

All B jns similar.

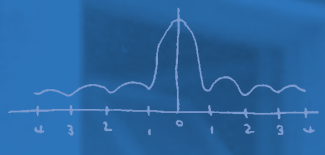
Structure is apparently at $\frac{2A}{2}$, $\frac{2A}{3}$, $\frac{2A}{4}$ etc.

2) measured 0 voltage current as function of field - no can.

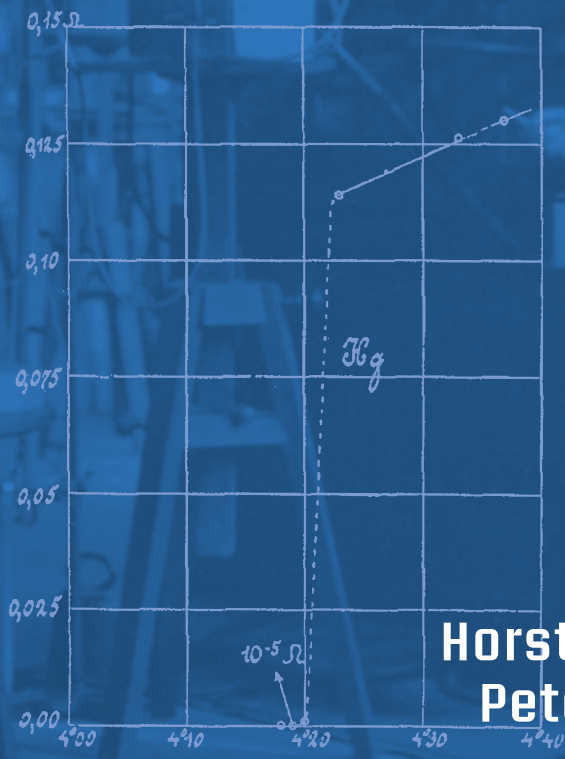
oscillates with about 30 mV period = 1.2 gauss.

Flux = $1.2 \times 2.4 \times 10^{-2} \times 780 \times 10^{-8}$
 width 2x per dist for lead foil
 $\approx 2.2 \times 10^{-7}$ = flux quantum.

Peculiarly see 4 dips and then some residual current



100 YEARS OF SUPERCONDUCTIVITY



Edited by
Horst Rogalla
Peter H. Kes

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Horst Rogalla and Peter H. Kes



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Contents

Preface	xvii
List of Authors	xix
Glossary	xxv
1 Early History	1
<i>Editor: Peter H. Kes</i>	
1.1 The Discovery and Early History of Superconductivity	
<i>Rudolf de Bruyn Ouboter, Dirk van Delft and Peter H. Kes</i>	
1.1.1 The Real Story	1
1.1.2 Elemental Superconductors	15
1.1.3 Superconductive Alloys, the Spongy Road to Type II Superconductors. . .	24
1.2 The Historical Context of Josephson's Discovery	
<i>A. B. Pippard</i>	
1.3 Further Reading	50
2 Theory	51
<i>Editor: Jan Zaanen</i>	
2.1 Ginzburg–Landau Equations	
<i>V. M. Vinokur and T. I. Baturina</i>	
2.1.1 Introduction	51
2.1.2 A History	52
2.1.3 The Equation	53
2.1.4 Consequences and Applications	58
2.1.5 Conclusion: Strings, the Universe, and All the Rest...	64
2.2 The Emergence of BCS	
<i>David Pines</i>	
2.2.1 Introduction	65
2.2.2 A Welcoming Environment	65
2.2.3 Starting Work with Bardeen	66
2.2.4 Polaron Theory	67
2.2.5 Effective Electron Interactions in Metals	67
2.2.6 Cooper's Pair Instability	68
2.2.7 Seattle and Stockholm	69
2.2.8 The Schrieffer Wave-Function	70
2.2.9 Deciphering, Teaching, and Applying BCS	70
2.2.10 BCS Theory	71
2.3 Theory of Superconductivity: From Phenomenology to Microscopic Theory	
<i>Lev P. Gor'kov</i>	
2.3.1 Introduction	72
2.3.2 Early Days	73
2.3.3 The 1950s	77

2.3.4	Microscopic Theory	79
2.3.5	Instead of Conclusion	91
2.4	A Modern, but Way Too Short History of the Theory of Superconductivity at a High Temperature <i>Jan Zaanen</i>	92
2.4.1	Introduction	92
2.4.2	Pushing BCS to the Limits: The Spin Fluctuation Superglue	94
2.4.3	The Legacy of Philip W. Anderson (I): Mottness	99
2.4.4	The Legacy of Philip W. Anderson (II): Resonating Valence Bonds and Their Descendants	100
2.4.5	Theory that Works: The Competing Orders of the Pseudogap Regime	106
2.4.6	Quantum Critical Metals and Superconductivity	110
2.5	Intrinsic Josephson Effect in Layered Superconductors <i>L. N. Bulaevskii and A.E. Koshelev</i>	115
2.5.1	Introduction: Layered Superconductors and Lawrence-Doniach Model	115
2.5.2	Vortex Matter in Layered Superconductors	118
2.5.3	Josephson Plasma Resonance	122
2.5.4	Radiation from Intrinsic Josephson Junctions	124
2.6	Mixed State Properties <i>Ernst Helmut Brandt</i>	125
2.6.1	Introduction	125
2.6.2	Abrikosov's Periodic Vortex Lattice Near B_{c2}	126
2.6.3	Distorted Vortex Lattice and Vacancy Near B_{c2}	127
2.6.4	Nonlocal Elasticity of the Vortex Lattice	129
2.6.5	Vortex Arrangements at Low Inductions	131
2.6.6	Vortex Lattice Solution for All κ and \bar{B}	132
2.6.7	Vortex Motion, Pinning, and Thermal Depinning	135
2.6.8	Anisotropic Superconductors	136
2.7	Thermomagnetic Effects in the Mixed State <i>R. P. Huebener</i>	137
3	Experiments	145
	<i>Editor: J. Mannhart</i>	
3.1	Tunneling and the Josephson Effect <i>John M. Rowell</i>	145
3.1.1	The Josephson Effect	153
3.2	The Discovery of Fluxoid Quantization <i>Dietrich Einzel</i>	161
3.2.1	Introduction	161
3.2.2	Theoretical Foundations	162
3.2.3	The Doll-Näbauer Experiment	163
3.2.4	The Deaver-Fairbank Experiment	165
3.2.5	The IBM Conference 1961	167
3.2.6	Post-1961	168
3.2.7	Summary and Conclusion	169
3.3	The Search for the Pairing Symmetry in the High Temperature Superconductors <i>Dale J. Van Harlingen</i>	170
3.3.1	Why the Symmetry Is Important	171
3.3.2	Determining the Symmetry	171
3.3.3	Samples	173
3.3.4	Parity	174

3.3.5	Penetration Depth	174
3.3.6	ARPES	175
3.3.7	Josephson Interferometry	177
3.3.8	Beyond d-Wave Symmetry	182
3.4	Half-Integer Flux Quantization in Unconventional Superconductors	
	<i>C. C. Tsuei and J. R. Kirtley</i>	182
3.4.1	The Design of the Tricrystal Experiments	183
3.4.2	Direct Observation of the Half Flux Quantization	187
3.4.3	Elucidation of the Nature of Half Flux Quantum Effect	191
3.4.4	Universality of the $d_{x^2-y^2}$ Pair State	192
3.4.5	Large-Scale Arrays of the Half Flux Vortices	194
3.4.6	Concluding Remarks	196
3.5	Electric Field Effect Tuning of Superconductivity	
	<i>Jean-Marc Triscone and Marc Gabay</i>	197
3.5.1	Preamble	197
3.5.2	Introduction	197
3.5.3	Electric Field Effect in Complex Oxides	197
3.5.4	Electric Field Effect in Superconductors: Physics and Lengthscales	199
3.5.5	Thomas Fermi Screening and Interface Quality	201
3.5.6	Field Effect Setups in a Nutshell	201
3.5.7	What's New?	203
3.5.8	Conclusions	206
3.6	The Grain Boundary Problem of High- T_c Superconductors	
	<i>J. Mannhart and D. Dimos</i>	206
3.7	Overview of the Experimental History, Status and Prospects of HTS	
	<i>M. R. Beasley</i>	213
3.7.1	The Allure of High Temperature Superconductivity	213
3.7.2	The Broad Sweep of History	213
3.7.3	From Onnes to Bednorz and Mueller	215
3.7.4	After Bednorz and Mueller	218
3.7.5	Prospects for Higher Temperature Superconductors	219
3.8	Vortex Matter in Anisotropic Superconductors	
	<i>Eli Zeldov</i>	222
3.8.1	Local Magnetization and Geometrical Barriers	223
3.8.2	Vortex Lattice Melting	225
3.8.3	Vortex Matter Phase Diagram	228
3.9	Further Reading	231
4	Materials	233
	<i>Editor: C. W. Chu</i>	
4.1	Introduction	
	<i>C. W. Chu</i>	233
4.2	The Route to High Temperature Superconductivity in Transition Metal Oxides	
	<i>A. Bussmann-Holder and K. A. Müller</i>	234
4.3	Superconductivity above 10 K in Non-Cuprate Oxides	
	<i>David C. Johnston</i>	239
4.3.1	Introduction	239
4.3.2	LiTi_2O_4	240
4.3.3	$\text{Ba}(\text{Pb}_{1-x}\text{Bi}_x)\text{O}_3$	242
4.3.4	$(\text{Ba}_{1-x}\text{K}_x)\text{BiO}_3$	244
4.4	Cuprates—Superconductors with a T_c up to 164 K	

	<i>C. W. Chu</i>	244
4.4.1	$\text{RBa}_2\text{Cu}_3\text{O}_7$	245
4.4.2	$\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$	250
4.4.3	$\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$	252
4.4.4	$\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3-\delta}$	253
4.5	Fe-Pnictides and -Chalcogenides	
	<i>Hideo Hosono</i>	255
4.5.1	Research Led to Discovery of Iron-Based Superconductors	255
4.5.2	Discovery of Iron-based Superconductors	257
4.5.3	Advances in Materials	260
4.5.4	Current Status	262
4.5.5	Perspective	263
4.6	Superconductivity in MgB_2	
	<i>Takahiro Muranaka and Jun Akimitsu</i>	265
4.6.1	Introduction	265
4.6.2	Crystal Structure of MgB_2	266
4.6.3	Electronic Structure of MgB_2	268
4.6.4	Two-gap Superconducting State of MgB_2	270
4.6.5	Conclusion	271
4.7	Fullerenes	
	<i>Kosmas Prassides and Matthew J. Rosseinsky</i>	272
4.7.1	Alkali Fulleride Superconductors	272
4.7.2	Fullerides with Increased Interfullerene Separations	274
4.7.3	Cs_3C_{60} —Fullerene Superconductivity Reborn	275
4.8	Elemental Superconductors	
	<i>K. Shimizu</i>	278
4.8.1	Periodic Table for Superconducting Elements	279
4.8.2	Experimental Technique	280
4.8.3	Example of Pressure-Induced Superconductivity in Elements	280
4.8.4	Summary: 3D Periodic Table for Superconducting Elements	282
4.9	Heavy-Fermion Superconductivity	
	<i>F. Steglich</i>	283
4.10	Ruthenate Superconductor Sr_2RuO_4	
	<i>Yoshiteru Maeno</i>	288
4.10.1	Same Crystal Structure but Different Unconventional Superconductivity	290
4.10.2	Novel Superconducting Phenomena	292
4.11	Magnetic Superconductors (and Some Recollections of Professor Bernd T. Matthias)	
	<i>M. Brian Maple</i>	293
4.11.1	Introduction	293
4.11.2	Localized Magnetic Moments in Conventional Superconductors	294
4.11.3	Coexistence of Superconductivity and Magnetic Order Involving the Same Set of Electrons	299
4.11.4	Some Thoughts about High Temperature Superconductors	304
4.11.5	Some Personal Recollections of Professor Bernd T. Matthias	305
4.12	Further Reading	307
5	SQUIDS and Detectors	311
	<i>Editor: A. I. Braginski</i>	
5.1	Introduction	
	<i>John Clarke, Arnold Silver and A. I. Braginski</i>	311

5.2	History and Device Fundamentals	
	<i>John Clarke and Arnold Silver</i>	313
5.2.1	Initial Discovery	313
5.2.2	Thin-Film Josephson Tunnel-Junction Quantum Interferometer	315
5.2.3	Point Contact Devices — dc SQUID	317
5.2.4	The rf SQUID	318
5.2.5	Linear SQUID Response and Single Flux Quantum Transitions	320
5.2.6	R-SQUID, Oscillators and Detectors	320
5.2.7	SLUGs at Cambridge	321
5.2.8	SQUIDs at Berkeley	324
5.2.9	The Square Washer SQUID	326
5.2.10	The rf SQUID Revisited	327
5.2.11	Today's SQUIDs	327
5.3	High- T_c SQUIDs	
	<i>A. I. Braginski</i>	328
5.3.1	Past and Present	328
5.3.2	High- T_c SQUID Limits of Performance	330
5.4	Geophysical Applications of SQUIDs	
	<i>C. P. Foley</i>	331
5.4.1	Introduction	331
5.4.2	Magnetic Measurements Used in Geophysical Prospecting	332
5.4.3	Early SQUIDs in Geophysical Prospecting	333
5.4.4	Transient ElectroMagnetics Using High- T_c SQUIDs	335
5.4.5	Tensor Gradiometry	338
5.4.6	Laboratory Systems	339
5.4.7	Final Comments	340
5.5	Application to Nondestructive Evaluation of Materials and Structures	
	<i>A. I. Braginski</i>	342
5.5.1	Past and Present	342
5.5.2	NDE Testing Methods Using SQUIDs	344
5.5.3	Bridge Testing	344
5.5.4	Airplane Testing	346
5.5.5	Two Examples of SQUID NDE Now in the Field	346
5.5.6	SQUID NDE Microscopy in Semiconductor Technology	348
5.5.7	Concluding Remark	349
5.6	SQUIDs — from Laboratory Devices to Commercial Products	
	<i>Ronald E. Sager</i>	349
5.6.1	Early SQUIDs as Laboratory Devices	349
5.6.2	First Commercialization of SQUIDs	350
5.6.3	SHE — Early SQUID Instrumentation	351
5.6.4	Quantum Design — Advanced SQUID Instruments	353
5.6.5	The Market for SQUID-based Instruments Today	356
5.6.6	Future Directions for SQUIDs in Laboratory Instrumentation	356
5.7	Electromagnetic and Particle Detection and Readout	
	<i>John Clarke, Kent Irwin and Peter Michelson</i>	358
5.7.1	DC SQUID Amplifiers	358
5.7.2	Transition Edge Sensors	361
5.7.3	Photon Energy Resolving Detectors	362
5.7.4	X-Ray Astronomy and Materials Analysis	363
5.7.5	Dark Energy and Cold Dark Matter	364
5.7.6	Dark Energy: Searching for Galaxy Clusters	366

5.7.7	Cold Dark Matter: WIMPs and Axions	368
5.7.8	Gravitational Radiation Detectors	369
5.7.9	Future Directions	371
5.8	Concluding Remarks <i>A. I. Braginski, John Clarke and Ronald E. Sager</i>	371
5.9	Further Reading	373
6	Qubits	375
	<i>Editor: J. E. Mooij</i>	
6.1	Qubits <i>J. E. Mooij</i>	375
6.1.1	Introduction	375
6.1.2	Early Experiments	376
6.1.3	Qubit Types	379
6.2	General Aspects <i>J. E. Mooij</i>	384
6.2.1	(De)coherence	384
6.2.2	Qubit Types, General Considerations	385
6.2.3	Recent Results	386
6.2.4	Future	387
7	Digital Electronics	389
	<i>Editor: Shinya Hasuo</i>	
7.1	Introduction <i>Shinya Hasuo</i>	389
7.2	Operating Principles of Digital Circuits <i>Theodore Van Duzer</i>	390
7.2.1	The Basic Switch	390
7.2.2	Logic Circuits	392
7.2.3	Memory	395
7.3	Digital Electronics in Japan <i>Shinya Hasuo</i>	397
7.3.1	The Dawn of Research on Digital Applications	398
7.3.2	Brief History of Japanese Projects on Superconducting Digital Electronics	399
7.3.3	Progress in the 1980s	402
7.3.4	Progress in the 1990s	403
7.3.5	Progress in the 2000s	405
7.4	Digital Electronics in the USA <i>Fernand (Doc) Bedard</i>	407
7.4.1	Cryotrons	408
7.4.2	Josephson Signal Processor (JSP)	409
7.4.3	Superconductive Crossbar Switch	410
7.4.4	Hybrid Technology Multi-Threaded Architecture (HTMT)	413
7.4.5	Superconducting Technology Assessment (STA)	414
7.5	Digital Electronics in Europe <i>Horst Rogalla</i>	415
7.5.1	The Early Days	415
7.5.2	European Projects	419
7.5.3	Organization of Superconducting Electronics in Europe	422
7.5.4	Road Ahead	423
7.6	Integrated Circuit Fabrication Process	

	<i>Mutsuo Hidaka</i>	424
	7.6.1 Circuit Elements	424
	7.6.2 Integration of Circuit Elements	427
	7.6.3 Planarized Multilayer Process	428
	7.6.4 Toward Further Progress	430
7.7	High-Speed Digital Circuits	
	<i>Akira Fujimaki</i>	431
	7.7.1 Principle of the Rapid Single Flux Quantum Circuit	432
	7.7.2 LSI Design Technology	433
	7.7.3 Demonstration of RSFQ LSIs	436
	7.7.4 New Directions in SFQ Circuits	439
7.8	History of Superconductor Analog-to-Digital Converters	
	<i>Oleg Mukhanov</i>	440
	7.8.1 Superconductor Parallel-Type ADCs	442
	7.8.2 Superconductor Oversampling ADCs	446
	7.8.3 Superconductor Materials for ADC Implementation: LTS vs HTS	456
	7.8.4 Conclusions	457
8	Microwave Applications	459
	<i>Editor: D. E. Oates</i>	
8.1	Microwave Measurements of Fundamental Properties of Superconductors	
	<i>D.E. Oates</i>	459
	8.1.1 Introduction	459
	8.1.2 Two-Fluid Model	460
	8.1.3 Microwave Measurement Techniques	462
	8.1.4 Early History	463
	8.1.5 Post World War II	463
	8.1.6 1960s and 1970s	464
	8.1.7 High- T_c Era	466
	8.1.8 Summary and Future Prospects	471
8.2	Applications of Passive Microwave Filters and Devices in Communication and Related Systems	
	<i>R. B. Hammond, N. O. Fenzi and B. A. Willemsen</i>	471
	8.2.1 Introduction	472
	8.2.2 HTS Filters for Cellular Telephone Base Station Receivers	473
	8.2.3 Other SC Passive Microwave Devices	483
	8.2.4 Summary and Looking Ahead	484
8.3	Superconducting Quantum Electronics Enabling Astronomical Observations	
	<i>T. M. Klapwijk</i>	484
	8.3.1 The Electrodynamics of Superconducting Films	485
	8.3.2 Photon-Assisted Tunneling with Superconductors	486
	8.3.3 Dynamic Pair Currents: Josephson Tunneling	487
	8.3.4 Passive Nonlinear Device: Quantum Mixing	488
	8.3.5 First Experimental Demonstration: Technology Base	489
	8.3.6 Submillimeter-Wave Astronomy	490
	8.3.7 From Proof-of-Principle to Demanding Use	491
	8.3.8 Nonequilibrium Mixers: Hot-Electron Bolometers	491
	8.3.9 Conclusions	492
8.4	Microwave Cooling of Superconducting Quantum Systems	
	<i>W. D. Oliver</i>	493
	8.4.1 Introduction	493

8.4.2	Superconducting Artificial Atoms	494
8.4.3	Microwave Cooling	496
8.4.4	Summary	499
8.5	Applications of Superconducting Microresonators	
	<i>Jonas Zmuidzinas</i>	499
8.5.1	Introduction	499
8.5.2	Linear Electrodynamics: A Brief Review	499
8.5.3	Superconducting Microresonators	501
8.5.4	Superconducting Microresonator Detectors	505
8.5.5	Parametric Amplifiers	510
8.5.6	Other Applications	511
8.5.7	Summary	511
8.6	Further Reading	511
9	Quantum Metrology	515
	<i>Editors: Richard E. Harris and Jürgen Niemeyer</i>	
9.1	Introduction	
	<i>Richard E. Harris and Jürgen Niemeyer</i>	515
9.2	Josephson Voltage Standard — The Ultimate Precision	
	<i>Jaw-Shen Tsai and James E. Lukens</i>	518
9.3	The First Josephson Voltage Standards	
	<i>Thomas J. Witt</i>	522
9.4	First Josephson Junction Array Voltage Standard	
	<i>Tadashi Endo</i>	525
9.4.1	Introduction	525
9.4.2	First Josephson Array	526
9.4.3	Applications of the Multiple Josephson Junction	527
9.4.4	Conclusion	528
9.5	How the DC Array Standards Were Developed	
	<i>Jürgen Niemeyer</i>	528
9.5.1	Introduction	528
9.5.2	Single Junction Design	529
9.5.3	Circuit Design and First Realization	530
9.5.4	1 Volt Circuits	532
9.5.5	10 Volt Circuits	533
9.6	Making the Josephson Voltage Standard Practical	
	<i>Clark A. Hamilton</i>	535
9.7	Programmable Josephson Voltage Standards: from DC to AC	
	<i>Johannes Kohlmann</i>	540
9.7.1	Introduction	540
9.7.2	Principles and Fundamentals of PJVS	540
9.7.3	Overdamped Josephson Junctions for PJVS	540
9.7.4	Realization of Series Arrays	543
9.7.5	Applications	545
9.7.6	Conclusions and Outlook	545
9.8	Quantum-Based Voltage Waveform Synthesis	
	<i>Samuel P. Benz</i>	546
9.9	Superconductivity and the SI (Metric) System Based on Fundamental Constants	
	<i>Edwin Williams and Ian Robinson</i>	553
9.10	Further Reading	557

10 Medical Applications	559
<i>Editor: Harold Weinstock</i>	
10.1 Introduction	
<i>Harold Weinstock</i>	559
10.2 Medical Applications of Magnetoencephalography	
<i>Cosimo Del Gratta, Stefania Della Penna, Vittorio Pizzella and Gian-Luca Romani</i>	562
10.2.1 Introduction: The Origin of Magnetoencephalography	562
10.2.2 Basics of MEG	564
10.2.3 First MEG Studies	569
10.2.4 A Step Ahead: Technological Developments	572
10.2.5 Brain Mapping and Clinical Studies	577
10.2.6 Recent Developments and Perspectives	580
10.3 MCG Instrumentation and Applications	
<i>Riccardo Fenici, Donatella Brisinda, Anna Rita Sorbo and Angela Venuti</i>	582
10.3.1 A New Boost in the 1980s	582
10.3.2 The History of High Resolution MCG	585
10.3.3 From Magnetic Field Mapping to 3D Cardiac Source Localization	588
10.3.4 From 3D localization to Magnetic Source Imaging	591
10.3.5 To Shield or Not to Shield? The History of Unshielded MCG	592
10.3.6 Clinical Perspectives	595
10.3.7 Detection of Myocardial Ischemia and Viability (Rest and Stress MCG)	595
10.3.8 3D Electro-anatomical Imaging of Arrhythmogenic Substrates and Pre-interventional Virtual Programming of Ablation Procedures	598
10.3.9 Arrhythmogenic Risk Assessment	599
10.3.10 Fetal Magnetocardiography	600
10.3.11 Conclusions	601
10.4 MRI (Magnetic Resonance Imaging) Instrumentation and Applications	
<i>Jim Bray and Kathleen Amm</i>	602
10.4.1 Basic Principles of MRI	603
10.4.2 History of MRI — A General Electric (GE) Perspective	604
10.5 Ultralow Field NMR and MRI	
<i>John Clarke</i>	610
10.5.1 Introduction	610
10.5.2 Background	610
10.5.3 Why ULF NMR and MRI?	611
10.5.4 Ultralow Field NMR	611
10.5.5 Ultralow Field MRI	612
10.5.6 T_1 -weighted Contrast Imaging	614
10.5.7 T_1 Contrast in Ex Vivo Prostate Tissue	616
10.5.8 Research in Other Institutions	617
10.5.9 A Perspective	618
10.6 Superconductivity in Medical Accelerators for Cancer Therapy	
<i>Peter A. Zavodszky</i>	619
10.7 Further Reading	625
11 Wires and Tapes	627
<i>Editor: David Larbalestier</i>	
11.1 The Long Road to High Current Density Superconducting Conductors	
<i>David Larbalestier</i>	627
11.1.1 Overview	627

11.1.2	Onnes's Vision for Superconducting Conductors and 10 T Magnets	628
11.1.3	Alloyed Superconductors, Type I and type II Transition and the Collective Failure to Understand It.	630
11.1.4	Theory and the Long Disconnect from Experiment	634
11.1.5	The 1960s: The Age of High Critical Current Densities and, Finally, High Field Magnets	635
11.1.6	Coexistence: High Temperature and Low Temperature Superconductors — 1987 to Present	636
11.1.7	Superconducting Conductors beyond the 2011 Centennial	638
11.2	Nb-Ti — from Beginnings to Perfection	
	<i>Peter J. Lee and Bruce Strauss</i>	643
11.2.1	The High Field Revolution in Retrospect	643
11.2.2	The High Field Revolution—The One that Was Noticed	643
11.2.3	First International Conference on High Magnetic Fields	644
11.2.4	God Save the Queen	645
11.2.5	The Slow Emergence of Nb-Ti	646
11.2.6	Rutherford CEBG/IMI Strand and the 1968 Brookhaven Summer School	648
11.2.7	Filamentary Superconductors	649
11.2.8	After the 1968 Summer School	650
11.2.9	Making Multifilamentary Strand	651
11.2.10	The First Strain Measurements	652
11.2.11	The Birth of Nb-46.5wt%Ti	652
11.2.12	Manufacturing of Cable for the Fermilab Tevatron	655
11.2.13	Toward a Complete Description of Nb-Ti	656
11.2.14	Nb-Ti as a Commodity	660
11.3	History of Nb ₃ Sn and Related A15 Wires	
	<i>Kyoji Tachikawa and Peter J. Lee</i>	661
11.3.1	Introduction	661
11.3.2	Chronological Progress in the Fabrication of Nb ₃ Sn and V ₃ Ga Wires	662
11.3.3	Bronze-Processed Nb ₃ Sn Wires	666
11.3.4	Internal Sn-Processed Nb ₃ Sn Wires	667
11.3.5	Conclusions and Future Outlook	669
11.4	Bi-Ca-Sr-Cu-O HTS Wire	
	<i>Martin W. Rupich and Eric E. Hellstrom</i>	671
11.4.1	Introduction	671
11.4.2	2223 Wires	674
11.4.3	2212 Conductors	681
11.4.4	Conclusions	688
11.5	Coated Conductor: Second Generation HTS Wire	
	<i>A. P. Malozemoff and Y. Yamada</i>	689
11.5.1	Texturing the Template	691
11.5.2	REBCO HTS Layer Deposition	694
11.5.3	Artificial Pinning	699
11.5.4	Drivers for 2G HTS Wire	700
11.6	The MgB ₂ Conductor Story	
	<i>René Flükiger and Hiroaki Kumakura</i>	702
11.6.1	Reasons for Excitement at the Unexpected Discovery of Superconductivity in MgB ₂	702
11.6.2	The Effect of Carbon or Carbon-based Additives on the Transport Properties	703
11.6.3	Factors Influencing the Transport Properties of MgB ₂ Conductors	704
11.6.4	The Fabrication Methods of MgB ₂ Wires and Tapes	705

11.6.5	Densification Effects in MgB ₂ Wires	708
11.6.6	Perspectives for Further Development of MgB ₂	709
11.7	Further Reading	711
12	Large Scale Applications	713
	<i>Editors: Peter Komarek, Bruce Strauss, Steve St. Lorant, Luca Bottura and Al McInturff</i>	
12.1	Introduction	
	<i>Steve St. Lorant</i>	713
12.2	The History of Superconductivity in High Energy Physics	
	<i>Steve A. Gourlay and Lucio Rossi</i>	716
12.2.1	Introduction	716
12.2.2	Accelerators	719
12.2.3	Detectors	721
12.2.4	Main Characteristics of Accelerator Magnets	723
12.2.5	The Benefits of Superconductivity	724
12.2.6	Early History	726
12.2.7	The Large Hadron Collider	728
12.2.8	Applications in Japan	731
12.2.9	RF Superconductivity	732
12.2.10	New Applications	735
12.3	Magnet Engineering—Study in Stability and Quench Protection	
	<i>Luca Bottura and Al McInturff</i>	737
12.3.1	Outline	737
12.3.2	The Infancy of Superconducting Magnet Technology	737
12.3.3	The Appeal of Nb ₃ Sn and the First Stumbling Steps	738
12.3.4	Malleable Nb-Based Alloys: Technology Goes to Industry	739
12.3.5	Training and Degradation, the Discovery of Stability	739
12.3.6	Stabilization Strategies	740
12.3.7	Cryogenic Stability	740
12.3.8	Adiabatic Stability	741
12.3.9	Dynamic Stability	742
12.3.10	MultiFilamentary Wires and Twisting	743
12.3.11	Cable Stability: The Invention of Rutherford Cable and CICC	743
12.3.12	Stability in the New Millennium	746
12.3.13	Quench and Protection—a Burning Issue	747
12.3.14	Hot Helium Bubbles	748
12.3.15	Coda	749
12.3.16	Appendix: Recollections and Reminiscences	749
12.4	The History of Fusion Magnet Development	
	<i>Jean-Luc Duchateau, Peter Komarek and Bernard Turek</i>	753
12.4.1	General Introduction	753
12.4.2	The Large Coil Task (LCT)	753
12.4.3	Early Work on Poloidal Field Coils for Tokamaks	755
12.4.4	<i>Tore Supra</i>	755
12.4.5	Tokamaks with Superconducting Magnet Systems in Recent Time	759
12.4.6	ITER as a Worldwide Collaboration Project in Thermonuclear Fusion	760
12.4.7	Superconducting Magnets for Stellarator-Type Fusion Devices	767
12.5	Electric Power Applications of Superconductivity	
	<i>William Hassenzahl and Osami Tsukamoto</i>	769
12.5.1	Introduction	769
12.5.2	Fault-Current Limiters	772

12.5.3	SMES	777
12.5.4	Superconducting Rotating Machines	782
12.5.5	Superconducting Cables	788
12.5.6	Superconducting Transformers	792
12.5.7	Conventional Transformer Characteristics	794
12.6	Magnetic Separation	
	<i>Christopher Rey</i>	797
12.6.1	Introduction	797
12.6.2	Principles of Magnetic Separation	797
12.6.3	Magnetic Separation Dynamics	799
12.6.4	Open Gradient Magnet Systems	800
12.6.5	Matrix/Filter Systems	800
12.6.6	Characteristics of High Gradient Magnetic Separation	801
12.6.7	Magnetic Separation Equipment	802
12.6.8	Applications of Magnetic Separation	806
12.6.9	Summary	811
12.7	Superconducting Induction Heating of Nonferrous Metals	
	<i>Niklas Magnusson and Larry Masur</i>	811
12.7.1	Conventional Aluminum, Copper and Brass Induction Heating	811
12.7.2	AC Superconducting Induction Heating	812
12.7.3	DC Superconducting Induction Heating	812
12.7.4	Commercial Deployment	814
12.7.5	Simple Technical Design	815
12.7.6	Low Frequency Billet Heating	815
12.7.7	A Field Report: Experiences with Operation	817
12.8	Superconducting Magnets for NMR	
	<i>Gerhard Roth</i>	817
12.8.1	Introduction	817
12.8.2	Stability	819
12.8.3	Homogeneity	820
12.8.4	Cryostat	822
12.8.5	Major NMR Magnet Development Steps	823
12.8.6	Nb ₃ Sn Technology	824
12.8.7	Subcooling Technology	826

Preface

Superconductivity came as a big surprise. But more amazing perhaps is that even a hundred years after its discovery this peculiar phenomenon continues to bring us new surprises. The research of superconductivity is characterized by times of relative quietness, interrupted by periods of exciting activities, often preceded by fundamental breakthroughs that later won Nobel Prizes in physics or chemistry. “Fundamental” can in this case both relate to an emerging theoretical insight and to a new class of materials displaying entirely unforeseen properties. In both cases, the prospect of new applications has been an important drive for commercial ambitions.

In the meantime, applications of superconductivity have found a place in science and industry; just like superconductivity in general, there were periods of quiet progress and stormy phases, but overall a steady progress took place, e.g., high- T_c superconductors were judged in the beginning as “never applicable in high magnetic fields” because of their grain boundary problem. In the meantime, they are essential building blocks for the creation of very high permanent fields: the result of excellent ideas and the cooperation between fundamental and applied scientists. Superconducting magnets for MRI can be found in any major hospital, and high-energy physics without superconducting magnets is practically unthinkable.

A similar breathtaking development took place in superconducting electronics: quantum-limited detectors, quantum-information processing, MEG and MCG, high-speed computing, and analog-to-digital and digital-to-analog converters with quantum precision, incorporating tens of thousands of Josephson junctions, are available. It seems to be a question only of time (and cooling) until they will enter the industrial product cycle.

In this centennial book on superconductivity many authors who themselves were responsible for the important steps forward, or were very close to those pioneers, report on the historical developments. The contributions represent their personal views and therefore this book does not provide the ultimate answers to all questions about superconductivity. Nonetheless it has become a very interesting collection of recollections and reviews of almost all the subdisciplines of superconductivity. The first three chapters concentrate on the interesting stories of the discovery and the succeeding gradual progress of theory and experiment. Much emphasis is given to the important developments in the early 1950s and 1960s. From then on superconductivity started to penetrate society and most applications today are based on the innovations of those years. But long before superconductivity could celebrate its centennial, a genuine revolution occurred with the discovery of the high temperature superconductors. A new episode began which is nicely described in a number of articles that bring this book up to the present time.

Originally it was the intention to present a small booklet (about 50 pages) to the attendants of the Superconductivity Centennial Conference taking place in the Netherlands in September 2011. This project quickly grew out to a book project of now more than 800 pages — primarily due to the excitement of scientists and engineers intending to show how far superconductivity has come after 100 years. Due to the limitation in space we had to restrict the number of contributions and many famous colleagues who would have deserved to take part in the project had to be left out. Even extending the size of the book to more than 800 pages did not help — superconductivity has become a vast field.

Being editors of the book was an exciting task, extremely enjoyable and nerve-wracking — hard deadlines melt in the sun of wonderful science and engineering! And preparing a book in \LaTeX was

an experience on its own. The help of students of the University of Twente (M. Garcia, W.A.G. Vessies, S. Waanders) and of the CU in Boulder (P. Lippert) is appreciated. The work of Daan Boltje in Leiden, Troy Christensen in Houston, and Peter Lee and Dmytro Abraimov in Tallahassee was essential to finish chapters 1, 2, 4 and 11. Finally our thanks to all authors, who were too engaged to stick to the page limits, and to the section editors, who did a wonderful (and difficult) job to organize and edit their chapters and to keep the excitement of the authors in balance with the available space in the book.

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Glossary

Glossary of Frequently Used Acronyms, Symbols, Terms and Physical Constants

We list here the fundamental physical constants, symbols, terms and also acronyms appearing throughout this book. Some of the terms, necessary to understand this book, are briefly defined.

Fundamental Physical Constants

$c = 2.997925 \times 10^8$ m/s	velocity of light
$e = 1.6022 \times 10^{-19}$ C	electron charge
$h = 6.6261 \times 10^{-34}$ Js	Planck constant
N_A	Avogadro constant
$\hbar = h/2\pi = 1.0546 \times 10^{-34}$ Js	Planck constant
$\Phi_0 \equiv h/2e = 2.0678 \times 10^{-15}$ Vs	flux quantum
$k_B = 1.3807 \times 10^{-23}$ J/K	Boltzmann constant
$\epsilon_0 = 8.8542 \times 10^{-12}$ As/Vm	permittivity of vacuum
$\mu_0 = 4\pi \times 10^{-7}$ Vs/Am	permeability of vacuum

Symbols and Terms

A	vector potential (vectors are denoted by bold, Roman symbols)
B	magnetic induction, $\mathbf{B} = \text{curl } \mathbf{A}$
H	magnetic field
E	electric field
$B = \mathbf{B} $	magnetic induction (magnitude)
$H = \mathbf{H} $	magnetic field (magnitude)
$E = \mathbf{E} $	electric field (magnitude)
c	specific heat
H_c	thermodynamic critical field
H_{c1}	lower critical field, field at which flux penetrates into a type II superconductor
H_{c2}	upper critical field, field at which the normal state comes back. Between H_{c1} and H_{c2} the material is in the Shubnikov phase (mixed state)
λ	magnetic penetration depth
λ_L	London penetration depth
ξ_0	coherence length, size of a Cooper pair
ξ	Ginzburg-Landau coherence length, length scale describing variation of

	Cooper pair density
κ	Ginzburg-Landau parameter, $\kappa = \lambda/\xi$, parameter distinguishing between type I and type II superconductors
β_A	Abrikosov parameter, determines the structure of the Abrikosov vortex lattice
a_0	lattice parameter of Abrikosov vortex lattice
σ	electric conductivity
ρ	electric resistivity
l	electron mean free path
F, f	Helmholz free energy, Helmholtz free energy density
m	electron mass
n_s	density of superconducting electrons
\mathbf{v}_s	average velocity of superconducting electrons
\mathbf{p}_s	momentum of superconducting condensate
$\mathbf{v}_F, \mathbf{p}_F$	Fermi velocity, Fermi momentum
ϵ_F, E_F	Fermi energy
$N(E_F)$	density of electronic states at the Fermi energy
\mathbf{j}, \mathbf{J}	electric current density
Δ_χ	generalized phase difference over Josephson junction
γ	Sommerfeld constant of electron specific heat
$\Delta(T)$	temperature dependent energy gap
V	BCS parameter determining the strength of the electron-phonon interaction
ω_D	Debye frequency
ω_P	Josephson plasma frequency
γ	anisotropy parameter of a layered superconductor
J_0	interlayer Josephson critical current
λ_J	Josephson length
s	layer thickness in a layered superconductor
$\Phi_{\alpha\beta}$	elastic matrix of a vortex lattice
b	reduced magnetic induction, $b = H/H_{c2}$
c_{ii}	elastic moduli of a vortex lattice
c_{11}	uniaxial compression modulus
c_{44}	tilt modulus
c_{66}	shear modulus
η	friction coefficient of a moving vortex lattice
κ	heat conductivity
ν	Nernst coefficient
$\beta_{dc} \equiv 2LI_c/\Phi_c$	dc SQUID parameter
$\beta_{rf} \equiv 2\pi LI_c/\Phi_0$	rf SQUID parameter
C	electric capacitance, heat capacity
$\delta \equiv \varphi_1 - \varphi_2$	phase difference across a Josephson junction
E	energy

$\epsilon(f)$	energy resolution of a SQUID
f	frequency
Φ	magnetic flux
$\phi(r, t)$	phase of the function of state
I	electric current
I_B, I_b	bias current
I_0, I_c	critical current (at which, for given B and T the superconductor normalizes)
I_c	critical current
J_c	critical current density
J_{Cu}	current density in the copper
J_e	engineering critical current density
$J_{overall}$	overall current density
L	electric inductance
ω	angular frequency
ω_c	cutoff or critical frequency
$\Psi(\mathbf{r}, t) = \Psi(\mathbf{r}, t) \exp[i\phi(\mathbf{r}, t)]$	macroscopic function of state
\mathbf{r}	space vector
R, r	electric resistance
R_n	normal state resistance of a Josephson junction
S_B	spectral density of magnetic field noise
$S_\Phi(f)$	spectral density of the flux noise
$S_I(f)$	spectral density of current noise
$S_V(f)$	spectral density of voltage noise
T_c	critical temperature (of transformation to superconducting state below T_c)
T_N	noise temperature of an electric device, circuit
t	time
τ	time constant
V, U	electric voltage
V_Φ	flux-to-voltage transfer coefficient (of a SQUID)
V_g	energy gap voltage

Acronyms

2212	$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+X}$ (X denotes deviation from stoichiometry)
2223	$\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+X}$
1G	1 st generation $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+x}$ wire
2G	2 nd generation $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ coated wire
A15 compounds	a group of superconducting chemical compounds
AC, ac	alternating current
ACJVS, ac	Josephson voltage standard

ADC	analog to digital converter
ADR	all-digital receiver
AEC	alkaline earth cuprate phase in BSCCO system
APC	artificial pinning center
BCS	Bardeen-Cooper-Schrieffer theory of superconductivity
Bi-2201	$\text{Bi}_2\text{Sr}_2\text{CuO}_{6+x}$
BSCCO	superconductors in the Bi-Sr-Ca-Cu-O system
BW	bandwidth
BZO	barium zirconate
CC	correction coils in a tokamak
CICC	cable-in-conduit conductor (cables of strand inside tube through which He coolant flows)
CDMC	old dark matter
CF	copper free phase in BSCCO system
CMB	cosmic microwave background (radiation)
CMS	compact muon solenoid
CPW	coplanar waveguide
CQOS	complementary quasidevice junction SQUID
CS	central solenoid, in a tokamak
CT-OP	controlled over-pressure processing—process used by Sumitomo Electric for 1G processing
CVD	chemical vapor deposition
CW	continuous wave
DC, dc	direct current
DE	dark energy
dipole	beam-bending electromagnet with two poles; the b_1 normal multipole coefficient in the expansion of the complex magnetic field
dodecapole	the b_6 normal multipole coefficient in the expansion of the complex magnetic field; a magnet with twelve poles
DVM	digital voltmeter
EB	electron beam
EMI	electromagnetic interference
EPR	electron spin paramagnetic resonance
FCL	fault current limiter
FEL	free electron laser
FET	field effect transistor
FWHM	full width half maximum
FPGA	field programmable gate array
GB	grain boundary (usually in high-temperature superconductor)
GLAG	Ginzburg-Landau-Abrikosov-Gorkov theory of superconductivity
G-M	Gifford-McMahon

GZO	gadolinium zirconate
HEMT	high electron mobility transistor
Hexed	filaments drawn through hexagonal die so that they can be stacked efficiently
HF, hf	high frequency
HTS	high-temperature superconductor (cuprate)
I	insulator
IBAD	ion beam-assisted deposition
IC	integrated (electric) circuit
ID	Inside diameter
IR	infrared
IT	internal tin process for making Nb ₃ Sn strand
JJ	Josephson junction
JNT	Johnson noise thermometry
JVS	Josephson voltage standard
LED	light emitting diode
LHe	liquid helium
LN₂	liquid nitrogen
LTS	low-temperature superconductor
MCG	magnetocardiography (biomagnetic imaging of heart fields/currents)
MEG	magnetoencephalography (biomagnetic imaging of brain fields/currents)
MFL	magnetic flux leakage NDE technique
MHD	magnetohydrodynamic(s)
MIITS	The energy balance defining the basic parameters for quench protection in a magnet, unit thereof
MOCVD	metal-organic chemical vapor deposition
MOD	metal-organic deposition
MPMS	magnetic property measuring system
MRI	magnetic resonance imaging
N	normal conductor
NDE	nondestructive evaluation (of materials and structures)
NMR	nuclear magnetic resonance
octupole	The b_4 normal multipole coefficient in the expansion of the complex magnetic field; a magnet with eight poles
OD	outside diameter
OFHC Cu	oxygen-free high conductivity copper
OP	overpressure processing — used for BSCCO conductors
OPIT	oxide powder in tube
PAIR	preanneal intermediate rolling — process to make 2212 conductor developed by NRIM
pancakes	planar magnetic coils
PECVD	plasma enhanced chemical vapor deposition

PF	poloidal-field coils, in a tokamak
pinning	effect used to inhibit movement of flux lines (vortices)
PJVS	programmable Josephson voltage standard
PLD	pulsed laser deposition
PMD	phase modulation-demodulation
PIT	powder in tube
quadrupole	The b_2 normal multipole coefficient in the expansion of the complex magnetic field; a magnet with four poles
QOS	quasi-one Junction SQUID
Quench	superconducting magnet enters non-superconducting state
QRQ	quarter rate quantizer
QVNS	quantized voltage noise source
RABITSTM	rolling assisted bi-axially textured substrate
REBCO	rare-earth cuprate (generic)
RF, rf	radio frequency
rms	root-mean-square
ROSAT	rotation-symmetric arranged tape-in-tape — conductor geometry for 2212 conductors developed by Hitachi
RRPTM	rod restacked process, an IT Nb ₃ Sn strand design developed by OST
RRR	residual resistivity ratio
RSFQ	rapid single flux quantum
RSJ	resistively shunted junction (free of hysteresis Josephson tunnel junction)
S	superconductor
SASE	self-amplified stimulated emission
SC	superconducting; superconductor
SCFCL	superconducting fault current limiter
sextupole	The b_3 normal multipole coefficient in the expansion of the complex magnetic field; magnet with six poles
SF	self field
SFQ	single flux quantum
SINIS	superconductor-insulator-normal-insulator-superconductor
SIS	superconductor-insulator-superconductor (tunnel junction, trilayer)
SLUG	superconducting low-inductance undulatory galvanometer
SMES	superconducting magnetic energy storage
SNS	superconductor–normal conductor–superconductor (proximity junction, trilayer)
SNR	signal-to-noise ratio
SQUID	superconducting quantum interference device
SCCO/Ag	bismuth strontium calcium copper oxide superconductor. The Ag indicates the substrate.
SRF	superconducting radio frequency
STO	SrTiO ₃ (strontium titanate)
SZE	Sunyaev-Zel'dovich effect

TEM	transmission electron microscopy
TEM	transient electromagnetics (geophysical exploration method)
TES	transition-edge sensor (superconducting detector of energy change)
TF	toroidal (magnetic) field in a tokamak
TDC	time to digital converter
V/F	voltage to frequency
WIMP	weakly interacting massive particle
YBCO	$\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$
YSZ	yttria stabilized zirconia

Institution, Experiment and Instrument Acronyms

AI	Atomics International
AIST	National Institute of Advanced Industrial Science and Technology, Japan
AMSC	American Superconductor Corporation
ANL	Argonne National Laboratory
ASC	Applied Superconductivity Conference
BIPM	Bureau International des Poids et Mesures, Paris, France
BNL	Brookhaven National Laboratory
BOC	British Oxygen Company
BTL	Bell Telephone Laboratories
CEA	Commissariat à l'Énergie Atomique et aux Énergies Alternatives, France
CEBAF	Colliding Electron Beam Facility
CEGB	Central Electricity Generating Board (UK)
CERN	European Organization for Nuclear Research
CESR	Cornell electron positron storage ring
CGPM	General Conference on Weights and Measures
CSIRO	Commonwealth Scientific and Industrial Research Organization, Australia
DESY	Deutsches Elektronen-Synchrotron
DOE	US Department of Energy
EAST	Experimental Advanced Superconducting Tokamak: Chinese experimental tokamak
EPAC	European Particle Accelerator Conference
ESCAR	Experimental Superconducting Electron Ring, at LBL
ETL	Electrotechnical Laboratory, Japan; former name of AIST
FLUXONICS	European network for superconducting electronics
FNAL	Fermilab (Fermi National Accelerator Laboratory)
FSU	Florida State University
FZ-Karlsruhe	Forschungszentrum Karlsruhe, Germany. Renamed KIT, Karlsruhe Institut für Technologie
GE	General Electric Corporation
GSI	Helmholtzzentrum (Gesellschaft) für Schwerionenforschung, Darmstadt

Harwell	United Kingdom Atomic Energy Authority (UKAEA) Research Establishment at Harwell
HEP	high energy physics
HERA	Hadron Electron Ring Accelerator, at DESY, Deutsches Elektronen-Synchrotron
IEEE	Institute of Electrical and Electronics Engineers
IGC	Intermagnetics General Corporation.
IMI	Imperial Metal Industries
IPHT	Institute für Photonische Technologien, Germany
IPK	International Prototype of the Kilogram
IPP	Max Planck Institute for Plasmaphysics, “Institut für Plasmaphysik”
IREE	Institute for Radio Electronics and Engineering
ISABELLE	Intersecting Storage Accelerator + “belle” at BNL
ISTEC	International Superconductivity Technology Center (Tokyo)
ITER	International Thermonuclear Experimental Reactor
IUPAP	International Union of Pure and Applied Physics
J-PARC	Japan Proton Accelerator Research Complex
JAERI	Japan Atomic Energy Research Institute
JINR	Joint Institute for Nuclear Research, Dubna, Russia
JLAB	Thomas Jefferson National Accelerator Facility (TJNAF)
JT-60SA	Experimental tokamak program preceding ITER, in Japan
KAERI	Korea Atomic Energy Research Institute
KAIST	Korea Advanced Institute of Science and Technology
KEK	High Energy Accelerator Research Organization, Japan
KERI	Korea Electro-Technology Research Institute
KSTAR	Korea Superconducting Tokamak Advanced Research
LAMPF	Los Alamos Meson Physics Facility
LASL	Los Alamos Scientific Laboratory, now LANL, (“National”)
LBNL/LBL	Lawrence Berkeley National Laboratory
LEP	large electron positron collider, CERN
LHC	large hadron collider, CERN
LHD	large helical device superconducting: stellarator in operation in Japan
MCA	Magnetic Corporation of America
METAS	Federal Office of Metrology, Switzerland
MIT	Massachusetts Institute of Technology
MSU	Michigan State University (location of National Superconducting Cyclotron Laboratory, NSCL)
MSU	Moscow State University
NAL	National Accelerator Laboratory (founded 1967), renamed Fermilab in 1974
NBS	National Bureau of Standards, USA; former name of NIST
NIST	National Institute of Standards and Technology, USA
NMI	National Measurement Institute

NML	Former name of national measurement institute in Australia
NPL	National Physical Laboratory, Great Britain
NRIM/NIMS	National Research Institute for Metals, now National Institute for Materials Science (Japan)
NST/NKT	Nordic Superconductor Technologies A/S is a subsidiary of Denmark's NKT Holding A/S
OI	Oxford Instruments
ORNL	Oak Ridge National Laboratory
PTB	Physikalisch-Technische Bundesanstalt
RCA	Radio Corporation of America
RHIC	Relativistic heavy ion collider (at BNL)
RMI	Formerly Reactive Metals, Inc., now RMI Titanium Company Extrusion Plant
Rutherford	Rutherford Appleton Laboratory (RAL) — when not referring to physicist Ernest Rutherford
SI	International system of units
SIS	Schwerionen Synchrotron at GSI, Darmstadt, Germany
SNS	spallation neutron source
SSC	superconducting super collider
SST1	Experimental tokamak in India with superconducting components
SEI	Sumitoma Electric Industries
Tevatron	Adopted name for the Energy Saver/Doubler hadron collider at FNAL
Tore Supra	Combination of “torus” and “superconductor,” a French tokamak
TOSKA	Usually understood to be a composite of “tokamak,” “supraleiter” and “Karlsruhe,” Germany, a test facility
TRIAM	Tokamak at the Research Institute for Applied Mechanics (RIAM) at Kyushu University, Japan
UNK	Accelerator at JINR, Dubna, Russia. Acronym unknown
UTSI	University of Tennessee Space Institute
W7-X	Wendelstein 7-X: superconducting stellarator under construction in Germany
WDG	Wire Development Group — research collaborations organized by American Superconductor Corp. that has worked on 1G and 2G wire

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1

Early History

Editor: Peter H. Kes

1.1	The Discovery and Early History of Superconductivity <i>Rudolf de Bruyn Ouboter, Dirk van Delft and Peter H. Kes</i>	1
1.2	The Historical Context of Josephson's Discovery <i>A. B. Pippard</i>	29
	Acknowledgments	50
1.3	Further Reading	50

1.1 The Discovery and Early History of Superconductivity

Rudolf de Bruyn Ouboter, Dirk van Delft and Peter H. Kes

1.1.1 The Real Story

On July 10, 1908, in his laboratory at Leiden University, the great Dutch physicist Heike Kamerlingh Onnes (1853–1926) experienced the most glorious moment of his career¹. That day, after 25 years of hard work and perseverance, of building up from scratch a cryogenic laboratory and organizing superb technical support to run it, he liquefied helium, opening up an entire new research field of low temperature physics. In a triumphant report to the Royal Dutch Academy of Arts and Sciences (KNAW) this historical fact is documented in great detail^{2,3}. Therefore it is remarkable that reliable details about his serendipitous discovery of superconductivity three years later are hard to come by. Lack of information has led to speculations about the discovery, in particular about the doubtful role played by a sleepy “blue boy”⁴, and about the possible disappearance of Kamerlingh Onnes’s laboratory notebooks. Enough reason, then, to have a close look at the Kamerlingh Onnes archive, stored at Boerhaave Museum in Leiden, to see whether any new clues could be found about the discovery of superconductivity — that most important consequence of the ability to reach liquid-helium temperatures.

Of course, it is roughly known when the first two experiments were carried out. Kamerlingh Onnes’s two earliest reports to the KNAW about zero resistance and “supraconductivity,” as this

¹ Dirk van Delft, *Freezing Physics. Heike Kamerlingh Onnes and the Quest for Cold*, KNAW, Amsterdam (2008)

² H. Kamerlingh Onnes, *Proc.* 11 (1909) 168, *Comm.* 108 (July 1908)

³ The regular articles in *Communications from the Physical Laboratory at the University of Leiden* (Comm.) were reprinted in the English-language version of the *Proceedings of the KNAW* (Proc.) and are available from the KNAW at <http://www.dwc.knaw.nl/english/academy/digital-library/>

⁴ J. de Nobel, *Physics Today*, (Sept. 1996) 40–42

phenomenon was initially called, are dated 28 April⁵ and 27 May 1911⁶. According to the archive's inventory, two notebooks (numbers 56 and 57) should cover the period 1909–1912. But on the cover of number 56 is written "1909–1910," and 57 begins with entry dated 26 October 1911. So it does indeed seem as if a crucial notebook is missing. This would explain why so many speculations started to circulate! Another obscuring factor is Kamerlingh Onnes's terrible handwriting. He wrote his lab notes, in pencil, in small household notebooks. They are very hard to read. After a few desperate hours trying, one tends to give up. And that is a pity because, the cover notwithstanding, notebook 56 does indeed announce the 1911 discovery of superconductivity (see Figure 1.1). The entry reads: "De meting van temperatuur is gelukt. Kwik nagenoeg nul. Herhaald met goud. (The temperature measurement was successful. [The resistance of] Mercury practically zero. Repeated with gold)". That looks very much like the discovery of superconductivity.

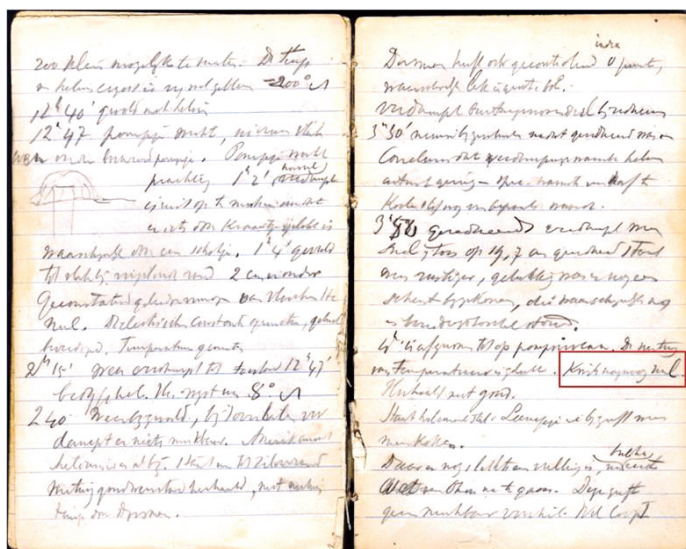


FIGURE 1.1: A crucial page from the entry for 8 April 1911 in Kamerlingh Onnes's notebook 56. The highlighted sentence *Kwik nagenoeg nul* means "Mercury[']s resistance is] practically zero [at 3.0 K]" announcing the first observation of superconductivity. The sketch of the functioning stirrer is seen on the left page. (Archive of the Boerhaave Museum, Leiden.)

When Kamerlingh Onnes took lab notes, he always started by writing down the date. In this case: the day was April 8, but he did not write the year! He dated the second experiment with mercury May 23, again without giving the year. It gets worse: Between those dates, he and Albert Perrier, a visitor from Lausanne, performed an entirely different experiment on the paramagnetism of liquid and solid oxygen. For that experiment the entry reads 19 May 1910. The year was specified this time, but the wrong one! It should have been 1911.

Why did Kamerlingh Onnes make that mistake? It is probably because an extensive series of similar experiments with Perrier had been carried out at the end of 1909 and during the first few months of 1910. In any case, that little slip of the pencil has led many astray. It is the most likely

⁵ H. Kamerlingh Onnes, *Proc.* 13 (1911) 1274, *Comm.* 120b (Apr. 1911)

⁶ H. Kamerlingh Onnes, *Proc.* 14 (1911) 113, *Comm.* 122b (May 1911)

reason that researchers exploring the archives were disappointed and, until now, did not look more closely at the notes. Had they made the effort, they would have found the excitement over the first successful transfer of liquid helium to a separate cryostat, the exact dates of the first resistivity experiments on a superconducting material, who was involved, and what their roles were. The notes also reveal that some nice stories about those events will always remain nice, but will never become true.

“Mercury practically zero”: with this note a new field of physics was born. But probably at that moment Kamerlingh Onnes was simply thinking how right he had been to choose mercury. Zero resistance was what he expected to find in extremely pure metals at liquid-helium temperatures⁷. After he liquefied hydrogen in February 1906, he started a program to investigate the resistance of metals at low temperatures. There was a practical reason —thermometry— but he also had a purely scientific interest.

One of the issues in those days was the question what would happen to the resistance of a metal as its temperature approaches absolute zero⁸. It was accepted that electrons were responsible for the electric conductance and that the resistance was due to the scattering of electrons by the ions of the metal crystal. Would the scattering amplitude decrease fast enough with falling temperature to yield zero resistance at zero temperature? Or would the mobility of the electrons also diminish at lower temperature, thus resulting in zero *conductivity* at absolute zero? If nature would follow the latter prescription — put forward by Lord Kelvin in 1902⁹ — the resistance of a pure metal would first fall with decreasing temperature, go through a minimum, and finally go up to infinity at absolute zero.

In the earliest investigations at liquid hydrogen temperatures in Leiden, Kamerlingh Onnes and his assistant Jacob Clay studied the resistance R versus temperature T in very thin gold and platinum wires¹⁰. Before July 1908 the lowest available temperature was 14 K, at which solid hydrogen sublimates under reduced pressure. That was low enough to observe that the almost linear decrease of R with T at higher temperatures starts to level off to an almost constant value. In one of his KNAW reports, Kamerlingh Onnes even mentioned a trace of a minimum in the $R(T)$ plot which indicates that he originally believed in Kelvin’s model. But the effect could equally well be due to the measuring accuracy.

The almost linear $R(T)$ behavior of Pt above 14 K made that metal suitable as a secondary thermometer. It was much more convenient than the cumbersome helium gas thermometer. Only one calibration point at the temperature of liquid nitrogen was sufficient to provide a sufficiently accurate and reproducible temperature scale. For many decades these Pt resistors were fabricated in the Leiden Physics Laboratory, and provided an extra source of income. But a disadvantage of these temperature standards was the rather large size: 10 cm long and about 1 cm wide.

The calibration point was needed because, according to Matthiessen’s rule, the resistance depended on the chemical and physical purity of the material. For instance, Kamerlingh Onnes showed that the resistance increase due to adding small admixtures of silver to the purest available gold was temperature independent and proportional to the concentration of added silver. So, improving purity would yield metal wires of very low resistance that could serve as secondary thermometers at temperatures far below 14 K.

Those very low temperatures came within reach after the successful liquefaction of helium in July 1908. But the race for absolute zero must have taken a great deal of Kamerlingh Onnes’s energy, because in the fall of 1908, after visiting the First International Congress of Refrigeration in Paris, he collapsed. It took until June 1909 before he could resume his experiments. In his KNAW report he

⁷ R. de Bruyn Ouboter, *IEEE Transactions on Magnetism*, MAG-23 (1987) 355

⁸ Per Fridtjof Dahl, *Superconductivity, its historical roots and development from mercury to the ceramics oxides*, AIP, New York (1992) 13–49

⁹ Lord Kelvin, *Phil. Mag.* 3 (1902) 257

¹⁰ H. Kamerlingh Onnes and J. Clay, *Proc.* 9 (1906) 213, *Comm.* 95d (June 1906)

reminded his audience how close to failure he had been in July 1908, because at the time he only had a very provisional, too high estimate of the critical pressure of helium from the law of corresponding states. Therefore he repeated the helium circulation at a much lower pressure and produced as much as 60 mL “without serious difficulties”. In a further attempt to solidify helium the pressure was reduced to 2.2 mm. At such low pressures the thermo-molecular corrections are substantial and instead of “2.5 K, perhaps 2 K” one can conclude in retrospect that Kamerlingh Onnes already had reached about 1.4 K. In a few subsequent experiments the helium gas thermometer was improved and the margin of errors of this instrument was so greatly reduced that the temperatures in the famous paper with the $R(T)$ plot of mercury¹¹ were reliable within 0.1 K.

The next important requirement was transferring helium from the liquefier, which lacked adequate space for experiments, to a separate cryostat. Considering the technology of those days this step was a real challenge. Thanks to the notebooks, we can follow quite closely the strategy followed by Kamerlingh Onnes, his technical manager of the cryogenic laboratory, Gerrit Jan Flim, and his master glassblower, Oskar Kesselring.

The first entry about the liquid-helium experiments in notebook 56 is dated Saturday 12 March 1910. It describes the first attempt to transfer helium to a separate cryostat. An extensive report can be found in the proceedings of the “Kältecongress, Wien, October 1910.” It is accompanied by a few beautiful drawings made by Flim, for example, the one showing the setup of the experiment displayed in Figure 1.2. The only content of the cryostat consisted of a double-walled container in which an even smaller one was connected to an impressive battery of pumps. “The plan is transfer, then decrease pressure, then condense in inner glass, then pump with Burckhardt [pump to a pressure of] 1/4 mm [Hg], then with Siemens pump [to] 0.1 mm.” Because there was nothing but glass inside the container, the experiment worked well and a new low-temperature record was registered: roughly 1.1 K. The goal of the next experiment, four months later, was to continue measuring $R(T)$ for the Pt resistor that had previously been calibrated down to 14 K. But the experiment failed because the extra heat capacity of the built-in resistor caused violent boiling and rapid evaporation of the freshly transferred liquid helium. So it was decided to drastically change the transfer system. And that would take another nine months.

Meanwhile, interest in the low temperature behavior of solids was growing rapidly. Specific heat experiments carried out in Berlin and Leiden exhibited unexpected decreases with descending temperatures. Einstein gave a qualitative explanation by modeling the energy distribution of the atomic degrees of freedom in terms of “Planck vibrators” (phonons)¹². For the first time, the quantum world was connected to low temperature phenomena. Inspired by Einstein and a publication of Riecke, Kamerlingh Onnes worked out his own model for scattering of electrons by Planck vibrators. It described the decrease in resistance with diminishing temperatures reasonably well¹³. He probably wanted to check his model at lower temperatures and did not want to wait until the new liquid-transfer system was ready. Therefore he decided to expand the original liquefier so that it could house a platinum resistor. Thus, on 2 December 1910, he made the first measurement of $R(T)$ for a metal at liquid helium temperatures. Cornelis Dorsman assisted with the temperature measurements and student Gilles Holst operated the Wheatstone bridge with the galvanometer. Because of its sensitivity to vibrations, the galvanometer had been placed in a room far away from the cryogenic laboratory with all its heavy, thumping pumps.

The outcome of the experiment was striking. It is shown in Figure 1.3a together with some older data of Au resistors¹³. The resistance of Pt became constant below 4.25 K. There was no longer any doubt that Lord Kelvin’s theory was wrong, the electron mobility did not freeze out near absolute zero. The resistance had fallen to a residual value that presumably depended on the impurity of the

¹¹ H. Kamerlingh Onnes, *Proc.* 14 (1912) 685, *Comm.* 124c (Nov. 1911)

¹² A. Einstein, *Annalen der Physik* 22 (1907) 180-190

¹³ H. Kamerlingh Onnes, *Proc.* 13 (1911) 1107, *Comm.* 119b (Febr. 1911)

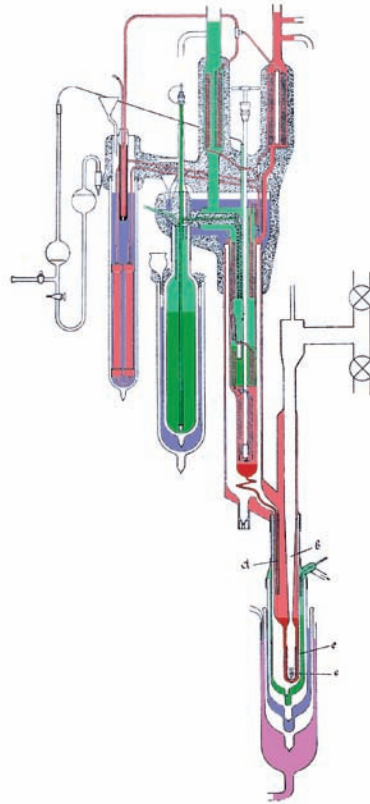


FIGURE 1.2: Set-up used in the first attempt (March 12, 1910) to transfer helium from the liquefier to a separate cryostat in which experiments could be done. The far right shows a drawing of the cryostat consisting of several containers of glass fitting inside one another. Most of the containers are in the form of a thermos bottle or Dewar (a double-walled glass container, pumped vacuum and usually covered with silver coatings on the inside walls; for visibility the coatings were not applied here). The outer vessel contained alcohol at 30–40°C to prevent condensation of water vapor on the glass. The outer Dewar contained liquid air, the middle one liquid hydrogen, and the inner Dewar **c** was supposed to be filled with liquid helium coming from the liquefier on the left, entering through the double-walled tube **d**. The bottom part of insert **b** was double walled and could be filled with liquid helium by condensation of helium gas. Subsequently, it could be evacuated to isolate the liquid helium inside **b** from the liquid helium in the cryostat. By pumping on the helium in **b** a new low temperature record was obtained. The left part of the drawing shows the liquefier with the Joule-Thompson valve clearly visible². [The original drawing (like the ones in Figure 1.4 and 1.5) was published in the Communications from the Physic Laboratory of the University of Leiden (referred to as Commun.). Colors have been added to indicate various cryogenic fluids: alcohol (pink), liquid air (purple), liquid and gaseous hydrogen (dark and light green respectively), and liquid and gaseous helium (dark and light red, respectively).]

wires. Those impurities could be either intrinsic or caused by the drawing process for the fabrication of thinner and longer wires to get higher resistances. Based on his model, Kamerlingh Onnes concluded that resistors of sufficiently pure platinum or gold should become zero at liquid-helium temperatures.

On 21 December 1910 and 27 January 1911 two more experiments were started up in the same

Kamerlingh Onnes adapted Riecke's theory by replacing the thermal energy $k_B T$ by $E_T = 3R\beta\nu/[\exp(\beta\nu/T) - 1]$, where k_B is Boltzmann's constant, R the gas constant, ν the frequency of Planck vibrators, and $\beta = h/k_B$ with h Planck's constant. The resistance ratio then could be written as $R(T)/R_0 = \sqrt{T E_T / T_0 E_0}$, where '0' refers to 0 °C. The parameter $\beta\nu$ depended on the material properties related to the elastic constants of the vibrators, for instance the melting temperature. With this model he computed the $R(T)/R_0$ dependence of Pt, Ag, Au, and Pb and found down to hydrogen temperatures reasonable agreement with the data of the purest wires. At 4.3 K, however, the model yielded immeasurably low values for all those metals.

In a communication to the first Solvay Conference Kamerlingh Onnes also reported the first data for mercury (see Figure 1.3b). Down to a temperature of 14 K there was reasonable agreement with the predictions of his model (see below). We now can reproduce why he was so eager to continue his investigations with mercury. As he later also explained there were two reasons: by using his model he could compute $R(T)/R_0$ at a few relevant temperatures, say 20 K, 14 K, 4.3 K, and 3.0 K. If we repeat his exercise with the value of $\beta\nu$ he chose for Hg^a, namely $\beta\nu = 30$, we obtain 5.0×10^{-2} , 2.7×10^{-2} , 0.13×10^{-2} , and 0.024×10^{-2} , respectively. The two latter values were within the sensitivity range of his equipment and the resistance ratio would nicely fall off to zero at the lowest temperatures. Furthermore, the Leiden laboratory had a lot of experience with the purification of mercury by distillation, and it would not be contaminated by the necessity of drawing a thin wire. (The liquid mercury in a capillary simply freezes at 234 K [−39°C].)

^a H. Kamerlingh Onnes, *Proc.* 13 (1911) 1093, *Comm.* 119b (Febr. 1911)

set-up, but they failed because of some technical difficulties. Again Flim was in charge of the helium liquefier and Kamerlingh Onnes took notes in his little notebook. Dorsman and Holst were present to assist with the experiments. Dorsman left in the summer of 1911, but Holst stayed until the end of 1913. He apparently enjoyed helping Kamerlingh Onnes with his research, rather than working on his thesis which was more like a routine project and much less exciting for a young researcher with ambitions.^{1,14}

The discovery

At the beginning of April 1911, the new cryostat was ready for its first cooldown. It was a masterpiece of technical design, demonstrating the amazing levels of glassblowing skill and fine mechanical construction. An extensive description with detailed drawings, reproduced in Figure 1.4, appeared in June 1911¹⁵. The transfer tube had been replaced by a double-walled, vacuum-pumped glass siphon, externally cooled by a counter flow of liquid air forced through a copper capillary coil wound around it. The liquefier and the cryostat could be separated from each other simply by closing a valve operated from above. Another important contraption, necessary to establish a well-defined

¹⁴ Holst received his doctorate in Zürich in September 1914. In *Commun.* 144d an abstract of his thesis (on the thermodynamic properties of ammonia and methylchloride) is given. At the end he writes (translated from German): "At the end of this work it is my pleasant duty to thank Professor H. Kamerlingh Onnes for his kindness to put all the equipment necessary for this research at my disposal. The time, during which I had the honor to be his assistant and more in particular the years during which I had the pleasure to assist him with his own research, will always remain a period of my life of which I will only be able to think with a feeling of deep gratitude".

¹⁵ H. Kamerlingh Onnes, *Proc.* 14 (1911) 204, *Comm.* 123a (June 1911)

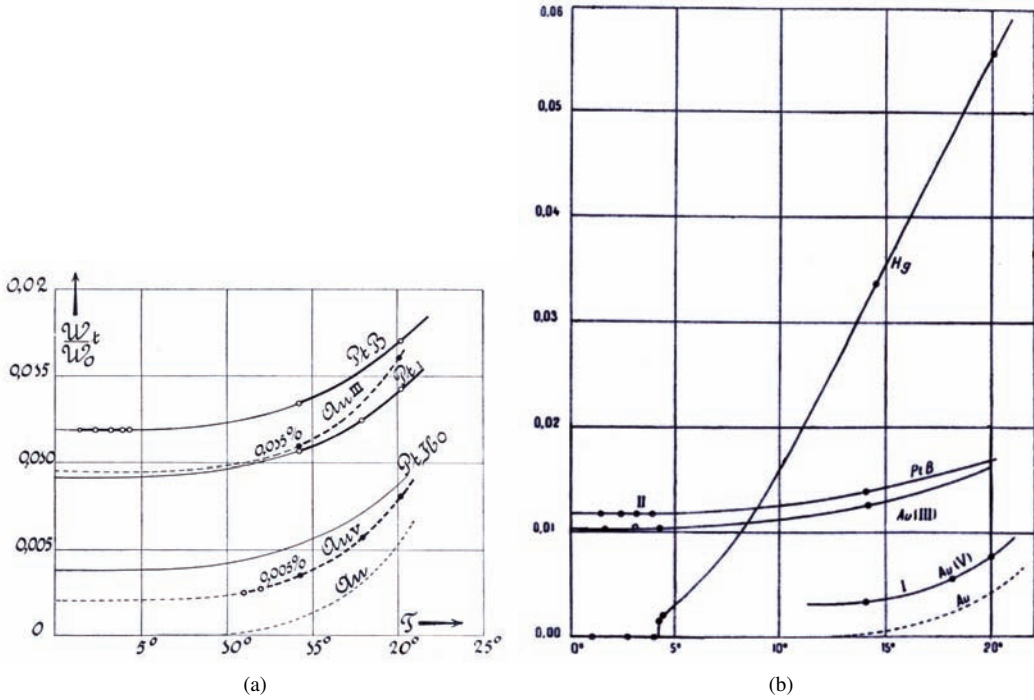


FIGURE 1.3: Resistance ratios of some metals versus temperature T (Kelvin). Left panel (a): Several platinum and gold resistors of various purities measured at different hydrogen temperatures. Pt-B was the first resistor ever to be cooled to helium temperatures in the experiment of 2 December 1910. The constant resistance below 4.3 K contradicted Kelvin’s model for conductance⁹; the electrons did not freeze onto the ion lattice at absolute zero. The remaining resistance was due to scattering of the electrons on impurities. By making the metal wires purer, both chemically and physically (by annealing out the lattice disorder), the resistance was shifted downward over a constant value, demonstrating that Matthiessen’s rule is valid down to the lowest temperatures. Right panel (b): The resistance ratio of Pt and Au compared to that of mercury (Hg). I denotes the temperature range of liquid hydrogen, II that of liquid helium¹³.

temperature at the site of the measuring devices, was a stirrer connected to a magnet at the top of the cryostat that could be moved up and down by a motor. The action of valve and stirrer could be directly followed through uncoated strips in the silvered vacuum glasses. Kamerlingh Onnes wrote “Niveau (van helium) vlak onder bovenrand pompje (= de roerder). Pompje werkt prachtig. [Level (of helium) just below upper rim little pump (= the stirrer). Pump works splendidly]”. In his notebook next to a little sketch visible in Figure 1.1 it shows how “It is peculiarly charming to see this little pump ejecting the light liquid over its upper edge when the level of the liquid helium sinks a little below it.” The main purpose of the experiment was to test the transfer of liquid helium to the experimental cryostat. But according to notebook 56, inside the cryostat were installed: “1^e transparent helium gas thermometer [...], 2^e resistor gold, 3^e thermo-element AuAg, 4^e resistor mercury, 5^e resistor constantin, 6^e conductivity liquid helium and dielectric constant”. So experiments could be done—just in case the helium transfer worked.

The mercury resistor was constructed by connecting seven U-shaped glass capillaries in series, each containing a small Hg reservoir to prevent the wire from breaking during cooldown. In Figure 1.5 one can see a similar design used in an experiment later that year. The electrical connections were

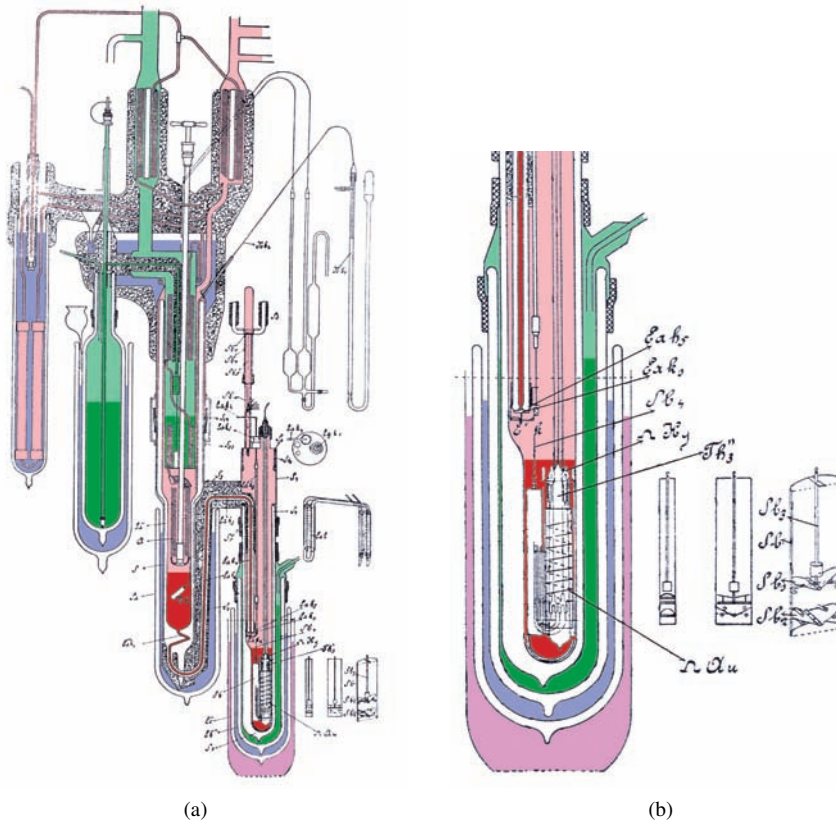


FIGURE 1.4: Set-up in which Heike Kamerlingh Onnes and coworkers carried out the 8 April 1911 experiment that first revealed superconductivity (same color scheme as in Figure 1.2). Left panel (a): On the left the liquefier with extended Dewar is schematically displayed. The liquid helium could be transferred through the double-walled vacuum-pumped siphon that could be closed with a valve (*Ea k1*) at the end inside the cryostat. Right panel (b): Blow-up of the lower part of the cryostat. Handwritten by Gerrit Flim are labels for the mercury and gold resistors (Ω Hg and Ω Au), the gas thermometer (*Th3*), components at the end (*Ea kn*) of the transfer tube from the helium liquefier, and parts of the liquid helium stirrer (*Sb*), which is also shown enlarged in several cross sections at the right¹¹.

made by four platinum feedthroughs with thin copper wires leading to the measuring equipment outside the cryostat. Kamerlingh Onnes had followed Gilles Holst's suggestion to distill the mercury by using liquid nitrogen. Apparently that worked well, but the Hg wire was "yet not as pure as our former mercury".

To learn what happened on 8 April 1911, we just have to follow the notes in notebook 56. The experiment started at 7 a.m., and Kamerlingh Onnes joined in when they began to circulate helium at 11:20 a.m. The resistance of the mercury indicated the falling temperature. After 30 minutes, the gold resistor was at -140°C , and soon after noon the gas thermometer denoted 5 K. The valve also worked "very sensitively". Half an hour later, enough helium had been transferred to test the functioning of the stirrer (see above) and to measure the very small evaporation heat of helium.

The team established that the liquid helium did not conduct electricity, and they determined its dielectric constant. Holst made precise measurements of the resistances of Hg and Au and the temperature was determined by Dorsman. Then they started to reduce the vapor pressure. The helium

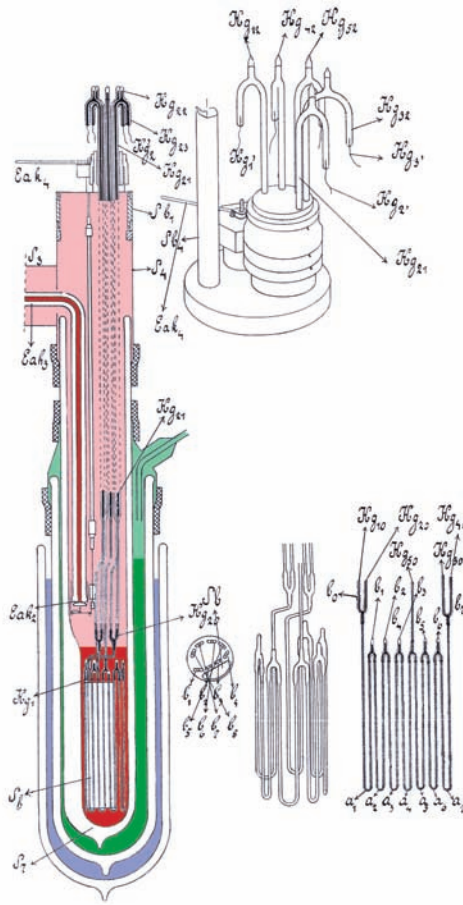


FIGURE 1.5: Cryostat with mercury resistor and mercury leads for the 26 October 1911 experiment (same color scheme as in Figure 1.2): seven U-shaped glass capillaries in series (inner diameter 0.07 mm), each with a mercury reservoir at the top and contact leads also made of glass capillaries filled with mercury. External contacts were made through Pt wires (denoted by Hgxx) shown in the top right drawing¹¹.

evaporated very quickly due to its small evaporation heat, they measured the specific heat, and stopped at a vapor pressure of 197 mmHg, corresponding to about 3 K.

Exactly at 4 p.m., says the notebook, the resistances of gold and mercury were determined again. The latter was in the historic entry “practically zero.” The notebook further records that the helium level stood quite still (“*Staat helemaal stil*”).

The experiments continued into the late afternoon. At the end of the day, Kamerlingh Onnes finished with an intriguing notebook entry: “Dorsman [who had measured the temperatures] really had to hurry to make the observations.” The temperature had been surprisingly hard to control. “It should be remarked that just before the lowest temperature [about 1.8 K] was reached, the boiling suddenly stopped and was replaced by evaporation in which the liquid visibly shrank. So, a remarkably strong evaporation at the surface.” Without realizing it, the Leiden team had also observed the superfluid transitions of liquid helium at 2.2 K. Two different quantum transitions had been seen for the first time, in one lab on one and the same day!

Three weeks later, Kamerlingh Onnes reported the results at the April meeting of the KNAW⁵. For the resistance of ultrapure mercury, he first told the audience, his model had yielded three predictions: (1) at 4.3 K the resistance should be much smaller than at 14 K, but still measurable with his equipment; (2) it should not yet be independent of temperature; and (3) at very low temperatures it should become zero within the limits of experimental accuracy. Those predictions, Kamerlingh Onnes concluded, had been completely confirmed by experiment. A look at Figure 1.3b clarifies why he came to that conclusion with only three data points (3.0 K, 4.3 K, and 14 K) at his disposal.

For the next experiment, on 23 May⁴, the voltage resolution had been improved to about 30 nV. The $R(T)/R_0$ at 3 K turned out to be less than 10^{-7} ! This value did not change anymore when T was lowered to 1.5 K. (The normalizing parameter R_0 was the calculated resistance of solid mercury extrapolated to 0 °C.) The notebook tells us that Ohm's law was checked at 4.3 K (supposedly both for the Au-III and Hg resistors). Then at 3:05pm:

“Now proceeded to resistance [measurements] at low temperatures”.[...] Everything is very regular now, no notion of violent boiling. All regarding installation had been disconnected from electrical wiring in building. It was feared that previous time this could have been of influence. Remains now [...] to suspect paper and paraffin. Evaporation seems decreased at these low temperatures. Now explored point between 190 mmHg and 760 mmHg [3.0 K and 4.3 K] because found resistance zero at just chosen point 3.2 K. At 4.00 [K] not yet anything to notice of rising resistance. At 4.05[K] not yet either. At 4.12 [K] resistance begins to appear.”

That entry contradicts the oft-told anecdote about the key role of a “blue boy” — an apprentice from the instrumentmaker's school Kamerlingh Onnes had founded. (The appellation refers to the blue lab coats the boys wore. As the story goes, the blue boy's sleepy inattention that afternoon had let the helium boil, thus raising the mercury above its 4.2 K transition temperature and signaling the new state — by its reversion to the normal conductivity — with a dramatic swing of the galvanometer.

The experiment was done with increasing rather than decreasing temperatures because that way the temperature changes slowly and the measurements could be done under more controlled conditions. Kamerlingh Onnes reported to the KNAW¹¹ that slightly above 4.2 K the resistance was still found to be only $10^{-5}R_0$, but within the next 0.1 K it had increased by a factor of almost 400. Such a fast increase was much more than his model could account for; see above and Figure 1.3b. He used the remainder of the paper to explain how useful this vanishing of the electrical resistance could be. It is interesting that the day before Kamerlingh Onnes submitted that report, he wrote in his notebook that the team had checked whether “evacuating the apparatus influenced the connections of the wires, as caused by deformation of the top [of the cryostat]. It is not the case”. Thus they ruled out inadvertent short circuits as the cause for the vanishing resistance.

That entry reveals how puzzled they were with the experimental results. Notebook 57 starts on 26 October 1911, “In helium apparatus mercury resistor with mercury contact leads (separate drawing made)”. This drawing, reproduced in Figure 1.5 and published in *Commun.*124c (30 December 1911), shows the team had spent the whole summer replacing the platinum feed-throughs and copper leads by mercury wires in glass capillaries that went all the way through the cryostat's cap. And they investigated how the new setup could be cooled down in a controlled fashion without breaking the mercury wires or the glass.

That was quite a challenge. In retrospect, the effort turned out to be a waist of time, but it was motivated by the important question of how small the resistance actually was. To improve voltage resolution, they sought to minimize the thermoelectric effect in the voltage leads. The idea was to do that by using the same material for both sample and leads and bringing the connections with Pt outside the cryostat where they can be thermally isolated from temperature variations. It didn't work, because the transition from solid to liquid mercury actually turned out to be the source of a considerable thermoelectric voltage of about 0.5 mV.

Still, the October experiment produced the historic plot, shown in Figure 1.6, of the abrupt ap-

pearance of mercury's resistance at 4.20 K. The part of the plot above the transition temperature is of particular interest because it shows a gradual increase with temperature beyond the jump. To obtain those data, the Leiden team had to go beyond the normal boiling point of helium. They did that by closing the helium inlet valve so that the vapor pressure could rise and thus raise the boiling temperature. That the resistance above the jump depended on temperature showed that the electrons at 4.2 K were still predominantly scattered by phonons (Planck vibrators). From the sudden jump it was clear that a totally new and unexpected phenomenon had been discovered, which Kamerlingh Onnes called "supraconductivity".

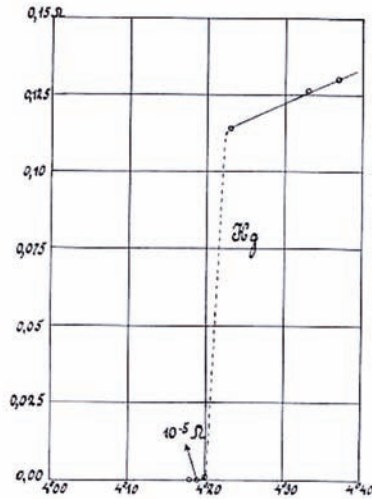


FIGURE 1.6: Historic plot of resistance (Ω) versus temperature (K) for mercury from the 26 October 1911 experiment shows the superconducting transition at 4.20 K. Within 0.02 K, the resistance jumps from unmeasurably small (less than $10^{-5} \Omega$) to 0.1 Ω .¹¹

Just one week later he reported his discovery in Brussels to the elite of the physics world at the very first of the historic Solvay Conferences. In the discussion "M. Langevin asked if other properties of the substance displayed similar sudden changes, as would be the case if mercury underwent a structural modification at 4.20 K". Apparently, Langevin was thinking of a phase transition, although he might have had a structural phase transition in mind. This was certainly Kamerlingh Onnes's interpretation, for "... should there exist such a new modification, it would differ from ordinary mercury at higher temperatures chiefly by the property that the frequency of the vibrators in the new state has become greater, and therefore the conductivity rises to the extremely large value exhibited below 4.19 K". So he still saw a way to stick to his model, but he also announced new experiments to investigate Langevin's suggestion.

Further on in notebook 57, we notice preparations in March 1912 for specific-heat experiments near the transition of mercury. Holst was put in charge. But there turned out to be experimental difficulties that could not satisfactorily be resolved. Eventually, Holst and Kamerlingh Onnes published a paper together on the specific heat and thermal conduction of Hg, but the accuracy of the measurements at helium temperatures was not sufficient to reveal any features at the transition temperature¹⁶. A month later they also tried to determine the thermo power of a mercury-platinum contact at temperatures around the transition. But again, experimental problems were in the way of

¹⁶ H. Kamerlingh Onnes and G. Holst, *Proc.* 17 (1914) 760, *Comm.* 142c (June 1914)

success.

Other Materials, Other Experiments

A notebook entry dated 20 June 1912 is very interesting: “Discussed with Holst ... alloying mercury with gold and Cd. Decided [to use] very small concentrations.” A few days later the experiment had already been carried out. The results were not published until the following March: “To my surprise the resistance (of the mercury with admixtures) disappeared in the same way as with pure mercury; much of the time spent on the preparation of pure mercury ... might therefore have been saved Even with the amalgam that is used for the backing of mirrors, the resistance was found [to be] 0 at helium temperatures. Later, December 1912, it was found that if it disappears suddenly, as with the pure mercury, it happens at a higher temperature.” In fact, the mercury period was closed with that experiment of December 1912. Not only did the Leiden team observe superconductivity in amalgam was observed, but they also discovered that lead and tin were superconductors with transition temperatures near 6 K and 3.8 K, respectively. These discoveries came as something of a relief. Since then the experiments were continued with these materials without worrying about laboratory problems peculiar to mercury: double distillation, broken threads, and very cumbersome cool down procedures.

The other notes stored in the Archives of the Boerhaave Museum concerning superconductivity are dealing with the persistent current experiments carried out in the spring and summer of 1914; see below. In the mean time Kamerlingh Onnes had published several papers on superconductivity¹⁷. They appeared early 1913 and gave a very open account of all the difficulties encountered with the mercury experiments. The destruction of superconductivity by a strong current surpassing a certain threshold value was a new issue. That depairing current or critical current, as it is called now, increased with diminishing temperature.

An experiment on 17 January 1914 revealed the destructive effect of a magnetic field on superconductivity. For Pb, the threshold value at 4.25 K was only 600 Gauss (60 mT)¹⁸. That must have been a great disappointment for Kamerlingh Onnes because on several occasions, for instance at the Third International Congress of Refrigeration in Washington-Chicago, he had dreamt aloud about coils made of superconducting material that could produce magnetic fields as high as a 100,000 Gauss (10 T). He finished the February 1914 paper with a nice twist: “An unforeseen difficulty is now found in our way, but this is well counterbalanced by the discovery of the curious property which is the cause of it”. Nowadays the 8-tesla bending magnets of the Large Hadron Collider at CERN approach that dream, but they do so with a niobium-titanium alloy whose critical magnetic field far exceeds those of the superconductors known on Kamerlingh Onnes’s time.

Kamerlingh Onnes next concentrated on the question of how small the “microresidual” resistance actually was in the superconducting state. He designed an experiment to measure the decay time of a magnetically induced current in a closed superconducting loop. He used the small lead coil which was made for the experiments about the magnetic field effect. To close the coil in itself the two ends were soldered together. And after lowering the temperature in presence of an external magnetic field a current could be induced in the superconducting closed loop by removing the magnet. From the decay time of the current and the self-induction of the coil the microresidual resistance R could be determined. With the upper bound for R being extremely small, it was to be expected that the decay time would be very large. For the Pb coil it was expected that the decay time would be more than 24 hours¹⁹.

To probe the decay of the current circulating in the closed loop after the induction magnet had been removed, he used a compass needle placed close to the cryostat and precisely to its east. To

¹⁷ H. Kamerlingh Onnes, Proc. 16 (1913) 113, Comm. 133a,b,c (Febr. 1913); Proc. 16 (1913) 113, Comm. 133d (May 1913)

¹⁸ H. Kamerlingh Onnes, Proc. 16 (1914) 987, Comm. 139f (Febr. 1914)

¹⁹ H. Kamerlingh Onnes, Proc. 17 (1914) 12, 278, 514, Comm. 140b (April 1914), 140c (May 1914), 141b (June 1914)

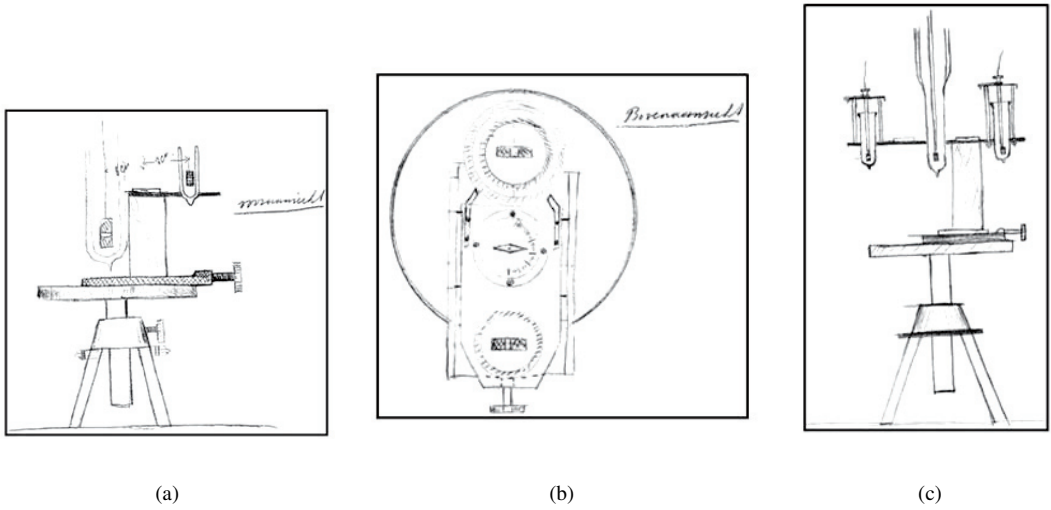


FIGURE 1.7: Original drawing by Gerrit Jan Flim showing the setup for the persistent-current experiments of 19 (a and b) and 29 May 1914. Left (a): front view (vooraanzicht) showing the lead coil in the helium cryostat and the copper compensation coil in the liquid air Dewar (actually, during the experiment, the lead and copper compensation coils were on the same height as the compass needle). Center (b): top view (bovenaanzicht) showing also the compass needle in the middle pointing north demonstrating good compensation of the fields from the Pb coil and that from the copper coil. Right (c): side view of the symmetric compensation set up with two copper coils in liquid air used in the experiment of 29 May 1914 (Archive of the Boerhaave Museum, Leiden).

improve the sensitivity, the earth field was compensated and to calibrate the supercurrent in the loop, he positioned an almost identical copper coil on the other side of the compass needle which had to compensate the effect of the superconducting coil. In Figure 1.7a, a sketch of the setup made by Flim is reproduced. Kamerlingh Onnes reported his first results to the KNAW on 24 April 1914: “During an hour the current [0.6 A] was observed not to decrease perceptibly. [...] A coil cooled in liquid helium and provided with current at Leyden, might, if kept immersed in liquid helium, be conveyed to a considerable distance and there be used to demonstrate the permanent-magnetic action of a superconductor carrying a current. I would have liked to show the phenomenon in this meeting in the same way as I brought liquid hydrogen here in 1906. But the appliances at my disposal do not yet allow the transportation of liquid helium”¹⁹.

Two decades later, such a travelling show had become possible. In 1932 six years after Kamerlingh Onnes’s death, Flim flew to London with a portable Dewar containing a lead ring immersed in liquid helium and carrying a persistent current of 200 A. He made the trip to demonstrate this most sensational effect of superconductivity at the traditional Friday evening lectures of the Royal Institution. That was the same grand venue at which James Dewar had demonstrated the liquefaction of hydrogen in 1899.

The analogies expressed by the title of the May 1914 paper are worth mentioning: “The imitation of an Ampère molecular current or of a permanent magnet by means of a supraconductor”. The latter effect is at the basis of superconducting levitation that we can demonstrate today on a human scale.

The precision of the first experiment, estimated to be about 10%, was further improved in two

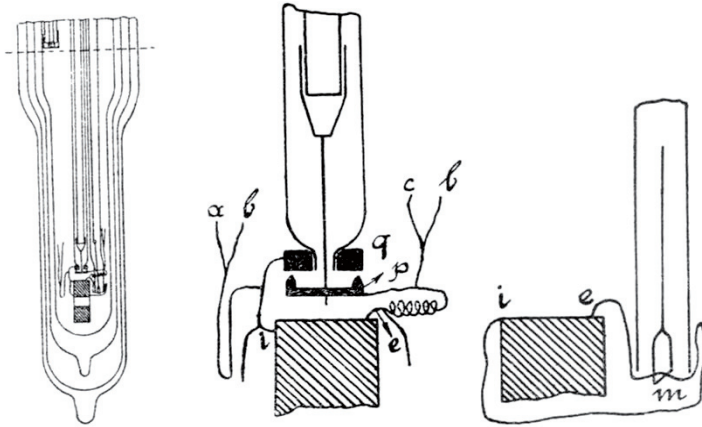


FIGURE 1.8: Design for the experiment on 20 June 1914 with cutting mechanism (right), the superconducting key (mechanical persistent mode switch) (center), and the cryostat with insert (left)¹⁹. The hatched element is part of the lead coil. All wires, as well as the ring *q* and the plate with protrusions *p*, are made of lead.

subsequent runs. The latter with two compensation coils of copper, both immersed in liquid air; see Figure 1.7b. It turned out that the change of the current was less than 1% per hour. That result raised the decay time to more than 4 days and diminished the upper limit of the resistance ratio to about 2×10^{-11} . In fact, that result was somewhat disappointing because it turned out to be only a factor of two lower than the ratio determined by means of the galvanometer. However, on spectators the impact of this direct observation of a persistent current was so much greater than all earlier reports, that this experiment of 1914 may be considered as the ultimate proof that superconductivity was indeed an entirely novel phenomenon.

The excitement spread quickly and widely. In Berlin Max Planck heard about it and wrote to Kamerlingh Onnes to express his amazement²⁰. Paul Ehrenfest, who had witnessed the experiment himself, told Lorentz that he was flabbergasted. “I attended a fascinating experiment at the laboratory. ... Unsettling, to see the effect of this ‘permanent’ current on a magnetic needle. It is almost palpable, the way the ring of electrons goes round and round and round in the wire, slowly and virtually without friction”²¹. Popular news media covered the spectacular phenomenon too. The Dutch newspaper *NRC* (*Nieuwe Rotterdamsche Courant*) invited Keesom to write an article that appeared in the issues of Friday and Saturday 10 and 11 July 1914²². On 30 June 1914 *Le Courier de la Presse* had reported “Une sensationnelle communication a été fait hier à l’Academie des Sciences: un courant électrique, une fois amorcé, peut durer indéfiniment ...”²²

Next Kamerlingh Onnes wished to supply a conclusive proof that the magnetic moment of the coil is really caused by a current. The essential elements for that experiment are displayed in Figure 1.8 on the right, reproduced from *Commun.* 141b¹⁹. This time the closed loop was constructed such that it could be cut from outside. Upon charging the coil and cutting the connection the current could escape only through a ballistic galvanometer which was connected to the coil on both sides of the

²⁰ Planck to Kamerlingh Onnes, 10 March 1915, Museum Boerhaave, Kamerlingh Onnes archive

²¹ Ehrenfest to Lorentz, 11 April 1914, Noord-Hollands Archief, Lorentz archive, inv. nr. 20

²² Museum Boerhaave, Kamerlingh Onnes archive

intersect. It worked and “the current does really flow through the coil” was the firm conclusion.

The same paper described two more experiments, both inspired by suggestions of colleagues in Leiden (Kuenen and Ehrenfest). Kuenen’s suggestion would nowadays be recognized as a mechanical persistent mode switch. The first such device is displayed in the center of Figure 1.8. It consisted of a lead ring mounted on a glass tube and a lead plate that could be pulled up against the ring providing a superconducting contact through three small protrusions on the plate pointing towards the ring. Ring and plate were connected through lead wires to the coil yielding a superconducting loop once the contact was made. In addition to the wires of the ballistic galvanometer (a and c), two more wires (b and d) were attached to the coil and an external current source. In this way the following experiment could be done: with open key and disconnected galvanometer an external current could be sent through the coil. Upon closing the key by applying sufficient pressure, the superconducting loop could be established, so that the ballistic galvanometer could be connected and the current source disconnected without disturbing the current in the loop. Finally, when the key was opened, the current produced a throw of the galvanometer. All this could be followed by monitoring the position of the compass needle next to the cryostat. And it all worked convincingly well¹⁹.

Ehrenfest came up with the idea that the experiment could be equally well performed with a lead ring. It worked perfectly. A current of 320 A was registered in a ring with a rectangular cross section of $3.0 \times 3.5 \text{ mm}^2$. Kamerlingh Onnes concluded correctly that the current density was the important quantity, but the value he computed, 30 A/mm^2 , was far too low. As we know today, the current is concentrated in a thin surface layer with thickness λ , the London penetration depth, which was introduced 20 years later, as will be discussed in Section 1.1.2.

1.1.2 Elemental Superconductors

The outbreak of the Great War in 1914 resulted in a period of silence which lasted until the mid 1920s. The only progress made was Silsbee’s explanation²³ of the linear relation between the (critical) threshold current of a tin wire and its diameter¹⁷. Silsbee proposed that superconductivity would be disturbed when the magnetic field at the surface produced by the current through the wire equals the critical value $\mu_0 H_c$ at the temperature considered, where μ_0 is the magnetic permeability of free space. New experiments in Leiden, first published in the thesis of Tuyn (July 1924), confirmed Silsbee’s conjecture²⁴. At about the same time an overview of $R(H, T)$ data of the then-known superconductors was published²⁵. That data showed, as can be seen in Figure 1.9, that the temperature dependence of the critical field follows a generic behavior that is well approximated by the parabola $H_c(T) = H_c(0)(1 - (T/T_c)^2)$. That critical field line thus separates a normal from a superconducting state and the resemblance with a thermodynamic phase diagram must have been compelling²⁶. Nevertheless it took more than a decade before that step was made.⁸

It was believed that the description of superconductivity had to rely on the theory of perfect conductivity—not unreasonable, because new experiments on the persistent current by Tuyn had reduced the upper limit of $R(4.2\text{K})/R_0$ to 10^{-13} . That belief culminated in the theory of Becker, Heller and Sauter²⁷. By combining Faraday’s law, $\text{curl } \mathbf{E} = -\partial\mathbf{B}/\partial t$, Ohm’s law, $\mathbf{E} = \mathbf{J}/\sigma$, and the conductivity $\sigma \rightarrow \infty$, it followed that $\partial\mathbf{B}/\partial t = 0$ so that, once in a state of perfect conductivity, the magnetic induction \mathbf{B} could not change anymore. A change of the applied magnetic field would therefore give rise to induced screening currents in the perfect conductor which would create a magnetic field that exactly compensated the applied field change in the interior. Those currents should

²³ F.B. Silsbee, *J. Wash. Acad. Sci.* 6 (1916) 597

²⁴ W. Tuyn, H. Kamerlingh Onnes, *Franklin Institute, Journal* 201 (1926) 379, *Comm.* 174a (1926); W.J. de Haas, J. Voogd, *Proc.* 14 (1911) 113, *Comm.* 212a (1931)

²⁵ W.J. de Haas, G.J. Sizoo, H. Kamerlingh Onnes, *Proc.* 29 (1926) 250, *Comm.* 180d (1926)

²⁶ W.H. Keesom, *Rapp. et Disc. 4^e Conseil Solvay* 288 (1924)

²⁷ R. Becker, G. Heller, F. Sauter, *Z. Phys.* 85 (1933) 772; G.L. de Haas-Lorentz, *Physica* 5 (1925) 384 (in Dutch)

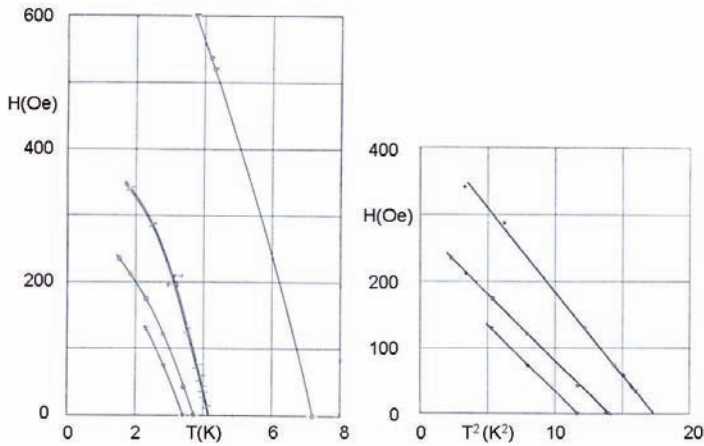


FIGURE 1.9: Left panel: the threshold curves of lead, mercury, tin, and indium (high to low T_c) in a linear plot of H_c versus T . Right panel: same H_c data (except for lead) plotted versus T^2 revealing the seemingly good quadratic temperature dependence $H_c(T) \approx H_c(0)(1 - (T/T_c)^2)$.^{24,25}

flow in a small, but finite layer at the surface with thickness $\lambda = (m/\mu_0 n e^2)^{1/2}$. For most known superconductors this layer was estimated to be about 10^{-4} mm ($-e$, m , and n respectively denote charge, mass, and density of the (relevant) conduction electrons). Interestingly, a few years earlier, the daughter of Lorentz had also obtained that result by equating the kinetic energy of the screening currents with the magnetic energy.²⁶ As has been schematically illustrated in Figure 1.10a and 1.10b, the state of a perfect conductor thus depends on its history. The perfect conductor therefore could not represent a thermodynamic equilibrium phase.

Thermodynamics

The first evidence that a superconductor was more than a perfect conductor and instead represented a state of thermodynamic equilibrium was provided by Keesom and Keesom²⁸ in specific heat experiments carried out in zero applied field. They had improved the sensitivity of earlier experiments of Keesom and Van den Ende so that for the first time a clear jump in the electronic heat capacity of tin at the critical temperature T_c could be observed; see Figure 1.11. In addition, they showed there was no latent heat at the transition and that below T_c the specific heat roughly varied as T^3 . The absence of a latent heat at T_c implied a phase transition of the second kind. The possibility of such a new kind of phase transition was introduced by Keesom²⁹ and Ehrenfest³⁰ for the theoretical analysis of the lambda transition that was just discovered in liquid helium. A student of Ehrenfest, Rutgers, used this analogy to derive a relation between the jump in the specific heat Δc and the derivative of the critical field at T_c ³¹

$$\Delta c = (c_s - c_n)_{T=T_c} = \mu_0 T_c \left(\frac{\partial H_c}{\partial T} \right)_{T=T_c}^2. \quad (1.1)$$

²⁸ W.H. Keesom, J.A. Kok, Proc. 35 (1932) 743, *Comm.* 221e (1932) and *Physica* 1 (1934) 175

²⁹ W.H. Keesom, *Commun. Suppl.* 75a (1933)

³⁰ P. Ehrenfest, *Commun. Suppl.* 75b (1933)

³¹ A.J. Rutgers, *Physica* 1 (1934) 1055

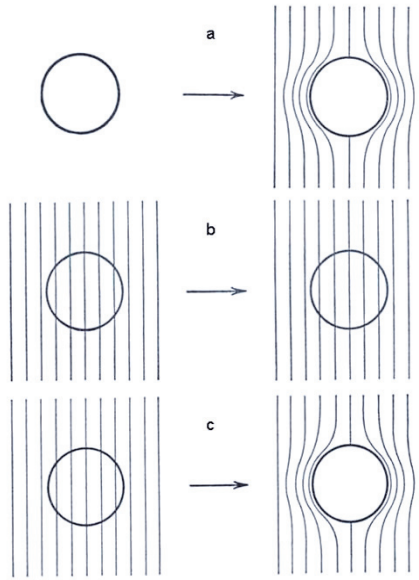


FIGURE 1.10: Difference between perfect conductor (a and b) and perfect diamagnetic (c). From left to right: a) sample cooled in zero field to T below T_c , then a magnetic field is applied. Magnetic induction B remains zero. b) Sample brought into magnetic field while in the normal state, then cooled to T below T_c . B doesn't change. c) Perfect diamagnetic brought into magnetic field $H \ll H_c(0)$ while in the normal state, then cooled through $T_c(H)$. At the transition to the superconducting state the magnetic field is spontaneously expelled.

That prediction agreed beautifully with the available experimental results for tin, and later for thallium as well³². Rutgers was a rather prudent person and did not want to publish his equation before it was certain that the transition of a superconductor was indeed a reversible transition between thermodynamic equilibrium phases. Cornelis Gorter, a student of De Haas, was more aware of the urgency of the developments and quoted Rutgers's findings in a pioneering thermodynamic analysis which he published in the spring of 1933³². To the regret of for instance Fritz and Heinz London³³, Gorter published his paper in the *Archives of the Teyler Museum in Haarlem*, an institution by which he was employed at the time³⁴. This guaranteed fast publication, but was also rather inaccessible. A later publication in *Physica* with Casimir as coauthor³⁵ included most of the contents of the paper in the archive.

In the first place, Gorter emphasized that the transition from the normal to the superconducting state in an applied magnetic field could be interpreted only in a simple way, if a configuration was chosen in which demagnetization effects would not play a role, for instance, a long wire with the axis parallel to the applied field. Only then, the destruction of superconductivity would occur sharply, in a well-defined way. Such a sharp transition was indeed observed in the experiments of De Haas and Voogd³⁶ on single crystals in the "longitudinal" configuration with much larger dimensions in the direction of the field than in the transversal directions. Moreover, the experimental data of Kok and Keesom²⁸ restricted him in his thermodynamic analysis to consider only those closed

³² C.J. Gorter, *Arch. Mus. Teyler* 7 (1933) 378

³³ G. Rickhayzen, *Theory of Superconductivity*, Wiley, New York, 1964, Chapter 1

³⁴ C.J. Gorter, *Rev. Mod. Phys.* 36 (1964) 3

³⁵ C.J. Gorter, H. B.G. Casimir, *Physica* 1 (1934) 306

³⁶ W.J. de Haas, J. Voogd, *Proc.* 34 (1931) 51, 192, *Comm.* 212c and 214c (1931)

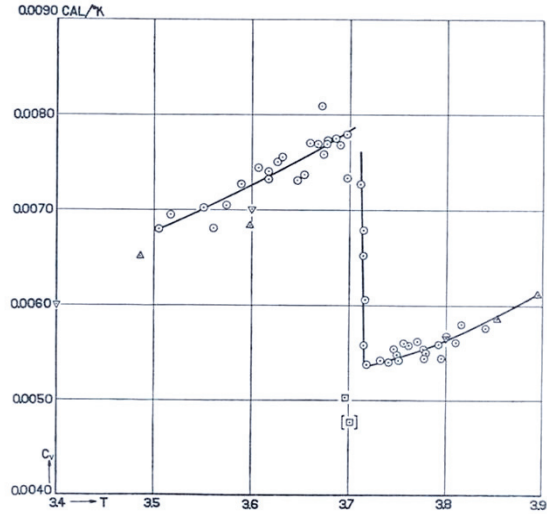


FIGURE 1.11: Temperature dependence of the specific heat of tin measured in ambient magnetic field; the first clear evidence of a jump in c at the superconducting transition²⁸.

rectangular loops in the $H - T$ diagram which contained the zero-field transition between normal and superconducting states. Following the loop in clockwise direction starting above T_c and going along $H = 0$, that automatically resulted in a superconducting state in which the induction $\mathbf{B} = 0$. That, according to Fritz London, “came very close to predicting the Meissner effect³⁷.”

Under these conditions the validity of Rutgers’s equation was equivalent to the statement that the second law of thermodynamics ($dQ/T = dS$) would apply for the transition in a magnetic field and that the transition would be reversible. Finally, Gorter concluded that in transversal field configurations (i.e., non-zero demagnetization) superconductivity would be destroyed in some parts of the specimen, while it could persist in other parts. Later on, this sequence of normal and superconductive layers was coined the “intermediate state”.

Within the above assumptions Gorter could compute the difference in free energy between the superconductor in zero field and that in the normal state by integrating the specific heat data of Keesom and Kok down from a temperature above T_c . From that calculation he obtained the field at which superconductivity would become thermodynamically unstable avoiding the discussion about the expected irreversibility of the field induced transition to the normal state³⁴. The good agreement with the measured data justified his approach from which the famous expression followed for the condensation free energy per unit volume, $\Delta f = f_s - f_n = -\mu_0 H_c^2(T)/2$.

Diamagnetics

At the end of the 1920s, new very-low-temperature facilities outside Leiden were founded and with that also new ideas for experiments emerged. At the Physikalisch-Technische Reichsanstalt (PTR) in Berlin Walther Meissner started to investigate the nature of the current distribution in superconducting cylinders in an applied transversal magnetic field³⁸. Assisted by Ochsenfeld he wanted to detect the changes in the magnetic field strength between two parallel, cylindrical su-

³⁷ F. London, *Superfluids*, vol. I, Dover, New York (1961) §2; 1st edition, John Wiley, New York (1950)

³⁸ W. Meissner, R. Ochsenfeld, *Naturwissenschaften* 21 (1933) 787

perconductors as they passed the transition to the superconducting state. In fact, Max von Laue, who was consultant at the PTR, had proposed to do the experiments and also assisted by calculating the expected field distribution outside the cylinders. Figure 1.12 shows the experimental set-up. A tiny search coil b , 1 mm wide and 15 mm long, probed the magnetic field strength between the mono-crystalline tin cylinders which were connected in series carrying a current J . The search coil was connected to a ballistic galvanometer and by flipping it over 180° the local field could be determined. When cooled through the superconducting transition a clear jump in the measured field strength was detected, indicating that the magnetic flux which had penetrated the cylinders in the normal state was entirely expelled from them at the transition to the superconducting state. On the other hand, no change was seen when the search coil was placed inside a hollow superconductor. They repeated the experiment by investigating several long, hollow, thick-walled cylinders in different external field configurations and each time confirmed that for pure superconductors the magnetic field distribution corresponded to zero induction in the bulk of the superconductor independent of the initial conditions (see Figure 1.10c). It implied that inside a superconductor an external magnetic field had to be completely compensated by the field generated by (super) currents in a layer at the surface.

The Meissner-Ochsenfeld effect came as a complete surprise and one can indeed state that $\mathbf{B} = 0$ signified a turning point in the history of superconductivity. It meant that a superconductor is not only a perfect conductor, it is above all a perfect diamagnetic. The theoretical implications are illuminated in Figure 1.10c: the magnetic flux should be spontaneously expelled from the pure superconductor. However, in practice, small impurities or inhomogeneities of the material can be sufficient to suppress the appearance of the perfect Meissner effect. In such “non-ideal” conditions frozen-in flux had been found. The shape of the specimen and the field configuration without demagnetizing turned out to be of importance; both are needed for the establishment of the pure Meissner effect. Moreover, being a purely magnetic effect, it was hard to recognize by relying only on resistivity experiments as was done by De Haas and collaborators. That probably was the reason why that fundamental phenomenon remained hidden for so many years.

Zero Induction

Immediately after the appearance of Meissner’s article its implications were picked up by Gorter³⁹. He wrote in a short letter to *Nature*: “A few weeks ago, Meissner and Ochsenfeld published a series of very interesting observations on the establishment of

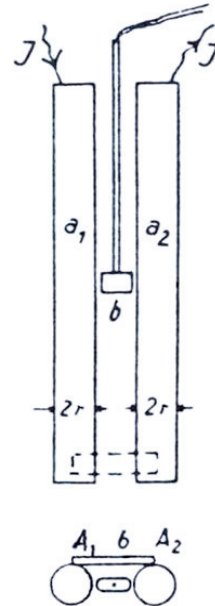


FIGURE 1.12: The Meissner-Ochsenfeld experimental setup (top and side view)³⁸. The pick-up coil b measured the magnetic field distribution between two monocrystalline tin cylinders. In that first experiment the cylinders were connected in series and a current I was applied (adapted from W. Meissner and F. Heidenreich, *Phys. Z.* 37 (1936) 451).

³⁹ C.J. Gorter, *Nature* 132 (1933) 931

superconductivity in a constant external field. Their results seem to indicate that in a superconductor B always equals 0." This point was indeed the missing link in his thermodynamic analysis earlier that year. The great importance of the Meissner-Ochsenfeld paper was immediately clear, but it also initiated a lot of scientific debates, since Gorter's interpretation was less obvious and not immediately accepted. While reading in Dahl's extensive history on superconductivity⁸ about the vivid discussions at the small conferences and meetings organized in 1933–1934, one gets the impression of surprisingly great difficulties in distinguishing between thermodynamic equilibrium ((i.e.) the Meissner state) and metastable equilibrium (i.e., flux conservation due to persistent currents). That caused a lot of confusion about the phenomena observed in the many beautiful experiments of Meissner and others, for instance, that no effect was seen in the detected magnetic field inside the hole of a hollow superconductor when the external field was changed.

Equally remarkable was the doubt about the relation between the jump in the specific heat at T_c and a phase transition of the second kind. To elucidate the characteristics of a second order phase transition, Gorter in 1934 introduced a model⁴⁰ to illuminate the reasoning leading to the Keesom-Ehrenfest relations^{29,30}. It goes as follows: suppose a vessel contains a small amount of liquid and its saturated vapor. The vessel is opaque so that the experimenter does not know what is happening inside, but he starts adding heat and measures the heat capacity. That consists of small contributions of the liquid and its saturated vapor, and a large contribution due to the evaporation of the liquid. If at T_c the evaporation of the last droplet takes place, it is clear that the heat capacity of the vessel will drop sharply to a lower value. The model also illustrates the notion of a free energy of condensation: when the temperature is lowered through T_c a gradual internal condensation takes place which finishes at $T = 0$. The amount of condensation energy follows from the area below the $\Delta c(T)$ curve.

The dispute about the interpretation of the Meissner-Ochsenfeld effect was eventually settled by a convincing experiment by Stark and Steiner.⁴¹ They fabricated a hollow cylinder of superconducting material and wound a pick-up coil with the windings going through the hole and connected that to a ballistic galvanometer. The magnetic field caused by a current flowing along the length of the superconductor was thus embraced by the coil. Upon switching on the current in the normal state a ballistic deflection was observed which was equal but opposite to the signal that was detected when the superconductor was cooled through its transition temperature, proving unambiguously that both the field and the current were expelled from the bulk of the superconducting cylinder.

The thermodynamics of superconductors was further confirmed by experiments of Kok, Van Laer and Keesom⁴². Simple expressions for the differences in entropy and specific heat along the threshold curve were obtained by substituting the quadratic formula for $H_c(T)$. For instance, the apparent T^3 behavior of the electronic specific heat in the superconducting state followed as a natural result. Nevertheless, Kok also noted that considerable deviations from the parabolic $H_c(T)$ curve could be observed for lead and mercury indicating that the quadratic behavior was not a law of nature⁴².

Two Electron Fluids

Gorter and Casimir⁴³ extended their thermodynamic treatment in a subsequent paper in which they introduced a phenomenological two-fluid model which was based on two general assumptions:

- a) The superconductor possesses an ordered internal state, the condensed state, and its free energy F_c is characterized by an internal order parameter $x_s(T)$ that represents the fraction of (superconducting) electrons condensed in the superconducting state; $x_s(T)$ varies from zero at T_c to unity at $T = 0$.

⁴⁰ W.H. Keesom, *Helium*, Elsevier, Amsterdam (1942) Section 5.32

⁴¹ J. Stark, K. Steiner, *Phys. Z.* 18 (1937) 277

⁴² J.A. Kok, *Nature* 134 (1934) 532; *Physica* 1 (1934) 1103; W.H. Keesom, P.H. van Laer, *Physica* 5 (1938) 193

⁴³ C.J. Gorter, H.B.G. Casimir, *Phys. Z.* 35 (1934) 963

- b) Because the superfluid fraction of condensed electrons x_s is completely ordered, it possesses no entropy. Therefore, the entropy of the system is entirely due to the non-condensed normal electrons indicated by a fraction $1 - x_s$ with free energy F_{nc} .

The two interpenetrating fluids were not supposed to be independent, which was taken into account by assuming that the thermodynamic functions of the normal fluid were proportional to some power of the normal fraction, $(1 - x_s)^r$, instead of being simply linearly proportional. With this arbitrary choice, the free energy took the form $F = x_s F_c(T) + (1 - x_s)^r F_{nc}(T)$ and by substituting $r = 1/2$ a satisfactory fit to the experimental results was obtained, especially the T^3 dependence of the specific heat. The function $F_c(T)$ was taken independent of T to assure that the superconducting condensate had no entropy. By minimizing F with respect to x_s the equilibrium value $x_s(T) = 1 - (T/T_c)^4$ was obtained, in addition to simple expressions for the thermodynamic quantities such as entropy and specific heat.

The theory of second order phase transitions was soon extended fundamentally by Landau in 1937.⁴⁴ It also played an important role in the phenomenological Ginzburg-Landau theory of superconductivity⁴⁵ (see the theory chapter in this book). In his famous paper of 1941 on the two-fluid description of liquid helium⁴⁶ Landau stressed that the fundamental property of that model is the simultaneous existence of two motions, a superfluid flow and a normal flow, rather than two species of particles, one with a “super” and the other with a “normal” label. And that principle should also hold for the corresponding two-fluid picture of superconductivity. In analogy to Kapitza’s experiment which showed a heat deficiency for superfluid helium streaming out of a superleak, Landau concluded that the supercurrent could not transfer heat. That phenomenon was supported by the absence of thermo-electric effects in superconductors⁴⁷.

London Equations

The Meissner effect proved that a superconductor in a magnetic field was in a single, thermodynamically stable state, at least, in absence of holes inside the material in which magnetic flux could be trapped. In order to describe the electromagnetic behavior of a pure superconductor within the Maxwell theory, one could try to replace Ohm’s law by a relation that would hold for the superconducting condensate. Such an equation should give complete diamagnetism, $\mathbf{B} = 0$, for a bulk superconductor in a longitudinal magnetic field, as well as for a superconducting wire with a transport current going through it. The brothers Fritz and Heinz London were the first to make this very important step⁴⁸. They proposed to introduce the relation (known as the 2nd London equation)⁴⁹

$$\text{curl } \Lambda \mathbf{j}_s = -\mathbf{B} \quad (1.2)$$

where $\Lambda = m/n_s e^2$ was a positive constant characteristic of the superconductor. By taking the curl on both sides and eliminating \mathbf{j}_s by applying $\text{curl } \mathbf{B} = \mu_0 \mathbf{j}_s$ (ignoring displacement currents) they obtained $\Lambda \mu_0^{-1} \text{curl curl } \mathbf{B} = -\mathbf{B}$. Since $\text{div } \mathbf{B} = 0$ that yielded

$$\Lambda \mu_0^{-1} \Delta \mathbf{B} = \mathbf{B}, \quad (1.3)$$

where Δ denotes the Laplace operator. The prefactor on the left defines a typical length scale, the London penetration depth, $\lambda_L = (\Lambda/\mu_0)^{1/2} = (m/\mu_0 n_s e^2)^{1/2}$. The above screening equation explained

⁴⁴ L.D. Landau, *Phys. Z. Soviet Union* 11 (1937) 26 and 545

⁴⁵ V.L. Ginzburg, L.D. Landau, *Zh. Eksperim. i Teor. Fiz.* 20 (1950) 1064

⁴⁶ L.D. Landau, *J. Phys. U.S.S.R.* 5 (1941) 71

⁴⁷ W.H. Keesom, C.J. Matthijs, *Physica* 5 (1938) 437 and earlier work quoted in that paper.

⁴⁸ F. London, H. London, *Proc. Roy. Soc. A* 149 (1935) 71; *Physica* 2 (1935) 341

⁴⁹ F. London, *Proc. Roy. Soc. A* 152 (1935) 24

the Meissner effect since it gave a local induction inside the superconductor that decays exponentially from its value at the surface $\mu_0 \mathbf{H}_e = \mathbf{B}_e$ to zero over a length of order λ_L which at zero temperature is about 10^{-4} mm. Also the supercurrent density was confined to the same thin surface layer. Historically, (1.2) was justified by considering the condensate of superconducting electrons and to apply an electric field E which would accelerate the superfluid according to $m\partial\mathbf{v}_s/\partial t = -e\mathbf{E}$. Together with $\mathbf{j}_s = -n_s e\mathbf{v}_s$, that yielded the first London equation

$$\frac{\partial \Lambda \mathbf{j}_s}{\partial t} = \mathbf{E}. \quad (1.4)$$

That equation alone leads to a screening equation in $\partial\mathbf{B}/\partial t$ with exponential decaying spatial solution in $\mathbf{B} - \mathbf{B}_0$, where \mathbf{B}_0 is the induction frozen in at the transition to the superconducting state.²⁷ In his first paper Gorter³² could get the thermodynamics right by choosing $\mathbf{B}_0 = 0$, but not the electrodynamics. That required the invention of the 2nd London equation (1.2). By introducing the vector potential \mathbf{A} , defined by $\mathbf{B} = \text{curl } \mathbf{A}$ and $\mathbf{E} = -\partial\mathbf{A}/\partial t - \text{grad } \phi$, (1.2) resulted in

$$\Lambda \mathbf{j}_s = \mathbf{A} \quad (1.5)$$

for a simply connected superconductor applying the appropriate (London) gauge. Finally, by substituting the empirical Gorter-Casimir temperature dependence for the density of superconducting electrons, $n_s(T)/n = x_s(T) = 1 - (T/T_c)^4$, it followed that the penetration depth very near T_c should diverge as $\lambda_L(T) = (\lambda_L(0)/2)/(1 - (T/T_c))^{1/2}$, expressing the loss of screening capability with decreasing density of superconducting electrons.

Penetration Depth

Being very small, the penetration depth could not be easily measured. The first to succeed was Shoenberg in Cambridge in 1939.⁵⁰ By using very fine-grained colloidal mercury and in virtue of the strong increase of λ_L near T_c he could determine the change in the magnetic susceptibility due to the temperature dependence of λ_L . The comparison with the theoretical temperature dependence displayed in Figure 1.13 turned out to be very good. However, the non-uniform grain size did not allow to accurately determine the value of $\lambda_L(0)$. Using better experimental techniques, Shoenberg and collaborators could eventually, in 1947, measure $\lambda_L(0)$ of a 20 μm thin mercury cylinder and got $7.6 \times 10^{-2} \mu\text{m}$, quite close to the estimated theoretical value.

Subsequently, Pippard⁵¹ realized a tenfold increase of sensitivity by using microwave techniques that became available after World War II. He could therefore investigate the effect of the electron mean free path on the penetration depth by alloying tin with indium⁵².

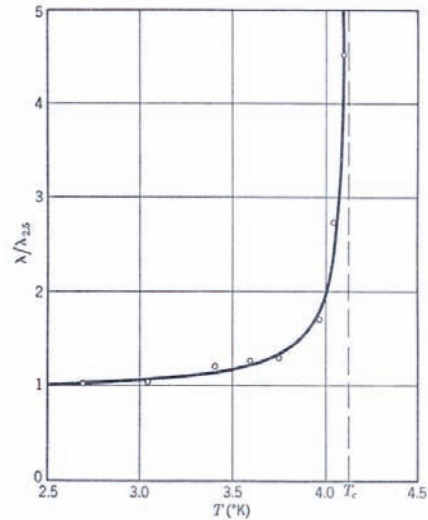


FIGURE 1.13: The temperature dependence of the penetration depth as determined by D. Shoenberg from measurements of the magnetic susceptibility of very fine grained colloidal mercury⁵⁰.

⁵⁰ D. Shoenberg, *Nature* 43 (1939) 433; *Proc. Roy. Soc.* A175 (1940) 49

⁵¹ A.B. Pippard, *Proc. Roy. Soc.* A191 (1947) 747

⁵² A.B. Pippard, *Proc. Roy. Soc.* A216 (1953) 547

It turned out that the simple local relation between \mathbf{j}_s and \mathbf{A} of (1.5) had to be amended for nonlocal effects according to:

$$j_s(r) = \int_V K((r-r')/\xi)A(r')dr'. \quad (1.6)$$

That is, the current density in a certain point r depends on the vector potential in a sphere around this point. The radius of the sphere is determined by the length scale over which the kernel $K(\mathbf{r}, \mathbf{r}')$ decays exponentially from unity in the center to $1/e$. In a superconductor this length scale, *the coherence length* ξ , represents the distance in which the amount of order of the superconducting condensate can change. In a pure superconductor this length scale is about equal to the coherence length ξ_0 introduced by Pippard. A few years later it was recognized that ξ_0 could be interpreted as the size of a Cooper pair. Using the Heisenberg uncertainty principle Pippard could estimate $\xi_0 \approx \hbar v_F / k_B T_c$, where v_F is the Fermi velocity. In 1953 he could explain with that formalism the deviations from the London theory that occurred when the coherence length was larger than the penetration depth. That happened to be the case in many pure elemental superconductors. Also the effect of changing the mean free path l by alloying could be qualitatively understood. Tin alloyed with a small amount of indium turned out to have a much greater penetration depth, without changing the thermodynamic properties like the critical temperature. Pippard proposed that the decrease of the mean free path would reduce the coherence length due to the extra scattering of electrons by the impurity ions and argued that $\xi^{-1} \approx \xi_0^{-1} + l^{-1}$.

Quantum Connection

Already in 1935 London had discussed a possible, quantum mechanical justification of the two London equations, referring to ideas of Bloch, Frenkel, and Landau⁵³. In 1948 he came back to this issue⁵⁴. The essential feature of superfluidity and superconductivity is, according to London, an internal condensation of a macroscopic number of particles in a single macroscopic ground state described by a macroscopic wave function. He further suggested that this state is characterized as “a kind of condensed state in momentum space which implies long-range order of the [average] momentum vector $\mathbf{p}_s = m\mathbf{v}_s - e\mathbf{A}$ in ordinary space [...]”⁵⁴. According to a theorem of Bloch (see, for a discussion, Reference 53, section 2.6), the wave function should be rigid upon applying a magnetic field, which for a singly connected isolated superconductor implied $\mathbf{p}_s = 0$, or $m\mathbf{v}_s = e\mathbf{A}$. By taking the curl or the time derivative of both sides, (1.2), (1.4), and (1.5) could be derived.

London also showed that $\mathbf{p}_s = \hbar \text{grad } \varphi$, where φ is the uniquely determined phase of the macroscopic wave function. He realized that this relation had very interesting physical consequences for multiply connected superconductors as, for instance, a hollow cylinder, because the macroscopic wave function should be single valued in any point. Consequently, the phase φ should change by 2π with each complete turn around the hole. If the circulation of \mathbf{p}_s was computed along a path around the hole, but inside the superconductor so that $\mathbf{v}_s = 0$, it immediately followed that the magnetic flux Φ enclosed by the path is quantized. As is well known, London^{37,54} predicted the flux quantum to be $\Phi_0 = h/e$, whereas it followed from the microscopic theory⁵⁵ that one should expect $h/2e$ because the superconducting electrons are bound in Cooper pairs⁵⁶. That prediction was confirmed in the beautiful experiments of Deaver and Fairbank⁵⁷ and of Doll and Näbauer⁵⁸ in 1961 (see Section 3.2 in Chapter 3).

⁵³ L. Hoddeson, E Braun, J. Teichmann, S. Weart (ed.), *Out of the Crystal Maze*, Oxford University Press, New York (1992)

⁵⁴ F. London, *Phys. Rev.* 74 (1948) 562

⁵⁵ J. Bardeen, L.N. Cooper, J.R. Schrieffer, *Phys. Rev.* 108 (1957) 1175

⁵⁶ L.N. Cooper, *Phys. Rev.* 104 (1956) 1189

⁵⁷ B.S. Deaver, W.M. Fairbank, *Phys. Rev. Lett.* 7 (1961) 43

⁵⁸ M. Doll, M. Näbauer, *Phys. Rev. Lett.* 7 (1961) 51; *Z. Physik* 169 (1962) 526

Crucial Developments

In the beginning of the 1950s a few crucial experiments helped to clarify the true mechanism of superconductivity. Those results had a major impact on the eventual development of the microscopic theory by Bardeen, Cooper and Schrieffer⁵⁵. Improved experimental techniques enabled Maxwell and Reynolds et al. to measure independently a small shift in the critical temperature as a function of the isotope mass of the mercury lattice⁵⁹; the lighter the mass of the isotopes the higher was T_c . That isotope effect indicated that the electron-phonon interaction played a crucial role and confirmed the conjecture made in 1950 by Fröhlich⁶⁰. Those experiments were soon repeated on tin isotopes and demonstrated the predicted square root dependence on the isotope mass M , $T_c \sim M^{-1/2}$ with high precision⁶¹.

A second series of high sensitivity experiments revealed the true behavior of the electronic specific heat c_{es} at very low temperatures. The T^3 dependence observed in the 1930s that so nicely fitted in the phenomenological two-fluid model, turned out to transpose at the lower temperatures into an exponential temperature dependence

$$c_{es} = \gamma T_c a \exp(-bT_c/T), \quad (1.7)$$

where γT is the electronic specific heat in the normal state, and a and b are constants of order unity. Within a few years (1953–1956) the exponential temperature dependence was found in several elements, first in vanadium by Corak et al.⁶² and later also in niobium and tin. It confirmed the existence of an energy gap Δ of order $k_B T_c$ in the electron excitation spectrum at the Fermi level between the superconducting ground state and the normal quasi-particle excitations. Fritz and Heinz London had already suggested the existence of such a gap in 1935⁴⁸ and experimental indications were first provided by Daunt and Mendelssohn in 1946.⁶³ Measurements of electromagnetic absorption in the far-infrared on thin superconducting films by Glover and Tinkham⁶⁴ definitively established the existence of an energy gap. Not only c_{es} , but also the entropy of the electrons goes exponentially to zero as the growing ratio between energy gap and temperature reduces the number of electronic excitations at low temperatures.

1.1.3 Superconductive Alloys, the Spongy Road to Type II Superconductors.

The hope of utilizing superconductivity began to rise again when De Haas and coworkers in Leiden started to investigate the behavior of superconducting alloys in a magnetic field. They found that superconductivity could survive in significantly stronger magnetic fields than were known for elemental superconductors. The most striking example was the eutectic of the lead-bismuth alloy ($\text{Pb}_{65}\text{Bi}_{35}$) with a threshold field of 1.4 T at 4.2 K, and even 2.1 T at 1.9 K.⁶⁵ On the other hand, when the critical current of a 0.3 mm diameter wire made of the same alloy was measured at 4.2 K a self field of only 30 mT was observed for a current of 23 A, and in an applied transverse field of 55 mT the wire could carry a current of only 11 A.⁶⁶ That was the more disappointing because the threshold field was expected to be 1.6 T. Clearly, the limiting behavior was not well understood.

⁵⁹ E. Maxwell, *Phys. Rev.* 78 (1950) 477; C.A. Reynolds et al., *Phys. Rev.* 78 (1950) 487

⁶⁰ H. Fröhlich, *Phys. Rev.* 79 (1950) 845; see also H. Fröhlich, *Proc. Roy. Soc. A*215 (1952) 291; J. Bardeen, D. Pines, *Phys. Rev.* 99 (1955) 1140

⁶¹ W.D. Allen, R.H. Dawton, J.M. Lock, A.B. Pippard, and D. Shoenberg, *Nature* 166 (1950) 1071, and W.D. Allen, R.H. Dawton, M. Bär, K. Mendelssohn, and J.L. Olsen, *Nature* 166 (1950) 1072

⁶² W.S. Corak, B.B. Goodman, C.B. Satterthwaite, and A. Wexler, *Phys. Rev.* 96 (1952) 1442

⁶³ J.G. Daunt and K. Mendelssohn, *Proc. Roy. Soc. A*185 (1946) 225

⁶⁴ R.E. Glover, M. Tinkham, *Phys. Rev.* 104 (1956) 844; 108 (1957) 243

⁶⁵ W.J. de Haas, J. Voogd, *Proc.* 33 (1930) 262 and 34 (1931) 56, *Comm.* 208b (1930) and 214b (1931)

⁶⁶ W.H. Keesom, *Physica* 2 (1935) 35

In a quite different experimental approach De Haas and Casimir-Jonker⁶⁷ studied the penetration of a transverse magnetic field in Bi_5Tl_3 and $\text{Pb}_{35}\text{Tl}_{65}$ samples. They prepared cylindrical rods and along the central axis was a narrow cavity which contained a bismuth wire with current and voltage leads. The resistance of bismuth is very sensitive to magnetic fields and a change of its resistance therefore revealed the penetration of field. We reproduced their results in Figure 1.14. The data points denote the fields at which penetration was first detected. They noted that on both sides of that critical field line the sample remained superconducting which was quite remarkable. They also depicted a shaded region in which the “resistance was gradually coming back rising to its value in the normal state.” Moreover, when the field was switched off, the resistance of the bismuth wire did not come back to its original value, indicating trapped magnetic induction in the cavity. Also Keeley, Mendelssohn, and Moore in Oxford had found magnetic hysteresis when pure lead was alloyed with only 4% bismuth⁶⁸.

Today, we know that these features are typical for type II superconductors with weak flux pinning and that—taking into account demagnetization—the lower line in the figure denotes half the lower critical field $H_{c1}(T)$ and the highest line represents the upper critical field $H_{c2}(T)$. A simple estimate from these data tells us that the Ginzburg-Landau parameter κ (see Chapter 2) of the Pb_5Tl_3 alloy must have been at least 3.0. Groups in Oxford⁶⁸, Toronto, and Kharkov reported similar behavior for alloys. Most prominent were the results of Shubnikov and coworkers at the Ukrainian Physical-Technical Institute in Kharkov^{69,70}.

Shubnikov was an authority in growing single crystals from the melt. This was the reason that De Haas invited him to work at his laboratory in Leiden. In 1926 he moved from Leningrad to Leiden where he set up the growth facility for the very pure bismuth single crystals in which he found the magnetoresistance oscillations, now known as the Shubnikov-De Haas effect. The bismuth wires used by Casimir-Jonker to probe the field penetration were actually made by Shubnikov. In 1930 he moved to Kharkov where he built up his own low temperature laboratory.

Two Types of Superconductors

Shubnikov must have been an excellent experimentalist. He developed a technique to measure the magnetic moment by rapidly withdrawing the sample from a coil surrounding it, which resulted

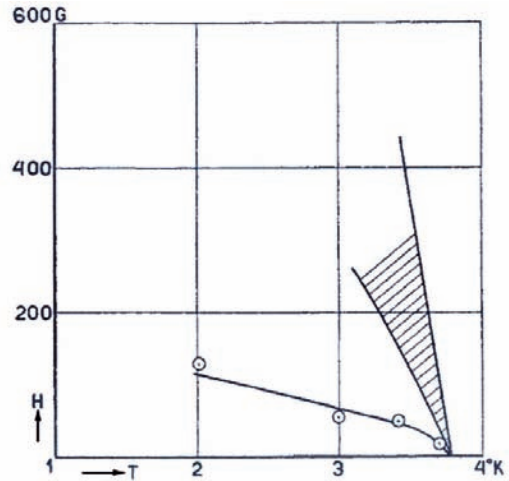


FIGURE 1.14: De Haas and Casimir-Jonker using the bismuth-wire technique, demonstrated the penetration of a transverse magnetic field into a sample of Bi_5Tl_3 .⁶⁷ The data points denote the fields at which penetration was first detected. On both sides of the line through the data the sample remained superconducting. The shaded area depicts the region in which the resistance was gradually rising to its normal state value.

⁶⁷ W.J. de Haas, J.M. Casimir-Jonker, *Nature* 135 (1935) 30; *Physica* 2 (1935) 935

⁶⁸ T.C. Keeley, K. Menselsohn, J.R. Moore, *Nature* 134 (1934) 773

⁶⁹ J.N. Ryabinin, L.V. Shubnikov, *Phys. Z. Sowjet Union* 7 (1935) 122; *Nature* 135 (1935) 581.

⁷⁰ See especially the more extensive review co-authored by V.I. Khotkevich and Yu.D. Shepelev in the memorial issue of the *Ukr. J. Phys.* 53 (2008) 42-52 with the English translation of the paper that originally appeared in *Zh. Eksp. Teor. Fiz.* 7 (1937) 221

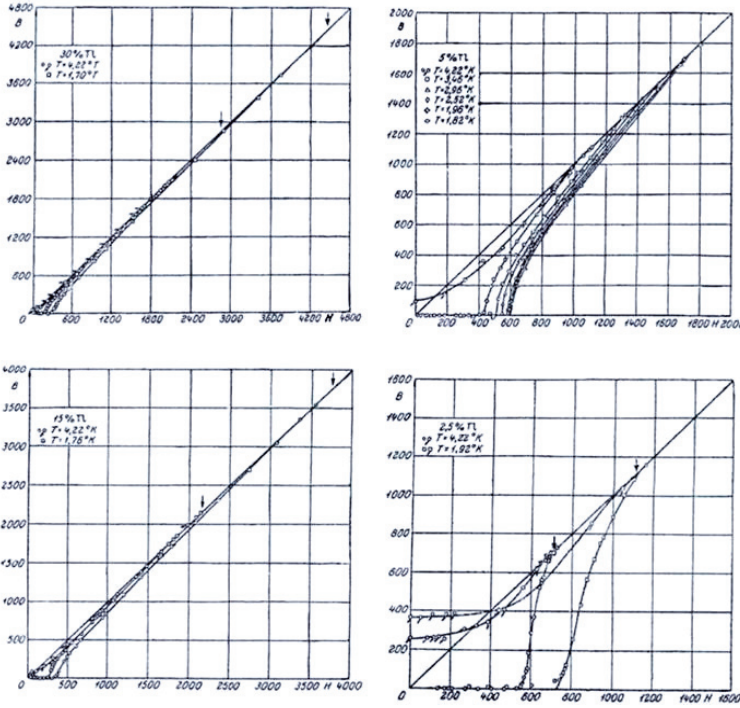


FIGURE 1.15: The $B(H)$ curves measured by Shubnikov and Ryabinin^{69,70} at several temperatures for single crystals made of $\text{Pb}_{1-x}\text{Tl}_x$ alloys with various compositions (only the results for $x = 0.3, 0.15, 0.05,$ and 0.025 are depicted here). Below the lower critical field H_{c1} the samples behaved as for a pure superconductor (no flux penetration, in accord with the Meissner effect, $B = 0$). Above H_{c1} flux started to penetrate until eventually at and above the upper critical field H_{c2} (denoted by the arrows) $B = H$. The symbols with a dash represent the data obtained in decreasing field. The observed hysteresis was most pronounced at low fields and for the lowest Tl concentrations.

in a deflection of the connected ballistic galvanometer. This method worked very well as he earlier demonstrated by obtaining the $B(H)$ curve of a poly-crystalline rod of Pb, thereby convincingly confirming the Meissner effect⁷¹. Directly measuring the magnetization gave substantially more information about the magnetic behavior than the techniques used by De Haas. This can be seen in Figure 1.15 where some $B(H)$ curves for increasing and decreasing fields at several temperatures are plotted for single crystals of PbTl alloys of various compositions^{69,70}. We immediately recognize the generic features of type II superconductors with κ values ranging between 1 and 5. Some hysteresis in the decreasing field curves due to weak flux pinning is also observed. The $H - T$ phase diagram resulting from one of these experiments (for a PbTl_2 single crystal) is given in Figure 1.16. The lower curve displays the field obtained from critical currents measured in wires of the same alloy in absence of an applied field. The dependence on the wire diameter showed that the superconductivity was destroyed by the field generated by the current at the surface of the wire. The value is low compared to the thermodynamic critical field and in retrospect we know that it actually should be closer to H_{c1} . It is amazing that such beautiful data were so long ignored. Although they were

⁷¹ J.N. Ryabinin, L.V. Shubnikov, *Nature* 134 (1934) 286

extensively discussed in Shoenberg's book⁷², it took 22 years before the theory that fully explained their meaning was published⁷³.

In one of his papers Shubnikov mentioned the results of specific heat measurements in a $\text{Pb}_{65}\text{Bi}_{35}$ alloy published earlier⁷⁴. There was no appreciable jump at T_c , which is remarkable since the slope of the threshold curve was so large. He concluded that the specific heat and the magnetic measurements were not in agreement with Gorter's theory³². Probably, Gorter wouldn't have denied this conclusion because he realized that the difference between dirty-alloy and pure-elemental superconductors must have had a deeper reason which he tried to understand on thermodynamic grounds⁷⁵, rather than blaming it on concentration variations and the "freezing in of flux" in "rings formed by regions of higher threshold value" as in Mendelssohn's sponge model⁷⁶. Quoting Per Dahl (reference 8, p.219): "This tenacious, albeit in the long run counterproductive model, was destined to exert an authoritative influence out of proportion to its worth for over two decades [...] distracting investigators from the final formulation of the theoretical underpinning of high-field superconductivity and discouraging concomitant progress in realizing the potentially enormous current densities that were then within sight." It is indeed strange that the sponge model remained so influential for over two decades, because one would expect that any of the typical length scales of superconductivity should play a role in comparison to the length scales of the material inhomogeneities that give rise to the hypothetical, multiply-connected superconducting sponge structure.

Gorter proposed the possibility of a fine partition in superconducting and normal regions (s- and n-regions) and argued that "there exists a minimum size k for the superconductor" (today we would identify k with the coherence length ξ). To avoid confusion we further will use ξ , and that the condensation energy "would decrease considerably as soon as the dimensions of the s-regions would become of the order of ξ ⁷⁵." Secondly, if the dimensions of the superconductive regions would become of the order of the penetration depth λ , the energy related to the screening will decrease. If now $\xi > \lambda$, there will be no tendency to form very small superconductive regions, and as soon as $H > H_c$ every trace of superconductivity will vanish. This appears to be on the whole in agreement with the behavior of single crystals of very pure metals. If, however, $\xi < \lambda$, small superconducting regions will be possible even at fields which are stronger than H_c . Gorter even estimated a value for the upper critical field, namely $(\lambda/\xi)H_c$. Above this value the small superconductive "blades or drops [...] will

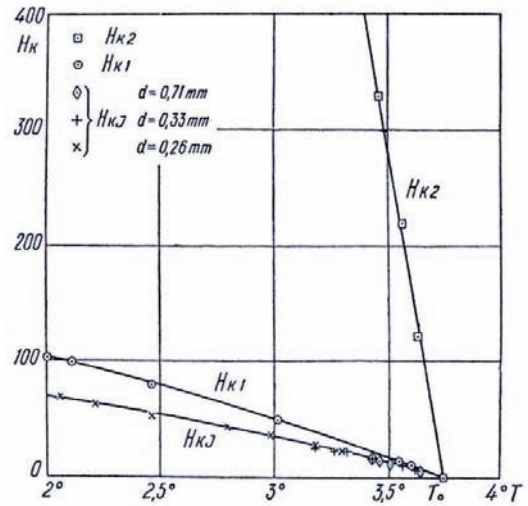


FIGURE 1.16: Phase diagram of PbTl_2 showing the lower and upper critical field data (H_{k1} and H_{k2} in Shubnikov's notation⁷⁰) as well as the data determined from the critical current measurements on wires of the same material with different diameters, H_{kJ} .

⁷² D. Shoenberg, *Superconductivity* (University Press, Cambridge, 1st edition 1938, 2nd edition 1952)

⁷³ A.A. Abrikosov, *Zh. Eksperim. i Teor. Fiz.* 32 (1957) 1442 [*Soviet Phys. - JETP* 5 (1957) 1174]

⁷⁴ L.V. Shubnikov, W.J. Khotkevich, *Phys. Z. Sowjet Union* 6 (1934) 605

⁷⁵ C.J. Gorter, *Physica* 2 (1935) 449

⁷⁶ K. Mendelssohn, *Proc. Roy. Soc. A* 152 (1935) 34

become impossible [...] and superconductivity will vanish entirely.” As we now know, this was very close to Abrikosov’s prediction⁷³. However, we should as well note here that Gorter concluded by saying that “these remarks [...] do not even offer a suggestion why λ should be especially large or ξ especially small for an alloy⁷⁵.”

Surface Energy

Almost at the same time Heinz London in Oxford⁷⁷ showed that the threshold field H_t in a thin superconducting layer parallel to the field and of thickness $d < \lambda$ is larger than H_c of the bulk, namely $H_t = (\lambda/d)H_c$. Measuring H_t would thus provide a way to determine the penetration depth. From that result London says “one is tempted to conclude that every superconductor in a magnetic field above H_c should split up into a great number of thin, superconducting laminae or fibres separated from each other by thin normal conducting regions, as then the superconductivity could persist at these higher fields.” He referred to Gorter’s paper, but ignored the possible role of a second length scale that comes into play at the interface between superconducting and normal regions, thus always obtaining a negative interface surface energy.

The question of the surface energy was taken up again in 1951 by Pippard^{78,51} who now explicitly introduced the coherence length expressing the range in which the gradual transition takes place from the ordered superconducting state to the disordered normal state, in contrast to the abrupt jump at the interface that was tacitly assumed in earlier discussions. (He apparently missed Gorter’s paper, but corrected that later in a very interesting historical overview which has been reprinted as the next contribution in this centennial book.) Pippard continued by discussing the relation between the surface energy of an n-s interface and the purity of the material, coming to the conclusion that “in very impure metals and alloys [the surface energy] will probably be negative, the range of order being considerably less than the penetration depth. It is thus understandable why ‘super-cooling’ is observed only in pure metals and why there is in alloys a persistence of superconducting regions in fields greater than critical.”

The ultimate theoretical derivation of the $n - s$ interface energy was eventually given by Ginzburg and Landau⁴⁵. The intention of their paper was to describe the properties of the intermediate state and therefore they limited their attention to situations in which the surface energy was positive. But with their paper they paved the way for the final attack and the theoretical prediction of two types of superconductors by Abrikosov⁷³. He introduced referring to the experimental results of Ryabinin and Shubnikov^{69,70}, the distinction between type I and type II superconductors depending on the sign of the $n - s$ interface energy. The type II superconductors are characterized by a mixed state consisting of superconducting regions encircling normal filaments containing one quantum of magnetic flux which form a triangular flux line lattice. When two years later Lev Gorkov showed that the Ginzburg-Landau equations could be derived from the microscopic BCS theory⁷⁹ and how to deal with mean free path effects, the GLAG (Ginzburg-Landau-Abrikosov-Gorkov) theory was born (see Chapter 2, Theory) providing the tools to explain the properties of all sorts of superconductors from first principles.

It should be mentioned though, that before 1961 the GLAG theory did not receive much attention from the scientific community in the Western world. That changed drastically after the discovery by Kuntzler et al.⁸⁰ of very high critical fields in Nb₃Sn in combination with high critical currents: 1 kA/mm² at 8.8 T. Eventually, Goodman bridged the gap when in 1962 he drew attention to the GLAG theory and demonstrated its ability to account quantitatively for the behavior of Pb-Tl al-

⁷⁷ H. London, *Proc. Roy. Soc.* A152 (1935) 650

⁷⁸ A.B. Pippard, *Proc. Camb. Phil. Soc.* 47 (1951) 617, *Proc. Roy. Soc.* A216 (1953) 547

⁷⁹ L.P. Gorkov, *Zh. Eksperim. I Teor. Fiz.* 37 (1959) 1407 [*Soviet Phys. JETP* 10 (1960) 998]

⁸⁰ J.E. Kunzler, E. Buehler, F.S.L. Hsu, and J.H. Wernick, *Phys. Rev. Lett.* 6 (1961) 89

loys.⁸¹ Finally, any doubt about the exact magnetic structure of type II superconductors evaporated when the decoration experiments of Essmann and Träuble⁸² in 1967 visualized the triangular lattice structure.

1.2 The Historical Context of Josephson's Discovery

A. B. Pippard

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⁸¹ B.B. Goodman, *IBM J. Research Develop.* 6 (1962) 63

⁸² U. Essmann, H. Träuble, *Phys. Lett.* 24A (1967) 526

THE HISTORICAL CONTEXT OF JOSEPHSON'S DISCOVERY

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In an introductory talk like this you might expect a complete history of superconductivity from 1911 onward. I was not a physicist in 1911; I never met Kamerlingh Onnes and I cannot tell you how it was then, nor am I going to try. I am going to start considerably later, about the time of the B. C. S. theory. I am not a historian, and when one starts to think about writing history, one realizes that historians may not be skilled in physics, but they certainly have expertise of their own. It is quite difficult to both write history and be involved in discovery. The thing which normally saves historians from being completely bogged down in detail is that they let enough time elapse between the events and the writing for almost everything to be forgotten; then it is possible to reconstruct the bits you care about and let the trivial details fade into insignificance. Because we are not talking about that sort of time lapse here it is very hard to separate the details from the important things. We feel the urge to find out what people were really thinking as the discoveries were made, but this is an extremely hard task.

Most of you probably have read Watson's book "The Double Helix" and his account of the discovery of the form of the DNA

Note: This paper is based on the opening talk presented by Sir Brian Pippard to the participants at the NATO Advanced Study Institute on Small-Scale Superconducting Devices. The talk was recorded and it represents essentially the transcript. The editors have requested that Professor Pippard allow us to maintain the informal nature of his talk in order to give the reader the flavor of his remarks. We encouraged only slight editing for clarity.

molecule. Watson was basing his story on copious notes and letters which he wrote at the time and was able to do a magnificent job of reconstruction. I was in Cambridge at the time that this work on the double helix was going on in the Cavendish laboratory. I can assure you that the flavor which comes through in Watson's book is very close to what I remember it to have been. To tell an equally good story of superconductivity would require someone with almost perfect recall and also with very good notes to make sure that his memory is not falsified by subsequent interpretations. I cannot promise you that this is what I can manage in this paper. The double helix is the only example that I know which gets at all close to the feel of events. One of the troubles one has in reconstructing important scientific events is that anyone working on a difficult problem goes through a great many fanciful interpretations. A lot of nonsense goes on in his mind until the moment when suddenly the right idea appears, and that usually comes through as a moment of enlightenment - sudden enough to drive out completely any feeling for what it was like before, so that almost immediately it is impossible to reconstruct the process of thought which led to that inspiration. Already history has begun to be blurred. One can try to go back and plot out the main lines which led to the new insight. However, once having seen the truth it is impossible to give an exact description of what it is like not to be able to see the truth. All I promise then is that I have done my best to find out what happened, but I cannot guarantee that any of the details are right.

I was, as far as the Josephson effect was concerned, an observer of the events but a very poor observer. One reason is that you could hardly find two people whose minds worked on more different lines than Brian Josephson and myself, so that I was never able to understand what he was talking about. The other thing is that one is not told at the time that something important is happening. It is only afterwards - years afterwards - that people will say, "You ought to have taken more notice of what was happening, because it was obviously important." All I can say is that it was not obviously important at the time - it was obviously interesting, but that is quite another matter. If something is interesting but you don't actually understand it, you can hardly recall it very closely. Apart from that, I was interested in other things at the time. It was only a few months since I had commissioned a high magnetic field laboratory. I was concerned with the behavior of electrons in high magnetic fields and had no deep interest in superconductivity at that time, apart from certain outstanding problems that I had a few students working on. My mind was going on other things, so I didn't take all that much notice. This is why I cannot present you with the evidence of a notebook in which I say "On January the third, Josephson told me that he had solved the Hamiltonian."

Well, where shall we start? I think the best thing is to go back a little into history. It is very easy to overestimate the importance of the Josephson effect when the major part of this NATO Institute is devoted to its applications. I am not saying that the Josephson effect is not important, but it is not the only important thing that happened in superconductivity about that time, and I think it is wise to get some perspective on it. How one gets perspective depends on taste, and one way (a bit curious perhaps) is through numerical research. I have studied Physics Abstracts and counted the number of papers published year by year on superconductivity and compared their total with the total number of papers published. This (as illustrated in Fig. 1) shows how the subject of superconductivity was far from dying as a result of B. C. S. theory. Normalization to the total number of papers is to allow for the overall five-fold expansion in the number of papers published in physics annually in this period. Far from superconductivity coming to an end in 1957, the B. C. S. theory represents the moment when it took off both in terms of the proportion of physicists actually publishing papers and (even more striking) in absolute numbers; in ten years there is a twelve-fold increase in the number of published papers, from 66 to 830. Some of this represents the rise of letter journals. (It may not represent more work done but just shorter papers

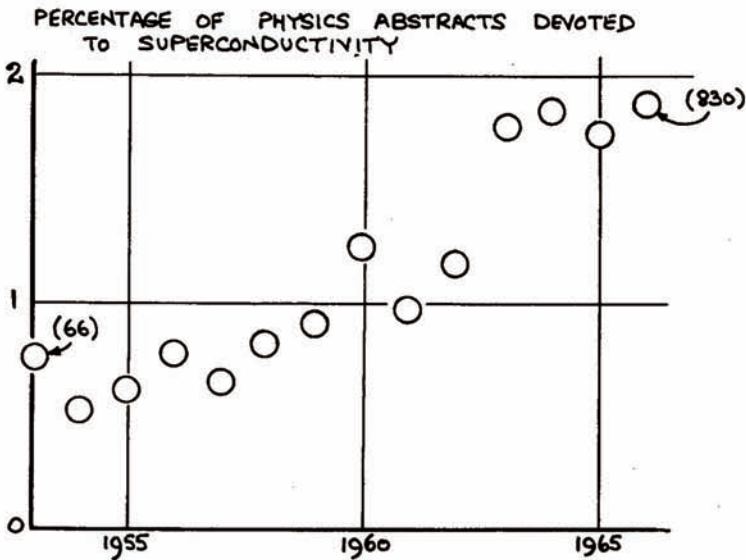


Fig. 1 A graph of the number of papers on superconductivity in Physics Abstracts from 1953 to 1966.

being published, with still less in each paper even than before.) The data in Fig. 1 stops in 1965-66 since it was quite clear looking at later Physics Abstracts that the curve was still increasing and my patience was exhausted. There is an enormous amount of applications work in superconductivity nowadays. Although 1957 was the year of the B.C.S. theory, this rise in papers is not associated just with B.C.S. nor with the Josephson effect which was discovered in 1962. Some of the bump in 1960 is perhaps the result of Giaever's discovery of tunneling, but there is a general rise of interest at this time in all areas of superconductivity. Another very important factor, of course, was the emergence of technical superconductivity; high-field alloys and devices must account for a great deal of the increase. Before we leave the simple numerology of the subject, there was a conference at Colgate on the science of superconductivity in August 1963, which was published in the Reviews of Modern Physics. The published proceedings ran to 330 pages. Although the conference took place one and a half years after Josephson, only 40 pages were devoted to tunneling - just over 10% - whereas 130 pages, more than one-third of the work, was concerned with high field superconductors and with transition metal alloys. Nowadays, technical applications of superconductivity are separately listed in Physics Abstracts and they overwhelm, by quite a large factor, the papers published on small-scale devices. Let us not then be too parochial when we are talking about small-scale devices. We are not the only pebble on the beach, there is quite a large rock standing quite close by.

Bearing in mind that many factors were responsible for the large increase of papers in superconductivity, I have traced historically four rather closely related fields, and have listed in Table I, against the year, some of the milestones. I hope nobody will be offended at being left out, for it is not meant to be anything like a complete list, but it includes some of the more significant developments. Let us start with the third column, dealing with type II superconductors which are possibly less intimately related to the main theme than the others. I start in 1935, when there was already quite a lot of experimental work by Mendelssohn, Shubnikov and others showing that alloy superconductors behave quite differently from pure superconductors. In 1935, Gorter specifically suggests that it is a short mean-free-path effect which is responsible for the peculiar properties of alloy superconductors. He doesn't know why, however. His ideas are in contrast to Mendelssohn's that alloys are inhomogeneous and form a superconducting sponge which can trap the flux. The war came along and the next significant event is the Ginsburg and Landau theory in 1950. I have put my own name there in 1951. These two developments are quite independent (it takes time for Russian papers to filter through). I revived Gorter's idea (without knowing he had had it already) in a more specific

Table I: Milestones in Superconductivity

	From Energy Gap to Tunneling	Weak Links	Type II Superconductors	Fundamental Theory
1935			Gorter	
1946	Ginsburg Daunt and Mendelssohn			
1950			Ginsburg and Landau	Frölich Maxwell
51			Pippard	
52				
53	Goodman			
54				
55				
56	Glover and Tinkham			Cooper
57			Abrikosov	Bardeen, Cooper Schrieffer
58		Meissner		Anderson
59			Gorkov	
1960	Giaever Nicol, Shapiro and Smith	Parmenter		
61			Kunzler, Buehler, Hsu & Wernick [Goodman]	
62	Cohen, Phillips and Falicov			
63	Josephson Anderson & Rowell Shapiro			
64	Zimmerman and Silver	De Gennes		

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FROM ENERGY GAP TO TUNNELING

- 1946 Ginsberg: Superconductivity (book; in Russian).
Daunt & Mendelssohn: Proc. Roy. Soc. A185, 225 (1946).
First suggestions of energy gap to account for London equations (G), and absence of Thomson heat (D & M).
- 1953 Goodman: Proc. Phys. Soc. A66, 217 (1953).
Experimental evidence for energy gap from thermal conductivity.
- 1956 Glover and Tinkham: Phys. Rev. 104, 844 (1956).
Absorption of far infrared reveals gap directly.
- 1960 Giaever: Phys. Rev. Lett. 5, 147 (1960).
Discovery of N-S tunneling through oxide layer.
Nicol, Shapiro & Smith: Phys. Rev. Lett. 5, 461 (1960).
Giaever: Phys. Rev. Lett. 5, 464 (1960).
S-S tunneling; explicit exhibition of zero-voltage tunneling current, discussed as metallic bridge (G) or uncommented upon (N, S & S).
- 1962 Cohen, Phillips and Falicov: Phys. Rev. Lett. 8, 316 (1962).
Tunneling Hamiltonian.
Josephson: Phys. Lett. 1, 251 (1962).
Prediction of pair tunneling through oxide layer separating superconductors.
- 1963 Anderson & Rowell: Phys. Rev. Lett. 10, 230 (1963).
Observation and recognition of Josephson tunneling.
Shapiro: Phys. Rev. Lett. 11, 80 (1963).
Stepped characteristic with microwave irradiation.
- 1964 Zimmermann and Silver: Phys. Lett. 10, 47 (1964).
Double-junction device as forerunner of fabricated interferometers.

WEAK LINKS

- 1958 Meissner: Phys. Rev. 109, 686 (1958).
Evidence of supercurrents through normal metals not caused by superconducting bridges.
Parmenter: Phys. Rev. 118, 1173 (1958).
Application of BCS theory to NS sandwiches.
- 1964 De Gennes: Rev. Mod. Phys. 36, 225 (1964).
Refinement of earlier theories of proximity effect.
Anderson and Dayem: Phys. Rev. Lett. 13, 195 (1964).
Supercurrents through narrow bridges.

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TYPE II SUPERCONDUCTORS

- 1935 Gorter: *Physica* 2, 449 (1935).
Difference between dirty and pure superconductors tentatively related to mean free path.
- 1950 Ginsburg & Landau: *Zh. Eksperim. i Teor. Fiz.* 20, 1064 (1950).
Phenomenological theory.
- 1951 Pippard: *Proc. Camb. Phil. Soc.* 47, 617 (1951).
Coherence length shortened by collisions, leading to negative surface energy in impure superconductors.
- 1957 Abrikosov: *Soviet Physics J. E. T. P.* 5, 1174 (1957).
Flux-lattice solution of Ginsburg-Landau equations.
- 1959 Gorkov: *Soviet Physics J. E. T. P.* 9, 1364 (1959).
Derivation of Ginsburg-Landau equations from microscopic theory.
- 1961 Kunzler, Buehler, Hsu and Wernick: *Phys. Rev. Lett.* 6, 89 (1961).
Discovery of very high critical field in Nb_3Sn .
[Goodman: see *IBM Journal* 6, 63 (1962).
Draws attention of Western world to Abrikosov (1957).]

FUNDAMENTAL THEORY

- 1950 Fröhlich: *Phys. Rev.* 79, 845 (1950).
Electron-phonon interaction proposed as cause of electronic phase change.
Maxwell: *Phys. Rev.* 78, 477 (1950).
Reynolds, Serin, Wright and Nesbitt: *Phys. Rev.* 78, 487 (1950).
Isotope effect strongly supporting Fröhlich's proposal.
- 1956 Cooper: *Phys. Rev.* 104, 1189 (1956).
Pairing of electron states lowers energy.
Bardeen, Cooper and Schrieffer: *Phys. Rev.* 108, 1175 (1956).
- 1958 Anderson: *Phys. Rev.* 112, 1900 (1958).
Pseudo-spin formulation of BCS theory.

form and tried to give some reason why mean-free-paths, when they are short, can lead to negative surface energies and the possibility of high field superconductivity. Mine was essentially a qualitative idea, in contrast to Ginsburg and Landau who, as we all know, produced a phenomenological theory in which for the first time we get the famous concept of a wavefunction ψ describing the collective state of the superconductor. The (imaginary) gradient of the wavefunction $\nabla\psi$ is responsible for the current, in accordance with normal quantum mechanical principles. The gradient of the wavefunction squared, $|\nabla\psi|^2$, enters the Ginsburg-Landau equation in a way which represents in energy terms the difficulty of confining the wave function. You can't change the spatial distribution of particles without affecting their kinetic energy.

Here I am going to touch on personal history, because I think it illustrates how physics is not always as simple as it ought to be. We all know now that the Ginsburg-Landau theory has been established microscopically. Why in 1950 did it take such a long time for the Ginsburg-Landau theory to be recognized? Why, bearing in mind the extreme lucidity and clarity of their paper, didn't everybody accept it? Why, I ask in particular, did I not accept it, since I soon came to know it perfectly well? Well, there is quite a good reason for this. It wasn't merely the dislike of someone else's ideas, though we all suffer from that. It was that in the Ginsburg-Landau theory the parameter κ , whose size controls whether the superconductor is type I or type II, is determined by the penetration depth and by certain other parameters such as the transition temperature. The penetration depth in London theory, which the Ginsburg-Landau theory incorporates, is fixed by the number of superconducting electrons and their mass. In other words, the penetration depth is a fundamental parameter according to London. What made me skeptical, at that time, was that in the early 1950's we knew that the penetration depth was changed by scattering. When the mean-free path was made shorter, the penetration depth increased, as could be explained easily by a non-local equation. One didn't have to infer that the number of superconducting electrons changes because of scattering. But Ginsburg and Landau implied that when you alloy a superconductor, making the mean-free-path shorter, the penetration depth increases and κ changes because the fundamental parameters which go into the theory change. I found that quite unacceptable. I couldn't understand how the number of superconducting electrons could be altered by alloying without, shall we say, altering the transition temperature. Of course all this was cleared up satisfactorily later by Gorkov, but for some years there was a feeling that the Ginsburg-Landau theory was altogether too arbitrary. You read it now, post-1957, and see how beautifully it ties onto the B. C. S. theory. Believe me, however, it's quite different when you haven't got a theory of

superconductivity and chaps come out suddenly saying, "Let's write down a wavefunction ψ which will behave just like an ordinary wavefunction behaves in quantum mechanics, except that we will fudge up the boundary conditions because it is not convenient to have normal boundary conditions ...". You can say, "Well, Ginsburg and Landau are very clever chaps and they know much more than I do about it, but it doesn't necessarily mean they are right.". And it took quite a long time for Ginsburg and Landau to be accepted. It was only, I think, when Gorkov produced from the Green's function treatment of the B. C. S. theory an explicit demonstration of how the microscopic parameters could be interpreted, that the Ginsburg-Landau theory fell into place. So in the early 1950's there was a certain amount of conflict which wasn't helped, incidentally, by the fact that Ginsburg kept on writing small papers in which he said it would be much better if we interpreted the electronic charge as not being exactly e , but e times a small numerical factor which might be as large as 2! He didn't say it was exactly 2; instead he wanted to introduce a fudge factor of (say) 1.6, and Landau kept on telling him he couldn't just put in arbitrary numbers, and muttered darkly about gauge invariance going wrong if you did. So even Landau wasn't supporting Ginsburg, and the Soviet Union seemed to be falling apart at that time.

The same thing happened when Abrikosov developed the Ginsburg-Landau theory to produce the theory of vortices in type II superconductors. As he told the story at the time he received the Simon prize, Abrikosov was discouraged by Landau who loathed the theory and would have nothing at all to do with it for some years, so that it wasn't published till 1957. In this now classic paper Abrikosov shows how vortices (flux lines) can appear in the theory, which nobody took any notice of. I don't know when the Russians began to think seriously of it, but in the West we owe a debt to Goodman. He is on my list because at the IBM Conference in 1961 he drew attention to the existence of Abrikosov's paper. He said it would explain high field superconductors and flux penetration far better than any ideas that he (Goodman) and I had been developing. So there is a gap of about 7 years between Abrikosov's solution of the equations and the idea of type II superconductivity really becoming respectable. Meanwhile Kunzler and his colleagues at Bell Labs had found that Nb_3Sn has a critical field higher than 80 kG. This discovery represents the sudden recognition of the technical importance of superconductivity, and opens up the development of high-field superconducting magnets. At this point a new story begins, which is not relevant to my theme.

I thought it worthwhile going into this matter in some detail simply because, although it was high-field superconductivity that

acted as the prime stimulus to the development and application of Ginsburg-Landau, yet once Gorkov had firmly based the G-L equations, they were soon recognized as the natural way of discussing weak links and many other things. In making applications of superconductivity one hopes to be allowed to forget fundamental theory and rely on the simpler G-L phenomenological theory.

Turning to the fundamental theory, I propose to take a moment to talk a little more about the Russian connection. This is a personal recollection of an incident I found instructive. In the early summer of 1957 I went to Moscow for the first and only time. Up to then, ever since the War, there had been extremely poor contact between Russia and the Western world. This was one of the first moments when it was possible for scientists working on superconductivity in Russia and the West to talk, and we all found it extremely revealing to discover each other's misapprehensions about work on the other side. In the course of a few days spent in Moscow, I spent a lot of time arguing fiercely with Landau, Ginsburg and Lifschitz. They are excellent people to argue with; there's no one like a Russian for having a fight with - no holds barred, intellectually speaking - and we all had a good time. But I was seriously assailed by Landau particularly, who would have nothing to do with non-local electrodynamics. The London equation was good enough for superconductivity, and it was a monstrous thing to throw this beautiful London equation out and replace it by an ugly non-local equation which was quite unnecessary. I did my best to explain why it was necessary, but Landau was not a man to be easily convinced once his mind was made up. Eventually I promised that I would do an experiment to show, once and for all, that the penetration depth varied with the direction of current flow in a non-tensorial manner. This, they said, was the only thing which would persuade them that the London equations were wrong. And so we parted.

Round about the end of the same year, I was rather astonished to receive one morning in the mail a letter from the BBC Monitor Service. They listen to foreign broadcasts and hand on the information to anyone interested. They wrote to say that a few days before Professor Lifschitz had been giving a general talk on science, and had mentioned particularly the pleasure the Russian physicists had in talking with people from the West. He went on to say "... and if Dr. Pippard should happen to be listening to this broadcast, I would like him to know that in the discussions which took place earlier in the summer, it was he who was entirely right." Now I hadn't done any of the promised experiments, so this was a surprise, and I was gratified to find that these great scientists could change their minds so readily. Of course what had happened was quite simple. Cooper's letter on electron pairs had reached Russia in the *Physical Review* and

immediately Bogoliubov had worked out his theory of superconductivity* (Bogoliubov is not post-B. C. S., but contemporary with B. C. S., having a powerful formalism absolutely ready from his earlier work on superfluid helium). As soon as the essential idea of Cooper pairs was put to him he lost no time in developing his extremely tidy and mathematically satisfying formulation of superconductivity. It was this theory that convinced Landau and Ginsburg - they really didn't care any more about experimental evidence; what they wanted was a nice tidy theory that looked convincing, and they would then happily accept its consequences, even non-local electrodynamics. This is a lesson then on how to persuade your critics. Don't give them what they think they need, give them what you know they need (if you possibly can).

Brian Schwartz remarked in introducing me that when the B. C. S. theory came out, it was obviously correct and it seemed as though there was little more theory to be done. Now this raises an interesting historical point. He is quite right in saying that the majority of people working on superconductivity, once they realized what was in the B. C. S. paper, recognized its worth. It took a month or two, but not much more than that, for the majority to appreciate that this was, if not the right answer, so near that it really was a fundamental breakthrough. But when I say the majority, I don't mean all. I must exclude from the consensus a considerable proportion of the leading theoretical physicists of the world who disliked the theory very much! This was somewhat similar to what happened in 1950, when Fröhlich proposed a theory in which the electron-phonon interaction was responsible for superconductivity. It was supported by experimental evidence from the isotope effect discovered by Maxwell at NBS and the Rutgers group. Most of us working in the field then were convinced that the isotope effect substantiated the idea of electron-phonon interaction, but the reaction from many leading theorists was hostile. Why was there this adverse reaction to Fröhlich and to Bardeen, Cooper and Schrieffer? To some degree the criticism of Fröhlich's paper was justified; he quite correctly traced superconductivity to the electron-phonon interaction, but the detailed model he constructed is not right. But that wasn't what those who disagreed objected to. The real trouble lay in the fact that Fröhlich's electron-phonon interaction is something they had almost all thought of themselves and rejected for what seemed very good reasons. Fröhlich's criterion was that in superconductors the electron-phonon interaction is strong enough to cause electron-electron attraction. Earlier theorists who had discovered this attraction had, I think,

* This may not be correct. B. C. S. published a Letter in *Physical Review* early in 1957, and it was perhaps this, and not Cooper's Letter, that did the trick. At all events, Bogoliubov's paper was submitted to *Il Nuovo Cimento* before the main B. C. S. paper was published.

concluded that in these circumstances the lattice is unstable and a crystal modification occurs. Perhaps they were right in general, and superconductivity is the last resort of a metal which cannot find a better way of eliminating the embarrassing interactions between the electron and lattice. Anyone who had travelled that road and decided it led nowhere was understandably irritated by the suggestion that he had missed discovering the theory of superconductivity; and it was easy enough for the expert to discover flaws in the working out that enabled him to overlook any possible merits. I think by the time B. C. S. appeared, seven years later, the iron had entered into the soul of these eminent men. They had already been had once on the electron-phonon interaction, and when B. C. S. showed that this very mechanism which they had rejected was in fact capable of leading to the right theory, their response was distinctly ill-natured. For two or three years after the B. C. S. theory, many of the leading theoreticians were saying, "It's all very well, but the theory is not manifestly gauge invariant." I don't know quite what those words stand for, but what they really meant was that they weren't having the theory at any price. It didn't make the slightest difference, of course; everybody else had accepted it.

The more one had been involved in superconductivity, the less happily one accepted B. C. S. I confess I muttered away for six months or so after B. C. S. before I was finally convinced that muttering did no good, and it was better to join the majority. But my disinclination in no way reflected a private disappointment at having missed getting the answer first - I could never have hit on anything so clever as B. C. S. My reaction sprang from regret for the end of an era, when superconductivity as an unsolved mystery posed the sort of problem that keeps an experimental physicist happy. From now on the subject was basically different. I need not pursue the history of fundamental theory any further, but must note that my inclusion of Anderson's pseudo-spin formulation of the theory is not intended to imply that it was, in itself, a major advance; it did, however, provide the framework which inspired Josephson's first thoughts about tunneling.

Let's go on to tunneling, and approach it through the idea of an energy gap. Now we are in deep water. Who first thought there was an energy gap in superconductors? Mendelssohn tells us that this is an idea which was being bandied around at Oxford before the War,* but he and Daunt never had time to write it up

* Since delivering the talk I have looked at some of the pre-War literature, especially the abortive models of superconductivity developed by, among others, Slater and Welker. It is clear that the energy gap was part of the mental furniture of the time, even if its precise role was ill-defined.

until after the War, in 1946, as Table I records. Ginsburg published a book on superconductivity in 1946, in Russian of course, which seems to have passed out of recollection. I suspect the ideas in the book go back several years, before 1946. Ginsburg is quite explicit that the London equations can come out of an energy gap model, and he stands out as the one who has the most cogent physical reasoning behind why he thinks there ought to be a gap.

The gap was then lost sight of for a few years, until Goodman revived it, to interpret his measurements on thermal conductivity well below the transition temperature. He found that at very low temperatures the electronic conductivity was exponentially dependent on temperature, and suggested an energy gap. Now you might expect him to have referred back to Daunt and Mendelssohn, but he doesn't; instead, he refers back to Koppe who isn't even in Table I. This is because it is difficult to give fair credit to an incorrect theory, even when it provides helpful clues. I refer to Heisenberg's theory of superconductivity which, like so many theories in the pre-BCS days, was based on the wrong mechanism and worked out wrongly. Nevertheless, we in Cambridge had cause to remember it with gratitude, because when Heisenberg went wrong he did not cease to be enlightening. In fact, in my own experience, two things came out of Heisenberg's theory. One is that Goodman knew about it because Heisenberg had lectured in Cambridge. We had discussed his theory in great detail in Cambridge, and had not forgotten it even though we were unconvinced. Goodman knew an energy gap came out of the Heisenberg theory, as developed by Koppe, and took it over as possibly the only correct thing to emerge from this work.

The other valuable outcome that I recollect took place when, in the early 1950's, I found compelling evidence for the non-local character of the supercurrent equation (about which I had the argument with Landau). I needed to formulate the non-local theory, and remembered how Heisenberg had explained the supercurrent as arising by a curious take-over mechanism from the normal current. So if the normal current obeyed a local equation, so did the supercurrent, and that gave the London equation; but if the normal current was non-local, as in the anomalous skin effect (my own baby), so too was the supercurrent. So I wrote down what the Heisenberg theory would have given in the non-local case, and (hurray!) it fitted the experiments. Here again, although the reasoning behind Heisenberg's theory is totally wrong, it provided the incentive and the formalism which was needed. This is something which crops up whenever one traces the development of ideas; almost always they start wrong and finish up right. There can be very few creative scientists who do not remember the debt they owe to

other people's bad ideas which set their mind working in a new direction. The debt is greater still when we take another's good idea and improve it in a way he could not have imagined, and the apportioning of credit can then be difficult. I should not have broached this rather awkward topic but that it plays a part in the Josephson story, and I feel moved to try to resolve some of the tensions. But this comes later - let's get back to the energy gap.

Between 1953 and 1960 the energy gap gained acceptance steadily, and the matter was clinched by Giaever's tunneling experiments. He first found tunneling between a normal metal and a superconductor, and then a few months later between superconductors. His second paper jostles that of Nicol, Shapiro and Smith in *Physical Review Letters*, and both of them produce evidence of zero-voltage currents. Giaever remarks on this explicitly and says it is due to a superconducting bridge. Nicol, Shapiro and Smith publish a beautiful oscillograph showing the current at zero voltage, but they do not draw attention to it. Here is another instance of researchers having the data to make an important discovery, but unable to break away from their traditional notions. We had to wait until 1962 for Brian Josephson to take a good result and make it even better.

Since we have at last reached the central theme, I'll go into a little more detail of this particular discovery. Josephson started as a research student under my direction in October 1961. The reason for this choice is worth recounting. He had had a brilliant undergraduate career, first in mathematics and then in physics. At that point he felt that his understanding of practical matters was deficient, and he would therefore do a thesis in experimental physics in order to balance up his expertise and try to compensate for what was easiest for him - the mathematical formulation of problems. But for that, he would have started as a theoretical research student under John Ziman, probably, and I don't know where he would have gone - not into superconductivity at any rate. If you enjoy arid speculation you might try to guess if, and when, the Josephson effects would have been discovered; and you might also try guessing what it is we don't know now that he might have discovered in different circumstances. But the simple fact is that he came to me to do an experimental thesis. I suggested to him that he should study the variation of penetration depth with magnetic field in superconductors, as measured by microwaves. This is a problem which still remains unsolved. Josephson studied this and obtained experimental results, but did not add anything to the theoretical understanding. He did a perfectly satisfactory thesis, ultimately, but was rather side-tracked in the middle by his independent theoretical work. I think it must have been early in 1962 that he began this, and not long afterwards came to tell me about it. In retrospect I feel no

shame at not understanding him then. I don't know how many people here have read his 1962 paper in *Physics Letters*. If you have, read it again, and remember that the paper is the result of systematic pressure on my part and Phil Anderson's to get the ideas into an intelligible form. I still find it a very difficult paper, but the first versions were really in a class of their own, since he was a new research student with almost no experience of technical writing. I hope you will be sympathetic to my reaction, which was to tell him that I just didn't have a clue what he was talking about, and he had better go and talk to Phil Anderson, who was in Cambridge as a visitor at the time. Phil is a much more clever man than I am, of course, and he did understand, though I think he too had to work for it. A few months later John Bardeen was very doubtful about Josephson's ideas, and he was far from being alone in this. I think this shows how hard it is for someone with a new idea to visualize what other peoples' difficulties will be in accepting it. It was so clear to Josephson in his particular way of looking at it, that he could not understand why, for example, I should fail to see the point. He remarks in his Nobel lecture, "In 1961 Pippard had considered the possibility that a Cooper pair could tunnel through an insulating barrier such as that which Giaever used, but argued that the probability of two electrons tunneling simultaneously would be very small so that any effects would be unobservable. This plausible argument is now known not to be valid. However, in view of it, I turned my attention to a different possibility, that the normal currents might be affected by phase difference." Let's look at this point. If a single electron only has a probability of 1 in 10^{10} of getting through, the probability for two electrons to tunnel simultaneously is 1 in 10^{20} - as near impossible as no matter. It is quite easy therefore to conclude that no current flows in pairs. I put this argument to Brian Josephson early on, and I am quite sure that this criticism of his theory was in the minds of almost everybody who was thinking about pair tunneling. I asked, "How can the pairs get through?" and he explained that the wave-functions of the electrons in the pair are phase-coherent, so that you have to add the amplitudes before you square. The electrons do not tunnel independently, but more like a single particle, and the probability of a pair going through is comparable to the probability for a single electron. It is like interference in optics with phase-coherent waves mixing, and if he had only said that in his early publication, he would have had no difficulty in carrying the world with him. But can you find it said in his 1962 paper? Of course you can't; because he didn't see the existence of a difficulty. So for some months a lot of people (especially those who had been thinking about tunneling before) thought he might well be talking nonsense because his orders of magnitude for the effect were completely astray.

While I am trying to correct the record, let me make reference to Phil Anderson's account of the early days of the Josephson paper. In one paragraph he manages to create two obscurities, one important and one not important. He says that "we were all - Josephson, Pippard and myself as well as various other people who habitually sat at the Mond tea table and participated in the discussions of the next few weeks - very much puzzled by the meaning of the fact that the current depends on the phase (this is the famous formula $J = J_1 \sin \phi$ relation). I think," he continues, "that it was residual uneasiness on this score that caused the two Brians (Pippard and Josephson) to decide to send the paper to Physics Letters, which was just then starting publication, rather than to Physical Review Letters." I disregard the insult that I don't mind publishing wrong papers, if they are published obscurely; in fact the reason for the choice of journal is quite simple - Physical Review Letters has a page charge which is charged in dollars. At that time exchange regulations in England made it very difficult to get dollars. Therefore it was not published in Physical Review Letters, but in Volume 1 of the new European journal, Physics Letters. This is a trivial point; more important is Anderson's statement about the famous $J = J_1 \sin \phi$ relation. Here I have some difficulty because my recollection on this is quite at variance with what Anderson says. The interesting thing is that $J = J_1 \sin \phi$ is not to be found in Josephson's original paper, nor is it to be found in the fellowship thesis which he wrote later in the year. I believe that the equation was derived by Phil Anderson either at the time of these discussions or within the following months; he quotes it openly in his lectures given in the spring of 1963. There is no question but that Phil has been generous to a fault in what he has written about Josephson. He did an enormous amount to help Josephson get his ideas across, and some of the suggestions which are associated with Josephson are really Phil's. Although Josephson may have been aware, at the back of his mind, of the simple sine relationship, I believe it was Anderson who recognized its importance as a statement of the tunneling law, and also the related expression for the coupling energy of two superconductors as a cosine of the phase. I cannot find these formulae in anything Josephson wrote at that time. By 1963, though, in his article for the Colgate Conference, he quotes the sine relation in a way that leaves one uncertain whether he means it is actually in his original paper or implicit in it (which it certainly is). I'm sure the ambiguity is unintentional. This is not the only example of undue modesty on Anderson's part; he deserves great credit for recognizing two obstacles in the way of detecting Josephson tunneling: (1) The deleterious effect of stray magnetic fields such as the Earth's, and (2) much more subtle, room temperature noise getting down the leads. When Phil suggested they should be eliminated, John Rowell was able to exhibit a clear demonstration of Josephson tunneling.

I must try to make a few remarks about Josephson's own approach to the problem. I can't say much of value because, as I have already indicated, his habit of thought was (and remains) alien to mine. But I can paraphrase his own account. Anderson is on the scene from the start, but his role in this case is unconscious. Being on leave from Bell Labs and spending a year in Cambridge, he gave a course of lectures on solid state physics. At the end he devoted some time to the question of broken symmetry which was intriguing him at that time. Let me explain broken symmetry briefly. The lattice of a crystal has certain symmetry properties, say cubic symmetry, described by a set of rotations that transform it into itself. It is not isotropic, for any other rotation leaves it looking different. However, if you write down the Hamiltonian describing the particles that make up the block of solid, the Hamiltonian itself contains only isotropic central forces. There are no symmetry elements corresponding to the symmetry of the solid crystal which results as the ground state solution. If the particles had been non-interacting, the ground state would have been isotropic, the lowest state of a quantum gas. As you start increasing the interaction between the particles there will come a time when there will precipitate out, as the lowest state, a new ground state which contains certain symmetry properties not present in the original Hamiltonian - a gas-to-solid phase transition has occurred. In a sense the ground state is still isotropic, for the solid lattice can be oriented in any direction, and an isotropic wave-function can be constructed as the superposition of all the degenerate states describing orientations. But this is physically unrealistic - what we observe is one particular orientation at a time.

Now this phenomenon, which is widespread and not confined to solid lattices, has excited the interest of many physicists, including Anderson, and has been a source of inspiration for general ideas about how physics works. He was talking about it in his lectures and used his pseudo-spin formulation of B. C. S. theory to show how the phase transition into the superconducting state could also be seen as a symmetry transition. This intrigued Josephson very much because when a symmetry is changed a new parameter enters, which in general we may refer to as the order-parameter. In superconductors the energy gap plays the role of order-parameter, and as Josephson pondered this in the light of Anderson's general discussion, he recognized that the energy gap alone was an incomplete specification - a phase must be associated with it; moreover (and all this is still consistent with general broken-symmetry theory) this phase was a variable which was non-commutative with respect to the number of electrons in the sample. The Heisenberg uncertainty principle applies to phase and number - if you know exactly how many electrons you have in the superconductor you can say nothing about the phase of the wavefunction. This is the case for two

pieces of superconductor quite separate from one another so that you can count the number of particles in each. On the other hand, Josephson saw if you take a single piece of superconductor and imagine dividing it into two, it is easy to transfer particles from one half to the other and correspondingly, you can have complete knowledge of the phase. Therefore you have a superconducting junction between one half and the other, because the Ginsburg-Landau equations tell one how the supercurrent is related to phase. Thus Josephson recognized early on that the uncertainty relation of phase and number distinguished clearly between superconductors which were separate and superconductors which were joined together. He then asked himself what happened in the intermediate case when they are weakly joined together. I find it particularly interesting to see the weak link appearing as the primary concept, with the oxide barrier coming later as a way of realizing it, and not the other way round - a theory of oxide barriers later being generalized to other sorts of weak link. Josephson recognized that if it was possible to transfer electrons, though with difficulty, from one superconductor to another; you could know something about the number and something about the phase. And since electron number is closely related to the current between the two, and so also is phase, through the G-L theory, he was on the way to describing the properties of a weak link. But, as he points out in the passage I quoted, he was also convinced by the argument against pair tunneling.

At precisely the right moment Cohen, Falicov and Phillips provided the formalism he needed, with their tunneling Hamiltonian, and first he looked at it to see what effect a knowledge of phase would have on the normal current. Not finding what he knew he needed there, he concentrated on the supercurrent and found pair tunneling as one element of the solution. It may be worth recording that a complete analysis of the tunneling Hamiltonian is an extremely formidable undertaking; Cohen, Falicov and Phillips tackled the simpler case of superconductor-normal tunneling, but were daunted by the superconductor-superconductor case. The thorough way they had approached the formulation of the problem prevented them in the end from seeing the wood for the trees. Josephson's advantage lay in his having started from a very general conception of what he wanted, so that he could seize on those features of the tunneling theory that appealed to his physical sensibilities. This is why I lay stress on the idea of weak links rather than tunneling.

Now weak links, though not so named, had been around for some time. In 1958 Meissner published a lot of careful work on the junction of two superconductors with a thin normal film between them. He provided a clear demonstration of the proximity effect (the normal metal between two superconductors

carrying pairs and enabling supercurrents to pass from one superconductor to another). Two years before Giaever, and four before Josephson, then, he was talking about superconductors being joined together by weak non-superconducting links. But his conception of what was going on in the weak links is not radical like Josephson's; nor is that of Parmenter who, following Meissner's results, wrote a very solid and systematic account of the proximity effect based on the B. C. S. theory. There were many of us at that time wondering, more or less deeply, about the proximity effect, and we agreed that it was perfectly possible for this superconductor to infect that normal metal with superconducting pairs so that the supercurrent could pass from one side to the other. But our thought was strictly limited to the idea of the normal metal becoming a sort of dilute superconductor, passing current according to G-L, that is, proportional to the gradient of the wavefunction just as in a normal superconductor. It never entered any of our minds that the current could be a periodic function of the phase difference, $\sin \phi$; the essential idea of a weak link was missing. Since Josephson, we recognize the weak link as one in which the behavior of the electrons between the two superconductors is determined by what is going on in the superconductors themselves, and not by the local state of affairs at each point between. And the difference is crucial - it permits the current to be periodic in the phase difference - but it took several years for many of us to see just how significant the difference is in practical terms.

I could really stop here, but perhaps should make a comment on the last entries in Table I, marking the beginning of the device era. I have put Zimmerman and Silver here as the key contributors and that may not be fair. I know other people, Mercereau and others, whose names should also be mentioned. But Zimmerman and Silver published the first description I can find of a device with two Josephson junctions separated by a macroscopic gap. What they did was to take a strip and a V-shaped wire, both of Nb, and they bent the wire over the strip so that it contacted the two sides and left a gap in between. They then showed interference fringes in the critical current as a function of magnetic flux through the loop. I think this is the progenitor of the macroscopic devices based on the Josephson effect.

Well, to sum up, I have tried to show some of the windings in the interconnected research paths leading to the Josephson effects, to bring out the mixture of logic and illogic, inspiration and desperation, and how we get things wrong. And of course this is still the way things are done. John Clarke will tell you that his discovery of the Slug was the result of imperfectly formulated ideas providing the inspiration for an elegant and useful end-product, and almost everyone who believes himself

to have made a significant discovery will admit that the first inklings had their origin in something read or heard, and very likely misunderstood. The final result is none the worse because it was reached by stumbling - it is only our pride which is hurt when we fail to measure up to that perfection of progress that the great men of the past always seemed to achieve. Or did they? If we wish to boast of our achievements, let us not point to the unerring pursuit of truth by a logically faultless thinking-machine, but to the even more astonishing way in which truth can be caused to emerge from the toils of error and stupidity.

Acknowledgments

We would like to acknowledge Bertram Schwarzschild, editor of *Physics Today*, for the editorial improvements of Section 1.1.1 and Louwrens van Dellen for his assistance with the addition of colors to the historic drawings.

1.3 Further Reading

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2

Theory

Editor: Jan Zaanen

2.1	Ginzburg–Landau Equations <i>V. M. Vinokur and T. I. Baturina</i>	51
2.2	The Emergence of BCS <i>David Pines</i>	65
2.3	Theory of Superconductivity: From Phenomenology to Microscopic Theory <i>Lev P. Gor'kov</i>	72
2.4	A Modern, but Way Too Short History of the Theory of Superconductivity at a High Temperature <i>Jan Zaanen</i>	92
2.5	Intrinsic Josephson Effect in Layered Superconductors <i>L. N. Bulaevskii and A.E. Koshelev</i>	115
2.6	Mixed State Properties <i>Ernst Helmut Brandt</i>	125
2.7	Thermomagnetic Effects in the Mixed State <i>R. P. Huebener</i>	137
	Acknowledgments	144

2.1 Ginzburg–Landau Equations

V. M. Vinokur and T. I. Baturina

I dedicate this contribution to Vitaly Ginzburg, in grateful memory of his wonderful personality, his kind encouragement, and generous help.

V. M. Vinokur

2.1.1 Introduction

In 1950 Vitaly Ginzburg and Lev Landau introduced in their seminal work¹ (which will be referred to as **GL** hereafter) the equations which have been known ever since as Ginzburg–Landau (GL) equations and which became among the most universal equations of modern physics. Ginzburg–Landau equations either in their original or modified form describe a wealth of phenomena and systems including superconductivity and superfluidity, nonlinear waves in active media, pat-

¹ V.L. Ginzburg and L. D. Landau, *Zh. Eksp. Teor. Fiz.* 20 (1950) 1064

tern formation and liquid crystals and supersymmetric conformal field theories². Ginzburg-Landau equations were one of the first nonlinear theories to demonstrate solutions in the form of topological singularities. Historically, GL theory was an extension of the Landau theory of second-order phase transitions³ onto the quantum phenomenon of superconductivity. It was based on the idea that the normal metal-superconducting state transition is, in the absence of a magnetic field, a thermodynamic second-order transition. An order parameter Ψ of the GL theory is an averaged wave function of superconducting electrons. Because of its (comparative) simplicity and physical transparency, GL theory has become one of the most universal and powerful tools in studies of superconductivity. In what follows, we briefly review the history and the content of GL theory and discuss its most standard applications.

2.1.2 A History

The discovery of superconductivity marked the beginning of a new era in physics, and it is no wonder that the brightest minds in physics strived to understand and reveal its nature and underlying mechanisms. The collegial work and intense scientific exchange, including strong yet forgiving and mutually supportive critique, brought a deserved reward to the scientific community: two theories that are justly considered to be among the top scientific achievements of the second part of 20th century. The first of these was the Ginzburg-Landau theory, which became a foundation for the phenomenological description of superconductivity. The second of these major achievements, which came 7 years later, was the microscopic theory of John Bardeen, Leon Cooper, and Robert Schrieffer⁴. Explosive theoretical efforts were triggered by Walther Meissner and Robert Ochsenfeld's experimental breakthrough⁵: 22 years after the discovery of superconductivity they demonstrated that superconductors expel magnetic fields irrespective of the route by which the superconducting state was achieved, either by cooling the sample in the applied magnetic field, below some magnetic field-dependent critical temperature T_c or by switching on the field after the cooled sample turned superconducting. The magnetic field B in the superconducting sample remains zero, as long as the applied magnetic field does not exceed some temperature-dependent field $H_c(T)$. This discovery was of primary importance, since it allowed us to consider the equality of magnetic induction to zero in the bulk of superconductor as a characteristic of the superconducting state, which hereafter acquired a status of a thermodynamic state of matter. In 1934, Cornelis ("Cor") Gorter and Hendrik ("Henk") Casimir provided strong evidence for the fact that superconductivity is an equilibrium phenomenon⁶. A year later the brothers Fritz and Heinz London published equations describing the linear electrodynamics of superconductors that explained the Meissner-Ochsenfeld effect⁷. They argued that the conventional Ohm's law $\mathbf{j} = \sigma \mathbf{E}$ should be replaced in superconductors simply by Newton's law of motion $\partial \mathbf{j} / \partial t = (n_s e^2 / m) \mathbf{E}$, where n_s is the density of the superconducting electrons, since the motion of the superconducting charges must be dissipationless. Making use of Maxwell equation $\text{curl } \mathbf{E} = (1/c)(\partial \mathbf{B} / \partial t)$, one arrives at the relation $(\partial / \partial t)[\text{curl } \mathbf{j} + (n_s e^2 / (mc)) \mathbf{B}] = 0$, meaning that the quantity in the brackets is conserved. As in the bulk of a superconductor must be $\mathbf{j} = 0$ and

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³ L. D. Landau, *Sov. Phys. JETP* 7 (1937) 19; *ibid.* 7 (1937) 627

⁴ J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Phys. Rev.* 106 (1957) 162

⁵ W. Meissner and R. Ochsenfeld, *Naturwiss.* 21 (1933) 787

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⁷ F. London and H. London, *Proc. Roy. Soc. A* 149 (1935) 71