

BCS theory of superconductivity: it is time to question its validity

J E Hirsch

Department of Physics, University of California, San Diego La Jolla, CA 92093-0319, USA

E-mail: jhirsch@ucsd.edu

Received 25 May 2009

Accepted for publication 6 August 2009

Published 3 September 2009

Online at stacks.iop.org/PhysScr/80/035702

Abstract

The time-tested Bardeen–Cooper–Schrieffer (BCS) theory of superconductivity is generally accepted to be the correct theory of conventional superconductivity by physicists and, by extension, by the world at large. There are, however, an increasing number of ‘red flags’ that strongly suggest the possibility that BCS theory may be fundamentally flawed. An ever-growing number of superconductors are being classified as ‘unconventional’, not described by the conventional BCS theory and each requiring a different physical mechanism. In addition, I argue that BCS theory is unable to explain the Meissner effect, *the* most fundamental property of superconductors. There are several other phenomena in superconductors for which BCS theory provides no explanation. Furthermore, BCS theory has proven unable to predict any new superconducting compounds. This paper suggests the possibility that BCS theory itself as the theory of ‘conventional’ superconductivity may require a fundamental overhaul. I outline an alternative to conventional BCS theory proposed to apply to all superconductors, ‘conventional’ as well as ‘unconventional’, that offers an explanation for the Meissner effect as well as for other puzzles and provides clear guidelines in the search for new high temperature superconductors.

PACS numbers: 74.20.–z, 74.20.Fg

1. Introduction

In the progress of science, it is often the case that a theory is superseded by a new theory without being negated. An example is classical mechanics, that was superseded by quantum mechanics and special relativity but retained its validity for length scales and speeds familiar in everyday life. Then there are other cases where theories thought to be correct for a long time are negated by new theories that end up replacing them [1]. Examples of the latter are Ptolemy’s theory of planetary motion (negated by Copernicus’ theory), the phlogiston theory (negated by Boyle’s theory of caloric energy), and the theory of fixed continents with land bridges (negated by Wegener’s theory of continental drift). There are many other such examples [1], and the purpose of this paper is to suggest that Bardeen–Cooper–Schrieffer (BCS) theory may become one of them.

In this paper, what I mean by ‘BCS theory’ is the BCS pairing theory through the electron–phonon interaction mechanism as formulated in the original BCS paper [2], and

its extension to include the effect of a retarded interaction, generally known as Migdal–Eliashberg theory [3, 4]. This theoretical framework is generally believed to describe the superconductivity of ‘conventional’ superconductors, both type I and type II, including all the elements and thousands of compounds [5, 6]. Then there are other classes of materials discovered in recent years generally believed not to be described by BCS theory, as discussed later in this paper.

In various realms of human activity, there are ‘established truths’ over long periods of time that may subsequently be completely overhauled¹. Before that happens there are usually anomalies [1], or ‘red flags’, that signal inadequacies of the established scheme, that are disregarded for a long time. In science, as argued by Lightman and Gingerich [8], anomalies are often recognized as such only *after* a new theoretical framework is found that explains them. They coined the term ‘retrorecognition’ for this phenomenon. What is perceived as true and real and time-tested can change

¹ I discuss elsewhere analogies between the situation with BCS theory and such situations in other contexts [7].

radically from one day to the next. This will happen if BCS theory is proven wrong, either by an incontrovertible experiment or an alternative theory or both. Today, the vast majority of physicists believe this possibility is unthinkable. However, I will discuss a number of ‘red flags’ in favor of this possibility. Most importantly, I argue that BCS theory has an unrecognized fundamental flaw, its inability to explain the most fundamental property of superconductors, the Meissner effect, and that this calls the validity of the entire framework into question, including the validity of London’s electrodynamic description of superconductors [9]. Also, I point out that BCS theory is completely unable to predict superconductivity in new materials. I discuss several other reasons that make the BCS scheme suspect. In the last section, I outline an alternative to BCS theory proposed to describe all superconducting materials ([10] and references therein).

2. Why BCS theory is generally accepted as valid

There are good reasons why a set of incorrect beliefs can go unchallenged for a long time [11]. Here, I list some of the factors that I propose contributed to make BCS theory successful for so long without being necessarily correct.

2.1. Kernel of truth

Parts of BCS theory are certainly correct and represented an important advance when first proposed: the concepts of Cooper pairs, of macroscopic phase coherence, and the existence of an energy gap are incontrovertible. These elements of the theory led to explanation and even prediction of puzzling experimental data such as nuclear magnetic resonance (NMR) relaxation rate [12] and Josephson tunneling [13]. However many other aspects of BCS theory and especially the electron–phonon mechanism I suggest are not correct despite being universally accepted.

The fact that part of a theory is correct of course does not make the entire theory correct. The BCS electron–phonon mechanism of superconductivity may have been convincing around 1970 as a ‘universal’ mechanism for all known superconductors [14]. By now, as discussed below, there are at least ten different classes of materials that clearly cannot be explained by the electron–phonon mechanism, each requiring its own different mechanism if BCS theory is assumed to be correct.

2.2. Eminence of key proponent

Just the year before he proposed BCS theory (1957), John Bardeen had been awarded the Nobel prize in physics for the invention of the transistor; he had a long and distinguished career in theoretical physics, and had been working and publishing on the problem of superconductivity for over 20 years. In 1956, he had published an authoritative review on superconductivity [15]. The fact that Bardeen was regarded as an authority in superconductivity at the time is evidenced by the fact that the *New York Times* wrote a story on the BCS theory of superconductivity less than a month after it appeared in print [16].

2.3. Early doubters proven wrong

There were early doubts about the validity of BCS theory because its ‘proof’ of the Meissner effect failed to satisfy gauge invariance [17]. However, it was later shown that the BCS derivation was valid in the particular case of a transverse gauge and plausible arguments were given for generalizing the theory to an arbitrary gauge [18]. Thus, the early doubts were allayed and as a consequence the theory became more firmly established.

As I will argue later, these early discussions did not really address the essence of the Meissner effect, which remained unexplained within BCS theory. But the fact that the early doubts had been resolved undoubtedly led to the general belief that all doubts concerning the Meissner effect within BCS had been discussed at length and resolved and there was no point to rehash them.

2.4. Selected few get to participate

One does not become an expert in BCS theory overnight. A background in many-body theory and second quantization is required as well as in solid-state physics and statistical physics. Concepts such as off-diagonal long-range order and broken gauge invariance are rather subtle. Beginning students asking interesting questions such as how can one possibly explain the Meissner effect, or why the theory is unable to predict new superconductors, are told to wait until they master the advanced mathematics and physics required to really understand it, or else go elsewhere. By the time they have mastered this technology, they have forgotten the interesting questions they had or have convinced themselves that they are no longer relevant.

2.5. Gatekeepers and non-gatekeeper participants

The ‘gatekeepers’ of BCS theory are those relatively few physicists who have performed detailed Eliashberg calculations of first-principles bandstructures and electron–phonon interaction parameters to calculate superconducting properties of real materials. The vast majority of physicists that use BCS theory do so with model Hamiltonians that do not have a clearcut justification nor very direct connection to real materials. The gatekeepers tell us that their calculations reproduce the measured superconducting T_c ’s, gaps, isotope effect, structure in tunneling characteristics, etc of real materials, and thus prove beyond doubt that BCS-electron–phonon theory describes conventional superconductors. The rest of physicists blindly trust the gatekeeper’s statements.

However, the BCS ‘gatekeepers’ have a lot to lose from BCS theory being wrong. They have invested considerable time and effort in becoming expert in these calculations, and benefit from the status quo. They have funding to perform such work, their work is being cited by the non-gatekeeper participants, and their careers advance. They are the best qualified to question BCS theory but have no strong incentive to do so, hence they may overlook ‘red flags’ that suggest problems with BCS theory.

2.6. Red flags and early questioners

The BCS theory was widely accepted soon after the publication but some early questions were raised whether the electron–phonon mechanism applied to the transition metal superconductors [19–21]. However, by 1969 when Park’s treatise on superconductivity was published [14] it was universally accepted that BCS-electron–phonon theory described all known superconductors.

Except for one persistent gadfly: Bernd Matthias, a well-respected solid-state experimentalist who had been making superconducting materials in his lab for many years ([22] and references therein). In paper after paper and conference proceedings after conference proceedings in the 1960s and 1970s, Matthias argued that BCS theory could not possibly be the correct theory of superconductivity because it was unable to predict new superconducting materials. Matthias found many new superconductors through empirical rules that he devised, but found no guidance whatsoever in BCS theory. The physics community politely tolerated Matthias’ rantings and ravings but he did not produce any followers. When he passed away in 1980, the sole voice calling into question BCS theory went silent.

2.7. The alleged ‘smoking gun’

The most quoted reason given as convincing proof that BCS-electron–phonon theory describes conventional superconductors is the structure in tunneling characteristics detected in normal-insulator–superconductor tunneling experiments, where small wiggles in the tunneling conductance as function of voltage match the peaks and valleys of the phonon density of states as function of frequency measured in neutron scattering experiments in several materials, most notably Pb [23–25].

I am not disputing the interpretation that the structure in the tunneling conductance reflects the phonon spectrum. As Bernd Matthias said [22], ‘you can’t ever stop a crystal lattice from rattling’. Even the gap of ordinary semiconductors is modulated (but not caused!) by the electron–phonon interaction and shows an isotope effect [26]. What I am disputing is the interpretation that the small modulation (few %) of the tunneling conductance spectrum by the phonons is *proof* that superconductivity is caused by lattice vibrations and would not exist for infinite ionic mass.

The interpretation of tunneling results is cast in terms of the spectral function $\alpha^2 F(\omega)$, where $F(\omega)$ is the phonon spectral function determined from neutron scattering experiments. What is *not* emphasized is that α^2 is itself often a strong function of ω that is not directly accessible to experiment [27].

2.8. Role of physics journals

The most prestigious as well as the mainstream physics publications such as *Physical Review Letters*, *Science*, *Nature*, *PNAS*, *Physical Review B*, *International Journal of Modern Physics B*, etc, are completely silent about the possibility that BCS theory could be wrong, while being full of papers devoted to applications of BCS theory. Papers submitted to these journals casting doubt on the validity of BCS theory

to explain conventional superconductors are not accepted for publication².

2.9. Long timescale

One of the arguments physicists would give to discount the possibility that BCS theory could be wrong is that it has been around for so long, over 50 years. I would argue that because of the large number of vested interests and highly motivated gatekeepers that develop around a flawed scheme the timescale for it being overhauled may be much longer than most people would expect.

2.10. BCS theory as a ‘Ponzi scheme’

In a financial ‘Ponzi scheme’, old investors are paid off by funds contributed by new investors. The old investors spread the word that this is a good scheme and this induces more new investors to come in. I am certainly *not* suggesting that there is deliberate deception in the case of a scientific theory such as BCS, still I propose that a similar phenomenon occurs [7]. The payoff to the old ‘investors’ (established physicists) comes in the form of citations to their papers by younger physicists and awards of grant money through which the older physicists are expected to train the new generation of physicists. The grant money also provides for summer salary, equipment, travel funds and other perks for the older physicists. These payoffs depend on the existence of a crowd of younger physicists eager to get into the game and continue building up the theory, lured by the success of the older physicists as evidenced by their career advancement, prestige, prizes, etc. Questioning of the old theory is discouraged in many ways, and early questioning would result in the young physicist being denied career opportunities open to his/her non-questioning peers. The flawed scheme continues building up and reinforced by those that are allowed to enter, and everybody turns a blind eye to anomalies that could suggest something is wrong [8]. There are however many such anomalies (red flags) in the case of BCS theory, as detailed in the following section.

3. Red flags in BCS theory

3.1. Lack of transparency

It can certainly be said about BCS theory that it is anything but transparent. It is extremely hard to explain it to a non-physicist and even to a non-solid-state physicist, and it defies intuition. How can the very strong direct Coulomb repulsion between electrons be overcome by a small ‘second-order’ electron–ion-induced attraction? Why are some materials not superconducting at any temperature? How is it that sometimes a high phonon frequency leads to high T_c [28, 29] and sometimes a low phonon frequency (the soft-phonon story [30]) leads to high T_c ?

There is no simple intuitive criterion in BCS theory that allows one to understand qualitative trends in T_c in materials. The Debye-frequency prefactor in the BCS expression for the

² For example, before being submitted to *Physica Scripta* this paper was submitted for consideration for publication to other journals who declined to publish it based on the advice of referees.

critical temperature suggests that going down a column in the periodic table (where elements have the same valence-electron configuration) T_c should decrease due to the increasing ionic mass. This is *not* what happens [31]. There are no qualitative criteria that can be used to estimate even the order of magnitude of critical temperatures, nor whether a material is or is not a superconductor. The gatekeeper ‘experts’ tell us that T_c ’s depend on many subtle details and can go up and down with different combinations of phonon frequencies, electron–phonon coupling constants, band structure details, strength of Coulomb interactions and of spin fluctuations, etc [5, 24, 32–36]. The ‘Coulomb pseudopotential’ serves as the wildcard that ensures that theory will always fit experiment [37, 38].

3.2. Increasing number of epicycles

Given that initially the isotope effect was claimed to be the ‘proof’ that the electron–phonon interaction is responsible for superconductivity, an early observation not easily explained by BCS theory was the absence of isotope effect in certain elements like ruthenium [39] and osmium [40] and an inverse isotope effect in uranium [41]. However, it was argued that more elaborate versions of the theory could account for the observations ([42] and references therein) [43].

Another observation calling into doubt the conventional theory was the absence of a strong electron–phonon structure in the tunneling spectra of niobium [44, 45], the element with the highest T_c . However, it was argued that a more elaborate theory taking into account the proximity effect due to the complicated nature of the tunnel junctions could explain the observations [46].

The early transition metals Sc and Y as well as the late transition metals like Pd are not superconducting at ambient pressure; even though they would be expected to be so given their other properties, according to the conventional theory [47]. To explain this, it is necessary to invoke the Coulomb pseudopotential ‘wild card’, and it is argued that ‘antiferromagnetic spin fluctuations’ suppress the expected superconductivity of scandium and yttrium [48], and ‘ferromagnetic spin fluctuations’ suppress the expected superconductivity of palladium [49]. However, it is not explained why these fluctuations do not give rise to ‘unconventional’ superconductivity in those elements. For example, it was suggested for Pd a propensity to p-wave superconductivity induced by ferromagnetic spin fluctuations [50]. This was however disproved by the finding of s-wave superconductivity in *irradiated* Pd at 3.2 K [51]. Furthermore, some of those elements were recently found to display quite high superconducting transition temperatures under pressure (not predicted by theory), as discussed in the following section.

In 1969, when Parks’ treatise on superconductivity was published [14], there was general agreement that BCS theory with the electron–phonon mechanism explained all known superconductors. Particularly, interesting is the article in that treatise by Gladstone *et al* on ‘Superconductivity in the transition metals’ [47]. As mentioned earlier, doubts had been raised by Matthias and others whether other mechanisms of pairing may be at play in transition metals [19–22], which

were reviewed in this paper and dismissed. In fact one of its authors, Jensen, had been one of the early questioners of BCS-electron–phonon mechanism for lanthanum and uranium [21]. However, by 1969 he clearly had been brought ‘into the fold’: Gladstone *et al* paper concludes, referring to predictions of non-electron–phonon superconductivity in lanthanum, ‘Although initially these predictions appeared to be found experimentally, more recent work on cleaner samples gives no evidence that La is anything but a phonon-induced BCS superconductor’, and similarly for all other transition metals.

However, since 1970 at least ten distinct materials or families of materials have been discovered that exhibit superconductivity for which there is a consensus that they cannot be described by the electron–phonon BCS theory, or at least there are serious doubts whether they can, namely: (i) high T_c cuprates, hole-doped ($\text{YBa}_2\text{Cu}_3\text{O}_7$) and electron-doped ($\text{Nd}_{1-x}\text{Ce}_x\text{CuO}_{4-y}$); (ii) heavy fermion materials (CeCu_2Si_2 , UBe_{13} , UPt_3); (iii) organics ($\text{TMTSF}_2\text{PF}_6$); (iv) strontium–ruthenate (Sr_2RuO_4); (v) fullerenes (K_3C_{60} , Cs_3C_{60}); (vi) borocarbides ($\text{LuNi}_2\text{B}_2\text{C}$, $\text{YPd}_2\text{B}_2\text{C}$); (vii) bismuthates ($\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$, $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$); (viii) ‘almost’ heavy fermions (U_6Fe , URu_2Si_2 , UPd_2Al_3); (ix) iron arsenide compounds ($\text{LaFeAsO}_{1-x}\text{F}_x$, $\text{La}_{1-x}\text{Sr}_x\text{FeAs}$); (x) ferromagnetic superconductors (UGe_2 , URhGe_2). In addition, magnesium diboride (MgB_2) was believed initially to be outside the scope of BCS electron–phonon theory; however, that has changed by now. We return to this interesting material in the following subsection.

The ten materials or classes of materials listed above exhibit each different deviations from conventional BCS behavior, and/or their T_c is too high to be described by BCS-electron–phonon theory; however, there is also no indication that they can all be described by a single alternative mechanism or theory. Rather, new different mechanisms and theories have been proposed to describe each of these situations. If BCS theory is correct for the conventional superconductors, we would need new different theories to describe d-wave symmetry states, p-wave symmetry states, superconductivity arising near a Mott insulating state, antiferromagnetic spin-fluctuation-induced superconductivity, ferromagnetic spin-fluctuation-induced superconductivity, superconductivity induced by low dimensionality, charge-density-wave-induced superconductivity, superconductivity induced by inhomogeneity (stripes), d-density waves, quantum critical points, resonating valence-bond-induced superconductivity, etc to encompass all these new materials discovered since 1970.

The Proceedings of the series conference ‘Materials and Mechanisms of Superconductivity’, held every three years since 1988, and earlier the Proceedings of the d- and f-band superconductivity conferences held every two or three years since 1971, provide a large number of references for these multiplying entities.

The situation is analogous to the situation in astronomy shortly before the advent of Copernican theory. To explain an increasing number of astronomical observations using the Ptolemy paradigm of the earth as the center of the universe prevalent at the time, increasingly more complicated

models postulating an increasing number of epicycles to describe retrograde motion of planets had to be introduced. Similarly, for each new observation unexpected within the conventional BCS theory a new twist is added to the theory to explain the observation, or else the material is declared to be ‘unconventional’, hence not described by the conventional BCS-electron–phonon theory. The validity of conventional BCS theory for ‘conventional’ superconductors is *never* questioned.

3.3. Inability to predict yet ability to post-dict

Matthias repeatedly emphasized that BCS theory and its implications did not lead to the ability to *predict* whether a compound or a family of compounds would be superconducting. The situation has become even far more egregious since the 1970s up to today, with the advent of an ever-increasing number of ‘unconventional’ superconductors and the discovery of substantially higher temperature superconductivity in ‘conventional’ superconductors under applied high pressure.

For a while, the search for new higher T_c superconductors was directed at compounds with light elements, that would give rise to a high Debye frequency, which appears as a prefactor in the BCS expression for T_c . High T_c superconductivity was predicted for metallic hydrogen [29] and for metal hydrides [52]. Indeed, superconductivity around 10 K was found in thorium-hydride [53] and in palladium hydride [54]. Of course, it was very disappointing when substitution of hydrogen by the heavier isotope deuterium gave an even higher T_c [55], but theory found a ready way to explain it [56, 57], and even to this day theorists continue ‘predicting’ that metal hydrides will yield high-temperature superconductors [58].

Similarly, superconductivity was predicted for the light metal Lithium, the simplest of simple metals, at ambient pressure with critical temperature 1 K or higher [37, 59]. After many years, superconductivity at ambient pressure in Li was found but only at temperatures below 0.0004 K [60].

High T_c was predicted in quasi-one-dimensional materials, based on Little’s excitonic mechanism for superconductivity [61]. None of it was found.

Instead, a ‘soft-phonon’ scenario was developed to ‘predict’ relatively high T_c ’s in materials with low-frequency phonons [32, 62], in response to the experimental findings of such materials, e.g. the A15 family of compounds [63].

In 1972, Marvin Cohen and Phil Anderson ‘predicted’ that superconductivity with critical temperatures much above what existed at the time (~ 20 K) was impossible in any material [64], through the electron–phonon or any other mechanism. This did not prevent *Time* magazine from reporting in 1987, shortly after superconductivity above 90 K was experimentally discovered [65], that ‘*At the University of California, Berkeley, a group that included theoretical physicist Marvin Cohen, who had been among those predicting superconductivity in the oxides two decades ago, reproduced the 98 K record, then started trying to beat it*’ [66]. However, the first paper written by Cohen discussing superconductivity in an oxide was in 1964 [67], where he discussed the just discovered superconductivity

with $T_c = 0.28$ K in semiconducting SrTiO₃ and referred to his earlier work on possible superconductivity in semiconductors that *did not* mention *either* semiconducting *or* superconducting oxides. Subsequently, Cohen ‘predicted’ the carrier concentration dependence of T_c in Sr₂RuO₄, including its maximum at ~ 0.30 K, *after* it had been experimentally measured [68]. Never did Cohen consider in his printed work the possibility of superconductivity in oxides at higher temperatures until after it was experimentally discovered.

Magnesium diboride (MgB₂) was found to be superconducting in 2001 with a critical temperature of 39 K [69], completely unprecedented for a metallic compound with only s- and p-electrons. It was not predicted by theory, and it exhibits a small isotope effect. Nevertheless this has not prevented theorists from claiming that the conventional BCS-electron–phonon theory completely explains the high T_c of MgB₂ [70–73]. Based on these calculations theorists have now predicted higher T_c superconductivity in related compounds such as Li_{1-x}BC [74–76] and in BC₃ [77, 78]. None has been found in either system [79, 80].

As mentioned in the previous section, scandium is not superconducting at ambient pressure, and this is ‘explained’ by the Coulomb pseudopotential wildcard [48]. In 1979, Sc under pressure (~ 200 kbar) was found to be superconducting with $T_c \sim 0.35$ K [81], and in 2007, its critical temperature was found to rise to 8.2 K at pressures of 740 kbar [82]. None of this was predicted by theory, but subsequently calculated and claimed to be ‘in good agreement with experiment’ [83]. However, shortly thereafter, Scandium’s critical temperature rose by over a factor of 2, to 19.6 K at 1 Mbar pressure ([84] and references therein). Presumably, we will see shortly a theoretical ‘prediction’ of this remarkable increase.

More generally, there have been remarkable advances in achieving superconductivity with higher transition temperatures in the elements under high pressure in recent years, e.g. [84, 85]: lithium, $T_c = 16$ K ($T_c = 0$) at 800 kbar (at ambient pressure); boron, 11 K (0) at 250 kbar; sulfur, $T_c = 17.3$ K (0) at 1.9 Mbar; calcium, $T_c = 25$ K (0) at 1.6 Mbar; yttrium, $T_c = 19.5$ K (0) at 1.1 Mbar; lutecium, $T_c = 12.4$ K (0) at 1.7 Mbar; vanadium, $T_c = 16.5$ K (5.4 K) at 1.2 Mbar; zirconium, $T_c = 11$ K (0.55 K) at 300 kbar. None of these have been predicted by theory, but there is an ever-increasing number of theoretical ‘post-dictions’ of the observations [86–93].

For example, in a postdictive study of yttrium under pressure, it is claimed that theoretical calculations ‘provide a good interpretation of the measured increase of T_c in these metals’ [91], yet the results shown indicate that even an anomalously low Coulomb pseudopotential $\mu^* \sim 0.04$ yields a critical temperature substantially lower than the observed one [91]. Another postdictive calculation for Y under pressure claims that it ‘demonstrates strong electron–phonon coupling in this system that can account for the observed range of T_c ’ using a Coulomb pseudopotential value $\mu^* = 0.15$ [92], while acknowledging that their more detailed approach ‘has not yet provided—even for elemental superconductors—the physical picture and simple trends that would enable us to claim that we have a clear understanding of strong-coupling superconductivity’ [92].

3.4. Blind use of formalism

In order to explain the increasingly higher T_c 's found in supposedly 'conventional' materials, higher values of the electron–phonon coupling constant λ have to be used in the conventional formalism [34]. In fact, as early as 1975 values of λ as high as 2.5 were postulated to explain the T_c of Pb–Bi alloys [34]. To explain the superconductivity of Y under pressure a value of $\lambda = 2.8$ is used [92], and λ as high as 3.1 is assumed to explain the superconductivity of Li under pressure [89]. However, it has been convincingly shown analytically [94] that λ values larger than ~ 1 *should not be used* in the conventional formalism, because for $\lambda > 1$ the electron–ion system collapses to a narrow band of small polarons, whose description is outside the reach of the conventional theory. This result is confirmed by numerical simulation studies [95]. This finding is completely ignored and the conventional formalism continues to be routinely used irrespective of whether λ is small or large.

3.5. Inability to explain Chapnik's rule

There is a simple empirical rule that can predict with good accuracy whether or not a material is superconducting: the sign of its Hall coefficient. The vast majority of superconductors have positive Hall coefficient in the normal state, indicating that the transport of current occurs through holes rather than electrons [96–98]. The electron-doped cuprate superconductors only become superconducting in the doping and reduction regime where their Hall coefficient changes sign from negative to positive [99, 100]. The sign of the Hall coefficient is a far better predictor of whether a material is or is not a superconductor than any other normal state property [101], yet the conventional BCS–electron–phonon theory has no explanation for this observation. It would be of great interest to measure the Hall coefficient of non-superconducting elements that become superconducting under applied pressure, which should give further evidence for this correlation between the character of the normal state charge carriers and superconductivity.

3.6. Inability to explain the Tao effect

In a series of experiments beginning in 1999, Tao *et al* found that millions of superconducting microparticles in the presence of a strong electrostatic field aggregate into balls of macroscopic dimensions [102–104]. No explanation of this phenomenon exists within the conventional theory of superconductivity. Initially, the finding was attributed to special properties of high T_c cuprates, in particular, their layered structure [102], however, subsequent experiments for conventional superconducting materials all showed the same behavior [103, 104].

The conventional theory of superconductivity predicts that superconductors respond to applied electrostatic fields in the same way as normal metals do [105, 106], by forming chain-like structures. Hence Tao's observation represents a fundamental puzzle within the conventional understanding of superconductivity, yet no explanation of the effect has been proposed by defenders of the conventional theory of superconductivity. The response of superconductors to

applied electric fields is as fundamental a question as their response to applied magnetic fields.

3.7. Inability to explain the de Heer effect

In a series of experiments, de Heer and co-workers have discovered that small niobium clusters at low temperatures develop ferroelectric dipole moments [107–109]. They find strong evidence that the electric dipole moment is associated with pairing of valence electrons and mirrors superconducting properties of the bulk material. Such behavior is unexpected both for a normal metal as well as for a superconductor, and suggest a fundamental inadequacy of the conventional theory of superconductivity. The same behavior is found by de Heer in alloy clusters of Nb and in clusters of other transition metals that are superconducting in the bulk.

3.8. Inability to explain rotating superconductors

A superconducting body rotating with angular velocity $\vec{\omega}$ develops a uniform magnetic field throughout its interior given by [110, 111]

$$\vec{B} = -\frac{2m_e c}{e} \vec{\omega}, \quad (1)$$

where e and m_e are the charge and mass of the superfluid charge carrier, respectively, and c is the speed of light. This has been determined experimentally for both conventional superconductors [112–114], heavy fermion [115] and high T_c [116] superconductors. The associated magnetic moment is termed the 'London moment'.

What is remarkable about this observation is [117]: (i) The measured magnetic field is always *parallel*, never *antiparallel* to the angular velocity. This implies that the superfluid charge carriers have negative charge, i.e. they are electrons, not holes. This is despite the fact that the normal state carriers in all these materials are holes. (ii) The mass and the charge entering equation (1) correspond to the *free electron mass and charge*, even for materials like heavy fermion superconductors where the normal state effective mass is extremely different from the free electron mass. (iii) The magnetic field equation (1) is the same whether a superconductor is put into rotation or a rotating normal metal is cooled into the superconducting state.

The fact that it is the electron's bare mass rather than the effective mass, and the bare charge (negative) rather than the effective charge (positive) that enter into equation (1), is unexplained within the conventional theory of superconductivity [117]. In particular, it implies that the superfluid carriers 'undress' from their interaction with the ionic lattice [118, 119]. Instead, the conventional theory asserts that the carriers are tightly coupled to the lattice since the origin of the interaction that leads to superconductivity is precisely the interaction between the electrons and the ionic lattice.

Furthermore, for the magnetic field to develop when a rotating normal metal is cooled into the superconducting state, the superfluid electrons near the surface need to *slow down* in order to create the surface current that gives rise to the magnetic field equation (1), *and*, negative charge needs to

move *inward* to satisfy mechanical equilibrium [120, 121]. The conventional theory does not explain the origin of the forces giving rise to these effects, characterized as ‘quite absurd from the viewpoint of the perfect conductor concept’ by London [9].

3.9. Inability to explain the Meissner effect

The Meissner effect is the most fundamental property of superconductors. When a superconductor is cooled in the presence of a static magnetic field, a spontaneous electric current near the surface of the superconductor develops that nullifies the magnetic field in its interior [122]. The literature on the conventional theory of superconductivity does not ever address nor answer the following questions: (i) How do electrons near the surface of the sample acquire the superfluid velocity needed to screen the magnetic field in the interior? (ii) How is angular momentum conserved in the process? These are fundamental questions that relate to the very essence of the phenomenon of superconductivity.

To the first question, a conventional superconductivity theorist may answer that because the final state with supercurrent flowing has lower free energy than the initial state, the system will somehow get there. However, the supercurrent is a macroscopic effect and it should be possible to identify a macroscopic *force* that leads electrons near the surface to start moving all in the same direction to give rise to the required current. The conventional theorist may say³ that since the Meissner state has a lower free energy F , the ‘force’ on coordinate x is $-dF/dx$ and no further explanation is needed. However, this explanation is flawed.

Quite the contrary, there is an induced electric field according to Faraday’s law that exerts an electric force on the charge carriers in exactly the opposite direction to what is required [123, 124]. The superconductor has to overcome this azimuthal electric force with another force in the opposite direction acting on the superfluid carriers. $-dF/dx$, with dx in the azimuthal direction as required to generate the Meissner current, is *not* a real, physical, force. The only forces in nature that are relevant in this context (of course gravitational and nuclear forces are irrelevant) are the Lorentz electromagnetic force [120] and ‘quantum pressure’, the tendency of quantum particles to lower their kinetic energy by radially expanding their wavefunction [125]. Neither of these forces plays a role in the Meissner effect according to the conventional theory of superconductivity.

To answer the second question is even more difficult within the conventional theory [124]. Because the supercurrent in the final state carries mechanical angular momentum, and because the total angular momentum in the normal state is zero, there exists a ‘missing angular momentum’ [123]. A conventional superconductivity theorist may answer that the ionic lattice takes up the missing angular momentum. However the conventional theory offers no mechanism by which such an angular momentum transfer between superfluid electrons and the ionic lattice would take place [124, 126–128]. In particular, if the electrons transfer the required angular momentum to the lattice through scattering via impurities or phonons, there should be a

clear way to describe this process since the heavy ions are essentially classical objects. No such description has ever been given within the conventional theory and in [123] it is argued that it may be impossible within the conventional theory.

3.10. Deviation from Occam’s razor

Occam’s razor is the philosophical principle that states that the explanation of any phenomenon should make as few assumptions as possible. Alternatively, that the simplest solution to a problem is preferable to more complicated solutions. However, as reviewed above, to explain all superconductors known today one needs many different mechanisms and fundamentally different physical assumptions.

Why is this implausible? Because there are fundamental characteristics of superconductors that *are* shared by all of them, namely: the Meissner effect, the Tao effect, the London moment and the existence of macroscopic phase coherence (Josephson effect). These characteristics are remarkable and qualitatively different from the properties of non-superconducting matter. It would be remarkable if nature had chosen to achieve these properties in materials through many different physical mechanisms and qualitatively different superconducting states. The progress of science has shown again and again that true scientific advances in understanding always simplify previously existing theories and unify the description of seemingly different phenomena.

We can make a parallel here with atomic physics. The spectra of atoms is very complicated and certainly cannot be explained by a simple Balmer-like formula that works for hydrogen only. However, we do not need a different ‘mechanism’ or theory to explain the atomic spectra of alkali metals, transition metals, rare gases, etc. All can be understood from the same fundamental principles that were first understood in the context of the simplest atom, hydrogen. Where is the ‘hydrogen atom’ of superconductivity?

4. An alternative to BCS

For the past 20 years co-workers and I have been developing an alternative to BCS theory, the theory of hole superconductivity [10, 129]. Essential aspects of the theory are:

1. It applies to all superconducting materials, in contrast to other alternative theories of superconductivity that have been proposed for specific classes of materials. A single material that is superconducting through another mechanism would prove the theory of hole superconductivity wrong [130, 131].
2. Electron–hole asymmetry is the key to superconductivity; hole carriers in the normal state are necessary for superconductivity.
3. Electron–phonon interaction does not cause superconductivity; superconductivity is driven by a purely electronic mechanism and is associated with kinetic energy lowering [132].
4. Material characteristics favorable for high T_c are: (i) transport in the normal state dominated by hole carriers,

³ This is quoted from a referee’s comment.

- and (ii) excess negative charge in the substructures (e.g. planes) where conduction occurs [133].
5. The gap function versus energy has a slope of universal sign, giving rise to asymmetry in tunneling experiments of universal sign [134].
 6. Superconductors expel negative charge from their interior toward the surface in the transition to superconductivity [135].
 7. London electrodynamic equations are modified [127, 136]. Macroscopic charge inhomogeneity and a macroscopic outward pointing electric field exist in the interior of superconductors. Applied electric fields are screened by the superfluid over a London penetration depth distance λ_L rather than over the much shorter Thomas–Fermi distance.
 8. A macroscopic spin current flows within a London penetration depth of the surface of superconductors, a kind of ‘zero point motion’ of the superfluid (Spin Meissner effect) [126].
 9. The spin–orbit interaction plays a fundamental role in superconductivity [128].
 10. Superfluid carriers reside in mesoscopic orbits of radius $2\lambda_L$ and carry orbital angular momentum $\hbar/2$ [126, 137].

The theory offers a compelling explanation for the Meissner effect [120, 123, 126]: in essence, the azimuthal force propelling the electrons in the Meissner current is the magnetic Lorentz force acting on electrons moving radially outward. The superconductor expels negative charge from its interior toward the surface and the outflowing charge drags the magnetic field lines with it as in a classical plasma (Alfvén’s theorem) [138] (even though the physics is highly non-classical). The outward motion of charge is driven by kinetic energy lowering and results in a macroscopically inhomogeneous charge distribution.

The theory also offers compelling explanations for the Tao effect [139], the puzzles of rotating superconductors [120, 121], Chapnik’s rule [140] and the variation of T_c along the elements in the transition metal series [141, 142]. The ‘soft phonon’ story [30] and the propensity of superconductors to be close to lattice instabilities [143], conventionally understood as arising from strong electron–phonon interactions, are more simply explained from the fact that superconductors have nearly full bands and hence a lot of electrons in *antibonding* states [144]. The same principle predicts that non-superconducting materials at ambient pressure that become superconducting under high pressure [84, 85] necessarily develop structures with carriers in nearly full bands [145], and explains qualitatively why superconductivity is favored at high pressures: the externally applied pressure counters the outward pressure exerted by electrons occupying antibonding states, which would otherwise render the system unstable. As Matthias famously said [143], ‘From now on, I shall look for systems that should exist, but won’t—unless one can persuade them’. The criteria given in (4) above provide guidelines in the search for new superconducting compounds, they explain why high T_c is found in the cuprates and predict that high T_c will be found in MgB_2 and Fe–As compounds. They also predict [146]

(contrary to conventional theory [74–76]) that high T_c will *not* be found in Li_{1-x}BC because it has far less negative charge in the planes than MgB_2 .

Examples of experiments that could provide key evidence in support of this theory and against conventional BCS theory are:

1. Detection of spontaneous macroscopic electrostatic fields in or around superconductors, of magnitude comparable with the magnetic critical field (H_c or H_{c1}) in cgs units.
2. Measurement of a macroscopic spin current in the ground state of a superconductor, of the predicted magnitude, namely carrier density the superfluid density and carrier speed given by the speed of carriers in the critical charge current of the superconductor.
3. Measurement of a much steeper plasmon dispersion relation in the superconducting state than in the normal state [136].
4. Detection of ionizing radiation emitted by a superconductor of large volume under non-equilibrium conditions, of frequencies up to $\omega = 0.511 \text{ MeV } \hbar^{-1}$ [147].

As a historical footnote I point out that several elements of this theory are related to preBCS-proposed explanations of superconductivity that are not part of the conventional BCS theory, namely: (i) Heisenberg [148] and others proposed that currents exist in the ground state of superconductors, albeit charge rather than spin currents; (ii) Born and Cheng [149] proposed that superconductivity could only occur when the Fermi surface is close to the edges of the Brillouin zone; (iii) Slater [150] proposed that electrons in superconductors reside in orbits of radius ~ 137 lattice spacings; (iv) Kronig [151] proposed that superconducting electrons do not ‘see’ the periodic ionic potential [117, 118]; and (v) Koch [152] proposed an explanation of the Meissner effect based on a thermoelectric radial current of electrons flowing from the warmer interior to the cooler exterior of a metal becoming superconducting.

5. Discussion

This paper focused on BCS theory; however, it is clear that more generally it may apply to all realms of contemporary science, i.e. that the same factors at play in the BCS case may be allowing for the preservation and growth of many flawed scientific theories *at the present time* [153]. With the growth and specialization of knowledge, incoming students increasingly rely on ‘gatekeepers’ (professors, mentors, established scientists, etc) to guide them into the world of science. The gatekeepers have a vested interest in preserving the status quo. A beginning scientist with a revolutionary idea that could prove many established scientists wrong is likely to be strongly discouraged from pursuing it, and if she/he persisted would simply be denied entrance to the profession by being unable to secure a job. By the time a scientist is ‘established’ he or she has usually been sufficiently conditioned to conform to the established truths.

For the case of BCS, it would be desirable that journal editors look more favorably than they have up to now at

papers suggesting inadequacies of BCS theory⁴, and keep in mind the vested interests of referees that are likely to write negative reports on such papers. To the extent that such papers can be published in mainstream publications, they will encourage physicists, the younger generation as well as some of the long-time experts that may have started having doubts about BCS in view of the recent experimental discoveries, to consider alternatives to the conventional BCS theory. It would also be desirable that funding agencies devote at least a small fraction of resources to experimental and theoretical work that calls into question the conventional BCS theory, and that conference and workshop organizers consider inviting speakers whose research questions the validity of BCS theory for conventional superconductors rather than shun such topics⁵.

The half-century old BCS theory has proven incapable of ever predicting a high-temperature superconductor. It offers no useful guidelines in the search for new superconducting compounds. It has proven incapable of explaining the superconductivity of ten families of compounds discovered in the last 30 years. It cannot explain the Meissner effect nor the Tao effect nor the de Heer effect nor Chapnik's rule nor rotating superconductors. The field of superconductivity is in crisis [1]. It is high time to consider the possibility that the lack of progress in understanding high T_c cuprates and other 'unconventional' superconductors may be due to the fact that 'conventional' superconductors are not understood either. It is high time to seriously consider the possibility that the BCS theory provides no real understanding of the superconductivity of 'conventional' materials because it is fundamentally flawed, and that it may be destined to be overhauled just as other established scientific theories of the past have been overhauled.

References

- [1] Kuhn T S 1996 *The Structure of Scientific Revolutions* 3rd edn (Chicago: Chicago University Press)
- [2] Bardeen J, Cooper L N and Schrieffer J R 1957 Theory of superconductivity *Phys. Rev.* **108** 1175–204
- [3] Migdal A B 1958 Interaction between electrons and lattice vibrations in a normal metal *Sov. Phys. JETP* **7** 996–1001
- [4] Eliashberg G M 1960 Interactions between electrons and lattice vibrations in a superconductor *Sov. Phys. JETP* **11** 696–702
- [5] Allen P B and Mitrovic B 1982 Theory of superconducting T_c *Solid State Phys.* **37** 1–92
- [6] Carbotte J C 1990 Properties of boson-exchange superconductors *Rev. Mod. Phys.* **62** 1027–157
- [7] Hirsch J E 2009 BCS theory of superconductivity: the world's largest Madoff scheme? arXiv: 0901.4099v1 [physics.gen-ph]
- [8] Lightman A and Gingerich O 1992 When do anomalies begin? *Science* **255** 690–5
- [9] London F 1950 *Superfluids* volume I. *Macroscopic Theory of Superconductivity* (New York: Dover) pp 1–173
- [10] Hirsch J E 2006 The fundamental role of charge asymmetry in superconductivity *J. Phys. Chem. Solids* **67** 21–6
- [11] Shermer M 2002 *Why People Believe Weird Things: Pseudoscience, Superstition, and Other Confusions of Our Time* (New York: Henry Holt) pp 1–349
- [12] Hebel L C and Slichter C P 1957 Nuclear relaxation in superconducting aluminum *Phys. Rev.* **107** 901–2
- [13] Josephson B D 1962 Possible new effects in superconductive tunnelling *Phys. Lett.* **1** 251–3
- [14] Parks R D (ed) 1969 *Superconductivity* vol I and II (New York: Dekker)
- [15] Bardeen J 1956 *Theory of Superconductivity. Theoretical Part. Handbuch der Physik* vol 15 (Berlin: Springer) pp 274–369
- [16] Plumb R K 1957 Theory of metals in cold evolved *New York Times*, 28 December
- [17] Schafroth M R 1958 Remarks on the Meissner effect *Phys. Rev.* **111** 72–4
- [18] Rickayzen G 1959 Collective excitations in the theory of superconductivity *Phys. Rev.* **115** 795–808
- [19] Kondo J 1963 Superconductivity in transition metals *Prog. Theor. Phys.* **29** 1–9
- [20] Suhl H, Matthias B T and Walker L R 1959 Bardeen–Cooper–Schrieffer theory of superconductivity in the case of overlapping bands *Phys. Rev. Lett.* **3** 552–4
- [21] Kuper C G, Jensen M A and Hamilton D C 1964 Simple model for the superconductivity of lanthanum and uranium *Phys. Rev.* **134** A15–21
- [22] Matthias B T 1973 T_c 's—The high and low of it *Science and Technology of Superconductivity Volume 1* ed W D Gregory, W N Mathews and E A Edelsack (New York: Plenum) pp 263–88
- [23] Scalapino D J, Schrieffer J R and Wilkins J W 1966 Strong-coupling superconductivity I. *Phys. Rev.* **148** 263–79
- [24] Scalapino D J 1969 The electron–phonon interaction and strong-coupling superconductors *Superconductivity* ed R D Parks (New York: Dekker) pp 449–560
- [25] McMillan W L and Rowell J M 1969 Tunneling and strong-coupling superconductivity *Superconductivity* vol I ed R D Parks (New York: Dekker) pp 561–613
- [26] Haller E E 2005 Isotopically controlled semiconductors *Solid State Commun.* **133** 693–707
- [27] Weber W 1984 The phonons in high T_c A15 compounds *Physica B+C* **126** 217–28
- [28] Kortus J, Mazin II, Belashchenko K D, Antropov V P and Boyer L L 2001 Superconductivity of metallic boron in MgB_2 *Phys. Rev. Lett.* **86** 4656–9
- [29] Ashcroft N W 1968 Metallic hydrogen: a high-temperature superconductor? *Phys. Rev. Lett.* **21** 1748–9
- [30] Testardi L R 1972 Structural instability, anharmonicity, and high-temperature superconductivity in A-15-structure compounds *Phys. Rev. B* **5** 4342–9
- [31] De Launay J and Dolecek R L 1947 Superconductivity and the Debye characteristic temperature *Phys. Rev.* **72** 141–3
- [32] McMillan W L 1968 Transition temperature of strong-coupled superconductors *Phys. Rev.* **167** 331–44
- [33] Carbotte J P and Dynes R C 1968 Superconductivity in simple metals *Phys. Rev.* **172** 476–84
- [34] Allen P B and Dynes R C 1975 Transition temperature of strong-coupled superconductors reanalyzed *Phys. Rev. B* **12** 905–22
- [35] Papaconstantopoulos D A *et al* 1977 Calculations of the superconducting properties of 32 metals with $Z \leq 49$ *Phys. Rev. B* **15** 4221–6
- [36] Sanborn B A, Allen P B and Papaconstantopoulos D A 1989 Empirical electron–phonon coupling constants and anisotropic electrical resistivity in hcp metals *Phys. Rev. B* **40** 6037–44
- [37] Allen P B and Cohen M L 1969 Pseudopotential calculation of the mass enhancement and superconducting transition temperature of simple metals *Phys. Rev.* **187** 525–38
- [38] Papaconstantopoulos D A and Klein B M 1975 Superconductivity in the palladium–hydrogen system *Phys. Rev. Lett.* **35** 110–3

⁴ In this author's experience, European-based journals are notably more open-minded than US-based journals.

⁵ The conference series New3SC (New Theories, Discoveries and Applications of Superconductors and Related Materials) organized by JD Fan *et al* is a notable exception to the rule in that it fosters presentation of ideas that may question established views.

- [39] Geballe T H, Matthias B T, Hull G W Jr and Corenzwit E 1961 Absence of an isotope effect in superconducting ruthenium *Phys. Rev. Lett.* **6** 275–7
- [40] Geballe T H and Matthias B T 1962 Isotope effects in low temperature superconductors *IBM J. Res. Dev.* **6** 256–7
- [41] Fowler R D, Lindsay J D G, White R W, Hill H H and Matthias B T 1967 Positive isotope effect on the superconducting transition temperature of α -uranium *Phys. Rev. Lett.* **19** 892–5
- [42] Garland J W 1963 Mechanisms for superconductivity in the transition metals *Phys. Rev. Lett.* **11** 111–4
- [43] Capellmann H and Schrieffer J R 1968 Isotope effect of superconducting α -uranium *Phys. Rev. Lett.* **21** 1060–1
- [44] Bostock J *et al* 1976 Does strong-coupling theory describe superconducting Nb? *Phys. Rev. Lett.* **36** 603–6
- [45] Bostock J and Macvicar M L A 1979 Comment on the state-of-the-art of tunneling into superconducting niobium *Phys. Lett. A* **71** 373–6
- [46] Arnold G B, Zasadzinski J and Wolf E I 1978 A resolution of the controversy on tunneling in Nb *Phys. Lett. A* **69** 136–8
- [47] Gladstone G, Jensen M A and Schrieffer J R 1969 Superconductivity in the transition metals: theory and experiment *Superconductivity* vol II ed R D Parks (New York: Dekker) pp 665–816
- [48] Capellmann 1970 Incipient antiferromagnetism in scandium *J. Low Temp. Phys.* **3** 189–96
- [49] Berk N F and Schrieffer J R 1966 Effect of ferromagnetic spin correlations on superconductivity *Phys. Rev. Lett.* **17** 433–5
- [50] Fay D and Appel J 1977 Possibility of triplet pairing in palladium *Phys. Rev. B* **16** 2325–8
- [51] Stritzker B 1979 Superconductivity in irradiated palladium *Phys. Rev. Lett.* **42** 1769–73
- [52] Gilman J J 1971 Lithium dihydrogen fluoride—an approach to metallic hydrogen *Phys. Rev. Lett.* **26** 546–8
- [53] Satterthwaite C B and Toepke I L 1970 Superconductivity of hydrides and deuterides of thorium *Phys. Rev. Lett.* **25** 741–3
- [54] Koskiewicz T 1973 Superconductivity in the palladium–hydrogen system *Phys. Status. Solidi. b* **59** 329–34
- [55] Stritzker B and Buckel W 1972 Superconductivity in the palladium–hydrogen and the palladium–deuterium systems *Z. Phys.* **257** 1–8
- [56] Ganguly B N 1973 High frequency local modes, superconductivity and anomalous isotope effect in PdH(D) systems *Z. Phys.* **265** 433–9
- [57] Papaconstantopoulos D A, Klein B M, Economou E N and Boyer L L 1978 Band structure and superconductivity of PdD_x and PdH_x *Phys. Rev. B* **17** 141–50
- [58] Ashcroft N W 2004 Hydrogen dominant metallic alloys: high temperature superconductors? *Phys. Rev. Lett.* **92** 187002
- [59] Liu A Y and Cohen M L 1991 Electron–phonon coupling in bcc and 9R lithium *Phys. Rev. B* **44** 9678–84
- [60] Tuoriniemi J *et al* 2007 Superconductivity in lithium below 0.4 millikelvin at ambient pressure *Nature* **447** 187–9
- [61] Little W A 1964 Possibility of synthesizing an organic superconductor *Phys. Rev.* **134** A1416–24
- [62] Allen P B and Cohen M L 1972 Superconductivity and phonon softening *Phys. Rev. Lett.* **20** 1593–6
- [63] Testardi L R 1975 Structural instability and superconductivity in A-15 compounds *Rev. Mod. Phys.* **47** 637–48
- [64] Cohen M L and Anderson P W 1972 Comments on the maximum superconducting transition temperature *superconductivity in d- and f-band metals* ed D H Douglass (New York: AIP) pp 17–27
- [65] Wu M K *et al* 1987 Superconductivity at 93 K in a new mixed-phase Y–Ba–Cu–O compound system at ambient pressure *Phys. Rev. Lett.* **58** 908–10
- [66] Lemonick M D 1987 Superconductors! *Time Magazine* 11 May issue
- [67] Schooley J F, Hosler W R and Cohen M L 1964 Superconductivity in semiconducting SrTiO₃ *Phys. Rev. Lett.* **12** 474–5
- [68] Koonce C S, Cohen M L, Schooley J F, Hosler W R and Pfeiffer E R 1967 Superconducting transition temperatures of semiconducting SrTiO₃ *Phys. Rev.* **163** 380–90
- [69] Nagamatsu J, Nakagawa N, Muranaka T, Zenitani Y and Akimitsu J 2001 Superconductivity at 39 K in magnesium diboride *Nature* **410** 63–4
- [70] Choi H J, Roundy D, Sun H, Cohen M L and Louie S G 2002 First-principles calculation of the superconducting transition in MgB₂ within the anisotropic Eliashberg formalism *Phys. Rev. B* **66** 020513
- [71] Kong Y, Dolgov O V, Jepsen O and Andersen O K 2001 Electron–phonon interaction in the normal and superconducting states of MgB₂ *Phys. Rev. B* **64** 020501
- [72] An J M and Pickett W E 2001 Superconductivity of MgB₂: covalent bonds driven metallic *Phys. Rev. Lett.* **86** 4366–9
- [73] Mazin I I and Antropov V P 2003 Electronic structure, electron–phonon coupling, and multiband effects in MgB₂ *Physica C* **385** 49–65
- [74] Rosner H, Kitaigorodsky A and Pickett W E 2002 Prediction of high T_c superconductivity in hole-doped LiBC *Phys. Rev. Lett.* **88** 127001
- [75] An J M, Savrasov S Y, Rosner H and Pickett W E 2002 Extreme electron–phonon coupling in boron-based layered superconductors *Phys. Rev. B* **66** 220502
- [76] Dewhurst J K, Sharma S, Ambrosch-Draxl S C and Johansson B 2003 First-principles calculation of superconductivity in hole-doped LiBC: T_c = 65 K *Phys. Rev. B* **68** 020504
- [77] Ribeiro F J and Cohen M L 2004 Possible superconductivity in hole-doped BC *Phys. Rev. B* **69** 212507
- [78] Moussa J M and Cohen M L 2008 Constraints on T_c for superconductivity in heavily boron-doped diamond *Phys. Rev. B* **77** 064518
- [79] Zhao L, Klavins P and Liu K 2003 Synthesis and properties of hole-doped Li_{1-x}BC *J. Appl. Phys.* **93** 8653–5
- [80] Ueno A *et al* 2006 Scanning tunneling microscopy study on a BC3 covered NbB₂(0001) surface *Surf. Sci.* **600** 3518–21
- [81] Wittig J, Probst J, Schmidt F A and Gschneidner K A Jr 1979 Superconductivity in a new high-pressure phase of scandium *Phys. Rev. Lett.* **42** 469–72
- [82] Hamlin J J and Schilling J S 2007 Pressure-induced superconductivity in Sc to 74 GPa *Phys. Rev. B* **76** 012505
- [83] Nixon L W, Papaconstantopoulos D A and Mehl M J 2007 Calculations of the superconducting properties of scandium under high pressure *Phys. Rev. B* **76** 134512
- [84] Debessai M, Hamlin J J and Schilling J S 2008 Comparison of the pressure dependences of T_c in the trivalent d-electron superconductors Sc, Y, La and Lu up to megabar pressures *Phys. Rev. B* **78** 064519
- [85] Shimizu K, Amaya A and Suzuki N 2005 Pressure-induced superconductivity in elemental materials *J. Phys. Soc. Japan* **74** 1345–57
- [86] Papaconstantopoulos D A and Mehl M J 2002 First-principles study of superconductivity in high-pressure boron *Phys. Rev. B* **65** 172510
- [87] Christensen N E and Novikov D L 2006 Calculated superconductive properties of Li and Na under pressure *Phys. Rev. B* **73** 224508
- [88] Shi L and Papaconstantopoulos D A 2006 Theoretical predictions of superconductivity in alkali metals under high pressure *Phys. Rev. B* **73** 184516
- [89] Kasinathan D *et al* 2006 Superconductivity and lattice instability in compressed lithium from Fermi surface hot spots *Phys. Rev. Lett.* **96** 047004
- [90] Profeta G *et al* 2006 Superconductivity in lithium, potassium, and aluminum under extreme pressure: a first-principles study *Phys. Rev. Lett.* **96** 047003
- [91] Lei S, Papaconstantopoulos D A and Mehl M J 2007 Calculations of superconducting properties in yttrium and calcium under high pressure *Phys. Rev. B* **75** 024512
- [92] Yin Z P, Savrasov S Y and Pickett W E 2006 Linear response study of strong electron–phonon coupling in yttrium under pressure *Phys. Rev. B* **74** 094519

- [93] Singh P P 2007 Electronic structure and electron–phonon interaction in hexagonal yttrium by density functional calculations *Phys. Rev. B* **75** 125101
- [94] Alexandrov A S 2003 *Theory of Superconductivity. From weak to Strong Coupling* (Bristol: Institute of Physics Publishing)
- [95] Marsiglio F 1995 Pairing in the Holstein model in the dilute limit *Physica C* **244** 21–34
- [96] Kikoin K and Lasarew B 1932 Hall effect and superconductivity *Nature* **129** 57–8
Kikoin K and Lasarew B 1933 *Phys. Z. Sowjetunion* **3** 351
- [97] Papapetrou A 1934 Bemerkungen zur Supraleitung *Z. Phys.* **92** 513–22
- [98] Chapnik I M 1979 On the empirical correlation between the superconducting T_c and the Hall coefficient *Phys. Lett. A* **72** 255–6
- [99] Jiang W *et al* 1994 Anomalous transport properties in superconducting $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{Cu}_{4\pm\delta}$ *Phys. Rev. Lett.* **73** 1291–4
- [100] Fournier P *et al* 1997 Thermomagnetic transport properties of $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{Cu}_{4\pm\delta}$ films: evidence for two types of charge carriers *Phys. Rev. B* **56** 14149–56
- [101] Hirsch J E 1997 Correlations between normal-state properties and superconductivity *Phys. Rev. B* **55** 9007–24
- [102] Tao R, Zhang X, Tang X and Anderson P W 1999 Formation of high temperature superconducting balls *Phys. Rev. Lett.* **83** 5575–8
- [103] Tao R, Xu X, Lan Y C and Shiroyanagi Y 2002 Electric-field induced low temperature superconducting granular balls *Physica C* **377** 357–61
- [104] Tao R, Xu X and Amr E 2003 MgB_2 superconducting particles in a strong electric field *Physica C* **398** 78–84
- [105] Bardeen J and Schrieffer J R 1961 Recent developments in superconductivity *Prog. Low Temp. Phys.* **3** 170–287
- [106] Koyama T 2004 Comment on charge expulsion and electric field in superconductors *Phys. Rev. B* **70** 226503
- [107] Moro R, Xu X, Yin S and de Heer W A 2003 Ferroelectricity in free niobium clusters *Science* **300** 1265–9
- [108] Xu X *et al* 2007 Nonclassical dipoles in cold niobium clusters *Phys. Rev. B* **75** 085429
- [109] Yin S, Xu S, Liang A, Bowlan J, Moro R and de Heer W A 2008 Electron pairing in ferroelectric niobium and niobium alloy clusters *J. Supercond. Novel Magn.* **21** 265–9
- [110] Becker R, Sauter F and Heller C 1933 Ueber die Stromverteilung in einer supraleitenden Kugel *Z. Phys.* **85** 772–87
- [111] London F and London H 1935 Supraleitung und diamagnetismus *Physica* **2** 341–54
- [112] Hildebrandt A F 1964 Magnetic field of a rotating superconductor *Phys. Rev. Lett.* **8** 190–1
- [113] Hildebrandt A F and Saffren M M 1965 *Proc. 9th Int. Conf. Low Temperature Physics* ed J G Daunt *et al* (New York: Plenum) p 459
- [114] Bol M and Fairbank W M 1965 Measurement of the London moment *Proc. 9th Int. Conf. Low Temperature Physics* ed J G Daunt *et al* (New York: Plenum) pp 471–2
- [115] Sanzari M A and Cui H L 1996 London moment for heavy-fermion superconductors *Appl. Phys. Lett.* **68** 3802–4
- [116] Verheijen A A, van Ruitenbeek J M, de Bruyn Ouboter R and de Jongh L J 1990 Measurement of the London moment in two high-temperature superconductors *Nature* **345** 418–9
- [117] Hirsch J E 2003 Electron–hole asymmetry and superconductivity *Phys. Rev. B* **68** 012510
- [118] Hirsch J E 2005 Why holes are not like electrons. II. The role of the electron–ion interaction *Phys. Rev. B* **71** 104522
- [119] Frenkel J and Rudnitsky V 1939 Gyromagnetic effect in supraconductors *J. Exp. Theoret. Phys.* **9** 260–1
- [120] Hirsch J E 2003 The Lorentz force and superconductivity *Phys. Lett. A* **315** 474–9
- [121] Hirsch J E 2005 Spin currents in superconductors *Phys. Rev. B* **71** 184521
- [122] Meissner W and Ochsenfeld R 1933 Ein neuer Effekt bei Eintritt der Supraleitfähigkeit *Naturwissenschaften* **21** 787–8
- [123] Hirsch J E 2008 The missing angular momentum of superconductors *J. Phys. Cond. Matt.* **20** 235233
- [124] Hirsch J E 2007 Do superconductors violate Lenz’s law? Body rotation under field cooling and theoretical implications *Phys. Lett. A* **366** 615–9
- [125] Hirsch J E 2009 Electromotive forces and the Meissner effect puzzle arXiv: 0908.4096v2 [cond-mat.supr-con]
- [126] Hirsch J E 2008 Spin Meissner effect in superconductors and the origin of the Meissner effect *Europhys. Lett.* **81** 67003
- [127] Hirsch J E 2008 Electrodynamics of spin currents in superconductors *Ann. Phys., Berlin* **17** 380–409
- [128] Hirsch J E 2009 Charge expulsion, spin Meissner effect, and charge inhomogeneity in superconductors *J. Supercond. Novel Magn.* **22** 131–9
- [129] Hirsch J E 1989 Hole superconductivity *Phys. Lett. A* **134** 451–5
- [130] Hirsch J E 2002 *Hole Superconductivity in MgB_2 , Cuprates, and Other Materials* ed A Narlikar (New York: Nova Science Publishers) pp 38, 49–73
- [131] Marsiglio F and Hirsch J E 2008 Hole superconductivity in arsenic–iron compounds *Physica C* **468** 1047–52
- [132] Hirsch J E and Marsiglio F 1993 London penetration depth in hole superconductivity *Phys. Rev. B* **45** 4807–18
- [133] Hirsch J E 1993 Electron- and hole-hopping amplitudes in a diatomic molecule *Phys. Rev. B* **48** 3327–39
- [134] Marsiglio F and Hirsch J E 1989 Tunneling asymmetry: a test of superconductivity mechanisms *Physica C* **159** 157–60
- [135] Hirsch J E 2003 Charge expulsion and electric field in superconductors *Phys. Rev. B* **68** 184502
- [136] Hirsch J E 2004 Electrodynamics of superconductors *Phys. Rev. B* **69** 214515
- [137] Hirsch J E 2009 Why holes are not like electrons. III. How holes in the normal state turn into electrons in the superconducting state *Int. J. Mod. Phys. B* **23** 3035–57
- [138] Newcomb W A 1958 Motion of magnetic lines of force *Ann. Phys.* **3** 347–85
- [139] Hirsch J E 2005 Explanation of the Tao effect: theory for the spherical aggregation of superconducting microparticles in an electric field *Phys. Rev. Lett.* **94** 187001
- [140] Hirsch J E 2002 Why holes are not like electrons: a microscopic analysis of the differences between holes and electrons in condensed matter *Phys. Rev. B* **65** 184502
- [141] Hirsch J E and Marsiglio F 1989 On the dependence of superconducting T_c on carrier concentration *Phys. Lett. A* **140** 122–6
- [142] Hong X Q and Hirsch J E 1992 Superconductivity in the transition-metal series *Phys. Rev. B* **46** 14702–12
- [143] Matthias B T 1973 Criteria for superconducting transition temperatures *Physica* **69** 54–6
- [144] Hirsch J E 1989 Bond-charge repulsion and hole superconductivity *Physica C* **158** 326–36
- [145] Hirsch J E and Hamlin J J 2009 Why non-superconducting metallic elements become superconducting under high pressure arXiv: 0908.3496v1 [cond-mat.supr-con]
- [146] Hirsch J E 2003 Electronic dynamic Hubbard model: exact diagonalization study *Phys. Rev. B* **67** 035103
- [147] Hirsch J E 2007 Ionizing radiation from superconductors in the theory of hole superconductivity *J. Phys: Condens. Matter* **19** 125217
- [148] Heisenberg W 1948 Das elektrodynamische verhalten der supraleiter *Z. Nat. forsch. A* **3** 65–75
- [149] Born M and Cheng K C 1948 Theory of superconductivity *Nature* **161** 968–9
- [150] Slater J C 1937 The nature of the superconducting state. II *Phys. Rev.* **52** 214–22
- [151] Kronig R de L 1932 Zur Theorie der Supraleitfähigkeit *Z. Phys.* **78** 744–50
- [152] Koch K M 1940 Versuch einer elektronenphysikalischen Deutung des Meissner–Ochsenfeld-effektes *Z. Phys.* **116** 586–97
- [153] Charlton B G 2008 Zombie science: a sinister consequence of evaluating scientific theories purely on the basis of enlightened self-interest *Med. Hypotheses* **71** 327329