IOP Publishing Journal of Physics: Condensed Matter
J. Phys.: Condens. Matter **31** (2019) 174001 (5pp) https://doi.org/10.1088/1361-648X/ab02ad

Why have band theorists been so successful in explaining and predicting novel superconductors?

I I Mazin

Code 6393, Naval Research Laboratory, Washington, DC 20375, United States of America

Received 17 January 2019
Accepted for publication 29 January 2019
Published 27 February 2019

Abstract

In this contribution to the *J. Phys.: Condens. Matter* memorial issue in honor of Sandro Massidda I reflect on a phenomenon Sandro had been a part of. While theoretical condensed matter physicists have made, over the years, exciting and most elegant contributions to the theory of superconductivity (which, in and by itself, is one of the most beautiful constructs in theoretical physics), some of them of utmost importance, they have had less success in predicting and explaining superconducting states and mechanisms in specific materials. More down-to-earth computational materials scientists, who often go by the moniker 'band theorists', have been much more successful in applying (usually other people's) ideas in such circumstances. In this essay I give some examples, largely drawn from my own experience, and speculate on their meaning.

Keywords: band structure, superconductivity, computational materials science

The last several decades have witnessed impressive contributions of band theorists, now more often referred to as computational materials scientists, in the fields of conventional and unconventional superconductivity. While the former is amazing in terms of the accuracy and predictive power of such first principles calculations, it is less surprising than the latter, which is justly perceived to be a domain of 'high-brow science', well beyond direct capability of first principles calculations. In my opinion, these two successes have quite different reasons, and I will dicuss them both in the following text.

The first principles theory of (at that time conventional) superconductivity goes back to George Gaspari and Balazs Gyorrfy, who suggested the first, albeit rather approximate, technique for computing the electron–phonon coupling constant, λ, from *ab initio* band structure calculations [1], and fundamental theoretical works by Phil Allen, Dierk Rainer, Eugene Maksimov and many others, well summarized in Rainer's review [2]. As a result, a foundation of first principles calculations of the anisotropic Eliashberg functions was established (a special mention goes to collaborations between Phil Allen, mostly an analytical theorist, and band theorists, such as Bill Butler, Warren Pickett, and others). After establishing the technique of applying Sternheimer's perturbation theory [3] to the linear response in periodic solids by Baroni and his collaborators [4], the community witnessed rapid progress in calculating the Eliashberg function and solving the Eliashberg equation, first isotropic, and then anisotropic, from first principles. A parallel, very successful development, also based on these linear response techniques, was superconducting density functional theory [5]. As these two directions matured (Sandro was taking an active part in both developments), accurate calculations of the critical temperatures of simple classical superconductors, such as Nb or Mo, had become possible. The very fact that a quantity exponentially dependent on parameters (at least, in the weak coupling regime) was coming out basically right was perceived as curious, but not necessarily very enlightening. The fact that superconductivity of the doped fullerenes was clarified in 1991 on a very basic level, as being related to intramolecular bond-length-changing phonon modes by three independent groups [6–8], two of which entirely composed of band theorists, was left unappreciated, partially because it was later recognized that the full physical picture was more complicated than that.

This perception would change definitively in 2001 after the discovery of a 40 K superconductivity in MgB_2. Recognized gurus of strongly correlated matter, who had gained fame

 © 2019 IOP Publishing Ltd Printed in the UK

through high-Tc cuprates (we will get to this family later) proffered all sorts of theories to this effect, all of them, it turned out, spectacularly off mark. At the same time band theorists were able to identify both the essential physcs, aptly dubbed by Warren Pickett 'doping of covalent bonds' (we will get back to this concept later) [9], and the correct structure of the order parameter (two distinctly different gaps) [10]. In both cases the insight was based, in a profound and intimate level, on the very material-specific aspects of the electronic bands, Fermi surfaces, and the calculated Eliashberg function[1]. Lack of this detailed understanding of materials-specific electronic properties is what prevented bright minds fed on model Hamiltonians from uncovering the right physics. Their *modus operandi* was 'what exciting physics is possible?' rather than 'what is possible in this specific material?' (I will come back to this important difference later again).

It is instructive at this point to go back 12 years and look at the paper by Len Mattheiss *et al* [11]. This was, arguably, the first paper where a new superconducting compound was suggested theoretically and verified experimentally. Noteworthy, this prediction was made years before the computational soft- and hardware had developed to a level permitting full electron–phonon coupling calculations for complex solids. Rather, the prediction was based entirely on Len's band theorist's intuition. A few years earlier he had calculated the electronic structure of the so-called Sleight oxide, $BaBiO_3$, which had been known to superconduct at a few Kelvin upon doping Pb for Bi, despite having a very low density of states. Mattheiss found that the conducting electrons are primarily derived from the Bi orbitals, and correctly conjectured that doping the 'active' bands does not allow for full benefits for superconductivity. Thus, he proposed to substitute the fully ionized Ba for K, and, indeed, the critical temperature for the optimal doping was dramatically increased compared to that of $Ba(Bi,Pb)O_3$, eventually surpassing 30 K.

This example shows that the main advantage of computational material scientists over the model theories adepts is not, or, at least, mostly not, the access to accurate numbers cranked by a computer, but material-sensitive, chemistry-driven intuition developed through performing calculation and analyzing their results for many classes of materials.

With time, more and more accurate calculations for more and more complex systems have become possible, together with considerable progress in computing crystallographic stability, eventually leading to excellent 'brute force' predictions of entirely new superconductors. This development has recently culminated in two record-breaking discoveries, superconductivity in H_3S at 200 and in LaH_{10} at 250 K, both predicted theoretically as materials stable at high pressure and as high-temperature superconductors, and, in fact, both utilizing Pickett's concept of 'doped covalent bonds'.

This is probably less surprising given that the theory of phonon-driven superconductivity is well established (as long as the key conditions are satisfied, namely, $kT_c \sim \Delta \lesssim \omega_{ph} \ll E_F$), and materials in question are satisfactorily described by the density dunctional theory, DFT, (which is, by nature, a static mean field theory). What is astonishing is that band theorists (if not the band theory directly) have provided over the years a lot of insight into the physics of unconventional superconductivity in unconventional materials.

Historically, when it was first realized that the insulating state of the parent compounds of the high-Tc cuprates cannot be reproduced by DFT calculations, the first reaction was to deny the latter any relevance and utility. To lesser extent, similar fate was suffered by Eliashberg equations. This author was a part of a paper submitted originally to *Phys. Rev. Lett.* [12], which was rejected on the ground of its using the Zeyher–Zwicknagl theory [13], dismissed by the referee as 'uncritical utilization of the Eliashberg equations beyond their range of applicability', and calculating the electron–phonon coupling parameters from DFT, 'application of DFT to materials to which it has no relevance'. The excellent agreement with the experiment did not seem to waver the referee's conviction. Needless to say, DFT calculations of the electron–phonon coupling in optimally doped cuprates were later recognized as quite reasonable, and regardless of the nature of the superconducting gap, its effect on the phonon energy was correctly described by the Zeyher–Zwicknagl formalism.

It is instructive to recall the state of experimental affairs in the field of superconducting cuprates at that time. Both the ARPES techique and the sample quality would undergo dramatic progress in the coming decade, but at that time it was not even able to detect the Fermi surface in the optimally doped cuprates. Superconductivity in alleged absence of a regular Fermi surface in the normal state led to a plethora of highly exotic theories, including such notions as, for instance, 'pseudo Fermi surface' or anyon superconductivity. An idea that, at least in the optimally- and overdoped high-Tc superconductors, the concept of (renormalized) Fermi liquid may not be so out-of-touch with reality and the DFT Fermi surface may actually be meaninful was, at that time, advocated only by band theorists [14]. As we now know very well, this concept was correct, and improved experiments have confirmed it. For a while, it seemed impossible to distinguish spectroscopically the bonding-antibonding splitting in bilayer cuprates, which led to a new generations of intriguing physical theories, such as 'interlayer pair tunneling' [16]. Again, with time the experiment has converged to the DFT results [15], not the other way around, as it often happens with theories. Moreover, while there is still no consensus on the theory of superconductivity in cuprates, arguably the most popular direction takes the most intuitive, from the point of view of DFT, approach, wherein the pairing interaction has magnetic origin and the Fermi surface geometry and the character of spin fluctuations (both easily obtainable from DFT calculations) lead to a d-wave pairing. This point of view was advocated by Doug Scalapino, David Pines and others. Of course, they were basing their intuition on the experimental findings, but could have used DFT calculations as well.

This said, it is quite clear that the essential physics of the high-Tc superconductivity is beyond the scope of DFT, which brings us to another important aspect of the latter. DFT is a

[1] I cannot resist mentioning that Sandro Massidda has made an invaluable contribution into the study of MgB_2, having published 30 papers on this subject, with more than 1000 cummulative citation count.

quantitative theory, based on a well-defined set of approximations. It is in a unique position where both successes and failures of a theory add equally to our understanding of real physics in a particular system. Model calculations more often than not can be tuned (to avoid the word 'massaged') to agree with essentially any experiment. DFT has relatively few knobs (although its extentions such as DFT+U or DFT+DMFT have more), and therefore its failure clearly outlines the applicability of its fundamental assumptions to a given material. Moreover, depending on the manner in which it fails one can extract invaluable information about the system. For instance, the fact that DFT underestimates the tendency to magnetism in cuprates tells us about the importance of local physicis and local correlations there. Conversely, the fact that DFT *overestimates* the tendency to magnetism in Fe-based superconductors suggests that magnetism there is largely itinerant and suppressed by long-range spin fluctuations.

Let us continue our historical excursion. For decades, Cu-based superconductors occupied most of researchers' attention, however, there were interesting splashes time and again in the sea of superconducting materials. The first that comes to mind is A_3C_{60} (A = K, Rb, Cs). Superconductivity at record (not counting the cuprates) temperatures up to 40 K [17] at that time, was mentioned above. It is worth noting that it was not a brute force calculation that provided insight; in fact, full electron–phonon calculations as we know them now were not possible at that time, and when they became possible it turned out that they underestimate the calculated coupling constant by 40% (band calculations beyond DFT, such as hybrid or GW functional correct for this error). Rather, it was qualitative (and correct) understanding of the basic physics, which had emerged from relatively inaccurate DFT calculations.

Fast forward ten years, and we have a bunch of discoveries that would have been sensational before the cuprates, but only attracted moderate attention in 2001. I am speaking of several new superconductors discovered, or declared in that year: $MgCNi_3$, $ZrZn_2$, ε-Fe, and, of course, MgB_2. Among them we find, in this order, (i) a material with a very strong electron–phonon coupling, but with a rather modest critical temperature of 8 K [18], (ii) an experimental artifact, a several years later retracted claim of coexistence of superconductivity and ferromagnetism [19], (iii) a ferromagnet turned into a superconductor by pressure [20], and (iv) the record normal-pressure-Tc conventional superconductor [21]. In all these cases the original assessement of the community was to a larger or smaller extent off the mark. In the first case, the original paper was pointing out an analogy with the $LnNi_2B_2C$ family, which are 2D superconductors, and expressed a justified surprise that in a 3D analogue T_c is much lower. This paper advocated for an unconventional superconductivity, having no gauge for the strength of the electron–phonon coupling. Early DFT calculations, however, have identified a very strong coupling with rotational phonon modes [22] (with, it was later found, a strong anharmonic component [23]), with a strong pair-breaking due to proximity to magnetism.

In the second case, the original paper was aiming at triplet pairing, postulating a microscopic coexistence with ferromagnetism; DFT calculations, again, showed strong coupling with particular phonons, and the calculated electronic and magnetic properties did not look encouraging for triplet pairing—nothing explicit, just a general impression. Correspondingly, Singh and Mazin [24] offered three possible scenarios, ordered by their likelihood: sample inhomogenuity, a Fulde–Ferrel state, or, least likely, triplet pairing. Indeed, a few years later it was found [25] that [19] had observed surface superconductivity.

Finally, in the third case it was found that when Fe loses its ferromagnetism at pressures above 15 GPa it transforms into a hexagonal structure know as ε-Fe and becomes superconducting. The original paper was calling ε-Fe 'non-magnetic' and referred to decades-old predictions (including one involving Sandro Massidda) [26] that the electron–phonon coupling in Fe, *if the magnetism could be entirely suppressed*, would be strong enough to provide for measureable superconductivity. When band theorists took a closer look at this experiment, they found that (1) ε-Fe at this pressures is not *non-magnetic*, but *paramagnetic*, sporting large, but disordered and strongly fluctuating magnetic moments [27] and (2) electron–phonon coupling depends on the pressure very weakly, while superconductivity exists only in a very narrow pressure range [28]. These two finding were in contradiction with the original proposal of the phonon-driven superconductivity, but rather pointing toward a spin-fluctuations-induced, uncoventional pairing. Subsequent experiments found unusual sensitivity to disorder, indicating such an unconventional pairing [29].

Let us once again return to the fourth case, MgB_2, which was, arguably, the most important discovery in superconductivity since the cuprates. The computational part, even while challenging at that time, was rather trivial, as was the much touted prediction of a two-gap superconductivity [10] (curiously, the 'model Hamiltonian' theorists were quite at loss with this compound, apparently still under the spell of the incorrect claim of a 30 K T_c limit for conventional superconductors, see [30]; they were proposing such exotic mechanisms as acoustic phonons, resonant valence bond, etc, overlooking the simple solution). What was not trivial was a new concent in phonon-driven superconductivity, introduced by Warren Pickett [9], which has proven instrumental for recently dicovered record-Tc hydorgen based superconductors: doped covalent bonds.

An opposite idea, of the utility of soft modes, had been circulated in the community for decades, even though many theorists were warning that the classical soft modes are only soft at particular points in the Brillouin zone and thus do not have enough phase space to boost superconductivity. The soft mode concept was based on the mathematically correct statement that phonons with frequencies close to $2\pi T_c$ are the most efficient in increasing the critical temperature [30], and that the classical expression for the electron–phonon coupling includes inverse force constants, which can written as $\lambda_{\nu,\mathbf{q}} \propto 1/\Phi = 1/M\omega^2_{\nu,\mathbf{q}}$, where M is some effective ionic mass. Obviously, lowering ω will increase λ in the exponent, which should be more important than the prefactor ω. Or is it?

Pickett's observation related to the dual character of the electron–phonon coupling: while indeed $\lambda \approx \eta/\Phi$, where η is an electronic factor characterizing the sensitivity of the electronic structure to ionic displacements, and Φ is some measure of the force constants, the force constants themselves depend on η, roughly as $\Phi \approx \Phi_0 - 2\eta$, where Φ_0 is the unscreened force constants parameter. Thus, η cannot be too large, because of the danger of the lattice becoming unstable. Doping covalent bonds is difficult to effect, but, if it can be done, it achieves two goals. First, the electronic structure strongly depends on ionic displacements modulating the covalent bond lengths (such are modes responsible for high T_c in both A_3C_{60} and in MgB_2), providing for large η, and the unscreen force constants are hard for covalent bonds, thus providing for a large Φ_0. Taken together, one can have a large λ and a large ω. This is exactly what happens in MgB_2. The E_g modes, mainly responsible for superconductivity, have large Φ_0, of the order of 10^7 a.m.u $\times$ cm^{-2}, which is reduced by a factor of three by the electron–phonon coupling—and still the phonon frequencies remain high, on the order of 500 cm^{-1}. The same physics appears to be crucial for the recently discovered record-temperature superconductors H_3S [31] and LaH_{10} [32] (which, incidentally, were both predicted computationally). A novel element there is that ultra-high pressures were instrumental in doping the H-involving covalent bonds, simply because compression severly limits possibilities of a system (which is obviously unhappy to have metallic covalent bonds) to assume a different crystal structure and get read of this undesired property.

Between 2001 and 2018 a number of interesting novel superconductors were discovered, and in explaining most, if not all of them, band theorists played an important and often a leading part. I will not dwell on those, having shown enough very diversified examples already. One milestone is however hard to pass over: Fe-based superconductors. These are the only truly high-Tc unconventional superconductors besides cuprates. The history of MgB_2 had repeated itself again, in the sense that outstanding theorists were suggesting all sort of highly exciting scenarios, but it was band theorists who came up with the basic idea (now understood to be a big oversimplification, but still covering the basic physics) of a novel pairing state dubbed $s_\pm$ since then [33]. There was a simple reason for that. This novel superconducting state basically results from a fortuitous combination of a particular Fermi surface geometry and a particular type of magnetic ordering these systems are close to. Both things are something band theorists calculate routinely and have a good intuition about.

Which brings us to the crucial question: what is the advantage that band theorists, a.k.a. computational materials scientist, have? The author of this essay is of firm opinion that theorists doing model calculations are generally smarter than us, and have deeper knowledge of the theory of superconductivity. Despite that, their intuition as regards specific superconducting materials seems to work less well. A seemingly unrelated, but in reality quite similar question is, why are solid state chemists, and not physicists, responsible for the lion's share of novel superconductors discovered in the last several decades? Materials-dependent intuition may be the key. Arguably, the most interesting question a theoretical physicist can ask is, what can happen, in principle? Answers to this question often lead to most interesting toeretical models, exciting possibilities, new concepts. An alternative question to ask is, what can happen *in this specific material*? Generically, this question is more boring, but also more productive as regards understanding a concrete superconductor. A correct answer to this question requires both a profound understanding of the microscopic physics, specific features of electronic bands, phonon spectra, magnetic orders, and an intuitive feeling based on a dozen, if not hundreds of previous calculations indicating what is possible in which material. Last but not least, in order to predict something one need not necessarily invent something new, but rather be aware of all hypothetical ideas that had been floated around, sometimes decades ago, by smarter-than-us theorists. It is worth noting that the two gap superconductivity had been studied, as a purely theoretical concept, as early as the late 50s [34]; the $s_\pm$ superconductivity in the early 70s [35]. Without knowing this general (and, until some time, purely abstract) frameworks it would be hard to associate actual superconductivity in MgB_2 and in LaFeAsO with these phenomena.

In conclusion, I would like to express my gratitude to my many brothers-in-arms, who over the years worked in the same field, applying band structure calculations to superconductivity, as Sandro, for instance, did. I am also thankful to my senior colleagues, my teachers and role models: Ole Andersen, Warren Pickett, Phil Allen, as well as to those who initiated me into the theory of superconductivity: Eugene Maksimov, David Kirzhnits, Vitaly Ginzburg.

Acknowledgments

The author was supported by the U.S. Office of Naval Research through the Naval Research Laboratory's basic research program.

ORCID iDs

I I Mazin https://orcid.org/0000-0001-9456-7099

References

[1] Gaspari G D and Gyorffy B L 1972 *Phys. Rev. Lett.* **28** 801
[2] Rainer D 1982 *Physica B + C* **109** 1671
[3] Sternheimer R M 1954 *Phys. Rev.* **96** 952
[4] Baroni S, Giannozzi P and Testa A 1987 *Phys. Rev. Lett.* **58** 1861
[5] Oliveira L N, Gross E K U and Kohn W 1988 *Phys. Rev. Lett.* **60** 2430
[6] Varma C M, Zaanen J and Raghavachari K 1991 *Science* **254** 989
[7] Schlüter M, Lannoo M, Needels M, Baraff G A and Tománek D 1992 *Phys. Rev. Lett.* **68** 526
[8] Mazin I I, Rashkeev S N, Antropov V P, Jepsen O, Liechtenstein A I and Andersen O K 1992 *Phys. Rev.* B **45** 5114
[9] An J M and Pickett W E 2001 *Phys. Rev. Lett.* **86** 4366
[10] Liu A Y, Mazin I I and Kortus J 2001 *Phys. Rev. Lett.* **87** 087005

[11] Mattheiss L F, Gyorgy E M and Johnson D W Jr 1988 *Phys. Rev.* B **37** 3745
[12] Thomsen C, Cardona M, Friedl B, Rodriguez C O, Mazin I I and Andersen O K 1990 *Solid State Commun.* **75** 219
[13] Zeyher R and Zwicknagl G 1990 *Z. Phys.* B **78** 175
[14] Mazin I I 1989 *Sov. Phys.—Usp.* **32** 489
[15] Pickett W E, Singh D J, Krakauer H and Cohen R E 1992 *Science* **255** 46
[16] Wheatley J M, Hsu T C and Anderson P W 1988 *Phys. Rev.* B **37** 5897
[17] Rosseinsky M J, Ramirez A P, Glarum S H, Murphy D W, Haddon R C, Hebard A F, Palstra T T M, Kortan A R, Zahurak S M and Makhija A V 1991 *Phys. Rev. Lett.* **66** 2830
[18] He T *et al* 2001 *Nature* **411** 54
[19] Pfleiderer C, Uhlarz M, Hayden S M, Vollmer R, Löhneysen H V, Bernhoeft N R and Lonzarich G G 2001 *Nature* **412** 58
[20] Shimizu K, Kimura T, Furomoto S, Takeda K, Kontani K, Onuki Y and Amaya K 2001 *Nature* **412** 316
[21] Nagamatsu J, Nakagawa N, Muranaka T, Zenitani Y and Akimitsu J 2001 *Nature* **410** 63
[22] Singh D J and Mazin I I 2001 *Phys. Rev.* B **64** 140507
[23] Ignatov A Yu, Savrasov S Y and Tyson T A 2003 *Phys. Rev.* B **68** 220504
[24] Singh D J and Mazin I I 2002 *Phys. Rev. Lett.* **88** 187004
[25] Yelland E A *et al* 2005 *Phys. Rev.* B **72** 214523
[26] Wohlfarth E P 1979 *Phys. Lett.* A **75** 141
Freeman A J, Continenza A, Massidda S and Grossman J C 1990 *Physica* C **166** 317
[27] Steinle-Neumann G, Stixrude L and Cohen R E 2004 *Proc. Natl Acad. Sci.* **101** 33
[28] Mazin I I, Papaconstantopoulos D A and Mehl M J 2002 *Phys. Rev.* B **65** 100511
[29] Jaccard D, Holmes A T, Behr G, Inada Y and Onuki Y 2002 *Phys. Lett.* A **299** 282
[30] Mazin I I 2008 *Physica* C **468** 105
Bergmann G and Rainer D 1973 *Z. Phys.* **263** 59
[31] Drozdov A P, Eremets M I, Troyan I A, Ksenofontov V and Shylin S I 2015 *Nature* **525** 73
[32] Drozdov A P, Minkov V S, Besedin S P, Kong P P, Kuzovnikov M A, Knyazev D A and Eremets M I 2018 (arXiv:1808.07039)
Somayazulu M, Ahart M, Mishra A K, Geballe Z M, Baldini M, Meng Y, Struzhkin V V and Hemley R J 2019 *Phys. Rev. Lett.* **12** 027001
Drozdov A P *et al* 2018 (arXiv:1812.01561)
[33] Mazin I I, Singh D J, Johannes M D and Du M H 2008 *Phys. Rev. Lett.* **101** 057003
[34] Suhl H, Matthias B T and Walker L R 1959 *Phys. Rev. Lett.* **3** 552
Moskalenko V A 1959 *Fiz. Met. Met.* **4** 503
[35] Aronov A G and Sonin E B 1973 *Sov. Phys.—JETP* **36** 556