

The Next Breakthrough in Phonon-Mediated Superconductivity

W. E. Pickett

Department of Physics, University of California, Davis, California, 95616

If history teaches us anything, it is that the next breakthrough in superconductivity will not be the result of surveying the history of past breakthroughs, as they have almost always been a matter of serendipity resulting from undirected exploration into new materials. Still, there is reason to reflect on recent advances, work toward higher T_c of even an incremental nature, and recognize that it is important to explore avenues currently believed to be unpromising even as we attempt to be rational. In this paper we look at two remarkable new unusually high temperature superconductors (UHTS), MgB_2 with $T_c=40$ K and (in less detail) high pressure Li with $T_c=20$ K, with the aim of reducing their unexpected achievements to a simple and clear understanding. We also consider briefly other UHTS systems that provide still unresolved puzzles; these materials include mostly layered structures, and several with strongly bonded C-C or B-C substructures. What may be possible in phonon-coupled superconductivity is reconsidered in the light of the discussion.

I. MOTIVATION

The appearance of several startling examples of superconductivity in the past six year or so is prompting re-evaluation of our thinking about the one pairing mechanism for which there is a precise and controlled theoretical foundation, to wit, phonon-mediated coupling. This strong-coupling Migdal-Eliashberg (ME) theory, formalized in detail by Scalapino, Schrieffer, and Wilkins,¹ has had numerous successes in the *quantitative* description of the frequency dependence of the complex superconducting gap function, the deviation of the critical field from its weak-coupling analytic form, etc. Its implementation has not been so precise in predicting the critical temperature T_c because the retarded Coulomb repulsion μ^* is difficult to calculate; nevertheless the underlying theory of T_c is understood to be in good shape.

So a question arises: when we have a material-specific, quantitative theory that works, why is it that we are nearly always surprised by the most interesting new cases of “unusually high T_c superconductivity” (UHTS), which here we will consider to be around 20 K or higher. (The high T_c cuprates, the real HTS materials, are a separate class and will not be considered here.) In this paper we will attempt to clarify issues that are involved in several of these UHTS materials, and to illuminate some of issues in the *understanding* of the ME theory. The aim of this paper is to provide a generalized conceptualization of some of the new surprises. The aim is not, unfortunately, to predict the next breakthrough, as the title misleadingly implies, although a provocative limit will be mentioned.

One relevant system that will not be addressed here is the fulleride superconductors A_xC_{60} , with values of T_c up to 40 K being achieved.² There is an enormous literature on this system, with many of the important papers being cited in a recent review.³ It is rather unfortunate that we do not have the space-time nor the energy to include fullerides, as some of its important characteristics overlap strongly with

those we discuss here. There are however correlation effects that complicate the theoretical description, and therefore the comparison, with materials discussed here, and it would not be prudent to draw parallels or contrasts in this paper.

For different reasons no discussion of PuCoGa_5 (with its surprising $T_c=18$ K)⁴ will be included. This heavy-fermion UHTS is a very different kind of material than any that will be discussed in this article, and no doubt requires a very different theoretical approach.

II. MgB_2 , THE QUEEN OF PHONON COUPLING

A. Background

The discovery by Akimitsu’s group⁵ in 2001 of $T_c = 40$ K in MgB_2 was unimaginable within the context of conventional understanding at the time, as will be elaborated further in this paper. The measurement of the boron isotope shift⁶ quickly established a phonon mechanism, and the structural and electronic simplicity allowed many groups to dive into study of the mechanism. The understanding of the mechanism arose quickly^{7–16} and is in reasonable quantitative agreement with data. The truly remarkable aspect of this Queen of superconductivity’s personality traits is her complete and utter scorn for the conventional wisdom of phonon-coupled superconductivity (“Matthias’s rules”).

Broken rule #1: MgB_2 is not cubic nor is it close, and this is one of its key characteristics. The all-important σ band is (quasi) two-dimensional (2D), so although it is rather lightly (self-)doped with holes, its density of states is comparable to what it would be with heavier doping. In addition, the sp^2 bonding in the B graphene layer provides it with stronger bonds than if it had three-dimensional (3D) sp^3 bonds. This distinction in sp^2 versus sp^3 bonding is why graphite is more strongly bound than is diamond.

Broken rule #2: There are no d electrons; previous emphasis was on intermetallic compounds, *viz.* Nb₃Sn, where d electrons played the central role. MgB₂ takes advantage of the fact that sp^2 and sp^3 bonds are the strongest in nature, stronger than the $d-d$ bonds in transition metal compounds that had ruled the conventional superconductivity roost. The strong bonds lead to extremely large electron-phonon matrix elements; we return to this below.

Broken rule #3: There is no special e/a (*electron/atom*) ratio that tunes the Fermi level to a peak in the density of states $N(E)$, because $N(E)$ has no peaks and furthermore its magnitude is embarrassingly modest. MgB₂ exchanges large $N(E)$ for very large matrix elements. This rule of large $N(E_F)$ is justified by the expression for the coupling strength λ ,

$$\lambda = \frac{N(E_F) \langle I^2 \rangle}{M \langle \omega^2 \rangle}, \quad (1)$$

with the other quantities being the mean square electron-phonon matrix element $\langle I^2 \rangle$ averaged over the Fermi surface, the ion mass M , and the mean square renormalized (physical) phonon frequency. (It will not be necessary for the purpose of this paper to delve into the complexities that arise in compounds with more than a single type of atom.) Since T_c increases monotonically with λ (all other characteristics kept fixed) and clearly it is proportional to $N(E_F)$, then a higher density of states is desirable. [We point out below the incorrectness of this argument; $\langle \omega^2 \rangle$ also depends on $N(E_F)$.]

The rule of light elements. This rule was not included in the conventional list, because it was not clear there was any real correlation between T_c and mass in the best intermetallic superconductors; Nb₃Sn was as good a Nb₃Al, for example, and a little better than the much lighter V₃Si. Theoretically, however, it was accepted that having a high energy boson doing the coupling [$T_c \sim \omega_{boson} \exp(-1/\lambda)$] provides a higher energy scale, and therefore lends hope for driving T_c skyward. Metallic hydrogen is the limiting case (barring the formation of a condensed system of muonium atoms, for which the μ^+ lifetime becomes an issue). Ashcroft's prediction 35 years ago that it would be a high temperature superconductor¹⁷ remains unverified, but also remains unretracted. A recent compilation of the values of T_c for elemental metals¹⁸ shows the high values to be concentrated toward the low mass end of the spectrum.

A more microscopically based overview of the interrelationships between large susceptibilities [$N(E_F)$, $\chi(q)$], large matrix elements, strong interatomic forces, and atomic masses was provided by Allen,¹⁹⁻²¹ who also focused on the limitations posed by structural instabilities as coupling became too strong. What is sobering to recognize is that the behavior of MgB₂ lies within conventional Migdal-Eliashberg theory; it was only our biases (as codified

in Matthias's rules) that MgB₂ abused. What MgB₂ really did in spectacular fashion was to violate a rule we probably were often not consciously aware that we followed (although we certainly "understood" it).

Broken unwritten rule A. The unwritten rule, the "eleventh commandment" of successful electron-phonon systems, can be phrased as *thou shalt not put all of thine eggs into one basket*. Successful electron-phonon coupling system should refrain from being too pushy, the coupling had to be spread out over most (preferably all) phonons, *i.e.* many baskets. Extremely strong coupling to any given phonon was the recipe for banishment from superconducting materials, via structural instability. The decomposition of the coupling strength λ into contributions from individual phonons (mode λ 's, λ_Q) by Allen²² made the connection clearer, and has also been the key to understanding coupling strength in the UHTSs. This *many-baskets* rule was not so clearly codified but nevertheless was quite clear: there were several examples where coupling strength got unusually strong at certain values (or localized regions) of phonon wavevector Q . The phonon branch softened, as parameters were twiddled to increase the coupling the phonon became unstable, and this enhanced T_c . Certainly these softened branches correlated closely with increased T_c , and there was a manifestation of the increased strength of the coupling. The first instance was probably the TaC-HfC pair measured by Smith and Glaser²³, and was followed by the Nb₃Sn-Nb₃Sb distinction.²⁴ The theory provided understanding of these connections, and also the means²⁵ to obtain the enhancement of the coupling (as long as anharmonic corrections were not important). If the renormalization became too strong, however, the compound transformed to a structure with weaker coupling (Peierls-type distortion due to strong Kohn anomaly, or a band Jahn-Teller transformation if $N(E_F)$ became too large), or the structure would not form at all ("covalent instability").

B. The Secrets of MgB₂

MgB₂ made, to put it kindly, fools of those of us who believed that focusing of coupling strength into a few modes was folly. [The author was a fervent believer in this 'evident truth.'] Only two of the nine phonon branches are strongly coupled, these being the doubly degenerate B-B bond-stretching modes in the 2D layers. And of these branches, only those with $Q < 2k_F$ are strongly coupled, and this set comprises only 12% of the area of the zone. Thus only 3% of the MgB₂'s phonons are carrying the load, with "mode λ_Q " values of $\sim 20-25$; the other 97% have values two orders of magnitude smaller and serve mainly to complicate the analysis and confuse the understanding, which is ac-

tually exceedingly simple. Neglecting these (97%) dismal wannabes, a very good estimate of the coupling strength can be obtained with a handful of easy computations and the back of a clean standard-size envelope.¹⁶

The explanation is most easily visible in the calculation of the phonon spectrum of hole-doped LiBC, whose crystal and electronic structure is much like those of MgB₂ (as are the predicted phonon anomalies²⁶) except the matrix elements are even larger. The phonon dispersion curves, before and after hole-doping, are shown in Fig. 1. The enormous Kohn anomalies are sharper than those published for MgB₂, possibly because it is a little more 2D-like, but more so because the phonon momentum grid used in the calculation is much denser than has been done for MgB₂. Just as simple considerations based on the circular Fermi surface suggest, renormalization is confined to $Q < 2k_F$, but the strength of renormalization is unprecedented. The extreme phonon softening and broadening, and the sharp Kohn anomalies, have been experimentally verified in MgB₂.^{27–29}

Predictions of the sort that give realistic values for MgB₂ suggest that in Li_xBC, T_c could be as much as twice as high.^{26,30} Li_xBC was reported a decade ago by Worlè *et al.*,³¹ but was not checked for superconductivity. Recent attempts at Li deintercalation have either not been successful.^{32–36} or have not produced a metallic material.^{37,38}

C. Extrapolating from MgB₂

Staying within the MgB₂ paradigm, one can ask the perverse question: why is T_c of MgB₂ **only** 40 K? why isn't it 60 K, or 100 K? Is it within the realm of possibility that an MgB₂-type material could be a room temperature superconductor? It is worthwhile to pursue this line of reasoning, neglecting for the time being that the biggest lesson that history has taught us is that every qualitative jump in T_c does not result from scientific scheming but, maddeningly, simply from serendipity. [Examples: high T_c cuprates; fullerenes; MgB₂. In none of these systems was the remarkable superconductivity foreseen. The exception: T_c up to 35 K in (Ba,K)BiO₃ was actually the outgrowth of systematic scientific scheming at Bell Labs by Mattheiss and coworkers.³⁹]

Fortunately, MgB₂ did not break the essential rule for good electron-phonon coupled superconductors: that Migdal-Eliashberg theory provides the description of not only T_c but the wavevector and frequency dependence of the superconducting gap. The underlying theory is still the one we understand, so one can pursue the theoretical game of varying specific materials characteristics individually, do learn what their influence is.

One of the first issues to consider, and one not directly related to Matthias's rules, is the doping

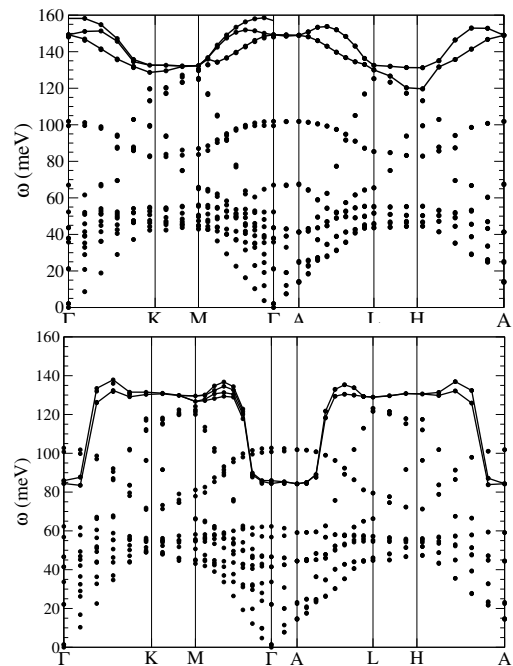


FIG. 1: Calculated phonon dispersion curves for the MgB₂ spinoff Li_xBC. Top panel: phonons for the semiconducting $x = 1$ compound, with the B-C bond-stretching modes emphasized by connecting the calculated points. Bottom panel: corresponding phonons for 25% hole doping ($x=0.75$). The Kohn anomaly at $Q = 2k_F$ is like the one in MgB₂ but more extreme. It is also a sharper drop at $2k_F$ than published results for MgB₂ because the phonons were calculated on a denser mesh. The relation to the model calculation in Fig. 2 is clear.

dependence of λ and T_c . This dependence arises mainly from the scale k_F of the Fermi surface (we neglect the renormalization of interatomic forces and bands). An analytic (front of the envelope) calculation leads to the results pictured in Fig. 2 and the remarkable implications. The coupling strength λ_Q is confined to $Q < 2k_F$ and decreases as k_F (hole doping) increases. However, the phase space, that is, the Fermi surface volume, increases in exactly a manner that leaves λ itself constant: the total coupling strength is independent of the doping level. The next result, directly following, is that the phonon renormalization does not change, even though an increasing fraction of the phonons are renormalized. Thus simple doping changes the number of phonons that are renormalized (following the *many-baskets* theme) but the mode λ 's are decreased, so doping is ineffective in effecting an increase in T_c in a system like MgB₂.

The first broken rule, about symmetry of the crystal structure, cannot be fixed in a continuous way, since the hexagonal structure of MgB₂ cannot be morphed into a cubic counterpart in any way that provide a useful comparison (although a quasi-2D electronic structure may be connected continuously to a 3D one). Likewise, p electrons cannot be

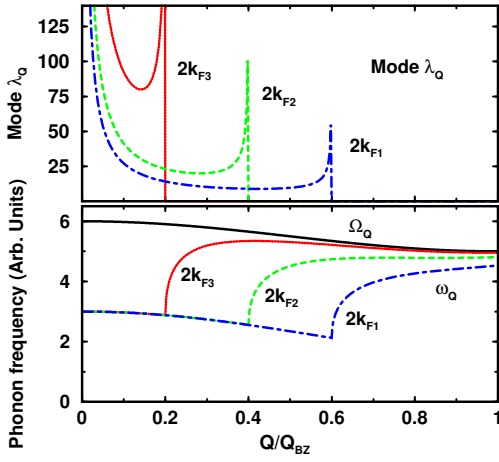


FIG. 2: Results of circular Fermi surface model showing the change in the mode λ_Q (top panel) and the renormalization of the bond-stretching mode (bottom panel). Three values of $2k_F$ are pictured; $2k_F$ increases with additional hole doping. Features to note: values of the mode λ_Q decrease with increased doping, but more modes have the large mode λ_Q , and as a result the total λ is independent of doping level; the amount of renormalization (bottom panel) is independent of the doping level, even though more phonons get renormalized as $2k_F$ increases.

squeezed continuously into d electrons, again a question of symmetry. The Queen has violated these two rules in a nonnegotiable fashion, as in a royal decree.

The third rule does involve a variable quantity, $N(E_F)$, which *can* be changed by varying the effective mass m^* or by encountering a non-parabolic dispersion relation. However, $\langle I^2 \rangle$ enters the equations multiplied by $N(E_F)$ so they can be considered together. It gets better than that: the unrenormalized phonon frequency Ω enters similarly, except in the form of its inverse square. Simply put, once phonon renormalization in this 2D system has been incorporated, one can express^{7,9,15} λ in terms of the intrinsic material parameters encapsulated in λ_o :

$$\lambda = \frac{\lambda_o}{1 - \lambda_o}; \lambda_o = \frac{d_B^2 N(E_F) \langle I^2 \rangle}{M\Omega^2}. \quad (2)$$

Here d_B is the band (Fermi surface) degeneracy; for MgB_2 there are two Fermi surfaces $d_B = 2$ and a reward of $d_B^2=4$.

With this form we can consider the variation of λ_o to be due to variation of $N(E_F)$, $\langle I^2 \rangle$, or d_B . Keeping in mind the frequency prefactor in the equation for T_c , which is the renormalized frequency (and depends on λ_o in a known way), the change in T_c can be obtained. For numerical realism in the strong coupling regime we are probing, we must use instead of the McMillan equation the Allen-Dynes equation,⁴⁰ which gives the correct strong-coupling limit $T_c \propto \sqrt{\lambda}$. For the results we present in Eq. 3, μ^* has been adjusted to provide the reference value $T_c = 40$ K for MgB_2 when first-principles results

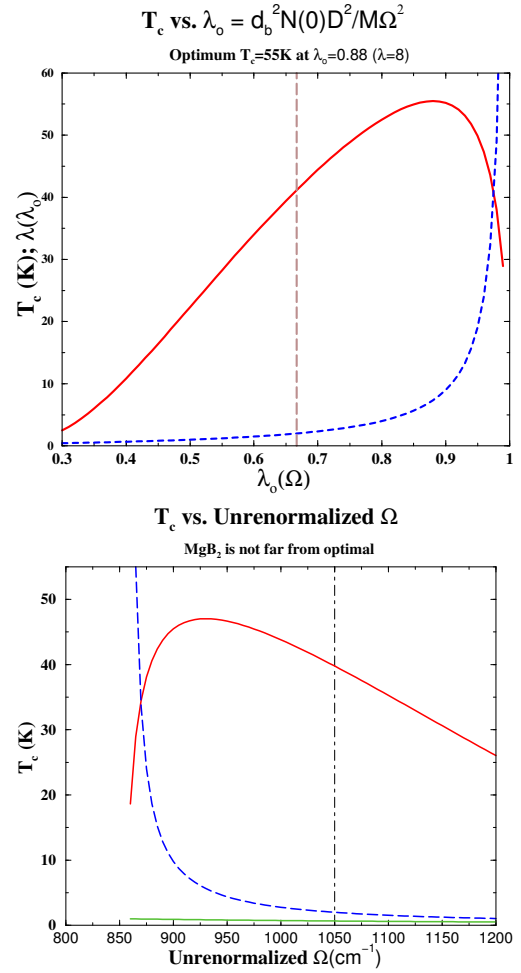


FIG. 3: Change in T_c with variation of chosen characteristics of MgB_2 . Top panel: the solid line shows the variation of T_c with $d_B^2 N(E_F) \langle I^2 \rangle$ for fixed bare frequency. Renormalization of the frequency by strong coupling finally drives T_c downward, before the frequency vanishes at $\lambda_o = 1$. Bottom panel: variation of T_c with unrenormalized frequency Ω , showing the optimal value somewhat above the critical value of 850 cm^{-1} . The vertical line in each panel indicates where MgB_2 lies: fairly close, but not at the optimal position.

are used for the other quantities. [The AlB_2 phonon frequency $\Omega = 1050 \text{ cm}^{-1}$ was taken as the unrenormalized frequency.]

The top panel of Fig. 3 shows, in addition to the trivial but instructive behavior of $\lambda(\lambda_o)$, the variation of T_c as $d_B^2 N(E_F) \langle I^2 \rangle$ is varied, *i.e.* varying λ_o at fixed Ω . It is seen that a higher band mass, or larger matrix element, can increase T_c by only $\sim 30\%$ to 55 K (where $\lambda \sim 7-8$); at this point the renormalized frequency crashes toward zero and in spite of a divergent λ (achieved by a vanishing denominator $M < \omega^2 >$) T_c drops to zero. The other variation to consider is that of keeping the electronic characteristics fixed by varying the unrenormalized frequency. It is found that reducing Ω initially leads to an increase in T_c , but after only a 15% increase at around

$\Omega \sim 900 \text{ cm}^{-1}$ (again, $\lambda \sim 7-8$), at which point the renormalized frequency again comes crashing down and T_c vanishes. Strictly, it seems in both cases that T_c does not vanish before the system becomes unstable. What we see is that our old conventional picture finally wins out: increased coupling strength leads to instability after only a rather modest enhancement of T_c for the case of MgB_2 . The Queen loses her head after all.

So, is there no way to win, no scenario that gives room temperature superconductivity? The lesson of Fig. 3 really is that the instability limit $\lambda_o \rightarrow 1$ must be avoided, and at least in these scenarios the ultra-strong coupling $T_c \rightarrow \sqrt{\lambda}$ scaling,⁴⁰ derived for fixed frequencies, is not part of the parameter space. However, if λ_o can be kept near its optimum value of 0.9 and the frequency (prefactor) increased, then there is no limitation on the increase. This situation might be obtained in two ways. One is to increase the numerator and denominator of λ_o proportionately; make the electronic coupling stronger while also making the underlying (unrenormalized) lattice stiffer. The increase in T_c then follows the increase in the frequency prefactor, which although renormalized is still increasing. MgB_2 , and B-doped diamond even more so, capitalize on a stiff underlying lattice, but hard lattices are limited at around the diamond example. The alternative is to apply pressure, and indeed pressure is seen to enhance T_c impressively in many systems.

The other possibility, based on the fact that $M < \omega^2 >$ is actually a force constant and is mass independent (hence λ_o is mass independent), is to fix all material parameters and simply reduce the nuclear masses. This is really the “metallic hydrogen” limit mentioned above, and such variation of masses via isotope substitution is quite limited in practice.

D. Boron-doped Diamond: MgB_2 in 3D

Although B-doped diamond does not (yet) fit our $\sim 20 \text{ K}$ criterion as a UHTS, it is quite instructive to consider it because of its relationship to MgB_2 . Diamond, doped at the 2-4% level by boron, has been shown⁴¹⁻⁴⁶ to be superconducting up to 11 K in bulk or thin film form. Application of ME theory, presuming that the material is a degenerate p-type semiconductor, shows⁴⁷⁻⁵¹ strong electron-phonon coupling of a magnitude that will account for its observed T_c . ARPES data has verified that the Fermi level indeed lies within the diamond valence bands at the expected energy⁵² rather than in an impurity band as has been speculated.^{53,54}

The calculations show this system to be a 3D analog of MgB_2 ; indeed one of the papers is so titled.⁴⁷ Holes are doped into the strongly bonding states, which are very strongly coupled to the C-C bond stretch modes – just the story of the high T_c in MgB_2 . In terms of the quantities involved in the

coupling of MgB_2 (above), the comparison is the following. The unrenormalized frequency, the 1330 cm^{-1} mode of diamond, is higher than its MgB_2 analog (the Raman mode of AlB_2 at 1050 cm^{-1} ; thus the lattice is stiffer.⁵⁵ The $\langle I^2 \rangle$ matrix elements are larger than in MgB_2 , due again to the shorter stronger C-C bond compared to B-B. Yet the renormalized frequency, $\omega \approx 1000 \text{ cm}^{-1}$ remains higher than that of MgB_2 ; this is the prefactor in the T_c equation and also is good. The only shortcoming, and a severe one, is that diamond is 3D, which means that the $N(E) \propto \sqrt{E_o - E}$ increases slowly with doping below the band edge E_o . As a result $N(E_F)$ is much smaller than in MgB_2 , by about a factor of four.

III. LITHIUM UNDER HIGH PRESSURE

The unexpected superconductivity of MgB_2 is perhaps matched by the subsequent discovery that the free-electron metal Li, upon being subjected to 35-50 GPa pressure, corresponding to a volume of only 40-50% of its zero pressure value, becomes superconducting⁵⁶⁻⁵⁸ at up to 20 K. Since the upper limit of T_c in Li at ambient pressure has been decreased⁵⁹ to 100 μK , this increase represents at least a five order of magnitude due to pressure. This 20 K value gives Li the highest T_c among elemental superconductors. How can it happen that a simple s-electron metal, still in a simple close-packed structure (fcc) suggestive of conventional metallic bonding, can produce the strength of electron-phonon coupling that is necessary, as studies have shown.⁶⁰⁻⁶²

Those papers can be consulted for the details, but the basic physics goes like this. Reduction of the atomic volume by a factor of ~ 2 doesn't produce enormous changes in the band structure; the new, and crucial, feature is the appearance and growth in size of necks joining spherical Fermi surfaces along $\langle 111 \rangle$ directions, as for the well known Fermi surface of Cu. There is also flattening (with respect to spherical) of the Fermi surfaces between the necks that has some import; see below. These necks also develop primarily 2p character, thus Li is transforming from an s electron metal into an s-p metal. This p character provides at least the possibility of some directional, ‘covalent’ character to the bonding, with the possibility that this may enhance electron-phonon coupling.

With the increase of pressure in the 20-38 GPa range where the fcc phase is stable, the transverse T_1 branch of the phonon spectrum (and only this branch) softens and becomes harmonically unstable around 25-30 GPa,⁶⁰⁻⁶² reflecting the renormalization that results from strong electron-phonon coupling. Searching through the phonon scattering processes from/to the Fermi surface, which is quantified

by the “nesting function”

$$\xi(Q) = \sum_k \delta(\varepsilon_k) \delta(\varepsilon_{k+Q}), \quad (3)$$

reveals that the fairly innocuous looking Fermi surface geometry actually focuses the phase space for scattering processes into a few regions,⁶⁰ including the one (Q near the zone boundary K point) where the phonon branch becomes unstable. The regions where the mode $\lambda_Q > 5$ have also been mapped,⁶¹ and they appear to coincide with the regions of intensity in $\xi(Q)$.

What has this enormous, and unanticipated, increase in T_c with pressure in Li to tell us about the bigger picture? (1) Li is cubic here, with the simplest of structures, so there is no low-dimensionality effect operating here. (2) Li is an $s-p$ electron material at reduced volume, a quality in common with MgB_2 . (3) The electron-phonon coupling strength is *not* driven by a large $N(E_F)$, again similar to MgB_2 . (4) Very much like MgB_2 , Li obtains its coupling strength from a relatively small fraction of the phonons: the region around $Q = (2/3, 2/3, 0)2\pi/a$ has strongest coupling, but only to phonons with transverse polarization $\langle 1\bar{1}0 \rangle$. In the case of Li, however, the sharp structure in Q of the coupling strength does drive the system to structural instability, at least in harmonic approximation. Thus the mechanism driving the increase in T_c is self-limiting already at experimental conditions as the conventional theory^{19–21} would lead one to expect. Current data suggest, however, that the high T_c survives the structural change at 40 GPa, and displays somewhat higher T_c in the higher pressure phase.⁵⁶

IV. OUTSTANDING PUZZLES IN EP SUPERCONDUCTIVITY

In this section we mention additional UHTS materials with $T_c \sim 20$ K or higher whose origin is unexplained.

A. Electron-doped Hf & Zr Nitridochlorides

Electron doping (for example by intercalating Li) of HfNCl leads to $T_c = 25$ K; for Li_xZrNCl the value is 12–15 K; these values depend only weakly on doping.^{63–66} The structure consists of graphene-like honeycomb double sheets of alternating Zr and N, in such a way that each atom is bonded with three of the other type within a layer, and with one of the other type in the neighboring layer. Layers of Cl on either side of this double layer results in an insulating slab that is formally $\text{Zr}^{4+}\text{N}^{3-}\text{Cl}^-$. These closed shell sheets are van der Waals bonded in the undoped material, and Li intercalation leads to electron doping – one electron per Li – and 2D metallicity and superconductivity. There is considerable

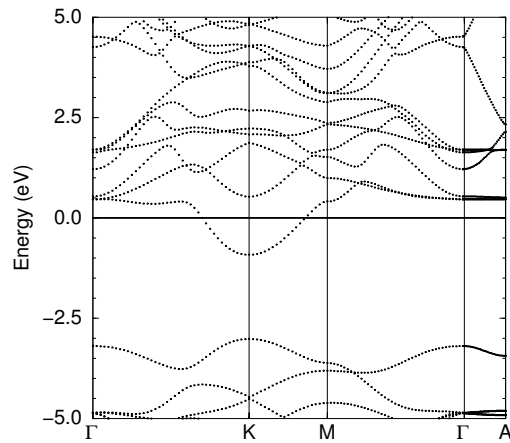


FIG. 4: Band structure of the electron-doped layered nitride $\text{Na}_{0.25}\text{ZrNCl}$, showing the single light-mass band into which the electrons are doped. The band minimum, and center of the resulting Fermi surfaces, lie at the zone corner symmetry points K. Note from the lack of dispersion along Γ -Z the strong two-dimensionality of the electronic structure around the Fermi level.

covalence⁶⁷ to the Zr-N bonding, however, so this cannot be pictured simply as an ionic system.

The electron is doped into a small mass band [light carriers, low $N(E)$], shown in Fig. 4, with primarily Zn $d_{xy}, d_{x^2-y^2}$ in-plane character and some N p_x, p_y involvement.^{67–70} There are circular Fermi surfaces at the zone boundary K symmetry points. A full calculation of the phonon dispersion and electron-phonon coupling spectrum by Heid *et al.* concludes⁷¹ that the coupling strength $\lambda = 0.5$ is insufficient to account for $T_c=15$ K in $\text{Li}_{1/6}\text{ZrNCl}$. The situation is clearly analogous to MgB_2 : 2D electronic system, circular Fermi surfaces. There being three (symmetry related but distinct) Fermi surfaces, there are two sorts of Fermi surface scattering processes: intrasurface, with $Q < 2k_F$; and intersurface, with $|Q - K| < 2k_F$. Note that here the point \vec{K} arises because the centers of the Fermi surfaces are separated by $Q \equiv K$, not because they also happen to be located at K . There are 3 intrasurface scatterings; there are 3! intersurface processes, for a total factor of $3^2=9$ similar contributions. Each has the same circular phase space factor $\xi(Q)$ discussed above for MgB_2 ; the intra- and inter-sheet matrix elements may differ, however. The point is that, whereas MgB_2 with its two Fermi surfaces takes advantage of the $2^2=4$ factor, in these nitridochlorides there is a more robust $3^2=9$ degeneracy factor. Unfortunately, the matrix elements and/or $N(E_F)$ magnitudes are not sufficient to take advantage of this degeneracy.⁷¹

The $\text{Zr} \leftrightarrow \text{Hf}$ comparison reveals a conundrum, which appears to be separate but could be the crucial clue. Why does the Hf system show $T_c = 25$ –26 K, while the Zr materials are all $T_c = 15$ K or a little less? Chemically, these isovalent $4d$ and $5d$

atoms are similar; in any case, the larger atom never gives a stiffer lattice so that tendency is backward. Regarding them as chemically equivalent, the difference could be viewed as an isotope shift (with masses differing by a factor of two). Again, the tendency is in the wrong direction, as it is the (twice as) heavy element which has the (60%) larger value of T_c . The simplest interpretation is that ME theory isn't working here, and other mechanisms must be considered. Bill and coworkers have suggested⁷² that an electronic mechanism may be operating; still there is the $Zr \leftrightarrow Hf$ question to address.

B. BKBO: A Case unto Itself

$Ba_{1-x}K_xBiO_3$ (BKBO), with T_c up to 35 K reported,⁷³ has been relatively heavily studied with no resolution of the source of its impressive superconductivity. The parent compound $BaBiO_3$ is a distorted perovskite with two inequivalent Bi sites, often interpreted formally as Bi^{3+} ($6s^2$ “lone pair” configuration) and Bi^{5+} (closed shell ion). Extensive electronic structure studies find very little actual charge difference between the sites, but these same local density functional studies are also unable to describe the ground state structural properties as well as can usually be done for an $s-p$ electron system (the valence-conduction orbitals are O $2p$ and Bi $6s$).

A density functional linear response calculation of the phonon spectrum, electron-phonon coupling, and T_c by Merregalli and Savrasov⁷⁴ failed to find an explanation of the superconductivity. The coupling strength $\lambda=0.34$ was found, well below the required strength. Possible resolutions include (1) electron correlation, although how to approach it is an open question (see below), (2) unconventional types of coupling to the lattice; after all, this system superconducts best near a structural phase boundary, (3) alloy issues (clustering or other short-range order), which could make the virtual crystal treatment of the electronic structure inapplicable, or (4) focusing of phonon scattering processes as in Li, which makes it numerically taxing to carry out the Q-integration to convergence to obtain the precise value of λ . The rounded cube Fermi surface does suggest nesting that could make alternative (4) worth revisiting.

One course of action is to look for correlations beyond LDA in this system. The focus is on the Bi cation and its tendency to favor the singlet-paired $6s^2$ configuration if electrons are available, and the lack of any magnetic behavior. This has been addressed in terms of a “negative U” interaction^{75,76} on the Bi ion, but a microscopic investigation into this possibility failed to turn up evidence for such interaction.⁷⁷

C. Assorted UHTSs: Any Rhyme or Reason?

There are a few other systems which fall under our classification as UHTS materials, but are as yet little understood.

C_2 Dumbbell Systems. The cubic compound Y_2C_3 , consisting of a bcc structure with Y occupying rather low symmetry (u, u, u) sites, and with interstitial dumbbells of C_2 molecules oriented along each of the cubic axes, superconducts^{78,79} at 18 K when synthesized at high pressure. Keeping in mind MgB_2 and B-doped diamond (and fulleride systems) with their strong coupling to high frequency B/C modes, it is natural to focus on the unusual C_2 dumbbells, which are essentially triple-bonded carbon molecules lying in the background electron gas provided by the Y carriers. Band structure calculations^{80,81} indicate a modest value of $N(E_F)$, but with an intriguing flat band very close to E_F in a limited region of the Brillouin zone. Singh and Mazin calculate⁸⁰ a C-C stretch mode frequency of 1442 cm^{-1} , higher than that of diamond. Its mode λ_Q was only about 10% of that from the Y mode they studied. It must be kept in mind, however, that coupling to a high frequency mode is more valuable for T_c than coupling to a soft mode. While it is suggested^{80,81} that phonons may provide the coupling in this system, the most distinctive feature of the structure, the C-C molecular dumbbells, does not seem to be a dominant force in the impressive value of T_c . On the other hand, the existing information is for only two phonons at a single Q value in a system with 60 branches, and recent experience teaches that as little as a few percent of the modes may drive T_c up to 30-40 K. Unfortunately, with 20 atoms in the primitive cell it is unlikely that full electron-phonon coupling calculations can be carried out in the near future.

Another dumbbell system is the class $Y_2C_2\mathcal{H}_2$, where \mathcal{H} is a negative halide ion (I, Br), with T_c up^{82,83} to 11.5 K. As for the Y_2C_3 systems, a C-C derived band lies very close⁸⁴ to the Fermi level. Again as for Y_2C_3 , it is unknown whether this band contributes strong electron-phonon coupling that drives the superconductivity in this system.

$Ba_2Nb_5O_x, BaNbO_{3-x}$. Materials in this class are reported to have T_c as high⁸⁵⁻⁸⁷ as high as 22 K. Values are strongly sample dependent, but T_c up to 18 K seems to be reproducible. The structure that is suggested to be responsible for the highest T_c is a perovskite oxynitride $BaNbO_xN_y$. In view of the enormous number of non-superconducting perovskite oxides, this could be a particularly significant achievement if it can be confirmed.

YPd_2B_2C . This compound is the highest T_c member (23 K)^{88,89} of the class of mostly Ni compounds⁹⁰ that have been studied most extensively because of the competition between magnetism (due to magnetic rare earths in place of Y) and superconductivity. This compound may be regarded as containing C-B-C trimers that link

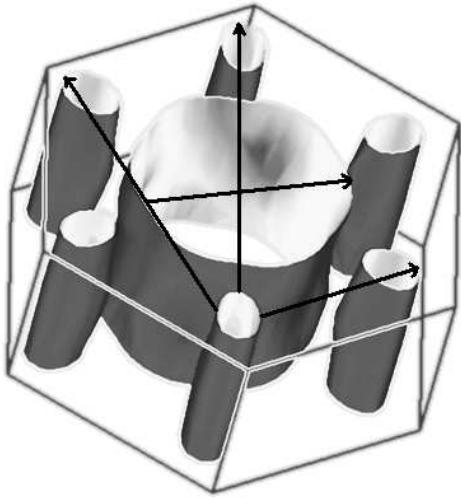


FIG. 5: Schematic picture of how to enhance total coupling strength while retaining a stable lattice. Additional scattering processes are introduced at large Q in the region of spanning vectors of Fermi surfaces arrayed around the Brillouin zone. In this figure three spanning vectors are shown, interconnecting the smaller sheets of Fermi surface.

YPd₂ layers. Indications from a rigid-potential treatment⁹¹ suggests the light atoms provide a majority of the coupling strength, but this tentative conclusion needs to be confirmed by more complete calculations.

V. THE DENOUEMENT

The primary theme of this paper, if one can be claimed, has been (a) to discuss how MgB₂ and a few other UHTS systems succeed in achieving impressive T_c by breaking old rules, and (b) to give some thought to the possibility of extending the positive attributes of these new and different superconductors. One observation is that MgB₂ puts all its reliance (coupling) on only a small fraction $\sim 3\%$ of its phonons. This works, as far as it goes. By varying various materials properties, we find there is no more than 20-30% to be gained in this type of system by increasing the raw coupling strength $[N(E_F) < I^2 >]$, also not much to be gained by starting with a stiffer system, and also that changes in the hole-concentration are ineffective for raising T_c . Increasing raw coupling *proportionately* with the stiffness of the underlying unrenormalized material is a possible avenue for increasing T_c . However, we are reaching the limits of stiff systems at ambient pressure. Thinking practically, application of such hard materials brings additional headaches – think of the prospect of winding your electromagnet coils with diamond wire.

This line of pursuit may not quite be hopeless. Since MgB₂ teaches us that putting lots of eggs into

one strong basket is an avenue to success, then it ought to be the case that putting even more and bigger eggs into *several* strong baskets ought to be even better. The mathematical justification is evident: renormalization of a phonon depends on λ_Q for the specific Q point, while λ is a sum over all Q . Whereas increasing coupling strength in a given region $Q < 2k_F$ reaches its limit (structural instability) in the way that was modeled in Sec. II, putting additional strength in other (non-overlapping) regions of the zone $|Q - Q_o| < 2k_F$ adds coupling strength while renormalizing *other* phonons, thus increasing λ while not threatening the overall stability of the lattice.

The way one goes about this is illustrated by the Fermi surface in Fig. 5. One designs an MgB₂-like material (*i.e.* quasi-2D with a stiff reference system) that has *several* cylindrical Fermi surfaces; in the example shown the new feature is the six (symmetry-related) Fermi surfaces along the Γ -K lines in a hexagonal lattice. The nesting vectors Q_n (those shown, and symmetry partners) form the centers of circles (cylinders, when shown in 3D) of radius $|Q - Q_n| < 2k_F$. These Kohn-anomaly-enclosed regions have radius $2k_F$, hence diameter of $4k_F$, and could comprise most of the Brillouin zone, so nearly all of the phonons are renormalized (and strongly coupled if the bare coupling is large). Then, if one is a clever enough materials designer, one manages to provide a large bare coupling $[N(E_F) < I^2 >]$ to every branch of the phonon spectrum rather than just two of nine as in MgB₂.

If one then manages to get all phonons as strongly coupled as in MgB₂ (instead of only $\sim 3\%$), then one achieves $\lambda \sim 25$ or so, with the lattice remaining stable. For MgB₂, the projected value of T_c (Allen-Dynes equation,⁴⁰ $\bar{\omega} = 60$ meV, $\mu^* = 0.15$) is of the order of 400-500 K. This estimate is in accord with the stated strong coupling limit $0.15\sqrt{\lambda} < \omega^2 >$ provided by Allen and Dynes,⁴⁰ which for these constants gives $T_c = 525$ K.

This analysis actually neglects the primary aspects of MgB₂-like systems, that 2D phase space is such that the total coupling from a circular Fermi surface is independent of its size, *i.e.* the doping level, and that the phonon renormalization (and impending structural instability) also do not depend on the doping level. Hence it is not strictly the fraction of the Brillouin zone that one can marshal that is important. Rather, it is the number of Fermi surfaces one can create – the “band degeneracy” factor d_B in Eq. 2. Whether they are hole-like or electron-like is not important, only that they are there and are quasi-2D. More, smaller sheets are better, up to a point; if they get too small (E_F very near a band edge) non-adiabatic effects arise, and getting into the very low carrier regime will introduce a poorly screened Coulomb interaction between carriers that will invalidate the present considerations.

Perhaps the most important feature that MgB₂

has introduced is a platform for distributing coupling strength relatively uniformly, something that decades ago was presumed to be the norm but may be instead the exception. The seemingly innocuous 3D system of fcc Li achieves a remarkable increase in T_c under pressure, but it arises from (broadened) ‘surface regions’ in specific locations in the zone. The corresponding phonons provide strong coupling but rapidly become unstable, in line with the classical understanding discussed in the Introduction. Building on “MgB₂-like” principles might yet lead to important enhancement of the superconducting critical temperature.

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