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# The next breakthrough in phonon-mediated superconductivity

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## Abstract

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),  $\text{MgB}_2$  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.

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## 1. Motivation

The appearance of several startling examples of superconductivity in the past six years 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 et al. [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  $\mu^*$  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  $\text{A}_x\text{C}_{60}$ , 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 fullerenes, 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.

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For different reasons no discussion of PuCoGa<sub>5</sub> (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.

## 2. MgB<sub>2</sub>, the Queen of phonon coupling

### 2.1. Background

The discovery by Akimitsu's group [5] in 2001 of  $T_c = 40$  K in MgB<sub>2</sub> 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 shift [6] 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 [7–13,15,14,16] 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<sub>2</sub> is not cubic nor is it close, and this is one of its key characteristics. The all-important  $\sigma$  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<sup>2</sup> bonding in the B graphene layer provides it with stronger bonds than if it had three-dimensional (3D) sp<sup>3</sup> bonds. This distinction in sp<sup>2</sup> versus sp<sup>3</sup> 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. Nb<sub>3</sub>Sn, where d electrons played the central role. MgB<sub>2</sub> takes advantage of the fact that sp<sup>2</sup> and sp<sup>3</sup> 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. MgB<sub>2</sub> 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  $\lambda$ ,

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

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  $\lambda$  (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; Nb<sub>3</sub>Sn was as good a Nb<sub>3</sub>Al, for example, and a little better than the much lighter V<sub>3</sub>Si. Theoretically, however, it was accepted that having a high energy boson doing the coupling [ $T_c \sim \omega_{\text{boson}} \exp(-1/\lambda)$ ] 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  $\mu^+$  lifetime becomes an issue). Ashcroft's prediction 35 years ago that it would be a high temperature superconductor [17] remains unverified, but also remains unretracted. A recent compilation of the values of  $T_c$  for elemental metals [18] 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 MgB<sub>2</sub> lies within conventional Migdal–Eliashberg theory; it was only our biases (as codified in Matthias's rules) that MgB<sub>2</sub> abused. What MgB<sub>2</sub> 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 "11th 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  $\lambda$  into contributions from individual phonons (mode  $\lambda^i$ 's,  $\lambda_Q$ ) by Allen [22] made the connection clearer, and has also been the key to understanding coupling strength in the UHTSs. This many-baskets rule was

170 not so clearly codified but nevertheless was quite clear:  
 171 there were several examples where coupling strength got  
 172 unusually strong at certain values (or localized regions)  
 173 of phonon wavevector  $Q$ . The phonon branch softened,  
 174 as parameters were twiddled to increase the coupling the  
 175 phonon became unstable, and this enhanced  $T_c$ . Certainly  
 176 these softened branches correlated closely with increased  
 177  $T_c$ , and there was a manifestation of the increased strength  
 178 of the coupling. The first instance was probably the TaC–  
 179 HfC pair measured by Smith and Glaser [23], and was fol-  
 180 lowed by the Nb<sub>3</sub>Sn–Nb<sub>3</sub>Sb distinction [24]. The theory  
 181 provided understanding of these connections, and also  
 182 the means [25] to obtain the enhancement of the coupling  
 183 (as long as anharmonic corrections were not important).  
 184 If the renormalization became too strong, however, the  
 185 compound transformed to a structure with weaker cou-  
 186 pling (Peierls-type distortion due to strong Kohn anomaly,  
 187 or a band Jahn–Teller transformation if  $N(E_F)$  became too  
 188 large), or the structure would not form at all (“covalent  
 189 instability”).

## 190 2.2. The secrets of MgB<sub>2</sub>

191 MgB<sub>2</sub> made, to put it kindly, fools of those of us who  
 192 believed that focusing of coupling strength into a few modes  
 193 was folly. (The author was a fervent believer in this ‘evident  
 194 truth’.) Only two of the nine phonon branches are strongly  
 195 coupled, these being the doubly degenerate B–B bond-  
 196 stretching modes in the 2D layers. And of these branches,  
 197 only those with  $Q < 2k_F$  are strongly coupled, and this set  
 198 comprises only 12% of the area of the zone. Thus only 3%  
 199 of the MgB<sub>2</sub>’s phonons are carrying the load, with “mode  
 200  $\lambda_Q$ ” values of  $\sim 20$ –25; the other 97% have values two orders  
 201 of magnitude smaller and serve mainly to complicate the  
 202 analysis and confuse the understanding, which is actually  
 203 exceedingly simple. Neglecting these (97%) dismal wannabes,  
 204 a very good estimate of the coupling strength can be  
 205 obtained with a handful of easy computations and the back  
 206 of a clean standard-size envelope [16].

207 The explanation is most easily visible in the calculation  
 208 of the phonon spectrum of hole-doped LiBC, whose crystal  
 209 and electronic structure is much like those of MgB<sub>2</sub> (as are  
 210 the predicted phonon anomalies [26]) except the matrix ele-  
 211 ments are even larger. The phonon dispersion curves,  
 212 before and after hole-doping, are shown in Fig. 1. The  
 213 enormous Kohn anomalies are sharper than those pub-  
 214 lished for MgB<sub>2</sub>, possibly because it is a little more 2D-like,  
 215 but more so because the phonon momentum grid used in  
 216 the calculation is much denser than has been done for  
 217 MgB<sub>2</sub>. Just as simple considerations based on the circular  
 218 Fermi surface suggest, renormalization is confined to  
 219  $Q < 2k_F$ , but the strength of renormalization is unprece-  
 220 dented. The extreme phonon softening and broadening,  
 221 and the sharp Kohn anomalies, have been experimentally  
 222 verified in MgB<sub>2</sub> [27–29].

223 Predictions of the sort that give realistic values for MgB<sub>2</sub>  
 224 suggest that in Li<sub>x</sub>BC,  $T_c$  could be as much as twice as high

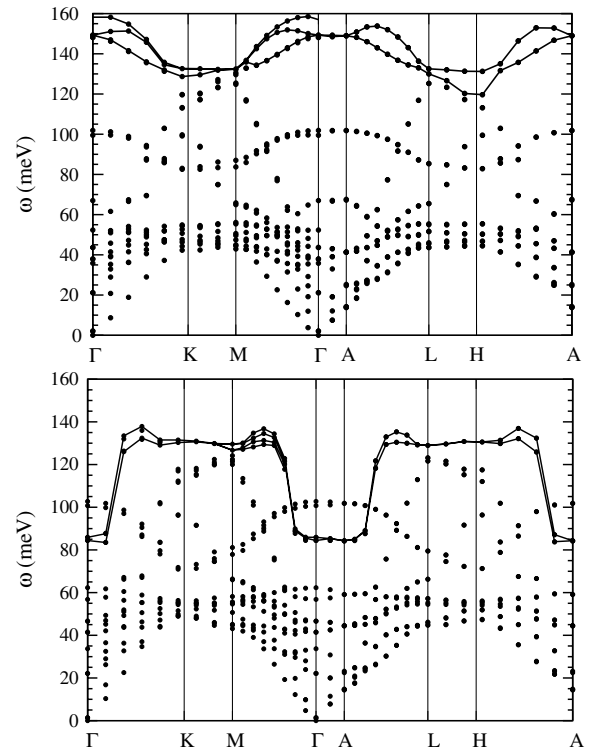


Fig. 1. Calculated phonon dispersion curves for the MgB<sub>2</sub> spinoff Li<sub>x</sub>BC. Top panel: phonons for the semiconducting  $x = 1$  compound, with the B–C bond-stretching modes emphasized by connecting the calculated points. Bottom panel: corresponding phonons for 25% hole doping ( $x =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

[26,30]. Li<sub>x</sub>BC was reported a decade ago by Worlë et al. [31], but was not checked for superconductivity. Recent attempts at Li de-intercalation have either not been successful [32–36], or have not produced a metallic material [37,38].

## 2.3. Extrapolating from MgB<sub>2</sub>

Staying within the MgB<sub>2</sub> paradigm, one can ask the per-verse question: why is  $T_c$  of MgB<sub>2</sub> only 40 K? why is not it 60 or 100 K? Is it within the realm of possibility that an MgB<sub>2</sub>-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; full-erides; MgB<sub>2</sub>. In none of these systems was the remarkable superconductivity foreseen. The exception:  $T_c$  up to 35 K in (Ba,K)BiO<sub>3</sub> was actually the outgrowth of systematic scientific scheming at Bell Labs by Mattheiss and coworkers [39].]

Fortunately, MgB<sub>2</sub> did not break the essential rule for good electron–phonon-coupled superconductors: that Mig-

dal–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 dependence of  $\lambda$  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  $\lambda_Q$  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  $\lambda$  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  $\lambda$ ’s are decreased, so doping is ineffective in effecting an increase in  $T_c$  in a system like  $\text{MgB}_2$ .

The first broken rule, about symmetry of the crystal structure, cannot be fixed in a continuous way, since the hexagonal structure of  $\text{MgB}_2$  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 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  $\Omega$  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]  $\lambda$  in terms of the intrinsic material parameters encapsulated in  $\lambda_0$

$$\lambda = \frac{\lambda_0}{1 - \lambda_0}, \quad \lambda_0 = \frac{d_B^2 N(E_F) \langle I^2 \rangle}{M \Omega^2}. \quad (2)$$

Here  $d_B$  is the band (Fermi surface) degeneracy; for  $\text{MgB}_2$  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  $\lambda_0$  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  $\lambda_0$  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),  $\mu^*$  has been adjusted to provide the reference value  $T_c = 40$  K for  $\text{MgB}_2$  when first-principles results are used for the other quantities. (The  $\text{AlB}_2$  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  $\lambda(\lambda_0)$ , the variation of  $T_c$  as  $d_B^2 N(E_F) \langle I^2 \rangle$  is varied, i.e. varying  $\lambda_0$  at fixed  $\Omega$ . 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  $\lambda$  (achieved by a vanishing denominator  $M \langle \omega^2 \rangle$ )  $T_c$  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  $\Omega$  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  $\text{MgB}_2$ . The Queen loses her head after all.

So, there is no way to win, no scenario that gives room temperature superconductivity? The lesson of Fig. 3 really is that the instability limit  $\lambda_0 \rightarrow 1$  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  $\lambda_0$  can be kept near its

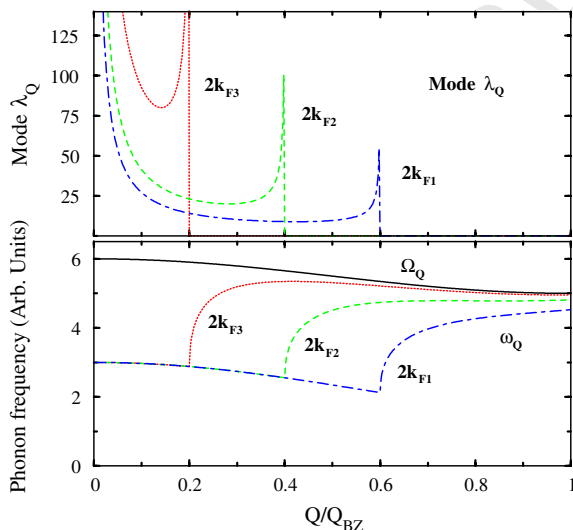


Fig. 2. Results of circular Fermi surface model showing the change in the mode  $\lambda_Q$  (top panel) and the renormalization of the bond-stretching mode (bottom panel). Three values of  $2k_F$  are pictured;  $2k_F$  increases with additional hole doping. Features to note: values of the mode  $\lambda_Q$  decrease with increased doping, but more modes have the large mode  $\lambda_Q$ , and as a result the total  $\lambda$  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.

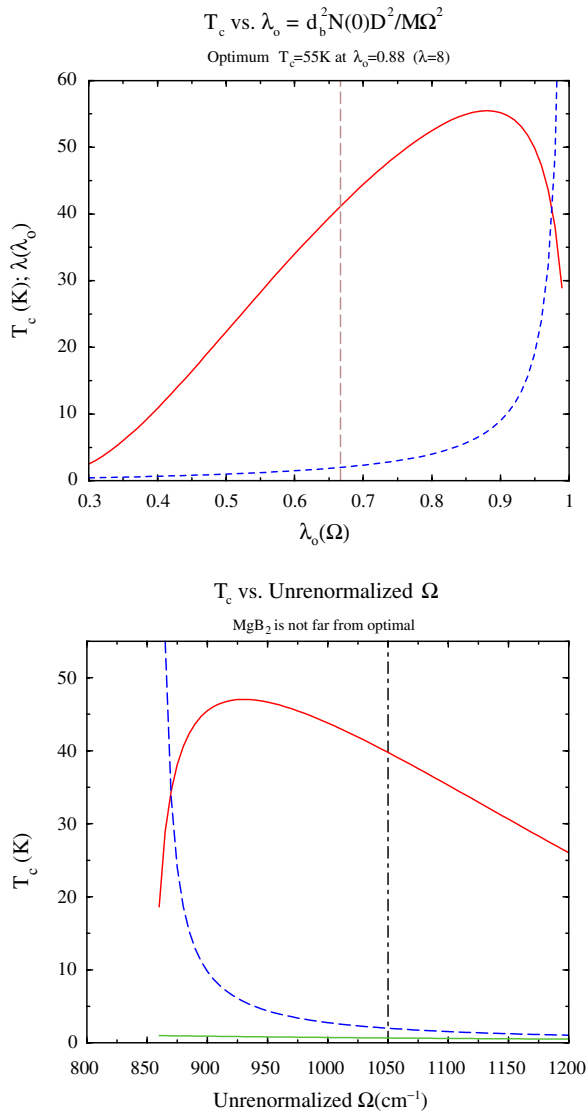


Fig. 3. Change in  $T_c$  with variation of chosen characteristics of  $\text{MgB}_2$ . Top panel: the solid line shows the variation of  $T_c$  with  $d_b^2 N(E_F) \langle I^2 \rangle$  for fixed bare frequency. Renormalization of the frequency by strong coupling finally drives  $T_c$  downward, before the frequency vanishes at  $\lambda_0 = 1$ . Bottom panel: variation of  $T_c$  with unrenormalized frequency  $\Omega$ , showing the optimal value somewhat above the critical value of  $850 \text{ cm}^{-1}$ . The vertical line in each panel indicates where  $\text{MgB}_2$  lies: fairly close, but not at the optimal position.

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  $\lambda_0$  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.  $\text{MgB}_2$ , 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  $M \langle \omega^2 \rangle$  is actually a force constant and is mass independent (hence  $\lambda_0$  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.

#### 2.4. Boron-doped diamond: $\text{MgB}_2$ in 3D

Although B-doped diamond does not (yet) fit our  $\sim 20$  K criterion as a UHTS, it is quite instructive to consider it because of its relationship to  $\text{MgB}_2$ . Diamond, doped at the 2–4% level by boron, has been shown [41–46] 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, shows [47–51] 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 energy [52] rather than in an impurity band as has been speculated [53,54].

The calculations show this system to be a 3D analog of  $\text{MgB}_2$ ; 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  $\text{MgB}_2$ . In terms of the quantities involved in the coupling of  $\text{MgB}_2$  (above), the comparison is the following. The unrenormalized frequency, the  $1330 \text{ cm}^{-1}$  mode of diamond, is higher than its  $\text{MgB}_2$  analog (the Raman mode of  $\text{AlB}_2$  at  $1050 \text{ cm}^{-1}$ ; thus the lattice is stiffer [55]. The  $\langle I^2 \rangle$  matrix elements are larger than in  $\text{MgB}_2$ , 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  $\text{MgB}_2$ ; 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  $N(E) \propto \sqrt{E_0 - E}$  increases slowly with doping below the band edge  $E_0$ . As a result  $N(E_F)$  is much smaller than in  $\text{MgB}_2$ , by about a factor of four.

### 3. Lithium under high pressure

The unexpected superconductivity of  $\text{MgB}_2$  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 superconducting [56–58] at up to 20 K. Since the upper limit of  $T_c$  in Li at ambient pressure has been decreased [59] to  $100 \mu\text{K}$ , 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  $\sim 2$  does not 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”

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

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  $\text{MgB}_2$ . (3) The electron–phonon coupling strength is not driven by a large  $N(E_F)$ , again similar to  $\text{MgB}_2$ . (4) Very much like  $\text{MgB}_2$ , 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  $\langle 110 \rangle$ . 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].

#### 4. 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.

#### 4.1. Electron-doped Hf and Zr nitrido-chlorides

Electron doping (for example by intercalating Li) of  $\text{HfNCl}$  leads to  $T_c = 25$  K; for  $\text{Li}_x\text{ZrNCl}$  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 covalence [67] 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. concludes [71] 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  $\text{MgB}_2$ : 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 three intrasurface scatterings;

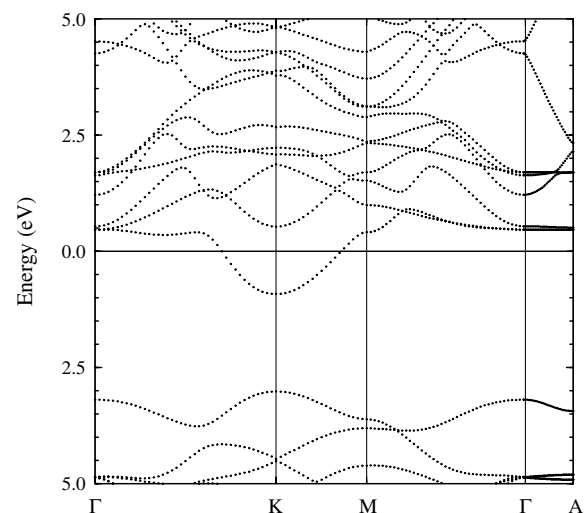


Fig. 4. Band structure of the electron-doped layered nitride  $\text{Na}_{0.25}\text{ZrNCl}$ , showing the single light-mass band into which the electrons are doped. The band minimum, and center of the resulting Fermi surfaces, lie at the zone corner symmetry points  $K$ . Note from the lack of dispersion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

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  $\text{MgB}_2$ ; the intra- and inter-sheet matrix elements may differ, however. The point is that, whereas  $\text{MgB}_2$  with its two Fermi surfaces takes advantage of the  $2^2 = 4$  factor, in these nitrido-chlorides 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 Zr  $\leftrightarrow$  Hf comparison reveals a conundrum, which appears to be separate but could be the crucial clue. Why does the Hf system show  $T_c = 25\text{--}26$  K, while the Zr materials are all  $T_c = 15$  K or a little less? Chemically, these iso-valent 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 suggested [72] that an electronic mechanism may be operating; still there is the Zr  $\leftrightarrow$  Hf question to address.

#### 4.2. BKBO: A case unto itself

$\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$  (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  $\text{BaBiO}_3$  is a distorted perovskite with two inequivalent Bi sites, often interpreted formally as  $\text{Bi}^{3+}$  ( $6s^2$  "lone pair" configuration) and  $\text{Bi}^{5+}$  (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 Savrasov [74] 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  $\lambda$ . 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].

#### 4.3. 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.

##### 4.3.1. $C_2$ dumbbell systems

The cubic compound  $\text{Y}_2\text{C}_3$ , 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  $\text{MgB}_2$  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 calculate [80] a C-C stretch mode frequency of  $1442\text{ cm}^{-1}$ , higher than that of diamond. Its mode  $\lambda_Q$  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  $\text{Y}_2\text{C}_2\mathcal{H}_2$ , where  $\mathcal{H}$  is a negative halide ion (I, Br), with  $T_c$  up [82,83] to 11.5 K. As for the  $\text{Y}_2\text{C}_3$  systems, a C-C derived band lies very close [84] to the Fermi level. Again as for  $\text{Y}_2\text{C}_3$ , it is unknown whether this band contributes strong electron-phonon coupling that drives the superconductivity in this system.

##### 4.3.2. $\text{Ba}_2\text{Nb}_5\text{O}_x$ , $\text{BaNbO}_{3-x}$

Materials in this class are reported to have  $T_c$  as high [85–87] 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  $\text{BaNbO}_x\text{N}_y$ . In view of the

enormous number of non-superconducting perovskite oxides, this could be a particularly significant achievement if it can be confirmed.

#### 4.3.3. $YPd_2B_2C$

This compound is the highest  $T_c$  member (23 K) [88,89] of the class of mostly Ni compounds [90] 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  $YPd_2$  layers. Indications from a rigid-potential treatment [91] suggests the light atoms provide a majority of the coupling strength, but this tentative conclusion needs to be confirmed by more complete calculations.

### 5. The denouement

The primary theme of this paper, if one can be claimed, has been (a) to discuss how  $MgB_2$  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  $MgB_2$  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  $[N(E_F)\langle I^2 \rangle]$ , 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  $MgB_2$  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  $\lambda_Q$  for the specific  $Q$  point, while  $\lambda$  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 Section 2, putting additional strength in other (non-overlapping) regions of the zone  $|Q - Q_0| < 2k_F$  adds coupling strength while renormalizing other phonons, thus increasing  $\lambda$  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  $MgB_2$ -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

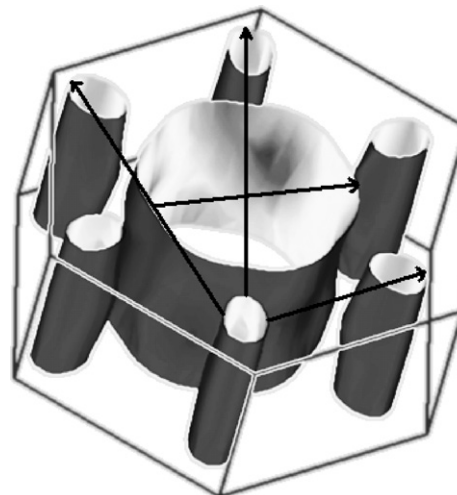


Fig. 5. Schematic picture of how to enhance total coupling strength while retaining a stable lattice. Additional scattering processes are introduced at large  $Q$  in the region of spanning vectors of Fermi surfaces arrayed around the Brillouin zone. In this figure three spanning vectors are shown, interconnecting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

the  $\Gamma$ - $K$  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  $[N(E_F)\langle I^2 \rangle]$  to every branch of the phonon spectrum rather than just two of nine as in  $MgB_2$ .

If one then manages to get all phonons as strongly coupled as in  $MgB_2$  (instead of only  $\sim 3\%$ ), then one achieves  $\lambda \sim 25$  or so, with the lattice remaining stable. For  $MgB_2$ , 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  $0.15\sqrt{\lambda\langle\omega^2\rangle}$  provided by Allen and Dynes [40], which for these constants gives  $T_c = 525$  K.

This analysis actually neglects the primary aspects of  $MgB_2$ -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  $\text{MgB}_2$  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 the classical understanding discussed in Section 1. Building on “ $\text{MgB}_2$ -like” principles might yet lead to important enhancement of the superconducting critical temperature.

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