Electron-Phonon Coupling in MgB_2-like Materials: Its Magnitude and Its Limits

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That very strong coupling of the B-B bond-stretching E_{2g} branch of phonons to the B $2p\sigma$ bonding hole states is responsible for the remarkable superconductivity in MgB_2 is well established. This entirely new manner of driving the superconducting T_c to high levels requires additional analysis. Here recent findings, such as how this strong coupling is related to possible structural instability, are discussed, and investigation into the practical limits of such coupling is initiated.

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I. INTRODUCTION

Although several aspects of the superconductivity near 40 K in MgB_2 discovered by Akmitsu's group[1] are now understood, there remain several puzzles, which include the following. (1) To what extent is the extremely strong coupling between the B σ band holes and the B-B bond-stretching modes really understood? This type of coupling is entirely new, as regards its microscopic origin and its strength. (2) Is the two-band character an intrinsic feature of this sort of superconductor, or a value-added item to provide added excitement in the field? (3) Is MgB_2 simply one of a kind (so far, it is), or can the operating principles be used to suggest other superconductors in this class? All of these questions have been attracting strong interest.

In this paper two specific questions will be addressed. First, we review recent analysis of electron-phonon (EP) coupling in MgB_2-like materials that reveals how remarkably strongly the bond-stretching modes are coupled. This brings up the questions of whether the theory remains valid, and whether such coupling can be increased, and by how much, and still retain crystal stability (a primary limiting mechanism for EP coupling). We focus on the implications for the validity of EP couping theory as it is presently being applied in MgB_2.

II. CONSEQUENCES OF TWO DIMENSIONALITY OF THE σ BANDS

Since the earliest theoretical work[2, 3] it has been clear that the covalent B-B bond that is driven to be metallic by the chemistry of MgB_2 is at the root of the remarkable superconductivity of MgB_2. The very large deformation potential $\mathcal{D}$ of the B $p\sigma$ band for stretching of the B-B bond was identified early on,[2] and several calculations[4–8] of the electron-phonon spectral function $\alpha^2F(\omega)$ have made this coupliing quite evident: this spectral density is dominated by a huge peak at the calculated frequency of the E_{2g} (bond stretching) mode.

Consideration of the Fermi surfaces (FSs) begins to clarify the degree to which the strong coupling is spread through, or rather focussed, in the phonon spectrum. The FS consists of two types: slightly fluted cylinders surrounding the Γ-A line (two of them), arising from B $2p_x, p_y(\sigma)$ states, and a more complicated, three dimensional sheet arising from the B $2p_z(\pi)$ orbitals. These Fermi surfaces, with calculations presented in most detail by Mazin and Kortus,[9] Rosner *et al.*[10], and Harima,[11] have been verified in detail by Carrington *et al.*[12] In fact, shifts of the σ and π bands by no more than ∼100 meV would make the correspondence exact.[10] The strong coupling involves the bond-stretching phonons with $Q < 2k_F$ that can scatter a hole from a cylinder, to a cylinder. Here and below, k_F is the average radius of the cylinders, and $Q = \sqrt{Q_x^2 + Q_y^2}$ is the in-plane wavevector. Detailed analysis, which involves in a central way the two dimensionality of the σ bands, shows[13] that all the bond stretching modes with $Q < 2k_F$ are renormalized by the same amount (a feature of the 2D susceptibility $\chi(Q)$[13]): the Kohn anomaly is not a downward cusp as in 3D, but rather an inverted plateau.

This 2D Kohn anomaly can be seen clearly in Figure 1, where the calculated phonon dispersion curves[14] for both undoped and doped LiBC are shown. Doping holes into the B-C σ bands, which are very much like those in MgB_2, introduces an extremely sharp and deep renormalization of the E_{2g} modes for $Q < 2k_F$. Similar behavior can be seen in the published phonon dispersion relations[3, 5, 7]. However, neither the sharpness nor the "inverted plateau" shape has been evident before, because the Q mesh in the phonon calculations has been much too coarse in all of the studies. The Q mesh in the $Li_{1-x}BC$ calculations[14] was much finer, and the

true behavior is evident in Fig. 1.

A. $Li_{1-x}BC$

It is appropriate to digress briefly. There has been much interest in possible other members of a "MgB_2 class" of superconductors that would share similar characteristics of EP coupling and also a high T_c. Hole-doped LiBC has been suggested as a serious possibility.[15] Its semiconducting electronic structure seems susceptible to hole-doping by Li depletion, and the broad band nature of all the bands in LiBC suggests that the doped-in holes, which would be partly σ in character, would be itinerant. Moreover, $Li_{1-x}BC$ had already been reported by Wörle *et al.*[16] to be synthesizable, with conductivity increasing with hole doping. A number of groups have synthesized and begun to characterize LiBC. [17–22] There are two reports of deintercalation of Li. Zhao, Klavins, and Liu reported evaporation of Li upon vacuum annealing, with no sign of superconductivity in the annealed samples.[22] Fogg *et al.* have reported[23] synthesis of Li-deficient $Li_{1-x}BC$ by high temperature annealing and also report no evidence of superconductivity in the susceptibility. The full story on the LiBC system remains uncertain.

B. Return to consequences of 2D character

The mode coupling strength $\lambda_{Q,\nu}$, whose average over the zone and over the N_ν branches ν gives λ, is[24]

$$\lambda_{\vec{Q},\nu} = \frac{2N_\nu}{\omega_{\vec{Q},\nu}N(0)}\sum_k |M_{k,k+Q}|^2\delta(\varepsilon_k)\delta(\varepsilon_{k+Q}) \quad (1)$$

The more usual picture for λ is the electron viewpoint, where it is given by the Fermi surface average of λ_k, expressing it as the weighted average of its values over the individual types of Fermi surface,

$$\lambda = <\lambda_k>_{FS} = \frac{N_\sigma(0)}{N(0)}\lambda_\sigma + \frac{N_\pi(0)}{N(0)}\lambda_\pi. \quad (2)$$

For MgB_2 in particular, it is important to consider both decompositions, as we now demonstrate.

For the E_{2g} branch that has very large EP matrix elements $\mathcal{M}$, the contribution from the σ bands (with their cylindrical Fermi surfaces) is

$$\lambda_{\vec{Q}}^{E_{2g}} = 4\frac{2N_\nu N^{2D}(0)}{\omega_{Q\nu}}4^2|\mathcal{M}|^2\hat{\xi}(Q), |Q| < 2k_F \quad (3)$$

where $4 = 2^2$ accounts for the two σ Fermi surfaces, the 2D phase space for electron-hole excitations is

$$\hat{\xi}(Q) = \sum_k \delta(\varepsilon_k)\delta(\varepsilon_{k+Q}) / \Big[\sum_k \delta(\varepsilon_k)\Big]^2 = \frac{1}{\frac{Q}{2k_F}\sqrt{1-(\frac{Q}{2k_F})^2}}, \quad (4)$$

and $N^{2D}(0)$ is the 2D DOS per spin for a single σ band. These mode $\lambda_{\vec{Q},\nu}$ values are related to the phonon linewidth $\gamma_{\vec{Q},\nu}$ by (for MgB_2)

$$\gamma_Q/\omega_Q = \frac{1}{N_\nu}\lambda_Q\frac{\pi}{2}N(0)\omega_Q \approx \lambda_Q \times \frac{1.6}{9} \times 0.35eV^{-1} \times 0.07eV \approx 0.004\,\lambda_Q \quad (5)$$

With usual values of $\lambda_Q \leq 1$, this relation gives the standard small linewidth $\gamma_Q << \omega_Q$. Due to the 2D FS nesting, both γ_Q and λ_Q are strongly Q dependent in MgB_2 (which may have experimental consequences), but because they are very large only in a limited region of Q space (see below), an average is not representative and is insufficient for an understanding and even for reasonable quantitative estimates.

To apply these relations in detail to MgB_2, the analysis goes as follows. On the σ surfaces, calculated and derived values (dHvA data [12] compared with theory) cluster around $\lambda_\sigma = 1 - 1.2$, here the conservative value $\lambda_\sigma = 1$ will be used. This total value arises from both the strongly coupled E_{2g} modes ($\lambda_\sigma^{E_{2g}}$), and all of the other modes (λ_σ^{other}). Comparing the calculated linewidths (equivalently, mode lambda) for the strongly coupled modes to the others (*i.e.* those with $Q < 2k_F$ compared to those with $Q > 2k_F$), we conclude that this arises almost entirely from the E_{2g} modes. To be conservative again, the following estimate will assume that only 80% arises from the E_{2g} modes. The fraction of phonon modes from which this arises is 2/9 of the branches, and – according to the latest de Haas-van Alphen data[12], and averaging the areas of the two σ cylinders – only 12.4% ($\approx \frac{1}{8}$) of the Brillouin zone lies in the region $Q < 2k_F$. These values imply that the value of $<\lambda_Q^{E_{2g}}> \times(2/9)\times(1/8) = \lambda_\sigma^{E_{2g}} \approx 0.8$ implies $<\lambda_Q^{E_{2g}}> \sim 38$. Then Eq. (5) gives the full linewidth $2\gamma_{E_{2g}} \sim 0.3 - 0.4\omega_{E_{2g}}$!

This number is remarkably large for a reasonably high frequency phonon. The point is clear: the E_{2g} modes with $Q < 2k_F$ are extremely strongly coupled, more strongly than anything that has been seen in other superconductors. This fact is clear

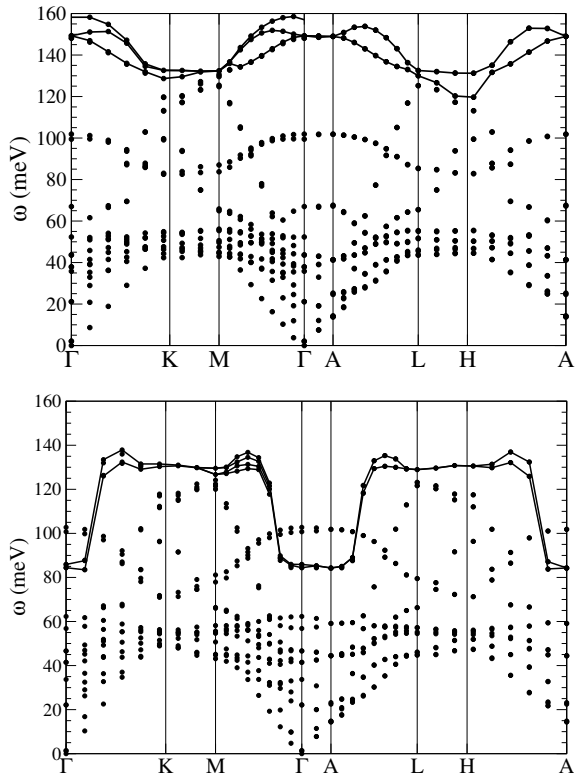

FIG. 1: Calculated phonon dispersion curves for (top) semiconducting LiBC and (bottom) hole doping corresponding to $Li_{0.75}BC$. The B bond-stretching modes are connected by heavy lines, to emphasize the extremely strong downward renormalization for $Q < 2k_F$ (ω_Q^2 decreases by ∼60%). The sharp and very strong Kohn anomalies at $2k_F$ along the various directions are apparent. See Ref. 14.

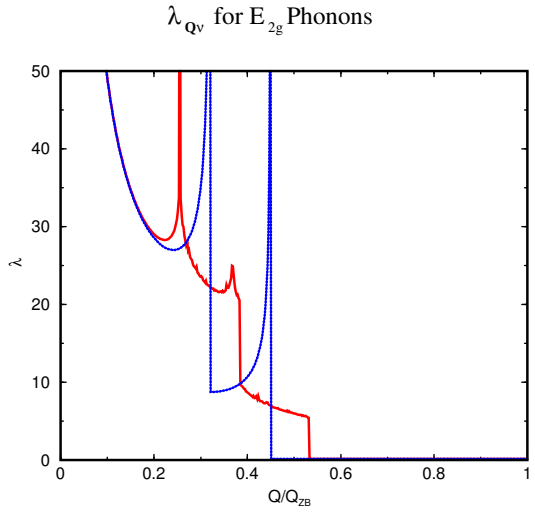

FIG. 2: Behavior of $\lambda_{Q_\parallel}$ ($Q_\parallel \equiv \sqrt{(Q_x^2 + Q_y^2)}$). The dotted line gives the behavior for two concentric 2D cylinder Fermi surfaces such as in MgB_2, with (integrable) divergences at $Q_\parallel \to 0$ as well as for $Q_\parallel = 2k_F$ for each of the two cylindrical Fermi surfaces. The full line shows the effect of k_z dispersion that is representative of MgB_2.

also for the similar material $Li_{0.75}BC$ in the calculated phonon dispersion curves of Fig. 1, where it can be seen that $\omega_{E_{2g}}^2$ (which is what arises naturally in the theory) is decreased by nearly 2/3 from its unrenormalized value. There is information on the linewidths from Raman scattering data, where $\gamma_{E_{2g}} \sim 0.3 - 0.4\omega_{E_{2g}}$ is found,[25] and from inelastic xray scattering where a similar result was obtained.[26]

III. VALIDITY OF MIGDAL-ELIASHBERG THEORY IN MGB_2

Occurrence of the prediction of overdamped modes from the theory indicates that use of the theory is invalid: for such strong coupling, the E_{2g} modes are not well-defined phonons. Even worse, since those modes are not phonons, then one can't be sure the others are, because harmonic phonon theory is a solution to the lattice dynamics problem only if *every* phonon is well defined. Although there is no reason to suspect that the situation is so bad as to have no well defined phonon at all, it should be kept in mind that, so far, the experimental evidence for any well defined phonon is not strong. The main evidence is from inelastic xray scattering, where it can only be said that some linewidths are less than the 8 meV energy resolution.[26]

Migdal theory for the coupled electron-phonon system therefore is not valid for MgB_2; the analysis we have been using in fact is not consistent because of this fact. It follows that the standard Migdal-Eliashberg theory that is being used to calculate the superconducting behavior of MgB_2 is unjustified. Eq. (5) has assumed very specifically that $\gamma_Q << \omega_Q$, but leads to a conclusion that violates this condition. The application of this theory to MgB_2 has been challenged on other grounds as well. Using careful frozen-phonon studies, Boeri and collaborators[27] have shown that the "anharmonicity" of the E_{2g} (B-B bond stretching) potential, which had been noticed by several groups, arises from the proximity of σ band edge to the Fermi level. As such, it is a "non-adiabatic" effect, but not in the usual sense because $\hbar\omega_{E_{2g}}$ is not really so close to the value of E_F. It is, rather, a combination of a relatively low Fermi energy, together with the extremely strong σ-band deformation potential for bond-stretching distortions. Thus it is

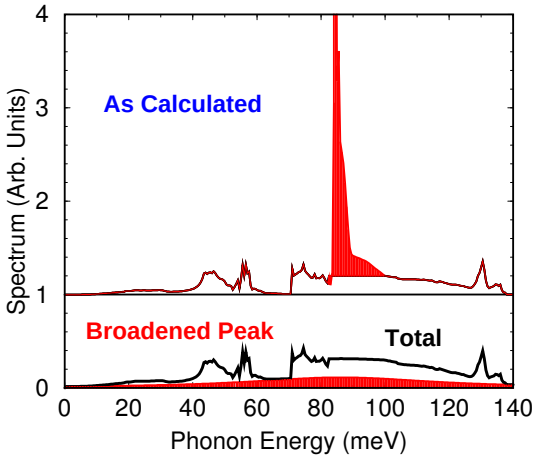

FIG. 3: The upper panel shows the $\alpha^2F(\omega)$ spectral function that was calculated by An *et al.*[13, 14] The lower panel shows the effect of broadening the contributions of the strongly coupled phonons (those within the peak near 85 meV) by a Lorentzian with a width equal to about 40% of the peak frequency (γ=35 meV): notice that the peak vanishes. A proper theory would probably not give the simple Lorentzian broadening that arises in conventional Migdal-Eliashberg theory.

an independent and new aspect of MgB_2, in which the extremely strong EP coupling is destroying the validity of Midgal theory. An *ad hoc* correction of this problem, treating this bond-stretching displacement as independent (which it is not, because it is so ill-defined), gives according to several groups an increase of the "frequency" of roughly 10 meV (or about 15%). Very recent calculations of the full third- and fourth order anharmonic corrections give the resulting increase of the E_{2g} mode frequency of only 5%.[28] So, interestingly, there is a negative feedback from this strong-coupling enhanced anharmonicity that helps keep the lattice stable. All things considered, it is clear that the coupling strength in MgB_2, extremely strong as it is, has not approached the limits of such coupling.

IV. HOW STRONG CAN MODE COUPLING BECOME?

These developments raise questions about the limits of crystal stability, and how much stronger the coupling could possibly be. The recent investigation of the EP coupling in quasi-2D bands such as in these materials revealed that the contribution from the 2D-like σ bands is independent of doping level, except indirectly due to changes in effective mass, or due to changes in the deformation potential arising from changes in screening. (Non-adiabatic effects of course depend on doping level.) Finally, there is no reason to exclude the possibility of "MgB_2-like" system with even higher T_c.

The dependence of EP coupling strength is given by

$$\lambda^\sigma \propto \frac{m^*}{\omega^2}\mathcal{D}^2 = \frac{m^*|\mathcal{D}|^2}{\Omega^2 - Bm^*|\mathcal{D}|^2} \qquad (6)$$

where m^* is proportional to the 2D density of states, ω is the frequency of the bond-stretching modes (subscript is suppressed) with $Q < 2k_F$, Ω is a reference, unrenormalized frequency, and $\mathcal{D}$ is the deformation potential for the σ bands at E_F. The constant B includes material independent quantities. Note especially the *independence* on 2D phase space (*i.e.* the value of k_F).[14] The dependence on $\mathcal{D}$ is leveraged by phonon softening in the denominator, but of course is finally limited by phonon softening as the mode is driven unstable. Then, of course, one must address the problem of the optimal value of λ: if λ is very large due to coupling to very low frequency modes, it does not lead to a high superconducting transition temperature. It is not fruitful to follow these relationships in more detail with these equations, because as pointed out in the previous sections, the theory has limited quantitative validity.

The numerator of Eq. (6) was at the root of the prediction that $Li_{1-x}BC$ (x = 0.2-0.5, say) should be a better superconductor than MgB_2: $\mathcal{D}_{LiBC} \approx \sqrt{2}\mathcal{D}_{MgB_2}$.[15] Fortunately, the value of Ω is larger for LiBC because the B-C bond is stronger than the B-B bond, which is also the underlying reason that the square of the deformation potential is almost a factor of two higher in $Li_{1-x}BC$. As noted earlier in this paper, the predictions for $Li_{1-x}BC$ have not yet been confirmed.

V. SUMMARY

Clearly EP theory needs to be extended for the case of MgB_2. There seems to be little doubt that the origin of the coupling is understood, and the electronic structure is described well, and that the EP coupling strength is quite different on the σ and π sheets of Fermi surface, making this a beautiful example of a two-band (or two-gap) superconductor. Both quantitative determinations of the properties of MgB_2, and a real understanding of what is happening in this bond-stretching-mode – σ-hole dynamical soup, remains to be sorted out using some extension of the theory.

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[1] J. Nagamitsu *et al.*, Nature **410**, 63 (2001).
[2] J.M. An and W.E. Pickett, Phys. Rev. Lett. **86**, 4366 (2001)
[3] J. Kortus *et al.*, Phys. Rev. Lett. **86**, 4656 (2001).
[4] Y. Kong *et al.*, Phys. Rev. B **64**, 020501 (2001).
[5] K.-P. Bohnen, R. Heid, and B. Renker, Phys. Rev. Lett. **86**, 5771 (2001).
[6] T. Yildirim *et al.*, Phys. Rev. Lett. **87**, 037001 (2001).
[7] A. Liu, I. I. Mazin, and J. Kortus, Phys. Rev. Lett. **87**, 087005 (2001).
[8] H. J. Choi *et al.*, Phys. Rev. B **66**, 020513 (2002); Nature **418**, 758 (2002).
[9] I. I. Mazin and J. Kortus, Phys. Rev. B **65**, 180510 (2002).
[10] H. Rosner, J. M. An, W. E. Pickett, and S. L. Drechsler, Phys. Rev. B **66**, 024521 (2002).
[11] H. Harima, Physica C **378-381**, 18 (2002).
[12] E. A. Yelland *et al.*, Phys. Rev. Lett. **88**, 217002 (2002); A. Carrington *et al.*, Phys. Rev. Lett. **91**, 037003 (2003).
[13] W. E. Pickett, J. M. An, H. Rosner, and S. Y. Savrasov, Physica C **387**, 117 (2003).
[14] J. M. An, S. Y. Savrasov, H. Rosner, and W. E. Pickett, Phys. Rev. B **66**, 220502 (2002).
[15] H. Rosner, A. Kitaigorodsky, and W. E. Pickett, Phys. Rev. Lett. **88**, 127001 (2002).
[16] M. Wörle, R. Nesper, G. Mair, M. Schwarz, and H. G. von Schnering, Z. Anorg. Allg. Chem. **621**, 1153 (1995).
[17] A. Bharathi, S. J. Balaselvi, M. Premila, T. N. Sairam, G. L. N. Reddy, C. S. Sundar, and Y. Hariharan, Solid State Commun. **124**, 423 (2002).
[18] J. Hlinka, I. Gregora, J. Pokorny, A. V. Pronin, and A. Loidl, Phys. Rev. B **67**, 020504 (2003).
[19] B. Renker, H. Schober, P. Adelmann, P. Schweiss, K.-P. Bohnen, and R. Heid, cond-mat/0302036.
[20] D. Souptel, Z. Hossain, G. Behr, W. Löser, and C. Geibel, Solid State Commun. **125**, 17 (2003).
[21] A. V. Pronin, K. Pucher, P. Lunkenheimer, A. Krimmel, and A. Loidl, Phys. Rev. B **67**, 132502 (2003).
[22] L. Zhao, P. Klavins, and K. Liu, J. Appl. Phys. **93**, 8653 (2003).
[23] A. M. Fogg, J. B. Claridge, G. R. Darling, and M. J. Rosseinsky, Chem. Comm. (2003, in press).
[24] P. B. Allen, Phys. Rev. B **6**, 2577 (1972); P. B. Allen and M. L. Cohen, Phys. Rev. Lett. **29**, 1593 (1972). A numerical correction is given in Eq. (4.27) of P. B. Allen, in *Dynamical Properties of Solids*, Ch. 2, edited by G. K. Horton and A. A. Maradudin (North-Holland, Amsterdam, 1980).
[25] J. W. Quilty *et al.*, Phys. Rev. Lett. **88**, 087001 (2002); H. Martinho *et al.*, cond-mat/0105204.
[26] A. Skukla *et al.*, Phys. Rev. Lett. **90**, 095506 (2003).
[27] L. Boeri, G. B. Bachelet, E. Cappelluti, and L. Pietronero, Phys. Rev. B **65**, 214501 (2002); Supercond. Sci. Technol. **16**, 143 (2003).
[28] M. Lazzeri, M. Calandra, and F. Mauri, cond-mat/0306650.