Extreme Electron-Phonon Coupling in Boron-based Layered Superconductors

J. M. An, 1 S. Y. Savrasov, 2 H. Rosner, 3 and W. E. Pickett 4

1 Lawrence Berkeley National Laboratory, Berkeley CA 94720
2 Department of Physics, New Jersey Institute of Technology, Newark, NJ 07102
3 Department of Physics, University of California, Davis CA 95616
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The phonon-mode decomposition of the electron-phonon coupling in the MgB$_2$-like system Li$_{1-x}$BC is explored using first principles calculations. It is found that the high temperature superconductivity of such systems results from extremely strong coupling to only $\sim$2% of the phonon modes. Novel characteristics of $E_{2g}$ branches include (1) “mode $\lambda$” values of 25 and greater compared to a mean of $\sim$0.4 for other modes, (2) a precipitous Kohn anomaly, and (3) $E_{2g}$ phonon linewidths within a factor of $\sim$2 of the frequency itself, indicating impending breakdown of linear electron-phonon theory. This behavior in borne out by recent inelastic x-ray scattering studies of MgB$_2$ by Shukla et al.

Superconductivity near $T_c \approx 40$ K in MgB$_2$ [1] has necessitated a re-evaluation of our understanding of phonon-coupled superconductivity, and illustrated vividly that there has been a substantial void in our conceptual understanding of this “conventional” mechanism of coupling, long thought to require $d$ electrons, high density of states, and high symmetry. The general theory of electron-phonon (EP) coupled superconductivity has long been available, [2,3] and some essential understanding of the mechanism in MgB$_2$ is now in place. [4–10] The particular structure and chemistry of MgB$_2$ creates holes in the B 2$p\sigma$ bands, and these holes are coupled very strongly to the B-B bond stretching vibrational modes. The predictions of band theory have been verified by angle-resolved photoemission [11] and de Haas – van Alphen measurements. [12–14] One new facet is an unusually strong anisotropy in the EP coupling, such that the Fermi surface (FS) averaged EP coupling strength $\lambda$ and Eliashberg function $\alpha^2F(\omega)$ do not give a precise account of $T_c$ or of thermal and spectroscopic data. It seems however that much can be accounted for by generalizing to a two-band model [9,10] of strongly coupled $\sigma$ holes and weakly coupled $\pi$ electrons, with $\lambda = \lambda_\sigma + \lambda_\pi \approx 0.6 - 0.8$.

In spite of success in accounting for many observations, this linear EP theory (with some ad hoc correction for anharmonicity) seems at best incomplete. The enormous linewidth $\gamma$ of the $E_{2g}$ mode, [15–18] ascribed to strong EP coupling plus anharmonicity, has not been accounted for quantitatively, and the predicted change in frequency and $\gamma$ at $T_c$ [9] is not observed. Non-adiabatic processes arising from the small filling of the $\sigma$ bands, and low Fermi energy $E_F$, have been proposed. [9,19,20] Boeri et al. provided needed clarification by demonstrating that $E_{2g}$ anharmonicity arises in MgB$_2$ from non-adiabatic effects, [21] due to the huge deformation potential. [4]

A second compound in the “MgB$_2$ class” that has been proposed recently is useful in clarifying these issues. LiBC is isostructural [22] and isovalent with MgB$_2$, having graphene-like B-C layers that are even more strongly bonded than are the B layers of MgB$_2$. The stoichiometric compound is semiconducting (due to the B-C difference), but Li deficiency that makes it a hole-doped metal has been reported. [22] Such hole doping introduces carriers into the B-C $\sigma$ bands, as occurs in MgB$_2$, and near rigid-band behavior has been demonstrated, making it a promising system for probing the carrier density dependence of EP coupling in MgB$_2$-class superconductors.

In this paper we focus on the decomposition of $\lambda$ into contributions (“mode $\lambda$’s”) from each phonon $\nu$ rather than its FS decomposition, and find startlingly high values $\lambda_\nu \approx 25$ for $E_{2g}$ modes. First principles calculations of $\alpha^2F$ for Li$_{0.75}$BC gives $\lambda=0.74$, making Li$_{1-x}$BC at this doping level quantitatively similar to MgB$_2$. The insulating end member of the Li$_{1-x}$BC system makes it pedagogically an ideal material to illustrate the novelty that MgB$_2$ has introduced into the physics of electron-phonon coupled superconductivity. Li$_{1-x}$BC is “MgB$_2$ with stronger coupling and variable carrier concentration,” and because its $\sigma$ FSs are (as in MgB$_2$) very close to cylindrical, the underlying physical processes can be modelled simply yet realistically. The essential revelations are: (1) the high temperature superconductivity arises from exceedingly strong coupling of only a small fraction (\sim2%, depending on doping) of the phonon modes, (2) a colossal sharp Kohn anomaly occurs – extreme renormalization by EP coupling upon doping from hard bond-stretching modes, and (3) the phonon linewidth due to decay into $\sigma$ band electron-hole pairs becomes comparable to the linewidth itself, making the bond-stretching modes poorly defined (at best), yet not unstable (due to their intrinsic hard nature). Just this strength of coupling and relative linewidths have been reported for MgB$_2$ by Shukla et al., obtained from inelastic x-ray scattering spectroscopy. [23] Moreover, [4] these effects occur continuously with doping and will allow a unique window into the non-adiabatic regime where the Fermi energy is comparable to the phonon frequency. These features apply directly to Mg$_{1-x}$Al$_x$B$_2$ as well.

A description of the band structure of Li$_{1-x}$BC was
The FSs for $x=0.25$ pictured in Fig. 1, consist of four B $2p - C 2p$ σ band cylinders with very small $k_z$ dispersion, and a π band FS. The σ cylinders are similar to those in MgB$_2$, with four (instead of the two in MgB$_2$) arising from the doubling of the unit cell along c due to alternate stacking of B-C layers. The phonon energies and EP matrix elements have been obtained from linear response theory [25] as implemented in Savrasov’s full-potential linear muffin-tin orbital code. [26,27] Because of the emphasis here on specific Fermi surface effects, a dense grid of Q points was chosen (a 16,16,4 grid giving 90 Q points in the irreducible wedge). For k-space integration a finer 32,32,8 grid was used, together with an adaptive tetrahedron integration scheme. The code was used previously for MgB$_2$ by Andersen’s group, [6] where the need for careful zone sampling was also emphasized.

For the semiconducting phase, the E$_{2g}$ phonons (Fig.2) are very hard, lying at 150 meV at the Γ point and not dispersing greatly. This high bond-stretching frequency, twice as high as in MgB$_2$, is due to the much stronger B-C bond, 9% shorter and having a 40% larger deformation potential for the σ bands. [24] The spectrum is indicative of a stable, strongly bonded material. For $x=0.25$, where it has become a metal (Fig.2), there is rather little difference in the spectra, except for $Q_{\parallel} < 2k_F \approx \pi/3a$ ($Q_{\parallel}$ is the component of the phonon wavevector $\vec{Q}$ lying in the plane). Within this region, however, the four E$_{2g}$-related modes display a precipitous Kohn anomaly at $2k_F$, and dip nearly discontinuously by 40%. (The decrease in $\omega^2$, which directly reflects the renormalization, is nearly 65%). Closely related renormalization of phonon modes in the Mg$_{1-x}$Al$_x$B$_2$ system has been noted by Renker et al. [28].

In Fig. 3 the phonon density of states (DOS) for $x=0$ and $x=0.25$ are contrasted, and also the calculated EP spectral function $\alpha^2F(\omega)$ for $x=0.25$ is compared with the DOS. For the DOS, doping moves the modes in the frequency range 135 - 155 meV to lower frequency; only from the dispersion curves of Fig. 2 it is clear where they end up (in the 85 meV region) because these modes are near the Γ point where phase space is small. The curve for $\alpha^2F(\omega)$ demonstrates what results: a tiny fraction of modes (quantified below) in the 85 meV region are extremely strongly coupled to the σ band holes, and leads to an inordinately strong contribution to λ, whose total value calculated from $\alpha^2F$ is 0.74. Although about half of the coupling arises from all other modes, it is the extremely strong coupling of small-Q E$_{2g}$ modes to σ holes that drives $T_c$, just as in MgB$_2$. The calculated value of $T_c$ using the Allen-Dynes equation [29] is 34 K assuming $\mu^* = 0.09$ as has been used previously [10] to obtain numerical agreement with the observed $T_c$ for MgB$_2$. Solution of the anisotropic Eliashberg equations [10] would give $T_c$ a few degrees higher.

The circular σ Fermi surfaces of MgB$_2$ and related materials allow an analytic treatment of EP coupling. The phonon energies ($\hbar=1$) are given by the poles of the lattice Green’s function

$$\omega^2_{Q\nu} = \Omega^2_{Q\nu} + 2\Omega_{Q\nu}\Pi(x,\omega_{Q\nu})$$

(1)

where the reference frequency $\Omega_{Q\nu}$ includes all self-energy effects except those arising from electron scattering within the σ bands; practically speaking, they are the energies shown in Fig. 2 for undoped LiBC. Taking for simplicity a single cylindrical Fermi surface with $N(\varepsilon)=m^*/2\pi$ per spin per unit area, and considering the E$_{2g}$ derived modes only, the phonon self-energy due to the σ carriers is

$$\Pi(x,\omega) = -2\sum_k |M_{k,Q}|^2 \frac{f_k - f_{k+Q}}{\varepsilon_{k+Q} - \varepsilon_k - \omega - i\delta}$$

$$\text{Re} \Pi(x,\omega) \approx -2|M_{g,Q}|^2 N(\varepsilon)|\chi^{2D}_L(Q)|$$

(2)

$$\chi^{2D}_L(Q) = (1 - \eta_Q) + [1 - \sqrt{1 - \eta_Q^2}] \theta(\eta_Q - 1)$$

(3)

Here $f_k \equiv f(\varepsilon_k)$ is the Fermi occupation factor, and the usual adiabatic approximation has been made. A mean square matrix element has been extracted from the sum, leaving the unitless Lindhard function $\chi^{2D}_L$. [30] The negative of $\chi^{2D}_L(Q)$ has much the form that is evident in the softened E$_{2g}$ branches with $Q < 2k_F$ in the bottom panel of Fig. 2. This behavior is illustrated by plotting $\omega_Q$ given by Eqs. 1-3 in the bottom panel of Fig. 4.

The “mode λ” $\lambda_{Q\nu}$ [31] for the E$_{2g}$ modes, defined such that it is an intensive quantity whose average over the zone and over the N$_\nu$ branches gives $\lambda_{2g}$ ($\lambda = \lambda_{2g} + \lambda_{other}$), is

$$\lambda_Q = \frac{2N_{\nu}}{\pi N(\varepsilon_F) \omega_Q^2} \gamma_Q = \pi \Omega_Q |M_{g2g}|^2 \xi(Q)$$

(4)

$$\xi(Q) = \sum_k \delta(\varepsilon_k)\delta(\varepsilon_{k+Q}) = N(0)^2 A_{BZ}^{\nu} \frac{\hat{\xi}(Q/2k_F)}{A_{FS}}$$

where $\xi(\eta) = \eta^{-1}(1 - \eta^2)^{-1/2} \theta(\eta)\theta(1 - \eta)$. Here $A_{BZ}$ is the basal area of the BZ and $A_{FS} = \pi(2k_F)^2$ is a doping-dependent area of renormalized E$_{2g}$ phonons. $Q \to 0$ requires somewhat more care [32] but involve negligible phase space for the present purposes. The important feature, aside from the magnitude, is that these mode λ’s scale inversely with $k_F^2$ as illustrated in Fig. 4, diverging for vanishing σ hole doping and indicating the breakdown of conventional EP theory (see below).

For $Q < 2k_F$, $\omega_Q$ and $\Omega_Q$ are nearly constant, so Eqs. (1) and (2) can be solved for $|M_{g2g}|^2$ and substituted into Eq. (4) to provide a simple expression for the mode $\lambda_Q$ ($Q < 2k_F$) in terms of $(\Omega_{g2g}^2 - \omega_Q^2)/\omega_{g2g}^2$. Similar expression have been used for Nb-Mo alloys [33] and for Pb alloys [34] to relate $\lambda$ to phonon softening. There is a simpler way to obtain the average mode $\lambda$ for E$_{2g}$
phonons. The total contribution is that obtained from the 85-100 meV region (see Fig. 3) of \( \alpha^2 F, \lambda_{2g} = 0.4 \). This arises from an average over all phonons, but only those in \( 3/4 \) of the BZ \((Q < 2k_F)\) and the upper four of 18 of the branches contribute. Hence the mean is \(< \lambda_{Q}^2 > = 0.4 \times (40/3) \times (18/4) \approx 25 \). The full \( Q \) dependence of the mode \( \lambda_Q \) for the \( E_{2g} \) branches is given by Eq. (4) and shown in the top panel of Fig. 4. The mean mode \( \lambda \) from all other phonons (equal to their contribution to \( \lambda \) since it includes 98\% of all modes) also is \( \lambda_{other} \approx 0.4 \), accounting for the total \( \lambda = 0.74 \) obtained from \( \alpha^2 F \).

The phonon relative halfwidth \( \gamma_Q/\omega_Q \sim 0.5 \lambda_Q / < \lambda_{2g} > \sim 0.5 \), an alarming result (this ratio is typically \( 10^{-2} - 10^{-3} \)) that reflects the fact that this phonon branch is so ill-defined from extremely strong EP coupling that Migdal theory (and Eliashberg theory) is no longer justified. Even so, this rough estimate is consistent with the large observed halfwidth \((15-18) \) of 125-175 cm\(^{-1}\) for the 600 cm\(^{-1}\) bond-stretching mode, indicating that the large linewidth and its strong increase with temperature is due to EP coupling rather than to anharmonicity, and the same conclusion has been reached by Shukla et al. \[23\].

Now we summarize and discuss some implications of these results. Use of Li\(_{1-x}\)BC has allowed us to identify and quantify the drastic phonon softening arising from the ultrastrong EP coupling to \( E_{2g} \) modes; comparable phenomena occur also in MgB\(_2\). Mode \( \lambda_{2g} \)'s \( \approx 25 \) and linewidths comparable to the frequency point to inadequacies of linear EP theory for these systems. Shukla et al. have reported \[23\] measurements of specific frequencies and linewidths of MgB\(_2\) from inelastic x-ray scattering. For five small-\( Q \parallel E_{2g} \) phonons with frequencies in the 500-550 cm\(^{-1}\) range, they obtained relative linewidths \( \gamma_Q/\omega_Q \approx 1/3 \), very consistent with our results above. For these modes, the average \( \lambda_Q = 26 \) (when normalized as we have done) are again exactly in line with the expectations outlined above.

This extremely strong and abruptly \( Q \) dependent EP coupling provides new insight into the relationship of limits on \( T_c \) and lattice instability. \[35\] Earlier study had produced arguments both that incipient lattice instabilities are helpful \([33,34]\) for \( T_c \), and that they are unhelpful because the low frequency modes are less useful for high \( T_c \), than higher frequencies (of the order of \( 2\pi T_c \)). \[36\] The lack of explicit dependence of \( \lambda_{2g} \) on \( k_F \) indicates that increase in \( T_c \), with doping will arise only from an increase of \( m^* \) (the heavy hole mass increases by 25\% from \( x = 0 \) to \( x = 0.5 \)) or increase of \( |M_{2g}|^2 \), either of which will further soften the \( E_{2g} \) modes and move the system closer to instability. What changes rapidly with doping is the coupling strength of the \( E_{2g} \) modes with \( Q < 2k_F \). The same total EP coupling strength is concentrated into increasingly fewer bond-stretching modes at lower doping levels. Thus in this system (where the two dimensionality of the electron dispersion is central) change of the doping level can lead toward (or away from) a lattice instability without any direct affect on \( T_c \) itself. These new features involving extremely strong coupling apply to Mg\(_{1-x}\)Al\(_x\)B\(_2\), where unexplained structural anomalies occur, as well as to Li\(_{1-x}\)BC.

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FIG. 1. Fermi surfaces of Li$_{0.75}$BC, with the Γ point at the center of the hexagonal zone. There are four cylinders, analogous to the two cylinders in MgB$_2$ but downfolded due to the doubled unit cell. The non-cylindrical surface arises from the weakly coupled π bands.

FIG. 2. Calculated phonon dispersion curves for (top) semiconducting LiBC and (bottom) strongly hole-doped and metallic Li$_{0.75}$BC, with $E_{2g}$-derived modes connected by heavy lines. The primary difference is the extremely strong renormalization downward ($\omega_Q^2$ decreases by ~60%) for $Q < 2k_F$; the extreme van Hove singularities along $\Gamma - K, M - \Gamma, A - L, H - A$ are apparent.

FIG. 3. Phonon DOS for LiBC and Li$_{0.75}$BC (top panel) where the primary difference is the disappearance of modes in the range 135 – 155 meV upon doping (from Fig. 1, they mostly lie in the 80-90 meV region). The shape of $F(\omega)$ and $\alpha^2F(\omega)$ for Li$_{0.75}$BC (bottom panel) revealing the extremely strong coupling to phonons in the 85 – 100 meV range.

FIG. 4. Characteristics of the model 2D electrons (see text) strongly coupled to $E_{2g}$ modes. Bottom panel: $E_{2g}$ branch versus Q; reference branch $\Omega_Q$ and renormalized branch $\omega_Q$ as in Eqs. (1)-(3), for three different values of $2k_F$. Top panel: Corresponding values of the mode $\lambda_Q$ given by Eq. 4, for the same three values of $2k_F$. 