Acoustic Phonon Anomaly in MgB$_2$

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Recent first principles calculations of the phonon dispersion curves in MgB$_2$ have suggested the presence of anomalies in some of the curves, particularly in the longitudinal acoustical (LA) branch in the $\Gamma$ to $A$ direction. Similar behavior has been observed in numerous other superconductors with $T_c$’s higher than those of standard electron-phonon BCS superconductors. Phenomenological calculations of the $\Gamma \rightarrow A$ LA dispersion based on both an acoustical plasmon and a “resonant polarization” mechanism are given here to emphasize the importance of these similarities.

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Single crystals of the new superconductor MgB$_2$ large enough for inelastic neutron scattering experiments have not yet become available, but first principles calculations of the phonon dispersion curves have appeared.

In Ref. 2, a well-defined anomaly appears in the dispersion of the LA mode in the $\Gamma$ to $A$ direction. This anomalous behavior is remarkably similar to that found in transition metal and transition metal carbide superconductors with high transition temperatures. Indeed, it has often been considered a signature of high-temperature electron-phonon superconductivity in these systems. Here, we call attention to and emphasize the potential importance of this similarity by carrying out model calculations in which the anomalies are produced both by an acoustical plasmon (AP) mechanism and by a parameterized, $q$-dependent, interband contribution to the dielectric response function.

Many superconductors with even moderately high transition temperatures show some type of anomaly in the phonon dispersion curves when compared to their low-$T_c$ or nonsuperconducting analogues. In this connection, the lattice dynamics in high-$T_c$ cuprate materials is currently being revisited. It now appears that there are effects in the optical modes and in the electronic structure that correlate with hole doping and that may be related to superconductivity.

We are mainly interested in anomalies in the LA dispersion curves because they are distinctive and prevalent, occurring in systems that have no optical modes as well as those that do. They were first observed and discussed for Nb ($T_c \sim 10K$) more than thirty years ago and somewhat later in the transition metal carbides. Figure 1 shows the LA dispersion curves for NbC, TaC, and HfC, which have transition temperatures of approximately 11K, 11K, and <1K, respectively. The anomalies are obvious for the first two materials but do not occur in HfC. Many other examples of this type of behavior could be given, notably the elemental materials Nb, V, and Ta where only acoustical modes occur. Also shown on Fig. 1 are the results from Ref. 2 of recent first-principles calculations for MgB$_2$ ($T_c = 38.5K$). While only four points were calculated in the $\Gamma$ to $A$ direction, they clearly show that the behavior is anomalous in the sense being used here.

Nakagawa and Woods found they could reproduce their phonon data for Nb with a Born-von Karman model utilizing numerous force constants. The need for such a complex model was thought to be indicative of a strong electron-phonon interaction. Ganguly and Wood observed that the anomalies may be produced by the interaction of acoustical plasmons and phonons. While it is difficult to reconcile this suggestion with the electronic band structure of Nb, as pointed out by Ruvalds, the notion that there is a connection between AP-like electronic modes and phonons persisted. The resonant electronic polarization arising from the double shell model of Weber et al. is somewhat related to the acoustical plasmon mechanism in that an additional mode which interacts with the “bare” phonons is introduced. First principles calculations that began to appear subsequently could replicate the anomalies but the assignments to specific mechanisms were often in conflict. However, the important roles of electronic polarization and details of the band structure were clear.

The acoustical plasmon concept was introduced by...
Pines in 1958 and subsequently applied to superconductivity by a number of authors. It is thought that APs may occur in systems in which heavy and light mass carriers coexist and the light carriers screen the heavy ones to produce an acoustical (ω → 0 as q → 0) excitation. Transition metal systems with the d electrons playing the role of heavy particles and the s electrons the light ones have been long seen as good candidates. In other systems, holes may be the heavy particles and electrons the light ones. In the simplest acoustical plasmon treatment of superconductivity in transition metals, the plasmons either replace entirely or simply complement the phonons in a standard BCS-type theory. An extensive criticism of AP-mediated superconductivity has been given based on system stability and other restrictive requirements. Nevertheless, while to our knowledge APs have not been shown to exist in any bulk material (see also Ref. 14), the concept is an intriguing one and based on sound theoretical arguments regardless of any role it may have in superconductivity. We note that acoustical plasmons have been proposed as existing in MgB$_2$, although not in the context of the present lattice dynamical discussion and in a much higher frequency range.

Magnesium diboride has the AlB$_2$ structure consisting of hexagonal layers of Mg interspersed between graphene-like B layers. Several calculations already contain the screening due to the continuum of light particles is included. The result of the full calculation was subsequently questioned by Ku et al. We emphasize that in any case the APs considered in these calculations are in a far different frequency range than those needed here, as will be seen in the following.

We write the q- and ω-dependent dielectric function as

$$\varepsilon(q,\omega) = 1 + \alpha^0 + \alpha^l + \alpha^h + \alpha^L,$$

and look for its zeros in a standard approach. \(\alpha^l\) and \(\alpha^h\) are the polarizabilities of the two distinct groups of light and heavy carriers and \(\alpha^0\) contains all other contributions to the electronic polarizability, e.g., from interband transitions; \(\alpha^L\) is the lattice contribution. Electronic polarizabilities are calculated in the free electron approximation:

$$\alpha^L_q(\omega) = \frac{8\pi e^2}{q^2} \sum_k \frac{n_{q+k} - n_k}{\omega + E_k - E_{q+k} + i\eta},$$

where \(E^i_k\) and \(n_k\) are the free-electron energy and Fermi function for the \(i = l, h\) particles, respectively.

Neglecting \(\alpha^L\) for the moment, an approximate expression for the dispersion of the APs can be obtained in the long-wavelength limit. Using the first terms of the expansions given by Lindhard

$$\alpha^L_q(\omega) \approx \left\{ \frac{3\alpha^0}{q^2 v_l^2} \omega_i^2 - \omega_0^2 / \omega^2 \right\} q v_i > \omega$$

$$q v_i < \omega.$$

$$\omega(p) = \frac{v_p q}{\sqrt{1 + q^2 l^2}}, \quad q v_h \ll \omega(p) \ll q v_l,$$

where \(v_p = v_h \sqrt{N_i / 3N_l}\) is the acoustical plasmon sound velocity, \(N_i\) is the density of states of the \(i\)th particle at the Fermi level, and \(l = \sqrt{\frac{3}{4\pi e^2 \epsilon_0 m_i}}\) is the screening length of light particles. The Landau damping of acoustical plasmons due to the continuum of light particles is neglected.

In a more complete calculation, we use Eqs. (1) and the full Lindhard expressions for \(\alpha^l\). To include the phonon contribution we use a simple, approximate expression for the lattice polarizability \(\alpha^L\)

$$\alpha^L_q(\omega) = -\omega_0^p(q) (\varepsilon^0 + \alpha^L_q(\omega)) / \omega^2,$$

and take in the \(\Gamma\) to \(A\) direction

$$\omega_0^p(q) = c_0 \sin \left( \frac{\pi q}{2q_0} \right),$$

where \(q/q_0\) is the fractional distance to the BZ boundary and \(c_0\) is adjusted to give the frequency of the LA phonon in MgB$_2$ at the zone boundary, as taken from Refs. 12.

This implies that the “bare” phonon frequency \(\omega_0^p\) already contains the screening due to \(\varepsilon^0\) and the light carriers, hence this screening is taken out in Eq. (8).

The results of such a calculation are shown in Fig. 3. The unperturbed or bare phonon dispersion curve is given by the dashed line and the acoustical plasmon by the dotted solid curve. The latter is Landau damped as it enters the heavy particle continuum at \(q_0 \sim 0.25\). Note again that the AP mode shown here is calculated without taking into account the phonon contribution. Also the bare phonon is before the interaction with heavy particles is included. The result of the full calculation \(\varepsilon = \varepsilon_0 + \alpha^l + \alpha^h + \alpha^L\) are shown by the solid line. After the phonon and heavy particles are allowed to interact, the phonon frequency rises above the unperturbed curve and continues to be affected even after the plasmon is damped, causing the anomalous behavior to develop. Interestingly, the perturbed phonon remains well-defined until it enters the heavy particle continuum where
Some of these effects will be discussed in more detail in phonon interaction was found to be strong in Ref. 2. We note that this is also the region where the electron- experiments should readily pick up this feature if it exists. 

We followed Fröhlich and Rothwarf a bit further by calculating $T_c$ from a modified BCS-like expression, $kT_c = \hbar \omega_{pm} \exp(-1/F)$. $\omega_{pm}$ was taken to be the frequency at which the plasmon enters the heavy hole continuum and $F$ was calculated as described in Refs. 14,17. Values of $T_c$ quite close to the experimental value could be found but they were very sensitive to the relevant parameters which could be changed over a fairly wide range without greatly changing the dispersion curves. Having in mind the known restrictions on the acoustical plasmon mechanism, we do not consider these results of direct, fundamental significance for the high transition temperatures in MgB$_2$, that is to say, we do not argue that superconductivity is produced by acoustical plasmons. However, the results do suggest that the electronic structure of this material leads to some resonance-like interaction of the electrons or holes with “bare” phonons. How this might come about from another viewpoint is illustrated by the following calculation.

In Eq. (6), $\alpha^h$, the polarizability of the heavy carriers, which gives rise to the acoustical plasmons, was replaced by a $q$-dependent polarization term, $\alpha^{ss}$, ascribed here to interband transitions that were previously included in the constant $\varepsilon_0$. $\alpha^{ss}(q)$ was chosen to be a “skewed Lorentzian” of the form

$$\alpha^{ss}(q) = \frac{a}{1 + b^2(q - q_0)^2}. \quad (7)$$

We initially fixed $q_0$ at 0.7 to locate the maximum in the vicinity of the dip in the phonon dispersion curve. Modification of the bare phonon dispersion and trial and error with the parameters $a$ and $b$ readily provided a satisfactory representation of the anomalous behavior. The results of three such calculations for different values of $q_0$ are shown by the upper curves on Fig. 3. We note that the importance of interband transitions has been emphasized in recent electronic structure calculations and particularly those of Refs. 23,24.

An interesting aspect of this calculation is that the $q$-dependence of $\alpha^{ss}$ correlates closely with that of the “supershell frequency”, $\omega_{ss}(q)$, in Weber’s double-shell model. Smith et al. calculated $\omega_{ss}(q)$ for TaC by assigning the free electron mass to the supershell. The supershell motion was then retained explicitly in the dynamical matrix rather than being transformed out as is usually done in the shell model. They found that $\omega_{ss}(q)$ for the longitudinal mode had a pronounced, asymmetrical dip centered at the position of the anomaly. Loosely speaking, the function of the supershell is to provide a “resonant polarization” mechanism to screen the relevant part of the dynamical matrix. This implies that the shell frequency should vary inversely with the square root of this polarization. Calculating the $q$-dependence of $\omega_{ss}$ in this way from Eq. (6) and comparing it with the $\omega_{ss}$

![FIG. 2: (a) An example of the calculation of the anomaly given by the acoustical plasmon mechanism, as described in the text. (b) The anomaly as a function of the mass of the heavy particle.](image-url)
extracted from Ref. 25 gives the results shown in the lower part of Fig. 3; the agreement is obviously quite good. The supershell frequencies have been normalized to one another at \( q = 0 \) and then shifted into the range of phonon frequencies. Of course, the introduction of a distinct, well-defined mode for the supershell in this region of \((\mathbf{q}, \omega)\) space is a rather drastic simplification whose implications are not clear. However, it is remarkable that the calculations of Ref. 26 also point to a sharp resonance in the vicinity of 2.5 eV attributed to interband transitions. In any case, the simple form in Eq. (7) does seem to capture much the same physics contained in the double shell model, and perhaps also that in less phenomenological treatments.

The calculations of the phonon spectra of MgB\(_2\) in Ref. 2 which show the anomalies, used a density functional theory (DFT), full-potential linear response, LMTO approach. The calculations of Ref. 2, which show the anomalies, used a mixed basis pseudopotential method and DFT. While the results of the two calculations are in general agreement, they differ strongly in the dispersion of interest here. Kong et al. 2 also calculated the electron-phonon interaction and found it to be particularly large in the vicinity of the anomaly. Since the calculations of Ref. 2 obtained the anomalies, their origin must be embedded in and, in principle, can be extracted from those calculations. Conversely, since the anomalies were not obtained in Ref. 2, a comparison of the two approaches is important from both a computational and a physical standpoint. As discussed above, attempts to identify a well-defined mechanism producing the anomalies in other materials in the 1970s were inconclusive and MgB\(_2\) may now provide an impetus to reconsider their origins. It will indeed be interesting to see how well these calculations fit the experimental lattice dynamical data when crystals large enough for neutron scattering become available. Of course, any hint of acoustical plasmon effects also would be of great interest.

To summarize, one recent first-principles calculation of the phonon dispersion curves in MgB\(_2\) shows anomalies in the LA branch similar to those found in other high-T\(_c\) electron-phonon BCS superconductors; however, another calculation did not give them. These anomalies can be calculated using an acoustical plasmon mechanism but the band parameters involved seem unrealistic. A resonant polarization mechanism in which interband transitions give a \( \mathbf{q} \)-dependent contribution to the dielectric response function is probably more realistic. A detailed analysis of the new MgB\(_2\) lattice-dynamical calculations and comparison with earlier calculations for transition metal materials should be invaluable in giving insight into the underlying mechanism.

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