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 Γ 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.[1,2] In Ref. 2, a well-defined anomaly appears in the dispersion of the LA mode in the Γ to A direction. This anomalous behavior is remarkably similar to that found in transition-metal[3] and transition-metal carbide[4] 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 parametrized, **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 analogs. In this connection, the lattice dynamics in high-T_c cuprate materials[5] is currently being revisited. It now appears that there are effects in the optical modes[6] and in the electronic structure[7] 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 ($T_c \sim 10$ K) more than 30 years ago[3] and somewhat later in the transition-metal carbides.[4] Figure 1 shows the LA dispersion curves for NbC, TaC, and HfC, which have transition temperatures of approximately 11 K, 11 K, and <1 K, 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 in Fig. 1 are the results from Ref. 2 of recent first-principles calculations for MgB_2 ($T_c = 38.5$ K). While only four points were calculated in the Γ to A direction, they clearly show that the behavior is anomalous in the sense being used here.

Nakagawa and Woods[3] 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[8] 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,[9] 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.*[10] is somewhat related to the acoustical plasmon mechanism in that an additional mode which interacts with the ''bare'' phonons is introduced. First-principles calculations[11,12] 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[13] in 1956 and subsequently applied to superconductivity by a number of authors.[14–17] It is thought that AP's may occur in systems in which heavy- and light-mass carriers coexist and the light carriers screen the heavy ones to produce an acoustical ($\omega \rightarrow 0$ as $\mathbf{q} \rightarrow 0$) excitation. Transition-metal systems with the d electrons playing the role of heavy

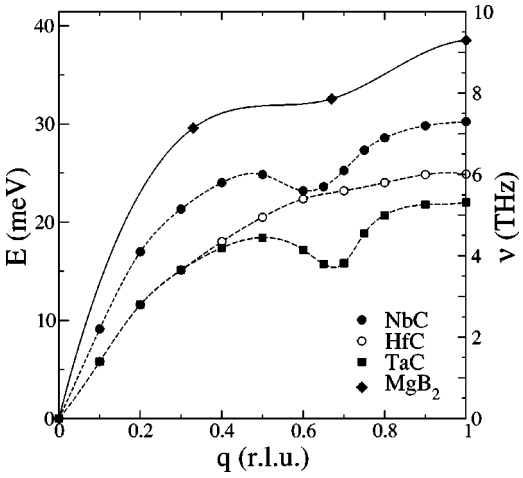

FIG. 1. Phonon dispersion curves along $(q,0,0)$ for NbC, TaC, and HfC; the anomalous behavior in the first two is evident. Data from the recent first-principles calculations for MgB_2 (Ref. 2) are also shown. Lines are guides to the eye, r.l.u. means reciprocal lattice units.

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.[18,19] Nevertheless, while to our knowledge AP's have not been shown to exist in any bulk material (see also Ref. 9), 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[20] 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 graphite like B layers. Several calculations[21–23] establish that the occupied bands consist of σ bands formed from boron sp^2 hybridized orbitals and π bands formed from the $2p_z$ orbitals directed along the *c* axis. Interactions with the Mg $3s$ orbitals result in the σ bands not being fully occupied, as in graphite, which creates holes at the top of the bands. The various calculations are in good agreement in showing a weakly dispersing band in the Γ to *A* direction lying just above the Fermi surface. Voelker *et al.*[20] have provided analytical fits to the bands they calculated, with the holes in the σ bands having high effective mass for motion along the k_z direction. This led those authors to investigate the possible existence of acoustical plasmons. They found evidence that they do exist but the validity of their calculation was subsequently questioned by Ku *et al.*[24] We emphasize that in any case the AP's 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

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

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

$$\alpha^i_{\mathbf{q}}(\omega)=\frac{8\pi e^2}{q^2}\sum_{\mathbf{k}}\frac{n^i_{\mathbf{q}+\mathbf{k}}-n^i_{\mathbf{k}}}{\omega+E^i_{\mathbf{k}}-E^i_{\mathbf{q}+\mathbf{k}}+i0}, \tag{2}$$

where $E^i_{\mathbf{k}}$ and $n^i_{\mathbf{k}}$ are the free-electron energy and Fermi function for the $i=l,h$ particles, respectively.

Neglecting α^L for the moment, an approximate expression for the dispersion of the AP's can be obtained in the long-wavelength limit. Using the first terms of the expansions given by Lindhard,[25]

$$\alpha^i_{\mathbf{q}}(\omega)\simeq\begin{cases}3\omega^2_{0i}/q^2v_i^2 & qv_i>\omega,\\ -\omega^2_{0i}/\omega^2 & qv_i<\omega.\end{cases} \tag{3}$$

v_i is the Fermi velocity of the ith particle, and $\omega^2_{0i}=4\pi e^2 n_i/m_i^*$ is the plasmon frequency, with m_i^* the effective mass and n_i the particle density; the imaginary parts are neglected. Substituting these in Eq. (1) and defining $1+\alpha^0=\varepsilon_0$ gives, for the acoustical plasmon frequency $\omega_p(q)$,

$$\omega_p(q)=\frac{v_p q}{\sqrt{1+q^2\lambda^2}},\quad qv_h\ll\omega_p(q)\ll qv_l, \tag{4}$$

where $v_p=v_h\sqrt{N_h/3N_l}$ is the acoustical plasmon sound velocity, N_i is the density of states of the ith particle at the Fermi level, and $\lambda=\sqrt{\varepsilon_0\hbar^2\pi/4e^2k_{F,l}m_l^*}$ 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 Eq. (1) and the full Lindhard expressions for α^i. To include the phonon contribution we use a simple, approximate expression for the lattice polarizability α^L,

$$\alpha^L_{\mathbf{q}}(\omega)=-\omega^0_{ph}(q)^2[\varepsilon^0+\alpha^l_{\mathbf{q}}(\omega)]/\omega^2, \tag{5}$$

and take in the Γ to *A* direction

$$\omega^0_{ph}(q)=c_0\sin\left(\frac{\pi}{2}\frac{q}{q_0}\right), \tag{6}$$

where q/q_0 is the fractional distance to the Brillouin zone (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. 1 and 2. This implies that the ''bare'' phonon frequency ω^0_{ph} already contains the screening due to ε^0 and the light carriers; hence, this screening is taken out in Eq. (5).

The results of such a calculation are shown in Fig. 2(a). 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 $q_c\sim 0.25$. 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 its width increases rapidly in the region of the anomaly due to the continuum of the heavy-particle contribution to the imaginary part of $\varepsilon(\mathbf{q},\omega)$. Neutron scattering experiments should readily pick up this feature if it exists. We note that this is also the region where the electron-phonon interaction was found to be strong in Ref. 2. Some of these effects will be discussed in more detail in a subsequent paper.

To obtain the curves in Fig. 2(a) we took the mass ratio $m_h^*/m_l^*=20$ and Fermi momentum ratio $k_{F,l}/k_{F,h}=2.4$. Here $n_l=10^{21}$ cm^{-3}, $n_h=0.75\times10^{20}$ cm^{-3}, $v_l=2.4\times10^7$ cm/s, and $v_h=5\times10^5$ cm/s. This corresponds to the choice of light mass $m_l^*=1.5m_0$. Also a value of $\varepsilon_0=30$ was

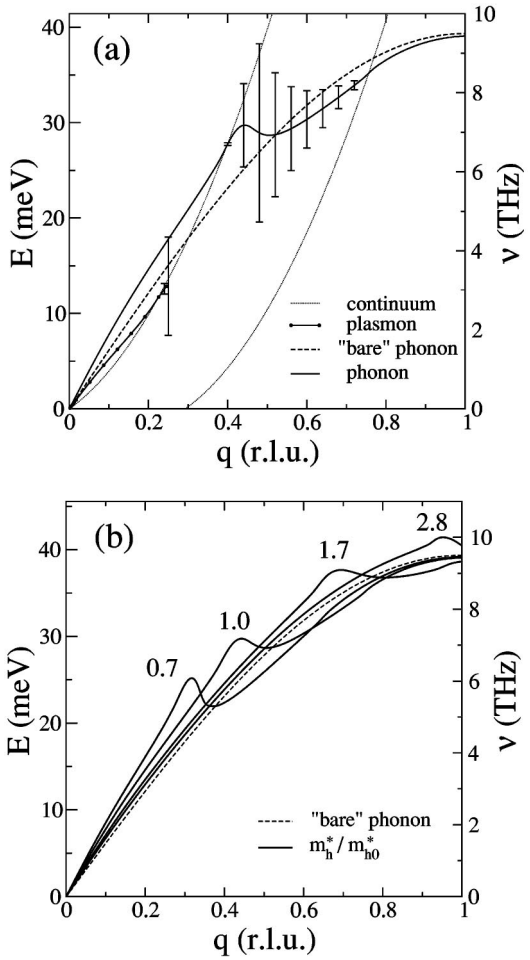

FIG. 2. (a) An example of the calculation of the anomaly given by the acoustical plasmon mechanism, as described in the text. (b) The anomaly as a function of the mass of the heavy particle.

assigned. As was the case with Nb, it is difficult to reconcile these parameter values with the published band structure calculations and this remains a serious drawback for the application of the acoustical plasmon concept to lattice dynamics.

Additional dispersion curves, obtained by changing the effective mass of the heavy particles over a limited range, are shown on Fig. 2(b). By varying other parameters, a wide variety of behavior can be obtained, which may be of interest for other materials.

We followed Fröhlich and Rothwarf a bit further by calculating T_c from a modified BCS-like expression, $kT_c = \hbar\omega_{pm}\exp(-1/F)$. Here ω_{pm} was taken to be the frequency at which the plasmon enters the heavy-hole continuum and F was calculated as described in Refs. 16 and 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,[18,19] 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

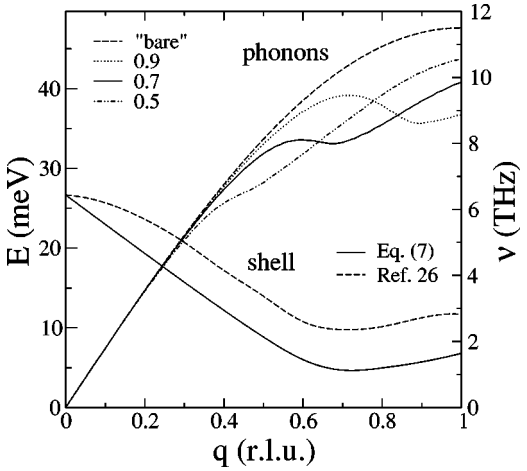

FIG. 3. Results for the resonant polarization mechanism as described in the text. The upper curves are for the phonon and the lower ones are for the supershell frequencies.

structure of this material leads to some resonancelike 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. (1), α^h, the polarizability of the heavy carriers, which gives rise to the acoustical plasmons, was replaced by a **q**-dependent polarization term α^{lh} ascribed here to interband transitions that were previously included in the constant ε^0. Here $\alpha^{lh}(q)$ was chosen to be a ''skewed Lorentzian'' of the form

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

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 in Fig. 3. We note that the importance of interband transitions has been emphasized in recent electronic structure calculations and particularly those of Refs. 20 and 24.

An interesting aspect of this calculation is that the q dependence of α^{lh} correlates closely with that of the ''supershell frequency'' $\omega_{ss}(q)$ in Weber's double-shell model.[10,11] Smith *et al.*[26] 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 ω_{ss} in this way from Eq. (7) and comparing it with the ω_{ss} ex-

tracted from Ref. 26 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. 24 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, linear muffin tin orbital (LMTO) approach. The calculations of Ref. 1, which show no anomaly, used a mixed basis pseudopotential method and DFT.[27] 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. 1, 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 **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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