INSTITUTE OF PHYSICS PUBLISHING SUPERCONDUCTOR SCIENCE AND TECHNOLOGY

Supercond. Sci. Technol. **16** (2003) 143–146 PII: S0953-2048(03)54516-X

The origin of phonon anharmonicity in MgB_2 and related compounds

L Boeri[1,2], G B Bachelet[1,2], E Cappelluti[1,2] and L Pietronero[1,2,3]

[1] INFM Center for Statistical Mechanics and Complexity and Dipartimento di Fisica, Università di Roma 'La Sapienza', Piazzale A. Moro 2, 00185 Roma, Italy
[2] INFM Unità di Roma 1 e Dipartimento di Fisica, Università di Roma I 'La Sapienza', Italy
[3] CNR, Istituto di Acustica 'O.M. Corbino', v. del Fosso del Cavaliere 100, 00133 Roma, Italy

E-mail: lilia@pil.phys.uniroma1.it

Received 9 October 2002
Published 30 December 2002
Online at stacks.iop.org/SUST/16/143

Abstract

The recent discovery of a superconducting transition at 39 K in MgB_2—made of alternating Mg and graphene-like B planes—has raised great interest, for both its technological and theoretical implications. It was clear since the very beginning that the properties of this material are related to an anomalous coupling between the charge carriers in the σ bands—due to in-plane bonds between Boron atoms—and the phonon mode (E_{2g}) which involves in-plane vibrations of the B ions. Theoretical studies have thus been focused on the search for possible anomalies in the e–ph coupling: one of the first results was the discovery that the E_{2g} phonon is highly anharmonic, but the connection between anharmonicity and T_c in this material is still a controversial point. We first present a detailed first-principles study of the E_{2g} phonon anharmonicity in MgB_2 and analogous compounds which are not superconducting, AlB_2 and graphite, and in a hypothetical hole-doped graphite $\left(C_2^{2+}\right)$; we then introduce an analytical model which allows us to relate the onset of anharmonicity with the small Fermi energy of the carriers in σ bands. Our study suggests a possible relation between anharmonicity and non-adiabaticity: non-adiabatic effects, which can lead to a sensible increase of T_c with respect to values predicted by conventional theory, become in fact relevant when phonon frequencies are comparable to electronic energy scales.

1. Introduction

The recent discovery of superconductivity with a T_c of 39 K in MgB_2 [1] has raised great interest in the study of metal-diboride compounds and similar layered systems, such as graphite and LiBC [2].

It is now widely accepted that superconductivity in these systems must be due to e–ph coupling; measurements indicate a strong isotope effect on T_c for Boron substitution [3]. However, the precise origin of such a remarkable critical temperature, higher than the theoretical upper bound of 25 K predicted by the standard Migdal–Eliashberg theory, is still not clear.

With this perspective it is important to investigate in detail the microscopic properties of these systems, in order to identify anomalous features in both vibrational and electronic spectra.

In the first part of this paper we present a detailed first-principles study of MgB_2 in comparison with similar materials, AlB_2, 2D graphite (C_2) and a hypothetical, hole-doped graphite, C_2^{2+}. From band-structure and frozen-phonon calculations, we identify the small Fermi energy of the conduction holes in the σ bands, together with a remarkable e–ph coupling, as being responsible for the strong anharmonicity of the E_{2g} phonon mode.

In the second section we present a simple analytical model which naturally underlines the relation between small Fermi energies and phonon anharmonicity.

In conclusion we discuss the possible implications of these findings on the superconducting properties of MgB_2 and analogous systems.

2. First-principles calculations

The local density functional [4] calculations presented in this section, based on Martins–Troullier pseudopotentials [5], were performed using the ABINIT code[4].

Band structures were computed at the experimental lattice parameters using an energy cut-off of 80 Ry; for **k**-space integration, which requires great care in these systems, we used two $15 \times 15 \times 10$ shifted Monkhorst–Pack grids in the full BZ.

2.1. Electronic properties

From the structural point of view, MgB_2 is very similar to graphite: its lattice is formed by graphene layers of B ions intercalated with planes of Mg atoms, sitting at the centre of each underlying hexagon; the alkali atoms are almost completely ionized and act as reservoirs of charge for the B planes, where conduction takes place. Mg sites can also be occupied by Al atoms: the main effect of this substitution is to dope the system with electrons. AlB_2 shares strong similarities with MgB_2, but it is not superconducting.

The electronic band structures of MgB_2, AlB_2 and C_2 present strong similarities: it is in fact possible to identify three mostly 2D σ bands, derived from (C)B s and $p_{x,y}$ orbitals, and two π bands (bonding and antibonding) derived from p_z-(Mg) orbitals. The main difference between MgB_2 and similar non-superconducting compounds is the position of the Fermi level (μ): in graphite and AlB_2 μ cuts the π band structure, well above the top of the σ bands $(\varepsilon_\sigma^{\rm top})$, which are then completely full. In MgB_2 μ happens to fall $\simeq$0.5 eV below the top of the σ bands, which thus give a sizable contribution to the Fermi surface [6].

From these observations it is easy to infer that the σ holes must play a primary role in superconductivity: further experimental evidences—Hall effect and dependency of T_c on doping—confirm this hypothesis.

For comparison with AlB_2 and MgB_2 we considered a model system, C_2^{2+}, consisting of a layer of graphite from which two electrons per cell are removed; the positive charge in excess is neutralized by adding a uniform negative background. C_2^{2+} is analogous to MgB_2, as μ is located $\sim$1 eV below the top of the σ bands.

2.2. Phonon properties

Isotope effect measurements indicate that the superconducting pairing is mainly due to phonon modes which involve only boron vibrations; at the Γ point there are three such modes, B_{1g} (out-of-plane), E_{2g}^a and E_{2g}^b (in-plane); these are also the three optical modes of 2D graphite.

It was shown in the literature both experimentally and theoretically [7, 8], that the E_{2g} mode experiences an extremely strong coupling with the σ bands. Frozen-phonon calculations show that in MgB_2 this mode exhibits a strong anharmonic character, as pointed out by Yildirim *et al* [9]. Under typical phonon displacements the σ bands at the Γ point undergo a very large splitting, which is the signature of a strong e–ph coupling: since the Fermi energy of the holes is very small, in this process one of the two σ bands is driven completely below the Fermi energy [10].

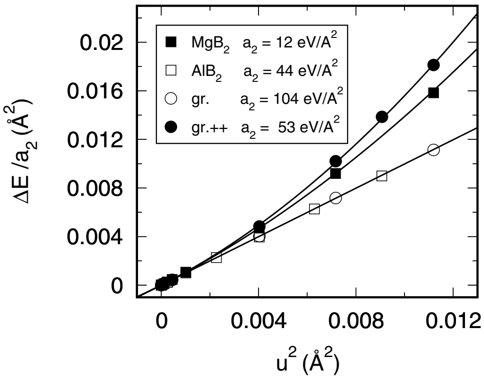

Figure 1. Energy ΔE for an E_{2g} phonon plotted as a function of u^2. The energy of each material is divided by a_2, the quadratic coefficient of a polynomial best-fit expansion of $\Delta E(u)$, so that harmonic phonons collapse on a single straight line corresponding to $y = x$. The solid lines are obtained fitting the data with our model (equation (2)); the corresponding parameters are shown in table 1.

Table 1. Input parameters for our analytical model—see equation (2)—, extracted from LDA data. N_σ and N_π were used as adjustable parameters: despite the extremely simplified DOS chosen, we obtained physically reasonable values, i.e. ($N_\sigma = 0.11$ st eV^{-1}, $N_\pi = 0.39$ st eV^{-1} for MgB_2; $N_\sigma = 0.07$ st eV^{-1}, $N_\pi = 0.30$ st eV^{-1} for C_2^{2+}).

	g (eV Å^{-1})	$\epsilon_\sigma^{\rm top}$ (eV)	a_2 (eV Å^{-2})
MgB_2	12.02	0.45	12
AlB_2	11.74	−1.63	44
gr.	28.29	−2.89	104
gr.++	30.86	1.17	53

We performed E_{2g} frozen-phonon calculations for MgB_2, AlB_2, C_2 and C_2^{2+} with distortions up to 0.1 Å. In AlB_2 and C_2 the E_{2g} phonon is perfectly harmonic up to distortions of 0.1 Å, while in MgB_2 and C_2^{2+} it is strongly anharmonic. Our results are summarized in figure 1.

We also calculated the effect of a phonon displacement on the band structure and observed that in all these systems the σ bands undergo splittings which are comparable with (AlB_2) or even larger than (C_2, C_2^{2+}) those of MgB_2; the main difference is that when the phonon is harmonic, the σ bands remain well below the Fermi level upon distortion (see figure 2). In contrast C_2^{2+}, where the Fermi energy is close to the top of the σ bands, we find a strongly anharmonic E_{2g} phonon.

3. The model

Our calculations suggest that the smallness of the Fermi energy, the large deformation potential and the anharmonic character of the E_{2g} phonon mode are strictly connected. This relation can be further investigated with a simple analytical model: the band structure of the system around the Fermi level can be schematized by two degenerate 2D σ bands, which extend up to an energy $\varepsilon_\sigma^{\rm top}$, and a π band which extends well

[4] The ABINIT code is a common project of the Université Catholique de Louvain, Corning Incorporated, and other contributors (URL http://www.pcpm.ucl.ac.be/abinit).

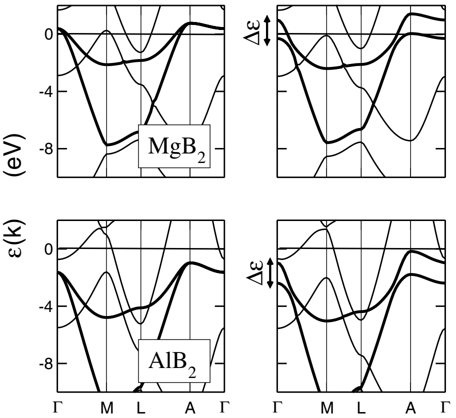

Figure 2. Band structures of MgB_2 (top) and AlB_2 (bottom), computed for the undistorted structure (left), and for an E_{2g} distortion of ∼0.1 Å (right).

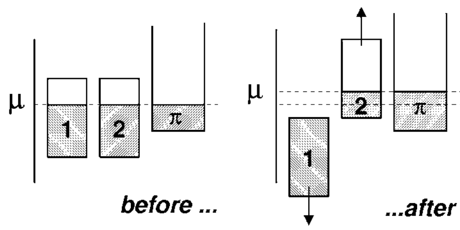

Figure 3. Schematic representation of the band structure of MgB_2 when the system undergoes large distortion: one of the σ bands is completely full, and the Fermi energy μ has to shift to keep the number of particles fixed.

beyond the Fermi level. The corresponding densities of states are $N_\sigma(\varepsilon) = N_\sigma, -W_\sigma \leqslant \varepsilon \leqslant \varepsilon_\sigma^{\mathrm{top}}, N_\pi(\varepsilon) = N_\pi - W_\pi \leqslant \varepsilon < +\infty$. The total energy of the undistorted system reads

$$E(u=0) = 2\sum_{\mathbf{k},i} n_i(\mathbf{k})\varepsilon_i(\mathbf{k}) + \sum_{\mathbf{k}} n_\pi(\mathbf{k}), \varepsilon_\pi(\mathbf{k}) \qquad (1)$$

where $\varepsilon_i(\mathbf{k})$ and $\varepsilon_\pi(\mathbf{k})$ represent the energy dispersion of the two σ and π bands respectively, and $n_i(\mathbf{k})$ and $n_\pi(\mathbf{k})$ represent the corresponding occupations; the factor 2 is for spin degeneracy. The LDA calculations show that the main effect of the lattice displacement is an almost linear splitting of the two σ bands in opposite directions, while the other bands remain substantially unchanged: this can be accounted for introducing a Jahn–Teller-like term in the total energy of the system, which can then be written as

$$E(u \neq 0) = 2\sum_{\mathbf{k},i} n_i(\mathbf{k},u)\varepsilon_i(\mathbf{k}) + \sum_{\mathbf{k},\pi} n_\pi(\mathbf{k},u)\varepsilon_\pi(\mathbf{k}) + 2gu\sum_{\mathbf{k}}[n_2(\mathbf{k},u) - n_1(\mathbf{k},u)] + \frac{M\omega_{2g}^2}{2}u^2. \qquad (2)$$

The first two terms on the right-hand side of equation (2) represent the band contribution to the total energy due to the u-dependent occupation of σ and π bands; the third term accounts for the Jahn–Teller coupling of E_{2g} phonon to the σ bands. The last term is an effective elastic energy, which includes ion–ion repulsive energy and the electronic contributions not explicitly included in our model bands.

The occupation numbers $n(\mathbf{k})$ appearing in equation (2) can be self-consistently calculated: $n_1(\mathbf{k},u) = f[\epsilon_1(\mathbf{k}) - gu - \mu(u)]$, $n_2(\mathbf{k},u) = f[\epsilon_2(\mathbf{k}) + gu - \mu(u)]$ and $n_\pi(\mathbf{k},u) = f[\epsilon_\pi(\mathbf{k}) - \mu(u)]$, where $\mu(u)$ is the Fermi energy at a phonon displacement u, and $f[x] = \theta(-x)$ is the Fermi function at zero temperature.

The Fermi energy $\mu(u)$ is obtained by imposing that the total number of particles is conserved upon distortion; it is then easy to obtain $E(u)$ from equation (2).

The model predicts two different regimes, depending on the values of the parameters g and $\varepsilon_\sigma^{\mathrm{top}}$:(a) $g|u| \leqslant \varepsilon_\sigma^{\mathrm{top}}$ and (b) $g|u| \geqslant \varepsilon_\sigma^{\mathrm{top}}$.

In case (a) the overall amount of spectral weight in the two σ bands is left unchanged by the phonon displacement, and the position of the Fermi level is not modified $\mu(u) = \mu(0)$. The total energy in this case is given by

$$E(u) = E(0) + \frac{M\omega_{2g}^2}{2}u^2 - 2N_\sigma g^2 u^2 \qquad (3)$$

i.e. our model gives the standard e–ph frequency renormalization.

In case (b) one of the two σ sub-bands becomes completely full upon distortion, so that it can no longer compensate for the loss of spectral weight in the other sub-band; the chemical potential has to shift so that the total number of particles is conserved (see figure 3):

$$\mu(u) = \frac{N_\sigma}{N_\sigma + N_\pi}\left(g|u| - \varepsilon_\sigma^{\mathrm{top}}\right). \qquad (4)$$

The expression of the total energy acquires an additional term:

$$E(u) = E(0) + \frac{M\omega_{2g}^2}{2}u^2 - 2N_\sigma g^2 u^2 + \frac{N_\sigma(2N_\sigma + N_\pi)}{N_\sigma + N_\pi}\left(g|u| - \varepsilon_\sigma^{\mathrm{top}}\right)^2. \qquad (5)$$

Our model predicts a sharp transition between harmonic and anharmonic behaviour when the distortion is large enough to drive one of the σ bands below the Fermi energy: this is the case of MgB_2 and C_2^{2+}. The non-analytic behaviour of the anharmonic term is due to the extreme simplifications of the model, in particular due to our completely flat DOS; choosing a more realistic DOS the transition is smoothed. Despite its simplicity, the agreement between our model and LDA calculations is extremely good: equations (3) and (5) can in fact be used to fit LDA data, with N_σ and N_π as adjustable parameters, while g, $\varepsilon_\sigma^{\mathrm{top}}$ and a_2 are extracted from the calculations. The results are shown in figure 2.

4. Conclusions

We have shown that the anharmonicity of the E_{2g} phonon in MgB_2 is strongly related to the small value of the Fermi energy of the charge carriers contained in the σ bands. We have also proved that a strong anharmonicity is not a unique feature of MgB_2, but it has to be expected in any system in which large e–ph coupling and small Fermi energies coexist.

In these kind of systems Migdal's theorem, on which the standard Migdal–Eliashberg superconductivity theory rests, is broken, and non-adiabatic effects come into play. A quantitative description of this regime, which can be found elsewhere [11], requires the use of quantum field theory techniques, and has been applied to fullerenes and other high-T_c superconductors [12–14].

Our main conclusion is that anharmonicity is a clear signature of an anomalous regime in which phonon and electronic energy scales become comparable and the standard ME theory cannot be safely applied; further investigation in this sense could lead to further insight into the mechanism of superconductivity in MgB_2 and similar compounds.

In this sense, our results [15] also suggest that hole-doped graphite could be an interesting system to look at for superconductivity: this is in agreement with the recently measured T_c of 35 K in graphite–sulfur [16] composite structures.

References

[1] Nagamatsu J *et al* 2001 *Nature* **410** 63
[2] Rosner H *et al* 2002 *Phys. Rev. Lett.* **88** 127001
[3] Hinks D G *et al* 2001 *Nature* **411** 457
[4] Hohenberg P and Kohn W 1964 *Phys. Rev.* **136** B864
Kohn W and Sham L J 1965 *Phys. Rev.* **140** A1133
[5] Troullier N and Martins J L 1991 *Phys. Rev.* B **43** 1993
[6] Kortus J *et al* 2001 *Phys. Rev. Lett.* **86** 4656
[7] Bohnen K-P, Heid R and Renker B 2001 *Phys. Rev. Lett.* **86** 5771
[8] Kong Y *et al* 2001 *Phys. Rev.* B **64** 020501
[9] Yildirim T *et al* 2001 *Phys. Rev. Lett.* **87** 037001
[10] An J M and Pickett W E 2001 *Phys. Rev. Lett.* **86** 4366
[11] Cappelluti E *et al* 2002 *Phys. Rev. Lett.* **88** 117003
[12] Pietronero L *et al* 1995 *Phys. Rev.* B **52** 10516
[13] Grimaldi C *et al* 1995 *Phys. Rev.* B **52** 10530
[14] Cappelluti E *et al* 2000 *Phys. Rev. Lett.* **85** 4771
[15] Boeri L *et al* 2002 *Phys. Rev.* B **65** 214501
[16] da Silva R Ricardo *et al* 2001 *Phys. Rev. Lett.* **87** 147001