Phonon dispersion and electron-phonon coupling in MgB$_2$ and AlB$_2$

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Abstract

We present a first principles investigation of the lattice dynamics and electron-phonon coupling of the superconductor MgB$_2$ and the isostructural AlB$_2$ within the framework of density functional perturbation theory using a mixed-basis pseudopotential method. Complete phonon dispersion curves and Eliashberg functions $\alpha^2F$ are calculated for both systems. We also report on Raman measurements, which support the theoretical findings. The calculated generalized density-of-states for MgB$_2$ is in excellent agreement with recent neutron-scattering experiments. The main differences in the calculated phonon spectra and $\alpha^2F$ are related to high frequency in-plane boron vibrations. As compared to AlB$_2$, they are strongly softened in MgB$_2$ and exhibit an exceptionally strong coupling to electronic states at the Fermi energy. The total coupling constants are $\lambda_{\text{MgB}_2} = 0.73$ and $\lambda_{\text{AlB}_2} = 0.43$. Implications for the superconducting transition temperature are briefly discussed.
Recently superconductivity has been observed in MgB$_2$ with an exceptionally high transition temperature for such a simple compound ($T_c \sim 39$ K) \cite{1}. This system has in the mean time received a lot of attention from many experimentalists as well as theorists since understanding superconductivity in this binary compound should be much easier than in the high-$T_c$ cuprate materials studied extensively for more than ten years now. This is due to the simpler lattice structure and the missing complication due to magnetism and strong electron-electron correlations. Already early experiments \cite{2-7} as well as theories \cite{8,9} have suggested that we are dealing here with an s-wave superconductor based on strong electron-phonon coupling although alternative coupling mechanisms have been discussed too \cite{10,11}.

Modern band-structure calculations together with ab initio determination of the phonon dispersion, electron-phonon coupling and solution of the Eliashberg equations to calculate the transition temperature should be the way to help understand the role played by the electron-phonon coupling in this material. Although during the past six weeks many contributions have been published concerning the electronic bandstructure \cite{8,9,12} only a few attempts have been made to proceed along the above mentioned roadmap to a deeper understanding of the electron-phonon coupling. Most investigations are restricted to calculations of the phonon modes for the $\Gamma$-point only \cite{2,13}. Estimates of the coupling strength are therefore not very accurate thus asking for a more complete treatment of the electron-phonon coupling in the whole Brillouin zone (BZ).

We have carried out such a systematic study of the lattice dynamics and the electron-phonon coupling using the mixed-basis pseudopotential method. To get a better understanding of the relevance of the electron-phonon mechanism we have studied two isostructural systems: MgB$_2$, which is superconducting, and AlB$_2$, for which no superconductivity has been found so far. This offers the possibility to compare the phonon dispersion curves to identify those which are strongly influenced by electron-phonon coupling even without calculating the coupling strength. Furthermore, the calculation of the Eliashberg function $\alpha^2F$ for both systems allows for a consistency check of the proposed phonon-mediated pairing mechanism.
Only very recently after completion of our study we became aware of a similar investigation by Y. Kong et al. [14] which calculated the full phonon dispersion, the electron-phonon coupling and $T_c$ for MgB$_2$ within the LMTO-method. Our calculations are very similar to those presented in Ref. [14], however, due to the parallel treatment of MgB$_2$ and AlB$_2$ they offer additional information.

In contrast to all other calculations presented so far we have structurally optimized both systems, thus we remain fully in the framework set by the theory. For comparison and checks of sensitivity of our results we have also studied certain phonon modes using the experimental structure. All our calculations are carried out using the mixed-basis pseudopotential method. For Mg and Al we have used well tested pseudopotentials of Martins-Trouillier-[15] and BHS type [16]. The boron pseudopotential was constructed according to the Vanderbild description [17] which led to a fairly deep p-potential for the boron atom which however could be dealt with very efficiently due to the mixed-basis formulation. The wave functions were constructed from localized s and p functions at the Boron sites supplemented by plane waves with an energy cut off of 16 Ry. Detailed tests were carried out to assure convergence with respect to the number of plane waves as well as with respect to k-point sampling [18]. Different Monkhorst-Pack k-point sets have been used up to 13824 k-points in the BZ together with a Gaussian smearing of 0.2 eV. The calculation of the phonon dispersion is based on a recently developed mixed-basis perturbation approach [19] which also allowed for the calculation of the electron-phonon coupling [20]. Finally, estimates of $T_c$ are obtained by solving the linearized form of the Eliashberg equations [21]. Structural parameters were found to be fairly insensitive to the k-point sets while individual phonon modes were very sensitive to the sampling thus pointing to strong electron-phonon coupling. All our calculations were carried out using the local exchange-correlation potential of Hedin and Lundqvist [22].

Since both systems crystallize in the so-called "AlB$_2$ structure" with alternating hexagonal (Mg,Al)-layers and graphite-like B-layers structural optimization required optimization of volume V and c/a ratio. Table 1 gives calculated results for V and c/a as well as the
bulk modulus $B$ together with the experimental values. For both systems a slightly smaller volume has been found by the theoretical treatment compared to the experimental one. This is a typical behavior in LDA-calculations. The $c/a$ ratio is slightly larger. The electronic bandstructure obtained for MgB$_2$ is very similar to the ones obtained by other groups with hole pockets around the $\Gamma$-point extending along the $\Gamma$-$A$-direction. AlB$_2$ has a very similar bandstructure, however, due to the additional electron density no hole pockets around $\Gamma$ and the $\Gamma$-$A$-direction exist.

In Table 2 we have summarized our phonon results for the $\Gamma$-point obtained from calculations based on the experimental structure as well as on the optimized one. With the exception of the $E_{2g}$-mode (in-plane boron mode) all other modes are fairly insensitive to structural changes as can be seen from Table 2. The same holds also true for the sensitivity with respect to $k$-point sets. All previous calculations of the $\Gamma$-point phonon modes for MgB$_2$ agree very well with these results with the exception of the $E_{2g}$-mode where shifts of $\pm 100$ cm$^{-1}$ have been observed. As extensive studies have shown, this is mostly an effect of $k$-point sampling and indicates strong electron-phonon coupling for this mode. Comparing these results with those obtained for AlB$_2$ the most dramatic changes occur again for the $E_{2g}$ mode which stiffens substantially and becomes the highest one, and the $B_{1g}$ mode (out of plane boron mode) which is strongly softened.

We have measured the $E_{2g}$ mode by Raman scattering from samples of commercially available MgB$_2$ and AlB$_2$ powders. The samples showed clear x-ray diffraction patterns and consisted of crystalline grains up to 10 $\mu$m (MgB$_2$) and 50 $\mu$m (AlB$_2$). Measured spectra showed only one prominent line in agreement with space group P6/mmm and were not particularly polarization dependent. Typical results are presented in Fig. 1. The experimental result for AlB$_2$ is in almost perfect agreement with the calculated one. For MgB$_2$ the Raman line is very broad, however, the peak position agrees reasonably well with the calculated one while the linewidth is likely to be due to strong electron-phonon coupling (see discussion below).

Having studied carefully the $\Gamma$-point modes we calculated also the full phonon dispersion
for both systems. Results are presented in Fig. 2 which were obtained by determining the
dynamical matrix on a (6,6,6) reciprocal lattice grid in the hexagonal Brillouin zone. The
results for MgB$_2$ agree very well with those of Ref. [14] and give thus additional credibility
to the theoretical treatment.

Comparing the phonon density-of-states shown in Fig. 2 certain features are worth men-
tioning. The biggest difference between the two systems is showing up in the intermediate
region of phonon frequencies where AlB$_2$ shows nearly a gap due to the strong dispersion of
the relevant modes while for MgB$_2$ this gap has nearly completely disappeared. High density
of states at the upper and lower end of the frequency range show up in both systems. To
compare with recent measurements by inelastic neutron scattering [24] we have calculated
also the generalized density-of-states (weighted by the inelastic scattering cross section and
the mass) broadened by a Gaussian with a width of 4 meV. The result in Fig. 3 should be
compared directly with Fig. 1 in Ref. [24]. An almost perfect agreement with respect to
peak positions, shoulders and even with the relative ratio of contributions is obvious. We
don’t find any indication of a peak in the spectra near 17 meV, as observed by Sato et al.
[25].

In the dispersion curves shown in Fig. 2, the layered structure of the crystals is reflected
in a weak dispersion of the optical branches along Γ-A and in an anisotropy in the slopes
of the acoustic branches in agreement with experiments [26]. Besides many similarities two
very significant differences between AlB$_2$ and MgB$_2$ can be seen. The first one is related
to the branches which evolve from the doubly degenerate E$_{2g}$-mode at the Γ-point. In MgB$_2$,
these branches are strongly renormalized towards lower frequencies mostly near Γ and along
the Γ-A direction. This is probably related to the hole pockets found in the electronic
bandstructure of MgB$_2$ which are absent in AlB$_2$. The second distinctive difference is the
behavior of branches starting from the B$_{1g}$-mode which in MgB$_2$ are significantly harder in
certain regions of the BZ than in AlB$_2$.

To address the superconducting properties we have calculated the so-called Eliashberg
function $\alpha^2F(\omega)$, using a very fine (36,36,36) k-point grid in performing the Fermi-surface
average of the electron-phonon matrix elements \[27\]. Results are presented in Fig. 4. For MgB\(_2\) we find indeed a very large contribution to \(\alpha^2 F\) in the intermediate region between 60 and 70 meV, which is mainly due to strongly softened in-plane vibrations of the boron atoms as mentioned above. At \(\Gamma\), for the \(E_{2g}\)-mode this strong coupling results in a very large linewidth of 15 meV in accordance with the broad feature seen in the Raman spectrum (Fig. 1). For AlB\(_2\), in contrast, the biggest contributions show up at very high frequencies as well as in the regime of the acoustic modes, however, they are substantially smaller than the main contribution in MgB\(_2\). From the Eliashberg function we calculate the electron-phonon coupling constant

\[
\lambda = 2 \int_0^\infty d\omega \frac{\alpha^2 F(\omega)}{\omega}
\]

which gives \(\lambda_{\text{MgB}_2} = 0.73\) and \(\lambda_{\text{AlB}_2} = 0.43\). For the logarithmically averaged phonon frequencies as defined in Ref. \[14\] we find 60.9 meV and 49.9 meV for MgB\(_2\) and AlB\(_2\), respectively. The values for MgB\(_2\) agree well with the results of Ref. \[14\]. The fairly large value of \(\lambda\) for AlB\(_2\) however is unexpected.

Within the dirty limit of superconductivity \[28\] the calculation of the transition temperature \(T_c\) requires the knowledge of \(\alpha^2 F\) and the Coulomb pseudopotential \(\mu^*\) \[21\]. As commonly done, we treat \(\mu^*\) as an adjustable parameter. A \(T_c\) of 40 K for MgB\(_2\) is obtained for \(\mu^* = 0.05\). The same \(\mu^*\)-value leads to \(T_c \sim 9\) K for the system AlB\(_2\). This result is in contrast to the experimental situation where no superconductivity has been found so far for AlB\(_2\). There are basically two possibilities to reconcile the theoretical results with the experimental situation. One possibility is a different screening in AlB\(_2\) compared to MgB\(_2\) which has been speculated about in Ref. \[29\], leading to different values for \(\mu^*\). Alternatively, the approximation of an isotropic superconductor (dirty limit) might not hold. Due to the fact that we have dealt with both systems on equal footing new questions have emerged which need further studies.

We have presented here first principles calculations of the phonon dispersion and electron-phonon coupling for two systems MgB\(_2\) and AlB\(_2\) which crystallize in the same lattice struc-
ture, however, which have fairly different phonon dispersion curves. These results are in excellent agreement with measured quantities. The calculation of the superconducting temperature, however, has a problem which might be due to approximations involved or due to the fairly restricted knowledge about the Coulomb pseudopotential $\mu^*$. 

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TABLES

TABLE I. Structural parameters of the optimized geometries. Experimental values (in brackets) are taken from Refs. [30,26].

|           | V (Å³)       | c/a          | B (Mbar) |
|-----------|--------------|--------------|----------|
| MgB₂      | 28.481 (29.010) | 1.153 (1.142) | 1.47 (1.20) |
| AlB₂      | 24.617 (25.578) | 1.09 (1.084)  | 1.84     |

TABLE II. Comparison of the calculated Γ-point phonon frequencies for the experimental (I) and optimized (II) geometries. Values are given in meV (cm⁻¹).

| Mode | MgB₂ | AlB₂ |
|------|------|------|
|      | I    | II   | I    | II   |
| E₁u  | 39.9 (322) | 40.5 (327) | 33.0 (266) | 36.6 (295) |
| A₂u  | 48.9 (394) | 50.2 (405) | 48.6 (392) | 52.1 (420) |
| E₂g  | 66.5 (536) | 70.8 (571) | 118.3 (954) | 125.0 (1008) |
| B₁g  | 86.3 (696) | 87.0 (702) | 59.9 (483) | 61.3 (494) |
FIGURES

FIG. 1. Micro-Raman spectra obtained from polycrystalline grains of MgB$_2$ and AlB$_2$ at room temperature ($\lambda = 514.5$ nm)

FIG. 2. Theoretical phonon dispersion curves along high-symmetry lines of the hexagonal BZ (notation after [31]) and density-of-states (DOS) of MgB$_2$ and AlB$_2$. Dots represent actually calculated modes, lines are obtained by Fourier interpolation.

FIG. 3. Calculated generalized phonon density-of-states of MgB$_2$. Values for the incoherent scattering cross sections are taken from Ref. [24].

FIG. 4. Calculated Eliashberg functions $\alpha^2 F(\omega)$ for MgB$_2$ and AlB$_2$. 
Raman intensity (arbitrary units)
