Effect of Al doping on the optical phonon spectrum in Mg$_{1-x}$Al$_x$B$_2$

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Raman and infrared absorption spectra of Mg$_{1-x}$Al$_x$B$_2$ have been collected for 0 ≤ x ≤ 0.5 in the spectral range of optical phonons. The x-dependence of the peak frequency, the width and the intensity of the observed Raman lines has been carefully analyzed. A peculiar x-dependence of the optical modes is pointed out for two different Al doping ranges. In particular the onset of the high-doping structural phase previously observed in diffraction measurements is marked by the appearance of new spectral components at high frequencies. A connection between the whole of our results and the observed suppression of superconductivity in the high doping region is established.

The recent discovery of superconductivity below 39 K in MgB$_2$ has stimulated a great deal of effort among the scientific community and a large number of theoretical and experimental papers have been published within few months. The debate on the origin of this unexpected superconductivity is still open, although both experimental and theoretical works indicate that MgB$_2$ is a BCS-like system. In this framework, the obvious relevant interaction in the superconducting transition is the electron-phonon (e-ph) coupling. Owing to the simple hexagonal structure (space group P6$_{3}$$\overline{m}$mm), four zone-center optical modes are predicted for MgB$_2$: a silent B$_{1g}$ mode, the E$_{2g}$, A$_{2g}$ modes, and the infrared active E$_{2u}$ and A$_{2u}$ modes. While the doubly-degenerate E$_{2u}$ and E$_{2g}$ modes are ascribed to in-plane stretching modes of the boron atoms, both non-degenerate A$_{2u}$ and B$_{1g}$ modes involve vibrations along the perpendicular direction (c axis). It is quite a general statement that the E$_{2g}$ mode is expected to allow for the strongest e-ph coupling, and then to play a relevant role in superconductivity. Raman experiments carried out on MgB$_2$ have shown that the spectrum is dominated by a quite large and asymmetric band around 600 cm$^{-1}$, ascribed to the E$_{2g}$ mode. The anomalous width of this phonon peak has been interpreted as a signature of the e-ph coupling.

Up to now, no other isostructural boride (XB$_2$) has shown the peculiar high temperature superconductivity of MgB$_2$. In particular, MgAl$_2$ is not superconducting. Indeed, several studies on the Mg$_{1-x}$Al$_x$B$_2$ compounds have shown that superconductivity is progressively suppressed for increasing x and vanishes for x>0.5. In order to achieve a deeper understanding of the effects of Al doping, we have studied the evolution of the phonon spectrum of Mg$_{1-x}$Al$_x$B$_2$ in the 0 ≤ x ≤ 0.5 range by means of both Raman and infrared spectroscopy.

Pure MgB$_2$ and Al doped polycrystalline samples have been synthesized at high temperature by direct reaction of the elements in a tantalum crucible under argon atmosphere. The samples, which show an average grain dimension around 1-2μm, have been characterized by x-ray diffraction and by resistivity measurements, in order to determine, in particular, the x-dependence of the superconductivity transition temperature Tc.

The Raman spectra were measured in back-scattering geometry, using a micro-Raman spectrometer with a CCD detector and an adjustable notch filter. The sample was excited by the 632.8 nm line of a 16 mW He-Ne Laser. The confocal microscope was equipped with a 20X magnification objective which gives a laser spot about 10 μm$^2$ wide at the sample surface. The Raman shift explored ranges between 200 and 1100 cm$^{-1}$, the low frequency limit being due to the notch filter cutoff. Since the laser spot impinges on a few sample grains, the relative intensities of the observed spectral features were slightly different from point to point, depending on the random orientation of the grains. For each sample, Raman spectra were thus collected from different points and then averaged.

As shown in Fig. 1a, the spectrum of the undoped MgB$_2$ sample is dominated by a band centered around 600 cm$^{-1}$, in agreement with previous Raman experiments reporting a band centered between 580 and 630 cm$^{-1}$, characterized by a large width (200-300 cm$^{-1}$) and a relevant asymmetric shape. A close inspection of the MgB$_2$ spectrum of Fig. 1a reveals two weak shoulders on the low- and the high-frequency side of the 600 cm$^{-1}$ band ($\nu_2$), around 400 ($\nu_1$) and 750 cm$^{-1}$ ($\nu_1$), respectively. Although the origin of the central $\nu_2$ band is still questioned, it is generally assigned to the Raman-active mode E$_{2g}$, to which theoretical predictions attribute a peak frequency $\nu_2$ ranging from 470 to 660 cm$^{-1}$. It is worth noticing that further spectral contributions observed in previous Raman experiments have been ascribed to peaks in the phonon density of states (around 430, 620, 710 and 780 cm$^{-1}$) derived from neutron scattering experiments in a disordered or defective system, the momentum selection rules can indeed be violated, and the Raman (or infrared absorption) spectrum can reflect the phonon density of states.

The Raman spectrum was fitted by a combination of
three contributions, each described by a Damped Harmonic Oscillator (DHO), since this profile has been successfully used in modelling broad phonon line-shapes in strongly correlated systems. The complete fitting function here used is:

\[
S(\nu) = \left[1 + n(\nu)\right] \frac{A_i \nu \Gamma_i}{\nu^2 + \Gamma_i^2} + \sum_{i=1}^{N} \frac{A_i \nu \Gamma_i}{(\nu^2 - \nu_i^2)^2 + \nu^2 \Gamma_i^2}
\]

(1)

The first term represents a large DHO function centered at \(\nu=0\). It takes into account the wide unstructured background, which is a common feature of strongly correlated systems such as manganites and cuprates. The second term accounts for \(N\) phonon peaks, where \(\nu_i\), \(A_i\), and \(\Gamma_i\) are their peak frequency, amplitude and linewidth, respectively. The quantity \(n(\nu)\) is the Bose-Einstein thermal population factor. In Fig. 1a we report the best fit spectrum, the \(\nu_1\), \(\nu_2\), and \(\nu_3\) components, and the tail of the background centered at \(\nu=0\). As discussed above, the \(\nu_2\) peak (centered at 605±10 cm\(^{-1}\)) can be ascribed to the \(E_g\) mode, while the \(\nu_1\) (at 415±20 cm\(^{-1}\)) and \(\nu_3\) (at 780±30 cm\(^{-1}\)) peaks probably reflect optical bands in the phonon density of states.

The spectra of the doped Mg\(_{1-x}\)Al\(_x\)B\(_2\) samples are well reproduced by using Eq. (1) if, for \(x>0.2\), the phonon number \(N\) is increased from 3 to 4. In Fig. 1b we report the Raman spectra for different Al doping after background subtraction. The \(\nu_3\) contribution becomes well detectable in the \(x=0.08\) spectrum. Both its intensity and peak frequency increase on further increasing \(x\). For \(x>0.1\), a new component \((\nu_4)\) appears around 850 cm\(^{-1}\) and, for \(x>0.25\), the \(\nu_3\) and \(\nu_4\) peaks become the dominant contributions to the Raman spectrum. It is interesting to note that the spectrum at \(x=0.5\) resembles that of the end-series compound (AlB\(_2\)), which is dominated by an intense and narrow peak centered around 980 cm\(^{-1}\).

Infrared absorption measurements were performed above 400 cm\(^{-1}\) by using a Bomem MB100 interferometer operating with a resolution of 10 cm\(^{-1}\). Following a standard procedure, we measured the infrared signals transmitted by a pure CsI pellet \((I_o(\nu))\) and by the sample powder dispersed in a CsI pellet \((I(\nu))\). The optical density \(O_d(\nu) = \ln(I_o(\nu)/I(\nu))\) is proportional to the optical conductivity of the sample and thus provides the spectral shape of the sample absorption. When this procedure is employed for measuring a powder metallic sample, the phonon spectrum is strongly reduced in intensity by the screening from free charges, and superimposed to a broad and intense background (see for example the case of metallic La\(_{2-x}\)Sr\(_x\)CuO\(_4\) powder). The far infrared \(O_d(\nu)\) of the measured Mg\(_{1-x}\)Al\(_x\)B\(_2\) are affected by intense backgrounds (see for example the MgB\(_2\) case in Fig. 2a), which prevent reliable fits of the spectra. However, once the background is subtracted, one obtains a clear picture of the effect of Al doping on the far infrared spectrum of Mg\(_{1-x}\)Al\(_x\)B\(_2\), as shown in Fig. 2b. The x=0 spectrum (see Fig. 2b) can be described by considering a broad peak centered around 460 cm\(^{-1}\), accompanied by a very broad band around 600 cm\(^{-1}\). Since the infrared active \(E_{1g}\) and \(A_{1g}\) phonons are predicted around 330 and 400 cm\(^{-1}\), the two observed bands might be ascribed to peaks in the phonon density of states, which become infrared active due to disorder, as noted above. Our MgB\(_2\) spectrum is qualitatively in agreement with that previously reported, where a broad peak centered around 480 cm\(^{-1}\) is accompanied by further components at higher frequencies. Our data (see Fig. 2b) show that the 460 cm\(^{-1}\) peak becomes more evident with increasing the Al content. For \(x>0.17\) a new absorption peak appears around 700 cm\(^{-1}\) and strongly increases with further increasing doping. Both Raman and infrared spectra thus give evidence that the Al doping induces substantial modifications of the MgB\(_2\) optical properties in the high-doping region. In particular, the appearance of new high-frequency contributions at high doping indicates remarkable structural changes.

A quantitative description of the Al doping effects can be achieved by analyzing the best-fit parameters of the Raman spectra. The \(\nu_1\) peak does not significantly vary with doping, its peak frequency and width being almost constant in the 0-0.5 \(x\) range \((\nu_1 \approx 415\) cm\(^{-1}\), \(\Gamma_1 \approx 100\) cm\(^{-1}\)). More interesting information can be extracted from the \(x\) dependence of the peaks at higher frequencies. In Fig. 3 we report the best fit parameters \(\nu_i\) and \(\Gamma_i\) \((i=2, 3, 4)\) as a function of \(x\). In discussing these results, we stress that two different structural phases have been observed in x-ray diffraction measurements: a low-doping (LD) phase in the \(0<x<0.10\) range and a high-doping (HD) phase in the \(x>0.25\) range. The two phases are structurally incompatible and a two phase region \(\text{LD + HD}\) at intermediate \(x\) \((0.10<x<0.25)\) has been proposed. Novel diffraction studies confirm a structural change around \(x=0.16\) and transmission-electron-microscopy observations revealed for \(x>0.10\) the existence of a superstructure, with doubled lattice constant along the \(c\)-axis. The existence of three major ordered phases for \(x<0.10\), at \(x=0.30\) and at \(x=0.50\), and an overall disordered phase for \(0.10<x<0.30\) have also been suggested.

As shown in Fig. 3a, where vertical lines at \(x=0.10\) and at \(x=0.25\) separate the three regions, \(\nu_2\) and \(\nu_3\) are nearly constant in the stable LD region, which is structurally characterized by small variations of the lattice parameters. The onset of the HD phase in the intermediate-x-region is marked by the appearance of the new spectral feature \((\nu_4)\). When the system enters in the pure HD phase, \(\nu_3\) and \(\nu_4\) strongly increase with \(x\), while \(\nu_2\) remains nearly constant. The latter result is well consistent with the assignment of the \(\nu_2\) peak to the in-plane \(E_{2g}\) stretching mode of the boron atoms, since the \(a\) (in-plane) lattice parameter do not significantly vary with \(x\). At the moment, our results do not allow a complete assignment of the observed Raman lines, possible through a polarization analysis of Raman
spectra from high-quality single crystals. We just note that the increase of the $\nu_3$ and $\nu_4$ values, simultaneous to the remarkable compression of the c (out-of-plane) lattice parameter, when x increases in the HD phase, suggests that the $\nu_3$ and $\nu_4$ peaks could be ascribed to out-of-plane vibrations.

As concerning the widths $\Gamma_i$ reported in Fig.3b, their values are affected by large errors in the LD phase owing to the nearly unstructured Raman spectra (see Fig.1). Bearing in mind the importance of the e-ph interaction on the width of the $\nu_2$ ($\Gamma_2$) phonon, the most interesting information is the x dependence of $\Gamma_2$. As a matter of fact, consider in addition the observed suppression of superconductivity and the remarkable narrowing of the $\nu_2$ peak and thus the e-ph interaction strongly decreases when x increases in the HD phase. The overall decrease of $\Gamma_3$ and $\Gamma_4$ may also reflect the decrease of the e-ph interaction with increasing x.

Although a comparison among the absolute intensities of different spectra may be questionable, a comparative analysis of the peak integrated intensities $I_i$ can be safely performed. In Fig. 4a the $I_2/I_3$ and $I_2/I_4$ values as a function of x are reported. It is well evident that both the ratios decrease for x>0.25, albeit $I_2/I_3$ is much steeper than $I_2/I_4$. This result clearly reflects the progressive transformation of the structure from the LD to the HD phase. The comparison between the x-dependence of $T_c$ reported in Fig. 4b and the intensity ratios reported in Fig. 4a clearly shows the correlation between superconductivity and the phonon structures, i.e. the structural properties of Mg$_{1-x}$Al$_x$B$_2$. The relevance of the $\nu_2$ mode with respect to the $\nu_3$ and in particular to the $\nu_4$ mode (characteristic of the HD phase) clearly decreases with increasing x in the HD phase, and conversely the transition to the superconducting state tends to be inhibited.

In conclusion, the measured Raman and infrared spectra give clear evidence of the structural difference between the low-doping and the high-doping phases of Mg$_{1-x}$Al$_x$B$_2$. The x-dependence of the $\nu_2$ peak supports its assignment to the $E_{2g}$ mode. Therefore, the remarkable narrowing of the $\nu_2$ phonon observed for x>0.25, implying the decrease of the e-ph interaction, can be related to the suppression of superconductivity. Moreover, the decrease of the critical temperature can be directly related to the decrease of the relative intensity of the $\nu_2$ ($E_{2g}$) mode with respect to the $\nu_3$ and $\nu_4$ modes which dominate the high-doping phase.

Figure captions

Fig. 1 - a) Raman spectrum of MgB$_2$ and the best fit curve from Eq.1 (solid line). The three phonon contributions (solid lines) and the $\nu = 0$ background (dashed line) are also shown separately. b) The Raman spectra of Mg$_{1-x}$Al$_x$B$_2$ at x=0, 0.08, 0.17, 0.25, 0.33, 0.41, 0.50 after background subtraction. The spectra are shifted vertically for clarity.

Fig. 2 - a) Far infrared optical density of MgB$_2$. The intense background is very evident (dashed line). b) Optically dense of Mg$_{1-x}$Al$_x$B$_2$ at x=0, 0.17, 0.33, 0.41, 0.45 after background subtraction. The spectra are shifted vertically for clarity.

Fig. 3 - Best fit values of $\nu_i$ (a) and $\Gamma_i$ (b) (i=2,3,4) as function of x from the analysis of the Raman spectra. Vertical dashed lines indicate the x=0.10 and x=0.25 values.

Fig. 4 - a) Intensity ratios of the peak integrated intensities $I_2/I_3$ and $I_2/I_4$ as a function of x from the analysis of Raman spectra. b) $T_c$ as a function of x from Ref.16. The vertical dashed lines indicate the x=0.25 value.

1. J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, J. Akimitsu, Nature 410, 63 (2001)
2. S.L. Bud’ko, G. Lapertot, C. Petrovic, C.E. Cunningham, N. Anderson P.C. Canfield, Phys. Rev. Lett. 86, 1877 (2001)
3. T. Takahashi, T. Sato, S. Souma, T. Muranaka, J. Akimitsu, Phys. Rev. Lett. 86, 4915 (2001)
4. G. Rubio-Bollinger, H. Suderov, S. Vieria, Phys. Rev. Lett. 86, 5582 (2001)
5. J.M. An, W.E. Pickett, Phys. Rev. Lett. 86, 4366 (2001)
6. J. Kortus, I.I. Mazin, K.D. Belashchenko, V.P. Antropov, L.L. Boyer, Phys. Rev. Lett. 86, 4656 (2001)
7. Y. Kong, O.V. Dolgov, O. Jepsen, O.K. Andersen, Phys. Rev. B 64, 020501 (R)
8. A.F. Goncharov, V.V. Struzhkin, E. Gregoryanz, J. Hu, R.J. Hemley, H. Mao, G. Lapertot, S.L. Bud’ko, P.C. Canfield, cond-mat 0104042 (2001)
9. K.P. Bohnen, R. Heid, B. Renker, cond-mat 0103319 (2001)
10. J. Hlinka, I. Gregora, J. Pokorny, L. Plecnik, P. Kus, L. Satrapinsky, S. Benacka, cond-mat 0105275 (2001)
11. X.K. Chen, M.J. Kostantinovic, J.C. Irwin, D.D. Lawrie, J.P. Franck, cond-mat 0104009 (2001)
12. K. Kunc, I. Loa, K. Syassen, R.K. Kremer, K. Ahn, cond-mat 0105402 (2001)
13. J.S. Slusky, N. Rogado, K.A. Regan, M.A. Hayward, P. Khalifah, T. He, K. Inumaru, S.M. Louie, M.K. Haas, H.W. Zandbergen, R.J. Cava, Nature 410, 342 (2001).
14. A. Bianconi, D. Di Castro, S. Agrestini, G. Campi, N. L. Saini, A. Saccone, S. De Negri, M. Giovannini, cond-mat 010321 (2001)
15. Y.Y. Xiang, D.N. Zheng, J.Q. Li, L. Li, P.L. Lang, H. Chen, C. Dong, G.C. Che, Z.A. Ren, H.H. Qi, H.Y. Tian, Y.M. Ni, Z.X. Zhao, cond-mat 0104366 (2001).
16. A. Bianconi, D. Di Castro, S. Agrestini, N. L. Saini, A. Saccone, S. De Negri, M. Giovannini, G. Profeta, A. Continenza, G. Satta, S. Massidda, A. Cassetta, A. Pifferi, M. Colapietro (unpublished)
17. G. Satta, G. Profeta, F. Bernardini, A. Continenza, S. Massidda, cond-mat 0102358 (2001)
18. T. Yildirim, O. Gulseren, J.W. Lynn, C.M. Brown, T.J. Udovic, H.Z. Qing, N. Rogado, K.A. Regan, M.A. Hayward, J.S. Slusky, T. He, M.K. Haas, P. Khalifah, K. Inumaru, R.J. Cava, cond-mat 0103469 (2001)
19. R. Osborn, E.A. Goremychkin, A.I. Kolesnikov, D.G. Hinks, Phys. Rev. Lett. 00, 000, 2001
20. S. Yoon, H.L. Liu, G. Schollerer, S.L. Cooper, P.D. Han, D.A. Payne, S.W. Cheong, Z. Fisk, Phys. Rev. B 58 (2795 (1998)
21. A. Congeduti, P. Postorino, E. Caramagno, M. Nardone, A. Kumar, D.D. Sarma, Phys. Rev. Lett. 86, 1251 (2001)
22. P. Dore, G. De Marzi, R. Bertini, A. Nucara, P. Calvani, M. Ferretti, Physica C 350, 55 (2001)
23. C.S. Sundar, A. Bharathi, M. Premila, T.N. Sairam, S. Kalavathi, G.L.N. Reddy, V.S. Sastry, Y. Harikaran, T.S. Radhakrishnan, cond-mat 0104354 (2001)
Figure 1

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