Superconductivity, superstructure, and structure anomalies in $Mg_{1-x}Al_xB_2$

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(Received 21 December 2001; published 12 March 2002)

The presence of a superstructure is identified to play a key role for the modifications in both superconductivity and structure transitions in the $Mg_{1-x}Al_xB_2$ system. This superstructure occurs along the *c*-axis direction, and can be well interpreted by Al-layer ordering. The optimal composition of the superstructure phase is $MgAlB_4$, a superconductor with $T_c \sim 12$ K. Raman spectrum of $MgAlB_4$ gives rise to a sharp peak at around 941 cm^{-1}. Brief diagrams illustrating the superconductivity and structural features of $Mg_{1-x}Al_xB_2$ ($0 \leqslant x \leqslant 1$) materials are presented.

DOI: 10.1103/PhysRevB.65.132505 PACS number(s): 74.62.Bf, 61.14.Lj, 68.37.Lp

Magnesium diboride (MgB_2), as a phonon-mediated high-T_c superconductor, has attracted considerable interest from both theoretical and experiential points of view.[1–5] The superconducting transitions in the MgB_2 materials synthesized under a variety of conditions seem to be at around the limit of $\mathbf{T}_c$ as suggested theoretically several decades ago for BCS. Recent theoretical calculations show that the strong coupling in the MgB_2 superconductor originates fundamentally from the in-plane optical phonon related to the vibrations of B atoms.[6,7] Doping Al on the Mg site can introduce electrons into the bands and, moreover, leads to the loss of superconductivity.[3] In our recent investigations of $Mg_{1-x}Al_xB_2$ ($0 \leqslant x \leqslant 1$) materials, measurements of physical properties and microstructure have revealed a rich variety of phenomena resulting from Al ordering with which we will be concerned in the following context.

The polycrystalline samples used in present study were prepared by the solid-reaction method. Stoichiometric amounts of Mg, Al, and B were mixed and compacted in to pellets. These pellets were wrapped with Ta foils and then enclosed in several evacuated quartz tubes. The quartz tubes were placed in a box furnace and heated at a rate of 50 °C/h, held at 600 °C for 8 h, at 800 °C for 5–8 h and finally at 980 °C for 6–10 h followed by furnace cooling to room temperature. Measurements of physical properties and structure indicated that the samples with the $0.4 < x < 0.65$ could show up evidently different features in connection with conditions of sample preparation, such as, the sizes of crystalline grains, microdefects, and the superconductivity. The experimental measurements on samples with large crystalline grains (~ 1 μm) clearly suggest the presence of a new superconducting phase at $x = 0.5$, which could become more or less dubious in the samples with small crystalline grains (< 0.1 μm). This fact is found to result from phase separation commonly observed in the doping range of $0.25 < x < 0.6$. Recent studies[3,8] on the $Mg_{1-x}Al_xB_2$ samples nominally with an averages size of crystalline grains less than 0.1 μm suggested the loss of superconductivity in association with the appearance of phase separation. In order to investigate the correlation among crystal structure, microstructural features, and superconductivity, we have carried out our study on numerous samples with large crystal sizes. The noticeable results obtained in our investigations, as discussed below, are an evident connection between the superconductivity and Al ordering phenomena. The Raman spectra were obtained in a Renishaw 1000 Raman spectrograph using the 514.5-nm line of an Ar-ion laser, which was focused on to the sample with an intensity of about 1 W/cm^2. Specimens for transmission-electron microscopy (TEM) observations were polished mechanically with a Gatan polisher to a thickness of around 50 μm and then ion milled. The TEM investigations were performed on a H-9000NA electron microscope with an atomic resolution of about 0.19 nm.

Figure 1(a) shows a series of the x-ray diffraction spectra of the $Mg_{1-x}Al_xB_2$ samples with $x = 0$, 0.17, 0.5, 0.75, and 1.0, illustrating remarkable modifications of the 002 reflection peak along with the increase of Al concentration. Two broad peaks for samples ranging from 0.09 to 0.25 have been

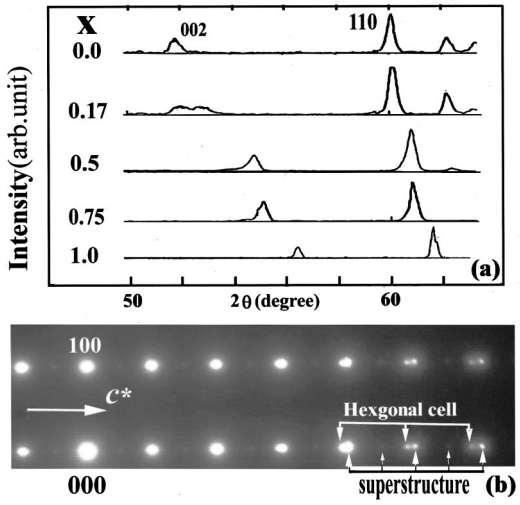

FIG. 1. (a) A series of x-ray diffraction spectra of $Mg_{1-x}Al_xB_2$, illustrating the evolution of (002)-reflection peak. (b) Electron-diffraction pattern showing the presence of additional superstructure reflections in the $x = 0.17$ sample.

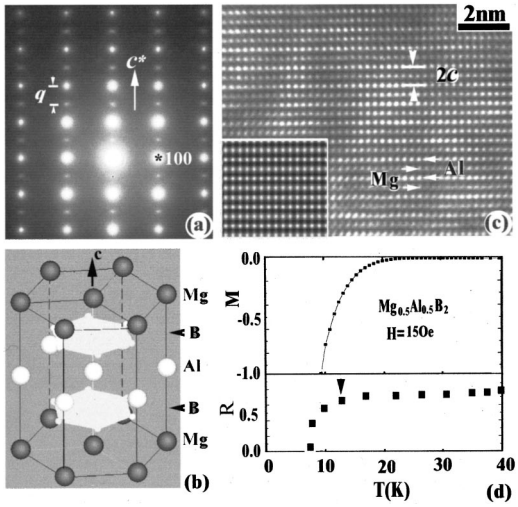

FIG. 2. (a) An electron-diffraction pattern of the superstructure phase $MgAlB_4$, with the wave vector of $q=c^*/2$. (b) A schematic structural model of $MgAlB_4$. (c) High-resolution TEM image clearly exhibiting ordered Al and Mg layers along c direction. Inset shows a calculated image. (c) Temperature dependence of normalized magnetization (upper panel) and resistivity (lower panel) showing superconductivity in a $MgAlB_4$ sample.

observed as reported previously.[3] Our systematic study suggests that all $Mg_{1-x}Al_xB_2$ materials with x ranging from either 0.09 to 0.25 or 0.70 to 0.8 exhibit complex structural and physical behaviors likely to originate from essential structural inhomogeneity. Direct evidences of the presence of two phases in these specific regions have been obtained by TEM investigations. Figure 1(b) shows an electron-diffraction pattern for $x=0.17$, indicating the coexistence of two structural phases in this material. The remarkable structural feature in this pattern is the appearance of a new superstructure phase with noticeably different cell parameters, as indicated by arrows. In order to characterize the essential origins of the structural anomalies in $Mg_{1-x}Al_xB_2$ system, we have performed an extensive structural analysis by means of x-ray diffraction, TEM observations and energy dispersive x-ray microanalysis. This superstructure could be commonly found in the materials with x in the large range of 0.1–0.75. However, in a number of materials, in particular, with x ranging from 0.1 to 0.35 and 0.65 to 0.80, intergrowth lamella of the superstructure with the hexagonal structure, as well as complex domains in connection with compositional phase separation, have been evidently observed. This superstructure phase can be fundamentally understood by Al ordering along the c-axis direction, and has an optimal composition of $Mg_{0.5}Al_{0.5}B_2$ ($MgAlB_4$ phase).

Figure 2(a) shows an electron-diffraction pattern taken from an $Mg_{0.5}Al_{0.5}B_2$ crystal, exhibiting the superstructure spots at the systematic $(h,k,1+1/2)$ positions. Detailed analyses suggest that this superstructure results directly from an ordered arrangement of Al and Mg layers along the c-axis direction. A brief schematic model for this superstructure is displayed in Fig. 2(b), clearly illustrating the atomic layers. Figure 2(c) shows a high-resolution electron micrograph of $MgAlB_4$ crystal taken along the [010] zone-axis direction,

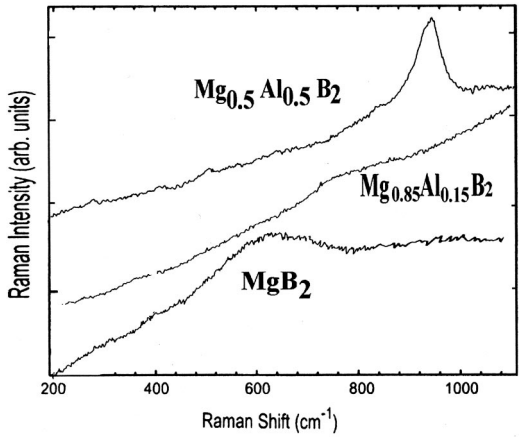

FIG. 3. Raman spectra of $MgAlB_2$, $Mg_{0.85}Al_{0.15}B_2$, and $Mg_{0.5}Al_{0.5}B_2$, illustrating a sharp Raman peak at around 941 cm^{-1} for the superstructure phase. The excitation wavelength is 514.5 nm.

exhibiting the atomic layers and superstructure along the c direction. In combination with theoretical simulations, we could identify the essential structural properties of this superstructure phase. Image calculations, based on the schematic model of Fig. 2(b) together with the resultant structural distortions, were carried out by varying the crystal thickness and the defocus value. A calculated image with the defocus value of -40 nm and the thickness of 10 nm is superimposed on the image, and appears to be in good agreement with the experimental one. Figure 2(d) shows the temperature-dependent magnetization (upper panel) and resistivity (lower panel) for an $Mg_{0.5}Al_{0.5}B_2$ sample. The superconducting transition can be clearly recognized in either magnetization or resistivity with T_c (onset) at around 12 K.

Figure 3 shows the Raman spectra for samples of MgB_2, $Mg_{0.85}Al_{0.15}B_2$, and $Mg_{0.5}Al_{0.5}B_2$. The remarkable feature revealed in these Raman spectra is the appearance of a sharp peak at around 941 cm^{-1} for the $x=0.5$ sample, in stark contrast with the broadened Raman band for the MgB_2 superconductor.[9,10] Systematic measurements of Raman spectra on the $Mg_{1-x}Al_xB_2$ samples suggest that this peak is essentially in connection with the appearance of the new superstructure in the $Mg(Al)B_2$ materials; which becomes clearly visible as Al concentration rises to $x=0.4$, then its intensity increase gradually and gives rise to a sharp peak for $x=0.5$. Afterwards, this peak becomes broadened along with the increase of x and keeps to be visible till $x=0.7$. It is well demonstrated for MgB_2 that E_{2g} mode is the Raman active one among the zone-center modes of $B_{1g}+E_{2g}+A_{2u}+E_{2u}$. It is a doubly degenerate mode for the crystal lattice with $P6/mmm$ symmetry. The observed Raman band at 620 cm^{-1} MgB_2 can be well assigned at this mode in good agreement with theoretical calculation.[10] The large linewidth of the observed band has been mainly attributed to large electron-phonon coupling in this kind of materials.[9] According to the structural analysis of $MgAlB_4$, [also see the proposed structural model of Fig. 2(b)], the $MgAlB_4$ crystal lattice has the same space group of $P6/mmm$. Hence, the observations of the frequency increase of the Raman band

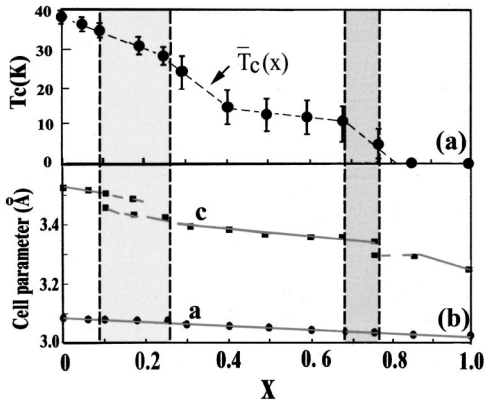

FIG. 4. Composition dependence of (a) superconducting temperature (T_c) and (b) basic structural parameters (a and c) for $Mg_{1-x}Al_xB_2$, anomalies in both structural and physical properties in association with Al ordering can be clearly recognized.

and the alternation of its shape suggest the evident changes in both structural features and the electron-phonon coupling along with the appearance of superstructure. Furthermore, our recent studies showed that Al ordering could also lead to the structural changes within the *a-b* plane. Further experimental measurements together with theoretical analysis are in progress.[11]

Figure 4(a) illustrates T_c as a function of the Al concentration (x). In this figure, we have shown the average result of $T_c(x)$ obtained from various sets of samples prepared by the method as describe above. The abrupt decrease of T_c between $x=0.25$ and 0.4 is apparently in connection with a phase transformation from the conventional hexagonal structure to the superstructure. In the range of $x=0.40-0.6$, the superconducting critical temperature T_c decrease gradually with the increase of Al concentration, and seemingly giving rise to a linear relationship between T_c and x. Furthermore, in the vicinal region of $x=0.5$, T_c decreases so slowly that we can recognize a plateaulike behavior in T_c. This is quite analogous to the interesting behavior observed in the well-known high-T_c superconductor $YBa_2Cu_3O_y$, in which oxygen stoichiometery, as well as oxygen/vacancy ordering, significantly affects the physical properties and yields a plateau in T_c at ~60 K.[12] *In situ* TEM observations show that the superstructure in the $Mg_{0.5}Al_{0.5}B_2$ sample is very stable without distinguishable changes in the temperature range of 100–500 K. It is also noted the superconducting transition depends markedly on the process of sample preparation, which can be either sharp or broadened dependent on the synthesis conditions. The other evident decrease of T_c occurs in the range of $x=0.7-0.8$, which is found to be in association with the disappearance of the superstructure as revealed in our TEM investigations. In other words, a phase transformation from the superstructure to AlB_2-like hexagonal structure occurs in this region. This transition seemingly appears in a narrow range neighboring $x=0.75$. Actually, we only observed clear evidence of phase separation in the $x=0.75$ material. A further study of the structural properties related to this phase transition is in progress. Materials with high Al concentrations of $x>0.8$ entirely lose superconductivity as measured in our experiments. Figure 4(b) shows the composition dependence of the basic lattice parameters, a and c, for a series of the well-characterized $Mg_{1-x}Al_xB_2$ materials. Evident anomalies become visible in the multiphase ranges of $0.09<x<0.25$ and $0.7<x<0.8$. Those coincide perfectly with the modifications of superconductivity. These facts suggest that the Al concentration and its ordered state significantly affect the physical properties of $Mg_{1-x}Al_xB_2$ materials and result in a rich variety of structural and physical issues. The further study of these issues may prove fruitful.

In conclusion, the $Mg_{1-x}Al_xB_2$ exhibits a variety of remarkable structural and physical properties in connection with Al ordering along the c-axis direction, such as structural transformations, phase separations, and the anomalous modifications in superconductivity. Measurements of Raman spectra have revealed a new sharp peak at around 941 cm^{-1} in the superstructure phase $MgAlB_4$. Though recent theoretical literatures about the electronic structure have performed for $Mg_{1-x}Al_xB_2$ and other related systems,[13] the presence of the Al ordering in a large intermediate range of $0.1<x<0.75$ will definitely lead to a further examination of the theoretical results.

The authors would like to express many thanks to Professor G. C. Che, Professor Y. L. Liu, Miss S. L. Jia, Professor D. N. Zheng, and Professor L. P. You for their assistance. The work reported here was supported by ''Hundreds of Talents'' program organized by the Chinese Academy of Sciences, People's Republic of China.

[1] J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, and J. Akimitsu, Nature (London) **410**, 63 (2001).
[2] S. L. Bud'ko, G. Iapertot, and C. Petrovic, Phys. Rev. Lett. **86**, 1877 (2001).
[3] J. S. Slusky, N. Rogado, K. A. Regan, M. A. Hayward, P. Khalifah, T. He, K. Inumaru, S. Loureiro, M. K. Haas, H. W. Zandbergen, and R. J. Cava, Nature (London) **410**, 343 (2001).
[4] Alexander F. Goncharov *et al.*, Cond-mat/0104042 (unpublished).
[5] J. Q. Li *et al.*, Chin. Phys. Lett. **18**, 680 (2001).
[6] P. C. Canfield *et al.*, Phys. Rev. Lett. **86**, 2423 (2001).
[7] J. M. An and W. E. Pickett, Cond-mat/0102391 (unpublished).
[8] J. Y. Xiang *et al.* (unpublished).
[9] X. K. Chen *et al.*, Cond-mat/0104005 (unpublished); K.-P. Bohen, R. Heid, and B. Renker, Cond-mat/0102468 (unpublished).
[10] A. F. Goncharov *et al.*, Cond-mat/0104042 (unpublished).
[11] F. M. Liu and Y. L. Liu *et al.* (unpublished).
[12] J. Cava *et al.*, Nature (London) **329**, 423 (1987).
[13] S. Suzuki, S. Higai, and K. Nakao (unpublished).