Article ID: 1003－6326(2003)04－0912－05

Influence of doping effect on structure and superconducting properties of MgB_2 ①

XIONG Yu-hua(熊玉华)[1], LI Pei-jie(李培杰)[1], ZHANG Xiao-ping(张晓平)[2]
ZHAO Yong-gang(赵永刚)[2], CAO Bi-song(曹必松)[2], ZENG Da-ben(曾大本)[1]
(1. Department of Mechanical Engineering, Tsinghua University, Beijing 100084, China
2. Department of Physics, Tsinghua University, Beijing 100084, China)

Abstract: $Mg_{1-x}M_xB_2$(M= Li or deficiency) compounds were prepared and their structure and superconducting properties were studied. The results show that nearly single-phased $Mg_{1-x}Li_xB_2$ samples have been obtained while $x \leqslant 0.3$. With increasing x, lattice parameters a decreases and c shows no obvious change, and the superconducting transition temperature T_c of $Mg_{1-x}Li_xB_2$ decreases. Moreover, loss of superconductivity occurs for sample with $x = 0.5$. For $Mg_{1-x}B_2$ nearly single-phased samples can be obtained at $x = 0$. MgB_2 coexists with MgB_4 phase and some minor impurity phases while $0 < x < 0.5$. With the increase of x, a and c of MgB_2 decreases and increases, respectively, and T_c decreases. The obvious difference in the superconductivity of $Mg_{1-x}Li_xB_2$ and $Mg_{1-x}B_2$ suggests that Li indeed dopes into the structure of MgB_2.

Key words: $Mg_{1-x}Li_xB_2$; $Mg_{1-x}B_2$; lattice parameter; superconducting transition temperature
CLC number: TM 26+2, O 511 **Document code:** A

1 INTRODUCTION

The recent discovery of superconductivity in the binary intermetallic compound MgB_2[1] has stimulated worldwide excitement in the scientific community and resulted in a flurry of both experimental and theoretical work[2-8]. The superconducting transition temperature T_c of MgB_2 is 39 K, which is almost twice as large as the record values of T_c for the conventional intermetallic superconductors. Its structure is very simple, consisting of alternating layers of Mg atoms and B atoms. Hall effect measurements show that the Hall coefficient of MgB_2 is positive like those of high T_c cuprate superconductors and its carrier density at 100 K is $1.5 \times 10^{23}/cm^3$, which is very high compared to those of Nb_3Sn and the optimally doped $YBa_2Cu_3O_y$[9]. A significant boron isotope effect was observed, suggesting a phonon-mediated BCS superconducting mechanism in MgB_2[5, 6]. On the other hand, it is proposed that the theory of hole superconductivity may also account for the superconductivity in MgB_2[7, 8]. So the mechanism for the occurrence of superconductivity in MgB_2 is still an open question.

Doping has been proved to be a very powerful method to study the physical properties of cuprates. Up to now, there have been some studies on the doping effect of $Mg_{1-x}M_xB_2$ or $MgB_{2-x}M_x$ in which M are the doping elements[11-16]. Slusky et al[11] have studied the electron doping effect of Al on the structure and superconducting transition temperature of MgB_2 and found that T_c decreases with Al doping. It is also found that Be cannot dope into Mg sites and $Mg_{1-x}Be_xB_2$ has the same T_c as pure MgB_2[12]. It was reported later that Be can react with B to form $BeB_{2.75}$, which shows superconductivity at 0.72 K[17]. Investigation indicates that 10% Zn could be doped in the MgB_2 structure, leading to an increase of both lattice parameters[13]. Since electron doping and isoelectronic substitution of Mg could not increase T_c of MgB_2, it is necessary to investigate the hole doping effect of MgB_2. It has been put forward that $Mg_{1-x}Li_xB_2$ is a key compound to test two possible superconducting mechanisms of MgB_2, that is BCS mechanism and hole superconducting mechanism due to their different predictions on the behavior of T_c upon hole doping. BCS mechanism predicts the increase of T_c due to Li doping. However, according to the hole superconductivity mechanism, MgB_2 is already over doped, further doping with holes by Li doping will decrease T_c[8]. Thus, it is important to prepare $Mg_{1-x}Li_xB_2$ and get the T_c dependence on Li doping. Moreover, since the structural and superconducting properties of $Mg_{1-x}B_2$ can be used as reference for investigation on doping effect, $Mg_{1-x}B_2$

① **Foundation item:** Project(JZ2001001) supported by the Basic Research Foundation for Tsinghua University of China
Received date: 2002－06－17; **Accepted date:** 2002－08－26
Correspondence: XIONG Yu-hua, PhD; Tel: +86-10-62773639; E-mail: yuhau-xiong@mail.tsinghua.edu.cn

samples are prepared and their superconductivity are studied at the same time in this work.

2 EXPERIMENTAL

$Mg_{1-x}Li_xB_2$ samples with x = 0, 0.1, 0.15, 0.2, 0.25, 0.3 and 0.5 as well as $Mg_{1-x}B_2$ samples with x = 0, 0.1, 0.2, 0.3, 0.4 and 0.5 were prepared by the solid-state reaction method. The starting materials were Mg flakes (99.9% purity), amorphous B powder (99.99% purity), and Li in lump form (99.99% purity). For $Mg_{1-x}Li_xB_2$, the stoichiometric elements were combined in glove-box under an argon atmosphere, and were put into a sealed Ta tube which was subsequently sealed in a quartz ampoule. For $Mg_{1-x}B_2$, the needed elements in the nominal ratio were combined in a sealed stainless steel tube. After that, the quartz ampoule and stainless tube were placed in a box furnace and heated at 950 ℃ for 2 h, then quenched to room temperature. The phase analysis of the samples was performed using Rigaku Dmax-RB X-ray diffractometer with Cu K_α radiation. AC susceptibility of the samples from room temperature to liquid helium temperature was measured. T_c of the samples was determined with superconducting quantum inlerference device.

3 RESULTS AND DISCUSSION

3.1 Phase analysis

Fig. 1 shows the X-ray diffraction patterns for $Mg_{1-x}Li_xB_2$ samples with x = 0, 0.1, 0.3. It can be seen that they are very similar while $x \leqslant 0.3$, and they are basically consistent with the reported X-ray diffraction pattern of MgB_2[10], indicating that the samples are nearly single-phased. However, some unidentified peaks occur in the X-ray diffraction pattern for sample with x = 0.5, showing that the sample may contain impurity phases. It can be found that the diffraction angles for (100), (101) and (110) crystal planes dramatically increase with increasing doping amount, especially the (100) and (110) crystal planes, while that for (002) plane remains unchanged. Using the diffraction angles and Bragg's formula, lattice parameters a and c can be obtained.

The X-ray diffraction patterns for $Mg_{1-x}B_2$ with x = 0 and 0.3 are shown in Fig. 2. It can be found that the pattern of sample with x = 0 is consistent with that of MgB_2 except a small peak of MgO. While x = 0.3, some extra peaks appear besides the peaks of the MgB_2 phase. Careful analysis shows that the major extra peaks belong to MgB_4 phase, while some low peaks may be related to some impurity phases. That is, the MgB_2 phase coexists with the MgB_4 phase and minor amount of impurity phases for

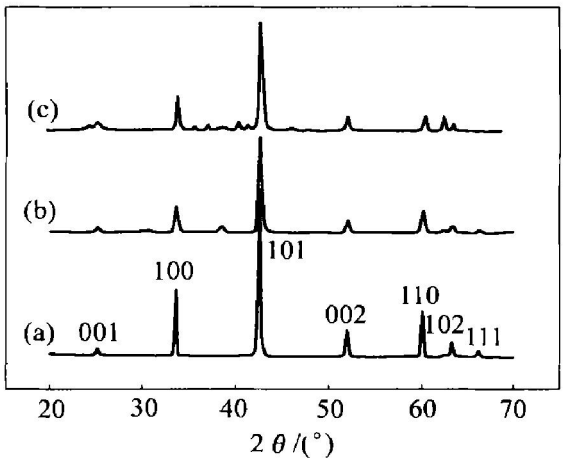

Fig. 1 X-ray diffraction patterns for $Mg_{1-x}Li_xB_2$ with different doping amounts
(a) —x = 0; (b) —x = 0.1; (c) —x = 0.3

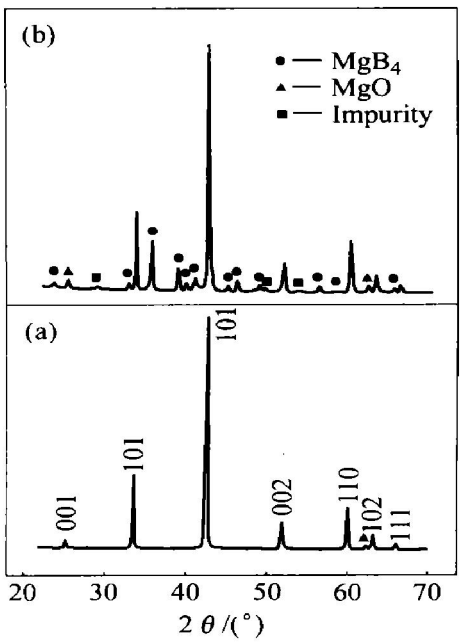

Fig. 2 X-ray diffraction patterns for $Mg_{1-x}B_2$ with x = 0(a) and 0.3(b)

samples with $0 < x \leqslant 0.5$. Moreover, the amount of the MgB_4 phase increases and that of the MgB_2 phase decreases with increasing x. The calculation of the temperature-composition phase diagram of the Mg-B system under 101.325 kPa shows that for $Mg_{1-x}B_2$ ($0 < x < 0.5$), which corresponds to the range of atomic fraction of boron from 67% (x = 0, molar fraction) to 80% (x = 0.5), the MgB_2 and MgB_4 phases coexist below 1 550 ℃. Thus, the present results are consistent with their calculation. It is also found that the diffraction angles for (100) and (110) crystal planes of MgB_2 increase with increasing x, while that for (002) plane decreases, indicating that the lattice parameters of the MgB_2 phase also change with x.

3.2 Lattice parameters

For comparison, the variation of lattice parame-

ters a and c with x for $Mg_{1-x}Li_xB_2$ (x = 0, 0.1, 0.15, 0.2, 0.25, and 0.3) and $Mg_{1-x}B_2$ (x = 0, 0.1, 0.2, 0.3, 0.4, and 0.5) samples is shown in Fig. 3. One can see that for $Mg_{1-x}Li_xB_2$, the in-plane lattice parameter a decreases with increasing x, which can be understood by considering the fact that the ion radius of Li^+ (0.6 Å) is smaller than that of Mg^{2+} (0.65 Å), and the lattice parameter c, the distance between the adjacent B layers, keeps invariant within the experimental error. Therefore, Li doping mainly affects the in-plane coupling.

As to $Mg_{1-x}B_2$, its lattice parameter a reduces slower than that of $Mg_{1-x}Li_xB_2$ and c increases along with increasing x, which is due to the presence of Mg vacancies or B interstitial atoms. Thus, it can be concluded that the dependence of the lattice parameters on x for $Mg_{1-x}Li_xB_2$ is different from that for $Mg_{1-x}B_2$.

3.3 AC susceptibility

Fig. 4 illustrates the temperature dependence of the AC susceptibility for $Mg_{1-x}Li_xB_2$ samples with x = 0, 0.1, 0.3 and 0.5, and for $Mg_{1-x}B_2$ samples with x = 0 and 0.5, respectively. Fig. 4(a) clearly shows that the superconducting transition temperature T_c of $Mg_{1-x}Li_xB_2$ samples decreases with Li doping and superconductivity disappears for sample with x = 0.5. For $Mg_{1-x}B_2$, T_c decreases with increasing x and the amplitude of variation of the AC susceptibility around the transition temperature also decreases, indicating that the amount of the superconducting phase decreases. This is consistent with the X-ray diffraction results that the fraction of the MgB_4 phase increases and that of MgB_2 phase decreases with increasing x.

3.4 Superconducting transition temperature

Fig. 5 shows that the variation of the superconducting transition temperature T_c with x for $Mg_{1-x}Li_xB_2$ and $Mg_{1-x}B_2$. It can be found that for $Mg_{1-x}Li_xB_2$, T_c decreases rapidly with the increase in Li doping amount. For $Mg_{1-x}B_2$, T_c decreases only from 38.4 K to 36 K with the increase of x from 0 to 0.5. T_c decreases slowly with x for samples with $x \leqslant 0.2$ and then decreases relatively fast for samples with $x > 0.2$.

It should be pointed out that if Li does not dope into the structure of MgB_2, the experimental results of $Mg_{1-x}Li_xB_2$ are comparable to those of $Mg_{1-x}B_2$ samples. In the present study, the obvious difference in the lattice parameters, AC susceptibility and superconducting transition temperature of $Mg_{1-x}Li_xB_2$ and $Mg_{1-x}B_2$ can be found. Therefore, it can be concluded that Li indeed dopes into the structure of MgB_2.

Careful analysis shows that the effect of Li doping on T_c may be realized by two actions, namely, the reduction of the lattice parameter a or unit cell volume and hole doping. Fig. 6 illustrates the relation between T_c and the unit cell volume V. It can be seen that T_c decreases with the decrease of the unit

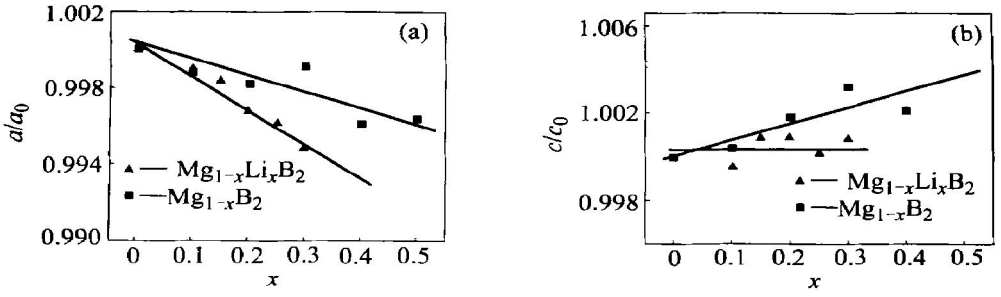

Fig. 3 Variation of lattice parameters a(a) and c(b) with x for $Mg_{1-x}Li_xB_2$ and $Mg_{1-x}B_2$

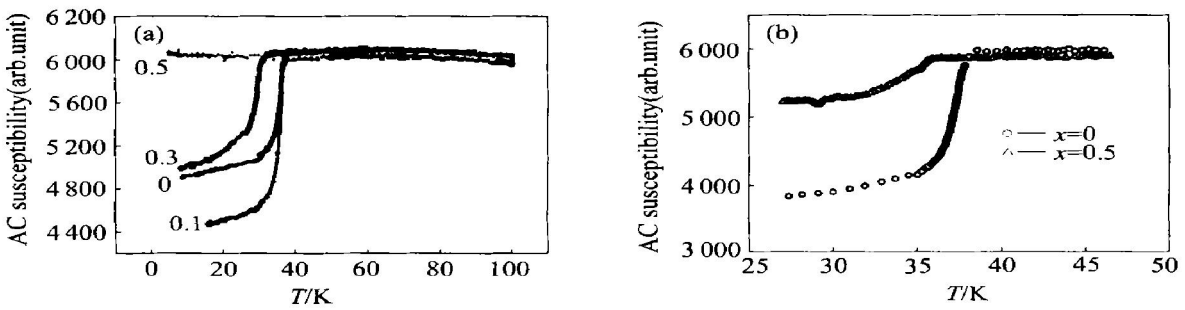

Fig. 4 Temperature dependence of AC susceptibility for $Mg_{1-x}Li_xB_2$ with different Li doping(a) and for $Mg_{1-x}B_2$(b)

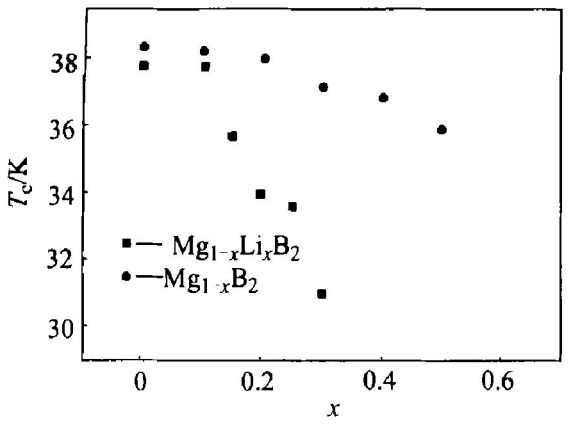

Fig. 5 Variation of T_c with x for $Mg_{1-x}Li_xB_2$ and $Mg_{1-x}B_2$ samples

cell volume. Some investigation on the influence of hydrostatic pressure on MgB_2 indicates that T_c of MgB_2 samples decreases linearly with the increase of the hydrostatic pressure[14, 19-20]. In these experiments, the hydrostatic pressure decreases both the in-plane and inter-plane B-B distance, leading to the decrease of T_c for MgB_2. The relation between T_c and V can be expressed as $d\ln T_c/dV = 0.18$ Ù$^{-3}$[19], or $d\ln T_c/d\ln V = 4.16$[20]. In the present study, Li doping decreases the in-plane B-B distance and has no effect on the inter-plane B-B distance, and decreases T_c. In addition, the values of $d\ln T_c/dV$ and $d\ln T_c/d\ln V$ are calculated to be 0.80 Ù$^{-3}$ and 23, respectively, which are much larger than those obtained in the hydrostatic pressure experiments. Provided that the chemical pressure (present work) and the physical pressure (in the hydrostatic pressure experiments) have the same effect on T_c of MgB_2, the above difference in ratios suggests that as for the T_c suppression in $Mg_{1-x}Li_xB_2$, there may be some contribution from hole doping besides the contribution from the contraction of the unit cell volume.

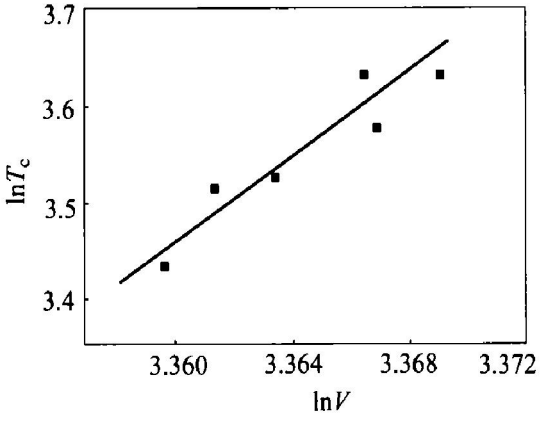

Fig. 6 Correlation between superconducting transition temperature T_c and unit cell volume for $Mg_{1-x}Li_xB_2$

4 CONCLUSIONS

1) $Mg_{1-x}Li_xB_2$ and $Mg_{1-x}B_2$ samples have been prepared by a solid-state reaction method. For $Mg_{1-x}Li_xB_2$, nearly single-phased samples can be obtained while $x \leqslant 0.3$. The lattice parameter a decreases and c has no obvious variation with increasing x. Li doping decreases T_c of $Mg_{1-x}Li_xB_2$ and superconductivity disappears for sample with $x = 0.5$.

2) For $Mg_{1-x}B_2$, nearly single-phased samples can be obtained for $x = 0$. However, MgB_2 coexists with MgB_4 phase and some minor impurity phases, and the amount of MgB_4 and MgB_2 increases and decreases, respectively with increasing x while $0 < x < 0.5$. The lattice parameters a and c of MgB_2 decreases and increases, respectively, and T_c decreases with the increase in x. T_c reduces to 36 K for sample with $x = 0.5$.

3) The obvious difference in the lattice parameters, AC susceptibility and superconducting transition temperature for $Mg_{1-x}Li_xB_2$ and $Mg_{1-x}B_2$ suggest that Li indeed dopes into the structure of MgB_2.

REFERENCES

[1] Nagamatsu J, Nakagawa N, Muranaka T, et al. Superconductivity at 39 K in magnesium diboride[J]. Nature, 2001, 410: 63 - 64.

[2] Finnemore D K, Ostenson J E, Budʹko S L, et al. Thermodynamic and transport properties of superconductivity $Mg_{10}B_2$[J]. Physical Review Letters, 2001, 86(11): 2420 - 2422.

[3] Karaperov G, Iavarone M, Kwok W K, et al. Scanning tunneling spectroscopy in MgB_2[J]. Physical Review Letters, 2001, 86(19): 4374 - 4377.

[4] Wen H H, Li S L, Zhao Z W, et al. Strong quantum fluctuation of vortices in bulk samples of the new superconductor MgB_2[J]. Chinese Physics Letters. 2001, 18(6): 816 - 819.

[5] Kortus J, Mazin I I, Belashchenko K D, et al. Superconductivity of metallic boron in MgB_2[J]. Physical Review Letters, 2001, 86(20): 4656 - 4659.

[6] An J M, Pickett W E. Superconductivity of MgB_2: Covalent bonds driven metallic[J]. Physical Review Letters, 2001, 86(19): 4366 - 4369.

[7] Hirsch J E. Hole superconductivity in MgB_2: a high T_c cuprate without Cu[J]. Physics letters A, 2001, 282(6): 392 - 398.

[8] Hirsch J E, Marsiglio F. Electron-phonon or hole superconductivity in MgB_2[J]. Physical Review B, 2001, 64(14): 144523.

[9] Kang W N, Jung C U, Kim Kijoon H P, et al. Hole carrier in MgB_2 characterized by Hall measurements[J]. Applied Physics Letters, 2001, 79(7): 982 - 984.

[10] Budʹko S L, Lapertot G, Petrovic C, et al. Boron isotope effect in superconducting MgB_2[J]. Physical Review Letters, 2001, 86(9): 1877 - 1880.

[11] Slusky J S, Rogado N, Regan K A, et al. Loss of su-

perconductivity with the addition of Al to MgB_2 and a structural transition in $Mg_{1-x}Al_xB_2$[J]. Nature, 2001, 410: 343－345.

[12] Felner I. Absence of superconductivity in BeB_2[J]. Physica C, 2001, 353(1－2): 11－13.

[13] Kazakov S M, Angst M, Karpinski J, et al. Substitution effect of Zn and Cu in MgB_2 on T_c and structure [J]. Solid State Communications, 2001, 119(1): 1－5.

[14] Lorenz B, Meng R L, Xue Y Y, et al. Thermoelectric power and transport properties of $Mg_{1-x}Al_xB_2$[J]. Physical Review B (condensed matter and material physics), 2001, 64(5): 052513－1－052513－4.

[15] Xu S, Moritomo Y, Kato K, et al. Mn-substitution effects on MgB_2 superconductor[J]. Journal of the Physical Society of Japan, 2001, 70(7): 1889－1891.

[16] Moritomo Y, Xu S. Effects of transition metal doping in MgB_2 superconductor. www. lanl. gov. cond-mat/0104568, 2001.

[17] Young D P, Goodrich R G, Adams P W, et al. Superconducting properties of $BeB_{2.75}$[J]. Physical Review B, 2002, 65(18): 180518.

[18] Liu Z K, Schlom D G, Li Q, et al. Thermodynamics of the Mg-B system: implications for the deposition of MgB_2 thin films[J]. Applied Physics Letters, 2001, 78(23): 3678－3680.

[19] Prassides K, Iwasa Y, Ito T, et al. Compressibility of the MgB_2 superconductor [J]. Physical Review B, 2001, 64(1): 012509.

[20] Tomita T, Hamlin J J, Schilling J S, et al. Dependence of T_c on hydrostatic pressure in superconducting MgB_2 [J]. Physical Review B, 2001, 64(9): 092505.

(Edited by LONG Huai-zhong)