Structural and superconducting properties of $MgB_{2-x}Be_x$

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(Received 5 November 2001; published 11 April 2002)

We prepared $MgB_{2-x}Be_x$ ($x=0$, 0.2, 0.3, 0.4, and 0.6) samples where B is substituted with Be. MgB_2 structure is maintained up to $x=0.6$. In-plane and interplane lattice constants were found to decrease and increase, respectively. The superconducting transition temperature T_c decreases with x. We found that the T_c decrease is correlated with in-plane contraction but is insensitive to carrier doping, which is consistent with other substitution studies such as $Mg_{1-x}Al_xB_2$ and $MgB_{2-x}C_x$. Implication of this work is discussed in terms of the two-dimensional nature of the σ band.

DOI: 10.1103/PhysRevB.65.172503 PACS number(s): 74.62.−c, 74.70.Ad, 61.10.−i

I. INTRODUCTION

The recent discovery of superconductivity in MgB_2 at $T_c=39$ K has drawn enormous attention to its structural and electrical properties.[1] The borons form the graphitic planes and magnesiums supply charges in the planes. The resulting carriers are holes in the σ-band.[2] Most theoretical works suggest that coupling of the σ hole with a B-plane phonon is the key ingredient of the superconductivity in this compound.[3–5] This phonon-mediated BCS mechanism is consistent with the boron isotope effect.[6]

There have been many attempts to change T_c through chemical substitution in Mg or B sites. For example, Al substitution on a Mg site[7] and C substitution on the boron plane are reported.[8] Such chemical substitutions change the physical quantities of the system such as hole density, lattice constants, etc. However, there is no detailed understanding of the effect of substitution on the observed T_c change even within the BCS frame.

In this paper, we prepared a series of $MgB_{2-x}Be_x$, where B is substituted with Be in the plane.[9] With this substitution, the in-plane B-B distance decreases while the interplane distance increases. Our thermopower measurement showed that the σ hole increases with Be, as reported in an independent paper.[10] We compare our result with other substituted compounds and find that the T_c change is insensitive to the carrier doping. Instead, we show that the in-plane B-B distance is closely correlated with the T_c change in the low-doping region. This result is consistent with the two-dimensional (2D) nature of the σ band.[4]

II. EXPERIMENT

Polycrystalline samples were synthesized with the powder metallurgical technique under high pressure. Starting materials were fine powders of Mg (99.8%, Alfa Aesar), amorphous B (99.99%, Alfa Aesar), and Be (99.+%, Alfa Aesar). Stoichiometric amounts of powders were mixed and pelletized. The pellets were placed in a tungsten vessel with a close-fitting cap, then reacted for 2 h at 850 °C under 20 atm of high-purity argon atmosphere.

An x-ray diffraction (XRD) θ-2θ scan measurement was performed using a Rigaku RINT d-max. Figure 1(a) shows the results for $x=0$, 0.2, 0.4, 0.6, and 1.0. Most of the reflections correspond to AlB_2-type patterns. Also, minor impurity phases such as MgO and BeO are found as indicated by ∇ and *, respectively. Note that the MgB_2 structure is maintained up to $x=0.6$. At higher compositions ($x=1.4$ and 2.0, not shown here), we find that $Be_{13}Mg$ becomes the main phase. In Fig. 1(b), the shifts of the (002) and (110) reflections are shown in expanded scales. As x increases, the (002)

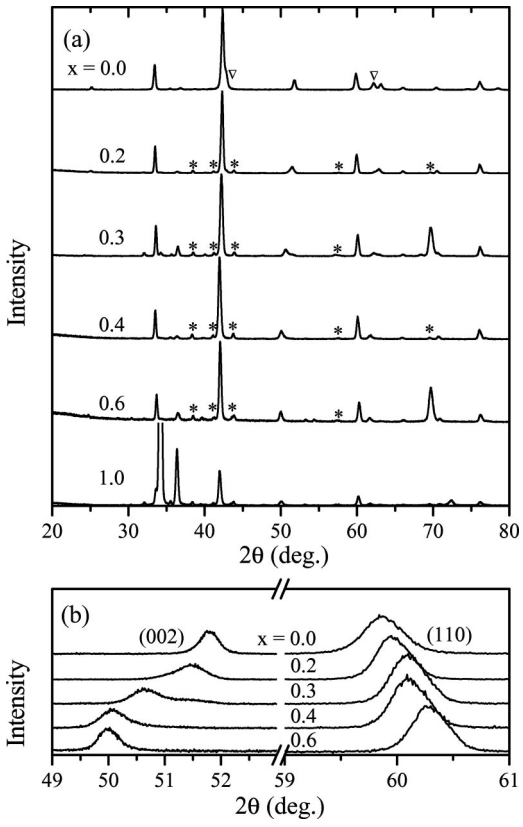

FIG. 1. (a) x-ray θ-2θ scan results of $MgB_{2-x}Be_x$ ($x=0$, 0.2, 0.3, 0.4, 0.6, and 1.0). Impurity peaks are indicated with symbols: MgO(∇) and BeO(*). (b) Shift of (002) and (110) reflections.

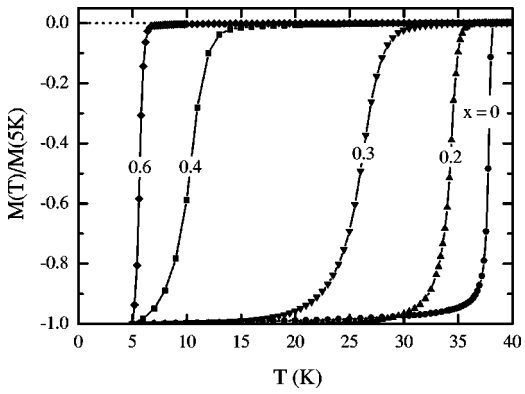

FIG. 2. Magnetization $M(T)$ of $MgB_{2-x}Be_x$. ZFC results are shown. External magnetic field $H=10$ Oe is used. Data are normalized with 5 K value.

reflection shifts to a lower angle while the (110) reflection moves to the opposite direction. This indicates that the in-plane lattice constant a decreases and the interplane distance c increases with x.[11] To obtain the lattice parameters, we performed refinement analysis using the RIETAN-2000 program[12] and used MgO and BeO as internal standards.

In order to study superconducting property, dc magnetization was measured using a dc superconducting quantum interference device (SQUID) magnetometer (Quantum Design). Figure 2 shows the magnetization $M(T)$ of $MgB_{2-x}Be_x$. In this measurement, samples were first zero-field cooled (ZFC) and data were measured with increasing temperature under $H=10$ Oe. Note that the superconducting transition temperature T_c decreases with x. In the figure, the magnetization is normalized with the saturated value at $T=5$ K. The transition width ΔT_c was determined from 10%–90% the transition.

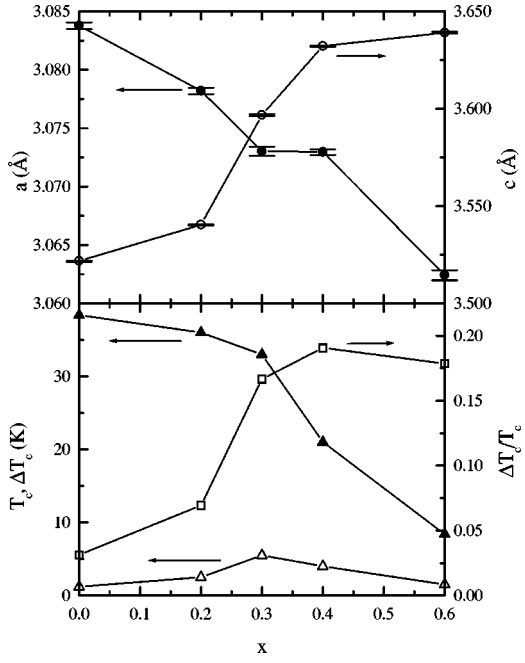

FIG. 3. Upper: lattice parameters a (●) and c (○) vs x. Lower: superconducting onset temperature T_c (▲), transition width ΔT_c (△), and the ratio $\Delta T_c/T_c$ (□) vs x. ΔT_c is determined from the 10%–90% transition of saturated magnetization.

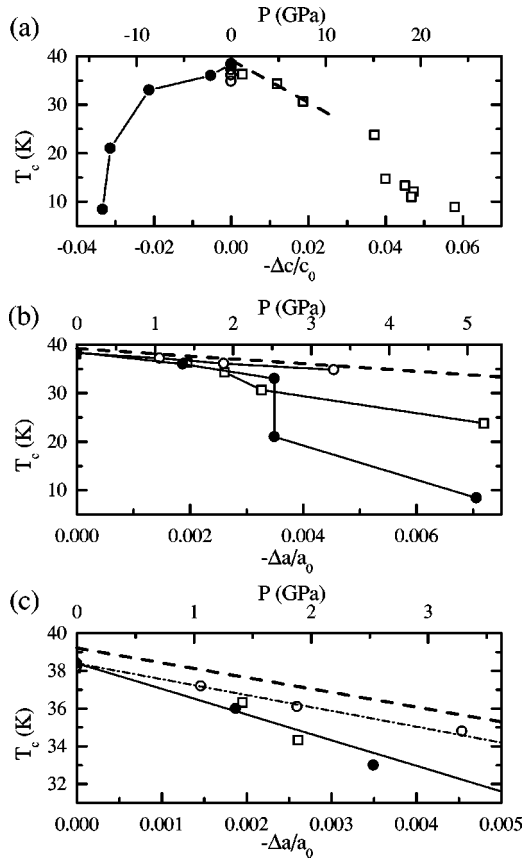

FIG. 4. T_c change with respect to lattice compression for various chemically substituted compounds. (a) T_c vs interplane lattice contraction $-\Delta c/c_0$. (b) T_c vs in-plane lattice contraction $-\Delta a/a_0$. (c) shows an expanded view of the low-doping region of (b). Experimental data are shown with symbols: $MgB_{2-x}Be_x$ (●), $Mg_{1-x}Al_xB_2$ (□), and $MgB_{2-x}C_x$ (○). Results of high-pressure measurement for pristine MgB_2 are shown for comparison (dashed lines), based on the experimental results below 1 GPa (Ref. 13). Solid and dash-dotted lines are guides for the eye.

III. RESULT AND DISCUSSION

In Fig. 3, we summarize the XRD and T_c results. The upper panel shows the lattice constants a and c. T_c and ΔT_c are shown in the lower panel. With Be doping, a decreases while c increases. Note that the change in c ($\sim$3.3%) is much larger than that in a ($\sim$0.7%). The transition temperature T_c decreases but ΔT_c shows a maximum near $x=0.3$. This is an interesting result, because normally the superconducting transition becomes broader with random substitutions. We associate this anomalous behavior of ΔT_c with the structural data: we note that the (002) reflection is the most broad at $x=0.3$ in Fig. 1(b), which indicates considerable distribution in the c value, possibly due to the two stable phases at $x=0$ and $x=0.6$. This effect may increase ΔT_c at intermediate x values. Considering the drastic change of T_c, the transition width will be more meaningful when it is nor-

malized with T_c. As shown with open squares, the ratio $\Delta T_c/T_c$ increases with x.

Now let us consider the T_c change. To see a possible correlation of T_c with lattice parameters, we first plot T_c vs c in Fig. 4(a). Our results for $MgB_{2-x}Be_x$ are shown as solid circles. For comparison, the results for $Mg_{1-x}Al_xB_2$ (open squares) (Ref. 7) and $MgB_{2-x}C_x$ (open circles) (Ref. 8) are also shown. In $MgB_{2-x}Be_x$, c expands with the substitution while it contracts in $Mg_{1-x}Al_xB_2$. For $MgB_{2-x}C_x$, c remains almost unchanged. For all these three different cases, T_c decreases and there is no correlation between T_c and c. This indicates that the inter layer distance is not directly related to T_c.

Next, we examine the T_c vs a relation in Fig. 4(b). For all samples, a shrinks with the substitutions. Along with the a decrease, T_c decreases linearly. With further contraction, sudden drops are found for $MgB_{2-x}Be_x$ and $Mg_{1-x}Al_xB_2$. This indicates some abrupt changes in the samples, for example structural instability like buckling or ordering in the plane. It is useful to compare the linear T_c decrease with the result of high-pressure experiments on pristine MgB_2 (dashed line): As external pressure is applied, the lattice is compressed and T_c is found to decrease.[13] [The dashed line in Fig. 4(a) represents the pressure result for c compression.] Note that the T_c decrease in substituted compounds is similar to the pressure line when the contraction ($-\Delta a/a_0$) is small.

In Fig. 4(c), we examine the low-contraction region more closely. Note that the data of the two compounds (Be, and Al substituted) fall nearly on the same line (see the solid guide line). It is interesting that the T_c change occurs in the same direction (decrease) for both electron [Al (Ref. 16)] and hole [Be (Ref. 10)] doping. In fact, such a behavior is predicted theoretically by An and Pickett[4]: their band calculation for MgB_2 shows that the in-plane σ band is highly 2D like and the DOS is nearly constant with energy. In this case, the Fermi level shift due to carrier doping will not affect T_c. Our observation is consistent with this prediction.

Our results suggest that the a contraction plays the key role in the observed T_c decrease. According to the BCS analysis of MgB_2,[17] the shrinkage in a leads to a decrease in the density of states (DOS), an increase in the phonon frequency, and a decrease in the electron-phonon coupling. As a result, T_c decreases.[14,15,18] Note that for Al- and Be-substituted samples, T_c decreases somewhat faster than the pressure line, suggesting that some additional effects such as, for example, structural randomness arise by the substitution. It is interesting that in $MgB_{2-x}C_x$, the slope is close to the pressure line, suggesting that the additional effects are minimal.[19] Our observation points to a possible T_c increase if a could be expanded.[20] In fact, Medvedeva *et al.* predicted that higher T_c may be obtained in lattice-expanded cases such as the hypothetical CaB_2.[21]

It is interesting to compare our results with the theoretical prediction on $MgB_{2-x}Be_x$ by Mehl *et al.*[11] According to their calculation, the lattice constant a increases with x, opposite to our observation. At this point, it is not clear where the discrepancy arises from. As one possibility, we speculate that Be substituted in the B plane may actually exist in a partially ionic state rather than in a perfect covalent state. In this case, the Be radius is smaller than its covalent radius, which can result in the in-plane contraction.[22]

IV. CONCLUSION

In this work, we studied the structural and superconducting properties of $MgB_{2-x}Be_x$ ($x=0$, 0.2, 0.3, 0.4, and 0.6). In-plane and interplane lattice constants were found to decrease and increase respectively with Be substitution. While T_c decreases with x monotonically, ΔT_c shows a maximum at $x=0.3$. From our results and other substitution studies (Al and C substitution), we found that the T_c change is correlated with the in-plane contraction and is independent of the carrier doping. This is consistent with the 2D nature of the σ band.

ACKNOWLEDGMENTS

This work was supported by Univ. of Seoul research fund (year 2000), by KRF-99-041-D00185 and by the KOSEF through the CSCMR. Work at POSTECH was supported by the Creative Research Initiatives of the Korean Ministry of Science and Technology.

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