Structural and superconducting properties of MgB$_{2-x}$Be$_x$

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We prepared MgB$_{2-x}$Be$_x$ ($x = 0, 0.2, 0.3, 0.4, 0.6$) samples where B is substituted with Be. MgB$_2$ structure is maintained up to $x = 0.6$. In-plane and inter-plane lattice constants were found to decrease and increase, respectively. 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$_x$B$_2$ and MgB$_{2-x}$C$_x$. Implication of this work is discussed in terms of the 2D nature of $\sigma$-band.

I. INTRODUCTION

The recent discovery of superconductivity in MgB$_2$ at $T_c = 39$ K has drawn enormous attention in its structural and electrical properties. The borons form the graphitic planes and magnesiums supply charges in the planes. The resulting carriers are holes in the $\sigma$-band. Most theoretical works suggest that coupling of the $\sigma$-hole with B-plane phonon is the key ingredient of the superconductivity in this compound. This phonon mediated BCS mechanism is consistent with the boron isotope effect.

There have been many attempts to change $T_c$ through chemical substitution in Mg- or B-sites. For example, Al-substitution on Mg-site and C-substitution on the boron plane are reported. Such chemical substitutions change physical quantities of the system such as hole density, lattice constants, etc. However, there is no detailed understanding on 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. With this substitution, the in-plane B-B distance decreases while the inter-plane distance increases. Our thermopower measurement showed that $\sigma$-hole increases with Be, as reported in the independent paper. 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 2D nature of the $\sigma$-band.

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 two hours at 850 °C under 20 atm. of high purity argon atmosphere.

X-ray diffraction (XRD) $\theta$$-\phi$ 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 the AlB$_2$-type patterns. Also, minor impurity phases such as MgO and BeO are found as indicated by $\nabla$ 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 (002) and (110) reflections are shown in expanded scales. As $x$ increases, (002) reflection shifts to the lower angle while (110) reflection moves to the opposite direction. This indicates that the in-plane lattice constant $a$ decreases and the inter-plane distance $c$ increases with $x$. To obtain the lattice parameters, we performed refinement analysis using the RIETAN-2000 program and used MgO and BeO as internal standards.

In order to study superconducting property, dc magnetization was measured using a dc SQUID magnetometer (Quantum Design). Figure 2 shows 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 $\Delta T_c$ was determined from 10 $\sim$ 90 % the transition.
III. RESULT AND DISCUSSION

In figure 3, we summarize the XRD and $T_c$ results. The upper panel shows the lattice constants $a$ and $c$, $T_c$ and $\Delta T_c$ 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 $\Delta T_c$ shows 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 $\Delta T_c$ 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 $c$ value, possibly due to the two stable phases at $x = 0$ and $x = 0.6$. This effect may increase $\Delta T_c$ at the intermediate $x$ values. Considering the drastic change of $T_c$, the transition width will be more meaningful when it is normalized 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$_x$B$_2$ (open squares) and MgB$_{2-x}$C$_x$ (open circles) are also shown. In MgB$_{2-x}$Be$_x$, $c$ expands with the substitution while it contracts in Mg$_{1-x}$Al$_x$B$_2$. 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 with $T_c$.

Next, we examine $T_c$ vs. $a$ relation in Fig. 4(b). For all the 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$_x$B$_2$. 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 experiment on pristine MgB$_2$ (dashed line): As external pressure is applied, the lattice is compressed and $T_c$ is found to decrease. (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) and hole (Be) doping. In fact, such a behavior is predicted theoretically by An et al. their band calculation for MgB$_2$ shows that the in-plane $\sigma$-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$_2$, the shrinkage in $a$ leads to decrease in the DOS, increase in the phonon frequency, and decrease in the electron-phonon coupling. As a result, $T_c$ decreases. 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. Our observation points to possible $T_c$ increase if $a$ could be expanded. In fact, Medvedev et al. predicted that higher $T_c$ may be obtained in lattice expanded case such as the hypothetical CaB$_2$.

It is interesting to compare our results with the theoretical prediction on MgB$_{2-x}$Be$_x$ by Mehl et al. 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 arise from. As one possibility, we speculate that Be substituted in the B plane may actually exist in partially ionic state rather than in prefect covalent state. In this case, Be radius is smaller than its covalent radius, which can result in the in-plane contraction.

IV. CONCLUSION

In this work, we studied structural and superconducting properties of MgB$_{2-x}$Be$_x$ ($x = 0, 0.2, 0.3, 0.4, 0.6$). In-plane and inter-plane lattice constants were found to increase and decrease respectively with Be-substitution. While $T_c$ decreases with $x$ monotonically, $\Delta T_c$ shows 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 $\sigma$-band.

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\[ T_c \] decreases with pressure at a slope \( \frac{\partial T_c}{\partial P} = -1.6 \text{ K/GPa} \) up to 1 GPa. Meanwhile, x-ray diffraction results by Goncharov et al. showed that lattice constant changes with pressure at a rate of \( \frac{\partial a}{\partial P} = -4.3 \text{ nm/GPa} \) and \( \frac{\partial c}{\partial P} = -8.6 \text{ nm/GPa} \) up to 12 GPa.

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