Thermoelectric power of MgB$_{2-x}$Be$_x$

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We investigated thermoelectric power $S(T)$ of MgB$_{2-x}$Be$_x$ ($x = 0, 0.2, 0.3, 0.4, \text{and} 0.6$). $S(T)$ decreases systematically with $x$, suggesting that the hole density increases. Our band calculation shows that the increase occurs in the $\sigma$-band. With the hole-doping, $T_c$ decreases. Implication of this phenomenon is discussed within the BCS framework. While the Mott formula explains only the linear part of $S(T)$ at low temperature, incorporation of electron-phonon interaction enables us to explain $S(T)$ over wide temperature range including the anomalous behavior at high temperature.

I. INTRODUCTION

Since the recent discovery of superconductivity in MgB$_2$, both theoretical and experimental efforts have been made to understand its structural and electrical properties. Most theoretical works suggest that coupling of the $\sigma$-hole with B-plane phonon is the key ingredient of the superconductivity. Boron isotope effect and other experimental data showed that the material is in the intermediate or strong BCS coupling regime ($\lambda = 0.7 \sim 1$).

Chemical substitution experiment has drawn much attention due to the possibility of obtaining higher superconducting transition temperature $T_c$. In general, by replacing Mg- or B-sites with other elements, physical parameters such as lattice constants and carrier density change. Therefore, study of $T_c$ shift in well-controlled substitution samples provides a chance to understand the superconductivity in detail. For the Mg-site substitution, several compounds such as Mg$_{1-x}$Al$_x$B$_2$ have been studied. For the B-site, C- and Be-substitutions have been reported.

It is important to know how these substitutions change the carrier density and how the change is related with $T_c$ shift. Thermoelectric power (TEP) measurement is a useful probe of the carrier density. For example, TEP experiment on Mg$_{1-x}$Al$_x$B$_2$ showed that the Al-substitution dopes electrons. Theoretical calculation on Mg$_{1-x}$Al$_x$B$_2$ suggested that the doping occurs largely in the $\sigma$-hole pocket. In the present paper, we report our results of TEP measurement and theoretical band calculation on MgB$_{2-x}$Be$_x$ samples where B is substituted with Be. In an earlier paper, we showed that in this compound, the MgB$_2$ phase is maintained up to $x = 0.6$. Also the lattice constants and $T_c$ changed systematically with Be-substitution. We find that the TEP decreases with $x$, opposite to that in Mg$_{1-x}$Al$_x$B$_2$, which suggests that hole is doped. Also, changes in the band structure indicate that the hole doping occurs mostly in the $\sigma$-band. Thus, Be-substitution brings about hole-doping into the boron plane. We consider the consequence of this effect on the transition temperature and argue that the hole density change plays only a second role in the $T_c$ shift.

Meanwhile, it is well known now that the temperature dependence of TEP is one of the unconventional features of MgB$_2$: At low $T$, TEP is linear in $T$ which is normal for most metals, but crosses over to a sublinear behavior as $T$ increases. There have been many interpretations of this phenomenon. We find that the crossover exhibits a systematic change with the Be-substitution. Further, we show that TEP in the whole $T$ region is explained by a single model function in which the electron-phonon interaction is explicitly taken into account.

II. EXPERIMENTAL

Polycrystalline samples used in this experiment were synthesized by a powder metallurgical technique using a high pressure furnace. Starting materials are fine powders (-325 mesh) of Mg (99.8%, Alfa Aesar), amorphous B (99.99%, Alfa Aesar), and Be (99.+, Alfa Aesar). Stoichiometric amounts of powders are mixed and pelletized. The pellets are placed in a tungsten vessel with a close-fitting cap, reacted two hour at 850 °C under 20 atm. of high purity argon atmosphere.

In MgB$_{2-x}$Be$_x$, the MgB$_2$ phase is maintained up to $x = 0.6$. Their structural and superconducting properties were reported elsewhere. We found that as a function of Be-substitution, lattice parameters show decreasing $a$-
and increasing $c$-values, and transition temperature $T_c$ decreases as summarized in Table I.

For TEP measurements, bar-shaped samples (with dimensions of $\sim 4 \times 0.5 \times 0.1 \text{ mm}^3$) were mounted on two resistive heaters. Gold wires were used for thermoelectric potential leads. Chromel-constantan thermocouples were used for the temperature gradient measurement. Sample ends and thermocouple beads were glued to the heater blocks by Stycast epoxy. In our measurement, thermopower from the contact wires was carefully calibrated.

### III. RESULT AND DISCUSSION

Figure 1 shows thermoelectric power $S(T)$ of MgB$_{2-x}$Be$_x$ samples. For MgB$_2$ ($x = 0$), $S(T)$ is linear in $T$ at low temperature above $T_c$. At higher $T$ (> 150 K), it crosses over to a sub-linear behavior. These features together with the large jump at $T_c$ ($\sim 1.4 \text{ } \mu \text{V/K}$) are consistent with the earlier reports. As boron is substituted with Be, the linear slope decreases. Also the crossover temperature is lowered. At $x = 0.6$, $S(T)$ changes sign at a low temperature.

Thermal diffusion of carriers gives rise to the linear-in-$T$ behavior in $S(T)$ at low temperatures. Kinetic transport theory shows that $S(T) = \frac{\pi^2 k_B^2 T}{3e} \sigma(E)/\sigma(E)$, where the dc-conductivity $\sigma(E)$ and its derivative $\sigma'(E)$ are calculated at the Fermi energy. In a single parabolic band system, it is approximated to the Mott formula:

$$S(T) = X_b T = \pm \left( \frac{\pi^2 k_B^2}{3e E_F} \right) T,$$

where $k_B$ is the Boltzmann constant, $\pm$ corresponds to the carrier sign, and $E_F$ is the Fermi energy relative to the band maximum (or minimum). However, MgB$_2$ is a multi band system where $\sigma$- and $\pi$-bands coexist. Also the Fermi surface is not spherical. Thus, Eq. (1) can be applied only approximately here. The positive value of $X_b$ in pristine MgB$_2$ suggests that the dominant carrier is hole. The decrease of $X_b$ with $x$ suggests that the hole density increases. To obtain $X_b$, we fit the linear part of $S(T)$ with Eq. (1) as shown by the dashed lines. Since the data are not extrapolated to zero, vertical shifts were needed in the fit.

To understand the behavior of $X_b$ more quantitatively, we calculated band structures of MgB$_{2-x}$Be$_x$ as shown in Fig. 2. Here we used the local density approximation (LDA) with the linearized augmented plane wave method. To account for the random substitution of Be, the virtual crystal approximation (VCA) was employed. Details of the calculation method were described by Mehl et al. In current work, the experimental lattice parameters in Table I were used. Four bands contribute to the Fermi surfaces: two $\sigma$-bands with B $p_{x,y}$ character give the 2D hole-type cylinders around the Γ-A line and two $\pi$-bands form the 3D honeycomb tubular networks. The latter consists of one electron-type at the $H$-point and another hole-type at the $K$-point. Note that the most prominent change with $x$ is the hole increase in the $\sigma$-bands. Change in the $\pi$-bands is relatively small. These results tell us that the Be-substitution does hole into the $\sigma$-bands.

It is interesting to note that $T_c$ decreases with the hole-doping, similarly to the electron-doped Mg$_{1-x}$Al$_x$B$_2$. Theoretical studies show that the superconductivity arise from the $\sigma$-band holes coupled with the B-plane phonons. $T_c$ of MgB$_2$ can be produced from the McMillan formula using the coupling constant $\lambda = 1.01$ and the Coulomb pseudopotential $\mu^* = 0.13$. Here $\lambda$ is proportional to the density of state (DOS) of the $\sigma$-bands at the Fermi energy, $N_h(E_F)$. From our band calculation, we find that $N_h(E_F) = 0.22$ (eV$^{-1}$ per cell) at $x = 0$ and $N_h(E_F) = 0.24$ (eV$^{-1}$ per cell) at $x = 0.6$. (The $\sigma$-bands are highly 2D-like and the DOS increases only slightly with hole doping.) Then $\lambda$ will increase proportionally to become 1.09 at $x = 0.6$, if we assume the other parameters determining $\lambda$ do not change. (see for example Eq. (3) of Ref. 3) This yields $T_c = 45$ K, which is in sharp contrast with the observed $T_c$ decrease. This suggests that the other parameters change significantly with the substitution and their effects overcome the $N_h(E_F)$ contribution. In another paper, we dealt with this issue and showed that the lattice constant change is the primary cause of the reduced superconductivity.

Now we consider the unusual behavior of $S(T)$, i.e., the deviation from the linear dependence at high $T$. In previous works, it has been attributed to the minor carrier contribution and to the phonon-drag effect. Here, we consider effect of electron-phonon interaction on $S(T)$. According to Kaiser, the interaction contributes to enhance the TEP through modifying the carrier mass and thus the thermal diffusion. Taking this effect into account, Eq. (1) is rewritten as

$$S(T) = [1 + \lambda \bar{\lambda}_s(T)] X_b T,$$

where $X_b$ is the slope in Eq. (1), $\lambda$ is the electron-phonon coupling constant, and $\bar{\lambda}_s(T)$ is a function which represents the $T$-dependent thermopower enhancement:

$$\bar{\lambda}_s(T) = \int_0^\infty d\omega \frac{\alpha^2 F(\omega)}{\omega} G_s \left( \frac{\hbar \omega}{k_B T} \right).$$

Here, the normalized Eliashberg function $\alpha^2 F(\omega)$ consists of the phonon density of states $F(\omega)$ and the coupling constant $\alpha$. $G_s(\hbar \omega/k_B T)$ is a function associated with thermal population of phonons. For MgB$_2$, we calculated $\bar{\lambda}_s(T)$ using $\alpha^2 F(\omega)$ reported by Liu et al. and fit the data with Eq. (2). Here we used $\lambda$ and $X_b$ as fitting parameters. For $x > 0$, the Be-substitution into the B-plane will change, probably significantly, the phonon structure. Thus $\alpha$ and $F(\omega)$ will depend on $x$. Since they are not known, we took the values of MgB$_2$ in
calculating $\lambda_s(T)$. Thus $\lambda$ and $X_b$ we estimate for $x > 0$ samples are under large uncertainties.

Figure 3(a) shows the fit for MgB$_2$ (solid line). The bare diffusion part ($X_bT$) and the enhancement part ($\lambda_s(T) \times X_bT$) are represented with dashed and dash-dotted line, respectively. The latter has a broad maximum at $T \sim 215$ K. Inset shows calculated behavior at higher temperature. Fig. 3(b) shows the fitting results for MgB$_{2-x}$Be$_x$. Note that the fit is reasonable except the small deviation for $x = 0.3$.

In Fig. 4, we summarize the linear slope $X_b$ obtained from our analyses. The fitting results using Eq. (1) and Eq. (2) are shown with the filled-circles and the triangles, respectively. Note that $X_b$ from the modified model is smaller than that from the bare diffusion model. This is due to the enhancement effect contained in Eq. (2). Also, we estimated $X_b$ from the band calculation (the dash-dotted line). Here the $F_{\sigma}$ in Eq. (1) was taken from the $\sigma$-hole bands, assuming contributions from the other bands are negligible. The band calculation result is closer to the modified model result at low doping region, $x \leq 0.3$, which supports the importance of the electron-phonon interaction effect. At $x = 0.3$, $X_b$ from the two fits exhibit a sudden drop. This drop may be related to the observed structural change in the same composition. The incomplete agreement between the fit result and the band calculation result may come from complex effects not included in this work such as the multi-band contributions and anisotropic transport.

Regarding the electron-phonon coupling constant (EPC), we obtain $\lambda = 0.90$ for MgB$_2$. This is in good agreement with the earlier reports of 0.7 $\sim$ 1.0. For $x > 0$, $\lambda$ increases to 0.98 ($x = 0.2$), 1.31 ($x = 0.3$), 1.34 ($x = 0.4$), and 1.47 ($x = 0.6$). This result is quite unusual because, as $T_c$ decreases with $x$, $\lambda$ is expected to decrease. Recent evidences show that MgB$_2$ has two gaps. In this case, EPC from transport measurement ($= \lambda_{tr}$) is different from the EPC which determines the superconducting $T_c$ ($= \lambda_{sc}$). Thus, the increase of TEP $\lambda$ ($= \lambda_{tr}$) does not necessarily contradict with the $T_c$ decrease. One should also keep in mind that the increase of TEP $\lambda$ may be simply an erroneous effect that arise from the uncertainties in $\alpha$ and $F(\omega)$ for $x > 0$ we mentioned above.

Now, let us consider the sign change in $S(T)$ of $x = 0.6$. Sign change in TEP is widely observed in many alloyed systems, for example, Ag-Au alloy$^{21}$ YBa$_2$Cu$_3$O$_{7-\delta}$, NbN$^{22}$, etc. In YBa$_2$Cu$_3$O$_{7-\delta}$, the change is observed as oxygen deficiency $\delta$ increases. In NbN$_x$, $S(T)$ is composed of the diffusive (positive in sign) and phonon-drag terms (negative in sign). At high $T$, the former is dominant while the latter prevails at low $T$. In the intermediate $T$, sign change occurs. It is tempting to interpret our observation similarly: the negative $S(T)$ may correspond to the phonon-drag effect. However, note that in the pristine MgB$_2$, the phonon-drag feature is not observed. Further, the feature, if any, should be suppressed with Be-substitution because the phonon-drag generally disappears as randomness is increased. Origin of the sign change is thus remains for future study.

IV. CONCLUSION

From the TEP measurement and band structure calculation on MgB$_{2-x}$Be$_x$ ($x = 0.2$, 0.3, 0.4, and 0.6), we found that the hole density increases with $x$ in the $\sigma$-bands. Thus, the Be-substitution dopes hole into the boron plane. The fact that $T_c$ shifts in the same direction (lowering) as the electron-doped case suggests that carrier doping is not the primary route to control the transition temperature in MgB$_2$. This result is consistent with the 2D nature of the $\sigma$-bands. Further, we showed that the anomalous behavior of TEP at high temperature can be explained by taking the electron-phonon interaction effect into account.

ACKNOWLEDGMENTS

This work was supported by KRF-99-041-D00185 and by the KOSEF through the CSCMR.

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FIG. 1. Thermoelectric power $S(T)$ of MgB$_{2-x}$Be$_x$ ($x = 0$, 0.2, 0.3, 0.4, and 0.6). Dashed lines represent linear fits to the data.

FIG. 2. LDA virtual crystal band structures of MgB$_{2-x}$Be$_x$ for $x = 0$ (top), 0.3 (middle), and 0.6 (bottom). The experimental lattice parameters are used. The horizontal reference at 0 denotes $E_F$.

FIG. 3. (a) Thermopower data of MgB$_2$ (open circles) and fit with the modified diffusion model (solid line). Dashed- and dash-dotted lines represent the diffusion and enhancement part, respectively. Inset shows the calculated behavior at higher temperature. (b) TEP data of MgB$_{2-x}$Be$_x$ (open circles) and the modified diffusion fit (solid lines).

FIG. 4. The linear slope $X_b$ of MgB$_{2-x}$Be$_x$. • : determined from the Eq. (1). ▲ : from the modified diffusive fit in Eq. (2). Theoretical results from the band calculations are shown with dash-dotted line. Solid lines are for eye-guide.

TABLE I. Physical properties of MgB$_{2-x}$Be$_x$. Transition width $\Delta T_c$ is determined from 10-90% transition.

| $x$  | $a$ (Å) | $c$ (Å) | $T_c$ (K) | $\Delta T_c$ (K) |
|------|---------|---------|-----------|------------------|
| 0    | 3.084   | 3.322   | 38.4      | 1.2              |
| 0.2  | 3.078   | 3.340   | 36.0      | 2.5              |
| 0.3  | 3.073   | 3.397   | 33.0      | 5.5              |
| 0.4  | 3.073   | 3.632   | 21.0      | 4.0              |
| 0.6  | 3.062   | 3.639   | 8.4       | 1.5              |
The graph shows the Seebeck coefficient ($S$) as a function of temperature ($T$) for MgB$_{2-x}$Be$_x$ with $x = 0$. The values of $S$ are given in $\mu$V/K, and the graph includes curves for different values of $x$. Arrows indicate specific points of interest on the graph.
