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, 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 σ 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.

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I. INTRODUCTION

Since the recent discovery of superconductivity in MgB_2,[1] both theoretical and experimental efforts have been made to understand its structural and electrical properties. Most theoretical works suggest that coupling of the σ hole with B-plane phonon is the key ingredient of the superconductivity.[2–4] Boron isotope effect[5] and other experimental data showed that the material is in the intermediate or strong BCS coupling regiem ($\lambda=0.7$–1).[6–12]

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 $Mg_{1-x}Al_xB_2$ have been studied.[6,13–15] For the B site, C and Be substitutions have been reported.[16,17]

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 $Mg_{1-x}Al_xB_2$ showed that the Al substitution dopes electrons.[18] Theoretical calculation on $Mg_{1-x}Al_xB_2$ suggested that the doping occurs largely in the σ-hole pocket.[10] 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.[17] We find that the TEP decreases with x, opposite to that in $Mg_{1-x}Al_xB_2$, which suggests that hole is doped. Also, changes in the band structure indicate that the hole doping occurs mostly in the σ 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.[18–20] We find that the crossover exhibits a systematic change with the Be substitution. Furthur, we show that TEP in the whole T region is explained by a single model function in which the electron-phonon interaction is explicitely 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.[17] 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 dimen-

TABLE I. Physical properties of $MgB_{2-x}Be_x$. Transition width ΔT_c is determined from 10–90 % transition (Ref. 17).

x	a (Å)	c (Å)	T_c (K)	ΔT_c (K)
0	3.084	3.522	38.4	1.2
0.2	3.078	3.540	36.0	2.5
0.3	3.073	3.597	33.0	5.5
0.4	3.073	3.632	21.0	4.0
0.6	3.062	3.639	8.4	1.5

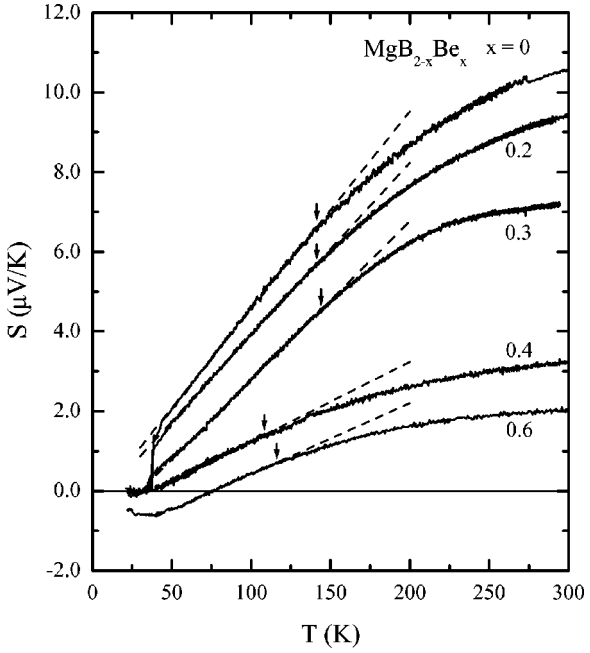

FIG. 1. Themoelectric power $S(T)$ of $MgB_{2-x}Be_x$ ($x=0$, 0.2, 0.3, 0.4, and 0.6). Dashed lines represent linear fits to the data.

sions of $\sim 4\times 0.5\times 0.1$ 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 sublinear behavior. These features together with the large jump at T_c (~ 1.4 μV/K) are consistent with the earlier reports.[18,19] 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 $S(T)=(\pi^2 k_B^2 T/3e)\sigma'(E)/\sigma(E)$, where the dc conductivity $\sigma(E)$ and its derivative $\sigma'(E)$ are calculated at the Fermi energy.[21] In a single parabolic band system, it is approximated to the Mott formula[21,22]

$$S(T)=X_b T=\pm\left(\frac{\pi^2 k_B^2}{3eE_F}\right)T, \tag{1}$$

where k_B is the Boltzman 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 multiband system where σ and π 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.[23]

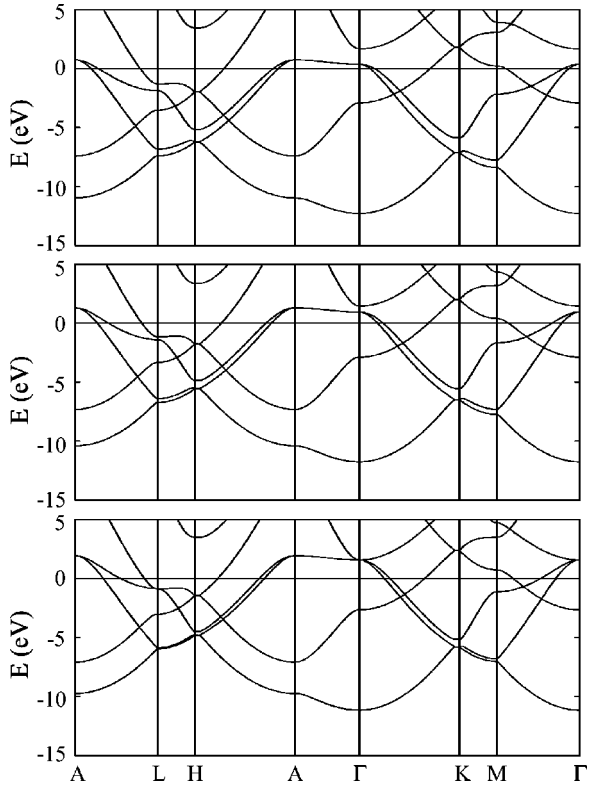

FIG. 2. LDA virtual crystal band structures of $MgB_{2-x}Be_x$ for $x=0$ (top), 0.3 (middle), and 0.6 (bottom). The experimental lattice parameters are used. The horizontal reference at 0 denotes E_F.

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.*[24] In current work, the experimental lattice parameters in Table I were used. Four bands contribute to the Fermi surfaces: two σ bands with B $p_{x,y}$ character give the 2D hole-type cylinders around the Γ-A line and two π-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 σ bands. Change in the π bands is relatively small. These results tell us that the Be substitution dopes hole into the σ bands.

It is interesting to note that T_c decreases with the hole doping, similarly to the electron-doped $Mg_{1-x}Al_xB_2$. Theoretical studies show that the superconductivity arise from the σ-band holes coupled with the B-plane phonons. $T_c=39$ K in MgB_2 can be produced from the McMillan formular using the coupling constant $\lambda=1.01$ and the Coulomb pseudopotential $\mu^*=0.13$.[3,4] Here λ is proportional to the density of state (DOS) of the σ 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 σ bands are highly 2D-like and the DOS increases only slightly with hole doping). Then λ will increase proportionally to become 1.09 at $x=0.6$, if we assume the other parameters determining λ 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,[17] 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,[18] the thermally activated transport,[19] and to the phonon-drag effect.[20] Here, we consider the 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.[25] Taking this effect into account, Eq. (1) is rewritten as

$$S(T)=[1+\lambda\overline{\lambda_s}(T)]X_bT, \tag{2}$$

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

$$\overline{\lambda_s}(T)=\int_0^\infty d\omega\frac{\alpha^2F(\omega)}{\omega}G_s\left(\frac{\hbar\omega}{k_BT}\right). \tag{3}$$

Here, the normalized Eliashberg function $\alpha^2F(\omega)$ consists of the phonon density of states $F(\omega)$ and the coupling constant α. $G_s(\hbar\omega/k_BT)$ is a function associated with thermal population of phonons. For MgB_2, we calculated $\overline{\lambda_s}(T)$ using $\alpha^2F(\omega)$ reported by Liu *et al.*[4,26] and fit the data with Eq. (2). Here we used λ and X_b as fitting parameters. For $x>0$, the Be substitution into the B plane will change, probably significantly, the phonon structure. Thus α and $F(\omega)$ will depend on x. Since they are not known, we took the values of MgB_2 in calculating $\overline{\lambda_s}(T)$. Thus λ 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 [$\lambda\overline{\lambda_s}(T)\times X_bT$] are represented with dashed and dash-dotted lines, respectively. The latter has a broad maximum at $T\sim215$ K. The inset shows calculated behavior at higher temperature. Figure 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 Eqs. (1) and (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 E_F in Eq. (1) was taken from the σ-hole bands, assuming contributions from the other bands are negligible.[27] The band calculation result is closer to the modified model result at low doping region $x\leqq0.3$, 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.[17] 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 multiband contributions and anisotropic transport.

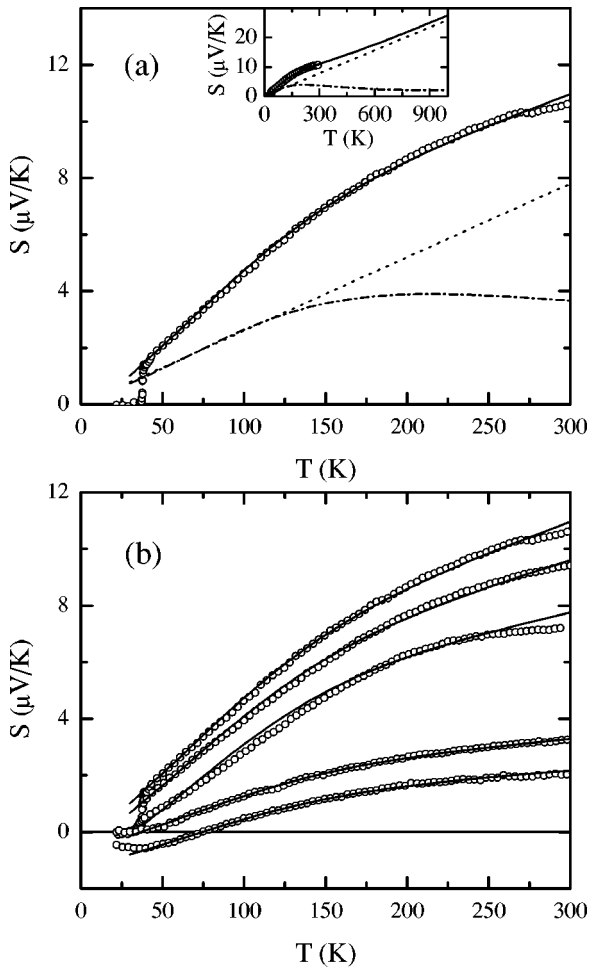

FIG. 3. (a) Thermopower data of MgB_2 (open circles) and fit with the modified diffusion model (solid line). Dashed- and dash-dotted lines represent the diffusion and enhancement part, respectively. The inset shows the calculated behavior at higher temperature. (b) TEP data of $MgB_{2-x}Be_x$ (open circles) and the modified diffusion fit (solid lines).

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 0.7–1.0.[2–4,8] For $x>0$, λ increases to 0.98($x=0.2$), 1.31(0.3), 1.34(0.4), 1.47(0.6). This result is quite unusual because, as T_c decreases with x, λ is expected to decrease. Recently, 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 ($=\lambda_{SC}$).[4] Thus, the increase of TEP λ ($=\lambda_{tr}$) does not necessarily contradict with the T_c de-

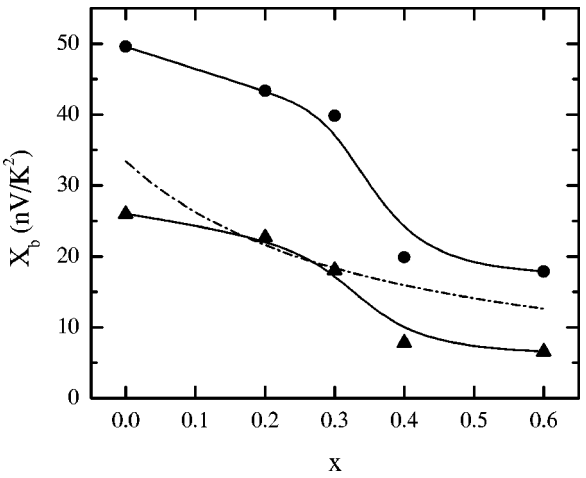

FIG. 4. The linear slope X_b of $MgB_{2-x}Be_x$. ● : determined from Eq. (1). ▲ : from the modified diffusive fit in Eq. (2). Theoretical results from the band calculations are shown with dash-dotted line. Solid lines are for guides for the eye.

crease. One should also keep in mind that the increase of TEP λ may be simply an errorneous effect that arises from the uncertainties in α and $F(\omega)$ for $x>0$ we mentioned above.[28]

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] $YBa_2Cu_3O_{7-\delta}$,[29] NbN_x,[30] etc. In $YBa_2Cu_3O_{7-\delta}$, the change is observed as oxygen deficiency δ 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.[21] 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. Furthur, 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 thus remains for future study.

IV. CONCLUSION

From the TEP measurement and band structure calculation on $MgB_{2-x}Be_x$ ($x=0$, 0.2, 0.3, 0.4, and 0.6), we found that the hole density increases with x in the σ 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 σ bands. Furthur, we showed that the anomalous behavior of TEP at high temperature can be explained by taking the electron-phonon interaction effect into account.

ACKNOWLEDGMENTS

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[27] The π-hole and the π-electron bands have similar 3D structure. Thus, their contributions to $S(T)$ may partly cancel each other.

[28] According to Kaiser, $S(T)$ enhancement is also possible by other mechanisms such as the velocity and time renormalization or the Nielson-Taylor higher-order diagram effects in the alloyed system (Ref. 25).

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