Pressure dependent thermoelectric power of MgB\textsubscript{2} superconductor

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We have measured temperature dependence of thermoelectric power (TEP) on MgB\textsubscript{2} superconductor under hydrostatic pressure. The sign and temperature dependence of TEP shows metallic hole carriers are dominant with activation type contribution at higher temperature. TEP increases with pressure while \( T_c \) decrease with ratio \(-0.136 \text{ K/kbar}\). The data are discussed in consideration of carriers from different bands and anisotropy of compressibility.

I. INTRODUCTION

The mechanism of superconductivity in MgB\textsubscript{2} superconductor has been of a great interest since its discovery. The conventional BCS type superconductivity is suggested from theoretical approaches. In this model, the light mass of boron in MgB\textsubscript{2} was attributed to have a strong electron-phonon coupling which enhances \( T_c \) of this material. On the other hand, the hole superconductivity model was also proposed where the superconductivity is driven by undressing of hole carriers.

Experimentally, various experiments have been done on this new superconductor and some of them could be used as a series of test for the theoretical models. Apparently, the BCS type superconductivity is supported by the experimental results of boron isotope effect, heat capacity, BCS like superconducting gap and high pressure measurement. But the hole superconductivity model also accounts for the observed results by itself or with some assumptions.

\( T_c \) of BCS superconductor can be expressed as McMillan formula

\[ T_c \sim \omega \exp(-1/\lambda), \]

where \( \omega \) is the phonon frequency and \( \lambda \) is the electron-phonon coupling constant. The pressure effect on \( T_c \) is manifest from \( \lambda \) by the relation of \( \lambda = N(\epsilon_F) < I^2 > /M < \omega^2 > \), where \( N(\epsilon_F) \) is the density of states at the Fermi level and \( < I^2 > \) is the electronic matrix element. By applying pressure, \( < \omega^2 > \) increases due to lattice stiffening and \( N(\epsilon_F) \) decreases as the bandwidth increases. In the hole superconductivity model, \( T_c \) was expected to increase with pressure if the pressure is to decrease in-plane boron-boron distance. Hall effect measurement under pressure was suggested to be a crucial test for this model.

Thermoelectric power (TEP) measurements under pressure will be a good probe to reveal the mechanism of superconductivity and to investigate transport properties in the normal state. By applying pressure, band parameters as well as electron-phonon coupling constant change, which will affect the absolute magnitude and the temperature dependence of TEP. In the simple metallic band model, TEP is proportional to \( N(\epsilon_F) \) or inversely proportional to the Fermi energy.

We report here the results of TEP measurements under hydrostatic pressure. The sign of TEP is positive indicating hole carrier is majority. The temperature dependence is metallic (linear with temperature) below \( \sim 120 \text{ K} \), above which negative contribution begins to appear. The magnitude of TEP increases and \( T_c \) decreases with pressure, which cannot be explained by a simple metallic band model. We tried several models to explain the temperature dependence of TEP at normal state. And then we adapt the models to account for the pressure dependence of TEP and decrease of \( T_c \) under pressure.

II. EXPERIMENTS

Polycrystalline sample used in this experiment was prepared at 950 \( ^\circ \text{C} \) under 3 GPa. The superconducting transition temperature was 38.4 K with transition width of 0.6 K. The bar shape sample (with dimensions of \( 4 \times 0.5 \times 0.1 \text{ mm}^3 \)) was mounted on two resistive heaters. Four gold wires were attached and two of them were used as thermoelectric potential leads for TEP measurements and as current feeding leads for 4-probe resistance measurements. Chromel-constantan thermocouples were used for the temperature gradient measurements. Sample ends and thermocouple beads were glued to the heater blocks by Stycast epoxy. 50:50 mixture of Daphne and Kerosene oil was used as a pressure medium in the self-clamped BeCu pressure cell. The pressure dependence of chromel-constantan thermocouples and gold lead wires were ignored, which are supposed to be very small. At room temperature, it was estimated that the TEP of chromel-constantan thermocouple increase by +0.7\%, and TEP of gold decrease by \(-0.07\mu\text{V/K} \) at 15 kbar. As it will be shown in the following section, the absence of pressure effect on TEP below \( T_c \) justifies our assumption. The detailed measurement set up will be published elsewhere.
III. RESULTS AND DISCUSSION

Fig. 1 shows the temperature dependence of resistivity under different pressure. The inset shows the low temperature expansion around $T_c$. The normal state resistivity and $T_c$ decrease with pressure. $T_c$ was defined as a temperature where the resistance reduces to one-half of the normal state resistance of just above $T_c$. The pressure dependence of conductivity change ratio ($\Delta \sigma / \sigma(1\text{bar})$) and $T_c$ was shown in Fig. 3: $T_c$ decrease with rate $-0.136 \pm 0.004 \text{K/kbar}$ whose value is in well agreement with previous reports.

Fig. 3 shows the temperature dependence of TEP at ambient pressure and under pressures of 14.8, 11.3, 9.2, 6.3 and 3.2 kbar and the inset shows the superconducting transitions. For one pressure of about 6.5 kbar, the temperature was increased from room temperature to 370 K, which is also shown in the same figure. The overall temperature dependence and the magnitude of TEP are very similar with previous reports, in which ambient pressure TEP was measured on the sample prepared without high pressure sintering. TEP is positive in the whole range of temperature and pressure, which indicates the majority carrier is hole as also evidenced by Hall effect measurement. The overall temperature dependence of TEP is universal regardless of pressure, i.e., linear $T$-dependence between $T_c$ and $\sim 120 \text{K}$ and gradual deviation from linear dependence at higher temperature. TEP increases with same curvature and same behavior extends to at least 370 K, the highest temperature in this measurement.

Superconducting transition is also clearly seen in the TEP measurements. Below the transition temperature, small offset of TEP was observed, $\sim -0.1 \mu \text{V/K}$ for 1 bar data and $\sim -0.2 \mu \text{V/K}$ for high pressure data. We believe that they are due to bad calibrations of gold lead wires in this temperature range where the temperature dependence of gold wire changes rapidly due to phonon drag. Nevertheless, the difference of magnitude of TEP below $T_c$ is within the error bars of our measurement setup ($\sim 50 \text{nV/K}$) and pressure independent except 1 bar data.

As for the pressure dependence of TEP, both the room temperature value and the slope of linear $T$-dependence increase with pressure. In our measurement set up, the pressure was initially increased from the ambient pressure to the highest value and the temperature dependence was measured. And then the pressure was released by few kbars followed by temperature dependence measurements. Fig. 4 shows the pressure dependence of TEP at room temperature and the slope of linear $T$-dependence of TEP. The pressure dependence of TEP at room temperature was measured during the initial pressurizing and the following successive temperature dependence measurements. TEP increases almost linearly by applying pressure with rate $+4.35(\pm 0.09) \times 10^{-2} \mu \text{V/kbar}$ at room temperature.

First, let us look into the temperature dependence of TEP. Due to the apparent linear $T$-dependence at the intermediate temperature region, we are tempted to account for the behavior by simple metallic diffusion TEP. In the simple metallic one band model, TEP can be expressed as

$$S = \frac{\pi^2 k_B^2 T}{3e} \left( \frac{N}{n} + \frac{\tau}{\tau_F} \right)$$

where $n$ is the carrier density and $\tau$ is the relaxation time. If we assume the relaxation time is energy independent, the linear $T$-dependence can be explained by above formula. According to the band structure calculations of MgB$_2$, two dimensional $\sigma$ bands and three dimensional $\pi$ bands, which originate from the boron $p_{x,y}$ and $p_z$ orbitals respectively, were shown. The $\sigma$ bands are partially filled with small dispersion along the $\Gamma$-$\Lambda$ line, which can produce large $(\sim N(\epsilon_F)$ from small energy dispersion) and positive (hole carriers) TEP signal. If we apply Eq. 2 to derive $N(\epsilon_F)$ from the observed linear $T$-dependence, $N(\epsilon_F)$ is estimated to be about 1.42 states/eV-carriers at 1 bar and increase to 1.67 states/eV-carriers at 14.8 kbar. According to And Pickett, the density of states of the two dimensional $\sigma$ band is $N(\epsilon_F)_{\sigma}=0.25$ states/eV-cell and the total number of holes for that band is 0.13/cell, which corresponds to 0.25/0.13=1.92 states/eV-\sigma carriers. The discrepancy of this value with the observed value is not surprising, because Eq. 1 is valid for single band and it should be modified when more than one band transport is involved.

When more than one band contributes TEP, total TEP is expressed as

$$S_{\text{tot}} = \frac{\sigma_1 S_1 + \sigma_2 S_2}{\sigma_1 + \sigma_2}$$

where $\sigma_1 (\sigma_2)$ and $S_1 (S_2)$ are conductivity and TEP from band 1 (band 2). If we have metallic hole band (suppose band 1) and metallic electron band (suppose band 2), and if we assume all metallic bands have similar temperature dependence of conductivity, the total TEP will be expressed as $S_{\text{tot}} = A_1 T - A_2 T = (A_1 - A_2) T$. $A_1 (A_2)$ is absolute magnitude of slope of linear $T$-dependence of TEP when TEP of band 1 (band 2) is probed exclusively. Therefore, TEP resulting from mixing of two metallic bands will show linear $T$-dependence again but its sign and magnitude depends on density of states of each bands. $S_{\text{tot}}$ will be positive if $N(\epsilon_F)_{\text{band1}} > N(\epsilon_F)_{\text{band2}}$ and negative in opposite case.

In the band structure calculation, an antibonding $\pi$ band from boron $p_z$ orbitals is supposed to be electron like, which has larger dispersion than the $\sigma$ bands. The anitbonding $\pi$ band will give smaller slope of the linear $T$-dependence with opposite polarity than the value obtained exclusively from the $\sigma$ band.

But when we look into the higher temperature region, which deviates from linear $T$-dependence, the above simple arguments can not explain such behaviors. The
temperature dependence of TEP from the $\sigma$ and the antibonding $\pi$ bands give same linear $T^-$ dependence, whereas the deviation becomes greater as the temperature increases.

The deviation of a linear $T^-$ dependence can be originate from the electron-phonon interaction which was not considered in Eq. 3. The phonon drag is the first candidate, which usually gives peak structure in the temperature dependence between $\theta_D/10$ and $\theta_D/5$, where $\theta_D$ is the Debye temperature. For MgB$_2$ superconductor, $\theta_D$ is estimated about 900 K. But in our results, there seems to be no such effects in the measured temperature range.

The phonon drag effect usually smeared out in the disordered metal, where the mass enhancement effect by electron-phonon interaction emerges in TEP instead. This effect was considered to account for the temperature dependence of high $T_c$ superconductors. TEP with electron-phonon enhancement can be expressed as, $S_{el-ph} = S_0(1+\lambda(T))$, where $S_0$ denotes the bare TEP without enhancement and $\lambda(T)$ is the electron-phonon coupling constant. The bare TEP behavior is recovered at high temperature, since $\lambda(T)$ goes to zero as phonon-phonon interaction dominates. When considering the fact that the TEP shows similar behavior up to 370 K, this effect seems to be less likely in MgB$_2$ superconductor.

Considering the two band model shown in Eq. 3, we can separate high temperature contribution from the total TEP. If we assign band 1 as a metallic TEP showing linear $T^-$ dependence (which comes from hole band and/or electron band), the additional negative contribution (from band 2) can be extracted by subtracting the linear temperature dependence from the observed TEP. We plot $\Delta S(= S(T) - AT)$ versus temperature in Fig. 4, where $A$ is the slope of linear $T^-$ dependence of TEP between $T_c$ and ~120 K.

Two notable features are shown in Fig. 4. The magnitude of $\Delta S$ increases with temperature and pressure, and the deviation begins to occur above same temperature regardless of pressure.

The temperature dependence of $\Delta S$ can be explained by assuming a existence of thermally activated carriers. In the situation where two types of charge carriers are involved; one is metallic and the other should overcome a energy gap $E_g$ to contribute transport, the total TEP can be expressed as,

$$S_{tot} = \frac{\sigma_1 AT + \exp(-E_g/2k_B T)(B + CE_g/2k_B T)}{\sigma_1 + \exp(-E_g/2k_B T)}$$

$$\approx AT + \frac{\exp(-E_g/2k_B T)(B + CE_g/2k_B T)}{\sigma_1}$$

(3)

The approximation is valid when the metallic conductivity is dominant compared to the activation type transport. The fitting was done by fixing $\sigma_1$ as $T^\gamma (n = 0, -1, -2)$ and liberating all other parameters. The best fitting curves are shown in the inset of Fig. 3, where the data were shifted by $-0.25 \mu V/K$ from the lower pressure data one by one. The fitting curves are obtained for temperature independent conductivity ($n=0$) and the fitted parameters are listed in Table. I.

$E_g$ is more or less pressure insensitive while the magnitudes of $B$ and $C$ increases with opposite sign. The increasing negative contribution shown in Fig. 3 seems to come from the increase of fitting parameter $B$. To derive physical properties from the fitting, we speculate the TEP of band 2 follows the TEP of intrinsic semiconductor with band gap $E_g$. TEP of intrinsic semiconductor can be written as

$$S_{semicon.} = \frac{k_B}{e} c \frac{m_e}{m_h}$$

where $c$ is the ratio of the electron to hole mobility ($\mu_e/\mu_h$). Usually when a semiconducting band is dominant in transport, TEP shows $1/T$ dependence and its sign exclusively depends on the mobility ratio. But when other competing bands are metallic bands, the contribution of TEP of semiconducting band decrease upon cooling due to the conductivity weighting and its sign depends on both mobility and effective mass ratio. Comparing Eq. 3 and Eq. 4, we listed the mobility and effective mass ratio in Table. I.

The origin of semiconducting hole carriers is not clear yet. One of the possibilities is that they originate from the lower band of the $\sigma$ bands when the $\sigma$ bands are splitted into two sub-bands due to electron-phonon interaction. It is believed that the $E_{2g}$ mode (in-plane boron-boron displacement) of MgB$_2$ splits the $\sigma$ band and the lower band is pushed down to the Fermi level. If the electron-phonon interaction is so strong, the splitting may push the lower band below the Fermi level, which results in a semiconducting hole band. Usually the $\sigma$ bands are believed to take an important role in the superconductivity of MgB$_2$ superconductor. Therefore, if our speculation is correct, one should consider reduced density of states and stronger electron-phonon coupling constants in theoretical estimation of $T_c$ of this material.

Now, we turn our attention to the pressure effect on normal state TEP and $T_c$. The increase of slope with pressure seems to be in apparent contradiction with McMillan formula because $N(\epsilon_F)$ increases with pressure but $T_c$ decreases. This discrepancy is due to the fact that the measured $N(\epsilon_F)$ from TEP contains contribution from all available bands as mentioned above to explain the magnitude of slope. If the pressure effect is to decrease inter-plane distance more significantly than the in-plane boron-boron distance, the increase of bandwidth of electron band (assumed to be antibonding $\pi$ band) is more dominant than that of the $\sigma$ band (in other words, $dN(\epsilon_F)/dP > dN(\epsilon_F)/dT$). Consequently, even when the total density of states decrease (as indirectly evidenced by the decrease of resistivity with
pressure), the measured slope of linear $T-$ dependence of TEP increases. The compressibility along the $c$-axis was found to be larger by 64% than along the $a$-axis, which support this idea.

TEP for Al doped MgB$_2$ was measured by Lorentz et al. and they also found an increase of slope and a decrease of $T_c$ upon electron doping. They attributed the decrease of $T_c$ to increase of the Fermi energy by doping, since the Fermi energy is close to an edge of decreasing density of state curves. But TEP results seems to be contradictory since TEP decreases for the increased Fermi energy in a simple one band metal. This inconsistency will be also explained by considering the role of electron band upon doping.

If we consider the pressure effect on the negative contribution at high temperature region (above $\sim 120$ K), the speculation of a semiconducting hole band should be examined. The pressure will decrease electron-phonon coupling by lattice stiffening, therefore the splitting of $\sigma$ band should be suppressed. Consequently, we expect the semiconducting energy gap ($E_g$) will reduce with pressure, which is not clearly seen in our measurements (see Table. I). The pressure effect seems to be rather dominant in the mobility and the effective mass term. It might be necessary to consider more complex situation like inter-band charge transfer to explain the observed TEP at high temperature region.

Within our model, we expect the anisotropic TEP measurement and/or the measurements under uniaxial stress will be helpful to understand the current observation. The sign of TEP and the temperature dependence of TEP will be quite different between in-plane and inter-plane direction. The in-plane TEP will be more or less same with polycrystalline sample data if our model is correct and the inter-plane TEP can be negative and linear at whole temperature range. And if a single crystal sample is compressed only along the $c$-axis while liberating expansion along the $ab$-plane, or vice versa, the behaviors of normal state TEP and $T_c$ will show different behaviors depending on the direction of compression.

**IV. CONCLUSION**

The temperature dependence of TEP under hydrostatic pressure was measured on MgB$_2$ superconductor. The results show that metallic hole carriers (presumably from the $\sigma$ bands) are important to explain temperature dependence of TEP. But the pressure dependence of $T_c$ and TEP needs contribution of carriers from other bands, i.e., metallic electron band and semiconducting hole band. The increase of TEP and the decrease of $T_c$ can be explained by the two metallic bands (hole and electron band). The density of states of both bands will decrease with pressure but the electron band will give larger effect due to the anisotropic compressibility. The deviation from the metallic TEP can be explained by the semiconducting hole band, whose contribution is only observable at higher temperature.

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TABLE I: Fitting parameters obtained from Eq. 3 to fit curves of Fig. 3. See text for the meaning of parameters.

| $P$ (kbar) | $E_g$ (K) | $B$ ($\mu$V/K) | $C$ ($\mu$V/K) | $\mu_e/\mu_h$ | $m_e/m_h$ |
|-----------|----------|---------------|---------------|--------------|-----------|
| ambient   | 1300     | -46.9         | 8.7           | 0.817        | 2.05      |
| 3.2       | 1280     | -49.4         | 8.9           | 0.814        | 2.13      |
| 6.3       | 1230     | -48.8         | 9.6           | 0.801        | 2.11      |
| 9.2       | 1270     | -52.2         | 9.6           | 0.800        | 2.23      |
| 11.3      | 1270     | -52.8         | 9.9           | 0.795        | 2.24      |
| 14.8      | 1270     | -54.8         | 10.3          | 0.788        | 2.32      |

FIG. 1: Temperature dependence of resistivity of MgB$_2$ under hydrostatic pressure. The inset shows expansion around $T_c$. The pressure shown here is 1bar, 3.2, 5.0, 5.7, 6.9, 8.8, 10.4, 12.2, 13.9 and 14.6 kbar from top to the bottom in the larger figure and from right to the left in the inset.
FIG. 2: (a) Change of conductivity (Δσ/σ(1bar)) at room temperature as a function of pressure (b) Tc versus pressure measured from the resistivity measurements.

FIG. 3: Temperature dependence of TEP of MgB2 under hydrostatic pressure. TEP increases as pressure varies as 1 bar, 3.2, 6.3, 9.2, 11.3 and 14.8 kbar. The data for temperature above 300 K was measured at 6.5 kbar. The definition of ΔS(T) is also shown. The inset shows low temperature expansion around Tc.

FIG. 4: Room temperature TEP and the slope of linear T-dependence of TEP as a function of pressure. Room temperature TEP was measured during initial pressurization (∆) and after temperature dependence measurements (○).

FIG. 5: Temperature dependence of ΔS(T)(= S(T) − AT) at different pressure. The inset shows fitting curves obtained from Eq. 3. The data in the inset were shifted by downward to show temperature dependence explicitly.
(a) 

\[ \Delta \sigma / \sigma(0) \text{ (\%)} \]

(b) 

\[ T_c (K) \text{ vs. } P \text{ (kbar)} \]

-0.136 K/kbar
\[ \Delta S = S(T) - AT \]

- 14.8 kbar
- 11.3 kbar
- 9.2 kbar
- 6.3 kbar
- 3.2 kbar
- 1 bar
$S_{RT} (\mu V/K)$ vs $P$ (kbar) diagram.
