Thermoelectric Properties of (Ca, Sr, Bi)$_2$Co$_2$O$_5$ Whiskers

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Thermoelectric properties of (Ca,Sr,Bi)$_2$Co$_2$O$_5$ (Co-225) single crystalline whiskers with a layered structure were measured over a wide temperature range 100–973 K. Both Seebeck coefficient and electrical resistivity exhibited fairly complex temperature dependences in this temperature range. The whole temperature range studied is divided into four distinct regions (I) to (IV), depending on observed characteristic temperature dependences of both Seebeck coefficient and electrical resistivity. From more or less linearly temperature dependent Seebeck coefficient in region (I) in combination with unique temperature dependences of both resistivity and Hall coefficient, we conclude the presence of a small pseudogap with a width of a few meV across the Fermi level. Complex magnetic properties are observed: the antiferromagnetic transition at 22 K but the hysteresis in the M-H curve remains up to room temperature. This is taken as evidence for the existence of Co atoms situated in different magnetic environments. The possession of large Seebeck coefficients exceeding 100 $\mu$V K$^{-1}$ in this system is attributed to the presence of the pseudogap at the Fermi level.

(Received January 22, 2001; Accepted March 22, 2001)

Keywords: thermoelectric properties, pseudogap, oxide whiskers

1. Introduction

The human race is currently using up only 30% of primary energy but is helplessly exhausting remaining 70% of it as heat into air. The development of a practical means to utilize this huge amount of heat energy is critically important to solve energy problems and to reduce the amount of CO$_2$ gas emissions. The thermoelectric power generation has been considered as a potential energy source in next decades. To realize thermoelectric power generation, however, it will be necessary to enhance the thermoelectric figure of merit, ZT, above unity, where ZT is defined as $S^2 T / \rho \kappa$ with the Seebeck coefficient $S$, absolute temperature $T$, electrical resistivity $\rho$ and thermal conductivity $\kappa$. Thus, the possession of high $S$ and low $\rho$ values is indispensably needed to realize an excellent thermoelectric performance. The Seebeck coefficient $S$ is expressed in the framework of the Boltzmann transport equation in the following form;

$$ S = \pi^2 k_B^2 T [\partial D(\varepsilon) / \partial \varepsilon]_{\varepsilon = \varepsilon_F} / 3 e D(\varepsilon_F), $$

where $k_B$, $e$ and $D(\varepsilon)$ represent the Boltzmann constant, an electric charge and the density of states at the energy $\varepsilon$, respectively. We see that the Seebeck coefficient takes either a positive or negative sign, depending on whether the holes or electrons serve as dominant carriers, respectively. In the free-electron model, eq. (1) is reduced to

$$ S_{free} = \pi^2 k_B^2 T / 2 e T_F, $$

where $T_F$ is the Fermi temperature defined as $T_F = \varepsilon_F / k_B$. Thus, the value of $S$ may be enhanced as high as we wish by reducing $T_F$ or the carrier concentration in a degenerate semiconductor. However, the reduction in $T_F$ along this line concomitantly results in a significant increase in resistivity and, hence, the reduction in the figure of merit. According to eq. (1), however, the value of $S$ may be increased to a high value while suppressing an increase in resistivity. This is in principle possible, provided that the derivative of $D(\varepsilon)$ at the Fermi level is increased but the value of $D(\varepsilon)$ itself is kept finite. Such a marginally metallic situation may be realized if the Fermi level falls in a steep declining slope of a pseudogap. Thus, we consider compounds having a deep pseudogap at the Fermi level to be a good candidate as thermoelectric materials.

Chemical stability of the material without involving harmful elements is also important to develop practical thermoelectric devices. At present, materials possessing a high thermoelectric performance are found in intermetallic compounds like Bi$_2$Te$_3$, CoSb$_3$, and Si-Ge alloys.$^{1-7}$ However, practical applications have been delayed because of the possession of their low melting points or decomposition temperatures, the content of harmful or scarce elements, and/or their insufficient conversion efficiency. Oxide compounds have been recently considered as an alternative candidate for thermoelectric device materials. The exploration of thermoelectric oxide materials has recently begun in earnest.$^{8-11}$ Indeed, NaCo$_2$O$_4$,$^{12,13}$ and (Ca$_2$Co$_2$O$_7$)$_x$Co$_2$O$_5$$^{14-16}$ have been demonstrated to exhibit very high thermoelectric performances. The Bi and Sr doped (Ca$_2$Co$_2$O$_7$)$_x$Co$_2$O$_5$ [(Ca,Sr,Bi)$_2$Co$_2$O$_5$; Co-225] compound possesses the Seebeck coefficient higher than 100 $\mu$V K$^{-1}$ while the $\rho$ value can be suppressed below about 1.6 $\times$ 10$^{-5}$ $\Omega$m above about 200 K.$^{16}$ In this paper, the thermoelectric properties of the Co-225 compounds grown as whiskers are presented and discussed with a particular emphasis on the relationship between the Seebeck coefficient and the formation of the pseudogap.

2. Experimental Procedures

Co-225 single-crystalline whiskers were prepared by using the so-called glass-annealing method.$^{16}$ CaCO$_3$, SrCO$_3$, Bi$_2$O$_3$, and Co$_2$O$_3$ powders were used as starting materials and mixed in proportion to Ca : Sr : Bi : Co = 1 : 1 : 1 : 2. The mixture was melted in air using an alumina crucible at 1573 K for 30 min. The glassy plates were obtained by in-
serting the melt between two copper plates and were subsequently heat-treated in a stream of O₂ gas at 1203 K for 1000 h to grow whiskers from their surface. As shown in Fig. 1, the whiskers were grown in a ribbon-like shape with 1–5 μm in thickness, 50–200 μm in width and less than 1.2 mm in length, being almost perpendicular to the surface of the precursor plates. The well-grown plane is identified as the crystallographic ab-plane of its monoclinic structure.

Measurements of the electrical resistivity ρ and the Seebeck coefficient S along the growth direction of a whisker in parallel to the ab-plane were performed in the temperature range 100–973 K. A commercial instrument (MMR Technologies Inc.) was used to measure S in the temperature range 100–700 K, while S values above 773 K were determined by taking a derivative of the thermoelectric voltage against temperature data measured with a laboratory-designed instrument. The value of ρ was measured using a standard DC four-probe method. Both S and ρ measurements were performed in air, when temperatures are higher than 773 and 350 K, respectively. The Hall coefficient R_H was measured by feeding the current to the ab-plane while magnetic field H of 9.0 T is applied along the c-axis using a commercial instrument (PPMS, Quantum Design). Both transverse and longitudinal magnetoresistance Δρ(H)/ρ(OT) [= (ρ(H) – ρ(OT))/ρ(OT)] was measured. The DC current is fed in parallel to the ab-plane of the whisker and magnetic field is also applied parallel to the ab-plane but perpendicular (transverse magnetoresistance) and parallel (longitudinal magnetoresistance) to the DC current. Silver paste was used to connect the lead wire with the sample. Temperature dependence of magnetic property was measured in zero-field cooling mode by applying magnetic fields parallel to its c-axis by using a SQUID magnetometer (MPMS, Quantum Design). Measurements of the magnetic hysteresis curve were carried out in the temperature range 5–300 K.

3. Results and Discussion

The [(Ca, Sr, Bi)₁₋ₓCoO₃], CoO₂ with x = 0.82 to 1.1 crystallizes into the rock-salt type layered structure with monoclinic symmetry.¹⁷ Because the average composition of the whiskers is (Ca, Sr, Bi)₁₋ₓCoO₂₋ₓ, they are simply referred to as the Co-225 in the following discussion. It constitutes a layered structure, in which two different layers are alternately stacked in the direction of the c-axis, as shown in Fig. 2.¹⁴ In the CoO₂ layer, each Co atom is surrounded by six O atoms in an octahedral configuration and the neighboring octahedra are edge-shared. On the other hand, Ca, Sr, Bi, Co and O atoms form a triple rock-salt layer (Ca, Sr, Bi)₂CoO₃. According to the X-ray and electron diffraction measurements, (Ca₂CoO₃)₃CoO₂ is characterized by the so-called “composite structure” in which a monoclinic [Ca₂CoO₃] sub-lattice and a monoclinic [CoO₂] sub-lattice interleave with each other.¹⁵ Here both sub-lattices are found to possess a common a-cell parameter but different b-cell parameters of 0.28 and 0.45 nm for the [CoO₂] and [Ca₂CoO₃], respectively.¹⁶

The temperature dependence of S and ρ is shown in Fig. 3. It is found that ρ remains lower than 1.6 × 10⁻⁵ Ωm while S is higher than 100 μV K⁻¹ over the temperature range 200–1000 K. Both ρ-T and S-T curves over a whole temperature range studied may be divided into four regions (I) to (IV), as marked in Fig. 3. Generally speaking, S value decreases with increasing T in semiconductors. In the Co-225 whiskers, however, S value increases almost linearly with increasing T in the region (I), where the ρ-T dependence is apparently typical of a semiconductor. In the region (II) where the ρ-T slope becomes slightly positive, S value continues to increase with T as in ordinary metals. The ρ-T slope becomes negative again in the region (III) but reverses its sign in the region (IV). Nevertheless, the value of S still continues to increase with increasing temperature up to the region (IV).

Figure 4 depicts the temperature dependence of R_H in the temperature range 5–300 K, which corresponds to the region (I) in Fig. 3. The R_H value becomes almost independent of T at T > 100 K. The carrier density is deduced to be as high as 3 × 10²⁷ m⁻³ in this temperature range from the
measured $R_H$. The Hall mobility is also estimated to be $1.5–2.3 \times 10^{-4} \text{m}^2\text{V}^{-1}\text{s}^{-1}$ from the product of the measured $R_H$ and $\rho$ in the range $T > 100 \text{ K}$ in the region (I). It is interesting at this stage to compare the observed mobility with that in $\text{NaCo}_2\text{O}_4$. The mobility we obtained is about 7 times as low as that of $\text{NaCo}_2\text{O}_4$ (12) since $\rho$ in the former is about 7 times higher than that in the latter while the carrier density deduced from $R_H$ is comparable with each other. The transmission electron microscope studies revealed that the present Co-225 whisker is essentially free from defects and impurity phases and its crystallinity is fairly high. (13) Thus, we believe that carriers at the Fermi level are rather immobile due presumably to the possession of a large effective mass.

The Seebeck coefficient in a semiconductor possessing a real gap is known to be inversely proportional to temperature. (18) However, the Seebeck coefficient we observed for the present Co-225 whiskers is almost linearly proportional to temperature. Judging from a sharp increase in $R_H$ below 100 K coupled with almost linearly increasing Seebeck coefficient in the region (I), we believe that a small pseudogap, rather than a real gap, exists in this system and that lowering the temperature below 100 K makes thermal excitations of electrons across the gap more difficult. The width of the pseudogap may be roughly estimated from the $\rho-T$ curve in 10–50 K to be a few meV or a few tens K.

For deep understanding of the electron transport mechanism, we consider it necessary to study magnetic properties of the Co-225 compound. The temperature dependence of the magnetization ($M/H$) curve for the Co-225 whisker was measured by applying magnetic field parallel to the $c$-axis. The results are shown in Fig. 5. Its temperature dependence exhibits a clear cusp and its inverse against $T$ shows a Curie-Weiss-type behavior at $T > 22 \text{ K}$ as shown in the inset. A line drawn through the data points below 150 K apparently crosses the temperature axis at a negative value. Hence, a cusp at 22 K may be indicative of the antiferromagnetic transition. However, it must be noted that the magnetization continuously increases with further decrease in temperature below 22 K, indicating the superposition of the magnetic interaction in different origins. Thus, we have measured the $M/H$ curve at various temperatures to gain further insight into the magnetism of this compound (Fig. 6). Surprisingly, a small hysteresis is observed over a wide temperature range 5–300 K. The magnitude of the hysteresis $\Delta M$ is found to decrease with increasing temperature.

Judging from the transmission electron microscopy studies, we consider the Co-225 compound studied in this experiment to be free from ferromagnetic impurity phases. Two possible magnetic interactions may be naturally considered: one from Co atoms in CoO$_2$ layer and the other Co atoms in the triple rock-salt layers. It has been reported that the rock-

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**Fig. 3** Temperature dependence of the Seebeck coefficient (■) and resistivity (●) for the Co-225 whisker.

**Fig. 4** Temperature dependence of the Hall coefficient for the Co-225 whisker.

**Fig. 5** Temperature dependence of magnetization $M/H$ for the Co-225 whisker taken under the magnetic field of 0.05 T. Inset shows the temperature dependence of its inverse $H/M$. 
salt-type CoO exhibits antiferromagnetic transition with the Néel temperature $T_N = 291$ K.\textsuperscript{19} Hence, Co atoms in the triple rock-salt layers would be responsible for the antiferromagnetic transition below 22 K. The lowering of $T_N$ to 22 K in the present Co-225 compound may be due to the weakening of magnetic interaction between Co and Co in the two-dimensional network of the triple rock-salt layer in contrast to the three-dimensional network of Co-O atoms in CoO. Instead, Co atoms in the CoO$_2$ layer are considered to remain ferromagnetic up to room temperature. Note that the curve in the inset of Fig. 5 is convex upward, suggesting the presence of two kinds of interactions. Further work is needed to clarify the origin of ferromagnetism in the Co-225 compound. At this stage, it is interesting to note that the Curie-Weiss behavior persists in the case of NaCoO$_2$ without any indication of magnetic ordering down to 5 K.\textsuperscript{20} The two-dimensional triangle network of Co atoms in the CoO$_2$ layer may hold a key role in the generation of ferromagnetism.

Figure 7 shows the magnetic field dependence of both transverse and longitudinal magnetoresistances, $\Delta \rho(H)/\rho(0T)$, measured in the geometry shown in the figure. As far as measuring temperature is below 30 K, both longitudinal and transverse magnetoresistances are found to be always negative. A decrease in resistivity with increasing magnetic field may be interpreted as the suppression of thermal fluctuations in magnetic moments. More interesting to be noted is the occurrence of a positive transverse magnetoresistance at 100 K. A positive transverse magnetoresistance is expected to occur when both electrons and holes coexist at the Fermi level and their numbers are unequal.\textsuperscript{21} We believe therefore that the positive transverse magnetoresistance observed at high temperatures is due to the presence of unequal number of electrons and holes in the pseudogap at the Fermi level and that the number of holes supersedes that of electrons at the Fermi level because of the possession of a positive Seebeck coefficient. Finally, we must note that a hysteresis is observed in the transverse magnetoresistance at 100 K, depending on ascending or descending stage of magnetic fields. Though the phenomenon is most likely related to the ferromagnetic Co layer, the reason why it disappears at lower temperatures is not clear at the moment.

4. Conclusion

The electrical and magnetic properties of the Co-225 whiskers were studied. The $\rho$-$T$ curve exhibited a semiconductor-like behavior below about 350 K. An apparent energy gap is estimated to be a few meV. From a more or less linearly temperature dependent Seebeck coefficient we conclude the presence of a small pseudogap across the Fermi level. The positive transverse magnetoresistance coupled with the positive Seebeck coefficient led us to believe that the electrons and holes coexist at the Fermi level and that the number of holes exceeds that of electrons. Complex magnetic properties were observed due to the presence of Co atoms situated in different environments. We believe that the Co-225 compound showing an increasing Seebeck coefficient beyond 150$\mu$V K$^{-1}$ above 400 K is very promising as a thermoelectric device material at high temperatures.

Acknowledgement

This work was supported by Industrial Technology Research Grant Program in ’00 (ID No. 00B60032c) from the New Energy and Industrial Technology Development Organization (NEDO) of Japan.
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