Thermoelectric power investigation of SmS under pressure

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Abstract. SmS undergoes a pressure-induced phase transition from a semiconducting to a mixed-valent state. Although the mixed valence state has been extensively studied, the semiconducting state with a divalent ionic state is not well understood yet. Here we report transport properties of the low-pressure semiconducting phase. Combining the thermoelectric power with the electrical resistivity, we observe that the mobility of electrons excited onto the conduction band is much greater than that of holes left behind in the valence band, the electron effective mass is nearly equal to the hole effective mass, and the relaxation time of the electron is much larger than that of the hole.

1. Introduction

SmS undergoes successive phase transitions under pressure ($P$). As $P$ increases, the system first undergoes a valence transition at a critical pressure ($\sim 7$ kbar at room temperature) from divalence (Sm$^{2+}$) to mixed valence (Sm$^{2+}$ and Sm$^{3+}$) accompanied by a color change from black to golden-yellow. With further increasing $P$ within the high pressure phase (named golden SmS), a magnetic transition occurs at a second critical pressure ($\sim 18$ kbar) \cite{1, 2}. According to a magnetic susceptibility measurement, the ground state at $P > P_c$ is antiferromagnetic \cite{3}. Golden SmS has attracted much interest because of its Kondo insulator behavior \cite{4}, but little is known about the low pressure phase (called black SmS). Here we focus on black SmS.

Black SmS is a narrow-gap semiconductor with an energy gap $E_g$ of the order of 0.1 eV at ambient pressure. $E_g$ is decreased by the application of $P$ as well as magnetic field $H$, and collapses to zero at an effective pressure $P_{\text{eff}} \sim 3 - 4$ kbar, where $P_{\text{eff}} = P + bH$ with $b = 0.14$ kbar/T \cite{5}. Above this pressure, the system becomes metallic \cite{6}. Of particular interest is to know what happens in the vicinity of the insulator to metal transition. In order to elucidate the black phase more in detail, we measure the thermoelectric power (TEP) $S$ and the electrical resistivity $\rho$ at the same pressure.

2. Experimental details

Single crystals of SmS were grown by the Bridgman method using a high-frequency induction furnace. We prepared two ingots with different starting compositions; stoichiometric sample \#8, and S-excess sample \#9. Samples with a typical dimension of $1 \times 1 \times 4$ mm$^3$ were cleaved for...
the present study. Electrical resistivity was measured by means of the conventional DC four-terminal method at ambient and high pressures. TEP was measured by means of the differential DC method at ambient and high pressures [7], using a thermocouple consisting of Au0.07at%Fe (abbreviated as AuFe hereafter) and Chromel wires of diameter \( \phi = 76 \mu m \). A strain gauge was used for a heater to generate a temperature gradient (\( \Delta T \)) between both ends of the sample. To obtain the Seebeck coefficient \( S \), we need to measure the voltage ratio, \( r = V_A/V_B \). Here, \( V_A \) and \( V_C \) is a voltage generated in the AuFe-sample-AuFe and the Chromel-sample-Chromel closed circuit, respectively. Then, \( S \) is evaluated using the following equation

\[
S = \frac{S_A - rS_C}{1 - r},
\]

where \( S_A \) and \( S_C \) indicate an absolute Seebeck coefficient of AuFe and Chromel, respectively.

An external pressure was applied using a NiCrAl-BeCu hybrid piston-cylinder with a WC piston. Daphne oil 7373 was used as a pressure transmitting medium. Pressure was determined using a superconducting transition of indium [8].

3. Results

Figure 1 shows the temperature dependence of \( S \) under pressure. At ambient pressure (left panel), we observe the 1/\( T \) dependence characteristic of a semiconductor. The absolute value of \( S \) is as large as about 300 \( \mu V/K \) at room temperature, and exceeds 1.4 mV/K at 40 K. The negative sign of \( S \) indicates that the electric current is carried dominantly by electrons.

At \( P = 0.78 \) kbar, the overall \( T \) dependence of \( S \) is same as the above, but its absolute value \( |S| \) decreases. This decrease in \( |S| \) arises from the reduction in the energy gap \( E_g \), as shown below. At \( P = 1.36 \) kbar, the 1/\( T \) dependence is still observed, but another feature appears at around 130 K, where a broad maximum emerges. At \( P = 1.81 \) kbar (right panel), in addition to the broad maximum, there emerges a shallow minimum at around 20 K. This is understood as follows: In the semiconducting state, \( |S| \) increases with lowering temperature, and then decreases toward zero for \( T \to 0 \) according to the thermodynamics. This gives rise to the minimum. With further increasing \( P \), this minimum becomes shallow and shifts toward high temperatures.

The inset of the right panel displays \( S \) in a log \( T \) vs log \( |S| \) plot at \( P = 2.04 \) kbar. We observe the nearly \( T \) linear dependence at low temperatures.

At \( P = 2.49 \) kbar (left panel), the system transforms into the golden phase. At room temperature, the sign of \( S \) is positive, in accordance with a previous result [7]. We also observe that \( S \) changes sign at a low temperature and shows a maximum below 10 K. Detailed results of the golden phase are given elsewhere [9].

Figure 2 compares the temperature dependences of \( S \) and the electrical resistivity \( \rho \). In the left panel, the result at \( P = 0.74 \) kbar is displayed. Corresponding to the semiconducting 1/\( T \) dependence of \( S \), we observe the resistivity to increase exponentially with lowering temperature. In the right panel, the result at \( P = 2.53 \) kbar is shown. With decreasing temperature, \( S \) initially increases, and then decreases below approximately 80 K before increasing again below about 30 K. As mentioned, the shallow minimum is ascribed to the gap formation. In the same temperature region where the semiconducting feature is observed in \( S \), we observe the resistivity to increase with lowering temperature. The gap energy obtained from these two methods will be compared below.

Figure 3 shows the temperature dependences of \( S \) and \( \rho \) together with the pressure dependence of \( E_g \). In the left panel, \( S \) is plotted against 1/\( T \) at pressures indicated in the figure. We evaluate some parameters using the relation [10]

\[
S = \frac{k_B}{e}\left(\frac{b-1}{b+1}\right)\frac{E_g}{2k_B T} + \frac{3}{4}\ln\frac{m_n}{m_p},
\]
where $b$ is the mobility ratio, $b = \mu_n/\mu_p$ ($\mu_n$ and $\mu_p$ are electron and hole mobility, respectively), $m_n$ and $m_p$ are the electron and hole effective mass, respectively, $k_B$ is the Boltzmann constant, and $e$ is the electron charge. From the slope of the broken straight line, we evaluate the “gap energy” $E_g^S$ defined as

$$E_g^S = \frac{b - 1}{b + 1} E_g.$$  \hfill (3)

The gap $E_g$ in the right-hand side is deduced from the slope of the broken straight line in the Arrhenius plot (middle panel). Thus obtained gap energies are summarized in the right panel. We observe the overall similar $P$ dependence for both the gap energies. This leads to that the prefactor of $E_g$ in eq. 3 is close to 1, leading to that $b \gg 1$. (Strictly speaking, since the prefactor is smaller than 1, $E_g^S$ should be smaller than $E_g$, contrary to the experiment. The
Figure 3. Pressure evolution of the gap energy. The slope of the straight line in the left and middle panel yields the gap energy $E_g^S$ and $E_g$, respectively. Pressure dependences of $E_g^S$ and $E_g$ are plotted in the right panel. Note that the overall feature is similar.

Figure 3. Pressure evolution of the gap energy. The slope of the straight line in the left and middle panel yields the gap energy $E_g^S$ and $E_g$, respectively. Pressure dependences of $E_g^S$ and $E_g$ are plotted in the right panel. Note that the overall feature is similar.

origin of this discrepancy is not clear.) Therefore, we have the relation, $\mu_n \gg \mu_p$, indicating that conduction electrons with 5d character are much mobile than holes in the valence band having the 4f character dominantly.

According to eq. 2, the quantity of $\ln \frac{m_n}{m_p}$ is evaluated from an interception of the straight line with the vertical axis. Then, the experimental results shown in the left panel of Fig. 3 yields the relation $\ln \frac{m_n}{m_p} \sim 0$, resulting in the relation $m_n \sim m_p$. Combining this with the mobility ratio obtained above, we have the relation $\tau_n \gg \tau_p$.

4. Summary
SmS is a semiconductor at ambient pressure. The energy gap $E_g$ deduced from both the electrical resistivity and the thermoelectric power decreases with increasing pressure, and collapses to zero at a pressure, which is roughly estimated as 3 kbar. In the vicinity of this pressure, the Seebeck coefficient shows the complicated behavior. In particular, we observed the emergence of a broad peak whose origin is unknown. Furthermore, using a combination of the resistivity and the thermopower, we obtained the following relations; $\mu_n \gg \mu_p$, $m_n \sim m_p$, and $\tau_n \gg \tau_p$.

References
[1] A. Barla, J. P. Sanchez, Y. Haga, G. Lapertot, B. P. Doyle, O. Leupold, R. Rüffer, M. M. Abd-Elmeguid, R. Lengsdorf and J. Flouquet 2004 Phys. Rev. Lett. 92 066401
[2] Y. Haga, J. Derr, A. Barla, B. Salce, G. Lapertot, I. Sheikh, K. Matsubayashi, N. K. Sato and J. Flouquet 2004 Phys. Rev. B 70 220406
[3] K. Matsubayashi, K. Imura, H. S. Suzuki, G. Chen, N. Mori, T. Nishioka, K. Deguchi and N. K. Sato 2007 J. Magn. Magn. Mater. 310 408
[4] G. Aeppli and Z. Fisk 1992 Comments Cond. Mat. Phys. 16 155
[5] K. Imura, K. Matsubayashi, H. S. Suzuki, K. Deguchi and N. K. Sato 2008 J. Phys: Conf. Series. 121 032014
[6] N. K. Sato et al. in preparation
[7] K. Imura, S. Kanematsu, K. Deguchi, H. S. Suzuki, K. Matsubayashi and N. K. Sato 2011 J. Phys. Soc. Jpn. Suppl. 80 SA077
[8] L. D. Jennings and C. A. Swenson 1958 Phys. Rev. 112 31
[9] K. Imura, S. Kanematsu, K. Matsubayashi, H. S. Suzuki, K. Deguchi and N. K. Sato 2011 J. Phys. Soc. Jpn. 80 113704
[10] N. E. Sluchanko et al. 2000 Phys. Rev. B 61 9906