Effect of pressure on thermopower and resistivity of EuCo\textsubscript{2}P\textsubscript{2}

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Abstract. The measurements of electrical resistivity $\rho$ and thermopower $S$ of the single-crystalline EuCo\textsubscript{2}P\textsubscript{2} have been performed at temperatures from 2 K to 300 K under hydrostatic pressures up to 3 GPa. The temperature dependence of $\rho$ and $S$ show drastic changes at the critical pressure $P_c$, indicating a large modification of electronic structure around the Fermi level due to a pressure-induced structural and magnetic phase transition. The magnetic phase transition temperature increases linearly with increasing pressure, and shows a sudden increase at the critical pressure $P_c$, which correspond to the change of magnetic state from the localized Eu(4f) sub-lattice magnetism into the itinerant Co(3d) sub-lattice magnetism.

1. Introduction

The rare-earth (R) transition metal (T) phosphides, RT\textsubscript{2}P\textsubscript{2}, which crystallize in the ThCr\textsubscript{2}Si\textsubscript{2}-type body-centered tetragonal structure, have a rich variety of the magnetic ground states such as 4f sub-lattice magnetism, 3d sub-lattice magnetism or magnetism of both sub-lattices \cite{1, 2, 3}. Additionally, superconductivity as well as intermediate valence behavior have been observed in this system \cite{4, 5}. One possible reason for such a richness is that this crystal structure can adapt to several elements with various atomic sizes. In this series, EuCo\textsubscript{2}P\textsubscript{2} is an antiferromagnet with a moment at Eu site of 6.9 $\mu_B$ and the Neel temperature of $T_N=66.5$ K at ambient pressure. It is reported that EuCo\textsubscript{2}P\textsubscript{2} undergoes a structural and magnetic phase transition at a pressure of $P_c \approx 3$ GPa from a long P-P distance phase, with magnetic Eu\textsuperscript{2+} and nonmagnetic Co, into a short P-P distance phase with nonmagnetic Eu\textsuperscript{3+} and magnetic Co with an estimated moment of 0.6 $\mu_B$ at the Co site \cite{6, 7}.

The results of band structure calculation for EuCo\textsubscript{2}P\textsubscript{2} reveal that the large electronic density of state (DOS) caused mainly by the Co 3d states lies near the Fermi level \cite{6, 8}. Since the electron scattering is sensitive to the electronic state in the vicinity of the Fermi level, a large pressure effect on the transport properties, especially near the critical pressure $P_c$, can be expected. Some studies on the transport properties of the Eu-based system with a valence instability have been performed \cite{9, 10}. However, as far as we know, no measurement of the transport properties of EuCo\textsubscript{2}P\textsubscript{2} under pressure was reported in the literature. In order to investigate the effect of pressure on the transport properties of EuCo\textsubscript{2}P\textsubscript{2}, we have measured the electrical resistivity $\rho$ and thermopower $S$ at temperatures from 2 K to 300 K under hydrostatic pressures up to 3 GPa.
2. Measurement procedures
A single-crystalline sample of EuCo$_2$P$_2$ used for the present measurements of $\rho$ and $S$ was prepared by a Sn flux method. The detailed procedures for sample preparation have been described in Ref. [11]. The size of the sample was about 0.05 $\times$ 1 $\times$ 2 mm$^3$. The measurements of electrical resistivity $\rho$ and thermopower $S$ were carried out by using the differential method with seesaw heating procedure [12] and the standard four-probe dc method, respectively. $\rho$ and $S$ were measured simultaneously at temperatures from 2 K to 300 K on the process of applying pressure. A clamp-type hybrid piston cylinder pressure cell [13] with Daphne oil 7373 as the pressure transmitting medium was utilized for the measurements of $\rho$ and $S$ under pressures up to 3 GPa. Chromel-constantan thermocouples were used for measuring probes because of small temperature dependence of pressure effect [14]. The directions of the current and the temperature gradient were made perpendicular to the $c$-axis.

3. Results and Discussion
The temperature dependence of $\rho$ of EuCo$_2$P$_2$ under pressures up to 2 GPa is shown in Fig. 1. With increasing temperature, $\rho$ at ambient pressure rapidly increases and shows a kink around 66 K, indicated by an arrow in Fig. 1, which is in agreement with the Neel Temperature $T_N$ reported in Refs. [6, 7]. $\rho$ increases with increasing pressure, especially in the high temperature region. The Neel temperature $T_N$ increases linearly with increasing pressure at the pressure range of $P \leq 2.0$ GPa. The temperature variation of $\rho$, however, shows almost the same feature. The inset of Fig. 1 depicts the temperature dependence of $\rho$ at $P=2.5$ GPa and 3.0 GPa. For the sake of comparison, $\rho$ at ambient pressure also shown in the inset of Fig. 1. The temperature dependence and the magnitude of $\rho$ at $P=2.5$ GPa indicate drastic changes as compared to those at $P \leq 2.0$ GPa, indicating the pressure induced phase transition at the critical pressure $P_c$, 2.0 $< P_c < 2.5$ GPa. In the high pressure phase at $P=2.5$ GPa, a kink in $\rho(T)$ at the magnetic phase transition temperature $T_N^* \approx 260$ K, indicated by an arrow in the inset of Fig. 1, is observed. $T_N^*$ is in good agreement with the literature data [6].

Figure 2 shows the temperature dependence of $S$ under pressures up to 2 GPa. At ambient
Figure 2. Temperature dependence of $S$ of EuCo$_2$P$_2$ under pressures up to 2 GPa. The inset shows the temperature dependence of $S$ at $P=2.5$ GPa and 3.0 GPa.

pressure, $S$ increases with increasing temperature, having a maximum around 60 K. $S(T)$ also indicates an anomalous behavior in the form of abrupt break at $T_N \approx 66$ K. With increasing pressure, $S$ deceases in the whole measuring temperature range and $T_N$ increases in the pressure range of $P \lesssim 2.0$ GPa. The additional anomalous behavior in $S(T)$ is observed around $T=10$ K. No phase transition around $T_N$ has been reported. The detailed investigation of this anomaly will be a subject of separate publication. Here we concentrate on the pressure-induced phase transition at $P_c$. The inset of Fig. 2 shows the temperature dependence of $S$ at $P \geq 2.5$ GPa. The temperature variation of $S$, as well as $\rho$, shows a dramatic change at the critical pressure $P_c$. No characteristic feature accompanied by the magnetic phase transition in the high pressure phase is observed in $S(T)$, as shown in the inset of Fig. 2. Since the large DOS mainly due to the 3d states lies near the Fermi level [6, 8], the transport properties of EuCo$_2$P$_2$ are strongly depend on the state of the Co 3d electrons. Then, it is considerable that the drastic changes of the features of $\rho(T)$ and $S(T)$ at $P_c$ indicate a large modification of the 3d electronic state around the Fermi level due to a pressure induced structural and magnetic phase transition, which should be connected with a difference between the variations of $\rho$ and $S$ at the magnetic phase transition temperature in the low pressure phase and those in the high pressure phase.

Figure 3 indicates the pressure dependence of the magnetic phase transition temperatures, $T_N$ in the low pressure phase and $T_N^*$ in the high pressure phase, obtained from $\rho(T)$ and $S(T)$ curves. $T_N$ increases with increasing pressure, $dT_N/dP \approx 6$ K/GPa, and shows a discontinuous jump at the critical pressure $P_c$, indicating the first order phase transition from the low pressure phase, with the magnetic Eu$^{2+}$ and nonmagnetic Co, into the high pressure phase with nonmagnetic Eu$^{3+}$ and magnetic Co [7]. $T_N^*$ in the high pressure phase slightly increases with increasing pressure.

In summary, the electrical resistivity $\rho$ and thermopower $S$ of the single-crystalline EuCo$_2$P$_2$ have been measured at temperatures from 2 K to 300 K under pressures up to 3 GPa. The features of the temperature dependences of $\rho(T)$ and $S(T)$ show qualitative and quantitative changes at the critical pressure $P_c$, indicating a large modification of electronic state, consist mainly of the Co 3d electron states, around the Fermi level due to a pressure induced structural and magnetic phase transition accompanied by the valence change of Eu. The magnetic
transition temperature linearly increases with increasing pressure, and shows a sudden increase at the critical pressure $P_c$, which correspond to the change of magnetic state from the Eu(4f) sub-lattice magnetism to the Co(3d) sub-lattice magnetism.

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