Pressure effect on the ferromagnetism of an off-center rattling system \( \text{Eu}_8\text{Ga}_{16}\text{Ge}_{30} \)

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Abstract. We report the pressure effect on the ferromagnetism of type-I clathrate \( \text{Eu}_8\text{Ga}_{16}\text{Ge}_{30} \) with \( T_C = 36 \) K by means of the resistivity \( \rho \) and Hall coefficient \( R_H \) measurements. With increasing pressure up to 11.4 GPa, \( T_C \) increases up to 45 K. The concomitant decrease of \( \rho \) is attributed to the increase of the carrier concentration because the normal part of \( R_H \) decreases with the ratio of \(-3.5\%{/GPa}\). At ambient pressure, \( \rho (T) \) has broad peak at \( T^* = 23 \) K. Upon pressurizing, the peak is weakened but remain visible at \( P = 11.4 \) GPa. Our findings suggest that the anomaly at \( T^* \) is not so sensitive to the cage size up to 11 GPa, where the cage volume is compressed to 87\% of the value at ambient pressure.

1. Introduction

Intermetallic clathrates showing low thermal conductivity and high thermopower have attracted much attention because of their potential in thermoelectric applications [1-3]. Among a large number of clathrate compounds, type-I clathrates \( X_8\text{Ga}_{16}\text{Ge}_{30} \) (\( X = \text{Ba}, \text{Sr} \) and \( \text{Eu} \)) have been most extensively investigated. The unit cell consists of two dodecahedra and six tetraakidecahedra composed of Ga and Ge atoms, which incorporate \( X_1 \) atoms \((2a \) site\) and \( X_2 \) atoms \((6d \) site\), respectively [4]. Neutron and x-ray diffraction studies revealed that the 6d site for \( X = \text{Sr} \) and \( \text{Eu} \) is split into four-fold sites displaced from the cage center, while the 6d site for \( X = \text{Ba} \) is not split [2, 5]. The reduced thermal conductivity for \( \text{Sr}_8\text{Ga}_{16}\text{Ge}_{30} \) and \( \text{Eu}_8\text{Ga}_{16}\text{Ge}_{30} \) was attributed to highly anhmonic and localized vibrations (so called rattling) of \( X_2 \) atoms in the tetraakidecahedral cage [2].

\( \text{Eu}_8\text{Ga}_{16}\text{Ge}_{30} \) is the only clathrate compound where magnetic ions fully occupy the guest positions in the cages. Furthermore, it is dimorphic, having type-I and type-VIII structures. The compounds of the two structures exhibit ferromagnetic transitions at \( T_C = 36 \) K and 10.5 K, respectively [1, 2, 6]. The divalent state of the Eu ions in the two compounds manifests itself in the Curie-Weiss-type temperature dependence of the magnetic susceptibility with the effective moment of 7.9 \( \mu_B{/\text{Eu}} \) and the saturated magnetization \( M_s \) of 7 \( \mu_B{/\text{Eu}} \). The magnetic and transport measurements for \( \text{Eu}_8\text{Ga}_{16-x}\text{Ge}_{30+x} \) with both type structures revealed that the thermal and transport properties depend on the carrier concentration, whereas \( T_C \) and \( M_s \) do not [1, 7, 8]. Pacheco et al. reported that the higher \( T_C \) in type-I than in type-VIII is due to the enhanced effective mass of the conduction electrons in type-I [7]. For type-I \( \text{Eu}_8\text{Ga}_{16}\text{Ge}_{30} \), both the electrical resistivity \( \rho \) and the temperature derivative of magnetization \( dM/dT \) exhibit peaks at \( T^* = 23 \) K in addition to the anomalies at \( T_C \) [8, 9]. The specific heat jump at
2. Experimental

A single-crystalline sample of Eu₈Ga₁₆Ge₂₉ was grown using a Ga self flux method, as described previously [9]. The elemental composition Eu : Ga : Ge was determined by the electron-probe microanalysis to be 8 : 15 : 29.5. The $\rho$ and $R_{\|}$ were measured for $P < 3$ GPa by an ac four-terminal method using a piston-cylinder pressure cell. The $R_{\|}$ was measured between 2 and 50 K under magnetic fields up to 6 T. The $\rho$ for $P \leq 11.4$ GPa was measured by a dc four-terminal method using a Bridgman anvil cell [12]. Daphne oil was used as a pressure medium in each pressure cell. The pressure was estimated by the pressure dependence of the superconducting transition temperature of tin.

3. Results and Discussions

Figure 1 shows the temperature dependence of $\rho$ under pressures. The $\rho(T)$ over the measured temperature range decreases upon pressurizing, probably as the result of the increase of the carrier concentration. The peak of $\rho$ at $T_C$ shifts to higher temperatures with pressure. The maximum of $\rho$ at $T^*$ shifts to higher temperatures and becomes broader, but remains visible even at $P=11.4$ GPa as shown in the inset of Fig. 1.

In order to examine the pressure dependence of the carrier concentration, we have measured the magnetic field dependence of the Hall resistivity $\rho_{xy}$ at 2 K far below $T_C$. The data at $P=0.1$, 1.32, and 2.81 GPa are depicted in Fig. 2. The $\rho_{xy}(B)$ increases with $B$ up to 0.5 T but decreases linearly with further increasing $B$. Empirically, $\rho_{xy}(B)$ of a ferromagnet is described by the formula, $\rho_{xy}(B) = R_o B + R_m \mu_0 M(B)$, where $R_o$ and $R_m$ are ordinary and extraordinary Hall coefficients, respectively [7]. The $R_o$ is inversely proportional to the carrier concentration, $n$, within the one carrier model. The initial increase of $\rho_{xy}(B<0.5 \text{ T})$ can be explained by the increase of $M$ in the ferromagnetic state. For $B > 0.5$ T, $M$ is saturated and therefore the first term of $R_o B$ gives rise to the linear dependence of $\rho_{xy}(B)$. Thus, $R_o$ can be determined from the slope of the linear fit to $\rho_{xy}(B)$ for $B > 0.5$ T. As shown in the inset, the absolute value of $R_o$ decreases with the ratio of -3.5%/GPa. This finding means the linear increase of the carrier concentration with pressure.

We summarize the pressure dependence of $T_C$ and $T^*$ of Eu₈Ga₁₆Ge₂₉ in Fig. 3. The $T_C$ increases linearly with an initial ratio of 0.94 K/GPa, and reaches 45 K at 11.4 GPa. The pressure dependence of $T_C$ allows us to determine the Grüneisen parameter for $T_C$, $\Gamma = -d\ln T_C/d\ln V$. Assuming the bulk modulus of 100 GPa, we obtain $\Gamma = 2.6$, which is same order of magnitude as those for Eu-filled skutterudites Eu₀₉Fe₄Sb₁₂ ($\Gamma = 6$), and Eu₀₄Co₄Sb₁₂ ($\Gamma = 9.6$) [13]. The $T^*$ increases to 26 K at 3 GPa, and stays at a constant value for $P > 3$ GPa.

At first, we discuss the reason for the increase of $T_C$ with pressure. The ferromagnetic ordering of Eu₈Ga₁₆Ge₂₉ arises by the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction of Eu²⁺ magnetic moments. Because $T_C$ is in proportion to the RKKY coupling constant, $J_{RKKY}$, $|\Gamma| = d\ln T_C/d\ln V$ is proportional to $d\ln J_{RKKY}/d\ln V$. Within the free-electron model, the $J_{RKKY}$ is described as $J_{RKKY} \propto F(k_F R_\parallel) = (2k_F R_\parallel)(2k_F R_\parallel) \sin(2k_F R_\parallel)/(2k_F R_\parallel)$, where $k_F$ and $R_\parallel$ are the Fermi wave number and...
the distance between the $i$-th and $j$-th Eu ions, respectively. It is noteworthy that $F(kF\rho_0)$ is independent of volume $V$, since $kF \propto V^{1/3}$ times $\rho_0 \propto V^{1/3}$ becomes constant. Then, the $J_{\text{RKKY}}$ remains constant against the change in volume, or pressure within this model. Experimentally, $T_c$ of Eu$_8$Ga$_{15}$Ge$_{29.5}$ is enhanced by applying pressure, whereas it is suppressed in a similar way with increasing $x$ in Eu$_8$Ga$_{16-}x$Ge$_{30+x}$ and $y$ in Eu$_8$Ga$_{16-y}$Ge$_{30+y}$Si$_{y}$ [8, 11]. The unit cell volume $V_{\text{cell}}$ is almost constant with increasing $x$ in Eu$_8$Ga$_{16-x}$Ge$_{30+x}$, whereas $V_{\text{cell}}$ decreases with increasing $y$ in Eu$_8$Ga$_{16-y}$Ge$_{30+y}$Si$_{y}$. These relations suggest that $T_c$ has no correlation with $V_{\text{cell}}$. Usually, the pressure dependence of $T_c$ of rare-earth compounds is caused by the change of the band structure near the Fermi level. Indeed, it was pointed out that the higher $T_c$ in type-I (36 K) than in type-VIII (10.5 K) results from the heavier effective mass of carriers in type-I, i.e., $m^*(\text{type-I})$$\geq$3$m^*$ (type-VIII) [7].

Next, we discuss the relation between $T^*$ and the cage size in Eu$_8$Ga$_{15}$Ge$_{30}$. The high-pressure x-ray diffraction study showed that the unit cell volume at $P$=11 GPa is compressed to 87% of the value at ambient pressure [14]. The lattice parameter, accordingly, is shrunk to 95.5%. From these data, we will estimate the cage size at $P$=11 GPa. A universal relation was found between the guest free space in the tetrakaidecahedron and the magnitude of thermal conductivity at 150 K in type-I clathrates [3]. The free space for guest vibration is written as $R_{\text{free}}=R_{\text{cage}}-r_{\text{cage}}-r_{\text{guest}}$, where $R_{\text{cage}}$ is the cage radius defined as the distance between the 6$d$ (guest) site and the 24$k$ (cage) site. At ambient pressure, $R_{\text{free}}$ for X$_8$Ga$_{15}$Ge$_{30}$ ($X$ = Ba, Sr and Eu) are 1.34, 1.50 and 1.58 Å, respectively [3]. Assuming that $R_{\text{cage}}$ is compressed by applying pressure, we obtain $R_{\text{free}}=1.39$ Å for $X$ = Eu at $P$=11 GPa. Because this value is close to that for $R_{\text{free}}$($X$=Ba) of the on-center counterpart, Eu atoms in the tetrakaidecahedral cage would return to center. This conjecture contradicts with the fact that the anomaly at $T^*$ remains even at 11 GPa. On the other hand, the anomaly at $T^*$ vanishes by changing the composition; increasing either $x$ up to 1.01 from 0.53 in Eu$_8$Ga$_{16-}x$Ge$_{30+x}$ or $y$ up to 7.3 in Eu$_8$Ga$_{16-y}$Ge$_{30+y}$Si$_{y}$ [8, 11], although the $V_{\text{cell}}$ hardly decreases [8, 11]. These findings suggest that $T^*$ has no correlation with the cage size. Instead, the carrier concentration increases in the three cases; with increasing $x$, $y$ and pressure in Eu$_8$Ga$_{16-}x$Ge$_{30+x}$, Eu$_8$Ga$_{16-y}$Ge$_{30+y}$Si$_{y}$, and Eu$_8$Ga$_{15}$Ge$_{29.5}$, respectively. Therefore, we conclude that the increase of the carrier concentration leads to the suppression of $T^*$. In order to reveal the origin of $T^*$,
more detailed structural and magnetic studies of $\text{Eu}_8\text{Ga}_{16-x}\text{Ge}_{30+x}$ with various values of $x$ are necessary.

In summary, we performed the resistivity $\rho$ and Hall coefficient $R_H$ measurements of type-I clathrate $\text{Eu}_8\text{Ga}_{15}\text{Ge}_{29.5}$ with $T_C = 36$ K and $T^* = 23$ K under high pressures up to 11.4 GPa. With increasing pressure, the $T_C$ increases up to 45 K at $P = 11.4$ GPa and broad peak at $T^*$ in $\rho(T)$ is weakened. The anomaly remains at $T^*$ even at $P = 11.4$ GPa. Contrary to our expectation, $T^*$ is found to be not so sensitive to the cage size up to 11 GPa, where the cage volume is compressed to 87% of the value at ambient pressure.

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