Multiple Ferromagnetic Structures in an Off-Center Rattling System Eu$_8$Ga$_{16}$Ge$_{30}$

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Abstract. We performed electrical resistivity $\rho$, magnetization $M$ and specific heat $C$ measurements on single crystals of a type-I clathrate compound Eu$_8$Ga$_{16}$Ge$_{30}$, where the guest magnetic ions of Eu$^{2+}$ in the tetrakaidecahedral cages are rattling among off-center positions. The jump of $C$ at the Curie temperature $T_C$ is only one third of the value expected for a uniform ferromagnet with $S=\frac{7}{2}$ from the mean-field theory. Both $\rho(T)$ and $dM(T)/dT$ show broad humps at $T^*=20-24$ K, where $C(T)$ has no anomaly. With increasing magnetic fields to 5 T, the $T^*$ in $\rho(T)$ shifts to 40 K. These observations indicate a crossover from a modulated structure to a uniform one on cooling through $T^*$.

Eu$_8$Ga$_{16}$Ge$_{30}$ is the only clathrate compound where magnetic ions fully occupy the guest positions in cages. This compound adopts two types of crystal structures, type-I and type-VIII. In the type-I, the Eu guest ions are encapsulated in two kinds of polyhedral cages of $E_{20}$ pentagonal dodecahedra and $E_{24}$ tetrakaidecahedra. On the other hand, the Eu guests in the type-VIII have one site in distorted polyhedral cages $E_{20+3}$. The type-I and type-VIII compounds exhibit ferromagnetic (FM) transitions at $T_C=36$ K and 10.5 K, respectively.[1, 2, 3] The divalent state of the Eu ions was indicated by the Curie-Weiss type temperature dependence of the magnetic susceptibility with the effective moment of 7.9 $\mu_B$/Eu and the saturated magnetization of 7 $\mu_B$/Eu. In the specific heat measurements of type-I samples, the jump at $T_C$ depends on samples, the reason of which has been unclear yet. The magnetic and transport properties of the type-I and type-VIII have been studied in detail on Eu$_8$Ga$_{16-x}$Ge$_{30+x}$ system.[3, 4, 5] In this system, the thermal and transport properties depend on the carrier density. The higher $T_C$ in the type I than in type-VIII was attributed to the enhanced effective mass of the conduction electrons in the type-I. By neutron diffraction experiments with single crystalline samples of type-I, magnetic peaks were observed below $T_C$.[2, 6] Sales et al. interpreted that the magnetic moments are directed along the [100] direction.[2] Chakoumakos et al. also reported that the preferred direction of the moments is along [100] and the projected saturation value of the Eu moments is 7 $\mu_B$.[6] By Mössbauer measurements, Hermann et al gave direct evidence for tunneling of Eu ions even in the ferromagnetically ordered state.[7]

On the other hand, there are several experimental facts which are at variance with the three dimensional Heisenberg-model. Srinath et al. evaluated magnetic entropy, $\Delta S_{mag}$, as a function of temperature from the magnetization $M(H,T)$ by adopting the thermodynamic...
Maxwell relation. In the case of a ferromagnetic transition of the three-dimensional Heisenberg system, the maximum of $\Delta S_{\text{mag}}$ should appear at $T_C$. The $\Delta S_{\text{mag}}$ of type-I shows its maximum value at 9 K far below $T_C=36$ K, whereas, in the type-VIII, $\Delta S_{\text{mag}}$ shows the maximum at 15 K close to $T_C$.\cite{8} In the optical reflectivity measurements, no difference was observed below and above $T_C$ in the type-I in contrast to the clear change in the type-VIII.\cite{9,10} The larger carrier density in type-I would smear out the possible change in the electronic structure. Furthermore, the guest magnetic ions of Eu$^{2+}$ in the tetrakaidecahedral cages in the type-I are rattling among off-center positions even within the FM state below $T_C$.\cite{2,11} Therefore, we expect that the FM state is modified by the rattling motion of the Eu$^{2+}$ ions.

Keeping this in mind, we have measured electrical resistivity $\rho$, magnetization $M$ and specific heat $C$ of several single crystals of Eu$_8$Ga$_{16}$Ge$_{30}$. We have found broad humps in both $\rho(T)$ and $dM(T)/dT$ at temperatures far below $T_C$. The jump of $C$ at $T_C$ is smaller than one third of that expected for a three dimensional Heisenberg system. These facts strongly suggest the existence of multiple ferromagnetic structures below $T_C$.

Single crystalline samples of Eu$_8$Ga$_{16}$Ge$_{30}$ were obtained using a Ga self flux method.\cite{12} High-purity elements of 4N Eu prepared by Ames Laboratory, 6N Ga and 5N Ge were sealed in an evacuated quartz ampoule with a composition of Eu:Ga:Ge=8:32:30. They were soaked above 1150°C for 2h in a box furnace, cooled over 6h to 720°C and slowly cooled over 100h to 620°C. The ampoule was quickly removed from the furnace and the remaining molten Ga flux was separated by centrifuging. Typical dimension of a single crystal with polyhedral surface facets is $10 \times 10 \times 5$ mm$^3$. The absence of secondary phase and the chemical homogeneity were confirmed by a scanning electron microscope. The atomic compositions were determined by electron-probe microanalysis (EPMA) by averaging over 10 different regions. The composition of Eu$_8$Ga$_{15.0}$Ge$_{29.5}$Vac$_{1.5}$ (Vac denotes a vacancy) was obtained by assuming the composition of Eu to be 8. Hereafter, this sample is denoted as Eu$_8$Ga$_{16}$Ge$_{30}$ for simplicity. The Ge compositions of 30±0.5 are close the ideal value, but the Ga compositions of 15.0-15.3 are less than the ideal value of 16. Therefore, defects should present in the Ga sites. The powder X-ray diffraction patterns were recorded at room temperature with Cu $K_{\alpha 1}$ radiation using Rigaku Ultima IV. The lattice parameter refined by the Rietveld analysis using RIETAN2000\cite{13} is 10.706(1) Å, which agrees with the reported value.\cite{3}

Magnetization was measured using a commercial SQUID magnetometer (Quantum Design MPMS) for 1.9-350 K in magnetic fields up to 5 T. Electrical resistance was measured by a standard four-probe AC method in a home-built system with a Gifford-McMahon type refrigerator. The resistance was also measured in various fixed magnetic fields up to 14 T in a longitudinal configuration, using a commercial Quantum Design PPMS. Specific heat was measured by a relaxation method at temperatures between 1.9 K and 300 K.

Figure 1 shows the temperature dependence of the electrical resistivity $\rho$ of Eu$_8$Ga$_{16}$Ge$_{30}$ in various magnetic fields up to 14 T. The data are vertically shifted for clarity. In zero field, the sharp and broad peaks appear at $T_C=36$ K and $T^*=25$ K, respectively, as indicated by the arrows. The sharp peak at $T_C$ is suppressed by the application of a low magnetic field of 0.5 T, whereas the broad peak at $T^*$ shifts to 40 K as the field is increased to 5 T. This fact strongly suggests that the anomaly at $T^*$ has a magnetic origin. Similar anomalies at $T^*$ are present in the data of $\rho(T)$ reported by Paschen et al.\cite{3} and Bentien et al.\cite{5}, although no attention was paid to the anomalies. We note that a broad hump or shoulder was observed in their samples with relatively high resistivity with the charge carrier concentration $n<0.633$ e$^-$/u.c. at 2 K. Actually, $\rho$ for the present sample is 0.8 mΩ cm at 2 K, which is comparable to that for their low carrier sample with $n=0.431$ e$^-$/u.c. at 2 K.\cite{5} Our magnetization measurements have revealed the presence of an anomaly in the vicinity of $T^*$. Figure 2 shows the temperature dependence of the magnetization $M$ and its temperature differentiation, $dM/dT$, in magnetic fields of $B=0.05$, 0.1, 0.5 and 1 T. As is common to a ferromagnetic transition, $M$ increases sharply below $T_C$. 


The $dM/dT$ has a shoulder at $T^*$ far below $T_C$. The increase of $T^*$ with increasing magnetic fields is consistent with the field dependence of the resistivity shown in Fig. 1. The anomaly at $T^*$ is therefore attributed not to a structural transition but to some magnetic origin.

In order to examine whether a phase transition occurs at $T^*$, we measured the specific heat. Figure 3 shows the temperature dependence of $C$. A jump of $C$ is observed at $T_C$, whereas no anomaly appears below $T_C$. This fact means that the anomaly observed at $T^*$ both in $\rho(T)$ and $dM(T)/dT$ could not result from a phase transition. The jump of $C$ at $T_C$, $8\Delta C$, was estimated by extrapolating the data below and above $T_C$, as indicated by the lines on the data in the inset of Fig. 3. The estimated value of $\Delta C$ is 7.3 J/K Eu-mol, being only one third of 20.1 J/K Eu-mol expected by the mean-field calculation for a ferromagnetic transition of the spin $S=\frac{7}{2}$ system.[14, 15] This suggests that the magnetic structure below $T_C$ is probably a modulated one, and it approaches to a uniform one with decreasing temperatures through $T^*$. Therefore, the anomaly at $T^*$ is the manifestation of the cross-over of the multiple ferromagnetic structures. Recently, we have grown single crystalline samples of Eu$_8$Ga$_{16}$(Ge,Si)$_{30}$ in aiming at investigating possible relationships between the off-center rattling and their FM transitions.[16] With substituting Si for Ge in the cage, we have found that the cage size decreases and the jump of $C$ at $T_C$ becomes more distinct. Moreover, the anomaly at $T^*$ disappears once Si is partially substituted for Ge in the cages. It should be recalled that the off-center rattling in Sr$_8$Ga$_{16}$Ge$_{30}$ changes to on-center one as Si is substituted for Ge.[17, 18] By the analogy, we propose that the modulated structure in Eu$_8$Ga$_{16}$Ge$_{30}$ is stabilized by the off-center rattling of Eu ions.

In summary, we performed electrical resistivity $\rho$ in magnetic fields, magnetization $M$ and specific heat $C$ measurements on Eu$_8$Ga$_{16}$Ge$_{30}$. The jump of $C$ at the FM transition temperature $T_C=36$ K is only one third of the value calculated by the mean-field model for the three dimensional Heisenberg system. In $\rho(T)$ and $dM(T)/dT$, we observed anomalies not only at

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**Figure 1.** Temperature dependence of the electrical resistivity of Eu$_8$Ga$_{16}$Ge$_{30}$ in magnetic fields up to 14 T. The data are vertically shifted for clarity.

**Figure 2.** Temperature dependence of the magnetization $M$ (top) and $dM/dT$ (bottom) of Eu$_8$Ga$_{16}$Ge$_{30}$ in magnetic fields of $B=0.05$, 0.1, 0.5 and 1 T.
Figure 3. Temperature dependence of the specific heat $C$ of Eu$_8$Ga$_{16}$Ge$_{30}$. The jump of $C$ at $T_C$, $8\Delta C$, was estimated by extrapolating the data below and above $T_C$, as indicated by lines in the inset.

$T_C$=36 K but also $T^*$=20-24 K. With increasing magnetic field to 5 T, the $T^*$ at the anomaly in $\rho(T)$ shifts to 40 K, indicating a magnetic origin for the anomalies at $T^*$. These results suggest that a magnetically ordered state with modulated moments appears at $T_C$, and it gradually changes to a uniform one through $T^*$. It should be examined whether the modulated structure results from the off-center rattling of the guest Eu-ions in the tetrakaidecahedral cage.

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