MAGNETIC PROPERTIES AND Eu VALENCE IN $\mathbf{EuCu_2(Si_xGe_{1-x})_2}$*

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We performed measurements of magnetic susceptibility (χ) and L_{III}-edge X-ray absorption spectroscopy (XAS) in $EuCu_2(Si_xGe_{1-x})_2$. For $0.70 \leq x \leq 0.80$, with decreasing temperature, the χ deviates from Curie–Weiss (CW) law with a Eu^{2+} state and exhibits almost temperature-independent behaviour at lower temperatures. The behaviour, which is roughly similar to that accompanied by the valence transition in $EuNi_2(Si_{1-x}Ge_x)_2$, cannot be interpreted only in terms of the valence change. The hybridization between $4f$ electrons and a conduction band should also be taken into consideration.

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1. Introduction

It is known that some Eu compounds show a valence fluctuation like Ce and Yb compounds. The valence fluctuation in Eu compounds takes place between non-magnetic Eu^{3+} and Eu^{2+} with a localized moment of $7\mu_B$. One of great interest in the valence fluctuation in Eu compounds is that the mean Eu valence strongly depends on temperature, magnetic field and pressure. For example, $EuPd_2Si_2$ exhibits a sharp but continuous valence transition from $Eu^{2.8+}$ and $Eu^{2.2+}$ at around 160 K [1]. Moreover, in such substituted systems as $EuNi_2(Si_{1-x}Ge_x)_2$ [2] and $Eu(Pd_{1-x}Pt_x)_2Si_2$ [3], a first-order valence transition is observed. In this study, we take notice of $EuCu_2(Si_xGe_{1-x})_2$ system which was reported to exhibit a Kondo-lattice type state by Levin *et al.* for the first time [4]. Recently, heavy fermion behaviour has been reported by Hossain *et al.* [5]. On the other hand, the compounds with $x = 0$ ($EuCu_2Ge_2$) and $x = 1$ ($EuCu_2Si_2$) are known to exhibit an antiferromagnetic ordering [6] and a valence variation with temperature from 100 K to 700 K [7], respectively. In order to investigate a relation

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between both of the phenomena and to compare with the behaviour of other Eu compounds, we performed measurements of magnetic susceptibility (χ) and L_{III}-edge X-ray absorption spectroscopy (XAS) in $EuCu_2(Si_xGe_{1-x})_2$.

2. Experimental details

The samples of $EuCu_2(Si_xGe_{1-x})_2$ were made by arc-melting, and annealed for 1 week at 900°C in an evacuated quartz tube. Powder X-ray diffraction patterns show that the samples have a single phase with the $ThCr_2Si_2$ type structure. Magnetic susceptibility $\chi = M/H$ was measured by means of a superconducting quantum interference device magnetometer (Quantum Design, MPMS) in fields of 0.5 T and 5 T in the temperature range from 2 to 300 K and from 2 to 50 K, respectively. The XAS measurement at Eu L_{III} edge was performed at the BL-9A of KEK Photon Factory by using a Si(111) double-crystal monochromator from 10 to 290 K [8]. The spectrum was analyzed by fitting to two subspectra which consist of a Lorentzian and an arctangent. The mean valence v was estimated from the relative intensities of the two subspectra [3].

3. Results and discussion

Figure 1(a) shows the temperature dependence of χ in the field of 0.5 T. Except for $x = 1$, the χ–T curves show a Curie–Weiss (CW) law with an effective moment of $7.0 \sim 7.3\mu_B$ at higher temperatures, corresponding to the divalent state. For $x = 0.70$, 0.75 and 0.80, with decreasing temperature, the χ deviates from the CW law and transfers to temperature-independent behaviour at lower temperatures. Here, the temperature where the χ begins

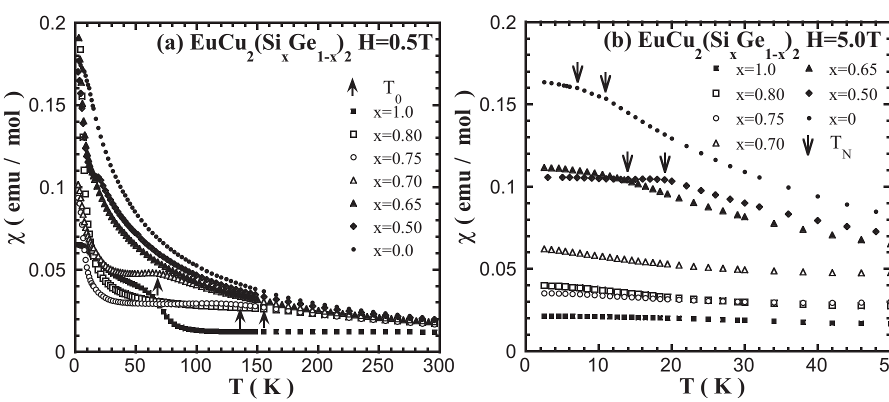

Fig. 1. Temperature dependence of χ in applied fields H of 0.5T (a) and 5T (b) in $EuCu_2(Si_xGe_{1-x})_2$.

to deviate from the CW law is defined as T_0. The T_0 increases with increasing Si concentration x. Such behaviour is roughly similar to that associated with the valence transition from Eu^{2+} to Eu^{3+} in $EuNi_2(Si_{1-x}Ge_x)_2$. However, the decrease in the χ with decreasing temperature is much smaller than that observed in $EuNi_2(Si_{1-x}Ge_x)_2$. At lowest temperatures, the χ for all the samples increases with decreasing temperature, which is possibly due to an extrinsic impurity since χ measured in the field of 5 T is suppressed, as shown in Fig. 1(b). Such an impurity, which is often observed, makes it difficult to investigate the ground state of valence fluctuating Eu compounds precisely. For $x = 1$, the χ is independent of temperature. The rise of the χ in the field of 5 T below 80 K (possibly due to an impurity) is also suppressed by magnetic field of 5 T. On the other hand, for $x = 0$, 0.50 and 0.65, the χ–T curve has a bend at lowest temperature, as shown in Fig. 1(b), which is ascribed to the antiferromagnetic ordering. Especially, for $x = 0$, the curve has two bends at 7.0 K and 11 K. Recently, similar two Néel temperatures have been reported also in $EuNi_2Ge_2$ [9].

Figure 2(a) shows the temperature dependence of the mean Eu valence v estimated from the XAS measurements in $EuCu_2(Si_xGe_{1-x})_2$. Except for $x = 0$, 0.50, with decreasing temperature, the valence is shifted toward a trivalent state. Compared with the behaviour observed in $EuNi_2(Si_{1-x}Ge_x)_2$ [2] and $Eu(Pd_{1-x}Pt_x)_2Si_2$ [3], the thermal variation of the v is much broader and smaller. For $x = 0.70 \sim 0.80$, the T_0 estimated from the χ–T curve is indicated as arrows in Fig. 2(a). The valence at the T_0 is found to be an almost common value of $2.4 \sim 2.45$, which appears to be a boundary between the temperature-independent nonmagnetic behaviour and the CW magnetic behaviour. For $x = 0$ and 0.50, the valence is almost independent of tem-

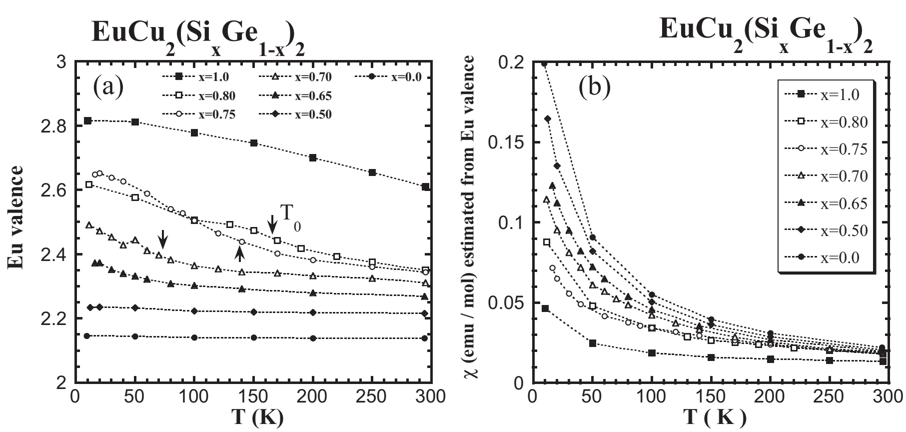

Fig. 2. Temperature dependence of Eu valence estimated from the XAS measurements in $EuCu_2(Si_xGe_{1-x})_2$ (a) and the χ estimated from the Eu valence (b).

perature. No anomaly is observed at T_N in the v–T curve. For $x = 0.65$, the valence at the lowest temperature is found to be close to 2.4, which suggests the antiferromagnetism is in the vicinity of the valence fluctuating state. Finally, in order to compare the valence with the χ, we estimated the susceptibility from the Eu valence as $\chi = \chi_2 p_2 + \chi_3 p_3$, where p_2 and p_3 are occupation probabilities of the Eu^{2+} and Eu^{3+} state estimated from the XAS measurements, respectively. The χ_2 is calculated from the CW law with a theoretical effective moment of Eu^{2+} and a Weiss temperature of -25 K. The χ_3 is the susceptibility of the Van-Vleck paramagnetism of Eu^{3+}. The calculated results are shown in Fig. 2(b). Compared with Fig. 1(a), it is found that the temperature-independent susceptibility observed for $x = 0.70 \sim 0.80$ below T_0 is not reproduced at all, which suggests that it is necessary to consider not only the valence change but also hybridizations between $4f$ electrons and a conduction band in order to interpret the behaviour of $EuCu_2(Si_xGe_{1-x})_2$. This should be associated with the Kondo-lattice state [4] and the heavy fermion behaviour [5].

4. Conclusions

We have reported the magnetic property and the Eu valence in $EuCu_2(Si_xGe_{1-x})_2$. For $0.70 \leq x \leq 0.80$, it is found that the χ deviates from the CW law, which is associated with the valence change observed by the XAS measurements. However, it is difficult to explain the temperature-independent susceptibility, which appears after the deviation, only in terms of the valence change. We propose that the hybridization between $4f$ electrons and a conduction band also plays an important role in the behaviour.

REFERENCES

[1] E. V. Sampathkumaran *et al.*, *J. Phys. C: Solid State Phys.* **14**, L237 (1981).
[2] H. Wada *et al.*, *J. Phys.: Condens. Matter* **9**, 7913 (1997).
[3] A. Mitsuda *et al.*, *J. Phys.: Condens. Matter* **12**, 5287 (2000).
[4] E. M. Levin *et al.*, *Sov. Phys. Solid State* **28**, 1736 (1986).
[5] Z. Hossain *et al.*, submitted to *Physica B.*
[6] I. Felner, I. Nowik, *J. Phys. Chem. Solids* **39**, 763 (1978).
[7] E.R. Bauminger *et al.*, *Phys. Rev. Lett.* **30**, 1053 (1973).
[8] M. Nomura, A. Koyama, *J. Synchrotron Rad.* **6**, 182 (1999).
[9] S.L. Bud'ko *et al.*, *J. Magn. Magn. Mater.* **205**, 53 (1999).