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Magnetic Susceptibility of liquid Gd-NM (NM = Cu, Ga, Ge) alloys

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Abstract. For rare earth alloys, the indirect interaction of RKKY is at work between rare-earth atoms. Therefore, the magnetism of them depends on the number of conduction electrons and the distance between rare-earth metals. In this work, to reveal the relationship between the number of conduction electrons and magnetic property of rare earth metal alloys, magnetic susceptibility measurements for liquid Gd-NM (NM = Cu, Ga, Ge) was performed by Faraday method. As the results, it was observed that the sign of paramagnetic Curie temperature of Cu-Gd alloys are positive at all composition, while Ga-Gd and Ge-Gd alloys show negative paramagnetic Curie temperature at certain composition. Moreover, it was indicated when the alloy at certain composition shows highest melting temperature, it has the lowest paramagnetic Curie temperature.

1 Introduction

Rare earth alloys are used for making various materials and they are known as useful materials. Among the rare-earth alloys, Al-REM (rare earth metal) alloys have been investigated for a long time, and it is widely known that they have interesting physical properties. Specifically, the rare earth-Al phase diagrams [1] contain a number of intermetallic compounds ranging from AlR_3 to $Al_{11}R_3$.

For rare-earth alloys, it is common sense that rare-earth atoms exist in R^{3+} or R^{2+} states at high temperatures in Al-based alloys and their magnetic moment per R-atom in the alloys shows the same value of pure rare-earth metals. However, former experimental results by Sidorov et al. indicated that the magnetic moment per R-atom of dilute Al-REM alloys is rather lower than for ions R^{3+} [2-4]. Given that alloys make intermetallic compounds, they claim this fact can be explained if REM ions exist not in form R^{3+}. And they claim that the existence of Al_2R quasimoleculars is highly probable in these alloys and their destruction starts only above melting point of Al_2R compound. Moreover, Uporova et al. reported the property of magnetic susceptibility of Al_2R alloys in a wide range of temperature [5] and

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they discovered the magnetic susceptibility of Al_2R alloys increase over the melting temperature of Al_2R.

The Al_2Gd alloy shows really high melting temperature and it is naturally considered that the Al_2Gd is the most stable in the Al-Gd alloys. In addition, Ga_2Gd alloy also show the highest melting temperature. On the other hand, in Ge-Gd systems, Ge_2Gd_5 shows the highest melting temperature in Ge-Gd alloys. In addition, in the case of Cu-Gd systems, they have lower melting temperature than the melting points of pure Gd and Cu. Cu, Ga and Ge belong to fourth period in periodic table and the valence are 1, 3 and 4, respectively. So we think the difference of height of melting temperature between Cu-Gd, Ga-Gd and Ge-Gd would depend on the number of conduction electrons of their alloys. In this study, we performed the magnetic susceptibility measurements for liquid Cu-Gd, Ga-Gd and Ge-Gd. The aim of this work is to reveal the relationship between the number of conduction electrons and magnetic susceptibility.

2 Experimental procedure

Magnetic susceptibility measurements were carried out using the Faraday method with a torsion balance [6]. The force applied to the sample in the cell was quantified by an automatic method of feedback current control. A Mohr's salt was used as a standard. The field strength, H, of the electromagnet was approximately 10 kOe with a 6.0 cm gap between pole pieces, and $H{\cdot}\mathrm{d}H/\mathrm{d}x$ was approximately 6.34 ± 0.04 $(\mathrm{k{\cdot}Oe})^2$/cm.

A Gd-NM (NM = Cu, Ga and Ge) alloy sample was placed in an magnesia cell with a magnesia stick, and was completely melted and homogenized under purified helium gas at a pressure of 20 kPa in a silicon carbide furnace. All measurements were carried out in the liquid state from about 1450°C down to the melting point. The chemical composition of each sample was determined by accurately measuring the mass of each component before mixing. After these measurements, we measured the sample mass and we re-calculate the accurate composition. The temperature of the liquid alloy was determined using Pt-Pt13%Rh thermocouples placed close to the sample.

3 Results

3.1 Experimental results

Figure 1 shows that the temperature dependence of magnetic susceptibility of liquid Gd_{1-c}-NM_c (Cu, Ga, Ge) alloys. The arrows show the melting temperature at the compositions. Since all of them decrease with increasing temperature, it is naturally considered that all of them follow Curie-Weiss law.

Figure 2 shows that the compositional dependence of magnetic susceptibility from 4f electrons, χ_{4f}, of liquid Gd_{1-c}-NM_c (Cu, Ga, Ge) alloys. In the case of Cu-Gd and Ga-Gd alloys, the magnetic susceptibility decrease linearly to some extent with increasing the amount of Cu and Ga composition. On the other hand, the magnetic susceptibility of $Ge_{0.2}Gd_{0.8}$ shifts downward from linear change. However, the magnetic susceptibility of Ge-Gd alloys roughly follows linear change.

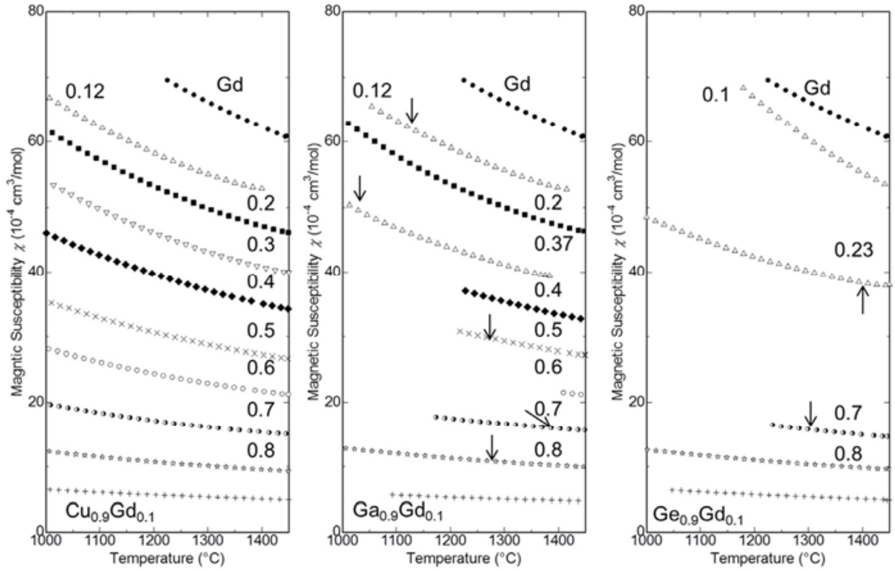

Fig. 1. Temperature dependence of magnetic susceptibility of $Gd_{1\text{-}c}NM_c$ (NM = Cu, Ga, Ge) alloys.

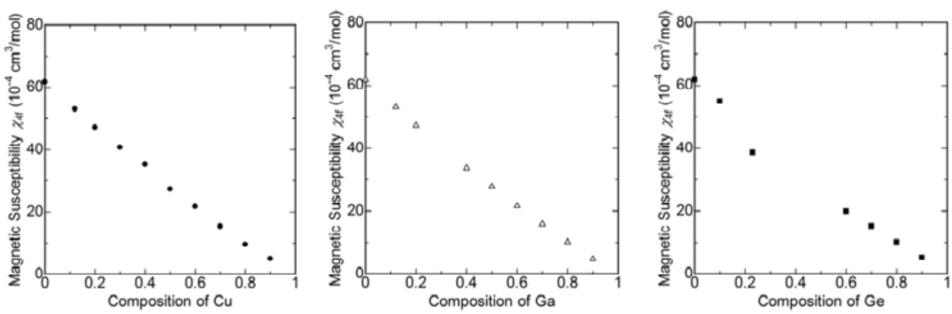

Fig. 2. Compositional dependence of magnetic susceptibility of $Gd_{1\text{-}c}NM_c$ (NM = Cu, Ga, Ge) alloys.

3.2 Analysis

In our experiment, the magnetic susceptibility of a liquid Gd-NM alloy is given by

$$\chi_{\mathrm{exp}} = \chi_{\mathrm{para}} + \chi_{\mathrm{dia}} + \chi_{\mathrm{4f}}, \tag{1}$$

where χ_{para} is the paramagnetic susceptibility due to conduction electrons, χ_{dia} is the diamagnetic susceptibilities due to Gd and NM ions and χ_{4f} denotes the magnetic susceptibility due to the localized 4f electrons. The diamagnetic susceptibility, χ_{dia}, was estimated by following formula.

$$\chi_{\mathrm{dia}} = (1\text{-}c)\,\chi_{\mathrm{dia}}(\mathrm{Gd}^{3+}) + c\chi_{\mathrm{dia}}\ (\mathrm{NM\ ion}) \tag{2}$$

We utilized the values of $\chi_{\mathrm{dia}}(\mathrm{Gd}^{3+})$ and χ_{dia} (NM ion) adopted in previous papers. We assumed that the total χ_{dia} for liquid Gd-NM alloys varies linearly with composition dependence. And the paramagnetic susceptibility, χ_{para}, was estimated by nearly free electron approximation [7, 8].

For all the compounds, since the magnetic susceptibility decreases with increasing temperature, they were approximated by the generalized Curie-Weiss law:

$$\chi_{4f} = \frac{C}{T-\theta} + \alpha \tag{3}$$

where C – Curie constant, θ – paramagnetic Curie temperature, α – the residual susceptibility at infinite temperature, respectively. And it is widely known that the Curie constant, C, can be denoted by

$$C = \frac{N_A p^2 \mu_B^2}{3k_B}, \tag{4}$$

where N_A is the number of Gadrinium atoms per mole, p is the effective number of Bohr magnetons, μ_B is Bohr magneton and k_B is Boltzmann constant.

Curie constants and paramagnetic Curie temperatures were obtained by fitted with Curie-Weiss law. In our fitting, we assumed the residual susceptibility for pure Gd as 0.00075 cm^3/mol. It was decided as the Curie constant of liquid Gd become appropriate value, which compared with the Curie constant in solid state. And we assumed that the residual susceptibility of other alloys decrease linearly with increasing the amount of NM composition.

3.3 Curie constant and the effective number of Bohr magnetons

Figure 3 shows the compositional dependence of Curie constant. The black circles, red triangles and blue squares show the Curie constant of Cu-Gd, Ga-Gd and Ge-Gd, respectively. In the case of Cu-Gd system, the curie constant decrease linearly with increasing the amount of Cu composition. However, in the case of Ga-Gd, the Curie constant at $Ga_{0.2}Gd_{0.8}$ shifts down and that at $Ga_{0.6}Gd_{0.4}$ shifts up from linear change. Moreover the Curie constant at $Ge_{0.1}Gd_{0.9}$ also shifts down with linear change.

Figure 4 shows the compositional dependence of the effective number of Bohr magnetons. In the case of Cu-Gd alloys, almost all the P values are around 8.0, which is equal to the pure Gd one. However the P of $Ga_{0.6}Gd_{0.4}$ is 9.0 and the P of $Ge_{0.1}Gd_{0.9}$ become 6.9. It can be interpreted that the surrounding environment around Gd atoms is different with pure liquid Gd atoms as shown in former studies [2-5].

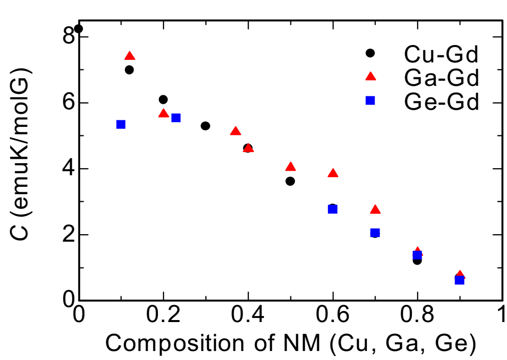

Fig. 3. The compositional dependence of Curie constant

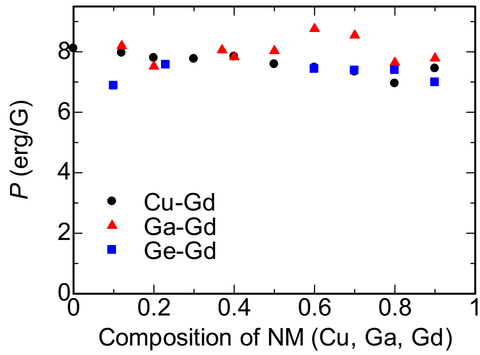

Fig. 4. The compositional dependence of the effective number of Bohr magnetons

3.4 Paramagnetic Curie temperature

The compositional dependence of paramagnetic Curie temperature is shown in Figure 5. In the case of Cu-Gd alloys, the paramagnetic Curie temperatures are positive at all composition. However, in the case of Ga-Gd alloys, they are negative at around c = 0.6 compositions. And in Ge-Gd alloys, it is easily considered that there may be negative paramagnetic Curie temperature at around c = 0.4.

For rare earth metals the indirect interaction of RKKY(Ruderman and Kittel [9], Kasuya [10], Yoshida [11]) type is at work between the rare-earth atoms. RKKY exchange integrals have oscillating and weak decay on distance:

$$H_{\mathrm{RKKY}} = -9\pi \frac{J^2}{\varepsilon_{\mathrm{F}}} \left(\frac{N_e}{N} \right)^2 f(2k_F R)\mathbf{S}_1 \cdot \mathbf{S}_2 \tag{5}$$

$$f(x) = \frac{-x\cos x + \sin x}{x^4}, \tag{6}$$

where $f(x)$ determines the space dependence of RKKY interaction.

The composition dependence of calculated $f(x)$ of Ga-Gd was shown in Figure 6. To estimate the $f(x)$, we assumed that the distance between Gd ions become longer linearly with decreasing the amount of Gd composition. And the both valence of Gd and Ga was approximated as 3. At a glance, the compositional dependence of paramagnetic Curie temperature looks like the composition dependence of $f(x)$. Specifically, both of them has local minimum at c = 0.6.

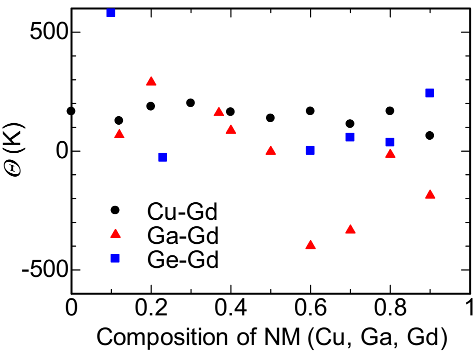

Fig. 5. The compositional dependence of paramagnetic Curie temperature

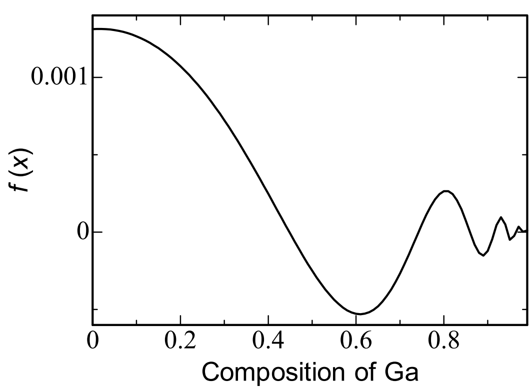

Fig. 6. The compositional dependence of $f(x)$

4 Discussion

For rare-earth alloys, the magnetism includes the effect of RKKY interaction. In brief, when the sign of $f(x)$ is positive, the magnetism become ferromagnetism and *vice versa*. In liquid state, although all of them show paramagnetism, there are differences whether it shows ferromagnetism or anti-ferromagnetism below Curie temperature or Néel temperature.

In our results, it is revealed that the paramagnetic Curie temperatures of Cu-Gd systems are positive in all composition. On the other hand, the sign of paramagnetic Curie temperature of Ga-Gd and Ge-Gd alloys show negative at specific compositions, which are c = 0.6-0.7, 0.9 in Ga_c-Gd_{1-c} systems and may be c = 0.2-0.5 in Ge_c-Gd_{1-c} systems. And, it is revealed that the compositional dependence of paramagnetic Curie temperature consists with the compositional dependence of $f(x)$.

While the melting temperature of Cu-Gd systems show lower value than the melting temperature of pure Cu and Gd, the melting temperature of $Ga_{0.66}Gd_{0.34}$ and $Ge_{0.38}Gd_{0.62}$ show the highest melting temperature in their system. In Ga-Gd and Ge-Gd systems, the sign of paramagnetic Curie temperature around $Ga_{0.66}Gd_{0.34}$ and $Ge_{0.38}Gd_{0.62}$ show negative and the sign of paramagnetic Curie temperature of eutectic composition show positive. The latter tendency is also shown in Cu-Gd systems. From these, we think that the sign of paramagnetic Curie temperature relates to the height of melting temperature.

4 Summary

The magnetic susceptibility measurements of Gd-NM (NM = Cu, Ga and Ge) alloys were carried out by using Faraday method. In all alloys, it is revealed that the magnetic susceptibility from 4f electrons follows Curie-Weiss law. Although the Curie constant of Cu-Gd systems decrease linearly with increasing the amount of Cu to some extent, the Curie constant become larger or smaller than linear change for Ga-Gd and Ge-Gd system. It can be interpreted that the surrounding environment of Gd shows difference with pure Gd systems. Moreover, while the sign of paramagnetic Curie temperature of Cu-Gd system is positive at all composition, for Ga-Gd and Ge-Gd liquid alloys paramagnetic Curie temperature become positive or negative depending on alloy composition. In addition it is indicated that the composition dependence of melting temperature follow the sign of paramagnetic Curie temperature and we think that the sign of paramagnetic Curie temperature relates to the height of melting temperature.

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