Magnetic Properties of Liquid RE-Co (RE = Dy, Er) Alloys

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The magnetic susceptibilities χ of liquid Dy-Co and Er-Co alloys have a large and negative temperature coefficient, which suggests that the Dy, Er, and Co ions in their liquid alloys are in the magnetic state. However, the temperature dependence of χ in both systems becomes weak near the content of 70 at% Co. It is interesting that the compositional dependence of χ for liquid Dy-Co and Er-Co alloys has a minimum at content of 80 at% Co, respectively. On the Co-rich side, the magnetic susceptibility of liquid Dy-Co and Er-Co alloys obeyed the Curie-Weiss law with regard to their temperature dependence of χ. On the rare earth-rich side, the magnetic susceptibilities of liquid Dy-Co and Er-Co alloys also exhibited Curie behavior with a reasonable value for the effective number of Bohr magnetons. The compositional dependence of χ_{4f} for liquid Dy-Co and Er-Co alloys was extracted by subtracting the corresponding data for liquid La-Co alloys from χ for the liquid Dy-Co and Er-Co alloys, respectively.

1 Introduction

Busch and colleagues [1] reported the electronic properties of liquid transition metal (TM), rare earth metal (RE), and their alloys. Schlapbach [2] reported more detailed dependence of magnetic susceptibility on composition with a minimum for liquid Ce-TM (TM = Fe, Co, Ni) alloys and found a continuous transition of Ce ions into the nonmagnetic state. Moreover, Singer et al. [3] extended and explained the compositional dependence of χ for liquid Ce-TM, Pr-TM, La-TM (TM = Fe, Co, Ni), and Sm-Fe alloys. In their paper [3], the compositional dependence of χ for liquid La-TM alloys plays an important role in understanding the magnetic susceptibility of liquid RE-TM (RE = Ce, Pr, Sm) alloys. Actually, the compositional dependence of χ_{4f} can be obtained by subtracting the corresponding data for liquid La-TM alloys from χ for liquid RE-TM (RE = Ce, Pr, Sm) alloys.

We attempt to obtain the magnetic susceptibilities as the functions of temperature and composition for liquid Dy-Co and Er-Co alloys. The magnetic susceptibility of liquid Dy-Co and Er-Co alloys consists of the two large terms due to the 3d- and 4f-electron states.

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The contribution of these two electron states provides a convenient sectionalization in the each region on the Co-rich and RE-rich (RE = Dy, Er) sides. Therefore, these two terms can be separated to obtain the temperature dependence of χ_{3d} and χ_{4f} for liquid RE-Co (RE = Dy, Er) alloys. The P_{eff} values for the Dy, Er, and Co ions in liquid Dy-Co and Er-Co alloys can thus be estimated from the temperature dependence of χ_{3d} and χ_{4f}. We investigate the trend of P_{eff} for Dy and Er ions on the basis of the s-f and indirect d-f interactions and compare the trend of Peff for Ce, Pr, Gd, Dy, and Er ions in liquid RE-Co alloys (RE = Ce, Pr, Gd, Dy, Er), respectively.

2 Experimental

Magnetic susceptibility measurements were made using the Faraday method with a torsion balance [4, 5]. The force applied to the sample in the cell was quantified by an automatic method of feedback current control. Mohr's salt (χ = 1.26 × 10^{-2} cm^3/mol at room temperature) was employed as a standard sample. The field strength H of the electromagnet was 10 kOe with a 6.0 cm gap between pole pieces, and $H \cdot dH/dx$ was 6.25 ± 0.12 $(kOe)^2$/cm.

The measurement system can be evacuated in a vacuum of 1.2 × 10^{-2} Pa and filled with a purified Ar gas at a pressure of 7 kPa. The RE-Co alloy sample was placed in a magnesia (MgO) crucible packed loosely with a MgO rod, and was completely melted and homogenized in a silicon carbide furnace under the above condition. The measurements of liquid Co and Er were carried out up to about 1570 °C. The measurements on the Co-rich side were carried out from the temperature between 1500 °C and 1550 °C to the melting point. The chemical composition of each sample was determined by accurately measuring the mass of each component before mixing. After this measurement, the decrease in weight of a 0.2 g sample was less than 4 mg. The temperature of the liquid alloy was determined using Pt-Pt13%Rh thermocouples placed close to the sample. The elemental purity was 99.9% for Dy, Er, and Co.

3 Results

As shown in Fig. 1(a), liquid Co has a large and negative temperature coefficient of magnetic susceptibility. On the Co-rich side, the magnetic susceptibilities χ of liquid Dy-Co alloys decrease with increasing Dy content up to 20 at% Dy and these temperature coefficients of χ become weak up to 30 at% Dy. With further increasing Dy content, the magnetic susceptibilities of liquid Dy-Co alloys increase with a large and negative temperature coefficient of χ. This suggests that the Co and Dy ions in the liquid Dy-Co alloys are in magnetic states. The values of χ for liquid Co and Dy are in good agreement with those obtained in the previous works [5, 6].

As shown in Fig. 1(b), the magnetic susceptibilities χ of liquid Er-Co alloys also decrease with increasing Er content up to 20 at% Er and these temperature coefficients of χ become weak up to 30 at% Er. With further increasing Er content, similarly, the magnetic susceptibilities of liquid Er-Co alloys increase with a large and negative temperature coefficient of χ. This suggests that the Co and Er ions in the liquid Er-Co alloys are in magnetic states. The limit of utility of MgO crucible may be up to the temperature of 1570 °C for liquid Er.

Figure 2 shows the compositional dependence of χ for liquid Dy-Co and Er-Co alloys at 1400 and 1500 °C. We added the compositional dependence of χ of liquid Gd-Co and La-Co alloys at 1350 and 1500 °C to do some more investigating. The compositional dependences of χ for liquid Dy-Co and Er-Co alloys decrease with decreasing Co content and exhibit a minimum at the compositions of 20 at% Dy and Er, respectively. The magnetic susceptibilities of liquid Dy, Er, and Gd are approximately 901, 693, and 663 × 10^{-5} cm^3/mol at the melting point, respectively.

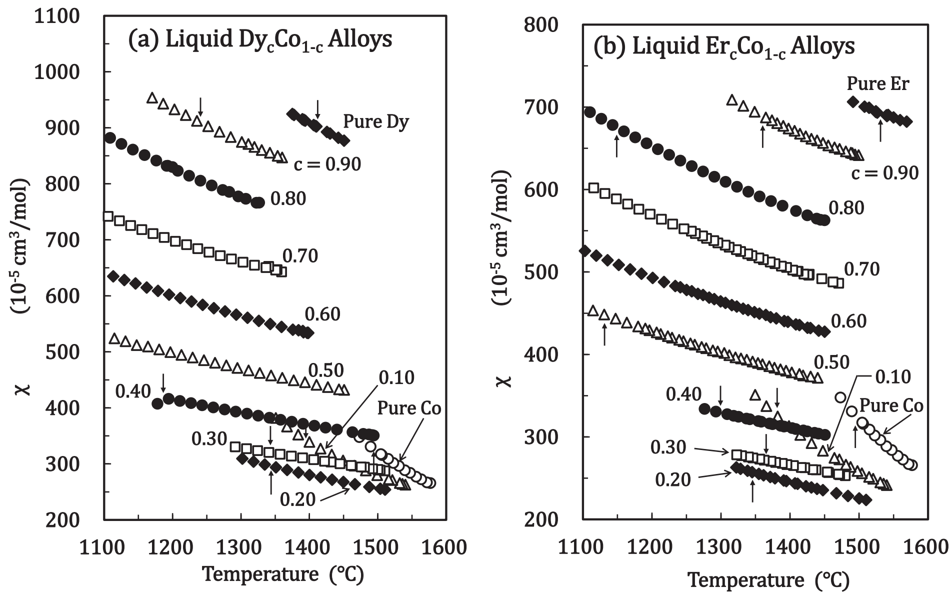

Fig. 1. Magnetic susceptibility of liquid RE_cCo_{1-c} alloys as a function of temperature. (a) liquid Dy_cCo_{1-c} alloys; (b) liquid Er_cCo_{1-c} alloys. The arrows indicate the melting point of the alloys. Experimental error is about 2.5%.

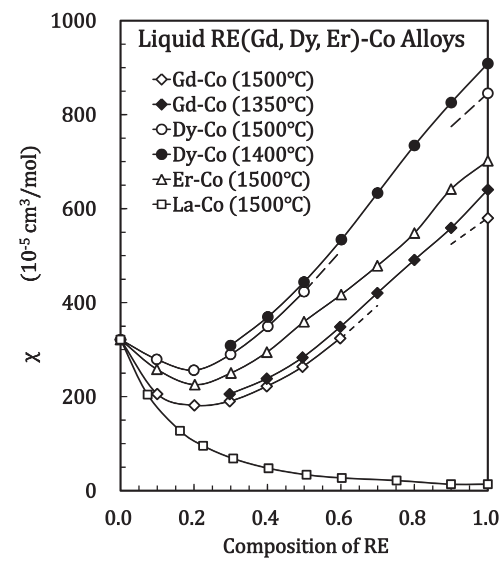

Fig. 2. Dependence of χ on composition for RE_cCo_{1-c} (ER = Dy, Er, Gd) alloys. The compositional dependence of χ for liquid La_cCo_{1-c} alloys was reported by Singer et al. [3]. The solid lines and dashed lines are drawn as guides for the eye.

4 Discussion

The magnetic susceptibility of a liquid RE-Co alloy is given by [5, 7]

$$\chi_l = [(1\text{-}c)\chi_{dia}(Co^+) + c\chi_{dia}(RE^{3+})] + \chi_{el} + \chi_{3d} + \chi_{4f} + \chi_{5d}, \quad (1)$$

where $\chi_{dia}(Co^+)$ and $\chi_{dia}(RE^{3+})$ are the diamagnetic susceptibilities due to the Co^+ and RE^{3+} (RE = Dy, Er, Gd) ions, respectively. The diamagnetic susceptibilities of Co^+, Dy^{3+}, Er^{3+}, and Gd^{3+} ions have been estimated by Bain and Berry [8], and Mendelsohn et al. [9], respectively. The diamagnetic susceptibility of Co ions in metals has been obtained by Banhart et al. [10]. The values of χ_{dia} for Co^+, Dy^{3+}, Er^{3+}, and Gd^{3+} ions employed in this work are -1.82, -1.90, -1.80, and -1.80 × 10^{-5} cm^3/mol, respectively. We assume that the total χ_{dia} for liquid Dy-Co, Er-Co, and Gd-Co alloys varies linearly with composition.

χ_{el} is the paramagnetic susceptibility due to conduction electrons, expressed as [7, 11]

$$\chi_{el} = \alpha(m^*, r_s)\mu_B^2 N(E_F), \quad (2)$$

where $N(E_F)$ is the density of states at E_F, which can be estimated from the nearly free electron model as follows: [7, 11]

$$N(E_F) = (V_a/2\pi^2)(2m/\hbar^2)^{3/2}E_F^{1/2}. \quad (3)$$

Here, V_a is the atomic volume and E_F is given by [7, 11]

$$E_F = (\hbar^2/2m)(3\pi^2 N_e/V_a)^{2/3}, \quad (4)$$

where N_e is the number of conduction electrons.

We assume that the E_F and $N(E_F)$ values are estimated by the linear interpolation of N_e and V_a from the RE side to the Co side. The 4s electrons of Co ions and the $6s^2$ electrons of RE ions are simply treated as conduction electrons. It is assumed that the 5d electrons of RE ions form independently the density of 5d-electron states.

We assume that the m^*/m ratio is 1.0 in liquid Co, RE, and their alloys. In this assumption, the enhancement factor for nearly free electrons is given by [12, 13]

$$\alpha(m, r_s) = \alpha(r_s) - 1/3, \quad (5)$$

where $\alpha(r_s)$ is the enhancement factor of free-electron theory. The dimensionless quantity r_s is defined as $(3.64 \times 10^8)/k_F$, where k_F is the Fermi wave number. The $\alpha(r_s)$ estimated by the random phase approximation increases slightly with increase r_s, and were determined to be 1.28, 1.28, 1.28, and 1.27 for liquid Dy, Er, Gd, and Co, respectively.

The compositional dependences of χ_{el} estimated using this approach deviate above slightly from the straight line connected on the Co side and RE (RE = Dy, Er, Gd) side, respectively. Assuming that the value of χ_{dia} for liquid RE-Co varies linearly with composition, we estimated the compositional dependence of (χ_{dia} + χ_{el}), as shown in Fig. 3. As a result, the compositional dependence of (χ_{dia} + χ_{el}) obtained in this procedure approximates a straight line on the scale shown in Fig. 3. As a result, the compositional dependence of (χ_{dia} + χ_{el}) obtained in this procedure approximates a straight line on the scale shown in Fig. 3. The values of V_a, χ_{dia}, and χ_{el} are shown in Table 1.

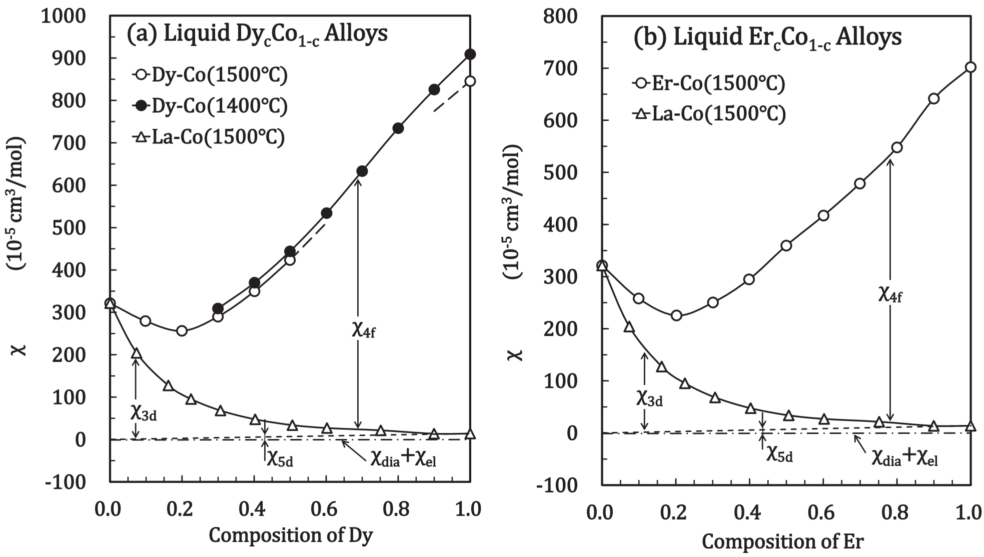

Fig. 3. Dependence of χ on composition for liquid RE_cCo_{1-c} alloys. (a) liquid Dy_cCo_{1-c} alloys; (b) liquid Er_cCo_{1-c} alloys. The compositional dependence of χ for liquid La_cCo_{1-c} alloys was reported by Singer et al. [3]. The base line is the compositional dependence of (χ_{dia} + χ_{el}). The solid lines and dashed lines are drawn as guides for eye.

Table 1. V_a, χ_{dia}, and χ_{el} for Co^+, Dy^{3+}, Er^{3+}, La^{3+}, Gd^{3+}, Pr^{3+}, and Ce^{3+} ions.

	Co^+	Dy^{3+}	Er^{3+}	La^{3+}	Gd^{3+}	Pr^{3+}	Ce^{3+}
V_a (10^{-23} cm^3/mol)	1.26	3.32	3.32	3.94	3.80	3.63	3.56
χ_{EXP} (10^{-5} cm^3/mol)	321	846	702	14	579	147	85
χ_{dia} (10^{-5} cm^3/mol)	-1.82	-1.90	-1.80	-2.00	-2.00	-2.00	-2.00
χ_{el} (10^{-5} cm^3/mol)	0.68	1.65	1.65	1.86	1.81	1.75	1.87
$\chi_{dia}+\chi_{el}$ (10^{-5} cm^3/mol)	-1.14	-0.25	-0.15	-0.14	-0.19	-0.25	-0.13

As mentioned above, the 5d-electrons of RE and La ions seems to form independently the density of 5d-electron states. Therefore, the magnetic susceptibility of χ_{5d} due to 5d-electron is given by [14]

$$\chi_{5d} = N_A \mu_B^2 \rho_{5d}(E_F)/[1-U\rho_{5d}(E_F)/2], \quad (6)$$

where U is the intra-atomic Coulomb interaction. The experimental χ value of liquid La corresponds to (χ_{dia} + χ_{el} + χ_{5d}) value. We can obtain the $\rho_{5d}(E_F)$ value of liquid La under the assumption that U = 2.0 eV. The $\rho_{5d}(E_F)$ obtained is 0.81 eV^{-1}·atom^{-1}, which is larger than the $\rho_{6s}(E_F)$ value of 0.60 eV^{-1}·atom^{-1}. The $\rho_{5d}(E_F)$ value may be really admixed by $\rho_{6s}(E_F)$, which forms the width of 5d-state. The magnetic susceptibilities of liquid TM-La alloys consists of (χ_{dia} + χ_{el}) value and χ_{5d} of eq. (7). The dependence of (χ_{dia} + χ_{el} + χ_{5d}) on composition obtained in this procedure approximates a straight line on the scale shown in Fig. 3.

According to their suggestion of March and Sayers [15], the magnetic susceptibility of liquid Dy-Co, Er-Co, and Gd-Co alloys consists of the two large terms due to the 3d-electron and 4f-electron states on the TM-rich side and RE-rich side. We compare the magnetic susceptibility of liquid RE-Co and La-Co alloys. The magnetic susceptibility of La-Co alloy is given by [5, 7]

$$\chi_2 = [(1-c)\chi_{dia}(Co^{+}) + c\chi_{dia}(La^{3+})] + \chi_{el} + \chi_{3d} + \chi_{5d}, \tag{7}$$

where $\chi_{dia}(La^{3+})$ are the diamagnetic susceptibilities due to La^{3+} ions. Roughly speaking, we can obtain the χ_{4f} value by subtracting eq. (7) from eq. (1) as follows;

$$\chi_{4f} \approx \chi_1 - \chi_2. \tag{8}$$

Assuming that ($\chi_{dia} + \chi_{el}$) is considerably smaller than χ_{3d} and χ_{4f}, we can obtain the χ_{4f} values of eq. (8) with a high degree of accuracy.

Figure 3(a) shows the dependence of χ on composition for liquid Dy-Co alloys. Assuming that the χ_{3d} of Co ions in liquid Dy-Co alloys may be little different from that in liquid La-Co alloys, we also plotted the dependence of χ on composition for liquid La-Co reported by Singer et al. [3]. This difference between the lines of liquid Dy-Co and La-Co alloys corresponds to the dependence of χ_{4f} on composition due to 4f-electrons. The base line exhibits the dependence of ($\chi_{dia} + \chi_{el}$) on composition due to the Dy and Co ions, and conduction electrons, which is a very small value compared with χ_{4f} and χ_{3d}. The dependence of χ_{3d} on composition decreases rapidly with decreasing Co content. The variation of χ_{4f}, χ_{5d}, and χ_{3d} are reasonable for the composition of Dy and Co.

Figure 3(b) shows the dependence of χ on composition for liquid Er-Co alloys. The dependence of χ on composition for liquid La-Co alloys exhibits the data reported by Singer et al. [3]. As shown in Fig. 3(b), the significant point of comparison is that the difference between the lines for liquid Er-Co and La-Co increases with increasing Er (or La) content. This difference corresponds to the dependence of χ_{4f} on composition due to 4f-electrons. The base line exhibits the dependence of ($\chi_{dia} + \chi_{el}$) on composition due to the Er (or La) and Co ions, and conduction electrons, which is a very small value compared with χ_{4f} and χ_{3d}. The dependence of χ_{3d} on composition decreases rapidly with decreasing Co content. The variations of χ_{4f} and χ_{3d} obtained in Fig. 3(b) are also reasonable for the composition of Er and Co.

Figure 4 shows the dependence of χ_{4f} on composition for liquid RE-Co (RE = Dy, Er, Gd) alloys. For liquid Gd-Co alloys, the dependence of χ_{4f} on composition was obtained by similar manner. Liquid RE-Co alloys have similar dependence of χ_{4f} on composition, which deviates below from straight line. The χ_{4f} values of liquid RE-Co alloys decrease with increasing temperature, which reflects the temperature dependence of the experimental χ value. It suggests that the RE ions in liquid RE-Co alloys are in the magnetic state over the wide composition range. It is known that the Curie-Weiss law describes the magnetic susceptibility in the magnetic state fairly well. For liquid RE-Co in the magnetic state, the third and fourth terms on the right-hand side of eq. (1) is given by [5, 7]

$$\chi_{4f,\ or\ 3d} = [N_A P_{eff}^2 \mu_B^2 / 3k_B(T-\theta)] + \alpha, \tag{9}$$

where N_A is the number of RE or Co atoms per mole. P_{eff} is the effective number of Bohr magnetons. The symbols θ and α are the paramagnetic Curie temperature and a residual susceptibility at infinite temperature, respectively [9].

In this work, the P_{eff} values of RE ions in liquid RE-Co alloys were obtained from the equation of $P_{eff}(RE^{3+}) = (3k_BT\chi_{4f}/N_A)^{1/2}\mu_B$ under the assumptions that $\theta = 0$ and $\alpha = 0$. On the Co side, the P_{eff} and θ for the Co ions in liquid RE-Co (RE = Dy, Er, Gd) alloys were obtained from the plots of $(1/\chi_{3d})$ vs T. The θ values obtained from this approach are 1450, 1340, and 920 K for liquid Co, $Dy_{0.1}Co_{0.9}$, and $Dy_{0.2}Co_{0.8}$ alloys, respectively. The θ values obtained for liquid $Er_{0.1}Co_{0.9}$, $Er_{0.2}Co_{0.8}$, $Gd_{0.1}Co_{0.9}$, and $Gd_{0.2}Co_{0.8}$ alloys are 1340, 790, 1140, and 730 K, respectively. The rapid decrease in χ of liquid RE-Co (RE = Dy, Er, Gd) alloys on the Co-rich side corresponds to the rapid decrease in θ which results from the reduction of exchange d-d interaction between Co ions.

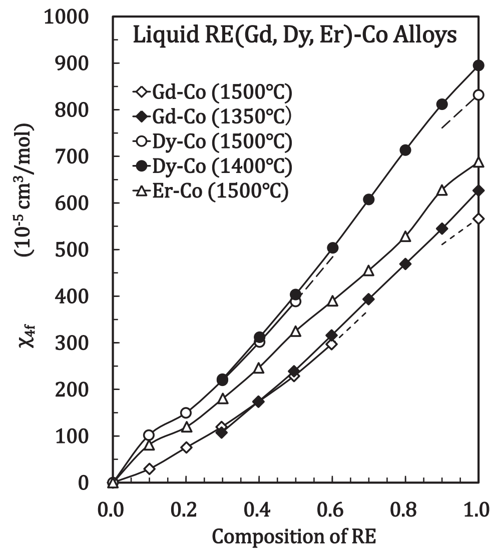

Fig. 4. Dependence of χ 4f on composition for liquid RE_cCo_{1-c} (RE = Dy, Er, Gd) alloys. The solid lines and dashed lines are drawn as guides for eye.

As shown in Fig. 5, we integrate the trends of P_{eff} (RE ions) in liquid RE-Co (RE = Dy, Er, Gd, Pr, Ce) alloys. The P_{eff} values of Ce and Pr ions were estimated from their data [2, 3] by the same manner. The P_{eff} values of Dy and Er ions are approximately 10.9 and 9.9, which are somewhat larger than the theoretical prediction of 10.6 and 9.6 estimated for Dy^{3+} and Er^{3+} ions [16], respectively. The P_{eff} value of Gd^{3+} ions is approximately 8.9, which is larger than the theoretical prediction of 7.9 estimated for Gd^{3+} ions [16]. A swell in P_{eff} for Gd^{3+} ions on the Gd-rich side may be attributable to the assumption of $\theta = 0$. If we can obtain an accurate θ value, we apply the general equation of $P_{eff} = [3k_B(T - \theta)\chi_{4f}/N_A]^{1/2}$ for the analysis of P_{eff}.

It is supposed that metallic RE alloys can be represented by an assembly of RE^{3+} ions embedded in a sea of conduction electrons [17]. In the case of heavy RE-TM alloys [17], the spin of TM ion lying near Gd^{3+} ion take the orientation contrary to the total spin of Gd^{3+} ion. Therefore, a gradual decrease in P_{eff} for liquid RE-Co (RE = Dy, Er, Gd) alloys may be attributed to the alignment of antiparallel moment due to the indirect d-f interaction by way of the conduction electrons [17]. It is well known that liquid Ce-Co alloys give rise to the continuous transition of Ce^{n+} ions with increasing Co content [2, 3]. The trend of P_{eff} for Ce^{n+} ions in liquid Ce-Co alloys is closely related to the continuous transition of Ce ions into the nonmagnetic state. We confirmed the transition of Ce^{3+} to Ce^{4+} ions by this treatment. On the other hand, the Pr ions are stable in liquid Pr-Co alloys. On the Co-rich side, the P_{eff} values correspond to the intermediate state between Co^{+} and Co^{2+} ions with the total spin $S = 1$ and 3/2, respectively. This indicates that the s-d interaction dominates the magnetic susceptibilities of liquid RE-Co alloys on the Co-rich side.

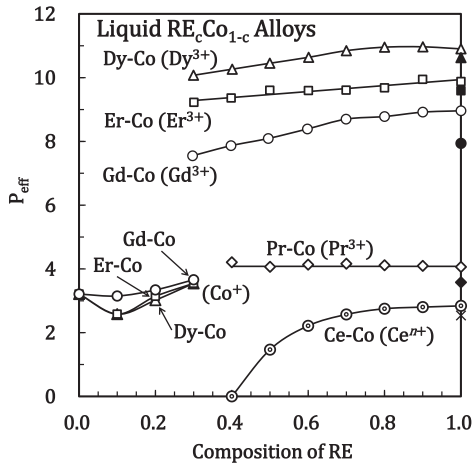

Fig. 5. Dependence of P_{eff} on composition for RE (RE = Dy, Er, Gd, Pr, Ce) and Co ions obtained in liquid RE-Co alloys. The closed traiangle, closed square and so on plotted on the RE side are the calculated values due to Van Vleck [16]. The solid lines are drawn as guides for the eye.

5 Conclusions

Based on the compositional dependence of χ for liquid La-Co alloys, those for liquid Dy-Co and Er-Co alloys can be divided into the two main terms due to the 4f- and 3d-lectrons. Using the Curie and the Curie-Weiss law, P_{eff} for Dy, Er, and Co ions can be estimated from the temperature dependence of χ divided partially. By the addition of Co, the gradual decrease in P_{eff} of Dy and Er ions in these liquid alloys may be attributed to the indirect d-f interaction by way of the conduction electrons. In the liquid RE-Co systems, the 4f-electron states involved with the s-f interaction predominates steadily over the wide composition rage.

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