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Curie temperatures and modified de Gennes factors of rare earth nitrides

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ABSTRACT

The Curie temperatures T_C of the nitrides of the rare earths (Gd, Tb, Dy, Ho, and Er), including binary systems, were investigated. T_C was found to be approximately proportional to the de Gennes factor, $\xi = (g-1)^2 J(J+1)$, where g is the Landé g-factor and J is the total angular momentum quantum number of a trivalent rare earth (RE). This proportionality was significantly improved by introducing a modified de Gennes factor, ξ_{bi}. The conventional de Gennes factor ξ indicates the exchange interaction given by the inner product of the effective spin components of ions of the same kind, whereas our modified de Gennes factor ξ_{bi} also considers interactions between different kinds of ions and statistical factors calculated on the basis of the binomial distribution. The good proportionality obtained between T_C and ξ_{bi} indicates that the spin components of RE ions interact with each other. This interaction is considered to be responsible for the ferromagnetism of these nitrides (including binary systems). These considerations were supported by the synthesis of and magnetization measurements on $Gd_xEr_{1-x}N$ ($x = 0, 0.25, 0.5, 0.75, 1$) samples.

1. Introduction

Rare earth (RE) nitrides form a class of materials with interesting electronic and magnetic properties [1–3], which originate from their open 4f shells. Recent theoretical calculations predict that they have variable electronic states (metallic, semiconducting, insulating, and half-metallicity) and magnetic properties (paramagnetism, ferromagnetism, and antiferromagnetism) [4–9].

The magnetism of RE nitrides has been investigated since the 1960s. NdN, GdN, TbN, DyN, HoN, and ErN exhibit ferromagnetism with Curie temperatures T_C of 28 [10], 58 K–75 [11–18], 42 [19], 26 [20], 18 [19], and 5 K [10], respectively. However, some controversy still remains about the magnetism of GdN. Some reports claim that GdN is ferromagnetic with a T_C of 65–75 K [11–17]. Li et al. reported that stoichiometric GdN is ferromagnetic [18]. Theoretical studies by Kuznietz [21] and Kasuya [22] indicate that the magnetism of GdN originates from the RKKY interaction, which is related to the cross-process between f–d mixing and f–d exchange interactions. The transition temperatures of RE intermetallic compounds [23,24] and RE alloys [25] have been described in terms of the de Gennes factor ξ, which indicates the exchange interaction of the spin component of the total quantum number [26]. On the basis of the variation in the magnetic transition temperature T_{MT} with the de Gennes factor ξ, the exchange interaction has been attributed mainly to the R–R exchange interaction in RNi_2Mn (R = Tb, Dy, Ho, and Er) [23], RNi_2, and RMn_2 [24]. Bozorth [25] reported that the T_{MT} values of RE metals and RE alloys exhibit a $\xi^{2/3}$ dependence (ξ values of alloys were obtained by averaging the ξ values of the alloy components weighted by their atomic fractions); however, no theoretical explanation was provided for this relationship.

We have investigated the magnetic properties of the RE nitrides LnN (Ln = Gd, Tb, Dy, Ho, or Er), including their binary systems, with the aim of using them in magnetic refrigeration for liquefying hydrogen [27–34]. Magnetic refrigeration generates a cooling heat of $Q = T\Delta S$, where ΔS is the magnetic entropy change [35]. A large ΔS can be extracted from a ferromagnet by sweeping an externally applied field and using a temperature close to the T_C. We found that these nitrides are ferromagnets with Curie temperatures below liquid nitrogen temperature, 77 K. To produce an efficient magnetic refrigeration system for cooling hydrogen from liquid nitrogen temperature to its liquefaction temperature (77–20 K), it is desirable to use several materials whose T_C values cover this wide range.

In this paper, we present the results of precise measurements of the correlation between T_C and the de Gennes factor. This is important not only for deriving a universal relation between T_C and ξ for RE nitrides (including binary systems), as has been done for RE metals and alloys, but also for gaining a deeper understanding of the magnetism of this class of materials.

2. Experimental

$Gd_xEr_{1-x}N$ ($x = 0, 0.25, 0.5, 0.75, 1$) samples were synthesized by carbothermic reduction in a nitrogen gas stream. Powders of Gd_2O_3 and Er_2O_3 (99.99% purity) and an appropriate amount of

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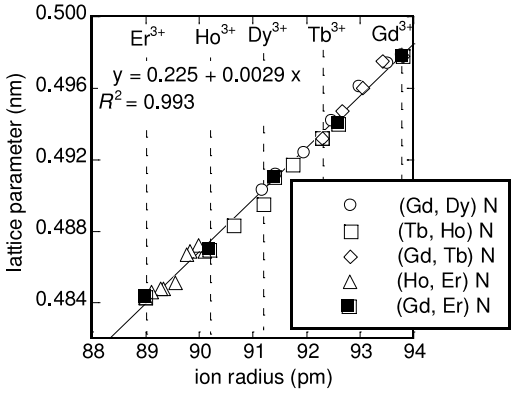

Fig. 1. Lattice parameter as a function of average radius for trivalent rare earth ions. The line was determined by the least mean square method.

amorphous carbon were thoroughly mixed with a mortar and pestle. The powder mixtures were shaped into pellets and heated at 1500 °C in a reaction tube through which 99.9995% purity nitrogen gas was flowed for 8 h. The phases in the products were identified from powder X-ray diffraction (XRD) patterns obtained using a diffractometer (RINT Ultima+; Rigaku Corp.) with Cu Kα radiation. Their magnetizations were measured using a magnetometer (PPMS or MPMS system; Quantum Design Corp.) under various applied fields H and at various temperatures T. The ferromagnetic Curie temperature, T_C, was calculated by drawing an Arrott plot [36].

3. Results and discussion

The XRD patterns obtained for $Gd_xEr_{1-x}N$ ($x = 0.25$, 0.5, 0.75) indicate that they are single phases of the mononitride with the NaCl structure. The lattice parameters of $Gd_xEr_{1-x}N$ were determined by Cohen's method, which demonstrated the validity of Vegard's rule, as we have previously reported [30,31]. Fig. 1 shows the lattice parameter plotted against the average radius of the trivalent ions of the constituent elements, together with previously reported data. The data for the binary nitrides are plotted against the effective ionic radius, which was calculated by weighting the radii of the two constituent elements by their atomic ratios. All the data points lie close to the line determined by the least mean square (LMS) method, indicating that all the nitrides belong to the same class of material. GdN and ErN have a lattice constant mismatch of about 3%. Fig. 2(a) shows the temperature dependences of the magnetization of the present $Gd_{0.5}Er_{0.5}N$ sample for various applied magnetic fields. The samples with other compositions exhibited similar behavior. Their T_C values were calculated from Arrott plots generated from data sets for magnetic field strengths of 5 T, 4 T, and 3 T in Fig. 2(b) and were 11 K, 26 K, and 37.5 K for $x = 0.25$, 0.5, and 0.75 in $Gd_xEr_{1-x}N$, respectively.

Fig. 3(a) shows T_C–ξ plots for the RE nitrides (including binary systems) that we have so far synthesized; the plots assume that the RE nitrides have trivalent states. The de Gennes factors of binary RE nitrides were obtained by weighting each ξ by the atomic fraction of the RE. All the data points lie relatively close to a line passing through the origin. The LMS method was applied and a correlation coefficient of $R^2 = 0.965$ was obtained. However, in view of its physical meaning and algebraic expression, we considered that it is not appropriate to apply the averaging method to binary RE nitrides for the following reason. The defining expression, $\xi = (g-1)^2 J(J+1)$, corresponds to the inner product of two parallel vectors of the same kind with magnitudes of $(g-1)\{J(J+1)\}^{0.5}$, which is the effective spin component along the direction of the total angular momentum **J**. Thus, the de Gennes factor indicates the exchange interaction between the spin components of the same kinds of ions. However, binary nitrides (e.g., $Gd_xEr_{1-x}N$) have three kinds of neighboring pairs (e.g., Gd–Gd, Gd–Er, and Er–Er) and thus three kinds of interactions. A more suitable averaging method is required for such systems. Although Fig. 3(a) exhibits a reasonable proportionality, careful observation reveals a discernible tendency to deviate from the LMS line, showing slight concavity; this deviation is most obvious in the plots of the present binary $Gd_xEr_{1-x}N$ samples.

We introduce the following three terms to account for the three interactions in binary nitrides:

$$\begin{aligned}
\xi_{\text{Gd–Gd}} &= (g-1)\mathbf{J}\cdot(g-1)\mathbf{J} = (g-1)^2 J(J+1)\\
\xi_{\text{Er–Er}} &= (g'-1)\mathbf{J}'\cdot(g'-1)\mathbf{J}' = (g'-1)^2 J'(J'+1)\\
\xi_{\text{Gd–Er}} &= (g-1)\mathbf{J}\cdot(g'-1)\mathbf{J}'\\
&= (g-1)\sqrt{J(J+1)}\cdot(g'-1)\sqrt{J'(J'+1)}
\end{aligned} \tag{1}$$

where J (J') is the quantum number and g (g') is the Lande g-factor of Gd^{3+} (Er^{3+}). For binary RE nitrides, the de Gennes factor was modified by assuming that it consists of three components, $\xi_{\text{Gd–Gd}}$, $\xi_{\text{Er–Er}}$, and $\xi_{\text{Gd–Er}}$. Assuming that the Gd^{3+} and Er^{3+} ions are randomly arranged, the modified de Gennes factor ξ_{bi} will be the expected value obtained by summing these three terms with statistical **factors** based on the binomial distribution. Note that there are 12 nearest-neighbor sites in the NaCl structure.

$$\xi_{\text{bi}} = x\sum_{n=0}^{12}\left(\frac{n}{12}\,{}_{12}C_n x^n(1-x)^{12-n}\xi_{\text{Gd–Gd}} + \frac{12-n}{12}\,{}_{12}C_{12-n}x^n(1-x)^{12-n}\xi_{\text{Gd–Er}}\right)$$

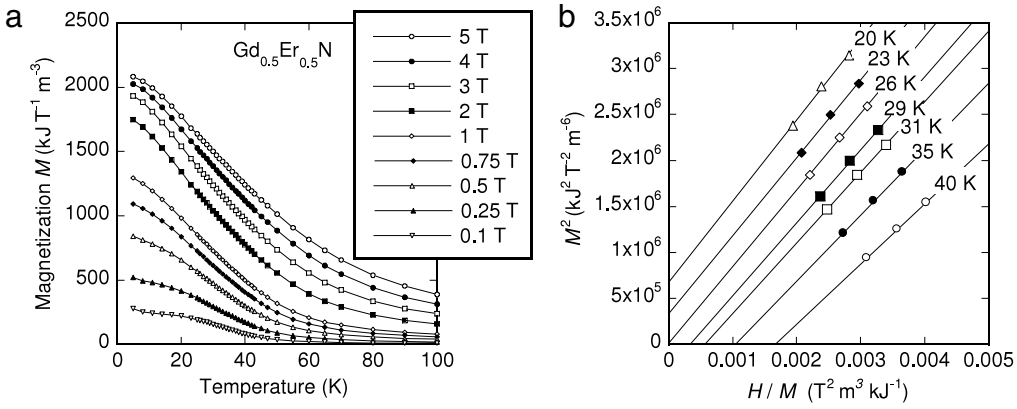

Fig. 2. (a) Magnetization data for $Gd_{0.5}Er_{0.5}N$ under different magnetic fields. (b) Arrott plot of data obtained under fields of 5, 4, and 3 T at seven different temperatures.

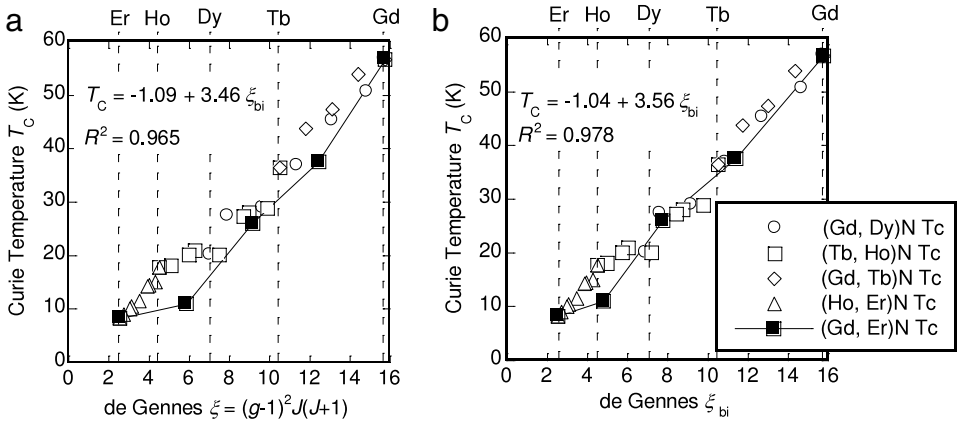

Fig. 3. Curie temperature of RE nitrides as a function of (a) the de Gennes factor $\xi = (g-1)^2 J(J+1)$ and (b) the modified de Gennes factor $\xi_{bi} = x^2\xi_{Gd\text{–}Gd} + 2x(1-x)\xi_{Gd\text{–}Er} + (1-x)^2\xi_{Er\text{–}Er}$.

$$+ (1-x)\sum_{n=0}^{12}\left(\frac{n}{12}\,{}_{12}C_n x^n (1-x)^{12-n}\xi_{Gd\text{–}Er} + \frac{12-n}{12}\,{}_{12}C_{12-n} x^n (1-x)^{12-n}\xi_{Er\text{–}Er}\right)$$
$$= x^2\xi_{Gd\text{–}Gd} + 2x(1-x)\xi_{Gd\text{–}Er} + (1-x)^2\xi_{Er\text{–}Er}. \quad (2)$$

In Fig. 3(b), T_C is replotted against ξ_{bi}; the data points for the binary samples are clearly closer to the LMS line. The correlation coefficient R^2 is 0.978, which is significantly higher than that (0.965) determined from the T_C–ξ plots in Fig. 3(a). The data points for $Gd_xEr_{1-x}N$ are much closer to the LMS line. Since Er and Gd have the greatest difference in the values of $(g-1)\{J(J+1)\}^{0.5}$ of all of the binary systems shown in Fig. 3(b), their values should be changed the most when the de Gennes factor is replaced by the modified de Gennes factor (i.e., $\xi \rightarrow \xi_{bi}$). Therefore, T_C will also consist of three components of the exchange interaction between nearest-neighbor RE ions; this is supported by theoretical calculations that predict that the exchange interaction is mainly the result of nearest-neighbor magnetic ions [37]. T_{MT} values for RE metals and alloys vary with $\xi^{2/3}$ [25], which indicates that in addition to nearest-neighbor ions, second-nearest-neighbor and third-nearest-neighbor ions that have higher metallicities may contribute to the magnetism produced by indirect RKKY interactions [37]. The ferromagnetism and T_C of RE nitrides are determined by the statistically averaged strength of interaction between randomly distributed nearest-neighbor pairs (e.g., Gd–Gd, Gd–Er, and Er–Er).

4. Conclusions

The T_C values of binary RE nitrides are found to have a slight concave deviation from linearity when they are plotted against the de Gennes factor ξ. This deviation was removed and a good proportionality was obtained by adopting a modified de Gennes factor ξ_{bi} that accounts for interactions between different kinds of ions and statistical **factors** due to their random arrangement. It was concluded that the spin components of nearest-neighbor RE ions mainly interact and give rise to the ferromagnetism of RE nitrides (including binary systems).

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