

THE SPIN REORIENTATION AND THE MAGNETIC ANISOTROPY IN $R_2Fe_{17-x}M_xCy$ ($R=Er, Tm, M=Al, Ga$)

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ABSTRACT- In order to consider the change of the magnetic anisotropy energy by the Al or Ga substitution for Fe, spin reorientation temperature T_{SR} and Curie temperature T_c in $R_2Fe_{17-x}M_x$ ($R=Er, Tm, M=Al, Ga$) have been studied both experimentally and theoretically. As a result, T_{SR} and T_c for $R_2Fe_{17-x}M_x$ shift toward higher temperature side with x ($0 \leq x \leq 2.0$). The ΔT_c , the difference of the T_c 's between $Er_2Fe_{17-x}Al_x$ and $Tm_2Fe_{17-x}Al_x$, is always about 10 K independent of Al-content. But in the case of Ga substitution, the ΔT_c increases with Ga-content; especially, the ΔT_c for $x=2.0$ is 43 K. This value of the ΔT_c is not explained by only the difference of the de Gennes factor G between Er^{3+} and Tm^{3+} , but it is thought that the values of J_{ErFe} and J_{TmFe} themselves are not equal. (J_{AB} : the exchange interaction between A and B.)

I. INTRODUCTION

The magnetic properties of the $R_2Fe_{17}N_x$ ($R=rare\text{-}earth$) have been extensively studied. $Sm_2Fe_{17}N_x$ has a small coercive force despite of a large anisotropy energy, and $Sm_2Fe_{17}N_x$ has not yet become a practical permanent magnet material.

The effect of the substitution for Fe by various elements has been studied in order to get the high Curie temperature T_c and the large anisotropy energy. Previously, Narashimhan et al. [1] reported in 1974 that in $Tm_2Fe_{17-x}Al_x$ the spin reorientation temperature T_{SR} and T_c shift toward higher temperature sides with x , and D. McNeely et al. [2] reported in 1976 the rise of T_c and the expansion of the unit cell volume in $Sm_2Fe_{17-x}Al_x$. Recently, Kato et al. [3] have measured the magnetization of $Sm_2Fe_{17-x}Al_x$ in a high field, and have reported that the spin reorientation (SR) occurs even in this compound with a canting angle of the spin axis. But according to their result, the easy direction of $Sm_2Fe_{17-x}Al_x$ does not orient to the c-axis at low temperatures ($T \leq T_{SR}$) as far as $x \leq 2$.

We have already measured the Al-content dependence of the T_{SR} in $R_2Fe_{17-x}Al_xC_2$, and have reported that T_{SR} becomes higher with the Al-

content [4]. By using the crystalline field model and the experimental results, it is seen that 2nd order crystalline field parameter $|A_2^0|$ increases and the molecular field $|H_m(0)|$ for $T=0$ K (R-Fe exchange interaction) decreases. The decrease of $|H_m(0)|$ is proportional to $(17-x)/17$ due to the substitution for Fe. It was also proved that the Al substitution increases the c-axis anisotropy energy of R ions having positive α_J . (α_J is 2nd order Stevens factor.)

Bao-gen Shen et al. [5] have measured the magnetic properties of $Sm_2Fe_{17-x}M'_x$ ($M'=Si, Ga$), and have reported that the T_c shifts toward higher temperature side with increasing x , and also the easy direction of $Sm_2Fe_{15}Ga_2$ orients to the c-axis at room temperature. But, this phenomenon is not seen in the substitution for Fe by Al and Si, and the Ga-substitution effect is in the same tendency as the one of the interstitial atoms (N, C) from the view point of enhancing the magnetic anisotropy energy.

Though α_J of Er^{3+} is positive, there is not SR in Er_2Fe_{17} . Then, in this paper, it is studied whether $Er_2Fe_{17-x}Ga_x$ ($x=0 \sim 2.0$) has SR by the effect of Ga-substitution as mentioned above. And also, the Ga-content-dependence of the T_{SR} is

studied in $\text{Tm}_2\text{Fe}_{17-x}\text{Ga}_x$ ($x=0 \sim 2.0$), and these experimental results are analyzed by means of the crystalline field model [6] and the molecular field expression for T_c [7]. Besides, the Al-content dependence of the T_{SR} in $\text{R}_2\text{Fe}_{17-x}\text{Al}_xC_{0.5}$ is also studied. The effect of the substitution for Fe by Al and Ga is discussed in the view point of the SR.

II. EXPERIMENTALS

All samples were prepared by arc-melting the high purity elements (99.9 % for Er and Tm, 99.99 % for Fe and Al, 99.999 % for Ga, respectively), and they were annealed in vacuum in sealed quartz tubes at 1100 °C for a week. It was confirmed by X-ray diffraction that the samples are of the single phase of the $\text{Th}_2\text{Ni}_{17}$ -structure.

The magnetization was measured by means of a vibrating-sample magnetometer between 77-400 K, and the magnetization of $\text{Er}_2\text{Fe}_{16}\text{Ga}$ was measured between 4.2-150 K. A weak field of 1 kOe was applied to measure T_{SR} precisely, where T_{SR} and T_c were defined as the inflection points in the temperature-dependence curves of the magnetization.

III. CALCULATION

There are two sites of 2b and 2d for an R ion in the hexagonal $\text{Th}_2\text{Ni}_{17}$ ($\text{P6}_3/\text{mmc}$)-type, and these two sites belong to the point group D_{3h} . Therefore, one must consider the crystalline field coefficients of A_2^0 , A_4^0 , A_6^0 , and A_6^6 , but in this paper only the A_2^0 and A_4^0 are taken into account. Especially, the A_2^0 is the most dominant parameter in determining the easy direction. As usual, A_2^0 values for both 2b and 2d sites are set equal. (The value of A_2^0 will be discussed in the section 4.)

Then the crystalline electric field Hamiltonian H_{CEF} [6] for the ground \mathbf{J} multiplet state is writ-

ten as follows ;

$$H_{CEF} = \alpha_J \langle r^2 \rangle A_2^0 O_2^0, \quad (1)$$

where $\langle r^2 \rangle$ is the average of r^2 over the radial wave function of the 4f electrons. The O_2^0 that operates to the ground multiplet state of an R ion is the Stevens operator.

The total Hamiltonian H_R for an R ion is expressed as follows ;

$$H_R = H_{CEF} + 2(g_J - 1)\mu_B \mathbf{J} \cdot \mathbf{H}_m(T), \quad (2)$$

where $\mathbf{H}_m(T)$ is the molecular field produced by the R-Fe exchange interaction, and it is assumed proportional to the magnetic moment of Fe in Y_2Fe_{17} . (The value of $|\mathbf{H}_m(0)|$ will be discussed in the section 4.)

The partition function Z is derived from Eq.(2), and the free energy of the total system per formula unit is given as follows ;

$$F = -2kT \ln Z + (17-x)K_{Fe}(T) \sin^2 \theta, \quad (3)$$

where $K_{Fe}(T)$ is the anisotropy energy per Fe atom, and the experimental value in Y_2Fe_{17} is taken as $K_{Fe}(T)$ from the ref. [8], and $K_{Fe}(0)$ is taken as -2.5 K. The T_c 's for Y_2Fe_{17} and $\text{Y}_2\text{Fe}_{17-x}\text{Ga}_x$ are different, and the values of $K_{Fe}(T)$ are not the same. But the T_c 's for these compounds are higher than room temperature, and the range of the present T_{SR} is located between 100 K and 250 K. Namely, it is thought that there is not so serious problem if the $K_{Fe}(T)$ values for Y_2Fe_{17} is used even in the present compounds. With the increase of x , the total anisotropy energy of Fe sublattice is reduced by the ratio of $(17-x)/17$ on the assumption that $K_{Fe}(T)$ is independent of the Ga-content. The direction of the magnetic moment of Fe at each temperature is obtained by minimizing Eq.(3) with respect to its angle θ for each temperature.

IV. RESULTS AND DISCUSSION

IV-1. Spin reorientation temperature

A. Al-substitution

The temperature-dependence of the magnetization in $Er_2Fe_{17-x}Al_xC_{0.5}$ ($x=0.5, 1.5, 2.0$) and $Tm_2Fe_{17-x}Al_xC_{0.5}$ ($x=0, 0.5, 2.0$) are shown in Figs.1 and 2, respectively. It is seen that the magnetization changes abruptly at T_{SR} ; the abrupt changes indicate the transition of the easy direction from the c -axis to the c -plane with rising temperature.

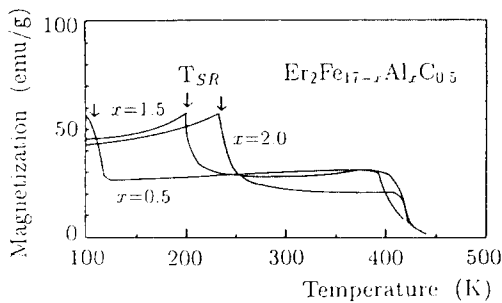


Fig.1. The temperature-dependence of the magnetization in $Er_2Fe_{17-x}Al_xC_{0.5}$.

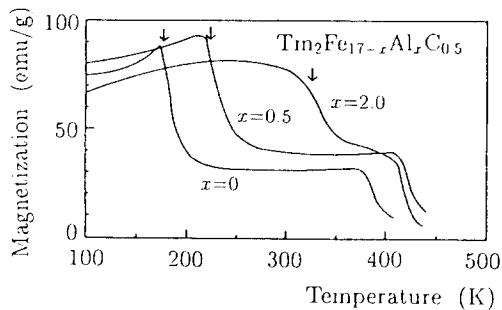


Fig.2. The temperature-dependence of the magnetization in $Tm_2Fe_{17-x}Al_xC_{0.5}$.

Since we have already measured the temperature-dependence of the magnetization in $R_2Fe_{17-x}Al_xC_2$ ($R=Er, Tm$), the T_{SR} as a function of the Al-content x in $R_2Fe_{17-x}Al_xC_y$ is shown in Fig.3. From this figure, the curves ($y=0.5, 2.0$) of the Al-dependence of T_{SR} have almost the same shapes between $R=Er$ and Tm ; especially, the curves of

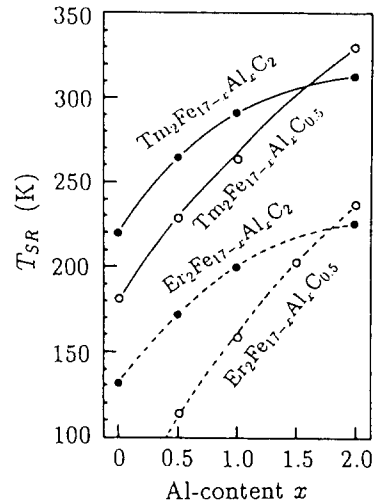


Fig.3. The observed T_{SR} as a function of Al-content x in $R_2Fe_{17-x}Al_x$.

$y=0.5$ for Er and Tm change almost linearly. Then, the T_{SR} 's of $R_2Fe_{15}Al_2C_{0.5}$ ($R=Er, Tm$) are higher than the ones of $R_2Fe_{15}Al_2C_2$ ($R=Er, Tm$).

B. Ga-substitution

The temperature-dependence of the magnetization for $Er_2Fe_{16}Ga$ between 4.2 K and 150 K is shown in Fig.4. No SR is observed in Er_2Fe_{17} , but it is clearly seen that the SR occurs in $Er_2Fe_{16}Ga$.

The T_{SR} as a function of the Ga-content x in $R_2Fe_{17-x}Ga_x$ ($R=Er, Tm$) is shown in Fig.5. It is seen that T_{SR} shifts toward higher temperature side with increasing x .

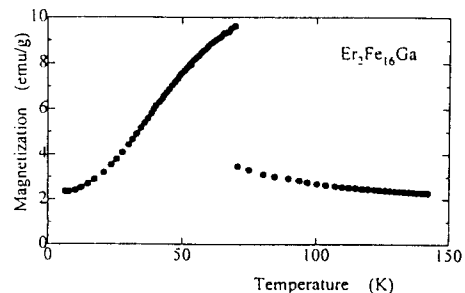


Fig.4. The temperature-dependence of magnetization in $Er_2Fe_{16}Ga$.

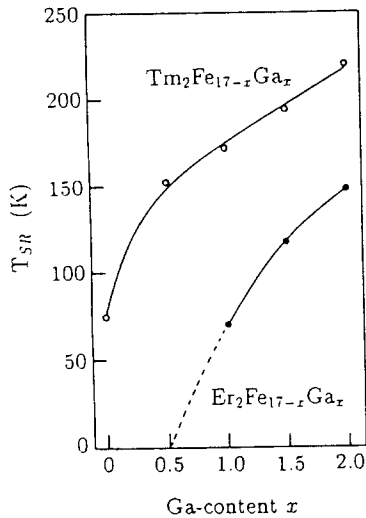


Fig.5. The observed T_{SR} as a function of the Ga-content x in $R_2Fe_{17-x}Ga_x$ ($R=Er, Tm$).

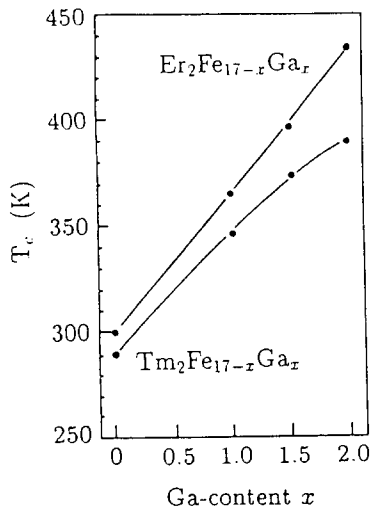


Fig.6. The observed T_c as a function of the Ga-content x in $R_2Fe_{17-x}Ga_x$ ($R=Er, Tm$).

IV-2. Curie temperature

The variation of T_c with x in $R_2Fe_{17-x}Ga_x$ ($R=Er, Tm$) is shown in Fig.6, and also the T_c 's in $R_2Fe_{17-x}Al_x$ ($R=Er, Tm$) were measured. In $R_2Fe_{17-x}Al_x$, it is seen that ΔT_c , the difference of T_c between $R=Er$ and $R=Tm$, is always constant with about 10 K, but the ΔT_c for $R_2Fe_{17-x}Ga_x$

increases with x ; especially, the ΔT_c in the case of $x=2.0$ is 43 K.

IV-3. Molecular field and Curie temperature

The T_c is almost determined by the value of Fe-Fe exchange interaction J_{FeFe} , but T_c 's differ with a kind of R due to the existence of R-Fe exchange interaction J_{RFe} . If J_{RR} is neglected, the expression of T_c for J_{FeFe} , H_m , and G becomes approximately as follows [7];

$$3k_B T_c \approx A + A + \frac{1}{2} \frac{2}{17-x} \frac{4H_m^2}{Z_{FeFe} J_{FeFe} S_{Fe}^2} G \quad (4)$$

$$H_m \equiv \frac{-Z_{RFe} S_{Fe} J_{RFe}}{2}$$

$$A \equiv Z_{FeFe} S_{Fe} (S_{Fe} + 1) J_{FeFe} ,$$

where Z_{AB} is the number of B atom neighbors of A atom, S_{Fe} is the Fe spin, G is the de Gennes factor, and H_m is the molecular field (J_{RFe}).

According to Eq.(4), the ΔT_c (the difference between the two T_c 's with different G and H_m values) is expressed as follows ;

$$3k_B \Delta T_c = \frac{1}{2} \frac{2}{17-x} \frac{4}{Z_{FeFe} J_{FeFe} S_{Fe}^2} \times (GH_m^2 - G'H_m'^2) \quad (5)$$

For example, in $R_2Fe_{14}B$, ΔT_c is about 10 K between $R=Er$ and Tm , and the Eq.(5) holds nearly good by the values of $Z_{FeFe}=10.5$, $J_{FeFe}=36$ K [9], $G^{Er}=2.55$, $G^{Tm}=1.16$, and $H_m^{Er}=H_m^{Tm}=150$ K. Then, the coefficient $2/(17-x)$ of Eq. (5) has to be changed to $2/14$ in $R_2Fe_{14}B$ -compound. Namely, in the case of ΔT_c of 10 K, it is thought that ΔT_c is explained by only the difference of G between Er^{3+} and Tm^{3+} , and the values of H_m^{Er} and H_m^{Tm} are the same ones. But the ΔT_c 's of $R_2Fe_{17-x}Ga_x$ ($R=Er, Tm$) are higher than 10 K, and increase with x . That is, the values of ΔT_c are not explained by only the difference of G , and it is thought that H_m is different between $R=Er$ and Tm .

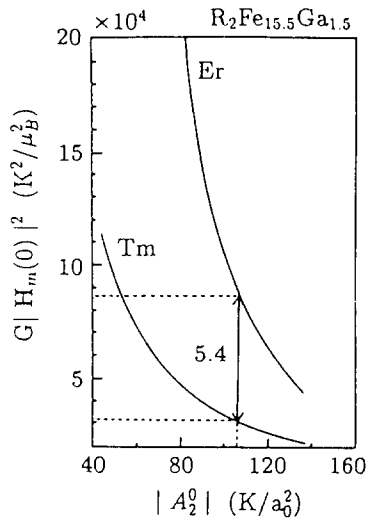


Fig.7. The combination of $|A_2^0|^2$ and $|H_m(0)|^2$. 5.4×10^4 K is the value of $\{G^{Er}(H_m^{Er})^2 - G^{Tm}(H_m^{Tm})^2\}$ estimated by the molecular field expression for T_c .

IV-4. Calculated results

The value of $\{G^{Er}(H_m^{Er})^2 - G^{Tm}(H_m^{Tm})^2\}$ in $R_2Fe_{15.5}Ga_{1.5}$ is estimated as 5.4×10^4 K by substituting the following values into Eq.(5) that $Z_{FeFe} = 10 - x$ [9], $J_{FeFe} = 25$ K, $S_{Fe} = 1$, $x = 1.5$, and $\Delta T_c = 22$ K. And the relation between the two parameters of $|A_2^0|^2$ and $G |H_m(0)|^2$ for $R=Er$ and Tm are shown in Fig.7 with the estimated value. (Two curves in Fig.7 show that the relations between the two parameters of the $|A_2^0|^2$ and the $|H_m(0)|^2$ for $R=Er$ and Tm reproduce well the observed T_{SR} in $Er_2Fe_{15.5}Ga_{1.5}$ and $Tm_2Fe_{15.5}Ga_{1.5}$, respectively.)

From Fig.7 $G |H_m(0)|^2$'s for $R=Er$ and Tm are obtained as 8.5×10^4 K and 3.1×10^4 K, respectively; the values of $|H_m(0)|^2$ for $R=Er$ and $R=Tm$ are required to be 183 K and 163 K, respectively, and the $|H_m(0)|^2$ and A_2^0 are also obtained in the cases of $x=1.0$ and 2.0 .

The values of A_2^0 and $|H_m(0)|^2$ for $R_2Fe_{17-x}Ga_x$ are shown in Table 1. It is noticed in Table 1 that the values of A_2^0 scarcely change in the range of $1.0 \leq x \leq 2.0$, but the values of $H_m(0)$ increase

Table 1 : The A_2^0 and $H_m(0)$ in $R_2Fe_{17-x}Ga_x$ ($R=Er, Tm$). $A_4^0 = -1.5$ (Ka_0^{-4}).

Compounds	A_2^0 (Ka_0^{-2})	$H_m(0)$ ($K\mu_B^{-1}$)
$Er_2Fe_{16}Ga$	-90	177
$Er_2Fe_{15.5}Ga_{1.5}$	-106	183
$Er_2Fe_{15}Ga_2$	-91	247
$Tm_2Fe_{16}Ga$	-90	168
$Tm_2Fe_{15.5}Ga_{1.5}$	-106	163
$Tm_2Fe_{15}Ga_2$	-91	190

with Ga-content x in spite of decreasing number of Fe atom per molecule by Ga-substitution. It is thought that the rise of T_{SR} in $R_2Fe_{17-x}Ga_x$ ($R=Er, Tm$) is caused by the increase of 3d-4f exchange interaction.

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