ANISOTROPIE ET MAGNÉTOSTRICTIONMAGNETOCRYSTALLINE ANISOTROPY IN RARE EARTHS AND THEIR ALLOYS

S. Chikazumi, K. Tajima, K. Toyama

MAGNETOCRYSTALLINE ANISOTROPY IN RARE EARTHS AND THEIR ALLOYS

S. CHIKAZUMI, K. TAJIMA (*) and K. TŌYAMA (**)
Institute for Solid State Physics, University of Tokyo, Roppongi, Tokyo, Japan

Résumé. — L'anisotropie magnétocristalline d'impuretés de terres rares dopant du Gd a été mesurée par la méthods du couple dans la gamme de températures 4,2-200 °K. Un calcul basé sur le modèle à un ion donne un accord raisonnable avec l'expérience pour les impuretés de terres rares lourdes, contrairement au cas de la plupart des terres rares légères. La dépendance en température de la constante d'anisotropie est très bien explicable en supposant que les moments des impuretés se comportent paramagnétiquement dans le champ d'échange produit par les spins des Gd environnants. La dépendance en température anormale pour l'impureté de Sm a été interprétée en terme de mélange de l'état de haut J excité par l'interaction d'échange avec le spin de Gd. Le métal Gd pur ne présente qu'une anisotropie relativement faible, qui, toutefois, a une dépendance en température compliquée. L'origine de cette anisotropie devrait être entièrement différente de celle des autres terres rares, car le Gd n'a pas de moment orbital. Par addition d'Y non magnétique un changement très important dans la dépendance en température de l'anisotropie de Gd a été observé. Un effet similaire a aussi été produit par l'application d'une forte pression hydrostatique.

Abstract. — Magnetocrystalline anisotropy of rare earth impurities doped in Gd metal was measured by torque method in a temperature range of 4.2 to 200 °K. Calculation based on the one-ion model agrees with experiment reasonably well for heavy rare earth impurities, while it does not for most of light rare earth impurities. Temperature dependence of the anisotropy constant can be explained fairly well by assuming that impurity moments behave paramagnetically in the exchange field produced by the surrounding Gd spins. Anomalous temperature dependence for Sm impurity was interpreted in terms of the mixing of the high J state excited by the exchange interaction with Gd spin. Pure Gd metal exhibits a relatively small anisotropy, which, however, exhibits rather complicated temperature dependence. The origin of this anisotropy should be entirely different from other rare earths, because Gd has no orbital magnetic moment. It was found that the addition of non-magnetic Y causes a drastic change in the temperature dependence of the anisotropy of Gd. A similar effect was also caused by the application of hydrostatic high pressure.

I. **Introduction.** — Rare earth metals exhibit an anomalously large magneto-crystalline anisotropy 10^2 to 10^4 times larger than 3 d transition metals, since their atomic magnetic moments are associated with more or less some orbital magnetic moment which has anisotropic wave functions in 4 f electron shell. The determination of the anisotropy constants of rare earth metals was first attempted by Liu and al. [1] for Dy through the observation of magnetization curves by using a field up to 18 kOe, which, however, was too weak to magnetize the specimen to a considerable extent. Rhyne and al. [2] and Belov and al. [3] measured torque curves for Tb, Dy and other rare earth metals in a field of about 150 kOe. It was found by Rhyne and al. [4] and also confirmed by Chikazumi and al. [5], however, that the application of the field higher than 150 kOe causes a permanent set of the crystal lattice as a result of the rotation of highly anisotropic moment, thus preventing the accurate determination of the anisotropy constants.

In the present experiments, one species of rare earth metals are intentionally introduced to Gd metals in a dilute form and a change in anisotropy was measured. Since Gd has no orbital magnetic moment, and accordingly exhibits only a small anisotropy, an introduction of an anisotropic rare earth ions changes the anisotropy dramatically, even if the content of the impurity metals is only a few per cent, thus allows the accurate measurement. Moreover, Gd has the maximum spin value $S = 7/2$, so that the exchange field of the host Gd metals is estimated to be as strong as 2 000 kOe, which is strong enough to rotate the anisotropic impurity moment in the crystal. The results were basically interpreted in terms of the interaction between 4 f orbitals and the crystalline field in Gd lattice.

Nature of the magnetocrystalline anisotropy in Gd metal itself is entirely different, since it has no orbital magnetic moment. It shows a relatively weak anisotropy but its temperature dependence is fairly complicated as has been studie by Graham [6], Corner and al. [7], Rodbell and Moore [8], and Féron and Pauthenet [9]. It was found that the application of a hydrostatic pressure and the introduction of non-magnetic Y modified these characters appreciably.

II. **Experimental procedure.** — All the rare earth alloys used in this experiment were prepared by melting low materials of 99.9 % purity by the argon arc. Single crystals were grown by the recrystallization, as described by Nigh [10], and were ground to a form of a sphere, 2.5 to 3.5 mm in diameter. The magnetocrystalline anisotropy was measured in the temperature range from. 4.2 to about 200 °K by means of a simple bearing-less torque magnetometer in which the torque was detected by paper strain gages attached to a part of the supporting rod. The field of 31 kOe was applied by a large rotatable electromagnet in the plane which contains the c-axis. The torque were recorded by X-Y recorder as a function of the rotation angle of the magnet.

III. **Magnetocrystalline anisotropy of dilute rare earth-Gd alloys.** — Figure 1 shows a torque curve measured at 4.2 °K for 1.8 % Tb-Gd alloys. It is seen that the anisotropy is quite large as compared

(*) Present address : Department of Physics, Tohoku University, Sendai.
(**) A visiting investigator from Department of Engineering Science, Osaka University, Osaka.

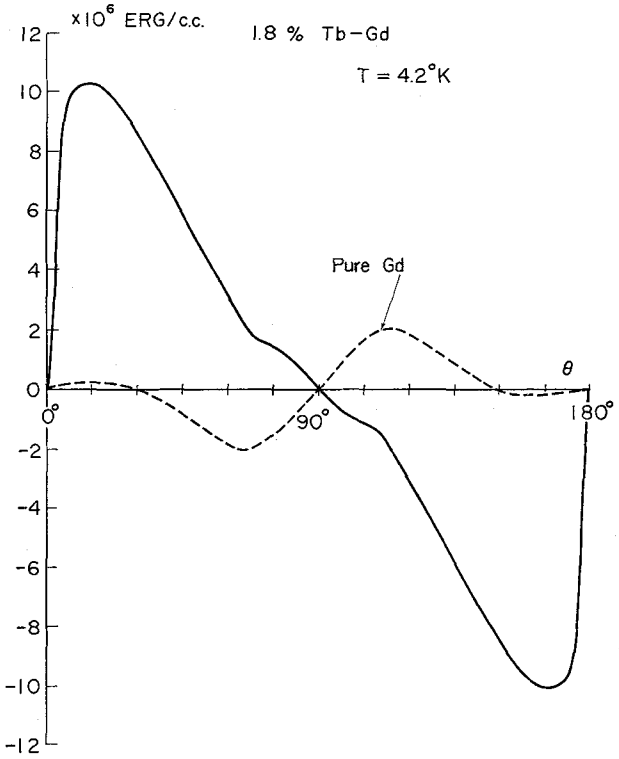

FIG. 1. — Torque as a function of the angle of the external field, θ, from the c-axis for the 1.8 % Tb-Gd alloy. The broken curve is for pure Gd. Both were measured at 4.2 °K in a field of 31 kOe.

with pure Gd (broken curve in figure 1), although the content of Tb is only 1.8 %. This means that the anisotropy of Tb is about 5.5×10^8 erg/cc which is in good agreement with the measurement of pure Tb by Rhyne and al. [2]. The shape of the curve is almost uniaxial, reflecting the symmetry of the hexagonal crystal. Sometimes the torque curve contains appreciable higher order harmonics as seen in figure 2 for 1.3 % Ho-Gd alloys. More complicated torque curves were observed for 1 % Pr-Gd (cf. Fig. 3) and for 1 % Nd-Gd (cf. Fig. 4). Sharp jumps of the torque

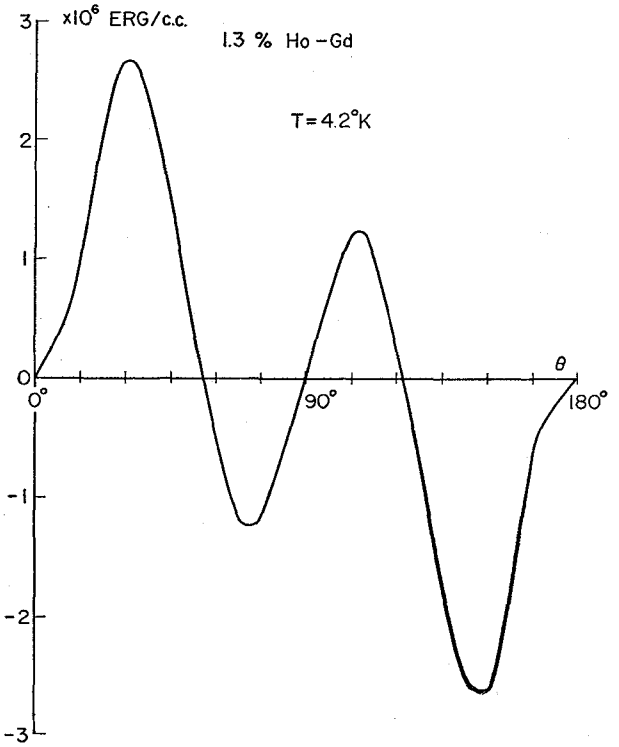

FIG. 2. — Torque curve for the 1.3 % Ho-Gd alloy.

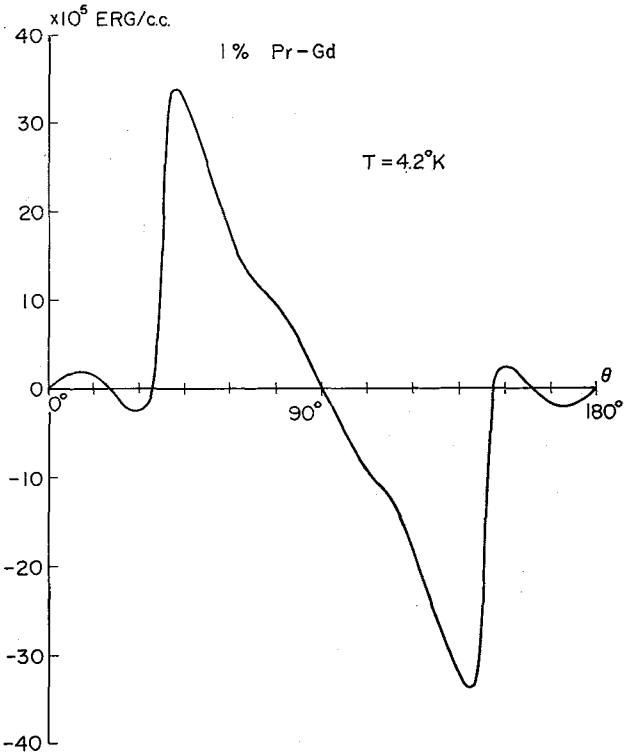

FIG. 3. — Torque curve for the 1 % Pr-Gd alloy.

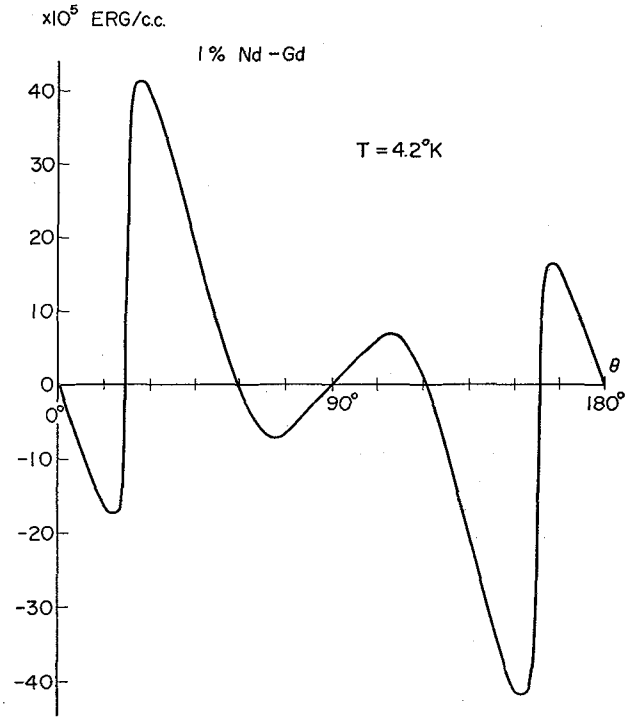

FIG. 4. — Torque curve for the 1 % Nd-Gd alloy.

are seen to occur at $\theta = 37^{\circ}$ and 23°, respectively. Apparently, such jumps are caused by the cross-over of the two descrete energy levels as the impurity J rotates from the c-axis. A similar effect was observed by Dillon and al. [11], Pearson and al. [12] for rare-earth doped YIG and theoretically interpreted by Kittel [13]. Actually such jumps were quickly smeared out as the temperature is raised up from 4.2 °K.

These torque curves were plotted as a function of the direction of the external field which is not necessarily the same as the direction of the impurity J. When the external field **H** makes the angle θ with the c-axis, it causes the rotation of the Gd spin, $\mathbf{S}_{Gd}$, which makes the angle, θ_h, with the c-axis. Impurity moment, **J**, may also be rotated through the exchange interaction with $\mathbf{S}_{Gd}$, thus makes the angle θ_i with the c-axis. Then the total energy of the system is given by

$$\begin{aligned} E = & -2(1-c)\,\mu_B\,S_{Gd}\,H\cos(\theta_h - \theta) \\ & - cg\mu_B\,JH\cos(\theta_i - \theta) \\ & - 2\,c\mu_B(g-1)\,JH_E\cos(\theta_i - \theta_h) \\ & + c\varepsilon_a(\theta_i)\,, \end{aligned} \tag{1}$$

where c is the concentration of the impurity atoms, μ_B the Bohr magneton, g the gyromagnetic factor, H_E the exchange field and ε_a the anisotropy energy which acts on the impurity atom. Equilibrium conditions for θ_h and θ_i are given by

$$\frac{\partial E}{\partial \theta_h} = 2(1-c)\,\mu_B\,S_{Gd}\,H\sin(\theta_h - \theta) - 2\,c\mu_B(g-1)\,JH_E\sin(\theta_i - \theta_h) = 0\,, \tag{2}$$

and

$$\frac{\partial E}{\partial \theta_i} = cg\mu_B\,JH\sin(\theta_i - \theta) + 2\,c\mu_B(g-1) \times JH_E\sin(\theta_i - \theta_h) + c\frac{\partial \varepsilon_a}{\partial \theta_i} = 0\,, \tag{3}$$

where $-\partial\varepsilon_a/\partial\theta_i$ is given by the torque reduced to per one impurity atom. Solving (2) and (3) with respect to θ_i, we have the deviation angle $\theta_i - \theta$ as a function of the torque. In figure 5, the solid curve represents the torque curve reduced to per one impurity Tb atom which is obtained after subtracting the torque curve for pure Gd from that for 1.8 % Tb-Gd alloy (cf. Fig. 1). After correcting the angle from θ to θ_i, the curve is sheared to the broken curve (Fig. 5). Maximum angle of correction in this case was 16°. Corresponding deviation of $\mathbf{S}_{Gd}$ from **H**, or $\theta_h - \theta$ was 6°. Exactly speaking, we have to take into consideration this correction for the torque curve for pure Gd before subtraction, but this effect is small, since the torque for Gd itself is very small. Figure 6 shows another example of angle correction for Tm. In this case, the maximum correction angle was 40° and the maximum $(\theta_h - \theta)$ was 5°. Effect of formation of spin transition layer around the impurity atoms was also neglected, because this effect is small in most cases.

After getting corrected torque curves, harmonic components were calculated by Fourier analysis. For uniaxial crystals, the magnetocrystalline anisotropy are expressed by

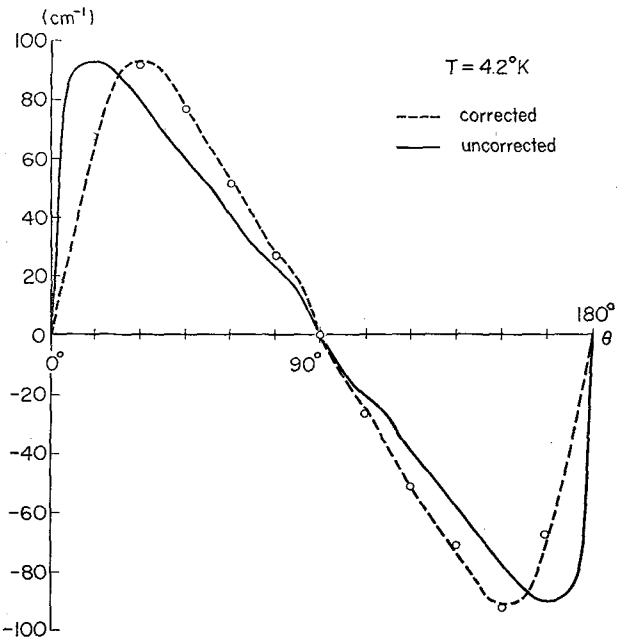

FIG. 5. — Torque curves reduced per one Tb atom as a function of the direction of external field (solid curve) and as a function of the direction of Tb moment (broken curve).

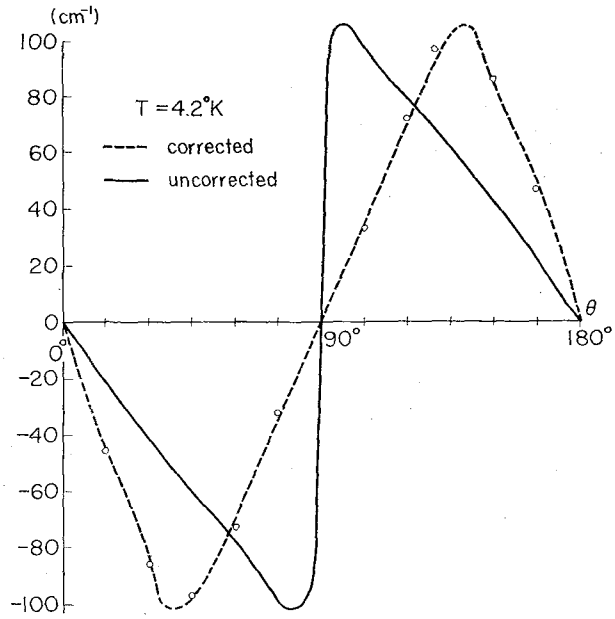

FIG. 6. — Torque curves for Tm atom as functions of the direction of the external field (solid curve) and of the direction of Tm moment (broken curve). Circles are calculated by eq. (4).

$$\varepsilon_a = DP_2(\cos\theta_i) + EP_4(\cos\theta_i) + FP_6(\cos\theta_i) + \cdots, \tag{4}$$

where P_2, P_4 and P_6 are Legendre polynomials and D, E, and F are the anisotropy constant per single atom. These values are tabulated in table I for various rare earth impurities. Values of D are also plotted as a function of the number of 4 f electrons in figure 7.

IV. Comparison with the calculation based on one-ion model. — The magnetocrystalline anisotropy of a rare earth impurity atom is caused by the inter-

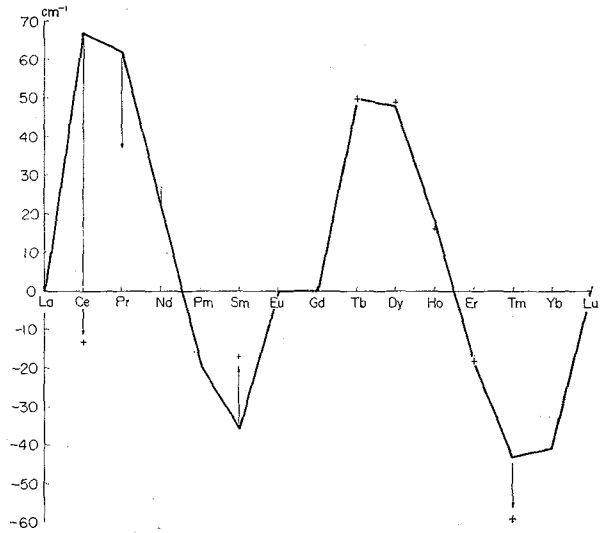

FIG. 7. — Values of the anisotropy constant D of doped rare earth atoms as a function of the number of 4 f electrons of the doped atoms. Solid lines represent the theoretical values, while crosses represent the experimental values. Some parameter was adjusted to fit both the values for Tb.

action of the anisotropically spreading 4 f orbitals with the non-zero crystalline field which is produced by the surrounding Gd ions. The shapes of the 4 f orbitals are schematically shown in figure 8. In the case of Tb which has eight 4 f electrons, the first seven electrons forms a half-filled spherical charge distribution and the last one with $l_z = 3$ has a pan-cake like charge distribution spreading perpendicular to the z-axis. As the electrons are added to Tb, as in the case of Dy, Ho, Er and Tm, the resultant charge distribution tends to be isotropic and then finally

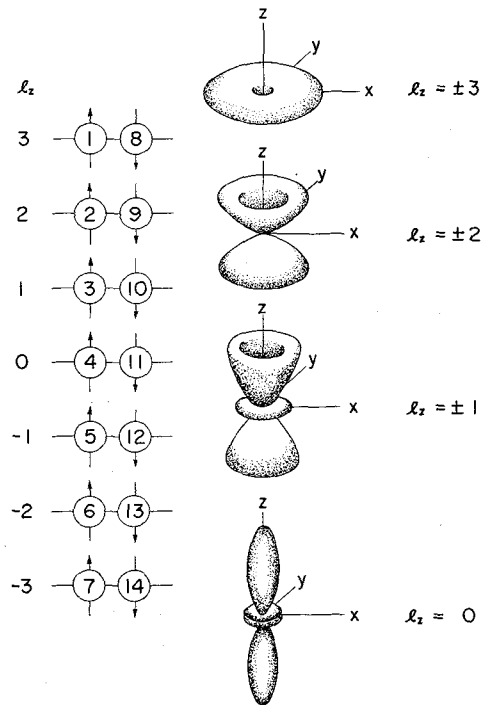

FIG. 8. — Shape of the 4 f orbitals for various l_z. Left hand figure indicates the order of occupation of 4 f electrons according to the Hund's rule.

extends its charge distribution along the z-axis, since $l_z = 0$ has a charge distribution along the z-axis (cf. Fig. 8). On the other hand, the crystalline field in Gd metal has a field gradient at each lattice site in such a way that it tends to attract the electron cloud along the c-axis, since $c/a = 1.599$ which is less than the ideal value 1.633. In the case of Tb, such a crystalline field rotates the pan-cake like orbitals so as to aline its z-axis perpendicular to the c-axis. In other words, the easy axis is in the c-plane ; that is $D > 0$.

According to the exact treatment along this line by Stevens [14], the anisotropy constants are driven as the formula

$$\begin{aligned} D &= A_2^0 < r^2 > \alpha J(J - \tfrac{1}{2}) \\ E &= A_4^0 < r^4 > \beta J(J - \tfrac{1}{2})(J - 1)(J - \tfrac{3}{2}) \\ F &= A_6^0 < r^6 > \gamma J(J - \tfrac{1}{2})(J - 1)(J - \tfrac{3}{2}) \times \\ &\qquad \times (J - 2)(J - \tfrac{5}{2}), \end{aligned} \tag{5}$$

where α, β, γ are Stevens factors [14] relating to the shape of the 4 f orbitals, $< r^n >$'s are the average of the radial part of 4 f wave function, and A_n^0's are the field gradients. According to the point charge approximation on nearest neighbours,

$$\begin{aligned} A_2^0 &= -1.22 \frac{ze^2}{a^3}\left(1.633 - \frac{c}{a}\right) \\ A_4^0 &= -\frac{ze^2}{a^5}\left[1.17 - 5.60\left(1.633 - \frac{c}{a}\right)\right] \\ A_6^0 &= \frac{ze^2}{a^7}\left[4.33 + 6.37\left(1.633 - \frac{c}{a}\right)\right], \end{aligned} \tag{6}$$

where z is the electric charges of the atom in the unit of e.

The radial part of the 4 f wave functions was calculated by Freeman and Watson [15] using a Hartree-Fock approximation for free ions. In metals, the 4 f wave function is expected to expand by various reasons as discussed by Kasuya [16]. We have chosen

$$\begin{aligned} < r^2 > &= 2.4 < r^2_{\text{F.W}} > \\ < r^4 > &= 2.3 < r^4_{\text{F.W}} > \\ < r^6 > &= 2.3 < r^6_{\text{F.W}} >, \end{aligned} \tag{7}$$

so as to have the best fit for D of Tb and also for the basal plane anisotropy of Tb (cf. [2]). Values of D, E, and F calculated by (5) with (6) and (7) using the $c/a = 1.599$ for host Gd at 4.2 °K and are tabulated in table I. Values of D are in excellent agreement with the observed values except for Ce, Pr, Sm and Tm. General tendency of the change in D with the number of 4 f electrons are more clearly seen in figure 7. Repetetion of the characteristic change from La to Gd, and Gd to Lu are well understood by the change in 4 f electron clouds as described above. Relatively large amplitude of D for light rare earths is due to the expansion of the 4 f shell, or the large $< r^n >$. Large deviation of D for Ce and Pr may be at least partly due to a large contribution of the crystalline field splitting relative to the exchange field. As for the disagreement of D for Sm we shall discuss in the next chapter.

TABLE I

Anisotropy constants for various rare earth impurities doped in gadolinium

Impurity	D (cm^{-1}) Observed	Theory	E (cm^{-1}) Observed	Theory	F (cm^{-1}) Observed	Theory
Ce	13	+ 67	+ 2	− 16	− 1	0
Pr	+ 31	+ 62	− 10	+ 21	− 3	+ 3
Nd	+ 30	+ 22	− 4	+ 13	− 7	− 4
Sm	− 16	− 36	+ 8	− 3	− 3	0
Tb	+ 50	+ 50	+ 10	− 11	+ 2	− 1
Dy	+ 49	+ 48	+ 4	+ 14	+ 2	+ 3
Ho	+ 15, + 16 (*)	+ 18	+ 3, + 3 (*)	+ 9	− 4, − 3 (*)	− 5
Er	− 18	− 18	+ 3	− 9	+ 3	+ 5
Tm	− 59	− 43	− 5	− 11	+ 2	− 2

(*) Two values in Ho were deduced from two specimens with different composition.

The reason for the poor agreement between theory and experiment for E and F may be due to i) neglection of the formation of spin transition regions about the impurity atoms, and also ii) the neglection of magnetostrictive deformation about the impurity atoms.

V. Temperature dependence of D of impurity rare earths. — Temperature dependences of anisotropy constants of rare earth impurities in Gd are generally monotonic as shown in figures 9 and 10 for D of heavy and light rare earths. This behaviour can be interpreted by regarding impurity rare earth moments as if they are paramagnetic ions under the action of the exchange field produced by host Gd. Then the

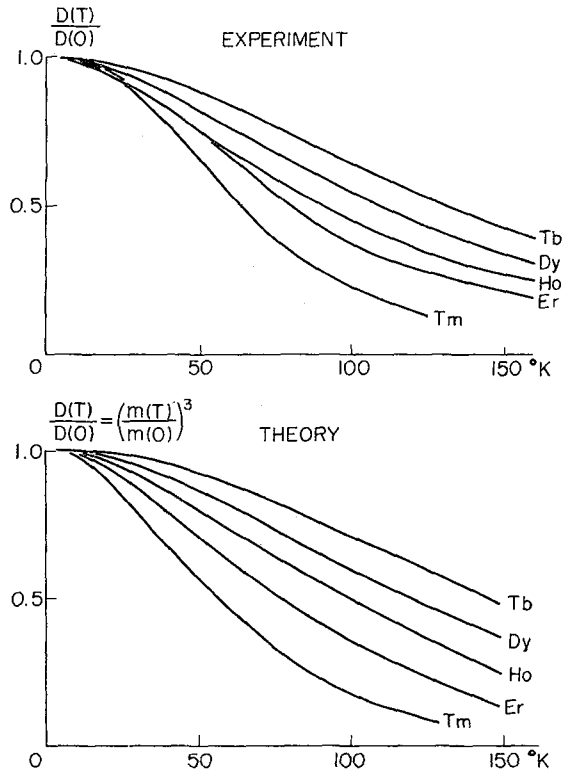

FIG. 9. — Temperature dependence of D for heavy rare earth impurities doped in Gd.

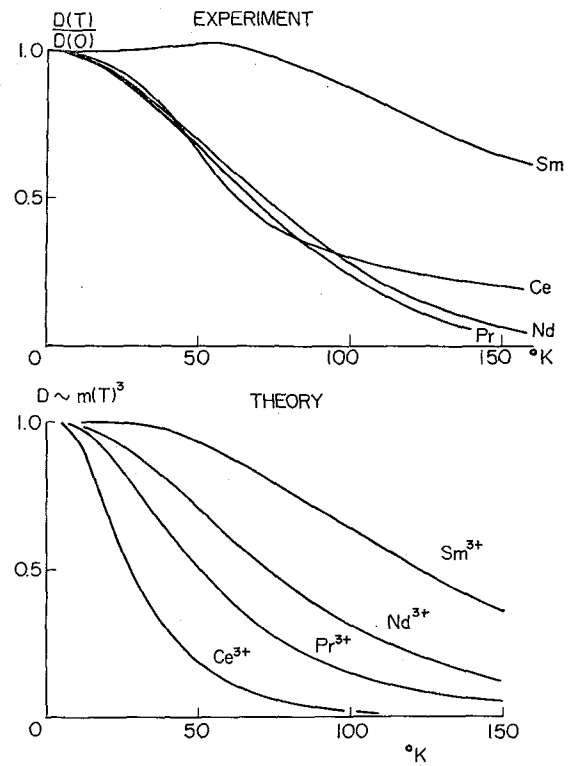

FIG. 10. — Temperature dependence of D for light rare earth impurities doped in Gd.

temperature dependence of magnetization of an impurity atom is given by the Brillouin function

$$\frac{m(T)}{m(0)} = B_J\left(\frac{2\,\mu_B(g-1)\,J}{kT}\,H_E\right). \qquad (8)$$

In this formula, H_E is the exchange field given by

$$H_E = \frac{3\,k\Theta_{Gd}}{M_{Gd}^2} < M_{Gd} >_T, \qquad (9)$$

where Θ_{Gd} is the Curie point of Gd and M_{Gd} and $< M_{Gd} >_T$ are the magnetic moment of Gd at 0 °K and thermal average of the moment at T °K, respectively. Since the n-th order anisotropy constant changes with temperature as

$$\frac{K_n(T)}{K_n(0)} = \left[\frac{m(T)}{m(0)}\right]^{\frac{1}{2}n[n+1]} \qquad (10)$$

as shown by Zener [17] and Keffer [18], we can calculate it with the aid of (8) and (9), where we use the experimental values for $< M_{Gd} >$ measured by Graham [19]. The calculated temperature dependence agree with experiment as seen in figures 9 and 10, for all the impurity atoms except for Ce and Sm. In the case of Sm, there is a tendency that D decreases with an approach to 0 °K. This may be due to a contribution of the excited state with $J = \frac{7}{2}$ which is higher than the ground state with $J = \frac{5}{2}$ by only $\Delta E = 900$ cm^{-1}. As the temperature decreases the mixing of the excited state will be increased through the increase of the exchange interaction which is about 300 cm^{-1}.

More details should be referred to ref. [20] and [21].

VI. **Magnetocrystalline anisotropy of Gd and Gd-Y alloys.** — Magnetocrystalline anisotropy of pure Gd is relatively small (about 0.2 % of Tb), since it has no orbital magnetic moment. Its temperature dependence is fairly complicated as shown by one of the curves in figure 11. It was found that the addition of non-magnetic Y changed its character completely (Fig. 11). As first discovered by Thoburn and al. [22], introduction of Y to Gd increases the magnetic moment per Gd. Figure 12 shows the recent experiment showing the changes in the saturation and effective moments with an increase of Y content in Gd (cf. [23]). From the inclination of this curve, we can figure out that some part, possibly conductive 5 d electrons of Y, may be polarized by 0.18 μ_B. Drastic change in the anisotropy may possibly come from such a polarization of 5 d electron.

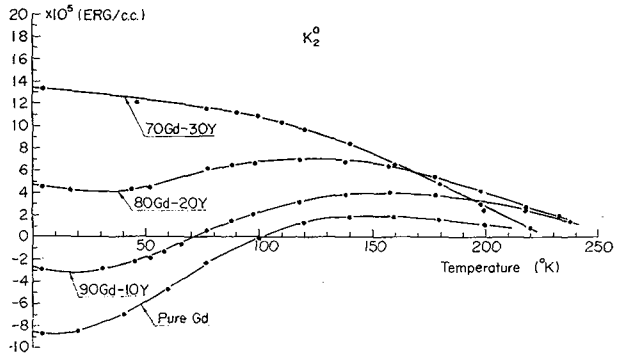

FIG. 11. — Temperature dependence of K_2^0 (values of D per unit volume) for Y-Gd alloys.

Pressure dependence of the anisotropy constants of pure Gd was measured at 77 °K (Fig. 13). It is interesting to note that the pressure dependence of the anisotropy constants are quite similar to their temperature dependences. This applies also to K_4^0 and K_6^0. These changes may be due to a modification of the polarization in 5 d electrons of Gd which is usually believed to be a cause of the deviation of saturation moment from 7 μ_B, that is 0.55 μ_B (cf. Fig. 12).

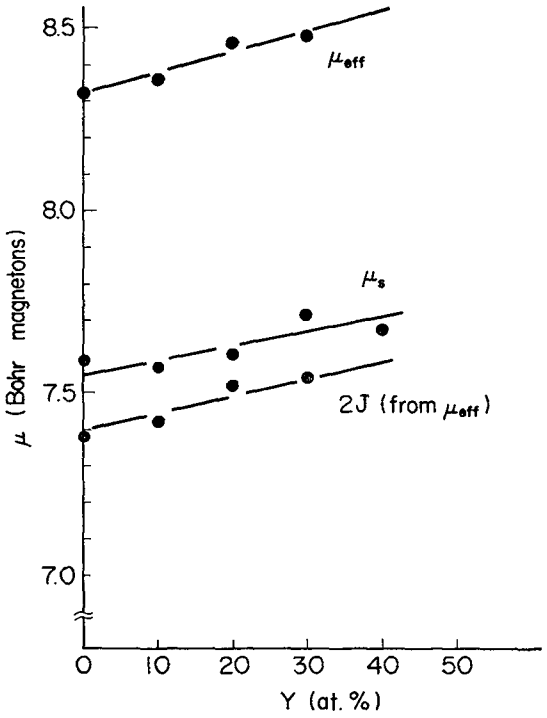

FIG. 12. — Change of magnetic moments per Gd atom with the concentration of Y in Gd-Y alloys. μ_s, μ_{eff} and 2 J represent the saturation moment, effective moment and the value of 2 J deduced from the effective moment.

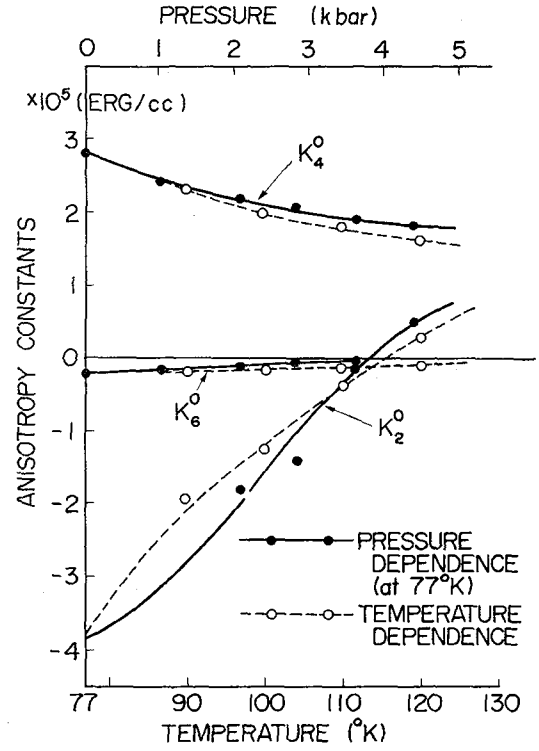

FIG. 13. — Pressure temperature dependences of K_2^0, K_4^0 and K_6^0 (values of D, E and F per unit volume) for pure Gd (cf. ref. [23]).

Acknowledgment. — The authors would like to express their thanks to Professors K. Yosida and H. Miwa for their valuable discussions.

References

[1] LIU (S. H.), BEHRENDT (D. R.), LEGVOLD (S.) and GOOD (R. H.), *Phys. Rev.*, 1959, **116,** 1464.

[2] RHYNE (J. J.) and CLARK (A. E.), *J. Appl. Phys.*, 1967, **38,** 1379.

[3] BELOV (K. P.), LEVITIN (R. Z.) and PONOMARJOV (B. K.), *J. Appl. Phys.*, 1968, **39,** 3285.

[4] RHYNE (J. J.), FONER (S.), MCNIFF (E. J.) and DOCLO (R.), *J. Appl. Phys.*, 1968, **39,** 892.

[5] CHIKAZUMI (S.), TANUMA (S.), OGURO (I.), ONO (F.) and TAJIMA (K.), *IEEE Trans. Magnetics*, 1969, **Mag-5,** 265.

[6] GRAHAM (C. D.), *J. Phys. Soc. Japan*, 1962, **17,** 1310.

[7] CORNER (W. D.), ROE (W. C.) & TAYLOR (K. N. R.), *Proc. Phys. Soc.*, 1962, **80,** 927.

[8] RODBELL (D. S.) and MOORE (T. W.), *Proc. Int. Conf. on Mag.* (Nottingham, 1964), 427.

[9] FÉRON (J. L.) and PAUTHENET (R.), *C. R. Acad. Sci. Paris*, 1969, **269,** 549.

[10] NIGH (H. E.), *J. Appl. Phys.*, 1963, **34,** 3323.

[11] DILLON (J. F.) and NIELSON (J. W.), *Phys. Rev. Lett.*, 1959, **3,** 30.

[12] PEARSON (R. F.) and COOPER (R. W.), *J. Appl. Phys.*, 1961, **32,** 265 S.

[13] KITTEL (C.), *Phys. Rev.*, 1960, **117,** 681.

[14] STEVENS (K. W. H.), *Proc. Phys. Soc.*, London, 1952, **A 65,** 209.

[15] FREEMAN (A. J.) & WATSON (R. E.), *Phys. Rev.*, 1962, **127,** 2058.

[16] KASUYA (T.), Magnetism IIB ed. Rado and Suhl Academic Press Inc., New York, 1966, 276.

[17] ZENER (C.), *Phys. Rev.*, 1954, **96,** 1335.

[18] KEFFER (F.), *Phys. Rev.*, 1955, **100,** 1692.

[19] GRAHAM (C. D.), *J. Appl. Phys.*, 1967, **38,** 1375.

[20] TAJIMA (K.) and CHIKAZUMI (S.), *J. Phys. Soc. Japan*, 1967, **23,** 1175 ; 1968, **24,** 1401.

[21] TAJIMA (K.), Thesis (Gakushuin Univ.), to be published in : *J. Phys. Soc. Japan.*

[22] THOBURN (W. C.), LEGVOLD (S.) and SPEDDING (F. H.), *Phys. Rev.*, 1958, **110,** 1298.

[23] TOYAMA (K.), TAJIMA (K.) and CHIKAZUMI (S.), to be published in : *J. Phys. Soc. Japan.*

[24] TOYAMA (K.), TAJIMA (K.) and CHIKAZUMI (S.), *J. Phys. Soc. Japan*, 1969, **27,** 1070.