

# High-Field Magnetization Process in R<sub>2</sub>Fe<sub>14</sub>B and R<sub>2</sub>Fe<sub>17</sub>N<sub>x</sub> Compounds (Magnetism)

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## High-Field Magnetization Process in $R_2Fe_{14}B$ and $R_2Fe_{17}N_x$ Compounds\*

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### Synopsis

General method of calculating magnetization curves in ternary system  $R$ -Fe- $X$  is given, where  $R$  is a rare-earth element and  $X$  a non-magnetic element such as B. In this method the ferromagnetism of Fe sublattice is treated phenomenologically, while exchange and crystal field acting on  $R$  ions are exactly taken into account. Experimental data on  $R_2Fe_{14}B$  and  $R_2Fe_{17}N_x$  systems are summarized in comparison with the calculated curves. Detailed analyses have shown that in the light  $R$  compounds the inter-multiplet mixing via the  $R$ -Fe exchange interaction is important especially for the first-order magnetization process, which often occurs at low temperatures with external fields along the hard direction.

### I. Introduction

During the last decades the performance of permanent magnets has greatly been improved by introducing rare-earth ( $R$ ) elements to their constituents. It is doubtless that the high coercivity of these magnets comes from the large magnetic anisotropy originated by the crystalline electric field (CEF) acting on  $R$  ions with large orbital angular momentum. Magnetization measurements up to the high-field region where the hard-axis magnetization saturates are indispensable in order to obtain the basic insight of the magnetic anisotropy. Since 1985 we have been investigating systematically the high-field magnetization in a series of  $Nd_2Fe_{14}B$ -type compounds using mainly single crystal samples.<sup>1)</sup> On the other hand we have developed the method of analyzing these magnetization curves, which consists of a simplified Hamiltonian taking exchange and crystal field at  $R$  ions into account, with Fe sublattice being treated phenomenologically.<sup>2)</sup> This method has proven to be applicable not only to the  $R_2M_{14}B$  system with  $M = Fe$  or  $Co$ <sup>3)</sup> but also to the pseudo-ternary system  $(R_{1-x}R'_x)_2Fe_{14}B$ <sup>4)</sup> or other  $R$ -Fe- $X$  systems such as  $R_2Fe_{17}N_x$ .<sup>5)</sup>

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In this paper we present the general method of calculating magnetization curves in  $R_h\text{Fe}_kX_l$  system, where  $R$  is a pure or mixed rare-earth element and  $X$  a non-magnetic element such as B. Experimental data on  $R_2\text{Fe}_{14}\text{B}$  will be shown together with the calculated curves. Recent data on  $\text{Sm}_2\text{Fe}_{17}\text{N}_3$  will also be given in the last section.

## II. Exchange and Crystal Field Model for $R_h\text{Fe}_kX_l$ System

We deal with magnetic properties of a system containing  $h$   $R$  and  $k$  Fe atoms as magnetic elements. In the case of  $R_2\text{Fe}_{17}\text{N}_x$  system,  $h = 2$  and  $k = 17$ , whereas for  $R_2\text{Fe}_{14}\text{B}$   $h = 4$  and  $k = 28$  since the  $f$  and  $g$  sites for the  $R$  ions must be subdivided magnetically into  $f_1, f_2, g_1$  and  $g_2$  sites. The total free energy of the system at temperature  $T$  in the external field  $\mathbf{H}$  is assumed to be given by

$$F(\mathbf{H}, T) = -k_B T \sum_{i=1}^h \ln \sum_s \exp[-E_s(i)/k_B T] + k \left\{ K_{\text{Fe}}(T) \sin^2 \theta - \mathbf{m}_{\text{Fe}}(T) \cdot \mathbf{H} \right\}, \quad (1)$$

where  $E_s(i)$  is the energy of  $s$ -th level of the  $R$  ion at the  $i$ -th site, and the second term expresses the anisotropy and Zeeman energy of the Fe sublattice;  $K_{\text{Fe}}$  is the uniaxial anisotropy constant per Fe atom,  $\theta$  the angle between the  $z$ -axis and the direction of Fe moment  $\mathbf{m}_{\text{Fe}}$ . Since the Fe-Fe exchange energy is assumed to be much larger than  $R$ -Fe exchange energy, the terms for the exchange energy and entropy of Fe sublattice are neglected in Eq. (1). The temperature dependences of the Fe anisotropy  $K_{\text{Fe}}(T/T_c)/K_{\text{Fe}}(0)$  and the Fe moment  $m_{\text{Fe}}(T/T_c)/m_{\text{Fe}}(0)$  are assumed to be identical with those of the corresponding compounds with non-magnetic  $R$  ions, such as  $\text{Y}_2\text{Fe}_{14}\text{B}$  or  $\text{Y}_2\text{Fe}_{17}\text{N}_x$ .

The energy  $E_s(i)$  in Eq. (1) is the eigenvalue of the following Hamiltonian for the  $i$ -th  $R$  ion.

$$\mathcal{H}_R(i) = \lambda \mathbf{L} \cdot \mathbf{S} + \mathcal{H}_{\text{CEF}}(i) + 2\mu_B \mathbf{S} \cdot \mathbf{H}_m(i) + \mu_B (\mathbf{L} + 2\mathbf{S}) \cdot \mathbf{H}, \quad (2)$$

where  $\lambda$  is the spin-orbit coupling constant and  $\mathbf{H}_m(i)$  is the molecular field at the  $i$ -th site due to the  $R$ -Fe exchange interaction. In the present model excited  $J$  multiplets for the  $R$  ion are taken into account in general, which have a definite influence on the magnetization values especially near first-order magnetization process (FOMP) in light  $R$  compounds. The second term of Eq. (2) is the CEF Hamiltonian for the  $i$ -th  $R$  ion:

$$\mathcal{H}_{\text{CEF}}(i) = \sum_{n,m} A_n^m(i) \sum_j V_n^m(x_j, y_j, z_j), \quad (3)$$

where  $A_n^m(i)$  is the CEF coefficient at the  $i$ -th site,  $V_n^m(x_j, y_j, z_j)$  is the tesseral function for  $j$ -th  $4f$  electron, and the summation  $j$  is over all the  $4f$  electrons. The non-zero terms in Eq.

(3) are determined depending on the point symmetry of the  $R$  ion site and appropriate choice of quantization axes; *e.g.* terms with  $(n, m)=(2,0), (4,0), (4,3), (6,0), (6,3), (6,6)$  are non-vanishing for  $\text{Sm}_2\text{Fe}_{17}\text{N}_3$  in which the Sm site has a trigonal symmetry. The matrix elements of  $\mathcal{H}_{\text{CJF}}$  can be calculated using the tensor-operator technique which has already been described<sup>2)</sup> in detail.

The total magnetization of the system for a given external field  $\mathbf{H}$  with a magnitude  $H$  and polar angles  $(\Theta, \Phi)$  at temperature  $T$  is calculated with a following procedure. For specific values of CEF parameters  $A_n^m(i)$  and molecular field parameter  $H_m(i)$  at 0 K, we diagonalize numerically the  $R$  Hamiltonian  $\mathcal{H}_R(i)$  given by Eq. (2), which is a Hermitian matrix with the dimension of  $\sum_f(2J+1) \times \sum_f(2J+1)$ , and calculate the total free energy  $F$  using Eq. (1), which must be minimized with respect to the polar angles  $(\theta, \phi)$  of  $\mathbf{m}_{\text{Fe}}$ . It should be noted that the direction of the molecular field is fixed to be antiparallel to the Fe moment. Then, using the set of angles  $(\theta_0, \phi_0)$  which gives the minimum value of  $F$ , the expectation value of  $-\mu_B(\mathbf{L}+2\mathbf{S})$ , hence the  $R$  magnetic moment  $\mathbf{m}_R$  will be obtained by using the eigenvectors of  $\mathcal{H}_R(i)$ . The total magnetization  $\mathbf{M}_t$  is thus given by

$$\mathbf{M}_t = \sum_{i=1}^h \mathbf{m}_R(i) + k \mathbf{m}_{\text{Fe}}(\theta_0, \phi_0). \quad (4)$$

What we normally observe is not the total magnetization but a component  $M$  along the field direction, which is easily computed using the relation  $M=\mathbf{M}_t \cdot \mathbf{H}/H$ .

### III. High Field Magnetization Results

The high-field magnetization measurements were carried out by using a sample-extraction method<sup>6)</sup> in steady magnetic fields of up to 26 T generated by a hybrid magnet system installed at High Field Laboratory of IMR. Figure 1 (a) shows the observed magnetization curves of  $\text{Pr}_2\text{Fe}_{14}\text{B}$  at 4.2 K and 290 K, together with the corresponding calculated curves. It should be noted that at 4.2 K both the [100] and [110] curves exhibit a sudden increase in magnetization, being a typical example of FOMP. The magnetization curves, however, still show the trend of increase after the FOMP, suggesting that the magnetic moments are not completely parallel to the direction of the external field at this stage. At room temperature the hard-axis magnetization saturates around 9 T. The saturation value, however, is slightly smaller than that along the [001] direction. The calculated curves based on the parameters  $A_n^m$  and  $H_m$  listed in Table I are in good agreement with the observed ones. The dashed lines at 4.2 K represent the results in which only the ground ( $J = 4$ ) multiplet is taken into account, which are apparently distinct from the solid lines including excited multiplets. This result demonstrates clearly that the effect of excited  $J$  multiplets are important even for Pr compounds especially around the FOMP.

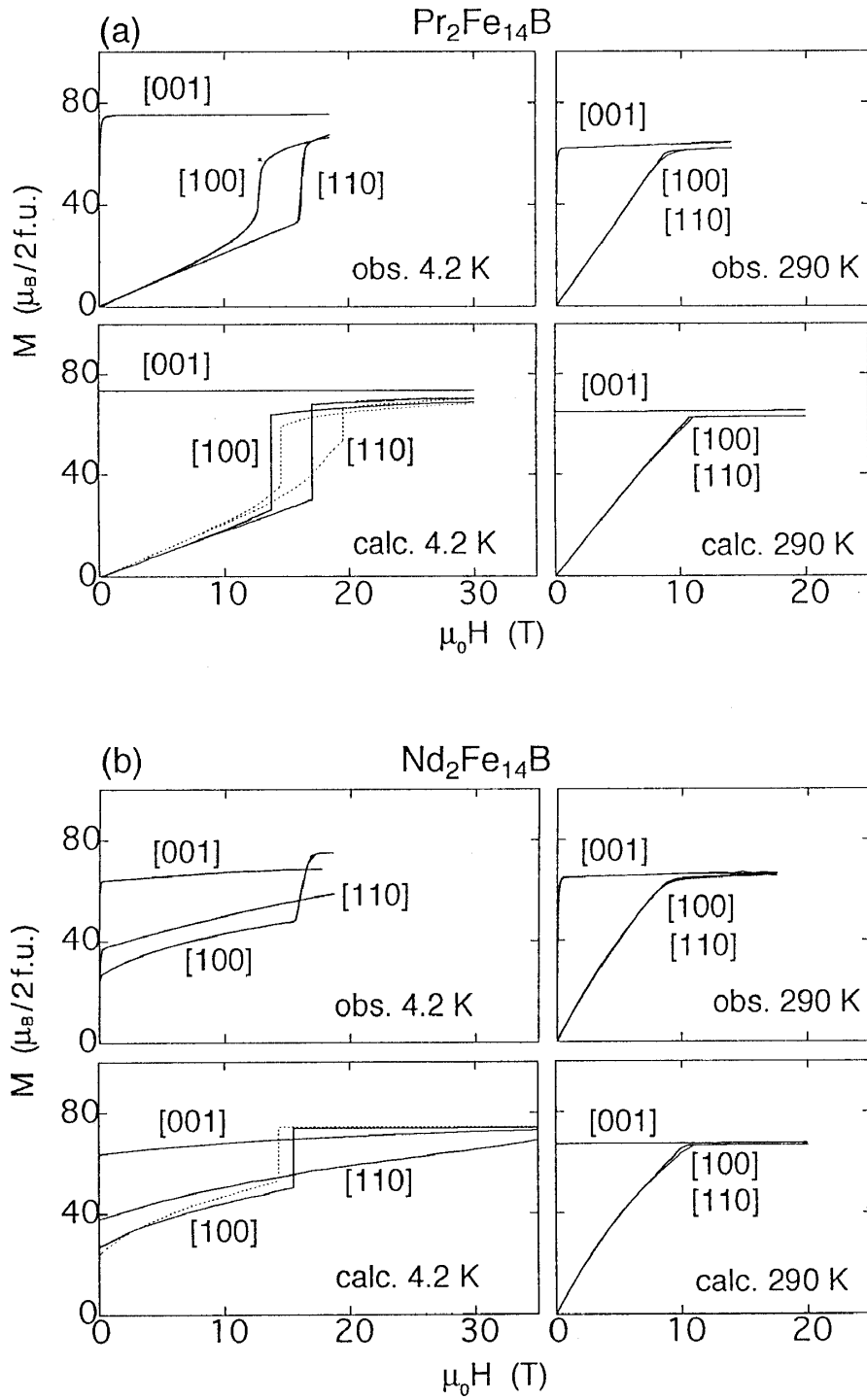


Fig. 1. Observed and calculated magnetization curves at 4.2 K and 290 K for (a)  $\text{Pr}_2\text{Fe}_{14}\text{B}$  and (b)  $\text{Nd}_2\text{Fe}_{14}\text{B}$ . Dashed lines of the calculation were obtained by taking only the ground  $J$  multiplet into account.



The results for  $\text{Nd}_2\text{Fe}_{14}\text{B}$  are given in Fig. 1(b). It is well known that the magnetization vector at 4.2 K is not parallel to the [001] direction but tilted at about  $32^\circ$  toward the [110] direction, which manifests in the [100] and [110] curves at 4.2 K having finite-magnetizations at zero field. The [100] curve at 4.2 K exhibits the FOMP, after which the magnetization becomes almost constant, in contrast to the case of the Pr compound. At room temperature, the anisotropy of saturation magnetization was also observed, although the difference in magnetization is not so large as that in the Pr compound. These features are seen to be nicely reproduced by the calculation, in which the dashed line was obtained by taking only the ground  $J$  multiplet into account. According to this calculation it has been found that the large difference in magnetization between the [100] and [001] directions above 17 T at 4.2 K is caused by the incomplete saturation of the [001] curve around this field range, this curve still continuing to increase at 35 T.

In the Sm compound, the easy axis of magnetization is the [100] direction in contrast to the Pr and Nd compounds. The Sm and Fe moments are not parallel but forming a non-collinear arrangement<sup>2)</sup> owing to the competition between the Sm-Fe exchange and the CEF interaction of  $A_2^{-2}$  terms. Observed and calculated magnetization curves are shown in Fig. 2, which exhibit a large magnetic anisotropy even at room temperature. The difference between the [100] and [110] curves is also remarkable, suggesting a significant contribution from the  $A_2^{-2}$  terms. It is well known that the energy interval between the excited and ground  $J$  multiplets in  $\text{Sm}^{3+}$  ion is relatively small, which results in a non-negligible mixing of these states. In the present calculation we have included, in addition to the ground ( $J = 5/2$ ) multiplet, the first ( $J = 7/2$ ) and second ( $J = 9/2$ ) excited multiplets. For comparison the results when only the ground multiplet is taken into account are also indicated by the dashed lines, which show apparently smaller anisotropy. It must be mentioned that the anomalous increase in magnetization observed in the [001] direction at 4.2 K is reproduced only by the inclusion of excited multiplets. This result suggests that the anomaly is related to the sixth-order CEF terms whose effect appears only through the excited multiplets because the sixth-order Stevens factor  $\gamma$  for the ground multiplet is zero for a  $\text{Sm}^{3+}$  ion.

For the  $R_2\text{Fe}_{14}\text{B}$  compounds with heavy  $R$  elements ( $R = \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}$  and  $\text{Tm}$ ), we have found that the magnetization curves and spin reorientation phenomena are explained satisfactorily within the ground  $J$  multiplet in terms of almost the same sets of parameters. We give here the results of Tb and Er compounds as shown in Fig. 3(a) and 3(b), respectively. The magnetization curves of the Tb compound exhibit the largest anisotropy among this series; the hard-axis magnetization at 15 T reaches only about a half of the easy-axis value at room temperature. The anisotropy in the Er compound, on the other hand, is very small owing to the competition between the Er and Fe sublattice. In fact the spin reorientation occurs at 323 K above which the Fe anisotropy dominates the

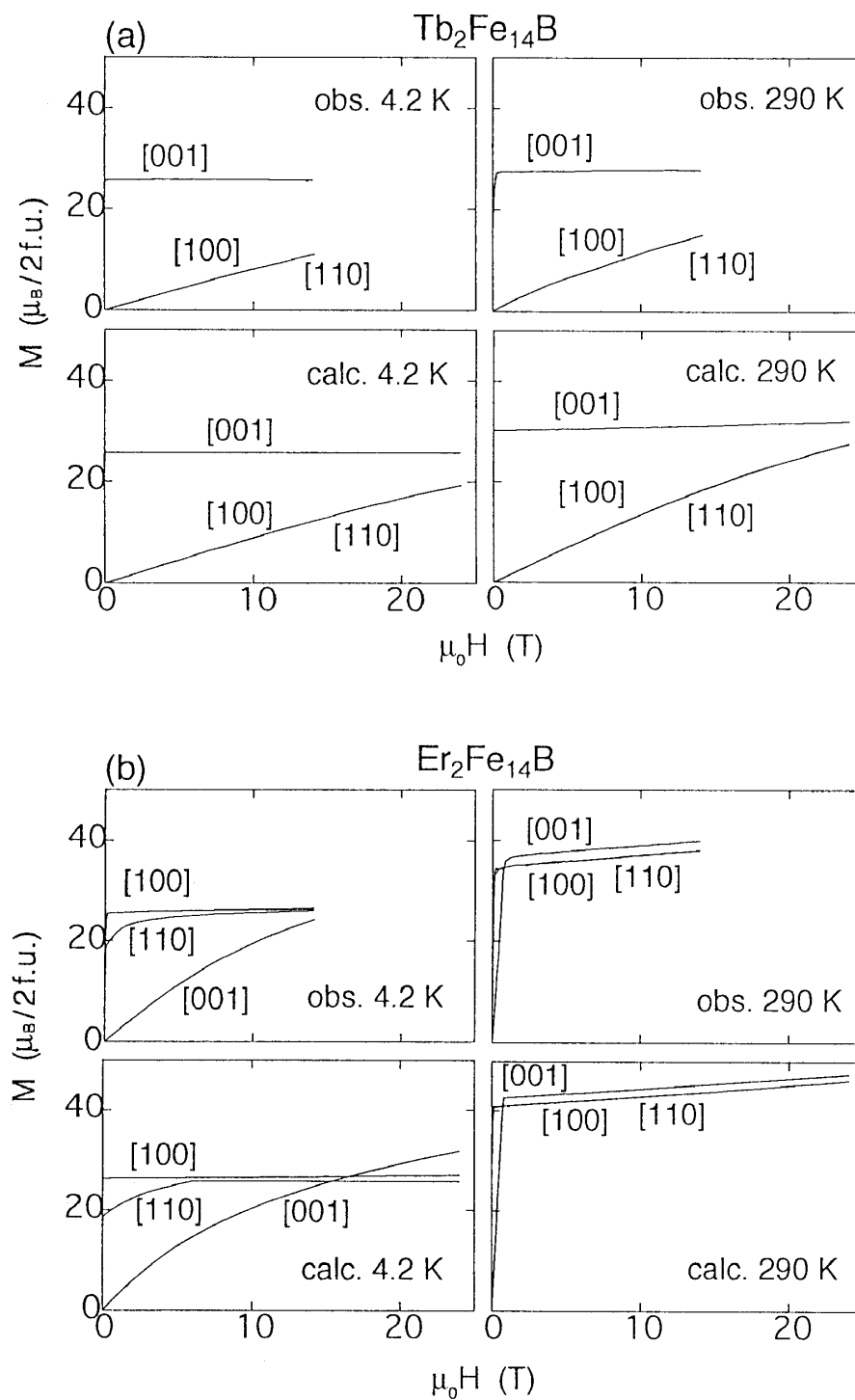


Fig. 3. Observed and calculated magnetization curves at 4.2 K and 290 K for (a)  $\text{Tb}_2\text{Fe}_{14}\text{B}$  and (b)  $\text{Er}_2\text{Fe}_{14}\text{B}$ . Parameters used for the calculation are given in Table I.



system. It should be noted that, in these heavy  $R$  compounds, the saturation magnetization is larger at room temperature than that at 4.2 K because of the ferrimagnetic coupling of  $R$  and Fe moments. The crossing between easy- and hard-axis curves in the Er compound, for example, can be explained based on the ferrimagnetic structure. In order to destroy this ferrimagnetic structure, one requires an extremely high magnetic field which is comparable to the magnitude of exchange field due to the  $R$ -Fe interaction. Recently we have calculated the magnetization process in  $R_2\text{Fe}_{14}\text{B}$  compounds with heavy  $R$  up to 250 T and found the occurrence of successive phase transitions<sup>7)</sup> from ferrimagnetism to the forced ferromagnetism via a spin-flop like phase. It is not easy to observe these transitions experimentally, since the lower critical fields for the Tb and Er compounds, for example, are as high as 132 T and 41 T, respectively. In the pseudo ternary system  $(\text{Er}_{1-x}\text{Tb}_x)_2\text{Fe}_{14}\text{B}$  with the  $x$  around 0.4, this critical field value has been found to become below 30 T owing primarily to the partial cancellation of CEF interactions arising from the Er and Tb ions and actually observed at 24 T for  $(\text{Er}_{0.6}\text{Tb}_{0.4})_2\text{Fe}_{14}\text{B}$  aligned polycrystal.<sup>8)</sup>

Next we show the results of  $\text{Sm}_2\text{Fe}_{17}\text{N}_3$  compound, to which much attention has recently been paid because of its high potentiality as a new permanent magnet material. Although the nitrogen content  $x$  of  $\text{Sm}_2\text{Fe}_{17}\text{N}_x$  can be increased up to more than 3, the sample with  $x = 3.0$  has proved to have the largest saturation magnetization and the highest uniaxial anisotropy.<sup>9)</sup> In the present sample, the nitrogeneration of the host alloy  $\text{Sm}_2\text{Fe}_{17}$  was performed at 738 K in a mixed gas of  $\text{NH}_3$  and  $\text{H}_2$ . The nitride powder was then annealed in an argon atmosphere and then dispersed in epoxy resin in an aligning field. The upper half of Fig. 4 shows the observed magnetization curves at 4.2 K and 296 K with fields applied parallel and perpendicular to the aligned direction. Although the hard-axis curve at 296 K almost saturates at 26 T, the saturation value is about 3 % smaller than the easy-axis value. Such an anisotropy of saturation magnetization was also observed in  $\text{Nd}_2\text{Fe}_{14}\text{B}$ -type compounds as shown in Figs. 1 and 3 and has been interpreted as an effect of strong CEF interactions. In the present case, however, the CEF is less important to this anisotropy, as will be shown below. At 4.2 K the magnetization along the hard axis is only 78 % of the easy-axis value in the field of 26 T and still exhibits the trend of increase. The field of saturation is estimated to be more than 70 T, which is much higher than the reported value ( $\sim 23$  T) of  $\text{Sm}_2\text{Fe}_{17}\text{N}_{2.2}$ .<sup>10)</sup> The calculated magnetization curves using a set of parameters listed in Table I are shown in the lower half of Fig. 4. By comparing with the experimental curves, overall features including the extremely large anisotropy at 4.2 K and the difference in saturation magnetization between the two directions at 296 K are well reproduced by this calculation. The dashed lines in the figure, on the other hand, designate the results in which only the ground  $J = 5/2$  multiplet of the  $\text{Sm}^{3+}$  ion is taken into account.

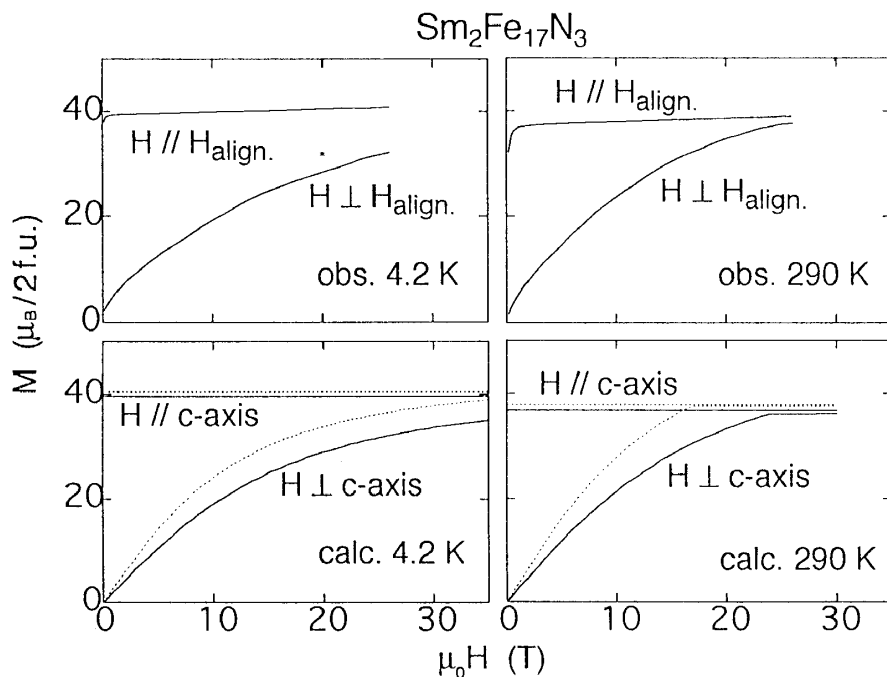


Fig. 4. Observed magnetization curves at 4.2 K and 296 K for  $\text{Sm}_2\text{Fe}_{17}\text{N}_3$  aligned powder and corresponding calculated magnetization curves with the parameters listed in Table I. Dashed lines of the calculation were obtained by taking only the ground  $J$  multiplet into account.

The exclusion of excited  $J$  multiplets significantly reduces the uniaxial anisotropy and enhances the magnitude of Sm magnetic moment. According to the detailed inspection of the calculated results, we have found an unusual magnetization process of Sm moments along the hard direction; at 296 K the Sm moment rotates against the field direction and finally becomes antiparallel to the field, while the Fe moment becomes parallel to the field. This fact means that the saturated state along the hard axis is ferrimagnetic, while along the easy axis the two moments are always parallel keeping the collinear ferromagnetic structure. When only the ground multiplet is treated, the Sm moment simply rotates toward the field direction. Observed anisotropy of the saturation magnetization at 296 K is thus attributed largely to this field-induced ferrimagnetism caused by the inter-multiplet mixing.<sup>5)</sup>

In conclusion, we have shown that the combination of high-field measurements and their numerical analyses given above are most useful for obtaining information about the CEF and exchange interaction in  $R_2\text{Fe}_{14}\text{B}$  and  $R_2\text{Fe}_{17}\text{N}_x$  systems. The present method will easily be applied to other rare-earth-transition-metal systems.

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