

High Field Magnetization and Spin Reorientation in $\text{Sm}_2(\text{Fe}_{1-x}\text{Al}_x)_{17}$ and $\text{Nd}_2(\text{Fe}_{1-x}\text{Al}_x)_{17}$ Single Crystals (Research in High Magnetic Fields)

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High Field Magnetization and Spin Reorientation in $\text{Sm}_2(\text{Fe}_{1-x}\text{Al}_x)_{17}$ and $\text{Nd}_2(\text{Fe}_{1-x}\text{Al}_x)_{17}$ Single Crystals*

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High field magnetization measurements have been performed for single crystals of $R_2(\text{Fe}_{1-x}\text{Al}_x)_{17}$ with $R = \text{Sm}$ and Nd . The magnetization along the c -axis has been found to show a small spontaneous component, indicating that the total magnetization vector is not within the c -plane but in the plane spanned by the b - and c -axes. The angle between the magnetization direction and the b -axis increases linearly with increasing x in the Sm system. The results are analyzed on the basis of the crystalline electric field theory.

KEYWORDS: $\text{Sm}_2(\text{Fe}_{1-x}\text{Al}_x)_{17}$, $\text{Nd}_2(\text{Fe}_{1-x}\text{Al}_x)_{17}$, high magnetic field, spin reorientation

1. Introduction

Magnetic properties of $R_2\text{Fe}_{17}$ (R : rare earth) containing interstitial nitrogens have been studied extensively, because of its drastic increase in Curie temperature T_C upon the nitrogen absorption¹⁾. The origin of the T_C enhancement has been attributed to the increase in the average Fe-Fe distance owing to the volume expansion of about 6%, which greatly enhances the exchange interactions²⁾. There is another important change upon the nitrogenation, which is the appearance of strong uniaxial anisotropy in the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$, while in the host $\text{Sm}_2\text{Fe}_{17}$ system, the direction of easy magnetization is within the c -plane. Some theoretical studies³⁾ dealt with this phenomenon in connection with the change of crystalline electric field (CEF) potential due to nitrogen atoms located at $9e$ site which is quite close to the Sm site. It seems likely, however, that a simple expansion of the lattice and/or a slight change in the c/a ratio of the hexagonal cell give rise to the change of the sign of CEF coefficients. Experimentally, high-field magnetization measurements on single crystal

samples are a powerful method to obtain a quantitative information about the CEF interactions. It is not easy, however, to grow a single crystal of such an interstitially modified system owing primarily to the huge volume expansion. This fact has been preventing us from obtaining a detailed information especially about the magnetic anisotropy. On the other hand, substitutional system $R_2(\text{Fe}_{1-x}M_x)_{17}$ with $M = \text{Al}$ or Ga also shows the increase of T_C with increasing M concentration^{4,5)} for $x \leq 0.2$, in which the rate of increase $\Delta T_C/T_C$ as a function of the volume change $\Delta V/V$ is similar to that of the nitrogen system. To investigate the correlation between such a volume expansion and CEF interaction at the R ion, we have grown the single crystals of $R_2(\text{Fe}_{1-x}\text{Al}_x)_{17}$ with $R = \text{Sm}$ and Nd , and measured the magnetization process under high magnetic fields systematically^{6,7)}. Numerical calculations of magnetization curves have also been performed to compare with the experiments and to give information on the CEF parameters.

2. Experimental

Single crystal samples of $R_2(\text{Fe}_{1-x}\text{Al}_x)_{17}$ with $R = \text{Nd}$, Sm and Y were grown by the Bridgman method using an Al_2O_3 crucible coated with BN in an atmosphere of high pressure Ar gas to avoid the

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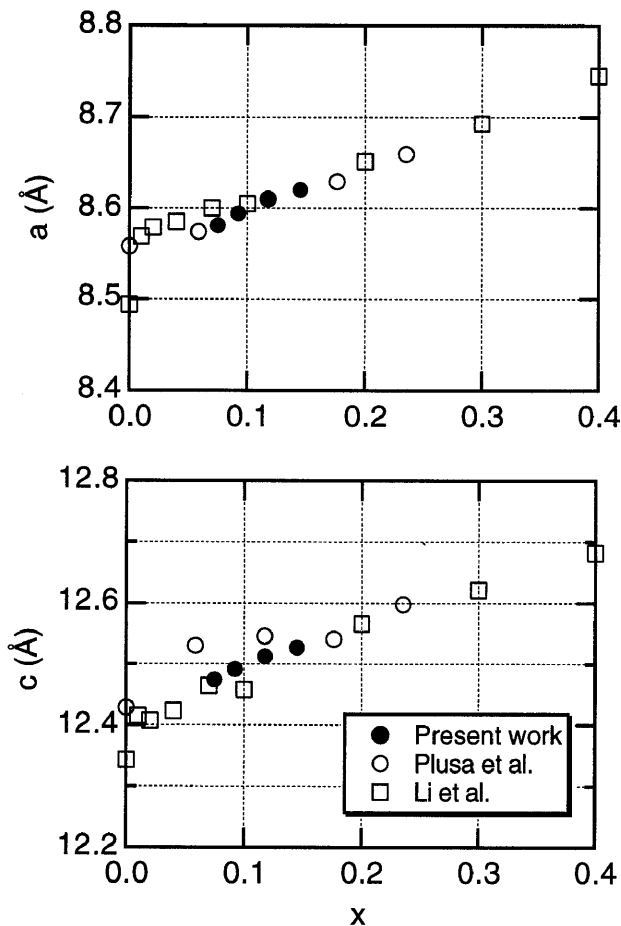


Figure 1. Hexagonal lattice constants a and c of $\text{Sm}_2(\text{Fe}_{1-x}\text{Al}_x)_{17}$ single crystals, obtained from X-ray diffraction measurements at room temperature. Results for polycrystalline samples by Plusa *et al.*⁹ and Li *et al.*¹⁰ are also shown for reference.

evaporation of R (especially of Sm). Final concentration of Al was precisely determined by using the inductively-coupled plasma method. X-ray powder diffraction measurements were carried out by using Cu-K α radiation, in which parts of the single crystals were pulverized to obtain fine powders. The diffraction data were analyzed by using a Rietveld profile-fitting technique implemented in the program RIETAN⁸.

In order to perform the high-field magnetization measurements, each crystal was embedded into a cube of epoxy resin so that the principal directions of the hexagonal cell a ([100]), b ([120]) and c ([001]) become parallel to the three cube axes, respectively.

High-field magnetization measurements were performed either by using a vibrating-sample method in fields of up to 150 kOe generated by a high-power water-cooled magnet or by sample-extraction method in fields of up to 230 kOe generated by a hybrid magnet, both of which are installed at High-Field Laboratory

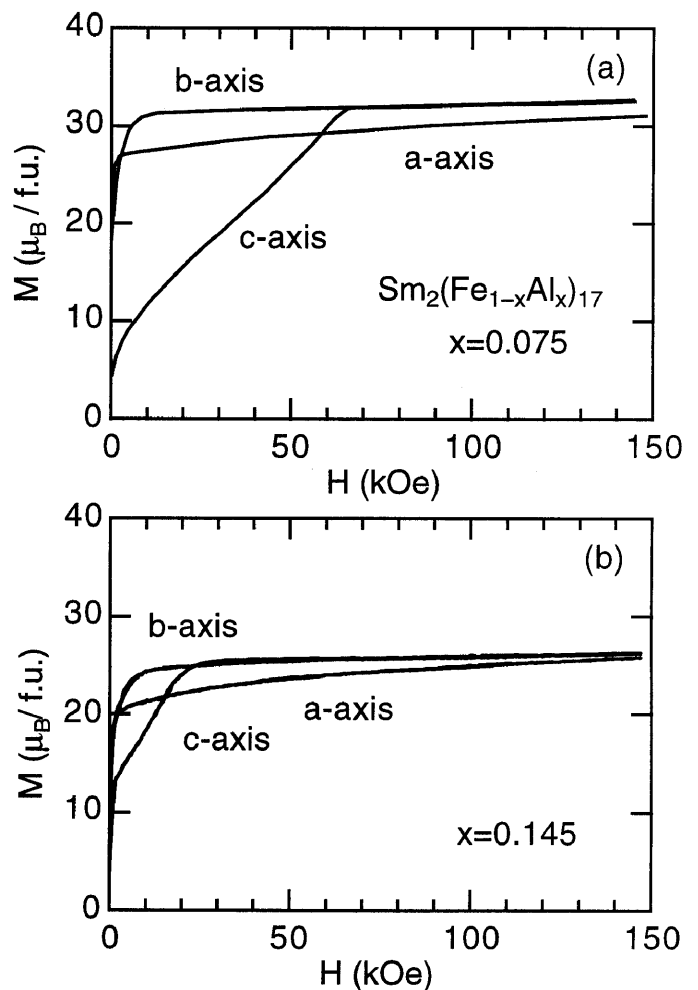


Figure 2. Magnetization curves of $\text{Sm}_2(\text{Fe}_{1-x}\text{Al}_x)_{17}$ single crystals with (a) $x = 0.075$, and (b) $x = 0.145$, measured at 4.2 K.

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3. Results and discussion

Figure 1 shows the lattice constants of single crystals of $\text{Sm}_2(\text{Fe}_{1-x}\text{Al}_x)_{17}$ as a function of Al concentration x . Both a and c increase with increasing Al concentration, in good agreement with the results for polycrystalline samples^{9,10}. We also confirmed that Curie Temperature T_C agree well with that for the polycrystalline sample⁹.

Figure 2 shows the magnetization curves measured at 4.2 K for the samples with $x = 0.075$ and 0.145. In the $x = 0.075$ sample, an appreciable anisotropy within the c -plane is observed, the magnetization along the a -axis being about 5 % smaller than that along the b -axis even in the field of 150 kOe. We have found, moreover, that the c -axis curve shows a finite spontaneous magnetization and

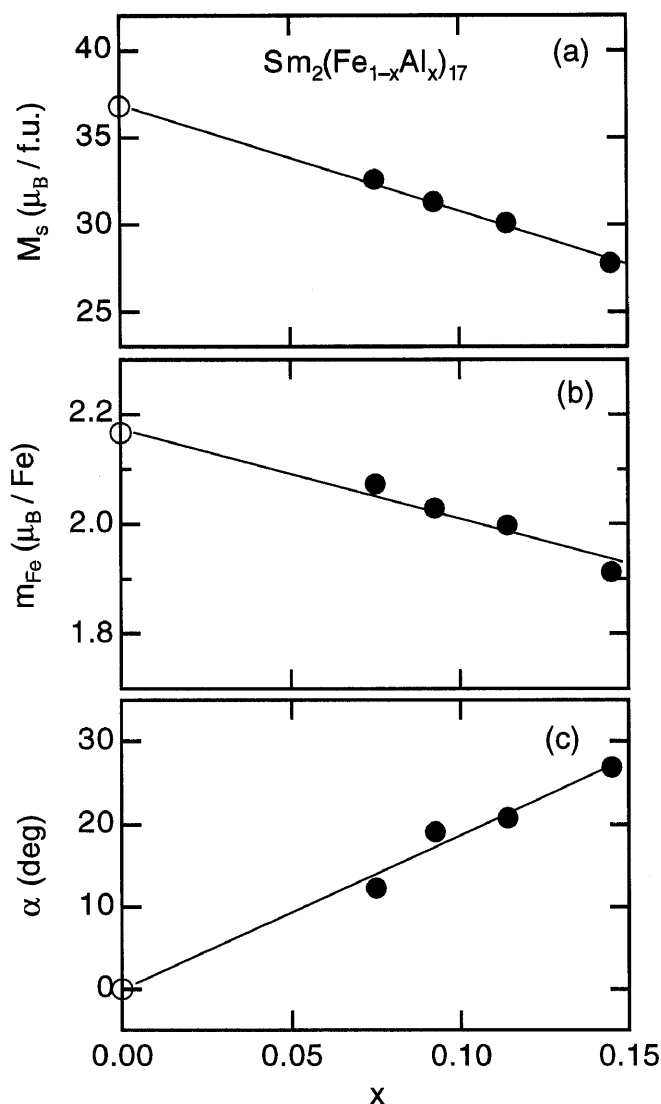


Figure 3. Spontaneous magnetization M_s (a), magnetic moment per Fe atom m_{Fe} (b) and out-of-plane angle α (c) in $\text{Sm}_2(\text{Fe}_{1-x}\text{Al}_x)_{17}$, plotted against the Al concentration x , deduced from the magnetization curves at 4.2 K. The data for $x = 0$ were taken by using the polycrystalline sample.

the ratio of spontaneous magnetizations along the a - and b -axes are nearly equal to $0.87 \approx \cos(\pi/6)$. These results thus show that the total magnetization vector is not within the c -plane but in the plane spanned by the c - and b -axes with an angle $\alpha = 12^\circ$ away from the b -axis. At room temperature the spontaneous magnetization along the c -axis is considerably small, showing that the out-of-plane angle α has been reduced to almost zero. Such a spin reorientation phenomenon can be originated from the competition between the CEF interactions at the Sm^{3+} ion and the anisotropy energy of Fe, and from the difference in their temperature dependences. Detailed results on

the temperature dependence of the magnetic behavior will be reported elsewhere.

Magnetization curves for the sample with $x = 0.145$ at 4.2 K given in Fig. 2(b) show that the c -axis curve also exhibits spontaneous magnetization, which is larger than that in the $x = 0.075$ sample. The field at which the c -axis magnetization saturates, on the other hand, reduced considerably in the $x = 0.145$ sample, indicating a rapid reduction of axial anisotropy by the further substitution of Al for Fe. It should also be noted that the difference in the high-field magnetization between a - and b -axes remains quite large even in the sample with $x = 0.145$.

In Fig. 3(a) the magnitude of spontaneous magnetization vector M_s , deduced from the extrapolated magnetization values to zero field along the three directions, is plotted against the Al concentration x . This result has shown that M_s decreases almost linearly with x , the rate of which is larger than that expected from the simple dilution of Fe by non-magnetic Al. We have deduced the magnetic moment per Fe atom m_{Fe} by assuming that the Sm magnetic moment m_{Sm} is negligible, as shown in Fig. 3(b). Considerable reduction of m_{Fe} with increasing x is observed in contrast to the fact that the concentration dependence of magnetization in a -Fe Al alloys can be explained by the simple dilution picture. A possible origin of the decrease in m_{Fe} is the preferential site occupation of Al, as already confirmed in $\text{Nd}_2(\text{Fe}_{1-x}\text{Al}_x)_{17}$ system by neutron diffraction¹¹⁾.

The out-of-plane angle α is plotted against x in Fig. 3(c), showing a linear increase with increasing x . Recently Wang *et al.*¹²⁾ have reported, according to the X-ray measurements of aligned powder sample, that the easy direction in $\text{Sm}_2(\text{Fe}_{0.81}\text{Al}_{0.19})_{17}$ is along the c -axis at room temperature. Their results are thus not inconsistent with the present work. Moreover, the interstitially modified system $\text{Sm}_2\text{Fe}_{17}\text{C}_{0.5}$, of which the volume is similar to that of $\text{Sm}_2(\text{Fe}_{0.925}\text{Al}_{0.075})_{17}$, has been reported to have a conical anisotropy, according to the X-ray diffraction of aligned polycrystals¹³⁾. These results therefore suggest that the easy direction is correlated with the unit cell volume in both substitutional and interstitial systems. In order to confirm this conjecture, of course, it is necessary to investigate systematically the dependence of α on both Al concentration and temperature.

It is important to note that the extrapolated value of α to $x = 0$ is zero, suggesting that the spontaneous

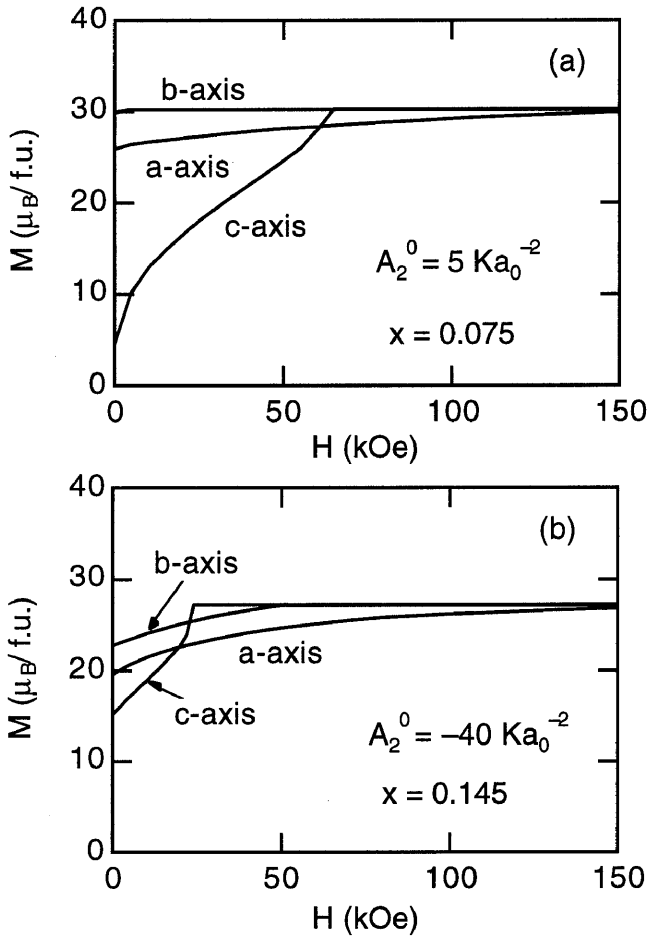


Figure 4. Two examples of calculated magnetization curves at $T = 0$ K for $\text{Sm}_2(\text{Fe}_{1-x}\text{Al}_x)_{17}$ with $x = 0.075$ (a) and $x = 0.145$ (b). The parameters used are as follows: $A_2^0 = 5 \text{ Ka}_0^{-2}$ for $x = 0.075$ and $A_2^0 = -40 \text{ Ka}_0^{-2}$ for $x = 0.145$; $A_4^0 = 16 \text{ Ka}_0^{-4}$, $A_6^0 = 2.5 \text{ Ka}_0^{-6}$, $A_6^6 = 100 \text{ Ka}_0^{-6}$, $A_4^3 = A_6^3 = 0$, and $H_m = 200$ K for both $x = 0.075$ and $x = 0.145$.

magnetization of $\text{Sm}_2\text{Fe}_{17}$ is actually within the c -plane. On the other hand, the anisotropy within the c -plane is almost independent of the Al content x , and so the $\text{Sm}_2\text{Fe}_{17}$ single crystal will exhibit the large in-plane anisotropy. The easy direction of $\text{Sm}_2\text{Fe}_{17}$ is therefore expected to be along the b -axis, which is consistent with the result of Mössbauer analysis by Bo-Ping Hu *et al.*¹⁴⁾. Direct evidence of these properties has so far been lacking owing to the difficulty of obtaining good single crystals of $\text{Sm}_2\text{Fe}_{17}$.

4. CEF analysis

Although the simple dilution picture cannot be applied to the Fe (Al) sublattice as described above, it is still useful to make the CEF analysis for the Sm sublattice to fit the observed magnetization curves. The

method of calculation is essentially similar to what we adopted for $R_2\text{Fe}_{14}\text{B}^{15)}$ and $\text{Sm}_2\text{Fe}_{17}\text{N}_3^{16)}$. The primary assumption in this model is that the magnitude of the Fe-Fe exchange interaction is large enough as compared with that of Fe- R interaction and, therefore, the Fe sublattice can be regarded as rigid, being treated phenomenologically. We can estimate the moment and anisotropy of the Fe (Al) sublattice from the experimental data of the corresponding Y compounds. This assumption may not be justified for $R_2\text{Fe}_{17}$ system, of which T_C is as low as 300 to 400 K. At low temperatures, however, these are still thought to be good approximations.

We first assume that the total free energy of the system is given by

$$F(\mathbf{H}, T) = -2kT \ln Z + 17(1-x) \left\{ K_{\text{Fe}}(T) \sin^2 \theta - \mathbf{m}_{\text{Fe}}(T) \cdot \mathbf{H} \right\} \quad (1)$$

where \mathbf{H} is the applied magnetic field and T the temperature. The second term of eq. (1) expresses the contribution from the Fe (Al) sublattice, where the anisotropy energy $K_{\text{Fe}}(T)$ and the magnitude of magnetic moment $m_{\text{Fe}}(T)$ per Fe are determined from the experimental data for $\text{Y}_2(\text{Fe}_{1-x}\text{Al}_x)_{17}$ single crystals¹⁷⁾ with corresponding x . The first term of eq. (1) is the Sm contribution, of which Z is the partition function defined by

$$Z = \sum_j^{\sum_j (2J+1)} \exp[-E_s / kT] \quad (2)$$

where E_s is the s -th eigenvalue of a Hamiltonian for Sm:

$$\mathcal{H}_{\text{Sm}} = \lambda \mathbf{L} \cdot \mathbf{S} + \mathcal{H}_{\text{CEF}} + 2(1-x)\mu_B \mathbf{S} \cdot \mathbf{H}_m + \mu_B (\mathbf{L} + 2\mathbf{S}) \cdot \mathbf{H} \quad (3)$$

where \mathbf{H}_m is the molecular field acting on Sm due to the Fe-Sm exchange interaction. According to the point symmetry of Sm in the $\text{Th}_2\text{Zn}_{17}$ structure, non-zero terms of the CEF Hamiltonian \mathcal{H}_{CEF} are written by

$$\mathcal{H}_{\text{CEF}} = A_2^0 \sum_j V_2^0(j) + A_4^0 \sum_j V_4^0(j) + A_4^3 \sum_j V_4^3(j) + A_6^0 \sum_j V_6^0(j) + A_6^3 \sum_j V_6^3(j) + A_6^6 \sum_j V_6^6(j) \quad (4)$$

where A_n^m is the CEF coefficient and $\sum_j V_n^m(j)$ is the unnormalized tesseral function for the j -th $4f$ electron

at the coordinate of (x_j, y_j, z_j) with the summation j over all the $4f$ electrons. The Cartesian coordinates in this formulation were taken so that the z - and x -axes become parallel to the hexagonal c - and b -axes, respectively. Since the effect of excited J multiplets on the magnetic properties of Sm-containing compounds is crucially important^{15,16}, the first excited $J = 7/2$ and second excited $J = 9/2$ multiplets are taken into account in addition to the ground $J = 5/2$ multiplet.

After performing some preliminary calculations, we have found that it is necessary to change the CEF parameters significantly for each Al concentration x , in order to reproduce the variation of magnetization curves with different x , especially to explain the changes in the c -axis curve. In Fig. 4(a) and 4(b), two examples of calculated magnetization curves for $T = 0$ K are shown, which correspond to the cases with $x = 0.075$ and 0.145 , respectively. Values of the second order CEF coefficient used are $A_2^0 = 5 K a_0^{-2}$ for $x = 0.075$ and $A_2^0 = -40 K a_0^{-2}$ for $x = 0.145$, where a_0 is the Bohr radius. Other parameters common to both cases are: $A_4^0 = 16 K a_0^{-4}$, $A_6^0 = 2.5 K a_0^{-6}$, $A_6^6 = 100 K a_0^{-6}$, $A_4^3 = A_6^3 = 0$, and $H_m = 200$ K. In these examples of calculation we needed to adopt a quite large value of A_6^6 so as to fit the observed large in-plane anisotropy. This value of A_6^6 is at least one order of magnitude larger than that in $\text{Ho}_2\text{Fe}_{17}$ ¹⁸, determined from the analysis of inelastic neutron scattering experiments. Although a quantitative information about the non-axial CEF coefficients for $R_2\text{Fe}_{17}$ or $R_2\text{Co}_{17}$ is scarcely published, results of $\text{Nd}_2(\text{Fe}_{1-x}\text{Al}_x)_{17}$ single crystals⁷, as shown next, and NdCo_5 ¹⁹ revealed the similar large in-plane anisotropy.

It must be emphasized that the sign of A_2^0 is different for the two cases; in general the negative A_2^0 tends to make the Sm moment align along the c -axis, against the Fe anisotropy energy. In contrast with the case of $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ in which the CEF energy is much larger than the Fe anisotropy energy¹⁶, the contribution from K_{Fe} is comparable to that from the A_2^0 terms here. In fact, present calculations have shown that m_{Fe} and m_{Sm} are noncollinear even at zero field, the angles between the two moments at $H = 0$ are 3.2° and 8.6° , respectively, for $x = 0.075$ and $x = 0.145$.

5. $\text{Nd}_2(\text{Fe}_{1-x}\text{Al}_x)_{17}$

In Fig. 5(a), we show the magnetization curves of

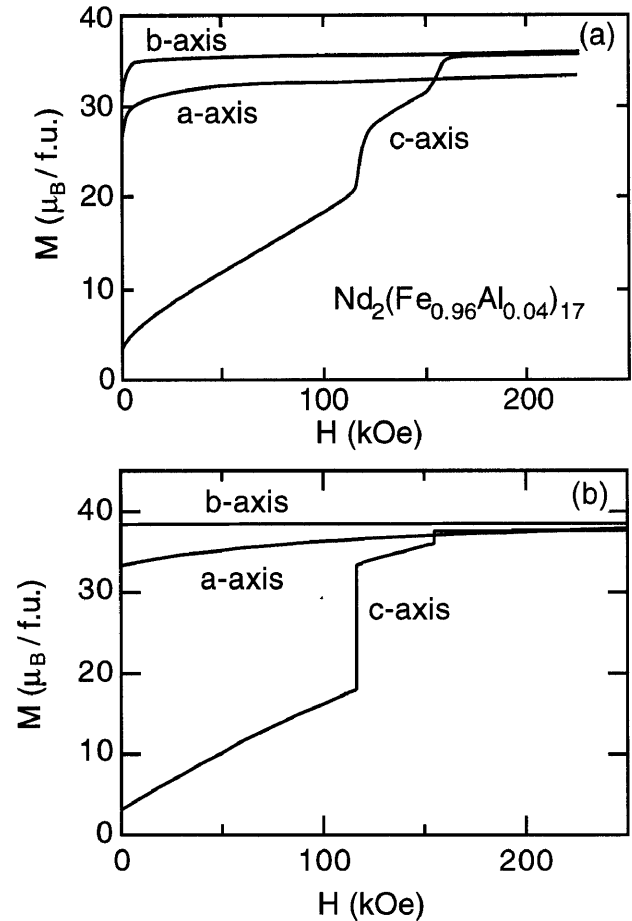


Figure 5. Magnetization curve of $\text{Nd}_2(\text{Fe}_{1-x}\text{Al}_x)_{17}$ with $x = 0.04$; observation at 4.2 K (a) and calculation for $T = 0$ K (b) with parameters given in text.

$\text{Nd}_2(\text{Fe}_{1-x}\text{Al}_x)_{17}$ with $x = 0.04$ measured at 4.2 K. As in $\text{Sm}_2(\text{Fe}_{1-x}\text{Al}_x)_{17}$, the easy direction is not within the c -plane but in the plane spanned by the b - and c -axes. The out-of-plane angle deduced is about 6° which is comparable to the value in the Sm compound with the same x as seen in Fig. 3. A sudden jump in magnetization has been observed at 115 kOe, when the external field was applied along the c -axis. This phenomenon can be regarded as the first-order magnetization process (FOMP), as observed in $\text{Nd}_2\text{Fe}_{14}\text{B}$ -type compounds¹⁵, and suggests that the higher order terms of the CEF potential of the Nd^{3+} plays an important role in this system. Moreover, the magnetization after the FOMP is not saturated but continues to increase gradually and, at 150 kOe, the second jump is observed, after which it coincides with that along the b -axis. It should be noted that such a double step jump of magnetization has been observed also in $\text{Tb}_2\text{Fe}_{17}$ single crystal²⁰.

An example of calculated magnetization curves for $T = 0$ K are shown in Fig. 5(b). Values of the molecular

field parameter and CEF coefficients used are $H_m = 250$ K, $A_2^0 = -500 \text{ K}\alpha_0^{-2}$, $A_4^0 = 15 \text{ K}\alpha_0^{-4}$, $A_4^3 = 0$, $A_6^0 = -4 \text{ K}\alpha_0^{-6}$, $A_6^3 = 150 \text{ K}\alpha_0^{-6}$ and $A_6^6 = 100 \text{ K}\alpha_0^{-6}$. Although the choice of the parameters is still not final, calculated curves well reproduce the observed features including two successive jumps and spontaneous magnetization along the c -axis. According to the calculation, both of these jumps arise from the sudden rotation of the magnetization vector toward the c -axis. In the first jump, moreover, we have found that the c -plane component also rotates from the [120] to [210] directions. Origin of this 60° rotation of in-plane component can be attributed to the competition of CEF potentials arising from A_6^3 and A_6^6 terms. Magnetization measurements and their analysis for samples with other Al concentrations are now in progress and will be reported elsewhere.

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