Magnetic Field Effect on Nitrogenation of $\text{Sm}_2\text{Fe}_{17}$

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Nitrogenation of $\text{Sm}_2\text{Fe}_{17}$ powder was performed under a zero field and a magnetic field of 5 T at 623, 673 and 743 K to clarify the magnetic field effect on nitrogenation. Applying a magnetic field of 5 T induced nitrogenation compared with zero-field nitrogenation, and almost fully nitride $\text{Sm}_2\text{Fe}_{17}\text{N}_{2.9}$ was obtained at 743 K. Mössbauer spectroscopy results suggested that a 5-T magnetic field promoted the phase transformation to the fully-nitride $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ phase. The magnetic field effect was discussed based on the magnetic energy gain and magnetic properties of host $\text{Sm}_2\text{Fe}_{17}$ and fully nitride $\text{Sm}_2\text{Fe}_{17}\text{N}_3$. [doi:10.2320/matertrans.MT-MN2019012]

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1. Introduction

Ferromagnetic (FM) nitride $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ ($0 < x \leq 3$) with a rhombohedral $\text{Th}_2\text{Zn}_{17}$ -type structure (space group $R\bar{3}m$) was synthesized using the N_2 gas-solid reaction technique on host $\text{Sm}_2\text{Fe}_{17}$.¹⁾ The host's cell volume expands by 6%–7% to accommodate three nitrogen atoms at the 9e-interstitial sites.²⁾ The fully-nitride (FN) $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ has high Curie temperature T_C of 746 K, high saturation magnetization $\mu_0 M_S$ of 1.51 T and large anisotropy field of 21 T at room temperature (RT).³⁾ Therefore, FN $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ is a candidate for permanent magnets.^{2,4)} However, $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ decomposes to α -Fe and SmN above 720 K.^{4,5)}

Magnetic field stabilizes the FM phase by gaining large magnetic energy (Zeeman energy) G_M . For example, magnetic fields induced FM phases of LaCo_5H_x ,^{6,7)} MnBi ^{8–12)} and MnAl .^{13,14)} Therefore, it is expected that magnetic fields will promote nitrogenation for $\text{Sm}_2\text{Fe}_{17}$. However, to the best of our knowledge, the magnetic field effect (MFE) on nitrogenation of the $\text{Sm}_2\text{Fe}_{17}$ system had not been reported in detail. Recently, to clarify the MFE on nitrogenation, we developed an in-field heat treatment furnace utilized for a 5-T cryocooled superconducting magnet with a 50 mm room-temperature bore.¹⁵⁾ In this paper, we describe a review of MFE on the nitrogenation of $\text{Sm}_2\text{Fe}_{17}$, which suggests competition between enhancement of phase transformation and suppression of diffusion processes by applying a magnetic field.

2. Experimental Procedure

The host $\text{Sm}_2\text{Fe}_{17}$ compound was prepared by induction melting of the constituent elements under an argon atmosphere and then annealed at 1423 K for 24 h in an argon atmosphere for homogeneity treatment.¹⁶⁾ The $\text{Sm}_2\text{Fe}_{17}$ ingot was crushed and pulverized into powder with particle size less than 53 μm in diameter. The lattice parameters a and c of $\text{Sm}_2\text{Fe}_{17}$ were 0.856 nm and 1.24 nm, respectively. The zero-field nitrogenation (ZFN) and in-field nitrogenation (IFN) of

5 T (IFN-5T) for the $\text{Sm}_2\text{Fe}_{17}$ powder were performed under a nitrogen gas pressure P_n of 0.1 MPa at nitrogenation temperature T_n of 623, 673 and 743 K for 24 hours in an applied magnetic field $\mu_0 H$ of 5 T. The IFN equipment is described in Ref. 15) in detail. The nitrogen content x in the nitrated powders was estimated from the increased sample mass after nitrogenation. Detailed sample preparation is reported in Ref. 17).

To examine the phases of ZFN and IFN-5T samples, X-ray powder diffraction (XRD) measurements were performed using $\text{Cu-K}\alpha$ radiation at RT. Magnetization M data were corrected using a superconducting quantum interference device magnetometer and a vibrating sample magnetometer. T_C of the sample was determined by differential scanning calorimetry under a zero field. ^{57}Fe Mössbauer spectroscopy experiments with a 1.85 GBq $^{57}\text{Co(Rh)}$ source were performed using a conventional constant acceleration method at RT. The velocity scale was calibrated with α -Fe which had a hyperfine field of 33.1 T. The values of the hyperfine parameters were refined using NORMOS.¹⁸⁾

3. Results

The estimated x in the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ powder prepared by ZFN and IFN-5T are listed in Table 1. In this table, the data for host $\text{Sm}_2\text{Fe}_{17}$ are also shown. It is clear that x of IFN-5T is larger than that of ZFN for all T_n . By applying a magnetic field of 5 T, x increased by 0.4–0.6 nitrogen atoms per formula unit. For condition of $T_n = 743$ K, almost FN $\text{Sm}_2\text{Fe}_{17}\text{N}_{2.9}$ was obtained using IFN-5T, while x was only 2.3 using ZFN. Magnetic field promotes nitrogenation for the temperature T range of 623–743 K. From XRD analysis for ZFN and IFN-5T samples,¹⁷⁾ we confirmed that the poor-nitride (PN) and FN phase coexisted in the nitride sample with $x \leq 1.9$. However, the XRD patterns for $x = 2.3$ and 2.9 did not show clearly the two phase coexistence of the PN and FN phases but a single nitride phase with a very small amount of α -Fe phase.¹⁵⁾ The determined lattice parameters for the nitride with $x = 2.3$ and 2.9 are listed in Table 1. The parameters of the nitride with $x = 2.9$ are comparable to the data for FN $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ reported in previous literature.²⁾

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Table 1 Conditions of zero-field nitrogenation (ZFN) and 5 T in-field nitrogenation (IFN-5T) for 24 h, nitrogen content x , lattice parameters, Curie temperature, relative fraction of poor-nitride phase (PN) and fully-nitride phase (FN), and average hyperfine field $\langle B_{\text{hf}} \rangle$.

	T_n	x	a	c	T_C	rel. fraction		$\langle B_{\text{hf}} \rangle$	
	(K)		(nm)	(nm)	(K)	PN	FN	PN (T)	FN (T)
ZFN	623	0.6	two phase		two phase	-	-	-	-
IFN-5T	623	1.0	two phase		two phase	-	-	-	-
ZFN	673	1.3	two phase		two phase	-	-	-	-
IFN-5T	673	1.9	two phase		two phase	-	-	-	-
ZFN	743	2.3	0.874	1.27	two phase	0.157	0.843	25.5	33.3
IFN-5T	743	2.9	0.874	1.27	746	0.082	0.918	25.7	33.2
Sm ₂ Fe ₁₇	-	-	0.856	1.24	391	1	0	21.5	-

Fig. 1 Magnetization curves of $\text{Sm}_2\text{Fe}_{17}$ (a), $\text{Sm}_2\text{Fe}_{17}\text{N}_{2.3}$ (ZFN) (b) and $\text{Sm}_2\text{Fe}_{17}\text{N}_{2.9}$ (IFN-5T) (c) at room temperature.

Figure 1 shows the magnetization (M - H) curves of $\text{Sm}_2\text{Fe}_{17}$ (a), $\text{Sm}_2\text{Fe}_{17}\text{N}_{2.3}$ (b) and $\text{Sm}_2\text{Fe}_{17}\text{N}_{2.9}$ (c) at RT. The saturation magnetic moments m_s were estimated to be $25.1 \mu_B/\text{f.u.}$ for $\text{Sm}_2\text{Fe}_{17}$, $31.3 \mu_B/\text{f.u.}$ for $\text{Sm}_2\text{Fe}_{17}\text{N}_{2.3}$ and $33.8 \mu_B/\text{f.u.}$ for $\text{Sm}_2\text{Fe}_{17}\text{N}_{2.9}$. The value of m_s for $\text{Sm}_2\text{Fe}_{17}\text{N}_{2.9}$ is comparable to that for FN $\text{Sm}_2\text{Fe}_{17}\text{N}_3$.²⁾ We confirmed that the magnetic moment m and remanence of the IFN-5T sample (Fig. 1(c)) are larger than those of the ZFN sample (Fig. 1(b)). IFN-5T induced the hard magnetic properties of $\text{Sm}_2\text{Fe}_{17}\text{N}_x$.

Fig. 2 Saturation moment for ZFN, IFN-5T and $\text{Sm}_2\text{Fe}_{17}$ at 10 K.

The thermomagnetization (M - T) curves of host $\text{Sm}_2\text{Fe}_{17}$, $\text{Sm}_2\text{Fe}_{17}\text{N}_{2.3}$ (ZFN) and $\text{Sm}_2\text{Fe}_{17}\text{N}_{2.9}$ (IFN-5T) in a magnetic field of 1 T were measured in the T range of 10–830 K, which was shown in Ref. 15). The M - T curves for $0.6 \leq x \leq 2.3$ did not show the Brillouin-function like curve but a superposition of two M - T curves,¹⁵⁾ suggesting that the PN and FN phase coexisted in the sample. The M - T curve of $\text{Sm}_2\text{Fe}_{17}\text{N}_{2.9}$ showed a single Brillouin-function curve.¹⁵⁾ The determined T_C of $\text{Sm}_2\text{Fe}_{17}\text{N}_{2.9}$ was 746 K, which is almost the same as that of FN $\text{Sm}_2\text{Fe}_{17}\text{N}_3$.²⁾ Figure 2 shows m_s at 10 K for the ZFN (open circles) and IFN-5T (solid circles). The magnetic field of 5 T enhanced the nitrogen content x and magnetic properties of $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ at each T_n .

Figure 3 shows the Mössbauer spectra of $\text{Sm}_2\text{Fe}_{17}$, $\text{Sm}_2\text{Fe}_{17}\text{N}_{2.3}$ and $\text{Sm}_2\text{Fe}_{17}\text{N}_{2.9}$ at RT. In this figure, dots and solid curves indicate experimental data and fitting curves, respectively. Since Fe atoms occupy 6c, 9d, 18f and 18h sites in the $\text{Th}_2\text{Zn}_{17}$ -type structure, the spectrum of $\text{Sm}_2\text{Fe}_{17}$ was fitted with four sub-spectra using hyperfine interaction parameters: site-occupation, isomer shift, quadruple splitting and hyperfine field B_{hf} . The determined average B_{hf} , $\langle B_{\text{hf}} \rangle$, was 21.5 T for $\text{Sm}_2\text{Fe}_{17}$, which is in good agreement with reported data (21.8 T) for $\text{Sm}_2\text{Fe}_{17}$.²⁾ The spectra of $\text{Sm}_2\text{Fe}_{17}\text{N}_{2.3}$ and $\text{Sm}_2\text{Fe}_{17}\text{N}_{2.9}$ were fitted with eight sub-spectra due to the PN and FN phases. The determined parameters of relative fraction and $\langle B_{\text{hf}} \rangle$ of $\text{Sm}_2\text{Fe}_{17}\text{N}_{2.3}$ and

Fig. 3 Mössbauer spectra of $\text{Sm}_2\text{Fe}_{17}$ (a), $\text{Sm}_2\text{Fe}_{17}\text{N}_{2.3}$ (ZFN) (b) and $\text{Sm}_2\text{Fe}_{17}\text{N}_{2.9}$ (IFN-5T) (c) at room temperature.

$\text{Sm}_2\text{Fe}_{17}\text{N}_{2.9}$ were shown in Table 1. The relative fraction of the FN phase of $x = 2.9$ (IFN-5T) was 92%, which is larger than that of $x = 2.3$ (ZFN). In contrast, the relative fraction of the PN phase of IFN-5T is smaller than that of ZFN. $\langle B_{\text{hf}} \rangle$ of the PN phase was determined to be 25.7 T for $x = 2.3$ (ZFN) and 24.9 T for $x = 2.9$ (IFN-5T), which were larger than that of $\text{Sm}_2\text{Fe}_{17}$. The determined $\langle B_{\text{hf}} \rangle$ of the FN phase was 33.3–33.4 T, which is in good agreement with reported data (33.3 T) of $\text{Sm}_2\text{Fe}_{17}\text{N}_3$.¹⁹ From Mössbauer spectroscopy experiments, it was found that both PN and FN phases existed in the nitrides with $x = 2.3$ and 2.9. The obtained results indicate that m_s of the PN phase is smaller than that of the FN phase but slightly larger than that of $\text{Sm}_2\text{Fe}_{17}$.

The results of this study showed that magnetic fields promoted phase transformation from the PN to the FN phase under at same T_n . That is, the equilibrium state of the N_2 gas-solid reaction probably was changed by applying a magnetic field to form the FN phase with large m .

4. Discussion

In this section, MFE on the nitridation of $\text{Sm}_2\text{Fe}_{17}$ is discussed. The gain of G_M , ΔG_M , can be driving force of the gas-solid reaction. ΔG_M of the Gibbs free energy tends to be more stable of a FM state with large m and promotes ferromagnet synthesis. So far, it has been reported that the reaction or phase transformations from the non-FM to FM phase was accelerated by magnetic fields.^{10,11,14,20}

Our results showed the two-phase coexistence of the FN and PN phases in $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ ($x < 3$), so that the field-

Fig. 4 Temperature dependence of the magnetic moments (a) and calculated moment $m(T,H)/m(0,H)$ (b) of $\text{Sm}_2\text{Fe}_{17}$ and $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ for $\mu_0 H = 1$ T (broken curve) and 5 T (solid curve). The open circles present the experimental data of $\mu_0 H = 1$ T.

induced phase transformation by ΔG_M is a possible mechanism. Assuming a simple model with only the Zeeman effect, ΔG_M under H can be written as

$$\Delta G_M = \mu_0 H \Delta m_s, \quad (1)$$

where μ_0 is the permeability of a vacuum and Δm_s is the change of the saturation moment.^{21,22} In the present case, Δm_s is expressed by

$$\Delta m_s = m_{\text{PN}} - m_{\text{FN}}, \quad (2)$$

where m_{PN} and m_{FN} are the magnetic moments for the PN and FN phases, respectively. The MFE direction is found by the sign of Δm_s .²² As shown in Fig. 3 of Ref. 15), FN $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ is ferromagnetic, but the PN phase is paramagnetic at $T_n = 623$ K, 673 K and 743 K, so that the sign of Δm_s and ΔG_M is negative in this T_n range. This indicates that the MFE promotes the phase transformation from the PN to FN phase.²²

It is difficult to evaluate magnetic moment of the PN phase in the M - T curve of $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ ($x < 3$) sample because of a superposition of two M - T curves.¹⁵ Since present IFN was conducted under a magnetic field of 5 T, we estimated $m(T,H)$ of $\text{Sm}_2\text{Fe}_{17}$ as the PN phase and $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ as the FN phase for $\mu_0 H = 5$ T based on a mean field theory for a simple two-sublattice model.^{2,23,24} The mean-field calculation is described in the appendix.

Figure 4 shows the temperature dependence of the magnetic moments (a) and calculated moment $m(T,H)/m(0,H)$ (b) of $\text{Sm}_2\text{Fe}_{17}$ and $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ for $\mu_0 H = 1$ T (broken curves) and 5 T (solid curves). In this calculation, the effective exchange parameters were $J^{\text{FeFe}} = 290$ K and $J^{\text{SmFe}} = 10$ K for $\text{Sm}_2\text{Fe}_{17}$, and $J^{\text{FeFe}} = 540$ K and $J^{\text{SmFe}} = 50$ K for $\text{Sm}_2\text{Fe}_{17}\text{N}_3$. The open circles in Fig. 4 show the experimental data collected under $\mu_0 H = 1$ T.¹⁵ The

Fig. 5 Nitrogenation temperature dependence of the change in magnetic energy ΔG_M under $\mu_0H = 5$ T, which was evaluated using eq. (1) and the change in magnetic moment Δm_s . The inset shows Δm_s deduced from Fig. 4(a).

Fig. 6 Field-induced nitrogen content Δx as a function of nitrogenation temperature T_n . The open circles indicate experimental Δx deduced from $\Delta x = x(\text{IFN-5T}) - x(\text{ZFN})$. The solid circles indicate Δx estimated by only ΔG_M . The inset shows that nitrogen content x as function of T_n for ZFN (open diamonds) and IFN-5T (solid diamonds).

calculated m - T curves represent the experimental data. The difference between the experimental data of $\mu_0H = 1$ T and calculated data of $\mu_0H = 5$ T is small. Therefore, we considered that the field-induced m was negligibly small within the present IFN-5T condition, and m_{PN} and m_{FN} under $\mu_0H = 5$ T were regarded as the experimental m of $\text{Sm}_2\text{Fe}_{17}$ and $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ for $\mu_0H = 1$ T, respectively. Since ΔG_M of an electron spin of $1 \mu_B$ in $\mu_0H = 1$ T corresponds to thermal energy of 0.67 K,²¹⁾ T_n dependence of ΔG_M for $\mu_0H = 5$ T was obtained, as shown in Fig. 5, which was evaluated using eqs. (1) and (2). Here, Δm_s was deduced from Fig. 4(a) (broken arrows), which is presented in the inset of Fig. 5. With decreasing T_n from $T_n = 743$ K, ΔG_M decreases: the gain of G_M becomes larger.

In Fig. 6, the field-induced nitrogen content Δx is shown as function of T_n . Here, the experimental Δx (open circles) was evaluated from the inset of Fig. 6: $\Delta x = x(\text{IFN-5T}) - x(\text{ZFN})$. If the field-induced nitrogen content ($\Delta x = 0.6$) from $x(\text{ZFN}) = 2.3$ to $x(\text{IFN-5T}) = 2.9$ is only due to ΔG_M (approximately 35 K) at $T_n = 743$ K, the change of the nitrogen content x was calculated to be $\Delta x = 1.0$ at $T_n = 673$ K and $\Delta x = 1.2$ at $T_n = 623$ K, as shown by the solid circles in Fig. 6. The experimental Δx at $T_n = 623$ K and 673 K were smaller than Δx estimated from ΔG_M . This result

suggests that only phase transformation mechanism from the paramagnetic PN phase to ferromagnetic FN phase is hard to explain the field-induced nitrogenation. As seen in Fig. 6, the nitrogenation due to the field-induced phase transformation is probably suppressed at lower T_n . We should consider other MFE mechanisms as well as the field-induced phase transformation in $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ powder.

Fujii *et al.* reported that the FN-phase grain growth (phase transformation) becomes dominant at the later stage in nitrogenation at 733 K under $P_n \geq 0.1$ MPa, exceeding the nitrogen diffusion process, which is important at the earlier stage.¹⁶⁾ That is, at first, nitrogen atoms diffuse into the $\text{Sm}_2\text{Fe}_{17}$ powder from the surface, which forms the PN phase. After that, the PN phase transforms the FN phase. This means that the amount of the PN phase is important for progressing the grain growth of the FN phase (phase transformation).

It was reported that the carbon diffusion in γ -iron²⁵⁾ and the diffusion process in Fe/Ga diffusion couples²⁶⁾ were suppressed by applying magnetic fields. If the nitrogen diffusion process for forming the PN phase is suppressed by applying a magnetic field, the competition of MFE between the enhancement of the phase transformation and suppression of the diffusion processes will occur. The nitrogen diffusion process is regarded as an activation type,^{4,16,27,28)} so that thermal effect of the diffusion is dominant at higher T_n such as 743 K, compared with the nitrogen diffusion process suppressed by MFE. In contrast, the field-induced suppression of the nitrogen diffusion process becomes more effective at lower T_n such as 623 K. This leads to smaller Δx than that estimated from the phase transformation from the PN to FN phase by ΔG_M . Now, further IFN experiments in fields up to 15 T are in progress to verify this scenario, which will be reported soon elsewhere. However, it should be noted that the present results clearly show the promotion of nitrogenation of the $\text{Sm}_2\text{Fe}_{17}$ magnet by applying a magnetic field under our IFN condition.

5. Conclusions

ZFN and IFN-5T for $\text{Sm}_2\text{Fe}_{17}$ powder were conducted under nitrogen gas pressure of 0.1 MPa at 623 , 673 and 743 K for 24 h to investigate the magnetic field effect on the nitrogenation to $\text{Sm}_2\text{Fe}_{17}\text{N}_x$. Nitrogenation of the $\text{Sm}_2\text{Fe}_{17}$ magnet was promoted by applying a magnetic field. Mössbauer spectroscopy results suggested that magnetic fields promoted the phase transformation from the poor-nitride to fully-nitride $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ phase. It was hard to explain the magnetic field effect on nitrogenation in $\text{Sm}_2\text{Fe}_{17}$ by only mechanism of the field-induced phase transformation due to gain of magnetic free energy.

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Mössbauer spectroscopy experiments were carried out at the Division of Isotope Science, Research Support Center, Institute for Research Promotion, Kagoshima University.

Appendix

In the simple model, $m(T, H)$ is expressed by

$$m(T, H) = 2m_{\text{Sm}}(T, H) + 17m_{\text{Fe}}(T, H), \quad (\text{A1})$$

where $m_{\text{Sm}}(T, H)$ and $m_{\text{Fe}}(T, H)$ are the magnetic moments of Sm and Fe atoms, respectively. Then, $m_{\text{Sm}}(T, H)$ and $m_{\text{Fe}}(T, H)$ are written by

$$m_{\text{Sm}}(T, H) = g\langle J \rangle \mu_B \quad (\text{A2})$$

and

$$m_{\text{Fe}}(T, H) = 2\langle S \rangle \mu_B, \quad (\text{A3})$$

where g is the Lande g-factor, $\langle J \rangle$ and $\langle S \rangle$ are thermal averages of the total angular momentum J of Sm and the total spin momentum S of Fe, respectively. The molecular field H_m acting on $m_{\text{Sm}}(T, H)$ and $m_{\text{Fe}}(T, H)$ can be written by

$$H_m(\text{Sm}) = \frac{(g-1)^2}{g\mu_B} J^{\text{SmSm}} z^{\text{SmSm}} \langle J \rangle + \frac{(g-1)}{g\mu_B} J^{\text{SmFe}} z^{\text{SmFe}} \langle S \rangle \quad (\text{A4})$$

and

$$H_m(\text{Fe}) = \frac{1}{2\mu_B} J^{\text{FeFe}} z^{\text{FeFe}} \langle S \rangle + \frac{(g-1)}{2\mu_B} J^{\text{SmFe}} z^{\text{FeSm}} \langle J \rangle, \quad (\text{A5})$$

respectively. Here, J^{SmSm} , J^{SmFe} and J^{FeFe} are the effective exchange parameters of the Sm–Sm, Sm–Fe and Fe–Fe interaction, respectively, and z^{ij} is the number of nearest neighbor j -atoms of an i -atom. In the Th₂Zn₁₇-type structure, Sm occupies the 6c site and Fe occupies the 6c, 9d, 18f and 18h sites. z^{ij} was determined to be $z^{\text{SmSm}} = 0$, $z^{\text{SmFe}} = 6$ (Sm–Fe(18f)) and $z^{\text{FeSm}} = 1$ (Fe(18f)–Sm). For four Fe sites, the average number of nearest neighbor Fe atoms of the Fe(6c)–Fe(6c) (one bond), Fe(9d)–Fe(18f) (four bonds), Fe(18f)–Fe(9d) (two bonds) and Fe(18h)–Fe(9f) (two bonds) was estimated to be 2.2, and $z^{\text{FeFe}} = 2.2$ was adopted in this calculation.

It was assumed that the crystalline electric field energy (magnetocrystalline anisotropy energy) is negligibly small in G_m for the T_C and T_n range, compared with J^{FeFe} in this calculation. The ground $J = 5/2$ multiplet and $g = 0.286$ for Sm³⁺ ion was only considered and $S = 1$ was adopted for the Fe-sublattice.

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