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Effect of conduction-electron polarization on the magnetism of hcp samarium metal

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Peculiar magnetic properties of hcp Sm are adequately described by the calculations based on the model with Sm^{3+} ions in a metallic matrix, taking into account the lowest three multiplets, the spin-orbit interaction, the crystal fields, and the exchange interaction, and together with the conduction-electron spin polarization. It is found that the effect of the conduction-electron polarization is essential to them. By the analyses, it is concluded that the conduction-electron moment is larger than the localized $4f$ one and that the polarity of the spin part of the magnetic moment enhanced by the conduction-electron polarization is positive to the total moment. This polarity of the spin moment, which is opposite to the case for the free Sm^{3+} ion, is furthermore experimentally verified by the magnetic measurements on the hcp SmNd and SmGd alloys. It is also elucidated through the calculations that the difference between the temperature dependence of the spin moment and that of the orbital one due to the admixture of the J multiplets, in general, results in a variety of temperature dependence of the ordered moment for each Sm^{3+} ion, just like the thermomagnetic behavior of ferrimagnets. [S0163-1829(97)01125-9]

I. INTRODUCTION

In analyzing the magnetic data of many substances containing the Sm^{3+} ion, some difficulties have often been encountered, which are attributed to the unique properties of this ion. First, the energy intervals between the consecutive J multiplets are relatively narrow, e.g., the first excited multiplet of $J=7/2$ is only about 1500 K above the ground multiplet of $J=5/2$. Therefore, the virtual transitions among the multiplets through the off-J matrix elements of the Hamiltonian and the thermal populations of the excited J levels have considerable influence on the magnetic properties.[1] Second, the spin and the orbital part of the localized $4f$ moment are coupled ferrimagnetically due to the spin-orbit interaction and the large cancellation between them occurs for the ground multiplet of $J=5/2$. In metallic cases, this makes the contribution of the conduction electron moment to the total moment quite substantial.[2–5] Furthermore, the magnetic behavior of the Sm^{3+} ion could be significantly modified in solids by the crystal fields and the exchange interaction.[6–11]

We have found before[12] that the melt-quenched Sm metal, which has an hcp structure, has peculiar magnetic properties as follows.

(1) The hcp Sm metal is a ferromagnet with the ordering temperature T_C of 160 K, which is exceptionally high compared with the value anticipated from the de Gennes factor for the ground J multiplet.

(2) The magnitude of the magnetization in the ordered state is about $0.1\mu_B$/ion, whereas the free-ion value for the ground state is $0.71\mu_B$/ion.

(3) The temperature dependence of the magnetization has a broad maximum, which does not seem to be attributed to the anisotropy nor the ferrimagnetic arrangement of the magnetic moments.

(4) The paramagnetic susceptibility decreases monotonically with increasing temperature up to 600 K, at which the transition from the metastable hcp phase to the normal one occurs. Namely, the minimum due to the thermal population of higher J multiplets, characteristic of the free Sm^{3+} ion, is not observed.

(5) The magnitude of the paramagnetic susceptibility is much larger than expected from Van Vleck's theory for the Sm^{3+} ion.

The purpose of this paper is to explain these magnetic behaviors of hcp Sm by calculating the temperature dependences of the ordered moment and the paramagnetic susceptibility on the basis of the model of Sm^{3+} in a metallic matrix. Though the Sm ions in some compounds are known to be divalent or mixed valent, those in pure metals such as hcp Sm are usually in a well-defined tripositive state and the lattice constants of hcp Sm, which can be smoothly extrapolated from those of hcp heavy rare-earth metals, also indicate that the electronic configuration of the Sm ion is $(4f)^5$.[13–15] Then it seems that the magnetic properties described above originate from the character of the trivalent ion. In this paper, despite some of the simplifications in the calculations, the experimental data will be satisfactorily explained and it will be shown that the effect of the conduction-electron polarization is essential to them. Furthermore, through the calculations, some general features of the Sm^{3+} moment will be also elucidated.

The plan of the remainder of this paper is as follows. The next section is devoted to the explanations of the theoretical aspects for the calculations, in which the excited J multiplets, the spin-orbit interaction, the crystal fields, the exchange interaction, and the conduction-electron spin polarization are taken into account. In Sec. III, the results of the numerical calculations, considering the lowest three multiplets, are compared with the experimental data, which have been newly measured in a temperature region extended down to 5 K. Some additional experimental results of the magnetic measurements on the hcp SmNd and SmGd alloys are also included in Sec. III to verify the adequacy of our point of view. Section IV is the concluding remarks.

II. THEORY

The starting point for the calculation of the ordered moment is the single-ion Hamiltonian for the $4f$ electrons. This is expressed by the sum of the spin-orbit interaction, the crystal-field potential, and the exchange interaction as follows:

$$\mathcal{H}=\lambda\mathbf{L}\cdot\mathbf{S}+\mathcal{H}_{\text{cryst}}-2J_{ff}\langle S_z\rangle S_z\,, \tag{1}$$

where λ is the spin-orbit interaction constant, J_{ff} is the interionic exchange integral, and $\mathbf{L}$, $\mathbf{S}$ are the $4f$ orbital and the $4f$ spin angular momentum operator, respectively. The notation $\langle\cdots\rangle$ means the thermal average. Here, the exchange interaction is written in a mean-field approximation and the assumption is made that the ordered moments are fixed to the z direction which is parallel to the hexagonal c axis. This is the most likely case when the Sm^{3+} ion is located at the hexagonal site in the trivalent rare-earth metals[16–18] and also supported by the consideration on the crystal fields as is shown below.

The crystal-field Hamiltonian relevant to the hcp structure can be decomposed into the following spherical harmonics:

$$\mathcal{H}_{\text{cryst}}=DO_2^0+EO_4^0+FO_6^0+GO_6^6, \tag{2}$$

where O_l^m are the equivalent operators[19,20] written in terms of the total orbital angular momentum $\mathbf{L}$. The numerical constants D, E, F, G have been calculated by Kasuya[21] using a point charge model as functions of the lattice constants a and c, the expectation values of r^l ($l=2,4,6$) with respect to the $4f$ radial wave function $\langle r^l\rangle$, and the effective point charge Z^*. With the experimental values of $a=3.64$ Å and $c=5.82$ Å at room temperature and nonrelativistic Hartree-Fock values of $\langle r^l\rangle$ calculated by Freeman and Watson,[22] we obtained the following values:

$$D=-4.47\times10^{-1}\cdot Z^* \quad (\text{K}), \tag{3a}$$

$$E=-1.31\times10^{-3}\cdot Z^* \quad (\text{K}), \tag{3b}$$

$$F=-2.57\times10^{-5}\cdot Z^* \quad (\text{K}), \tag{3c}$$

$$G=4.69\times10^{-4}\cdot Z^* \quad (\text{K}), \tag{3d}$$

which we use to estimate the magnitudes of the crystal fields. The signs of these crystal-field parameters indicate that hcp Sm has a strong anisotropy along the c axis for the positive value of Z^*.

The energy eigenvalues and eigenfunctions are obtained by diagonalizing the Hamiltonian and determining the expectation value of S_z self-consistently. Then we can calculate the total magnetic moment per each ion to be

$$m_{\text{total}}=m_{4f}+m_{\text{cond}}\,, \tag{4}$$

$$m_{4f}=-\mu_B\langle L_z+2S_z\rangle, \tag{5}$$

$$m_{\text{cond}}=-2\mu_B J\rho\langle S_z\rangle, \tag{6}$$

where m_{4f} and m_{cond} are the $4f$ moment and the conduction-electron moment, respectively. Equation (6) is derived from the so-called s-d Hamiltonian,[23,24] and J and ρ represent, respectively, the zero-wave-vector component of the exchange integral between the $4f$ and the conduction electrons and the density of states per atom at the Fermi level. We are neglecting here the orbital contribution of the conduction band.

In the paramagnetic region, the Hamiltonian under the external field H can be written as[2,23–25]

$$\begin{aligned}\mathcal{H}=&\lambda\mathbf{L}\cdot\mathbf{S}+\mathcal{H}_{\text{cryst}}+\mu_B\mathbf{H}\cdot(\mathbf{L}+2\mathbf{S})\\&+2\mu_B J\rho\mathbf{H}\cdot\mathbf{S}-2J_{ff}\langle\mathbf{S}\rangle\cdot\mathbf{S},\end{aligned} \tag{7}$$

where the last three terms on the right-hand side are regarded as a small perturbation. The formula for the α $(=x,y,z)$ component of the susceptibility has been recently derived by Stewart[26] using a perturbation theory as follows:

$$\chi_{\text{total}\alpha}=\chi_{4f\alpha}+\chi_{\text{cond}\alpha}+\chi_{\text{dia}}\,, \tag{8}$$

$$\begin{aligned}\chi_{4f\alpha}&=-N\mu_B\,\frac{\langle L_\alpha+2S_\alpha\rangle}{H_\alpha}\\&=-N\mu_B^2\left[\left(\sigma_{L_\alpha+2S_\alpha,L_\alpha+2S_\alpha}-\frac{2J_{ff}\sigma^2_{L_\alpha+2S_\alpha,S_\alpha}}{1+2J_{ff}\sigma_{S_\alpha,S_\alpha}}\right)\right.\\&\quad\left.+2J\rho\left(\frac{\sigma_{L_\alpha+2S_\alpha,S_\alpha}}{1+2J_{ff}\sigma_{S_\alpha,S_\alpha}}\right)\right],\end{aligned} \tag{9}$$

$$\begin{aligned}\chi_{\text{cond}\alpha}&=-2N\mu_B J\rho\,\frac{\langle S_\alpha\rangle}{H_\alpha}+\chi_{\text{Pauli}}\\&=-2N\mu_B^2 J\rho\left[\left(\frac{\sigma_{L_\alpha+2S_\alpha,S_\alpha}}{1+2J_{ff}\sigma_{S_\alpha,S_\alpha}}\right)\right.\\&\quad\left.+2J\rho\left(\frac{\sigma_{S_\alpha,S_\alpha}}{1+2J_{ff}\sigma_{S_\alpha,S_\alpha}}\right)\right]+\chi_{\text{Pauli}}\,,\end{aligned} \tag{10}$$

where χ_{4f}, χ_{cond}, and χ_{dia} are, respectively, the susceptibility associated with the $4f$ moments, that arising from the spin polarization of the conduction electrons, and the orbital diamagnetic one. The notation N is the number of the Sm^{3+} ion, $\chi_{\text{Pauli}}=2N\mu_B^2\rho$ is the Pauli paramagnetic susceptibility and $\sigma_{A,B}$ is

$$\begin{aligned}\sigma_{A,B}\equiv\Sigma_n P_n^0\Bigg(&-\frac{\langle n|A|n\rangle\langle n|B|n\rangle}{k_BT}\\&+2\Sigma_{m\neq n}\,\frac{\langle n|A|m\rangle\langle m|B|n\rangle}{E_n^0-E_m^0}\Bigg),\end{aligned} \tag{11}$$

where $E_n^0, |n\rangle$ and P_n^0 denote the unperturbed energy eigenvalue, the eigenfunction, and the normalized Boltzmann factor, respectively.[8]

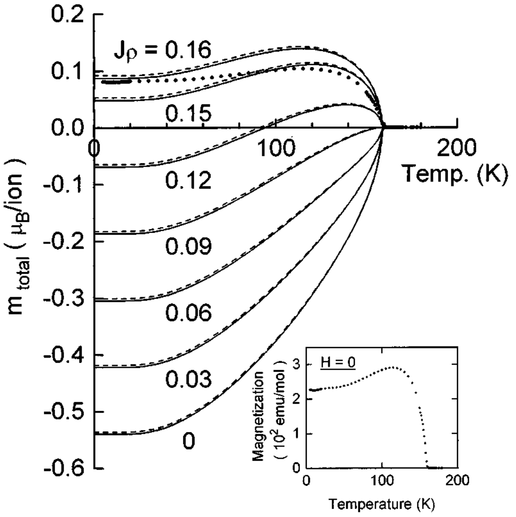

FIG. 1. Temperature dependence of the ordered Sm^{3+} moment in hcp Sm calculated for the various values of $J\rho$. For other parameters, $\lambda = 430$ K, $J_{ff} = 40$ K, and $Z^* = 2.0$ are used. Solid and broken lines represent the results of the calculation considering the lowest two multiplets ($J = 5/2$ and $7/2$) and the lowest three ones ($J = 5/2$, $7/2$, and $9/2$), respectively. The positive value means that the spin moment is larger than the orbital one and the negative value means the opposite case. Dots are the values deduced from the experimental thermomagnetic data shown in the inset, which were taken on a SQUID magnetometer.

The total susceptibility can be summed up into the following form, which we use for the calculation:

$$\chi_{\text{total}\alpha} = -N\mu_B^2\left(\sigma_{M_\alpha,M_\alpha} - \frac{2J_{ff}\sigma^2_{M_\alpha,S_\alpha}}{1+2J_{ff}\sigma_{S_\alpha,S_\alpha}}\right) + \chi_{\text{Pauli}} + \chi_{\text{dia}}, \tag{12}$$

where

$$M_\alpha \equiv L_\alpha + 2(1+J\rho)S_\alpha. \tag{13}$$

This formula indicates that the spin part of the ionic moment is modified by a factor of $1 + J\rho$ due to the interaction J [see Eq. (9)], similar to the ordered moment [Eqs. (4)–(6)]. This result is readily understood from the shape of the starting Hamiltonian of Eq. (7). Compared to Eqs. (8)–(10), this final expression is more convenient to the numerical calculation, as well as provides another physical interpretation described above.

III. RESULTS AND DISCUSSION

A. Ordered moment

The calculated ordered moment for various values of the parameters, λ, J_{ff}, Z^*, and $J\rho$, have been compared with the experimental data. The experimental values of the ordered moment for each ion (dots in Fig. 1) have been obtained from the thermomagnetic data for the field-cooled polycrystalline sample in a zero field, which is shown in the inset, with the assumption that each moment is completely fixed to the c axis in each crystal grain, which is then randomly oriented on the hemisphere on the field direction side for a field-cooled sample.

In the calculations, since the effective charge Z^* has only weak influence, e.g., the different values of Z^* by 1.0 makes the difference of T_C of about 10 K, we have adopted $Z^* = 2.0$ throughout, which is a reasonable value taking into account the shielding effects of the outer electrons. Then, the interionic exchange parameter J_{ff} has been chosen as $J_{ff} = 40$ K to fit T_C with the experimental value.

Theoretically the high T_C of hcp Sm is expected to be caused by the admixture of the excited J multiplets into the ground one.[27] But, the derived value of $J_{ff} = 40$ K, taking account of this effect, is still somewhat higher than the value extrapolated from the systematic variation of those for the hcp heavy rare-earth metals, which are obtained from the well-known relation $T_C = 2J_{ff}G/3k_B$, where G is the de Gennes factor. This implies that the systematic change in electronic structure, such as the density of states at the Fermi level and the exchange integral between the $4f$ and the conduction electrons, for the heavy rare-earth series might not be extrapolated smoothly to hcp Sm and that the high T_C of hcp Sm is originated from such a special situation in electronic structure as well as J multiplet structure.

Figure 1 shows the temperature dependence of the ordered moment calculated through Eqs. (4)–(6) with $J_{ff} = 40$ K, $Z^* = 2.0$ for various values of the parameter $J\rho$. The spin-orbit interaction constant λ has been taken to be 430 K throughout, which gives an energy separation of 1505 K between the ground J level and the first excited one for the free ion.

A variety of temperature dependence shown in Fig. 1 is originated from the difference between the temperature dependence of the spin moment and that of the orbital one, mainly due to the admixture of the first excited multiplet into the ground one. As is shown in Fig. 1, the influence of the second excited multiplet is small in this temperature range. Note that such a variety is not the case for the other rare-earth ions, where the excited multiplets are of little relevance and hence the ratio between the spin and the orbital moment is constant at any temperatures according to the Wigner-Eckart theorem.

For $J\rho = 0$, which means that the moment is arising only from the $4f$ electrons, the magnitude of the ordered moment at $T = 0$ K is reduced from the free-ion value for the ground multiplet of 0.71 μ_B/ion to about 0.54 μ_B/ion due to the J mixing caused mainly by the exchange interaction, but this is far from the experimental value of the order of 0.1 μ_B/ion. As $J\rho$ increases and the total spin moment begins to exceed the orbital one, a broad maximum as is seen in the experimental data appears in the calculated curve. It should be noted that in this case the conduction-electron moment is larger than the localized $4f$ moment and that the contribution of the latter to the total moment is negative.[28] The case of $J\rho = 0.15$–0.16 gives the ordered moment of the order of $0.1\mu_B$/ion, giving a good agreement with the experiment. This value of $J\rho$ is almost the same as has been obtained from the analysis of the neutron magnetic form factor for α-Sm by Moon and Koehler.[29] The higher value of

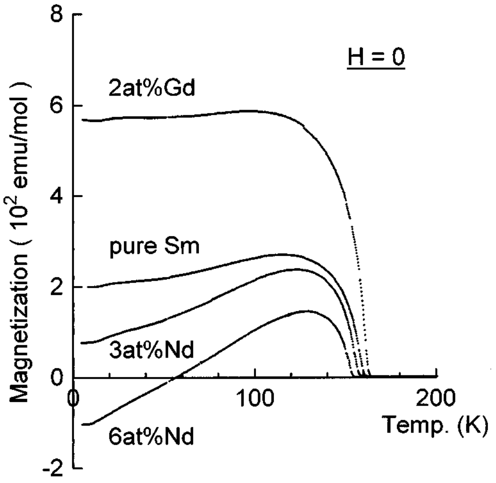

FIG. 2. The thermomagnetic curves for the melt-quenched hcp Sm metal and SmNd, SmGd, alloys in a zero field. The measurements were made on a vibrating sample magnetometer.

$J\rho$ for hcp Sm compared with those for the heavy rare-earth metals is also consistent with the high value of J_{ff} described above.

Our analysis predicts that for hcp Sm the resultant moment has a spin character rather than an orbital one. Then we have made magnetic measurements on hcp Sm containing a small amount of Nd and Gd to verify the adequacy of our point of view. It is known that in the hcp binary alloys between rare-earth elements the spin moment of each constituent couples ferromagnetically to whichever the constituent is, light or heavy rare earth.[30] This implies that if the spin moment indeed exceeds the orbital one, adding a small amount of lighter rare-earth elements such as Nd to hcp Sm would decrease the magnetization and a heavier rare earth such as Gd would increase it, and, in contrast, if the orbital moment is larger than the spin, the effect of addition would be opposite. Figure 2 shows the thermomagnetic curves for the field-cooled samples in a zero field. These results support the spin character of the Sm moment and suggest that our interpretation is essentially correct. Note that this spin character has little to do with the crystal-field induced sign reversal of $\langle S_z \rangle$ pointed out by Buschow *et al.*[9] and that, nevertheless, the Sm^{3+} ion in such a situation could behave just like the heavy rare-earth ion with respect to the magnetic coupling.

B. Paramagnetic susceptibility

Figure 3 shows the effect of $J\rho$ on the paramagnetic susceptibility with $\lambda = 430$ K, $J_{ff} = 40$ K, and $Z^* = 2.0$. Here, the values calculated by

$$\chi_{\text{total av}} = \frac{2}{3} \chi_{\text{total } x} + \frac{1}{3} \chi_{\text{total } z} \tag{14}$$

are used for the comparison with the experimental data, and the lowest three multiplets have been considered because of the higher temperature range than in the previous section.

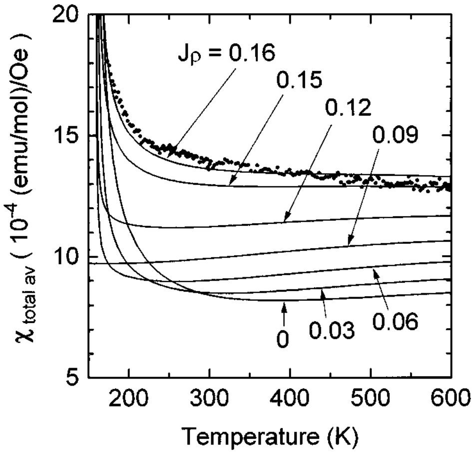

FIG. 3. Temperature dependence of the calculated paramagnetic susceptibility with regard to the polycrystalline hcp Sm metal for the various values of $J\rho$. For other parameters, $\lambda = 430$ K, $J_{ff} = 40$ K, $Z^* = 2.0$, and $\chi_{\text{Pauli}} + \chi_{\text{dia}} = -2 \times 10^{-4}$ (emu/mol)/Oe are used, and the lowest three J multiplets ($J = 5/2$, 7/2, and 9/2) are considered. Dots are the experimental values.

It can be seen that both the magnitude and the temperature dependence are strongly modified by $J\rho$. The increase of $J\rho$ makes the increase of the paramagnetic susceptibility over a wide temperature range and the disappearance of the minimum in the temperature dependence, whereas, without $J\rho$, any reasonable combinations of other parameters, λ, J_{ff} and Z^*, cannot make such a modification. The Curie-Weiss behavior suggested by Stewart[2] is approximately valid in a lower temperature region where the thermal populations of the excited multiplets are negligible.

The experimental data can be fitted well with $J\rho = 0.16$ and $\chi_{\text{Pauli}} + \chi_{\text{dia}} = -2 \times 10^{-4}$ (emu/mol)/Oe. This value of $J\rho$ is consistent with the analysis of the ordered moment described in Sec. III A. However, the value of $\chi_{\text{Pauli}} + \chi_{\text{dia}}$ is much smaller than that estimated from the susceptibility for the isostructural nonmagnetic metals of Y and Lu, e.g., 1.8×10^{-4} (emu/mol)/Oe.[31] In this sense, our analysis of the susceptibility has not yet met with the quantitative success.

In Fig. 4, the effect of $J\rho$ on $\langle S \rangle_{\text{av}}/H$ is shown, which is calculated as

$$\frac{\langle S \rangle_{\text{av}}}{H} = \frac{2}{3} \frac{\langle S_x \rangle}{H_x} + \frac{1}{3} \frac{\langle S_z \rangle}{H_z} \tag{15}$$

with $\lambda = 430$ K, $J_{ff} = 40$ K, and $Z^* = 2.0$. Experimentally this quantity correlates with the part of the Knight shift arising from the polarization of the conduction electrons through the exchange with the $4f$ electrons. It can be seen that $J\rho$ also causes the drastic change in $\langle S \rangle_{\text{av}}/H$. For $J\rho = 0$, the crossover temperature T_{CO}, at which $\langle S \rangle_{\text{av}}/H$ crosses zero, is calculated to be about 320 K. As $J\rho$ is increased from zero, T_{CO} becomes lower and approaches down to T_C, and around $J\rho \sim 0.09$ the direction of divergence is changed from the positive side to the negative one. For $J\rho$ larger than 0.09, the value of $\langle S \rangle_{\text{av}}/H$ is negative for all temperatures. Note that, for $J\rho \sim 0.09$, $\langle S_\alpha \rangle / H_\alpha$ is not very dependent on tem-

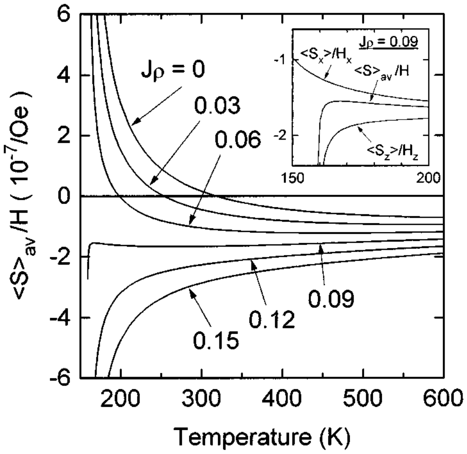

FIG. 4. Effect of the variation of $J\rho$ on the temperature dependence of $\langle S\rangle_{\mathrm{av}}/H$ calculated for hcp Sm. For other parameters, $\lambda = 430$ K, $J_{ff} = 40$ K, and $Z^* = 2.0$ are used, and the lowest three J multiplets ($J = 5/2$, $7/2$, and $9/2$) are considered. The inset shows the case of $J\rho = 0.09$ around T_C with the scale enlarged.

perature even just above T_C (see the inset). Such a peculiarity for the case of $J\rho \sim 0.09$ is also reflected in the unique temperature dependences of the ordered moment and the susceptibility around T_C (see Figs. 1 and 3). In this case, the compensation between the spin moment and the orbital one occurs in the vicinity of T_C and then the divergence of the susceptibility at T_C is almost depressed unlike the usual magnetic transition.

IV. CONCLUDING REMARKS

The numerical calculations of the temperature dependences of the ordered moment and the paramagnetic susceptibility with regard to the hcp Sm metal have been made. And it has been shown that the numerical results adequately describe the general trends of the peculiar magnetic behaviors of this metal and that the conduction-electron polarization effect is essential to them. Detailed results of the analyses are as follows.

(1) The effect of higher J multiplets to T_C is quantitatively evaluated and somewhat higher J_{ff} compared with those of hcp heavy rare-earth metals has been obtained. The derived high values of J_{ff} and $J\rho$ suggest that the systematic change in electronic structure for the heavy rare-earth series might not be extrapolated smoothly to hcp Sm, which is thought to be one of the reasons for the high T_C.

(2) In hcp Sm, the conduction-electron moment is greater than the localized $4f$ one and the total spin moment enhanced by the conduction-electron polarization exceeds the orbital part of the magnetic moment. This marginal cancellation between the conduction-electron moment and the $4f$ one, or between the spin and the orbital part of the magnetic moment, gives rise to the small magnetization. The polarity of the spin moment positive to the total one, which is opposite to the case of the free Sm^{3+} ion, has been, furthermore, experimentally verified by the magnetic measurements on the SmNd and SmGd alloys.

(3) The broad maximum in the temperature dependence of the magnetization in the ordered state is originated from the difference between the temperature dependences of the spin moment and that of the orbital one, due to the mixing of the excited J multiplets into the ground one.

(4) The high values of the paramagnetic susceptibility and the absence of the minimum in its temperature dependence can be explained qualitatively by the conduction-electron polarization effect.

An interesting conclusion deduced from the present analyses is the exotic thermomagnetic behavior, just like ferrimagnets, of the ordered Sm^{3+} moment due to the J mixing. This is a general property of the ordered Sm^{3+} moment, and hence we can expect various temperature dependences of each Sm^{3+} moment in magnetically ordered states. Especially in the case of metals, where the spin part of the magnetic moment is often enhanced by the conduction-electron polarization and tends to cancel or even to exceed the orbital part, the difference of the temperature dependences of the two due to the J mixing would be remarkably reflected in the thermal variation of the total moment. Such an interpretation of the thermomagnetic behavior of the ordered Sm^{3+} moment has never been proposed by anyone, as far as we know. We have also found, in this term, that when the compensation between the spin moment and the orbital one occurs around T_C the peak of the susceptibility would be suppressed and the magnetic transition is obscured in the M-T curve.

Another striking feature of Sm^{3+} shown in the calculations made is how drastically the magnetic properties are affected by the conduction-electron polarization effect. Prior to our study, this effect has been argued by Stewart,[2–5,26] mainly in the paramagnetic region since early 1970's and its importance has been pointed out. His quantitative estimations, however, have been limited within the cases considering the first excited multiplet of $J = 7/2$ as a perturbation. The present investigation illustrates that the thermal population of the excited multiplets should be considered to analyze the experimental data at around room temperature or above and also demonstrates that the analysis of the temperature dependence of the ordered moment, as well as the susceptibility, could be fruitful to estimate the true size of the conduction electron polarization and to elucidate the physics of Sm^{3+} in real metallic substances.

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[27] Since the de Gennes factor G is defined only in a subspace of given J, the relation $T_C = 2J_{ff}G/3k_B$ is not valid for the case that the excited J multiplets are also concerned. For the Sm^{3+} ion, taking account of the mixing of the first excited multiplet of $J = 7/2$ as a perturbation, the above relation is modified to be $T_C = 2J_{ff}G/\{3k_B(1-40J_{ff}/7\Delta)\}$, where G is the de Gennes factor for the ground multiplet and Δ is the energy interval between the first excited multiplet and the ground one. This implies that T_C for the Sm compound is positively shifted, in the first-order perturbation theory, by a factor of $(1-40J_{ff}/7\Delta)^{-1}$ compared with the case considering only the ground J multiplet. Our fit of T_C takes account of this effect in more complete form and results in $J_{ff} = 40$ K.

[28] Such a moment formation has been first pointed out theoretically for the paramagnetic state by Stewart (Ref. 3) and found experimentally in the polarized neutron-diffraction measurement on the CsCl-type compound SmZn by Givord *et al.* [D. Givord, P. Morin, and D. Schmitt, J. Magn. Magn. Mater. **15-18**, 525 (1980)].

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