Crystal field effects on the saturation magnetic moment of Sm³⁺ ion in ferromagnetic samarium compounds

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Abstract. The effects of cubic crystal fields on the saturation magnetic moment of Sm³⁺ ion in ferromagnetic compounds have been investigated. In samarium compounds with magnetic elements, the exchange field H_{ex} acting on Sm³⁺ ion is taken to be proportional to the sublattice magnetization of the magnetic element, while in compounds with nonmagnetic elements H_{ex} is taken to be proportional to the spin average of the Sm³⁺ ion and is determined self-consistently. In both types of compounds H_{ex} is assumed to be along [001] direction. The saturation magnetic moment is calculated by taking into account the admixture of excited ($J = 7/2$ and $J = 9/2$) levels into the ground ($J = 5/2$) level of Sm³⁺ ion by crystal fields and exchange fields. It is shown that depending upon the strength, the crystal fields quench or enhance the magnetic moment from the free ion value, and in some cases force Sm³⁺ ion to behave effectively like an $(L + S)$ ion rather than an $(L - S)$ ion. The crystal fields may have important bearing on the performance of samarium compounds as permanent magnet materials.

Keywords. Saturation magnetic moment; Crystal fields; Sm³⁺ ion; SmCo₅.

1. Introduction

The magnetic properties of compounds containing Sm³⁺ ions have been of considerable interest ever since the work of Van Vleck (1932). The Sm³⁺ ion possesses five electrons in the 4f shell which are responsible for its magnetic properties. The lowest spectroscopic term given by the Hund's rule is ⁶H ($S = 5/2$ and $L = 5$, where S is the spin angular momentum quantum number and L is the oribtal angular momentum quantum number). The spin-orbit interaction splits this term into a multiplet the component levels of which have J values ranging from $(L - S)$ to $(L + S)$, i.e., 5/2, 7/2, 9/2, .. 15/2, with $J = 5/2$ as the ground level. However, unlike in most other rare earth ions, the energy separation between the ground ($J = 5/2$) level and the first excited ($J = 7/2$) level of Sm⁺³ ion is only about 1400 ∼ 1500 K. As a result of the narrow multiplet width, there is sizable temperature-independent contribution, associated with the second-order Zeeman effect, to many observable quantities, such as the 4f-susceptibility X_t (Van Vleck 1932), the spin average $\langle S_z \rangle_{av}/H$ of Sm³⁺ ion (White and Van Vleck 1961), the 4f-induced hyperfine field $\langle H_z^{4f} \rangle_{av}/H$ at the samarium nuclear site in paramagnetic compounds (Günther and Lindgren 1964), etc. Here S is the spin operator of Sm³⁺ ion, H_{op}^{4f} is the operator for the magnetic field produced by the 4f electrons at the nuclear site, H is the applied magnetic field, and 'av' denotes the Boltzmann

Table 1. Saturation magnetic moment on samarium in some ferromagnetic compounds (Wallace 1968, 1971)

Compound	Curie temperature (K)	Saturation moment (μ_B)	Compound	Curie temperature (K)	Saturation moment (μ_B)
SmPt$_2$[a]	16	0·19	SmNi*	45	0·23
SmIr$_2$	37	0·24	SmNi$_2$*	21	0·25
SmAl$_2$	122	~0·1	SmNi$_3$*	85	0·33
SmRh$_2$	22	0·53	SmNi$_5$*	25	0·7

[a] Sankar (1974)   * Nickel is non-magnetic in these compounds.

average of the expectation value of the corresponding operator over all the multiplet levels.

In rare earth ions, where only the ground state is populated, both $\langle S_z \rangle_{av}/H$ and $\langle H_s^{4f} \rangle_{av}/H$ are proportional to the 4f susceptibility X_f. This, however, is no longer true in the case of Sm^{3+} ions. In fact, White and Van Vleck (1961) showed that in the case of free Sm^{3+} ion, because of the temperature-independent contributions, $\langle S_z \rangle_{av}/H$ changes sign passes through zero, or at a temperature of about 300 K, called the crossover temperature. This has, indeed, been observed in many samarium compounds (Jones and Hesse 1967, deWijn *et al* 1967, Jones 1969) by studying the 4f contribution, K_f, to the Knight shift of the nonmagnetic site, K_f being proportional to $\langle S_z \rangle_{av}/H$. On the other hand, in free Sm^{3+} ion, the 4f-induced hyperfine field $\langle H_s^{4f} \rangle_{av}/H$ at samarium nuclear site, with the inclusion of temperature independent terms, does not show a crossover, *i.e.*, does not pass through zero at any temperature (Günther and Lindgren 1964) but is still not proportional to the 4f-susceptibility.

Furthermore, because of the narrow multiplet width, the crystal fields also strongly admix the excited J levels into the ground level of Sm^{3+} ion leading to many interesting results. It has been shown (Malik and Vijayaraghavan 1971 *a*, 1971 *b*, Malik 1972, deWijn *et al* 1973) that the crystal fields may reduce the crossover temperature in $\langle S_z \rangle_{av}/H$ from 300 K to lower values as has been observed in SmPt$_2$ (Malik 1970) or even altogether suppress the Van Vleck type crossover as in SmSn$_3$ (Borsa *et al* 1967, Malik 1970), SmF$_3$ (Malik *et al* 1972) and SmAl$_2$ (Buschow *et al* 1967). Similarly, it has been shown (Malik and Vijayaraghavan 1974 *a*, Malik 1974) that the crystal fields introduce one or more crossovers in $\langle H_s^{4f} \rangle/H$ where none exists in the free Sm^{3+} ion.

The saturation magnetic moment of Sm^{+3} ion (at 0 K) in many ferromagnetic compounds is found to be considerably different from $g_J J = 0·71$, the value associated with free Sm^{3+} ion (here g_J is the Lande' g-factor of the rare earth ion). The magnetic moment values in a few samarium compounds are given in table 1. Further, in many compounds with magnetic elements, samarium behaves like an ion belonging to the second half of the rare earth series (Gd and above) rather than one belonging to the first half (Wallace 1968). In this paper we discuss the effects of crystal fields on saturation magnetic moment (Bleaney 1962) in cubic samarium compounds (Malik 1973) and show that, apart from considerably affecting the magnitude of the magnetic moment, the crystal fields may force Sm^{3+} ion to behave effectively like an $(L + S)$ ion rather than an $(L - S)$ ion.

2. The crystal field Hamiltonian and its matrix elements

The general crystal field Hamiltonian can be written as (Hutchings 1964)

$$\mathscr{H}_c = \sum_{n=0}^{\infty} \sum_{m=0}^{n} A_n^{\ m} \sum_i f_{nm}^{\ c} (r_i) = \sum_{n=0}^{\infty} \sum_{m=0}^{n} A_n^{\ m} \sum_i V_n^{\ m} (r_i) \tag{1}$$

where $f_{nm}^{\ c}$ or $V_m^{\ n}$, which have been tabulated by Hutchings (1964), are certain functions of cartesian coordinates of the electrons, and the summation involving i is over all the electrons of the partially filled shells (in our case the 4f shell) of the ion under consideration. The coefficients $A_n^{\ m} \langle r^n \rangle$, sometimes represented by $V_n^{\ m}$ also (Elliott and Stevens 1953), determine the strength of the crystal potential. Here $\langle r^n \rangle$ is the expectation value of the nth power of the radius of the 4f orbital. We need the matrix elements of $\mathscr{H}_c$ between different states in the $| f^N SLJM \rangle$ representation. For configurations containing equivalent electrons (i.e., electrons having same n and l quantum numbers) the terms with n-odd in eq. (1) vanish. Further, for f-electrons only terms with $n \leq 6$ give non-zero contribution. The point symmetry of the ion under consideration may require that some of the coefficients ($A_n^{\ m}$) in eq. (1) be zero. The term with $n = m = 0$ is a constant which gives a uniform shift of all the energy levels and is of no concern in the magnetic properties.

While working in a manifold of constant J, one can use the method of operator equivalents (Stevens 1962, Bleaney and Stevens 1953) and replace $f_{nm}^{\ c}$ or $V_n^{\ m}$ by the angular momentum operators

$$A_n^{\ m} \sum_i f_{nm}^{\ c} (r_i) = [A_n^{\ m} \langle r^n \rangle \theta_n] O_n^{\ m} = B_n^{\ m} O_n^{\ m} \tag{2}$$

where $\theta_n = \alpha, \beta, \gamma$ are respectively the operator equivalent factors for the second, the fourth, and the sixth degree terms in the crystal potential, and $O_n^{\ m}$ are the angular momentum operators. All these have been tabulated by Hutchings (1964). For calculations involving the crystal field effects on Sm^{3+} ion we also need the matrix elements of $\mathscr{H}_c$ between states belonging to different J manifolds. These too can be obtained by the method of operator equivalents extended to elements nondiagonal in J (Elliott and Stevens 1953, Judd 1954). However, it is convenient to use the methods of tensor algebra to obtain these matrix elements (Malik 1972). The crystal field Hamiltonian is written in terms of the tensor operators $C_m^{(n)}$ by making the following replacements

$$f_{n0}^{\ c} (r) = a_{n0} r^n C_0^{(n)} (\theta, \phi) \tag{3a}$$

$$f_{nm}^{\ c} (r) = a_{nm} r^n [C_{-m}^{(n)} (\theta, \phi) + (-1)^m C_m^{(n)} (\theta, \phi)] \quad m > 0 \tag{3b}$$

where a_{nm} are certain numerical factors, and the tensor operators $C_m^{(n)}$ are defined in terms of the spherical harmonics as

$$C_m^{(n)} (\theta, \phi) = \sqrt{\frac{4\pi}{2n+1}} \ Y_n^{\ m} (\theta, \phi) \tag{4}$$

The factors a_{nm} can be easily determined by comparing the two sides of eqs (3a, 3b); for example $a_{40} = 8$ and $a_{60} = 16$. The radial integration over the 4f wavefunction may be carried out in the rightmost expression in eqs (3a, 3b). The operators $C_m^{(n)}$ act only on the angular part of the wavefunction. Now the matrix elements of $C_m^{(n)}$ between different states in the $| f^N SLJM \rangle$ representation are needed.

These matrix elements are diagonal in the spin variables. The M-dependence of the matrix elements can be taken apart by the Wigner-Eckart theorem

$$\langle f^N \, SLJM \mid C_m^{(n)} \mid f^N \, SL'J'M' \rangle$$

$$= (-1)^{J-M} \begin{pmatrix} J & n & J' \\ -M & m & M' \end{pmatrix} (f^N \, SLJ \parallel C^{(n)} \parallel f^N \, SL'J') \tag{5}$$

The large parentheses denote the Wigner 3-j symbols which have been tabulated by Rotenberg *et al* (1959). The reduced matrix elements of $C^{(n)}$ can be written as (Wybourne 1965);

$$(f^N \, SLJ \parallel C^{(n)} \parallel (f^N \, SL'J')$$

$$= (-1)^{S+L'+J+n} \sqrt{(2J+1)(2J'+1)} \, (f \parallel C^{(n)} \parallel f)$$

$$\times \begin{Bmatrix} J & J' & n \\ L' & L & S \end{Bmatrix} (f^N \, SL \parallel U^{(n)} \parallel f^N \, SL') \tag{6}$$

where for the f electrons ($l = 3$)

$$(f \parallel C^{(n)} \parallel f) = (-1)^l (2l+1) \begin{pmatrix} l & n & l \\ 0 & 0 & 0 \end{pmatrix} \tag{7}$$

The curly parenthesis in eq. (6) denotes the Wigner 6-j symbol (Rotenberg *et al* 1959). The doubly reduced matrix elements of $U^{(n)}$ have been tabulated by Nielson and Koster (1964) and can also be obtained (Wybourne 1965) by using the coefficients of fractional parentage (abbreviated as $(\bar{\psi}_1 \{ \mid \psi)$ and $(\bar{\psi} \mid \} \psi_1'))$, *i.e.*

$$(\psi_1 \parallel U^{(n)} \parallel \psi_1') = N \sqrt{(2\bar{L}_1 + 1)(2\bar{L}_1' + 1)} \sum_{\bar{\psi}} (\psi_1 \{ \mid \bar{\psi})(\bar{\psi} \mid \} \psi_1')$$

$$\times (-1)^{\bar{L}+L_1+l+n} \times \begin{Bmatrix} L_1 & l & \bar{L} \\ l & L_1' & n \end{Bmatrix} \tag{8}$$

where N is the number of electrons in the 4f shell. Thus all the required matrix elements of the crystal field Hamiltonian can be completely determined.

3. Calculation of the magnetic moment

In order to demonstrate the effects of crystal fields on the saturation magnetic moment of Sm^{3+} ion we consider the case of a cubic samarium ferromagnet in which Sm^{3+} ions occupy a site of local cubic symmetry. For simplicity we assume [001] axis as the easy direction of magnetization. The exchange field, therefore, is along [001] axis which we take as the z axis. The Hamiltonian in the presence of spin-orbit coupling, the crystal field, the exchange field H_{ex} (which acts on S_z only) and the applied field H (which acts on $L_z + 2S_z$) can be written as

$$\mathcal{H} = \lambda L \cdot S + \mathcal{H}_c + 2\mu_B H_{ex} S_z + \mu_B H (L_z + 2S_z) \tag{9}$$

where μ_B is the Bohr magneton (taken positive), and λ is the spin-orbit coupling parameter assumed throughout this paper to be $\lambda/k = 410$ K which gives an energy separation of about 1435 K between $J = 5/2$ and $J = 7/2$ levels. The cubic crystal field Hamiltonian with $z \parallel [001]$ is given by (Hutchings 1964).

$$\mathcal{H}_c = \sum_i [A_4^0 f_{40}^c (r_i) + A_4^4 f_{44}^c (r_i) + A_6^0 f_{60}^c (r_i) + A_6^4 f_{64}^c (r_i)] \tag{10}$$

For the choice of [001] as the z axis, some of the coefficients in $\mathcal{H}_c$ are related, namely, $A_4^4 = 5A_4^0$ and $A_6^4 = -21A_6^0$ (we shall abbreviate $A_4^0 \langle r^4 \rangle$ as $A_4 \langle r^4 \rangle$ and

$A_6{}^0 \langle r^6 \rangle$ as $A_6 \langle r^6 \rangle$ and treat them as parameters in our calculations). The cubic crystal field Hamiltonian in terms of the tensor operators $C_m{}^{(n)}$ can be written as

$$\mathcal{H}_c = 8A_4 \langle r^4 \rangle \sum [C_0{}^{(4)} + \sqrt{\tfrac{5}{14}} (C_{-4}{}^{(4)} + C_4{}^{(4)})]$$
$$+ 16A_6 \langle r^6 \rangle \sum [C_0{}^{(6)} - \sqrt{\tfrac{7}{2}} (C_{-4}{}^{(6)} + C_4{}^{(6)})] \tag{11}$$

(We drop the arguments of $C_m{}^{(n)}$ as well as the summation index for the sake of brevity). The method outlined earlier can be used to evaluate the desired matrix elements of $\mathcal{H}_c$. The operators S_z and $L_z + 2S_z$, being vectors, connect states differing in J by 0 or ± 1, and their nonzero matrix elements can also be obtained by the use of tensor operator techniques. However, in this case the matrix elements can be written conveniently as

$$\langle SLJM \mid S_z \mid SLJM \rangle = (g_J - 1) M \tag{12 a}$$

$$\langle SLJM \mid L_z \mid SLJM \rangle = (2 - g_J) M \tag{12 b}$$

$$\langle SLJM \mid S_z \mid SLJ + 1\, M \rangle = \langle SLJ + 1M \mid S_z \mid SLJM \rangle$$
$$= \sqrt{(J+1)^2 - M^2} \, \langle J \| A \| J + 1 \rangle \tag{12 c}$$

$$\langle SLJM \mid L_z \mid SLJ + 1M \rangle = \langle SLJ + 1M \mid L_z \mid SLJM \rangle$$
$$= - \sqrt{(J+1)^2 - M^2} \, \langle J \| A \| J + 1 \rangle \tag{12 d}$$

where

$$\langle J \| A \| J + 1 \rangle = \left[\frac{(J+L+S+2)(-J+S+L)(J+L-S+1)(J+S-L+1)}{4(J+1)^2(2J+1)(2J+3)} \right]^{1/2} \tag{13}$$

Also

$$\langle SLJM \mid L \cdot S \mid SLJ + 1M \rangle = \tfrac{1}{2} [J(J+1) - L(L+1) - S(S+1)] \tag{14}$$

After having determined all the required diagonal and nondiagonal matrix elements of various operators, we construct the secular determinant of the Hamiltonian of eq. (9) between M states spanned by $J = 5/2, J = 7/2$ and $J = 9/2$ levels, and diagonalize it to obtain the energy eigenvalues E_m and eigenfunctions $\mid m \rangle$. The exchange splittings in ferromagnetic state are comparable to crystal field splittings and therefore both the interactions have to be treated equally. The neglect of $J = 11/2$ and other higher levels does not introduce significant error, because these levels lie far off in energy. On the other hand, the neglect of these levels considerably reduces the size of the matrix to be diagonalised. The magnetic moment is defined as

$$\mu = - \mu_B \langle L_z + 2S_z \rangle_{av} \tag{15}$$

where $\langle A \rangle_{av}$ of an operator A at any temperature is given by

$$\langle A \rangle_{av} = \sum_m \langle m \mid A \mid m \rangle \exp(- E_m/kT) / \sum_m \exp(-E_m/kT)$$
$$= \sum_m p(m) \langle m \mid A \mid m \rangle$$

where $p(m) = \exp(- E_m/kT)/\sum_m \exp(- E_m/kT)$. For calculations of the saturation magnetic moment at 0 K, $p(m) = 1$ for the ground state and zero for all other

states. The exchange coupling between a Sm^{3+} ion and another paramagnetic ion j is represented by the usual exchange potential $\vartheta \, S_{sm} \cdot S_j$ where ϑ is the exchange integral connecting the two ions. While calculating the saturation moment we distinguish between the compounds of samarium with nonmagnetic elements and those with magnetic elements. In the case of ferromagnetic samarium compounds with nonmagnetic elements such as $SmPt_2$, $SmRh_2$, $SmAl_2$, etc. (to be referred to as type I compounds) the exchange interaction is among the Sm^{3+} ions ($S_j = S_{sm} = S$) and in metallic compounds operates through the RKKY (Ruderman, Kittel, Kasuya, Yosida) mechanism (Ruderman and Kittel 1954, Kasuya 1956, Yosida 1957). We use the molecular field approximation which consists in writing the exchange interaction as $2\mu_B H_{ex} S_z$ where

$$2\mu_B H_{ex} = - \vartheta_{ff} \langle S_z \rangle_{av} \qquad (17)$$

and ϑ_{ff} is the exchange interaction constant between Sm^{3+} ions. On the other hand, in the case of ferromagnetic samarium compounds with magnetic elements (ME), such as $SmFe_2$, $SmCo_2$, etc. (to be referred to as type II compounds) the exchange field acting on the Sm^{3+} ion is mainly determined by its coupling with the magnetic element and can be taken to be proportional to the sublattice magnetization M_{ME} of the ME ion (Wolf and Van Vleck 1960).

Now for the type I compounds H_{ex} is determined by $\langle S_z \rangle_{av}$ of the Sm^{3+} ion itself, but $\langle S_z \rangle_{av}$ implicitly depends on H_{ex} through the eigenfunctions $| m \rangle$ and energy eigenvalues E_m. Thus the exchange field is to be determined self-consistently for a given value of ϑ_{ff}, for each set of crystal field parameters ($A_4 \langle r^4 \rangle$ and $A_6 \langle r^6 \rangle$)) and for each temperature. In order to accomplish this we start with $H_{ex} = 0$, $H = 10$ kOe and diagonalise the Hamiltonian of eq. (9) for given $A_4 \langle r^4 \rangle$ and $A_6 \langle r^6 \rangle$ and calculate $\langle S_z \rangle_{av}$. Typically we take $\vartheta_{ff}/k = 70$ K, which yields a Curie temperature of about 120 K (though dependent slightly on the crystal field parameters), and calculate the exchange field using eq. (17). This value of H_{ex} is used in the next iteration and the process repeated till self-consistent values of $\langle S_z \rangle_{av}$ or H_{ex} are obtained. The Hamiltonian of eq. (9) is then completely known and, therefore, the magnetic moment can be calculated. In a slightly different procedure, after the first iteration when a nonzero H_{ex} is generated, the applied field is set equal to zero and H_{ex} is built to self-consistency in the absence of H. However, since the exchange field dominates the applied field the results in the two cases do not differ significantly. One can also start with an approximate value of H_{ex} and $H = 0$ and obtain self-consistent values of H_{ex}. For the type II compounds, H_{ex} is already defined and no self-consistency is required. Here we take typically $| \mu_B H_{ex}/k | = $ const. $\times M_{ME}/k = 25$ K. In this paper only the results on saturation magnetic moment will be presented. The crystal field effects on the temperature dependence of the magnetization will be reported later (Malik and Vijayaraghavan 1974 *b*).

4. Results and Discussion

The calculated values of the saturation magnetic moment of Sm^{3+} ion as a function of $A_4 \langle r^4 \rangle$ and $A_6 \langle r^6 \rangle$ are shown in figure 1 for type I compounds. The curves are labelled with the values of $A_6 \langle r^6 \rangle/k$ in Kelvin and it may be recalled that we have taken [001] as the easy direction of magnetization and $\vartheta_{ff}/k = + 70$ K. It
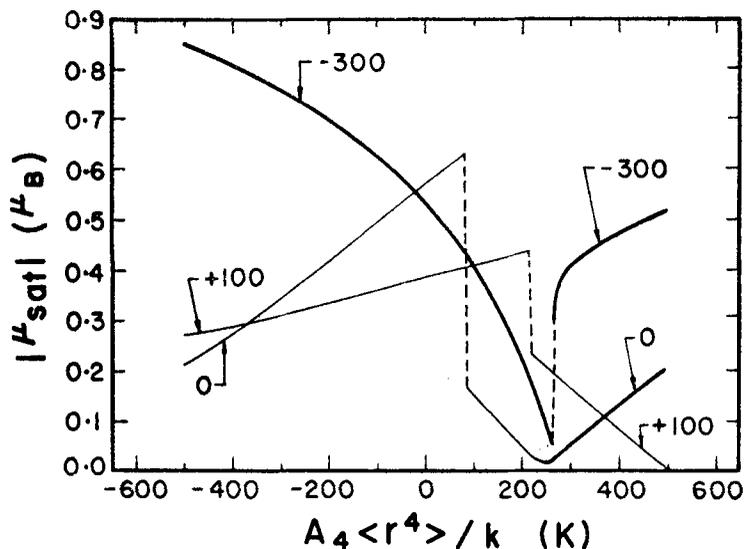
Figure 1. The variation of the saturation magnetic moment of Sm^{3+} ion in Type I compounds (see text) as a function of $A_4 \langle r^4 \rangle / k$ and $A_6 \langle r^6 \rangle / k$ (in Kelvin). The curves are labelled with the values of $A_6 \langle r^6 \rangle / k$ in Kelvin. Throughout $H_{ex} \parallel [001]$ and $\vartheta_{tt}/k = +70$ K.

is to be noted that the crystal fields, in general, tend to quench the magnetic moment from the free ion value $g_J J = 0.71$ (Bleaney 1962). However, it is interesting to note that in some cases an enhancement over the free ion value is also obtained. It is also noted that even in the free Sm^{3+} ion $(A_4 \langle r^4 \rangle = A_6 \langle r^6 \rangle = 0)$ the saturation moment is less than $g_J J$ due to the mixing of the higher J levels into the ground level. An expression for the saturation moment on free Sm^{3+} ion in the presence of mixing of $J = 7/2$ level into $J = 5/2$ level by exchange fields has been obtained by Stewart (1972), who has also shown the importance of the conduction electron polarisation contribution to the total magnetic moment in ferromagnetic samarium compounds.

The results for the type II compounds under the same conditions as above except that $| \mu_B H_{ex}/k | = 25$ K are shown in figure 2 and the findings are similar. Though we have considered here only cubic samarium compounds with [001] as the easy direction of magnetization, the results described above are quite general in nature and basically arise due to the admixture of excited J levels into the ground level by crystal fields and exchange fields. Therefore, essentially similar behaviour as above is expected when the easy direction of magnetization is other than [001] or even when Sm^{3+} ions occupy a site of lower than cubic symmetry.

Another interesting feature which we find from our calculations on both type I and type II compounds is that for some value of crystal field parameters $A_4 \langle r^4 \rangle$ and $A_6 \langle r^6 \rangle$, the calculated moment μ (or μ_{Sm}) is parallel to $\langle S_z \rangle_{av}$ (thin curves in figures 1 and 2) while for some other values of $A_4 \langle r^4 \rangle$ and $A_6 \langle r^6 \rangle$, the moment is antiparallel to $\langle S_z \rangle_{av}$ (thick curves in figures 1 and 2 and dotted lines in both the figures correspond to sudden changes in the magnetic moment values as a function of $A_4 \langle r^4 \rangle$). To appreciate the meaning of this result, we notice that for rare
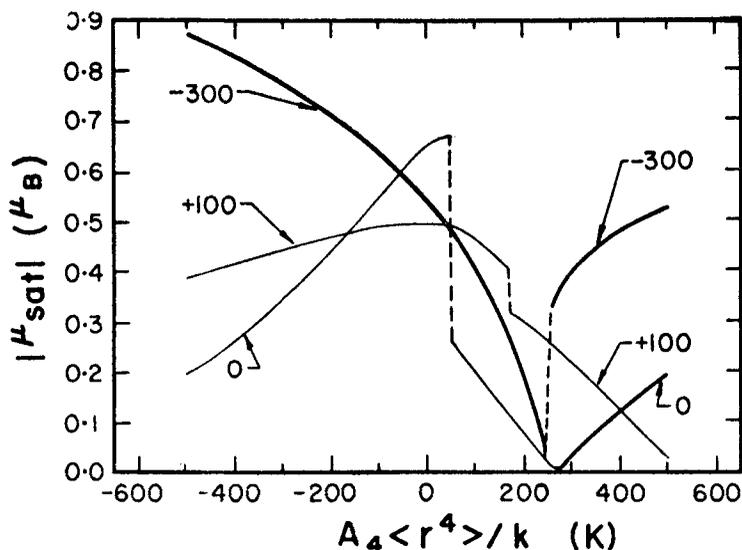
Figure 2. The variation of the saturation magnetic moment of Sm^{3+} in Type II compounds (see text) as a function of $A_4 \langle r^4 \rangle /k$ and $A_6 \langle r^6 \rangle /k$ (in Kelvin). The curves are labelled with the values of $A_6 \langle r^6 \rangle /k$ in Kelvin. Throughout $(\mu_B H_{ex}/k)$ $= +25$ K and $H_{ex} \parallel$ [001].

earth ions belonging to the first half of the rare earth series the total angular momentum J is aligned antiparallel to S ($J = L - S$), while for rare earth ions belonging to the second half (Gd and above) J is aligned parallel to S ($J = L + S$). But for normal rare earth ions the total magnetic moment is defined through J (or through $L_z + 2S_z$) and is aligned antiparallel to J (due to the negative gyromagnetic ratio of electrons). Therefore μ is parallel (antiparallel) to S for rare earth ions belonging to the first (second) half of the rare earth series. Thus it would appear that in the presence of strong crystal fields the Sm^{3+} ion behaves effectively like an $(L + S)$ ion, rather than an $(L - S)$ ion.

In compounds of rare earths (RE) with magnetic elements (ME) the sublattice coupling between the rare earth magnetic moment and magnetic element moment is generally found to be ferromagnetic for rare earth ions belonging to the first half and antiferromagnetic for rare earth ions belonging to the second half (Wallace 1968). This is explained by assuming an antiferromagnetic exchange interaction between the rare earth spin S_{RE} and the magnetic element spin S_{ME}. This interaction aligns S_{RE} antiparallel to S_{ME}, and by the reasoning given earlier (based on whether $J_{RE} = L - S_{RE}$ or $J_{RE} = L + S_{RE}$) we get J_{RE} parallel to S_{ME} for the first half (or ferromagnetic coupling of μ_{RE} and μ_{ME}) and J_{RE} antiparallel to S_{ME} (antiferromagnetic coupling of μ_{RE} and μ_{ME}) in the second half of the rare earth series. However, it is sometimes found that the sublattice coupling between the samarium magnetic moment and the magnetic element moment is antiferromagnetic, *i.e.*, it has the same sign as the coupling between μ_{RE} of the rare earths of the second half and μ_{ME} (table 2), and opposite to that between the magnetic element moment and the rare earth moment of the first half (Wallace 1968). This is exactly the behaviour to be expected in the presence of strong crystal fields. Thus the crystal fields might be responsible for the anomalous behaviour of samarium in compounds

Table 2. Sublattice coupling between rare earth and magnetic element moments in some ferromagnetic compounds (Wallace 1968)

Compound	Sublattice coupling*	Compound	Sublattice coupling*
(Pr, Nd) Co$_2$	F	(Pr, Nd) Co$_5$	F
SmCo$_2$	F	SmCo$_5$	AF
(Gd, Tb, Dy, Ho, Er, Tm) Co$_2$	AF	(Gd, Tb, Dy, Ho Er, Tm) Co$_5$	AF
CeFe$_2$	F	(Pr, Nd)$_2$ Co$_{17}$	F
SmFe$_2$	AF	Sm$_2$Co$_{17}$	AF
(Gd, Tb, Dy, Ho, Er, Tm) Fe$_2$	AF	(Gd, Tb, Ho, Er, Tm)$_2$ Co$_{17}$	AF

*F = Ferromagnetic   AF = Antiferromagnetic

such as $SmFe_2$, Sm_2Co_{17}, $SmCo_5$ and possibly Sm_6Mn_{23} in all of which the sublattice coupling between the samarium magnetic moment and the magnetic element moment is antiferromagnetic (Wallace 1968). The system $SmCo_5$ has gained wide importance as a material for making permanent magnets. However, $PrCo_5$ is somewhat superior in theoretical capability to $SmCo_5$ for such purposes because μ_{Co} and μ_{Pr} are coupled ferromagnetically but not μ_{Sm} and μ_{Co}, presumably because of the crystal fields in $SmCo_5$. Therefore, in order to improve the performance of $SmCo_5$ and other similar samarium compounds one might look into the possibility of substituting partially in place of Sm or Co some other suitable elements which reduce the crystal fields somewhat and thereby swing μ_{Sm} parallel* to μ_{Co}, but which at the same time do not diminish the total magnetic moment of the system. The usefulness of these compounds as permanent magnetic materials depends very much on the crystal field interactions.

From figures 1 and 2 it is obvious that identical values of the magnetic moments can be obtained by different choices of the combinations of $A_4 \langle r^4 \rangle$ and $A_6 \langle r^6 \rangle$. Therefore before attempting quantitative explanation of the magnetic moment in individual ferromagnetic samarium compounds, one has to estimate the crystal field parameters by fitting other available data such as the susceptibility, the Knight shift, the 4f-induced hyperfine field, etc. Moreover, the knowledge of the easy direction of magnetization, the exchange constant (or Curie temperature) or the exchange field, and the conduction electron polarisation contribution to the magnetic moment is also necessary. Attempts to quantitatively explain the magnetic moments in some ferromagnetic samarium compounds are in progress and the results will be reported later.

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* This is implied at 0 K or, in general, at temperatures much below 300 K. However, near 300 K, which is the normal working temperature of these magnets, the reduction in the crystal fields can at most make μ_{Sm} = 0 compared to a finite but oppositely aligned μ_{Sm} in the presence of strong crystal fields.

5. Conclusions

The effects of cubic crystal fields on the saturation magnetic moment of Sm^{3+} ion in ferromagnetic samarium compounds have been investigated. It has been shown that the crystal fields may either quench or enhance the magnetic moment over the free ion value. Further, it has been shown that, in the presence of strong crystal fields, the Sm^{3+} ion behaves effectively like an $(L + S)$ ion rather than an $(L - S)$ ion. This is more readily apparent in ferromagnetic compounds of rare earths (RE) with magnetic elements (ME), where the sublattice coupling between the RE moment μ_{RE} and the ME moment μ_{ME} is found to be ferromagnetic for rare earths having $J = L - S$, and antiferromagnetic for rare earths having $J = L + S$. However, μ_{Sm} seems to couple antiferromagnetically with μ_{ME} in $SmFe_2$, $SmCo_5$, Sm_2Co_{17} and Sm_6Mn_{23}. It is suggested that, excepting possibly in Sm_6Mn_{23}, the crystal fields might be responsible for such a behaviour of Sm in these compounds. Improvement in the performance of permanent magnetic materials such as $SmCo_5$ might be achieved by partial substitutions by other suitable elements which modify the crystal fields and thereby swing μ_{Sm} parallel* to μ_{ME}. This gain, however, should not be offest by the loss in overall magnetization caused by the substituting element.

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