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Crystal-field effects on the $4f$-induced hyperfine field on samarium in ferromagnetic compounds

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It is shown that in ferromagnetic samarium compounds, the crystal fields not only affect the magnitude of the $4f$-induced hyperfine field (H_{4f}) at the samarium nuclear site, but may also make it negative in contrast to the positive H_{4f} in the case of the free Sm^{3+} ion.

In a recent paper we have shown[1] that in paramagnetic samarium compounds the hyperfine field H_{4f}/H ($\langle H_z^{4f}\rangle_{\mathrm{av}}/H$ of Ref. 1) at the samarium nuclear site induced by the paramagnetism of $4f$ electrons may change its sign at one or more temperatures because of the mixing of ionic J levels of the Sm^{3+} ion by crystal fields and exchange fields, while in the case of the free Sm^{3+} ion H_{4f}/H is positive at all temperatures. Negative values of H_{4f}/H for samarium in the paramagnetic state have indeed been observed[2] for the first time using the perturbed-angular-correlation technique. In this paper we extend the calculations of H_{4f} to ferromagnetic samarium compounds and show that crystal fields not only affect the magnitude of H_{4f}, but could also make it negative. The experimentally observed hyperfine field at the Sm nuclear site in some cases may be negative, although so far it has been assumed to be positive in all cases.

Samarium forms ferromagnetic intermetallic compounds with several magnetic as well as nonmagnetic elements. A few typical examples of such compounds are SmAl_2 ($T_C = 120$ K),[3] SmCd (265 K),[4] SmIr_2 (37 K),[5] SmNi_2 (21 K),[6] SmCo_2 (240 K),[7] etc. In general, the hyperfine field on the samarium nucleus in any ferromagnetic compound is a function of several parameters, such as the crystalline electric field, the exchange field, the angle which the exchange field or the easy direction of magnetization makes relative to the local crystal-field axis, etc. Since these parameters vary from one compound to another, each system would have to be discussed individually. However, in order to demonstrate the effects of crystal fields on H_{4f}, we consider the case of a cubic ferromagnetic samarium compound in which Sm^{3+} ions occupy a site of a local cubic symmetry. Further, we assume [001] to be the easy direction of magnetization (although this depends upon the crystal-field parameters). Therefore, the exchange-field points along [001] we take as the quantization or the z axis. In Ref. 1 the cubic-crystal-field Hamiltonian $\mathcal{H}_C$ for $\hat{z}\parallel[001]$ was given in terms of the Cartesian coordinates of the $4f$ electrons. However, in order to calculate the matrix elements of $\mathcal{H}_C$ it is convenient to write it in terms of the tensor operators $C_m^{(n)}$ as

$$\begin{aligned}\mathcal{H}_C = {} & 8A_4\langle r^4\rangle \sum_i \left(C_0^{(4)}(\theta_i,\phi_i) + \sqrt{\tfrac{5}{14}}\,[C_{-4}^{(4)}(\theta_i,\phi_i) + C_{+4}^{(4)}(\theta_i,\phi_i)]\right) \\ & + 16A_6\langle r^6\rangle \sum_i \left(C_0^{(6)}(\theta_i,\phi_i) - \sqrt{\tfrac{7}{2}}\,[C_{-4}^{(6)}(\theta_i,\phi_i) + C_{+4}^{(6)}(\theta_i,\phi_i)]\right),\end{aligned} \qquad (1)$$

where the summation is over all the $4f$ electrons. The matrix elements of the tensor operator $C_m^{(n)}(\theta,\phi) = [4\pi/(2n+1)]^{1/2} Y_n^m(\theta,\phi)$ in the $SLJM$ representation (including those nondiagonal in J) can be easily evaluated.[8]

The Hamiltonian in the presence of spin-orbit interaction, the crystal, the exchange, and the applied fields becomes

$$\mathcal{H} = \lambda \vec{L}\cdot\vec{S} + \mathcal{H}_C + 2\mu_B H_{\mathrm{ex}} S_z + \mu_B H (L_z + 2S_z). \qquad (2)$$

Throughout we use $\lambda/k = 410$ K, which gives an energy separation of 1435 K between the ground ($J=\frac{5}{2}$) level and the first excited ($J=\frac{7}{2}$) level. The Hamiltonian given by Eq. (2) is diagonalized between the M sublevels arising from the lowest three multiplet levels ($J=\frac{5}{2}$, $\frac{7}{2}$, and $\frac{9}{2}$) to obtain the energy eigenvalues E_m and the eigenfunctions $|m\rangle$. The hyperfine field H_{4f} at any temperature is then given by

$$H_{4f}(T) = \sum_m \langle m|H_{\mathrm{op},z}^{4f}|m\rangle e^{-E_m/kT} \Big/ \sum_m e^{-E_m/kT}, \qquad (3)$$

where

$$\vec{H}^{4f}_{\mathrm{op}} = -2\mu_B \sum_i \{r_i^{-3}[\vec{l}_i - \vec{s}_i + 3\vec{r}_i(\vec{r}_i \cdot \vec{s}_i)/r_i^2]\} \quad (4)$$

is the operator for the hyperfine field at the rare-earth nuclear site arising from the orbital and the spin angular momenta of the $4f$ electrons. The matrix elements of the z component of $\vec{H}^{4f}_{\mathrm{op}}$ in the $SLJM$ representation are given by

$$\langle SLJM | H^{4f}_{\mathrm{op},z} | SLJM \rangle = -2\mu_B \langle r^{-3}\rangle \langle J || N || J\rangle M \quad (5a)$$

and

$$\langle SLJM | H^{4f}_{\mathrm{op},z} | SLJ-1M \rangle = -2\mu_B \langle r^{-3}\rangle \langle J || N || J-1\rangle (J^2 - M^2)^{1/2}, \quad (5b)$$

where $\langle r^{-3}\rangle$ is the expectation value of the inverse cube radius of the $4f$-electron orbital and $\langle J || N || J\rangle$ and $\langle J || N || J-1\rangle$ are certain multiplicative factors which for the Hund-rule ground multiplet have been defined in Ref. 1.

We confine our calculations to ferromagnetic samarium compounds with nonmagnetic elements (e.g., $SmAl_2$, SmCd, $SmIr_2$, etc.), so that the exchange interaction responsible for magnetic ordering is between Sm^{3+} spins. In the molecular-field approximation, the exchange field which the Sm^{3+} ions exert on each other can be written as

$$2\mu_B H_{\mathrm{ex}} = -\mathcal{J}_{ff} \langle S_z \rangle_{\mathrm{av}}, \quad (6)$$

where $\mathcal{J}_{ff}$ is the exchange-interaction constant and $\langle S_z\rangle_{\mathrm{av}}$ is the Boltzmann average of the expectation value of the z component of Sm^{3+} spin. Typically, we take $\mathcal{J}_{ff}/k = 70$ K, which yields a Curie temperature of about 120 K, though dependent slightly on the crystal-field parameters. Although H_{ex} is proportional to $\langle S_z\rangle_{\mathrm{av}}$, the latter itself depends implicitly on H_{ex} through the eigenfunctions $|m\rangle$ and the energy eigenvalues E_m obtained after diagonalizing the Hamiltonian of Eq. (2) containing H_{ex}. Thus the exchange field is to be determined self-consistent for a given value of $\mathcal{J}_{ff}$, for each set of crystal-field parameters $A_4\langle r^4\rangle$ and $A_6\langle r^6\rangle$ and for each temperature. To accomplish this we start with an approximate value of H_{ex} and a small value of H, diagonalize the Hamiltonian of Eq. (2) for a given combination of $A_4\langle r^4\rangle$ and $A_6\langle r^6\rangle$, and calculate $\langle S_z\rangle_{\mathrm{av}}$ and thus H_{ex}. This value of H_{ex} is used in the next iteration and the process repeated until self-consistently values of $\langle S_z\rangle_{\mathrm{av}}$ or H_{ex} are obtained. This completely determines the Hamiltonian and various quantities of interest can be calculated. The sign of H_{4f} is determined relative to the external field H applied in the positive z direction.

The hyperfine field at the samarium nuclear site has been calculated at 0 K for a range of crystal-field parameters $A_4\langle r^4\rangle$ and $A_6\langle r^6\rangle$. The experimentally estimated value of Bleaney[9] has been used for $\langle r^{-3}\rangle$. Figure 1 shows the plot of H_{4f} versus $A_4\langle r^4\rangle$ and the curves are labeled with the values of $A_6\langle r^6\rangle/k$ in deg kelvin. For a typical set of crystal-field parameters, namely, $A_4\langle r^4\rangle/k = 200$ K and $A_6\langle r^6\rangle/k = -100$ K, the expectation values of $H^{4f}_{\mathrm{op},z}$ (in MOe) for the lowest six levels (starting from ground level and going successively higher in energy) are, respectively, −2.03, −2.55, −0.8, +1.18, +0.38, and +2.78. However, at 0 K only the ground state contributes. In the case of the free Sm^{3+} ion we get $H_{4f} \cong 3.37$ MOe (throughout we refer to H_{4f} values at 0 K). It is to be noted from Fig. 1 that the crystal fields mostly bring about a reduction in H_{4f} compared to the free-ion value, though in some cases an enhancement in H_{4f} to the extent of 10% over the free-ion value also occurs. The most interesting point to be noted from Fig. 1 is that for some range of values of crystal-field parameters H_{4f} becomes negative. This is in striking contrast to the positive sign expected in the case of the free Sm^{3+} ion. (The dashed lines in Fig. 1 correspond to sudden changes in H_{4f} as a function of $A_4\langle r^4\rangle$ for the given value of $A_6\langle r^6\rangle$.) In most other rare-earth ions, the crystal fields cause only a reduction in H_{4f} from the free-ion value. The other two effects, namely, the enhancement and the sign change in H_{4f}, are peculiar to the Sm^{3+} ion and arise because of the admixture of excited ionic J levels into its ground level by crystal

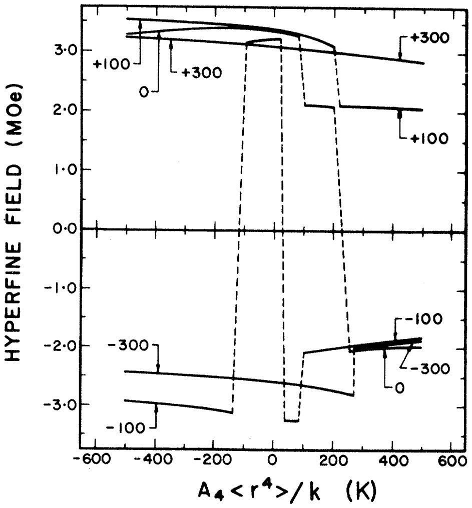

FIG. 1. Plot of the hyperfine field H_{4f} at 0 K vs $A_4\langle r^4\rangle$ for $\mathcal{J}_{ff}/k = 70$ K. Different curves correspond to different values of $A_6\langle r^6\rangle/k$ (in deg kelvin) given along with the curves.

fields. It is worthwhile remarking that the values of crystal-field parameters, for which H_{4f} becomes negative, fall typically in the range of values estimated in some samarium compounds, e.g., $SmAl_2$,[3] $SmSn_3$,[3] Eu(Sm)Al_2,[2] etc., from Knight-shift and hyperfine-field measurements. Thus it should be possible to observe experimentally the kind of effects discussed here in some ferromagnetic samarium compounds. Calculations have also been performed with different values of the exchange interaction constant $\mathcal{J}_{ff}$ and the results are similar to those described above.

Though we have considered a particular case of a cubic samarium compound with $\vec{H}_{ex} \| [001]$, similar behavior is expected when H_{ex} is along some other direction, or even when Sm^{3+} ions occupy sites of other than cubic symmetry. However, the range of crystal-field parameters for which H_{4f} is negative would depend on these details. Thus one cannot assume H_{4f} to be positive at the samarium nuclear site unless an explicit determination of its sign is carried out. It may be remarked that the hyperfine field at the nonmagnetic site is samarium intermetallic compounds, which is proportional to $\langle S_z \rangle_{av}$, is also strongly influenced by crystal fields, both in magnitude and sign. Experimental determination of the sign and magnitude of H_{4f} on the samarium nucleus in a few compounds is in progress. The crystal-field effects on the $4f$ contribution to the electric field gradient at the samarium nuclear site have also been investigated[10] and the results will be reported elsewhere.

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