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MAGNETIC SCATTERING AMPLITUDES OF SAMARIUM*

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ABSTRACT

Approximate ground states for the cubic and hexagonal sites in metallic Sm are calculated. The cubic ground state is adjusted to give rough agreement with observed neutron scattering amplitudes for high angle reflections. Large deviations occur at low scattering angles which are attributed to conduction electron polarization. The ratio of conduction spin polarization to 4f spin polarization is 0.15.

INTRODUCTION

We have recently determined the magnetic structure of metallic Sm through neutron diffraction experiments.^{1,2} In this paper we attempt to deduce characteristics of the ground state of metallic Sm by interpreting the observed magnetic scattering amplitudes.

The crystal structure³ of Sm has a large unit cell of nine layers along the $\vec{c}$ axis. Two-thirds of the sites have point symmetry $3m(C_{3v})$, with a near-neighbor coordination like that of a distorted HCP structure. The rest of the sites have point symmetry $\bar{3}m(D_{3d})$, with near-neighbors arranged as in a distorted FCC structure. The hexagonal sites order antiferromagnetically at 106°K with a structure which results in zero exchange field at the cubic sites, which then order independently at 14°K. The cubic-site structure has a magnetic cell which is four times larger than the chemical cell along both $\vec{a}$ and $\vec{c}$, resulting in magnetic Bragg peaks at very small scattering vectors where conduction electron polarization should be evident.

The combination of large unit cells and weak magnetic intensities resulted in a difficult experimental situation. A large cell produces a high density of Bragg spots in reciprocal space and a high incidence of simultaneous reflections. The effects of simultaneous reflections can be minimized by reducing the size of the sample but we were forced to use a fairly large crystal because the magnetic intensities were very weak. We estimate that all the magnetic amplitudes are subject to an error of about $\pm 15\%$ from simultaneous reflections. In addition there were serious background and resolution problems for many of the peaks. One should be cautious in ascribing significance to all details of the data.

Our general approach is to use standard theoretical approximations to identify the important parameters in the 4f electronic ground state, then vary these selected parameters to give rough agreement with the neutron amplitudes. The theoretical task is to

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calculate the effects of the crystal field and exchange on the free-ion ${}^6\text{H}_{5/2}$ ground state multiplet, taking into account a possible admixture from the ${}^6\text{H}_{7/2}$ multiplet which lies at about 1500°K.

THEORY

The basic model assumes localized 4f electrons in a crystal field of appropriate symmetry with an exchange interaction between different sites via polarization of the conduction electrons. Expanding the crystal field in spherical harmonics and making the molecular field approximation for the exchange term, the effective single-ion Hamiltonian for the 4f electrons becomes

$$H = V_2^0 + V_4^0 + V_4^3 + V_6^0 + V_6^3 + V_6^6 + 2\beta H_e S_z. \quad (1)$$

The magnitude and sign of the individual V_n^m terms depend on the site symmetry and the polar axis is along $\vec{c}$. We have assumed that the exchange field is also along $\vec{c}$, as indicated experimentally. It can be shown that the ground states we obtain are consistent with this assumption. We diagonalize that portion of the energy matrix involving states in the lowest lying multiplet ($J = 5/2$) and then use perturbation theory to estimate the admixture of states from the $J = 7/2$ multiplet. The problem simplifies greatly when only the $J = 5/2$ states are considered because then all matrix elements involving crystal field terms of the sixth order are zero.

In evaluating the crystal field terms we used the point charge model with $+3|e|$ on each lattice site and the lattice sums carried to convergence. We have used the values of $\langle r^n \rangle$ tabulated by Lewis⁴ based on relativistic Dirac-Slater wave functions. We do not expect accurate results from such a calculation but hopefully it should identify the important parameters and give the form of the approximate ground state. The exchange term was evaluated in the usual way by expanding $\langle S_z \rangle$ in powers of H_e , assuming $H_e = -\lambda \langle S_z \rangle$ and determining λ at the Néel point. The low-temperature ground state was then determined by a self-consistent requirement on $\langle S_z \rangle$.

For the cubic sites, considering only the $J = 5/2$ multiplet, the ground state has the form

$$\psi_G = \cos\alpha \left| \frac{5}{2}, \frac{5}{2} \right\rangle - \sin\alpha \left| \frac{5}{2}, -\frac{1}{2} \right\rangle. \quad (2)$$

We estimate $\sin\alpha = -0.306$, giving a 4f moment of $0.634 \mu_B$, while the saturation moment for the free ion is $0.714 \mu_B$. Our calculations show the $J = 7/2$ admixture to be quite small, so we adopt Eq. (2) as our approximate wave function.

For the hexagonal sites the point charge calculation indicates that the trigonal terms in Eq. (1) are very small and can be neglected. Within the $J = 5/2$ manifold, all non-vanishing matrix elements are diagonal and the predicted ground state is $|5/2, 5/2\rangle$. In this case the much larger exchange term produces a small admixture of the higher multiplet and we calculate an approximate ground state of

$$\psi_G = 0.996 \left| \frac{5}{2}, \frac{5}{2} \right\rangle - 0.084 \left| \frac{7}{2}, \frac{5}{2} \right\rangle. \quad (3)$$

This admixture causes an increase in the expectation value of L_z and an equal decrease in S_z , resulting in a net decrease in the total moment. We obtain a moment of $0.564 \mu_B$ for the state given by Eq. (3).

The calculation of elastic neutron scattering amplitudes involves the evaluation of

$$\langle \mu f \rangle \equiv \langle \psi_G | \hat{K} \times [\vec{M}(\vec{K}) \times \hat{K}] | \psi_G \rangle / \sin \beta, \quad (4)$$

where $\vec{K}$ is the scattering vector, $\vec{M}(\vec{K})$ is the Fourier inversion of the magnetic moment density and β is the angle between $\vec{K}$ and $\vec{M}(0)$. A general method for making this calculation has been given by Lovesey and Rimmer.⁵ A great reduction in the complexity of the calculations is achieved by making the dipole approximation, which for our cases becomes

$$\mu f = \langle \psi_G | (\langle j_0 \rangle + \langle j_2 \rangle) L_z + 2 \langle j_0 \rangle S_z | \psi_G \rangle, \quad (5)$$

where

$$\langle j_n \rangle = \int \rho(r) j_n(Kr) dr. \quad (6)$$

Fig. 1. Comparison of the dipole approximation with exact calculation of magnetic form factors for Sm^{3+} , $S_z = 5/2$.

$|5/2, 5/2\rangle$, we should expect a similar spread in the observed values when plotted against $\sin \theta / \lambda$. A complete analysis seems unwarranted

Here $\rho(r)$ is the ground state radial charge density and $j_n(Kr)$ is the spherical Bessel function of order n . In making this approximation we lose all information on the asphericity and noncollinearity of the magnetic moment distribution. A comparison between the dipole approximation and the exact calculation for various values of β for the $|5/2, 5/2\rangle$ state of Sm^{3+} is shown in Fig. 1. The exact calculation is by Davis⁶ using relativistic Hartree-Fock-Slater wave functions. The amplitudes have been normalized to unity by dividing by the net moment. Note that for $\sin \theta / \lambda$ from 0.3 to 0.7 the dipole approximation is very close to the exact calculation for $\beta = 27^\circ$ and is greater than the exact calculation for $\beta = 90^\circ$ by 8 to 15 percent. Since our approximate ground states are both predominantly

because of the approximate nature of our data. We will use the dipole approximation and attempt to adjust the ground-state wave function so that the calculated scattering amplitude gives an upper bound to the data for β varying between 30° and 90° .

COMPARISON OF THEORY AND EXPERIMENT

The magnetic intensities were reduced following standard procedures and placed on an absolute basis by comparison with nuclear intensities. The magnetic amplitudes for the cubic sites, obtained from the observed magnetic intensities, are shown in Fig. 2. The corresponding data for the hexagonal sites are not really worthy of analysis. All that can be said is that the level of scattering is about the same as in the cubic case, which is consistent with our approximate wave functions.

The expected scatter in the data of Fig. 2 is evident and there is a dramatic decrease in the amplitudes for small values of $\sin\theta/\lambda$. We expect any evidence of conduction electron polarization to show up at small scattering angles, so we will temporarily neglect the data inside of $\sin\theta/\lambda = 0.2$ in comparing with the calculation for the 4f electrons. For wave functions of the form given by Eq. (2) the dipole approximation simplifies to

$$\langle \mu f \rangle = g \langle \psi_G | J_z | \psi_G \rangle (\langle j_0 \rangle + 6 \langle j_2 \rangle), \quad (7)$$

Fig. 2. Magnetic scattering amplitudes for the cubic sites in metallic Sm compared with various calculations (see text).

with $g = 2/7$. Changing the admixture of the state with $J_z = -1/2$ does not change the shape of the calculated scattering function but does change the scale factor $g \langle J_z \rangle$. Curve A is drawn for $\sin\alpha = 0$ in Eq. (2) and curve B for $\sin\alpha = -0.306$, corresponding to our calculated ground state. We believe that curve C, drawn for $g \langle J_z \rangle = 0.571$, or $\sin\alpha = -0.409$, represents a better fit to the data based on the expected behavior of the dipole approximation as discussed in the previous section. We can get a larger admixture of the state with $J_z = -1/2$ by strengthening the V_4^3 crystal field term, or weakening the terms V_2^0 or V_4^0 . The changes in

crystal field parameters required to go from curve B to C are not excessive in view of the known shortcomings in a metallic point charge calculation. If curve C represents our best estimate of the 4f electronic contribution to the magnetic scattering, then the large deviations at small $\sin\theta/\lambda$, where the dipole approximation should be very good, must be ascribed to polarization of the conduction

electrons. We make the crude assumption that the total scattering amplitude is given by a 4f contribution corresponding to curve C, plus a conduction contribution made up of a linear combination of 5d and 6s terms,

$$\mu_f = (\mu_f)_{4f} + \mu_c [\alpha \langle j_o \rangle_{5d} + (1 - \alpha) \langle j_o \rangle_{6s}]. \quad (8)$$

The dashed curve in Fig. 2 is a least-squares fit of Eq. (8) to the low-angle observations, with μ_c and α as adjustable parameters. The $\langle j_o \rangle$ functions were calculated by Davis⁶ for a $(4f)^5(5d)^1(6s)^2$ configuration using relativistic Hartree-Fock-Slater wave functions for the free atom. The fitting procedure gave $\mu_c = -0.42 \pm 0.05 \mu_B$ and $\alpha = 0.77 \pm 0.24$. A fit of about equal quality was obtained using free-atom form factors but with Wigner-Seitz normalization. The use of free-atom form factors to represent the conduction electrons is certainly questionable, but it seems to give a surprisingly good fit to the data and is probably a reasonable method of extrapolating the data to $\sin\theta/\lambda = 0$ to obtain the total moment. The rough ratio of 3/1 for 5d to 6s spin may indicate a high density of 5d states at the Fermi surface. The apparent free-atom behavior of the conduction electron polarization in Sm is quite different from that deduced from neutron studies on Gd.⁷

We believe that the total moment per atom for the cubic sites is $(0.15 \pm 0.05) \mu_B$ and is made up of the following parts: a 4f orbital moment of $3.42 \mu_B$, a 4f spin moment of $-2.85 \mu_B$ and a conduction spin moment of $-0.42 \mu_B$. This gives a ratio of conduction spin to 4f spin of 0.15, as compared to a similar ratio in Gd of 0.08. If this conduction polarization persists in the paramagnetic region, it will have a major effect on the paramagnetic susceptibility, as discussed by Stewart.⁸ Unfortunately, his analysis of the Sm susceptibility data is wrong because he assumed all sites to be paramagnetic above 15°K.

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REFERENCES

1. W. C. Koehler, R. M. Moon, J. W. Cable and H. R. Child, AIP Conference Proc. No. 5, 1434 (1972).
2. W. C. Koehler and R. M. Moon (to be published).
3. A. H. Daane, R. E. Rundle, H. G. Smith and F. H. Spedding, Acta Cryst. 7, 532 (1954).
4. W. Burton Lewis, Proceedings of the Colloque Ampere, "Magnetic Resonances and Related Phenomena," Bucharest, 1970.
5. S. W. Lovesey and D. E. Rimmer, Rept. Prog. Phys. 32, 333 (1969).
6. H. L. Davis (private communication).
7. R. M. Moon, W. C. Koehler, J. W. Cable and H. R. Child, Phys. Rev. B 5, 997 (1972).
8. A. M. Stewart, Phys. Rev. B 6, 1985 (1972).