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MAGNETIC FORM FACTOR OF THULIUM METAL*

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The magnetic form factor of thulium at 4.2°K has been measured with polarized neutrons. With the exception of the two innermost reflections, the form factor is in excellent agreement with the theoretical $4f^{12}$ form factor. At low angles an additional contribution to the form factor is present. We have interpreted this as $5d$-like conduction-electron polarization, although the magnitude is unexpectedly large.

The crystal structure of thulium is hcp with $a = 3.537$ Å and $c = 5.504$ Å. At 4.2°K the magnetic structure[1,2] consists of ferromagnetic layers, in which the spins are aligned parallel (positive layers) or antiparallel (negative layers) to the c axis, stacked such that four positive layers are followed by three negative layers. The ordered moment per atom is $7\mu_B$, and the net ferromagnetic moment is $1\mu_B$ per atom. In the present experiment the magnetization density of this ferromagnetic component has been measured accurately with polarized neutrons. Recent magnetization measurements[3] on a single crystal of thulium give the saturated moment per atom as $(1.001 \pm 0.005)\mu_B$ in low fields applied parallel to the c axis. For fields greater than 28 kOe, applied in the same direction, thulium becomes ferromagnetic, with a saturation moment of $(7.14 \pm 0.02)\mu_B$ per atom. The $0.14\mu_B$ in excess of $7\mu_B$ has been attributed to conduction-electron polarization.[4] In the paramagnetic state (above 56°K) the effective moment is $7.61\mu_B$ per atom. The moments determined by neutron diffraction and magnetization experiments are consistent with the $4f^{12}$ configuration ($J = 6$, $L = 5$, $S = 1$, $g = 7/6$).

The form factor of terbium[5] has been measured with both polarized and unpolarized neutrons. Reference 5 contains a detailed discussion of the form-factor derivation, and of the nature of the spin distribution in the rare earths. In comparison with terbium the present experiment with thulium has two immediate advantages. Firstly, the ferromagnetic scattering amplitude in the forward direction (p_0) is less than the nuclear scattering amplitude (b), which is not the case in terbium with a ferromagnetic moment of $9\mu_B$ per atom; this is important in considering the sensitivity of the polarized-beam method at low scattering angles. Secondly, the asphericity in the spin distribution for thulium is theoretically greater than for terbium, and may be readily observed.

The cross section for polarized neutron scattering has been given by Blume,[6] and, considering the coherent elastic scattering only,

$$(d\sigma/d\Omega) \propto b^2 + 2\vec{P}\cdot\vec{\eta}_\perp b p_{\text{ferro}} + \eta_\perp{}^2 p_{\text{ferro}}{}^2 + \text{magnetic terms}, \quad (1)$$

where $\vec{P}$ is a vector in the direction of the neu-

tron polarization, in this case parallel or antiparallel to the c axis of the crystal. In the derivation of Eq. (1) the magnetic structure is assumed to be uniaxial; b is the nuclear coherent scattering length, $\vec{\eta}_\perp$ is the projection of a unit scattering vector on the basal plane, p_{ferro} is the ferromagnetic scattering length defined as

$$p_{\text{ferro}} = \left(\frac{\gamma e^2}{2mc^2}\right) \frac{1}{N} \sum_{l=1}^{N} f_l^{JM}(\vec{K}) g_l^J M_l. \qquad (2)$$

The sum is over all atoms in the magnetic unit cell ($N = 14$), $f_l(\vec{K})$ is the magnetic form factor with $\vec{K}$ the momentum transfer ($K = \sin\theta/\lambda$), and $g_l M_l$ (M, the magnetic quantum number is quantized along the c axis) the magnetic moment in μ_B of the lth atom. Assuming all atoms are in the $^3H_6$ state with $M_l = \pm 6$, Eq. (2) reduces to

$$p_{\text{ferro}} = (\gamma e^2/2mc^2)\, \mu f(\vec{K}),$$

where μ is the ferromagnetic moment per atom in μ_B. In a polarized-beam experiment the ratio of the Bragg-peak intensities for the two neutron polarization states ($P = \pm 1$) is measured. This ratio, the flipping ratio, allows an accurate determination of p_{ferro}/b to be made. The coherent elastic cross section for the 4^+, 3^- structure also contains purely magnetic terms, resulting in additional satellite reflections that are polarization independent.

The magnetic form factor for the free Tm^{3+} ion in the $J = 6$, $M = 6$ state may be written

$$f(\vec{K}) = \frac{(4\pi)^{1/2}}{7}\Big[(2\langle j_0\rangle + 5\langle g_0\rangle) Y_0^0(\hat{K}) + 5^{1/2}(\tfrac{1}{3}\langle j_2\rangle + \langle g_2\rangle) Y_2^0(\hat{K}) - \frac{1}{11}(4\langle j_4\rangle + 5\langle g_4\rangle) Y_4^0(\hat{K}) - \frac{13^{1/2}}{3\times 11\times 13}(25\langle j_6\rangle + 45\langle g_6\rangle) Y_6^0(\hat{K})\Big],$$

where $Y_l^m(\theta, \Phi)$ are spherical harmonics with $\theta = 0$ corresponding to the direction of the moment. The spin $\langle j_n\rangle$ and orbital $\langle g_n\rangle$ terms used in the calculation are those given by Blume, Freeman, and Watson.[7] $f(\vec{K})$ is normalized such that $f(0) = 1$. The apparent spin distribution is very aspherical, but has cylindrical symmetry about the moment direction and cannot be observed in the conventional polarized-beam method in which the scattering vector remains in the plane perpendicular to the moment direction.

The experiments were performed at the Ames Laboratory Research Reactor with a two-axis polarized-beam diffractometer. A feature of this instrument is that the detector may be elevated to a limited extent out of the plane perpendicular to the field direction (normal-beam method). Two thulium single crystals with dimensions $0.9\times 1.1\times 5$ mm and $1.2\times 1.0\times 11$ mm, with the long axis parallel to the c axis in each case, have been used, and the measurements were made at two incident neutron wavelengths (1.01 and 0.85 Å). The neutron-polarization and spin-flipping efficiency were >98% for both wavelengths. The corrections arising from incomplete polarization were small, and the corresponding uncertainties introduced in the observed p_{ferro}/b values were in all cases much less than the statistical uncertainties. Two samples and two neutron wavelengths were used to test for secondary extinction and multiple-reflection effects. For the smaller crystal the measured polarization ratios were identical for both wavelengths. In the larger crystal the values from the strong (11.0) and (10.1) reflections were clearly influenced by extinction, and were therefore rejected, but other values were in excellent agreement with those from the smaller crystal. Since the purely magnetic satellite reflections occur in layers corresponding to indices ($hk.1 \pm \tau$), where $\tau = 1/7$, considerable care was necessary in order to avoid contamination from these reflections. The crystals were maintained at 4.2°K in an applied field of 10 kOe. The flipping ratio of a strong low-angle reflection was observed as a function of applied field, and from this we conclude that the crystals are saturated in fields of less than 3 kOe, in agreement with magnetization measurements. A further source of systematic error arises if the thulium nucleus, which is a single isotope Tm^{169} with spin $\frac{1}{2}$, is polarized.[8] Since this effect has a $1/T$ dependence we have measured the flipping ratio of the (11.0) reflection at 1.8°K. No change from the value at 4.2°K was observed.

The experimental values for $\mu f(\vec{K})$ are given in Table I. Each value in the table is the average of a number of equivalent reflections and the quoted error is the standard deviation of the average. In all cases the values from equivalent reflections were in good agreement. The $\mu f(\vec{K})$ values were derived from the measured p_{ferro}/b values using $b = 0.69\times 10^{-12}$ cm, as given by

Table I. Theoretical and observed magnetic scattering amplitudes for thulium ($b_{coh} = 0.69 \times 10^{-12}$ cm).

hkl	$\sin\theta/\lambda$	$f_{calc}{}^{4f}$	$(\mu f)_{obs}$	$(\mu f)_{calc}{}^{4f}$ $\mu = 0.885\mu_B$
10.0	0.163	0.913	0.860 ±10	0.808
10.1	0.187	0.900	0.829 ±10	0.796
10.2	0.244	0.865	0.771 ±8	0.765
11.0	0.283	0.770	0.685 ±6	0.681
10.3	0.318	0.811	0.740 ±40	0.717
20.0	0.327	0.711	0.635 ±8	0.630
20.2	0.374	0.685	0.596 ±8	0.606
21.0	0.432	0.571	0.505 ±10	0.505
30.0	0.490	0.499	0.444 ±6	0.441
22.0	0.566	0.412	0.364 ±8	0.365
31.0	0.589	0.388	0.353 ±10	0.343
40.0	0.653	0.324	0.287 ±13	0.287
32.0	0.712	0.274	0.225 ±8	0.242
41.0	0.748	0.245	0.220 ±10	0.217
33.0	0.848	0.179	0.151 ±8	0.158

Koehler et al.[1] The error on this value is reported as $\pm 0.02 \times 10^{-12}$ cm, i.e., 3%. This uncertainty, which is not included in the errors given in Table I, introduces a constant scale factor to all the measured $\mu f(\vec{K})$ values.

In the analysis, we have assumed that the only contribution to the form factor at high angles is from the highly localized $4f$ moment. Thus, in Table I, by using $\mu = 0.885\mu_B$ the $(\mu f)_{calc}{}^{4f}$ may be brought into excellent agreement with all the experimental observations, except for the two innermost reflections. Figure 1, which also uses $\mu = 0.885\mu_B$, illustrates this agreement. The off-basal-plane reflections ($l \neq 0$) are included in the insert of Fig. 1, and confirm the asphericity in the magnetization density. From a suitably weighted least-squares analysis the error on $\mu = 0.885\mu_B$ in Table I is $\pm 0.005\mu_B$. However, if the error on b is included, the magnitude of the localized $4f$ ferromagnetic moment is $0.885 \pm 0.025\mu_B$ per atom.

So far the two innermost reflections have not been included in the analysis. By using the $4f$ moment contribution deduced from the higher angle reflections, $(\mu f)_{obs} - (\mu f)_{calc}{}^{4f}$ has been plotted on an expanded scale versus $\sin\theta/\lambda$ in Fig. 2. An additional contribution is clearly present for the two innermost reflections. The solid and dashed lines in Fig. 2 are the spherical part of the form factors for the densities of $5d$ and $6s$ electrons, respectively. For these calculations the free-atom wave functions given by Herman and Skillman[9] have been used. The $5d$

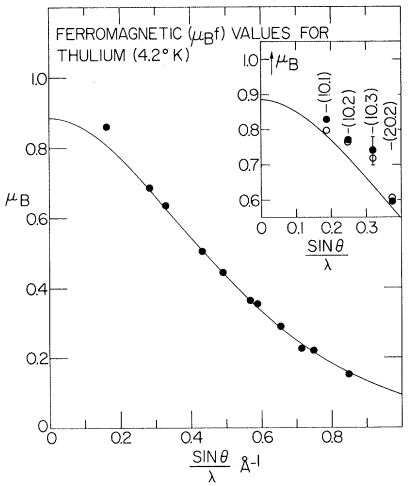

FIG. 1. Observed (closed circles) and theoretical $4f$ free-ion form factor for the ($hk.0$) reflections (i.e., scattering vector perpendicular to the moment) in thulium metal. The theoretical form factor (smooth curve) has been scaled by 0.885, this value being obtained from a least-squares fit with all experimental points except the two innermost reflections. The insert illustrates the same smooth curve together with the theoretical (open circles) and observed (filled circles) values of the form factor for certain reflections out of the basal plane.

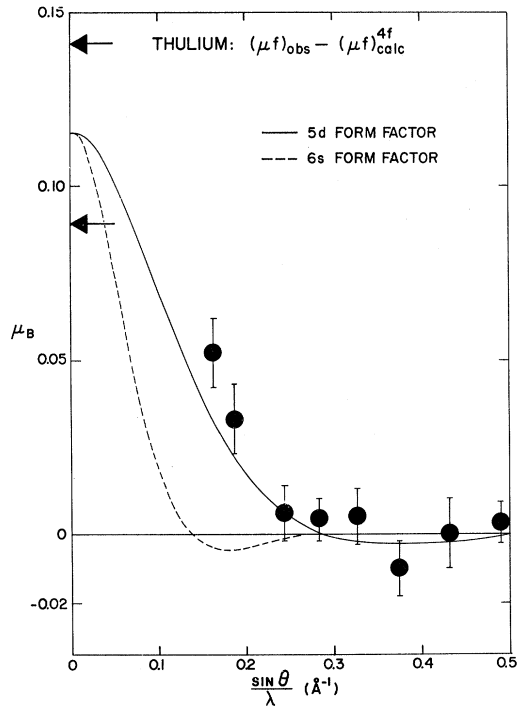

FIG. 2. A plot of $(\mu f)_{obs} - (\mu f)_{calc}{}^{4f}$ vs $\sin\theta/\lambda$ for the innermost reflections. The smooth curves are form factors for the $5d$ and $6s$ states using free-atom wave functions. The arrows on the ordinate axis indicate the uncertainty introduced in the normalization at $\sin\theta/\lambda = 0$ by the error of ±0.02 in b_{coh} for thulium.

and 6s form factors have been normalized to $0.116\mu_B$ in the forward direction. The value of $0.116\mu_B$ is obtained by subtracting the localized $4f$ moment ($0.885\mu_B$) from the magnetization value of $1.001\mu_B$ per atom. By subtracting $(\mu f)_{\text{calc}}^{4f}$ from $(\mu f)_{\text{obs}}$ we have assumed that the magnetization density consists of two parts, a localized $4f$ contribution plus a contribution from conduction-electron polarization. The conduction electrons in the rare-earth metals are generally assumed to be polarized via exchange coupling with the $4f$ moment. Augmented plane wave calculations[10] show that the conduction electrons for heavy rare-earth metals are mostly 5d like, and our observations would seem to confirm this behavior.

The magnitude of the 5d effect is, however, very large. In the ferromagnetic state the conduction-electron polarization is $0.14/7 = 2\%$ of the free-ion moment. If this polarization follows the four-plus, three-minus configuration of the $4f$ moments, its magnitude would be 2% of $1\mu_B$. The effect reported here is ~13%.

The reduction of 11% from the expected value of $1\mu_B$ in the localized ferromagnetic $4f$ moment may possibly be explained by a small deviation from the ideal four-plus, three-minus structure. Such a change can readily lead to the necessary reduction in the ferromagnetic component, while introducing only very small variations in the intensities of the satellite reflections. One may also argue that the value of the nuclear coherent scattering length used to derive $\mu f(\vec{K})$ is too low. However, if the form factor at low angles represents a 5d-type distribution, as suggested in Fig. 2, then the experimental value of $\mu f(\vec{K})$ extrapolates to $1\mu_B$ at $K = 0$, in agreement with magnetization measurements.

The effects observed here may be a property of the four-plus, three-minus structure of thulium. On the other hand, if the 11% reduction of the localized $4f$ moment is present also in the ferromagnetic state, then a reinterpretation of the data is required. We may, indeed, have to consider whether the $4f$ wave functions are themselves modified, especially in the outer regions of the unit cell, by the exchange coupling. In this case, the division of the form factor into contributions from a localized $4f$ moment and a conduction-electron moment would be incorrect.

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