Analysis of Mössbauer Hyperfine Structure in Thulium Metal below the Néel Temperature

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Mössbauer-effect measurements of the hyperfine structure of Tm^{169} below the Néel temperature are presented and analyzed. The interpretation is based on the neutron diffraction analysis of the magnetic structure, and assumes fast relaxation among the exchange-split levels of the lowest J multiplet. The assumption of slightly incommensurate magnetic and crystal unit cells is essential to the successful interpretation of the data, since it produces a continuous distribution of hyperfine fields, as is observed.

INTRODUCTION

IN a previous study[1] of the Mössbauer spectrum[2] of magnetically ordered thulium metal, complex hyperfine (hf) spectra were observed; these results were not understandable in terms of the known magnetic structure of this material as determined by neutron diffraction studies.[3] This paper presents a remeasurement of some of these experimental data, and a successful analysis of the observed spectra in terms of a simple model based on the neutron diffraction solution of the magnetic structure. Preliminary results have already been reported.[4]

Mössbauer-effect experiments on hfs are intermediate in both difficulty and power between neutron diffraction and magnetization measurements of magnetic ordering in solids. The observation of magnetic hfs (nuclear Zeeman effect) in Mössbauer experiments usually allows one to determine the magnetic field at the nucleus; this information can be related to the electronic wave functions. In particular, the technique can detect the existence of a number of magnetically inequivalent sites (through the observation of their different hf fields), but not, unless special techniques are used, the orientation of the fields or ion magnetic moments.

EXPERIMENTAL TECHNIQUE

Standard transmission geometry Mössbauer spectroscopy techniques were used. The source consisted of a thin layer of evaporated erbium metal containing Er^{169}, and was at room temperature. The absorber was a 10 mg/cm^2 layer of Tm metal evaporated in very high vacuum in an ion-pumped system; careful comparison between two absorbers made from different batches of vacuum-distilled Tm metal failed to reveal any differences in the observed spectra. The absorber temperature was measured and controlled for most of the measurements using a Cu–Au (2.1% Co) differential thermocouple with a liquid-H_2 reference. The short- and long-term temperature stability was better than 0.1°K. An argon-filled proportional counter was used to detect the γ rays, which were counted in a multichannel analyzer in the time mode. The velocity drive has been previously described.[5]

THEORY

Elliott has presented[6] a well-developed framework for the discussion of magnetic effects in rare-earth (RE) metals. The fundamental physical assumptions in this theory are (1) L–S coupling for the RE $4f$ electrons, (2) the Ruderman-Kittel interaction as the primary mechanism of cooperative effects, and (3) the crystal electric field (CEF) coupling with the $4f$ wave functions. The combination of (2) and (3) can explain some of the complex ordering effects found in the RE metals.

Unfortunately, in thulium metal ($4f$ ground-state $^3H_6$), the magnetic exchange, crystal field, and thermal population of excited states of the ground $4f$ manifold are all of approximately the same importance in the temperature range considered here. Additionally, the size of the effective exchange interaction is rapidly varying in space and with temperature, leading to an extremely complex situation. Thus an analysis of the problem from first principles is prohibitively difficult. Accordingly, we have chosen to use the existing experimental data on Tm magnetic structure to set up a simple model for the system, rather than working forward from first principles. This model gives exactly the most important (magnetic) part of the hf interaction and, well below the Néel temperature, is a fair approximation to the (much smaller) electric quadrupole term. As will be seen, the agreement between the calculations, which

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[4] R. L. Cohen, Phys. Letters **24A**, 674 (1967); and in *Proceedings of the International Conference on Hyperfine Interactions Detected by Nuclear Radiation*, edited by E. Matthias (North-Holland Publishing Co., Amsterdam, 1968).
[5] R. L. Cohen, Rev. Sci. Instr. **37**, 957 (1966).
[6] R. J. Elliott, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1965), Vol. IIA, p. 385.

involve *no* adjustable parameters, and the experimental results, is very good.

From a neutron diffraction study of Tm metal some years ago, Koehler *et al.*[8] obtained a very detailed picture of the magnetic ordering. We summarize their results here: The thulium ion moments, produced by the $4f$ electrons, lie along the c axis of the hcp crystal. At a temperature T, the magnetic moment for an ion at z can be written as a Fourier series

$$\mu(z, T)=\sum_n a_n(T)\cos[(2n\pi z/7c)+\theta_n], \qquad (1)$$

where $a_n(T)$ and θ_n are Fourier coefficients and c is the interplanar spacing. The data were good enough to determine the coefficients from $n=0$ to $n=3$. Above 56°K, all a's are 0, and there is no magnetic order. Between 40 and 56°K, only a_1 is nonzero, leading to a sinusoidal distribution of moments repeating every seven lattice layers. Below about 40°K, the other coefficients appear, leading to a net moment and a "squaring up" of the moment distribution (through the introduction of the harmonic components), which is complete below about 25°K, where every ion has approximately the theoretical maximum of $\pm 7\ \mu_B$. (This value is confirmed by the Mössbauer hfs results.) An approximate picture of the variation of the moments with temperature is shown in Fig. 1.

At all temperatures, the values of the coefficients providing the best fit to the diffraction data were such as to make Fourier series symmetric about $z=0$ (the θ_n coefficients are temperature-independent and all either 0 or π); this results in a duplication of some values of magnetic moment so that in the seven-atom magnetic unit cell there are four inequivalent sites with populations 1, 2, 2, and 2. These unequal magnetizations should produce four distinct hf spectra, with relative intensities proportional to their populations.

The hfs observed in Tm^{169} comes almost entirely from two sources: the internal magnetic field ($\mathbf{H}_{\rm int}$) (at the nucleus) produced by the spin and orbital angular momentum of the 12 $4f$ electrons of the Tm^{3+} ion, and the electric field gradient (EFG) resulting from the asymmetric charge distribution of the $4f$ electrons. The EFG tensor produced by the $4f$ electrons is in this case axially symmetric and has its major axis along $\mathbf{H}_{\rm int}$, so that V_{zz} and $\mathbf{H}_{\rm int}$ define completely the hf fields. The internal field and EFG interact respectively with the nuclear magnetic dipole and electric quadrupole moments to produce the observed hfs. (For a fuller discussion of these factors, see Refs. 7 and 8.) We proceed at this point under the assumption that the relaxation processes creating transitions between the $2J+1=13$ $4f$ wave functions in the ground-state J manifold are sufficiently fast to produce a well-defined V_{zz} and $\mathbf{H}_{\rm int}$. This is further discussed below.

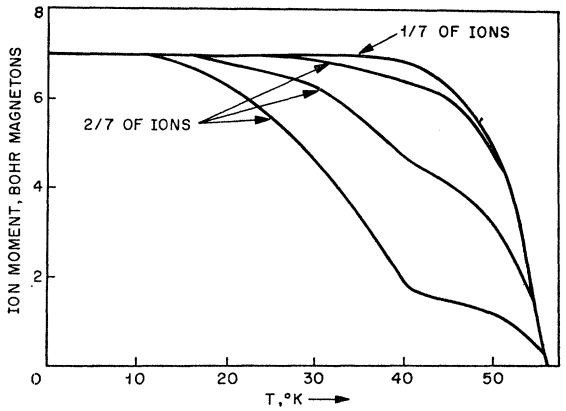

FIG. 1. Approximate thulium sublattice magnetization obtained by neutron diffraction measurements.

The internal magnetic field is composed of the following components[9]: the direct contribution of about 7 MOe due to the $4f$ electrons, core polarization due to the $4f$ electrons (about -100 kOe), conduction-electron polarization (CEP) due to the ion's own $4f$ electrons (about -40 kOe), and CEP due to the surrounding ions (about $+50$ kOe).[10] Under the assumption of L–S coupling, all terms except the last are proportional to $4f$ electron moment, so to an excellent approximation the internal field is proportional to $4f$ moment. Thus from the measured values of ion magnetization, we can calculate $H_{\rm int}$.

Determination of V_{zz}, however, requires more detailed knowledge of the $4f$ wave functions. Lacking a complete solution of these eigenvalues and eigenvectors, we proceed in the following way. The most important perturbation on the lowest ($J=6$) electronic state of the Tm ion is the conduction-electron exchange interaction with the $4f$ shell. The ordered moment at 0°K,[3] the internal field and quadrupole interaction measurement at saturation,[11] and a direct measurement of the crystal-field effects,[12] all show that at low temperatures the influence of the exchange interaction strongly dominates the crystal field from the surrounding ions. If we ignore the crystal-field effects, the $J=6$ level is split into 13 equally spaced levels characterized by $J_z=-6$, -5, $\cdots$, $+6$. This approximation breaks down badly near the Néel temperature, where the exchange splitting

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[8] R. L. Cohen, Phys. Rev. **134**, A94 (1964).
[9] S. Hüfner and J. H. Wernick, Phys. Rev. (to be published).
[10] The last 3 terms are relatively small and were approximated by scaling from the $S=\frac{7}{2}$ case discussed in Ref. 9 to the $S=1$ (Tm) case.
[11] The difference, discussed in Ref. 8, between the internal field in Tm metal and in Fe_2Tm, has been shown to be due to the existence of an extremely strong contribution to the internal field from the unusually large conduction-electron polarization in the Fe_2R compounds [R. E. Gegenwarth, J. I. Budnick, S. Skalski, and J. H. Wernick, Phys. Rev. Letters **18**, 9 (1967)].
[12] D. L. Uhrich, D. J. Genin, and R. G. Barnes, Phys. Rev. **166**, 261 (1968).

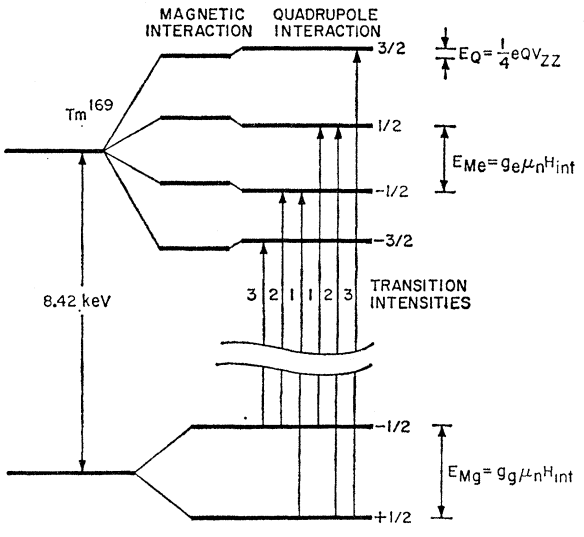

FIG. 2. Hyperfine splitting of nuclear energy levels of Tm^{169}. Six lines are expected, with intensities as shown.

approaches zero, but should be adequate where the ion magnetization is large. Each of these wave functions produces, at the nucleus, a magnetic field and electric field gradient

$$H_{\text{int}} \propto \langle J_z \rangle,$$

$$V_{zz} \propto \langle 3J_z^2 - \mathbf{J}^2 \rangle$$

(where the brackets signify the matrix elements of the operators on the angular part of the $4f$ wave functions). The relative populations of the various states will be determined by the Boltzmann factor $\exp(-m\Delta/kT)$, where $m=-6, \cdots +6$ is the value of J_z used to characterize the state, and Δ is the energy difference (for a particular temperature and ion) between the successive J_z levels. If we assume that the electronic spin-lattice relaxation is fast among the various levels (e.g., faster than about 10^{-10} sec), we get, for any particular ion, a time averaged moment, internal field, and EFG as follows:

$$\begin{aligned}\bar{\mu} &= g_J \langle J_z \rangle_{\text{av}} \mu_B \\ &= \frac{g_J \mu_B \sum_{-6}^{6} m \exp(-m\Delta/kT)}{\sum_{-6}^{6} \exp(-m\Delta/kT)} \\ &= g_J \mu_B F_1(\Delta, T) \qquad (2)\end{aligned}$$

(g_J the Landé g factor, 7/6 for the $^3H_6$ configuration),

$$\bar{H}_{\text{int}} = K_1 \bar{\mu}/g_J = K_1 F_1(\Delta, T), \qquad (3)$$

$$\begin{aligned}\bar{V}_{zz} &= K_2 \frac{\sum_{-6}^{6}(3m^2-42) \exp(-m\Delta/kT)}{\sum_{-6}^{6} \exp(-m\Delta/kT)} \\ &= K_2 F_2(\Delta, T), \qquad (4)\end{aligned}$$

leading to magnetic and electric parts to the hf energy levels of $g\mu_n K_1 F_1(\Delta, T)$ (g is the ground- or excited-state nuclear g factor) and $eQK_2F_2/4$ (Q the spectroscopic nuclear quadrupole moment), respectively (see Fig. 2). (K_1 and K_2 are constants involving radial integrals over the $4f$ wave functions, matrix elements, and shielding factors. The constants $K_1 g$ and $K_2 Q$ can be empirically determined using the values for the hyperfine parameters measured in the metal at low temperature or in Fe_2Tm. They are not treated as adjustable parameters in this paper.)

These equations are particularly useful in this analysis since, using the neutron scattering measurement of the ion moments, we can directly find, using Eq. (2), the value of Δ for each ion and temperature, and then straightforwardly calculate the hf energy perturbations. It should be emphasized that the magnetic part of the hf interaction is exactly determined, regardless of the model used for the $4f$ electron wave functions, but the quadrupole part is approximated, and the approximation should not be good for small ion moments.

EXPERIMENTAL RESULTS

Some of experimental results are shown in Fig. 3(a). Spectra taken at intermediate temperatures showed no anomalies. Our results are similar in over-all appearance to those of Ref. 1, but we do not find the satellite lines reported earlier at 29°K (our data not shown) and there is some difference in the temperature scale. The data at 5°K are similar to those already published,[1] and have similar values of linewidth (2–3 cm/sec) and over-all splitting (107 cm/sec). The ratio of excited- and ground-state nuclear magnetic moments, -2.22 ± 0.07, is also consistent with previous values of -2.17 ± 0.1 [8] and -2.33 ± 0.04.[1]

Using the model discussed previously, in which the magnetization repeats every seven lattice layers, giving four inequivalent magnetizations, we have generated, by summing four spectra, each composed of 6 Lorentzian lines with positions obtained from Eqs. (2)–(4) and appropriate amplitude, the spectrum to be expected from the neutron data at 40°K. This calculation is compared with experimental data at the same temperature (Fig. 4), and the agreement is seen to be poor. The problem is not simply one of detail; the predicted spectrum does indeed look like several well-resolved spectra, while the experimental result looks like one 6-line spectrum with the lines smeared to varying degrees. This discrepancy could not result from the approximate wave functions being used for the $4f$ electrons; an exact calculation would shift the positions of the lines slightly but would not change their sharpness. This lack of agreement between calculated spectra and the observations is very disturbing, since the calculations are so straightforward and inexorably linked to the neutron data. Fortunately, a trivial modification of the assumptions,

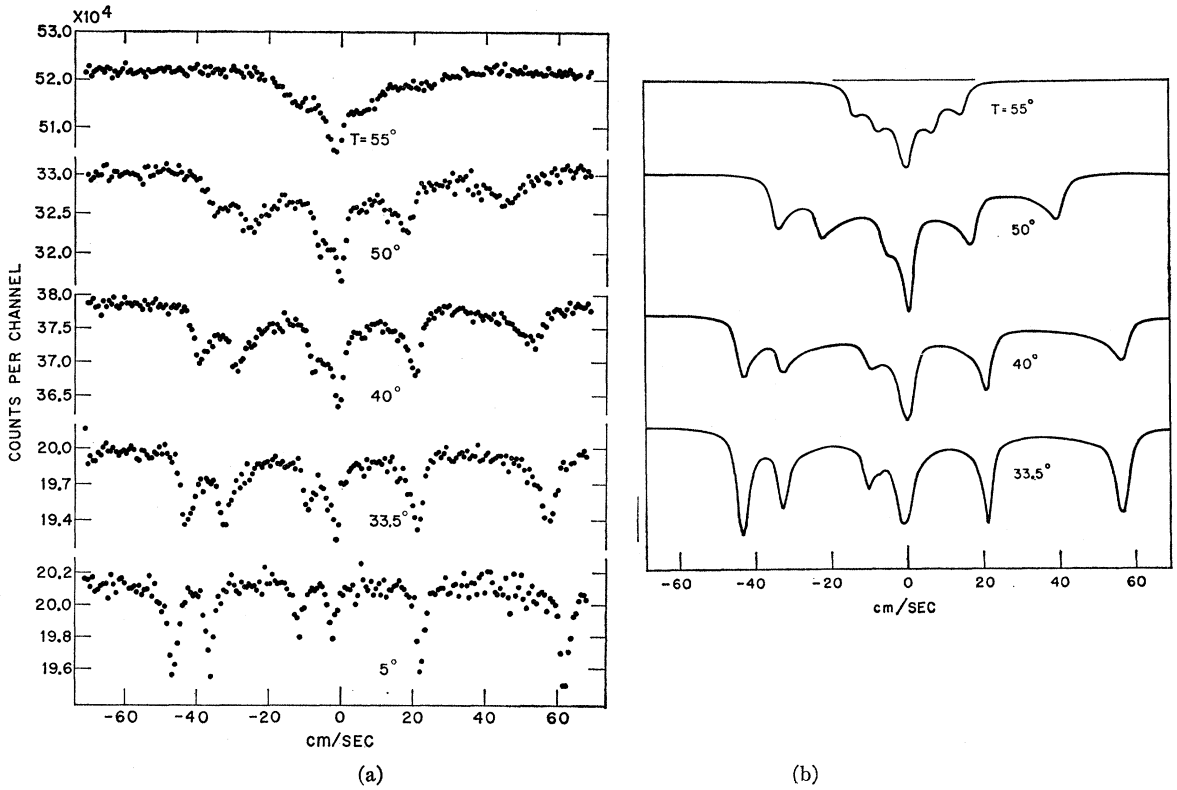

FIG. 3. (a) Hyperfine spectra of Tm^{169} metal at various temperatures. (b) Family of spectra at various temperatures calculated using model described in text with an essentially infinite number of magnetically inequivalent sites.

consistent with the results of the neutron diffraction measurements, provides excellent agreement between the experimental and theoretical results, as follows:

If we make the minor change of assuming that the magnetic structure repeats not every 7 layers [as in Eq. (1)] but $7+\epsilon$ ($|\epsilon| \ll 1$) layers, the magnetic structure becomes incommensurate with the lattice. This change produces not four inequivalent sites, but an essentially infinite number. Values of ϵ on the order of 10^{-3} are perfectly adequate to produce this effect and are not incompatible with the precision of the neutron results. The sole purpose of the constant ϵ is to destroy the commensurate relationship between the lattice constant and magnetization wavelength, and the predicted spectra on this model are totally independent of the exact value chosen. Results of calculations using this (infinite sublattice) model are shown in Fig. 2(b). [The plots were generated by summing a large number of 6-line spectra with hf parameters determined from the Eqs. (3) and (4) using ion moments obtained from the aforementioned modification of Eq. (1). It should be emphasized that the calculated spectra are produced directly from the neutron moment measurements, with no adjustable parameters or "fudge factors."]

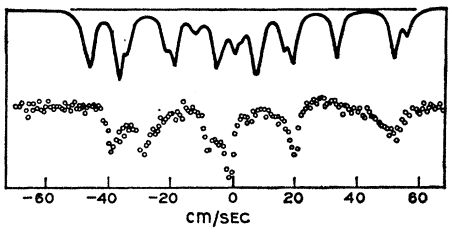

FIG. 4. Comparison of experimental data at 40°K with calculation based on the four-inequivalent-site model. Note poor agreement, especially near −20 and +20 cm/sec.

As can be seen, the over-all agreement between these calculations and the experimental results is good except near the Néel temperature. This is not surprising, since the model used breaks down badly as the ordering temperature is approached and the ion moments (and the exchange coupling) decrease. The remaining discrepancy is a small difference (less than 10% at worst, and visible only because of the high resolution of the Tm hfs) in over-all splitting between the calculated and observed spectra. The most likely cause of this difference is the following: It was previously mentioned that the neutron diffraction results provided only the first four Fourier coefficients for Eq. (1). The values of these four were chosen to provide exactly $\pm 7.0\ \mu_B$ at $T=0$ for each of the 7 ions per magnetic cell. The neglect of all the higher-order coefficients results in an overesti-

mate of the strength of these coefficients, and this results in calculated spectra with greater splitting than would be obtained if the entire series of coefficients was accurately known. The splitting in the spectra calculated here is indeed slightly larger than that experimentally observed.

The idea of a wave of magnetization incommensurate with the lattice may appear at first intuitively unreasonable; one might expect the wavelength to change slightly to provide a minimum energy configuration with the nodes (or loops) of the wave at the ion moments. However, there are similar systems in which the magnetization is indeed incommensurate with the lattice. For example, dysprosium has a flat spiral (helical) spin configuration between 90 and 180°K. The moments of the $4f$ electrons are parallel within each plane perpendicular to the c axis, and there is a temperature-dependent angle α between the directions of the moments in adjacent planes. A study[13] of the temperature dependence of α, which varies from 27° to 43° over the temperature range mentioned, shows no discontinuity at $\alpha=30°$.

Additionally, erbium metal shows a wave of magnetization in the temperature range 20 to 52°K, with the wavelength continuously varying from 4.1 to 3.5 c_0 over this range.[14] (This situation is similar to the one we are suggesting for Tm, but our experiment cannot, and the neutron results do not, detect any temperature variation of the magnetization wavelength. If ϵ were temperature-dependent, and there were some temperature for which $\epsilon=0$, the four-site spectrum shown in Fig. 4 should in principle be observable.) A recent study of erbium metal hfs by Mössbauer spectroscopy[15] did not analyze results in this temperature range using the neutron data of Ref. 14; however, an analysis very similar to that presented here was used to analyze the erbium spectra above 52°K.

It is of course possible that in our absorbers the magnetization wave was pinned on defects (for example, the unavoidable oxygen impurities), and that thulium of much higher purity would show the complex spectrum resulting from four inequivalent sites.

If the magnetization is indeed inherently incommensurate with the lattice, there is no force keeping it fixed in position, and it may be wandering through the lattice. The sharpness of the hf lines observed at 30°K allows us to estimate that at that temperature, any motion of the wave through the lattice is at 10 cm/sec or less. Higher velocities would result in rapid enough changes of ion moment with time to give greater broadening than is observed.

Recently the hfs of $ErAl_2$ below the ordering temperature was reported on and analyzed using a simple relaxation model.[16] Some of the qualitative characteristics of those results are superficially similar to ours, and we should distinguish between the two situations. The most commanding justification for our treatment is that in the temperature range about 30°K, where the lines are still sharp, relaxation spectra based on the model using four inequivalent sites look nothing like the observed data, because the existence of different sublattice magnetizations should be observed. There is an additional problem in that experimentally, the lines are observed to broaden as higher temperatures are approached. To get such behavior with the ferromagnetic relaxation processes occurring here, the relaxation time would have to *increase* (from about 3×10^{-11} sec at $T=20°$ to about 10^{-9} sec at $T=50°$) in a situation where the spin-lattice and conduction-electron relaxation mechanisms would be making the *decrease*. Thus, though we cannot completely exclude the possibility of some line broadening caused by relaxation effects, i.e., breakdown of the fast-relaxation approximation used to obtain Eqs. (3) and (4), the major features of the observed spectra must be explained on other grounds if the neutron scattering data are not to be ignored.

SUMMARY

In this work, hf spectra in Tm metal have been presented and analyzed. The essential feature of the analysis is the assumption of incommensurate magnetic and crystallographic unit cells, resulting in a continuous distribution of hf fields. This model successfully reconciles the results of earlier Mössbauer measurements with neutron diffraction measurements; they had previously been in apparent contradiction.

ACKNOWLEDGMENTS

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