# Temperature Dependence of the Periodicity of the Magnetic Structure of Thulium Metal*

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(Received 12 September 1969)

A neutron-diffraction investigation has been made of the variation with temperature of the characteristic wave vector of the magnetic structure of thulium metal. It has been found that this wave vector is slightly incommensurate with the lattice periodicity in the purely sinusoidal phase, increases with decreasing temperature, and locks into the seven-layer periodicity at 32 K, while the sine wave squares up symmetrically until a ferromagnetic component appears at 32 K, causing it to develop finally the antiphase structure found earlier by Koehler *et al.*

## I. INTRODUCTION

THE first neutron investigation to reveal the details of the magnetic structure of thulium metal was made by Koehler *et al.*[1] They found that a Néel temperature of 56 K below which a longitudinal sine wave of moments ordered along the $c$ axis developed, and furthermore that this sine wave began to square up at lower temperatures until at very low temperatures the structure became an antiphase domain arrangement with a four-up three-down full-ordered moment developed on the hexagonal layers. The results of Koehler *et al.* indicated that the magnetic periodicity was characterized by a seven-layer repeat distance throughout the temperature range below $T_N$. They were unable to establish the precise temperature at which the ferromagnetic component appeared although their results indicated that it came in smoothly at about 40 K.

More recently, anomalies have been observed in the ac susceptibility[2] and one of the Seebeck coefficients[3] at 32 K, while evidence from Mössbauer hyperfine data[4] indicates that the characteristic wave vector is not exactly commensurate with the lattice periodicity above 32 K. Accordingly, we have reexamined the magnetic structure of thulium metal by neutron diffraction using rather high-resolution and single-crystal samples believed to be of considerably greater purity than the ones used in the earlier investigation,[1] particularly with regard to nonmetallic elements. We have also utilized polarized neutrons to establish accurately the way in which the ferromagnetic component appears, and to study this component as a function of applied field.

## II. EXPERIMENTAL DETAILS

The single-crystal samples used in the experiment were essentially the same as those used in the transport measurements of Edwards and Legvold.[3] The two crystals used were in the form of parallelopipeds with the approximate dimensions of 1×1×6 mm, with the longest dimensions parallel to the [100] and [110] axes of the reciprocal lattice, respectively. The metallic impurity concentrations and resistivity ratios as measured for these crystals are given in Ref. 3. A further vacuum-fusion analysis after the spark cutting of the crystals indicated the following amounts of impurities for H, O, and N, in ppm by weight; O<207, H<9, N<5. The mosaic spreads of these crystals were estimated to be less than 10 min of arc. Most of the data were taken in the (100) plane of the first crystal using the neutron diffractometer at the Ames Laboratory Research Reactor, and collimations of 10-min arc both before and after the sample. The incident wavelength used was 1.16 Å from the (103) planes of a beryllium monochromator. The positions of the satellites due to the magnetic periodicity were analyzed by performing scans along the line between the 110 and 112 reciprocal-lattice points, in equal increments of $\mathbf{q}$ and taking the mean values of the peaks at the satellite positions, thus eliminating first-order resolution effects. The spectrometer angles were positioned to an accuracy of 0.01 deg. Changes in the lattice constant $c$ were corrected for by normalizing the $\mathbf{q}$ value obtained for each satellite by expressing it as a ratio to the difference in $\mathbf{q}$ between 110 and 112. In addition, possible small changes in the value of the lattice constant $a$ could result in a scan which makes a small angle with the true [001] direction. Such changes were corrected for and it was found that the correction factor was in fact negligible for the satellites studied. At the lowest temperatures where there are six distinct satellites between 110 and 112, each satellite position was used as an independent determination of the basic periodicity $\tau$. As the temperature was raised we relied mainly on the $11(0+\tau)$, $11(0+3\tau)$, $11(2-3\tau)$, and $11(2-\tau)$ satellites and at still higher temperatures only on the first harmonics. The results are shown in

* Work performed in part in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 2616.
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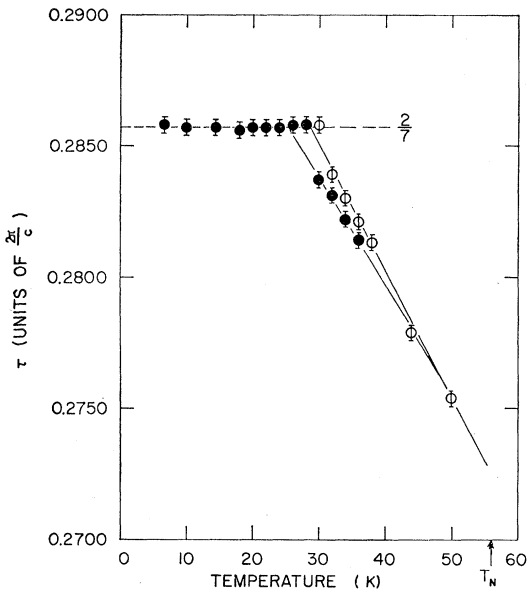


FIG. 1. Plot of the characteristic wave vector expressed as $(0,0,\tau)2\pi/c$ as a function of temperature. The full circles represent measurements taken with temperature descreasing and the open circles those taken with temperature increasing.

Fig. 1, where the error bars are obtained from a consideration of the spread in values for $\tau$ from such independent determinations. The most striking feature is that there is a small (estimated $\sim 3\%$ at $T_N$) but definite deviation of $\tau$ below the value of (0,0,2/7) corresponding to the seven-layer repeat distance in the temperature range from about 32 K to the Néel temperature. Thermal hysteresis in $\tau$ has also been observed as may be seen from Fig. 1. At temperatures below 28 K (decreasing temperature) and 30 K (increasing temperature) $\tau$ takes the constant value (0,0,2/7), within experimental error. The transition to the commensurate structure seems to be accompanied by a sudden change of $\tau$ when it gets close to the 2/7 value. At the higher temperatures, $\tau$ seems to decrease almost linearly with increasing temperature, the rate of change

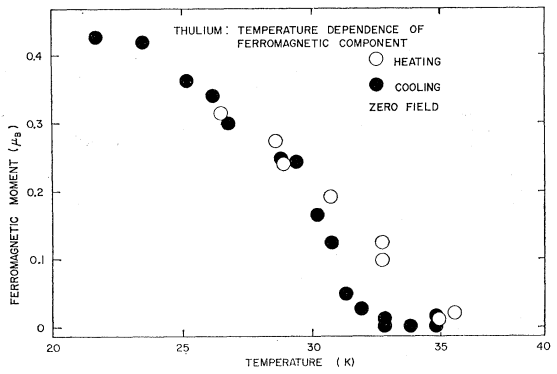


FIG. 2. Plot of the ferromagnetic component $\Psi_0$ as a function of temperature.

being $-0.0868$ degrees of interlayer turn angle per deg K for the temperature-increasing curve and $-0.0717$ degrees per deg K for the temperature-decreasing curve. Measurements made along the line between the 200 and 202 reciprocal-lattice points of the second crystal have confirmed the above behavior of $\tau$ although the temperatures for the transition to incommensuracy seem to be shifted upwards by roughly 2 K.

Between the temperatures at which $\tau$ becomes incommensurate and the Néel temperature, one might expect the satellites corresponding to the harmonics $2\tau$, $3\tau$, etc., to be split, since the positions $11(0+2\tau)$ and $11(2-5\tau)$ no longer coincide, and so on. No such splitting was observed, and our data showed that in fact in the incommensurate phase, the satellite $11(0+3\tau)$ appeared but *not* the $11(2-4\tau)$, and then the satellite $11(2-5\tau)$ appeared but not the $11(0+2\tau)$. An analysis of the relative amplitudes of the different harmonics as a function of temperature was complicated by extinction effects for the strong satellites, but seemed to indicate good quantitative agreement for the first, second, and

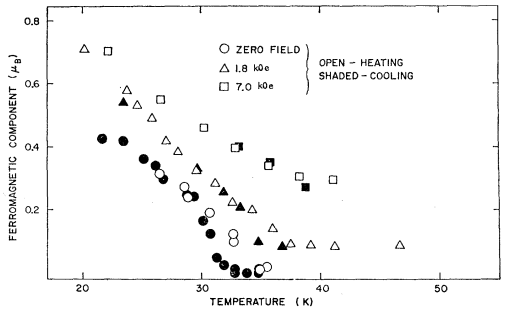


FIG. 3. Magnetic-field dependence of the ferromagnetic component $\Psi_0$ as a function of temperature.

third harmonics with the results of Koehler *et al.* and did not show any discontinuities at the transition to commensuracy. In order to establish the behavior of the ferromagnetic component, we studied a third crystal aligned with its [001] axis lengthwise using the Argonne polarized-neutron spectrometer situated at the Ames Research Reactor. The results are shown in Fig. 2, and indicate a sharp rise in ferromagnetic moment at a temperature of around 32 K and also exhibiting thermal hysteresis. Applying fields of up to 7 kOe both raised this Curie temperature and decreased the sharpness of rise of the ferromagnetic moment as indicated in Fig. 3. Measurements at 1.8 kOe in fact show a curve very reminiscent of that given by Koehler *et al.* for the ferromagnetic component $\Psi_0$.

## III. DISCUSSION

The incommensurability we observe in $\tau$ is certainly consistent with the evidence obtained by Cohen,[4] who was forced to postulate a slight incommensurability

above 32 K to explain the smearing out of some of the hyperfine lines in his Mössbauer data. We believe that the sharp change to a commensurate $\tau$ takes place at the same temperature as the ferromagnetic component $\Psi_0$ appears and that the slight difference in these temperatures as measured could well be within the sensitivity of temperature measurements. But if they are real, they could also possibly be due to differing strains in the differing samples. According to the theory of Elliott and Wedgewood,[5,6] the magnetic periodicity adopted by the moments is actually a function of the ordered moment rather than of the temperature directly. Hence one would expect a sudden jump in $\tau$ to be associated with the sudden appearance of the ferromagnetic component. Also, both the ferromagnetic component and $\tau$ show thermal hysteresis effects near the transition temperature.

The theory of magnetic ordering in the heavy rare-earth metals has also been discussed by Evenson and Liu[7] and Watson, Freeman, and Dimmock.[8] In the paramagnetic phase the nature of the Fermi surface produces a maximum in the Fourier transform of the Ruderman-Kittel-Kasuya-Yosida (RKKY) exchange interaction $J(\mathbf{q})$ at some value $\mathbf{q}_0$ such that when the moments begin to order it will be energetically favorable for them to adopt a periodicity with a characteristic wave-vector $\mathbf{q}_0$ at $T_N$. According to Elliott,[9] the anisotropy field in thulium metal keeps the moments aligned parallel to the $c$ axis, so initially a sinusoidal longitudinal wave (LW) structure will appear. As the temperature is decreased, the ordered moment increases and the superzone boundaries induced cause $\tau$ to change with temperature. The increase in $\tau$ with decreasing temperature has indeed been predicted by Elliott and Wedgewood[6] using a very simplified free-electron model for the bands. It should be noted that this behavior is in contrast to the trend for all the other heavy rare-earth metals. Watson, Freeman, and Dimmock[7] have discussed the superzone boundaries for a more realistic Fermi surface for thulium but have not studied its effect on the magnetic periodicity.

The theory of Elliott,[9] based on a free-energy argument, predicts that the amplitude of the sinuosoidal moment should saturate at $\frac{1}{2}T_N$, or 28 K. In fact the results of Koehler *et al.*[1] and our results indicate that it saturates at about 40 K. Below this temperature the structure can only decrease its free energy by inducing higher harmonics and hence begins to square up. Our observation that above the incommensurate-to-commensurate phase transition only the odd harmonics appear indicates that it begins to square up symmetrically, namely that there is a half-wave from 0 to $\frac{1}{2}\lambda$ which is *symmetric* about $\frac{1}{4}\lambda$ and subsequently inverted from $\frac{1}{2}\lambda$ to $\lambda$. There is no detailed theory at present as to how the structure actually squares up in detail, but from Elliott's theory it is reasonable to postulate that at the lowest temperatures the free energy is lowest for the maximum ordered moment developed on *each* atom and in such a way that the basic periodicity is close to the maximum in $J(\mathbf{q})$. This immediately implies that the structure must go commensurate at some stage and will choose the seven-layer repeat distance. Since there are an odd number of layers in this repeat distance, it also follows that a ferromagnetic component must be developed at some stage, and that the structure can no longer square up using only odd harmonics. The transition to commensurability provides it with a mechanism for developing the even harmonics, since now there is no distinction between the first and sixth, second and fifth, third and fourth, and seventh and zeroth harmonics, respectively, the last being the ferromagnetic component which then begins to grow rapidly below the transition temperature. A consideration of the relative amplitudes of the harmonics indicates that the structure does not exactly attain the four-three antiphase domain except at the lowest temperatures.

## ACKNOWLEDGMENTS

We wish to thank Dr. Sam Legvold for his generous cooperation and help and Dr. Allen Reese for helpful discussion.

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