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Magnetic transitions in single-crystal thulium

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Abstract. The magnetic transitions in a thulium single crystal have been investigated with magnetization, AC susceptibility and high-resolution calorimetric measurements. The results give clear evidence of the antiferromagnetic transition at 58 K, the squaring up of the magnetic moments between 42 and 35 K, and the ferrimagnetic transition at 33 K. The transition at 33 K is of first order with a latent heat of 0.8 ± 0.2 J mol^{-1}. The magnetic moment in the ferrimagnetic state measured with a SQUID magnetometer is $(1.025 \pm 0.001)\mu_B$ consistent with the expected 7.0 μ_B per atom and a 3, −4 antiphase domain structure. At 30 kOe a field-induced transition to ferromagnetic order takes place. In this state the moment is found to be $(7.060 \pm 0.001)\mu_B$. The excess moment of $6 \times 10^{-2}\mu_B$ for the ferromagnetic saturation magnetization in thulium is tentatively attributed to polarization of the conduction electrons.

1. Introduction

Thulium, like many of the heavy rare-earth elements, is an HCP metal. The magnetic structure has been studied with neutron diffraction by Koehler *et al* [1] and by Brun *et al* [2]. Between the Néel temperature ($T_N = 58$ K) and 40 K a sinusoidally modulated *c* axis structure exists. Owing to the strong crystal-field anisotropy of thulium the magnetic moments will remain parallel to the *c* axis in the whole temperture range below T_N. At about 40 K the amplitude of the sine wave modulation saturates. In order to decrease the free energy, higher harmonics are induced and the sinusoidal modulation begins to square up. At about 30 K a ferrimagnetic structure with a seven-layer repeat distance occurs [2] with the magnetic moments in three layers parallel to and in four layers antiparallel to the *c* axis, thus establishing an antiphase domain structure. The wave-vector which is slightly incommensurate with the lattice in the sinusoidal phase becomes commensurate with the lattice when the ferrimagnetic structure develops. In a recent x-ray diffraction study [3] this incommensurate-to-commensurate transition was found to be of first order.

The magnetization of thulium shows an increase below 40 K [4, 5] connected with the squaring up of the moments and exhibits no definite change at around 30 K due to the transition to the ferrimagnetic state. Nor was the latter transition observed in specific heat measurements [6, 7]. Anomalies which may be related to the ferrimagnetic

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transition have been observed only in a study of the Seebeck coefficient [8] and in high-resolution resistivity measurements on very pure thulium [9]. We report here a study of the magnetic transitions in thulium with magnetization, AC susceptibility and high-resolution calorimetric measurements. Our results give clear evidence of the ferrimagnetic transition as well as of the squaring up of the moments and the anti-ferromagnetic transition.

2. Experimental details

The measurements were made on samples from a single crystal of thulium. The crystal was obtained from Ames Laboratory (IA), the major impurities in atomic parts per million being as follows: F, 4; Na, <6; K, <10; Sc, <40; Mn, <70; Fe, 6.9; Ga, <30; C, 35; N, 45; O, 240; H, 525. From this crystal, samples with a mass of about 0.2 g were cut for the magnetic measurements and a mass of about 0.05 g for the calorimetric measurements. The samples for the magnetic measurements were in the shape of parallelepipeds with the *c* axis to within a few degrees parallel to one of the sample edges. After preparation the samples were annealed in vacuum (1×10^{-6} Torr) for 10 h at 680 °C.

The calorimetric measurements were performed with a sensitive high-resolution microcalorimeter. The sample and a dummy of equal thermal mass were connected via a differential thermocouple. The temperature of the sample was measured with another thermocouple also attached to the sample. The temperature was determined to an accuracy of 0.2 K. The measurements were made by varying the temperature linearly with time. The signal from the differential thermocouple due to energy changes in the sample was recorded as the rate of change in energy $\mathrm{d}Q/\mathrm{d}t$ against time and temperature. Further details of the measuring technique can be found in [10].

For the measurements of the susceptibility a low-field AC set-up previously employed in the study of the influence of magnetic fields and frequencies on the magnetic properties in erbium [11] was used. For each run the susceptibility χ was determined at constant magnetic field for different frequencies. The AC field amplitudes used were 8 A m^{-1} (0.1 Oe), 240 A m^{-1} (3 Oe) and 8000 A m^{-1} (100 Oe). The real (elastic) part χ' and the imaginary (viscous) part χ'' of the susceptibility were studied between 4 and 190 K for increasing temperature. The magnetization measurements were made with a SQUID magnetometer and with a vibrating-sample magnetometer. The maximum field used was 4×10^6 A m^{-1} (50 kOe). Appropriate demagnetization corrections were applied when necessary.

3. Results and discussion

3.1. Magnetization

The magnetic moment M of thulium measured with the SQUID magnetometer at 5 K and with the applied field along the *a* axis (open circles), the *b* axis (full circles) and the *c* axis (triangles) is plotted in figure 1. With the field parallel to the *c* axis, M was found to exhibit two distinct saturation levels with increasing field. At low fields the saturation is connected with the ferrimagnetic state. At higher fields the moments are decoupled into ferromagnetic order. This field-induced transition takes place at a critical field of about

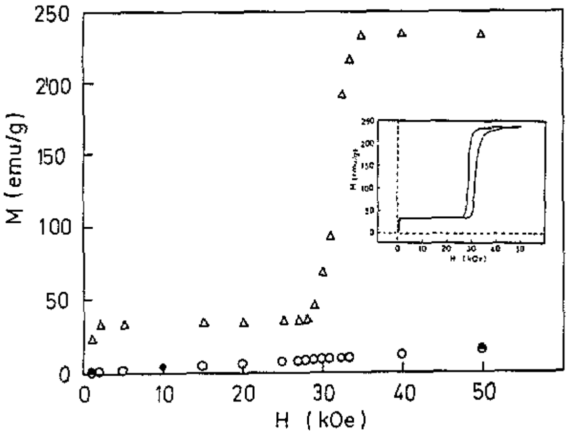

Figure 1. Magnetic moment of thulium at 5 K measured with a SQUID magnetometer to a maximum field of 50 kOe for different crystallographic orientations: ○, *a* axis; ●, *b* axis; △, *c* axis. The inset shows measurements on the same crystal at 4.2 K with a vibrating-sample magnetometer for increasing and decreasing values of the applied field.

30 kOe. Already at a field of 10% above this critical field the ferromagnetic alignment is almost complete as evidenced by the nearly constant values of the magnetization. The magnetic moment in the ferrimagnetic state calculated from the magnetization at 25 kOe is 33.88 ± 0.02 emu g^{-1} which corresponds to a moment of $(1.025 \pm 0.001)\mu_B$ per atom while in the ferromagnetic state at 50 kOe a saturation value of 233.23 ± 0.02 emu g^{-1} or a moment per atom of $(7.060 \pm 0.001)\mu_B$ is obtained. The ratio of the moment in the ferromagnetic state to that in the ferrimagnetic state is almost exactly 7 to 1. These results confirm beautifully the earlier experimental values of Richards and Legvold [4] $(1.001 \pm 0.005)\mu_B$ and $(7.14 \pm 0.02)\mu_B$ for the moments in the ferrimagnetic and ferromagnetic states, respectively, of thulium. The present results also agree with a net magnetic moment of $1\mu_B$ per atom obtained from neutron diffraction measurements by Koehler *et al* [1] for the 3, −4 antiphase structure of thulium with a moment per atom of $7.0\mu_B$.

The magnetization of thulium was also studied with a vibrating-sample magnetometer. The measurements were made at the same temperature as for the SQUID magnetometer results. The external field was directed along the *c* axis and was cycled between 0 and 50 kOe. The magnetization was recorded for both increasing and decreasing fields (see inset of figure 1). The magnetization values are consistent with the SQUID results. Furthermore both the ferrimagnetic and the ferromagnetic phases are found to exhibit hysteretic effects at the transitions.

The magnetization with the field directed along the *a* and *b* axes is considerably lower than for the *c* axis case. For both the *a* and the *b* axes the magnetization increases linearly with increasing field with no saturation noticeable up to 50 kOe. Also these results are in conformity with the observations in [4] and demonstrate that the *a* and *b* axes are hard-magnetization directions while *c* is an easy axis. There is no remanence in the magnetization for any of these directions.

The small increase in the *c* axis magnetization in excess of the expected value of $7.0\mu_B$ for full ferromagnetic saturation is assumed to be due to the polarization of the 5d conduction electrons via exchange interaction with the 4f electrons [12]). The present

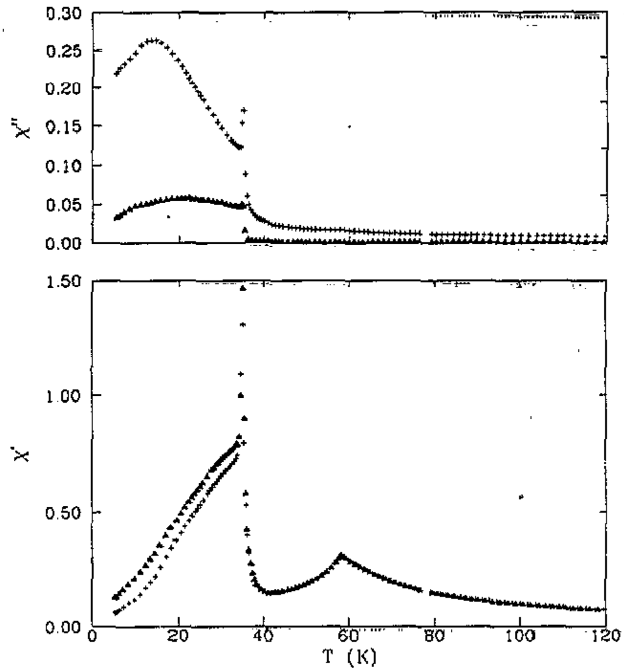

Figure 2. AC susceptibility versus temperature with the applied field of 0.1 Oe along the *c* axis for two frequencies: ▲, 100 Hz; +, 1000 Hz. For clarity, only a reduced number of data points are plotted in figures 2–4.

data give an electron contribution of $(0.060 \pm 0.001)\mu_B$ which is somewhat lower than the $(0.14 \pm 0.02)\mu_B$ found in [4]. An estimate with a simple exchange polarization model [13] leads to an approximate value of $0.1\mu_B$ for the conduction electron polarization in thulium.

3.2. AC susceptibility

The results of the AC susceptibility measurements are plotted in figures 2–4. In figure 2 the data for the measurements with the lowest applied field, 0.1 Oe, directed along the *c* axis are presented. The frequencies used were 100 Hz (full triangles) and 1000 Hz (crosses). A cusp in χ' is observed at 58 K of a shape typical for an antiferromagnetic transition. Below 42 K a rapid upturn in χ' starts, which results in a sharp maximum at 35 K followed by a steep decay in χ' to 33 K. Below this temperature, χ' declines more slowly towards liquid-helium temperature. Increasing the field to 3 Oe with the same field orientation (figure 3) does not give rise to any more pronounced change in the χ' curve except for a small increase in the part of χ' which lies below 33 K. For a field of 100 Oe (data not shown in the figures) a further enhancement of χ' below 33 K occurs while the data for the higher temperatures are almost unaffected. The calorimetric measurements (section 3.3) give a sharp energy peak at 33 K for this crystal, probably coming from the commensurate transition. This is, however, closely connected with the development of the ferrimagnetic antiphase structure. Even when taking possible differences in the thermometry of the calorimetric and the magnetic measurements into account we are inclined to assume that it is the break point in χ' at 33 K which marks the

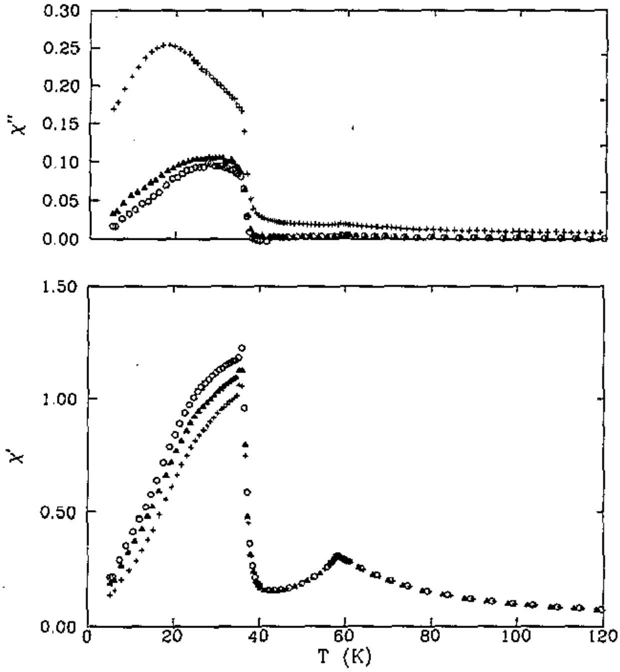

Figure 3. AC susceptibility versus temperature and frequency for a field of 3 Oe parallel to the *c* axis: ○, 10 Hz; ▲, 100 Hz; +, 1000 Hz.

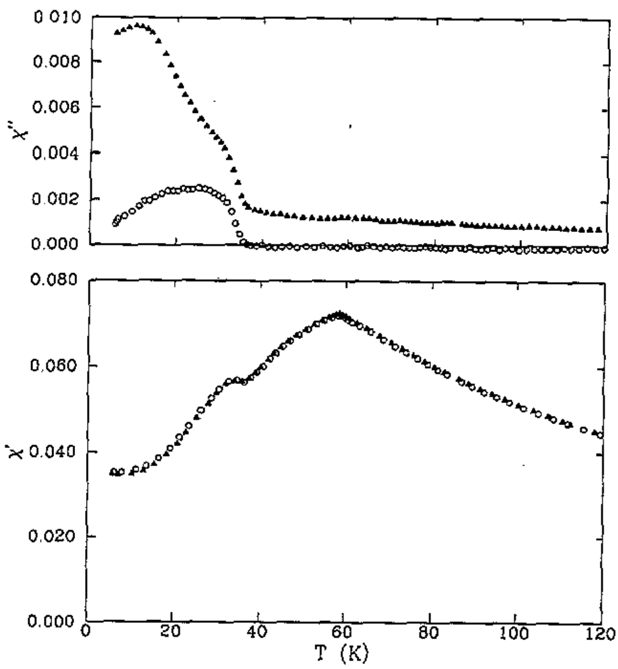

Figure 4. AC susceptibility versus temperature and frequency with the applied field of 100 Oe, parallel to the *b* axis: ○, 10 Hz; ▲, 100 Hz.

onset of the ferrimagnetic state in the susceptibility measurements. Support for this assumption is the observed increase in χ' with increasing field in the region below 33 K while the peak value at 35 K is not changed much. The enhancement of χ' with increasing field is due to motion of the ferrimagnetic domain boundaries. The growth of χ' below 42 K is in accord with the observation in [4] where the magnetization increase was attributed to the squaring-up process.

With the field directed along the *b* axis, the antiferromagnetic transition gives rise to a cusp in χ' at 58 K (figure 4) similar to that observed at T_N with the field parallel to the *c* axis. This might appear strange as there is no magnetic ordering in the basal plane in thulium. The behaviour at T_N can, however, be understood in terms of a coupling between the magnetization along the *c* axis and that in the basal plane [5]. The susceptibility at T_N when measured along the *b* axis is about a quarter of that along the *c* axis which is consistent with the strong magnetic anisotropy of thulium. The difference between the strengths of the applied field in figures 2–4 is of little importance in this connection. The strong peak in χ' at 35 K in figures 2 and 3 is virtually missing when measuring along the *b* axis. The small anomaly at about 35 K might, however, be a residue of this peak, possibly because of interaction between the magnetization along the *c* axis and the magnetic components in the basal plane.

The frequency dependence of χ' is very small except for temperatures below 33 K where χ' decreases with increasing frequency (see, e.g., figure 3). This is a consequence of the fact that the domain walls become less susceptible to the field oscillations as the frequency increases. The fact that χ' does not display any marked frequency dependence below 33 K with the field perpendicular to the *c* axis might indicate an orientation with the ferrimagnetic domain walls essentially perpendicular to this axis.

The imaginary part χ'' of the susceptibility is related to the AC losses in the sample. From figures 2–4 it is obvious that the general trend in χ'' is to increase with decreasing temperature at constant frequency. This behaviour is a typical eddy current effect. The increase in χ'' with increasing frequency is also due to eddy currents. Below about 35 K, χ'' shows a strong increase. This may be due to losses associated with the domain structure in the ferrimagnetic state.

3.3. Calorimetric measurements

The calorimetric measurements were made by continuously scanning the temperature between 15 and 65 K for both increasing and decreasing temperatures. On heating the sample, a narrow endothermic peak in dQ/dt occurred at 33.4 ± 0.2 K (figure 5). The energy change, obtained by integration of dQ/dt over time, is 0.8 ± 0.2 J mol^{-1} for this peak. On cooling the sample, a similar exothermic peak is obtained at 30.9 K. The sharpness of the energy peaks and the thermal hysteresis are characteristic of a first-order process. The transition temperature is close to the temperature reported in [2], 32 K, where the ferrimagnetic structure develops. The small difference in temperature between [2] and the present investigation may depend on the purities of the samples used. The thermal hysteresis observed in figure 5, 2.5 K, is of the same value as observed in [2] from the temperature variation of the characteristic wavevector of the magnetic structure.

For somewhat higher temperatures a small deviation in dQ/dt from the zero level occurred between about 35 and 42 K, which indicates a small energy change in the sample. At 58.2 K the antiferromagnetic transition gives rise to a sharp change in

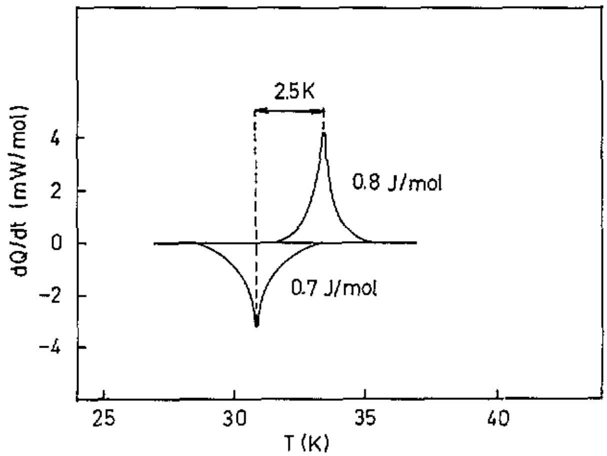

Figure 5. The change in energy content at the ferrimagnetic transition in thulium for increasing temperature (endothermic peak) and for decreasing temperature (exothermic peak). The zero line is drawn as a guide to the eye.

dQ/dt. No latent heat or thermal hysteresis is observed at the transition, which accordingly is of second order. The extended energy change between 35 and 42 K may tentatively be attributed to the squaring up of the magnetic moments.

The Néel temperature of 58 K obtained in the calorimetric and magnetic measurement is in agreement with the transition temperatures of 58 K observed in [4] from magnetization measurements and 56 K found by Koehler *et al* [1] from neutron studies. The calorimetric measurements give further clear evidence of the first-order nature of the transition at 33 K. At this transition, neutron studies [2] show that, concomitantly with the appearance of a ferromagnetic component in the scattering due to the development of the ferrimagnetic phase, the wavevector locks into a constant value, indicating the formation of a commensurate structure. We have previously studied calorimetrically the magnetic transitions in erbium [10]. The incommensurate-to-commensurate transitions in erbium are of first order with latent heats of 0.5–1 J mol^{-1}, while the ferromagnetic transition, which is also of first order, gives an energy change of about 20 J mol^{-1} because of the much larger deformation of the lattice in this case. The small energy peaks in figure 5 are probably essentially connected with the commensurate phase transition. One can, however, question, by comparing with the ferromagnetic transition in erbium, why no larger energy change due to the ferrimagnetic ordering is observed in thulium. Unfortunately there are no data available on the distortion of the lattice parameters at the ferrimagnetic transition in thulium. The deformation of the lattice at the ordering of the moments is, however, probably partly compensated in the antiphase domain structure which may explain the small energy effects. Another possibility is that the squaring up of the sine wave modulation below 42 K can be considered as a gradual change towards the ferrimagnetic state. The distortion of the lattice due to the ferrimagnetic ordering process will then be extended over a wider temperature interval and the transition will appear continuous.

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