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Magnetic ordering phenomena in TmS*

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ABSTRACT

Neutron diffraction data have been obtained from powder and single crystal specimens of TmS at temperatures ranging from room temperature to 1.7 K and in applied magnetic fields up to 42.8 kOe. In zero field TmS undergoes a transition, at about 3.9 K, to an antiferromagnetic structure which is almost the type two face-centered cubic structure. In this structure there are four G-type or (π, π, π) type antiferromagnetic sublattices such that the moments are parallel in (111) planes, alternating in sign from one such plane to the next. Superimposed on the ordering is a sinusoidal modulation with propagation vectors parallel to [110] directions. The structure is a multidomain one which gives rise to a very complex diffraction pattern. With polarization analysis it was possible to determine the moment directions in the domains. For example, in domains with propagation vector parallel to [110] the moments are parallel to [112]. From powder data taken at 1.7 K the maximum value of the Tm moment was estimated to be 4.0 μ_B . Diffuse streaks of magnetic origin with temperature and field dependence different from that of the satellites were observed which may influence our estimate of the magnitude of the ordered moment. The response of the magnetic reflections to applied magnetic fields can be understood, in part, in terms of domain repopulation.

INTRODUCTION

The thulium monochalcogenides TmS, TmSe, and TmTe have been studied intensively recently. They all have the simple rock salt crystal structure, and all exhibit magnetic ordering transitions at low temperatures as indicated by magnetic susceptibility and specific heat measurements.¹ Part of the current interest in these materials stems from the fact that the thulium ion behaves differently in the three compounds. In the sulfide thulium appears to be trivalent; in the selenide, at least for some compositions, it is considered to be in a mixed-valence state; and in the telluride, it is divalent. In all three cases the ordered configuration appeared to be an antiferromagnetic one.

Recently, neutron diffraction experiments on TmSe have revealed a very strong dependence of the type of magnetic ordering on the composition. Type I antiferromagnetic order with a small ordered moment appears to be characteristic of nearly stoichiometric samples.²

In this paper we report some results of a study of the magnetic structure of TmS. A polycrystalline specimen and one single crystal preparation have been investigated. These have room temperature lattice parameters, 5.417 Å, close to what is expected for Tm³⁺S. Magnetic measurements on the same crystal yield a molar Curie constant of 6.04 emu, somewhat smaller than the free ion value, and a Neel temperature near 5 K. We expect that the properties of TmS will be sensitive to composition and we intend to carry out further studies on well-characterized crystals of different composition.

RESULTS

Neutron powder patterns were obtained for a specimen of TmS at room temperature, at 30 K, and at 1.7 K at a neutron wavelength of 1.063 Å. The integrated intensities of the nuclear reflections in the 30 K pattern were found to be in good agreement with those expected for stoichiometric TmS and with currently accepted coherent scattering amplitudes. A postulated deficiency of 5% in the Tm content improves the intensity agreement but the change is just outside that produced by experimental uncertainties.

In addition to the nuclear reflections there was observed a strong paramagnetic scattering background on which was a broad diffuse maximum centered more or less at the superlattice position ($\frac{1}{2} \frac{1}{2} \frac{1}{2}$). A part of the 30 K pattern is illustrated in Fig. 1. As the temperature was lowered a number of additional reflections of magnetic origin appeared. These are shown in Fig. 1 also in a temperature difference pattern for intensities observed at 30 K and 1.7 K. We note several features of this difference pattern: (i) Magnetic intensity is associated with superlattice reflections whose indices are all odd, (ii) Except for the ($\frac{1}{2} \frac{1}{2} \frac{1}{2}$) which appears to be a single line the superlattice points shown all have closely spaced satellites, and (iii) The resolved magnetic reflections are not noticeably broader than the nuclear peaks. Such a distribution of magnetic intensity implies a modulated structure with a propagation vector nearly equal to the reciprocal lattice vector $\frac{1}{2}(\vec{b}_1 + \vec{b}_2 + \vec{b}_3)$ and having a component normal to it. In the sequence of measurements further analysis of the powder data was deferred until the single crystal was studied and we follow that procedure here.

Single crystal data were collected first with a $[1\bar{1}0]$ direction vertical and with a neutron wavelength of 1.252 Å. In Fig. 2 are shown θ -scans at a scattering angle fixed at the position calculated for the ($\frac{1}{2} \frac{1}{2} \frac{1}{2}$) superlattice peak. It is clear that the single line observed in the powder data at this position is

due to several magnetic reflections all having scattering angles equal to that of the $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ reflection. In order to identify and index these reflections we repeated the 0-scans at several representative temperatures with a 2 mm-wide horizontal mask over the counter opening. This mask was moved from the bottom to the top of the counter slit at about 1 mm intervals and a scan was taken at each position. The results of this procedure may be summarized as follows: (i) Three kinds of magnetic scattering were identified which we call peaks, streaks, and humps according to their width. (ii) All three types have rocking curve widths significantly broader than those of the nuclear reflections. (At the wavelength chosen a small but measurable second-order nuclear peak can be seen at the $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ position. In Fig. 2 this can best be seen as a sharp spike on the central peak observed at 8.43 K.) (iii) Of all the intensity measured in these scans only that of one pair of the streaks is in the scattering plane.

This is illustrated in the insert of the upper half of Fig. 3 which presents polarization analysis data for a $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ scan at 6.8 K. The field, $H = 1.2 \text{ kOe}$, was applied to provide a guide field for the polarized beam and it is sufficiently low that little change in the magnetic structure was produced. As shown there the "central peak" of the scans of Fig. 2 is produced by two peaks, labeled 1 and 4. At temperatures above about 4 K the inner reflections of the left-hand pair of peaks is produced by satellites 5 and 6, and of the right-hand pair by satellites 2 and 3. The outer member of the pair is produced by a streak, designated by a vertical line in the figure. Other streaks falling between but slightly outside of the satellite spots were observed also. As mentioned above, only the streak between satellites 5 and 6 has intensity in the scattering plane (defined by $[111]$ and $[\bar{1}\bar{1}2]$). The experiment was undertaken to establish the directions of the magnetic moments and these are, as shown at the satellite positions, parallel to $[\bar{1}\bar{1}2]$ directions. In the streaks the moments are parallel to one or another $[110]$ direction. To verify these observations, the crystal was reoriented by rotating it 90° about the $[111]$ direction and the experiment repeated. Satellites 1 and 4 are now in the scattering plane and the scattering from them is entirely non-spin flip indicating that the moments are parallel to the polarization direction. Satellites 2, 7 and 3, 6 have both spin-flip and non-spin-flip contributions showing that the moments have components normal and parallel to the polarization $\vec{P}$. The intensity ratio, about 3 to 1 spin flip to non-spin flip, again determines the moment direction. The streaks, now appearing directly above and below the $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ position are nearly completely spin-flip and thus have moments normal to $\vec{P}$.

Finally, in Fig. 4 we summarize the results obtained in the varying temperature scans. In the upper left-hand diagram a schematic representation of a typical scan is given. In that same diagram we show the temperature variation of the intensity at the point D which is a broad diffuse hump appearing under the "central peak" and a point C which is due in part to the diffuse streak between satellites 1 and 6 and 5 and 4 in Fig. 3 and in part to a diffuse hump under satellites 5 and 6. As the Néel point, 8.9 K as measured in the neutron scattering studies, is reached the intensities at C and D become identical and persist with slowly decreasing intensity to temperatures well above the ordering temperature. It is this contribution presumably which is seen in the powder pattern at 30 K. The component of C due to the streak disappears at T_N . The positions of the components of the left- and right-hand pairs of reflections vary with temperature and this is shown in the lower right-hand diagram. Above about 6 K the streak (outer) and satellite (inner) are resolved and one can measure the separations $\Delta\omega_2$ and $\Delta\omega_1$, respectively. At about 5 K the peaks are superposed and below 4 K the streak is inside the satellite position. This can be seen in the low temperature scans of Fig. 2. The position of the satellite varies rather little whereas that of the streak is changing markedly. To the extent that the intensity at the peak of the components of the left-hand pair can be separated, E and F in the upper-right diagram, the temperature dependence of the intensity is different. That of the streak appears to be approaching saturation at about 6 K whereas that of the satellite seems still to be increasing rapidly. Finally, in the lower left we show this difference by comparing the square root of the normalized intensity as measured for the sum of the two left-hand components with the corresponding quantity for the two central peak satellites.

CONCLUSIONS

The experimental results presented above are not completely understood but some conclusions can be drawn from them. If we consider only the sharp satellite peaks we can interpret the structure as a multidomain one with a propagation vector $\vec{\tau} = \frac{1}{2}(\vec{b}_1 + \vec{b}_2 + \vec{b}_3) + \Delta(\vec{b}_1 - \vec{b}_2)$ with $\Delta = 0.080$. The structure can be envisaged as being approximately the simple Type II antiferromagnetic structure with (111) sheets of like spin alternating in sign. Superimposed on this is an oscillatory component parallel to a [110] direction. The moment direction for that domain is parallel to the [112]. There are three domains associated with the reciprocal lattice vector $\frac{1}{2}(\vec{b}_1 + \vec{b}_2 + \vec{b}_3)$ and there

are four distinct such vectors for a total of 12 domains in all. A similar magnetic structure has been proposed for CeAl_2 .³ We have adopted this model to interpret the intensities observed in the powder pattern and obtain at 1.7 K a value of $\mu_{\text{max}} = 4.0 \mu_B$ for the value of the amplitude of the moment. Although the model accounts well for all the powder lines, we recognize that the moment value obtained from the powder data is open to question for we may not have accounted properly for all the magnetic scattering. We have not attempted as yet to analyze the single crystal intensities quantitatively because of the high degree of perfection of the crystal.

We can only speculate on the origin of the streak. It may be due to a second component of the moment with little or no correlation with the first. We have seen that the temperature dependence of the intensity and spacing of the streak scattering is different from that of the satellite; we know also that the two types of scattering respond differently to an applied magnetic field. It is possible, in rather modest applied fields, to prepare a single domain with the scattering appearing, for a given $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ lattice point, in a single pair of satellites with the moment normal to the field direction. Large hysteresis effects are observed.

We have deferred further quantitative analysis until we can obtain a series of well-characterized single crystal and powder specimens.

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Fig. 1. Neutron powder patterns for TmS. The upper curve is a partial diffraction pattern taken at 30 K. The lower one is formed from the difference of data taken at 1.7 K and 30 K. The magnetic intensities are found at or about the superlattice positions with all odd indices.

Fig. 2. Single crystal scans at various temperatures. These data are described in the text. The broad peaks between the central and outside groups are streaks of intensity. The whole group is superimposed on a diffuse hump which is most noticeable at low temperatures.

Fig. 3. Polarization analysis of $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ scattering. Upper half 6.8 K and $[1\bar{1}0]$ vertical, lower half 4.4 K and $[\bar{1}\bar{1}2]$ vertical. The moment directions in the domains responsible for the satellites are shown in each case.

Fig. 4. Summary of data from varying temperature scans.