RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 28, NUMBER 5 1 SEPTEMBER 1983

Modulated magnetic structure of the Kondo compound TmS

Y. Lassailly and C. Vettier
Institut Laue-Langevin, 156X Centre de Tri, F-38042 Grenoble Cedex, France

F. Holtzberg
IBM, Thomas J. Watson Research, Yorktown Heights, New York 10598

J. Flouquet
Centre de Recherches sur les Très Basses Températures, Centre National de la Recherche Scientifique, 166X Centre de Tri, F-38042 Grenoble Cedex, France

C. M. E. Zeyen
Institut Laue-Langevin, 156X Centre de Tri, F-38042 Grenoble Cedex, France

F. Lapierre
Centre de Recherches sur les Très Basses Températures, Centre National de la Recherche Scientifique, 166X Centre de Tri, F-38042 Grenoble Cedex, France

(Received 25 April 1983)

Single-crystal neutron-diffraction experiments have revealed a modulated antiferromagnetic structure in TmS below the Néel temperature $T_N = 5.2$ K. At 1.5 K the propagation vector $\vec{q}$ is $(\frac{1}{2}-\eta, \frac{1}{2}+\eta, \frac{1}{2})$ with $\eta = 0.075$ and the modulation amplitude $3.4\mu_B$ along the $[11\bar{2}]$ direction. No lock-in transition is observed even when hydrostatic pressure up to 16 kbar is applied. While the magnetic-transition temperature increases under presssure, the modulation amplitude appears to be pressure independent. Comparison is made with $CeAl_2$ and other chalcogenide Tm compounds.

Thulium monochalcogenides with the NaCl structure exhibit various types of behavior due to the different degrees of instability of the valence of thulium. In particular, Tm ions are divalent in TmTe,[1] whereas they show a homogenous intermediate-valence (IV) state in TmSe (Ref. 1) and are considered to be trivalent in TmS.[1] These three compounds order magnetically at low temperature. TmSe has a simple antiferromagnetic type-I structure with a magnetic moment of $1.7\mu_B$ along the [100] axis.[2] At very low temperature, below $T_N = 0.2$ K, TmTe (Ref. 1) is magnetically ordered. Earlier work on TmS (Ref. 3) has shown a complex magnetic structure. Using a better characterized sample, we have undertaken a further neutron scattering study in order to solve the magnetic structure of TmS and to investigate pressure-dependent effects for comparison with Tm compounds and the archetype of Kondo systems, $CeAl_2$.

The experiments were carried out at the high-flux reactor of the Institut Laue Langevin. Single-crystal intensities were measured on the 4-circle diffractometer D10 at a wavelength $\lambda = 2.35$ Å with a PG(002) monochromator and with a PG filter to reduce higher-order contamination. The sample was mounted in a full 4-circle continuous flow He-cryostat designed for the temperature range of 3–300 K. At lower temperatures, measurements were performed in a fixed scattering plane geometry on D10. This instrument was then used in a 3-axis mode with a PG(002) analyzer. Powder and single-crystal high-pressure data were obtained on the 2-axis diffractometer D1A at $\lambda = 2.98$ Å. A clamp alumina cell was used for high-pressure studies.[4]

Scans performed below the observed Néel temperature $T_N = 5.2$ K on a powder sample showed magnetic diffraction peaks. They correspond approximately to a propagation vector $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ confirming earlier work.[3] However, a more accurate description of the propagation vector was obtained from the present single-crystal data. Q scans revealed the existence of satellites on the corners of a hexagon (Fig. 1) which could be indexed as $\vec{Q} = \vec{\tau} \pm \vec{q}$, where $\vec{\tau}$ is a reciprocal-lattice vector, and $\vec{q}$ is the sum of a $\vec{q}_c(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ vector and a $\vec{q}_I(-\eta,\eta,0)$ incommensurable vector. At $T = 1.5$ K, η has the value of 0.075 ± 0.001 and reaches 0.085 at 5 K. It can be seen from Fig. 1 that the satellites were quite well resolved and that neither humps nor streaks, which had been reported earlier,[3] were present. Moreover, our observed value T_N is in complete agreement with resistivity and specific-heat measurements.[5]

The neutron-diffraction measurements allow us to determine both the magnitude and the direction of the Fourier components $\vec{m}_{\vec{q}}$ of the magnetic moment. In the inset of Fig. 1, different propagation vectors $\vec{q}$ are represented in the first Brillouin zone. The pair of satellites correspond to the Fourier components associated with $\vec{q}$ and $-\vec{q}$, respectively. A search was made for higher-order satellites; third-order satellites were absent even at very low temperature. Q scans were performed at different positions in reciprocal space to check for any eventual coupling between Fourier components and secondary-order parameters, as proposed for $CeAl_2$.[6] No indication for such coupling was found. Therefore TmS apparently exhibits a pure sinusoidal magnetic structure.

In the high-temperature paramagnetic phase, TmS crystallizes in the O_h^5 space group with one Tm atom per cell; the lattice parameter is 5.395 Å at $T = 1.5$ K. The point group of the $\vec{q} = (\frac{1}{2}-\eta, \frac{1}{2}+\eta, \frac{1}{2})$ vector is C_2. There are 24 vectors in the star of $\{\vec{q}\}$. In the magnetically ordered state

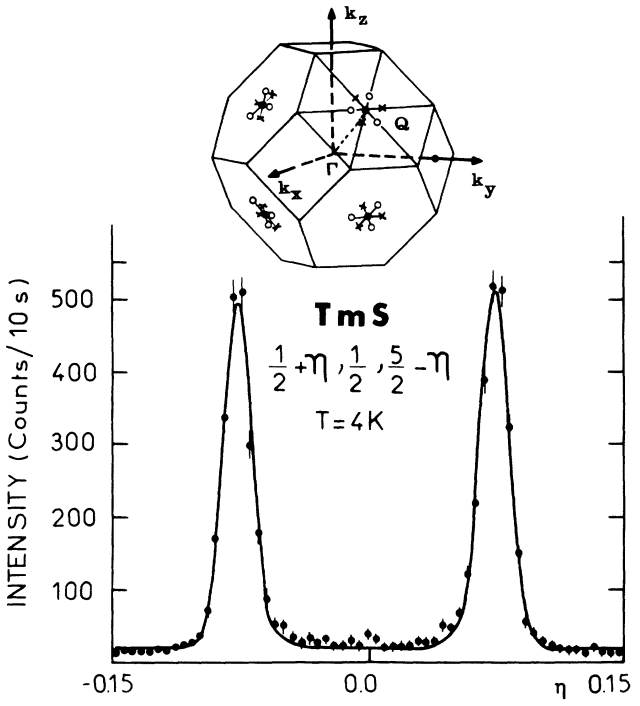

FIG. 1. Q scan around the $(\frac{1}{2},\frac{1}{2},\frac{1}{5})$ position performed on the 4-circle diffractometer D10 without analyzer. The insert shows that in the first Brillouin zone the nonequivalent $\vec{q}$ vectors (open circles) belong to the Q symmetry point characterized by the C_2 group. The magnetic satellites coming from the adjacent Brillouin zone (crosses) participate to a hexagon.

the magnetic distribution $\vec{M}(\vec{r})$ can be expanded in a Fourier series. In the case of a pure sine wave $\vec{M}(\vec{r})$ can be written as

$$\vec{M}(\vec{r}) = \sum_{\{\vec{q}\}} e^{-i\vec{q}\cdot\vec{r}}\vec{m}_{\vec{q}} \ . \tag{1}$$

A fundamental question is to determine how many members of the star would be present in the summation (1). As $\vec{q}$ is not equivalent to $-\vec{q}$, the $\{\vec{q}\}$ star is reduced to a set of 12 nonequivalent $(\vec{q}, -\vec{q})$ pairs. Thus $\vec{m}_{\vec{q}}$ and $\vec{m}_{-\vec{q}}$ couple to yield a real value for the magnetic moment. For a given domain i associated with a $\vec{q}_i$ vector, the magnetic cross section is given by

$$\frac{d\sigma}{d\Omega} = V_i A(\vec{Q}) f^2(Q) \sum_{\alpha\beta} \left(\delta_{\alpha\beta} - \frac{Q^\alpha Q^\beta}{Q^2}\right) m^\alpha_{\vec{q}_i} m^\beta_{-\vec{q}_i} \ , \tag{2}$$

where $\vec{Q} = \vec{\tau} \pm \vec{q}_i$, V_i is the domain population, and $f(Q)$ is the magnetic form factor of the Tm^{3+} ion. The coefficient $A(\vec{Q})$ includes scale factor, absorption, and extinction corrections, which were refined from the nuclear intensities at low temperature. Least-squares refinement of 220 magnetic intensities from the 12 magnetic domains leads to the conclusion that the $\vec{m}_{\vec{q}}$ vectors lie along $[11\bar{2}]$ directions. The Fourier component amplitude $2|m_q|$ is found to be $(3.4 \pm 0.2)\mu_B$ at $T = 1.5$ K from powder data. The adjusted domain populations V_i are slightly different but not so different that a multi-q structure could be ruled out. However, the simplest solution is to neglect coupling among the different $\vec{m}_{\vec{q}_i}$, and this leads to a single-q structure which can be described as an amplitude modulation of the magnetization propagating along the [110] direction. The magnetic moments $\vec{M}(\vec{r})$ are aligned along $[11\bar{2}]$ directions and (111) planes are antiferromagnetically coupled.

The assumption of a single-q structure leads to magnetic order in TmS, very similar to the structure observed in $CeAl_2$ (Ref. 7) which has been considered as the archetype of Kondo compounds. Tm ions in TmS are in a trivalent state close to the intermediate-valence regime.[8] The strong coupling to the conduction electrons leads, at high temperature, to Kondo contributions observed in the resistivity and in the susceptibility.[5] However, in contrast to $CeAl_2$, where the hierarchy between the main relevant parameters [the Kondo energy $k_B T_K$, the exchange coupling J_{ij}, and the crystal-field splitting (CF)] is well established ($k_B T_K$ is less than J_{ij} which, in turn, is much less than CF), TmS corresponds to a crossover regime where these parameters are of similar magnitude. Whatever the crystal-field scheme may be, the Kondo mechanism provides one of the conditions for the occurrence of a sinusoidal structure at low temperature (possibility of building a singlet ground state). However, the supplementary condition concerning the occurrence of a magnetic crystalline anisotropy is not verified since, up to now, well-defined crystal-field transitions have not been directly observed by neutron inelastic scattering. Only indirect assignments[5] may indicate that the triplet Γ_5 is the ground state and the doublet Γ_3 the first excited state. Such a picture is supported by the fact that the isostructural trivalent Kondo compound $Tm_{0.87}Se$ clearly exhibits this level scheme.[9] Furthermore, the amplitude of the magnetic moment ($3.4\mu_B$) in the ordered phase and high-field magnetization [$3\mu_B$ at $H = 100$ kOe at $T = 1.5$ K (Ref. 10)] are close to the $2.7\mu_B$ value of the Γ_5 level but too far from the value ($7\mu_B$) of the full orbital momentum $J = 6$.

Measurements under pressure can provide useful information about the valence state of Tm ions. Therefore we performed neutron scattering experiments on TmS under hydrostatic pressure up to 15.6 kbar. The incommensurate wave vector η and the Néel temperature increases with pressure: at $P = 8.3$ kbar, $T_N = 6.8$ K, $\eta(1.5\text{ K}) = 0.0801 \pm 0.001$, and at $P = 15.6$ kbar, $T_N = 7.15$ K, $\eta(1.5\text{ K}) = 0.082 \pm 0.001$, whereas the amplitude of the modulation seems to remain constant under pressure. From the lattice parameter variation, a compressibility K_V equal to 8.86×10^{-4} kbar^{-1} was determined. The observed pressure dependence of T_N agrees with susceptibility[11] and resistivity measurements.[12] From K_V and $T_N(P)$ a large positive magnetic Grüneisen coefficient

$$\Gamma_M = -d\log T_N / d\log V = 28$$

is found for TmS compared with $CeAl_2$ (where $\Gamma_M = -10$). TmS may correspond to the case where T_K decreases strongly with pressure, as shown by the behavior of the resistivity.[11] At sufficiently high pressure ($P > 100$ kbar), the pure trivalent regime of the Tm ions will be reached with a vanishing Kondo coupling. A simple model for TmS is that the pressure increase of T_N is related to the corresponding increase of the magnetic character (decrease of T_K), whereas for $CeAl_2$ the pressure decrease of T_N corresponds to the tendency towards a delocalization of the $4f$ electron (increase of T_K). It is also interesting to compare the pressure dependence of the magnetism in TmSe and TmS as Tm ions in TmSe may change from an intermediate-valent state to a trivalent state under pressure.

In accordance with TmS, the most important points are that at low pressure ($P < 30$ kbar) the magnetic structure of TmSe is a type-I AF (antiferromagnetic) structure,[13] probably with a doublet ground state, whereas above $P > 30$ kbar a new state appears corresponding to the disappearance of the insulating ground state and to a change in the magnetic structure presumably to type-II AF.[14,15] The high-pressure behavior of TmSe appears similar to that of TmS. This conclusion is reinforced by the facts that (i) in TmSe at high pressure Γ_M is nearly equal to 30, and (ii) in the ternary TmS-TmSe compound (not too far from the TmS composition) a similar volume dependence of T_N has been observed.[16] This similarity suggests the existence of a critical volume (or valence) at which important changes appear in the magnetic parameters, related to a modification in electronic conduction: insulating ground state for $P < 30$ kbar in TmSe, metallic for $P > 30$ kbar in TmSe and TmS. In TmSe the critical pressure may not coincide with an entry into the trivalent regime but may be reflected in the intermediate-valence regime itself as a pressure-induced crossover between divalent and trivalent states. Due to weak differences in the compressibilities and volumes the IV-3 + valence transition may be continuous.

In conclusion TmS exhibits an incommensurate modulated structure. Within the assumption of single-q structure, the magnetic moments are aligned along $[11\bar{2}]$ direction and (111) planes are antiferromagnetically coupled. In the light of our results, a multi-q structure cannot be rejected. The possibility of such a structure must be examined: experiments under symmetry-breaking fields should be performed to settle this question.

ACKNOWLEDGMENTS

Fruitful discussions with Dr. W. C. Koehler are gratefully acknowledged. The authors are indebted to S. Burke for a critical reading of the manuscript and to R. Chagnon for technical assistance.

[1]E. Bucher, K. Andres, F. J. Di Salvo, J. P. Maita, A. C. Gossard, A. S. Cooper, and G. W. Hull, Phys. Rev. B 11, 500 (1975); H. R. Ott and F. Hulliger, Z. Phys. B 49, 323 (1983).

[2]H. B. Muller, S. M. Shapiro, and R. J. Birgeneau, Phys. Rev. Lett. 39, 1021 (1977).

[3]W. C. Koehler, R. M. Moon, and F. Holtzberg, J. Appl. Phys. 50, 1975 (1979).

[4]D. Bloch, J. Paureau, J. Voiron, and G. Parisot, Rev. Sci. Instrum. 47, 296 (1976).

[5]J. Peyrard, J. Flouquet, F. Lapierre, Y. Lassailly, C. Vettier, and F. Holtzberg, J. Magn. Magn. Mater. 31–34, 433 (1983).

[6]S. M. Shapiro, E. Gurewitz, R. D. Parks, and L. C. Kupferberg, Phys. Rev. Lett. 43, 1748 (1979).

[7]B. Barbara, M. F. Rossignol, J. X. Boucherle, and C. Vettier, Phys. Rev. Lett. 45, 938 (1980).

[8]See, for example, N. Mårtensson, B. Reihl, R. A. Pollak, F. Holtzberg, and G. Kaindl, Phys. Rev. B 25, 6522 (1982).

[9]A. Furrer, W. Bührer, and P. Wachter, in *Valence Instabilities—1982 (Zürich),* edited by P. Wachter and H. Boppart (North-Holland, Amsterdam, 1982), p. 319.

[10]O. Pena, thesis (Grenoble, 1980) (unpublished).

[11]R. P. Guertin, S. Foner, and F. P. Missell, Phys. Rev. Lett. 37, 529 (1976).

[12]F. Lapierre, P. Haen, B. Coqblin, M. Ribault, and F. Holtzberg, Physica B 108, 1351 (1981).

[13]C. Vettier, J. Flouquet, J. M. Mignot, and F. Holtzberg, J. Magn. Magn. Mater. 15–18, 987 (1980).

[14]D. Debray, R. Kahn, D. L. Decker, A. Werner, M. Loewenhaupt, E. Holland-Mortiz, and D. K. Ray, in *Valence Fluctuations in Solids,* edited by L. M. Falicov, W. Hanke, and M. B. Maple (North-Holland, Amsterdam, 1981), p. 183.

[15]M. Ribault, J. Flouquet, P. Haen, F. Lapierre, J. M. Mignot, and F. Holtzberg, Phys. Rev. Lett. 45, 1295 (1980).

[16]B. Batlogg, H. Boppart, E. Kaldis, D. B. McWhan, and P. Wachter, in Ref. 9, p. 523.