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ANTIFERROMAGNETISM OF THE HEXAGONAL LAVES PHASE $ThMn_2$ □

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Magnetization, thermal expansions and neutron diffraction measurements have been performed on $ThMn_2$. Below T_N, one Mn atom (2a) in four remains nonmagnetic whilst the others order in a triangular configuration. The large anisotropic thermal expansions effects minimize the frustration of the Mn–Mn interactions.

1. Introduction

$ThMn_2$ crystallizes in the hexagonal Laves phase ($P6_3/mmc$). Mn atoms which lie on two nonequivalent sites (6h and 2a) are located at the top of a regular tetrahedron which form chains along the six fold axis. Owing to the smooth thermal variation of the magnetic susceptibility, $ThMn_2$ has been previously reported to be a Pauli paramagnet [1]. In fact careful measurements show a maximum in the results of the susceptibility which occurs at $T_N = 115$ K [2]. In this paper we report thermal expansion and neutron diffraction measurements.

2. Experimental and results

The sample was prepared by induction melting and was subsequently annealed for three days at 840 °C. Powder X-ray diffraction measurements were carried out between 2 and 300 K, using $CrK\alpha_1$ radiation ($\lambda = 2.2896$ Å). Neutron diffraction experiments were performed using a multidetector spectrometer with a neutron wave length $\lambda_N = 2.503$ Å in the Grenoble Nuclear Center.

For all temperatures, the crystallographic structure remained hexagonal. The thermal variations of the a and c lattice parameters, deduced from the Bragg angle of the (220) and (313) reflections are shown in fig. 1. Below $T_N = 115$ K, anomalous thermal expansion effects are observed for both the a and c parameters. As the temperature decreases, the c parameter contracts, whilst a expands. The relative changes of a and c extrapolated to 0 K are $\Delta a/a = 0.09\%$ and $\Delta c/c = -0.13\%$ respectively. However no significant volume anomaly is observed. Above T_N, the volumetric thermal expansion coefficient $\beta_V = (1/V)\,\Delta V/\Delta T$ is 0.8×10^{-4}/K which is twice as large as that observed in YCo_2 and YNi_2 compounds [3].

Several neutron diffraction patterns were obtained above and below $T_N = 115$ K. Above 115 K (fig. 2) the pattern contains only nuclear peaks. Consistent with the Laves phase structure, the agreement between the calculated and observed structure factors, using $b_{Mn} = -0.36 \times 10^{-12}$ cm and $b_{Th} = 0.98 \times 10^{-12}$ cm, was $R = 6\%$ where $R = |\Sigma I_{obs} - I_{cal}|/\Sigma I_{obs}$. Below T_N extra peaks

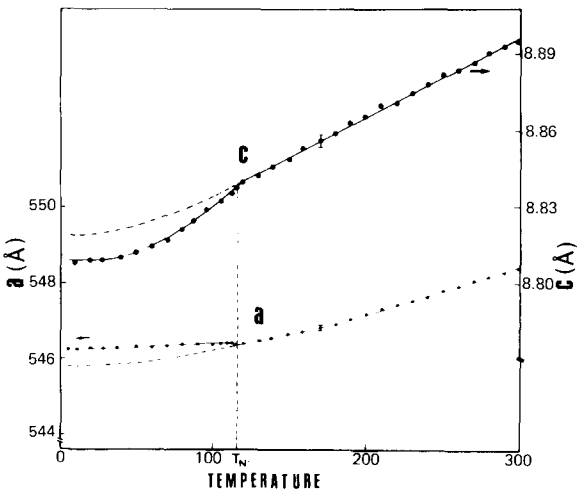

Fig. 1. $ThMn_2$. Thermal dependence of the lattice parameters determined from the (220) and (313) reflections.

□ Part of the B. Ouladdiaf's thesis.

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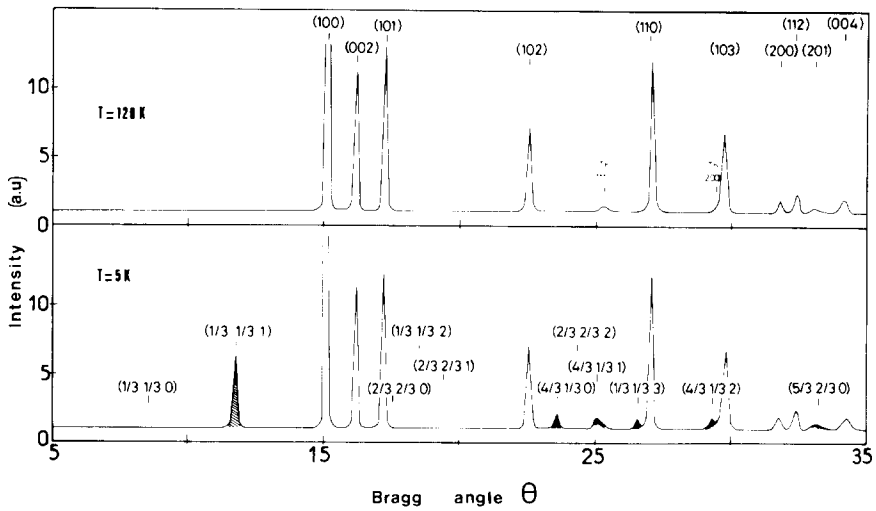

Fig. 2. Neutron diffraction pattern of $ThMn_2$ performed at 120 and 5 K with wave length $\lambda = 2.503$ Å. The magnetic peaks are hatched.

appear, their intensities increasing as the temperature is decreased. All the observed magnetic peaks can be indexed using the propagation vector $\boldsymbol{K} = [\frac{1}{3}\,\frac{1}{3}0]$. The absence of the $(\frac{1}{3}\,\frac{1}{3}0)$, $(\frac{2}{3}\,\frac{2}{3}0)$, $(\frac{1}{3}\,\frac{1}{3}2)$, $(\frac{2}{3}\,\frac{2}{3}1)$ and $(\frac{2}{3}\,\frac{2}{3}2)$ magnetic reflections indicates that along a chain of Mn tetrahedrae, the manganese atoms which are at $z = 0$ and $z = \frac{1}{2}$ are nonmagnetic. Furthermore the moments of the three manganese atoms in the 6h site which are at $z = \frac{1}{4}$ are coparallel and antiparallel to the three other manganese atoms at the same site but which are at $z = \frac{3}{4}$. Since $\boldsymbol{K} = [\frac{1}{3}\,\frac{1}{3}0]$, the direction of the moments rotates through an angle $2\pi/3$ from chain to chain. The projection into the basal plane of the magnetic structure is shown in fig. 3. The calculated and observed magnetic intensities are in

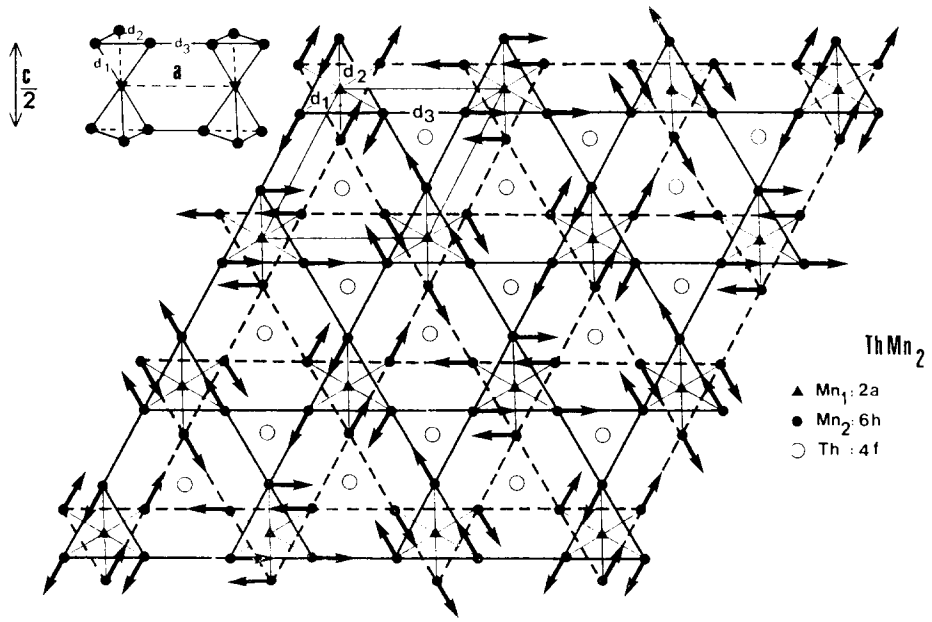

Fig. 3. Projection into the basal plane of $ThMn_2$ magnetic structure. Only Mn (6h) site are magnetic.

good agreement, with a reability factor $\Sigma | I^M_{obs} - I^M_{cal} | / \Sigma I^M_{obs}$ of 5.5% yielding a moment $m = (1.6 \pm 0.1)\mu_B$ for the manganese atoms on the 6h site.

3. Discussion

$ThMn_2$ orders antiferromagnetically below $T_N = 115$ K. The magnetic structure can be described as a stacking of magnetic atomic layers, perpendicular to the *c* axis, which are antiferromagnetically coupled. In each layer the magnetic arrangement shows two types of magnetic coupling: parallel alignment between Mn moments belonging to the same tetrahedron and triangular coupling between Mn moments belonging to the neighbouring chains. These properties enable the anomalous thermal expansion to be understood because of the strong dependence of the magnetic interaction with Mn–Mn distances [4]. In the paramagnetic state the Mn tetrahedrons are regular so that all the Mn–Mn nearest neighbour distances are equal with a value of 2.75 Å at 120 K. In α-Mn, the corresponding interactions are weakly negative and strongly dependent on interatomic distance [4]. In $ThMn_2$ due to the presence of exchange rings involving odd numbers of Mn interatomic distances, any antiferromagnetic ordering is frustrated. The nonmagnetic state of the Mn(2a) atoms reduce this frustration without requiring any change of the Mn(2a)–Mn(6h) distance (d_1 in fig. 3). The anomalous decrease of the c parameter arises from the increase of the d_2 interatomic distance between 6h atoms ($\Delta d_2/d_2 = -2\ \Delta c/c = 0.26\%$); such an increase reduces the negative interactions which are strongly frustrated because of the ferromagnetic coupling. The anomalous increase of the *a* parameter ($\Delta a/a = 0.09\%$) is less than $\Delta d_2/d_2 = 0.26\%$, since in order to improve the repartition of the frustrated energy in the 6h magnetic layers, the d_3 distance decreases ($\Delta a = \Delta d_1 = \Delta d_2$ and $\Delta d_3/d_3 = -0.06\%$) enhancing the negative interactions.

In conclusion the frustration of the magnetic interactions, which is inherent owing to the topology of the magnetic atomic arrangement, leads in $ThMn_2$ to:

i) The nonmagnetism of 2a Mn atoms
ii) A triangular configuration of the 6h magnetic moments between neighbouring chains.
iii) Large and anisotropic anomalous thermal expansion effects.

As in YMn_2, such frustration should give rise to magnetic short range ordering in the paramagnetic state. The progressive vanishing of this short range ordering when the temperature increases could favour an increase in the local amplitude of the 3d magnetization (e.g. on the 2a site). The study of the thermal variation of the paramagnetic neutron scattering will soon be performed at I.L.L.

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