Classification
Physics Abstracts
8.530

MAGNETIC STUDIES ON THE METALLIC PEROVSKITE-TYPE COMPOUND Mn_3SnN

D. FRUCHART and E. F. BERTAUT

Laboratoire de Cristallographie, C.N.R.S.,
166 X, 38042 Grenoble Cedex, France

and

Laboratoire de Diffraction Neutronique, C.E.N.-G.,
85 X, 38041 Grenoble Cedex, France

J. P. SÉNATEUR and R. FRUCHART

E.R. 155, I.N.P.G., Section de Génie Physique,
15 X, 38040 Grenoble Cedex, France

(Reçu le 17 septembre 1976, accepté le 27 octobre 1976)

Résumé. — Le composé métallique Mn_3SnN de structure-type pérovskite présente quatre phases cristallographiques et magnétiques ordonnées différentes. Les expériences de diffraction neutronique, les mesures magnétiques et la spectroscopie Mössbauer effectuées en fonction de la température font apparaître un comportement critique des propriétés magnétiques révélant l'existence de singularités dans la densité d'états.

Abstract. — Mn_3SnN is a metallic compound of perovskite-type structure which shows four different crystallographic and magnetically ordered phases. From neutron diffraction data, magnetic measurements and Mössbauer experiments performed at different temperatures it is concluded that the magnetic properties depend critically on the existence of singularities in the density of states.

1. Crystallographic and magnetic properties. — The metallic compound Mn_3SnN with perovskite-type structure shows four different crystallographic and magnetic phases. First-order transitions occur at $T_{t_1} = 186$ K, $T_{t_2} = 237$ K, $T_{t_3} = 357$ K. The transition at $T_c = 475$ K is second-order, the compound becoming paramagnetic and cubic. With increasing temperature we observe the successive crystallographic distortions :

$$T_{t_1} \xrightarrow{+} T_{t_1} \xrightarrow{(T_{t_1})'} T_{t_2} \xrightarrow{-} T_{t_3} \xrightarrow{+} T_c \xrightarrow{-}$$

$T_{t_1}^+$ indicates a quadratic distortion with $c/a > 1$, C a cubic cell and $T_{t_1}^-$ a quadratic distortion with $c/a < 1$ (Fig. 1a).

The compound has been studied by magnetic measurements in low (Fig. 1b) and high static fields, by paramagnetic susceptibility torque, neutron diffraction and Mössbauer effect on ^{119}Sn (Fig. 1c). A very weak magnetization ($< 10^{-2} \mu_B/\text{mole}$) vanishes between T_{t_3} and T_c , while a weak magnetization of $0.1 \mu_B/\text{mole}$ characterizes the $T_{t_1}^+$ quadratic phases. T_{t_1} is a magnetic compensation point (Fig. 1b). The

thermal variation of the paramagnetic susceptibility $\chi(T)$ may be analyzed as the sum of a Curie-Weiss like term and a temperature independent term. This corresponds to a Pauli type component [1] which has here the largest value ($\simeq 3 \times 10^{-3} \text{ uem/Oe/mole}$) measured in the series Mn_3MX ($X = \text{C}$ or N ; $M = \text{Ni, Cu, Zn, Ga, Ge, Rh, Ag, Sn, Sb, Pt}$). Above T_c incoherent neutron paramagnetic scattering is very weak ; this implies a loss of the magnetic moment localized on the manganese atoms. This is confirmed by the Mössbauer effect at the ^{119}Sn nucleus. When the temperature increases we observe an important decrease of the hyperfine field(s) which already in the 100-170 K range of temperature drops sharply (Fig. 1c). Magnetic measurements below 475 K in static fields as large as 15 T, performed at the *Service National des Champs Intenses* show that saturation is far from being reached. The M versus H curves characterize mainly the thermal behaviour of weak magnetizations previously described on figure 1b. Exchange interactions seem to be approximately equivalent to 200 T [2].

FIG. 1. — *a*) Thermal behaviour of the crystallographic parameters and the unit cell volume. *b*) Magnetization curves in low fields. *c*) Hyperfine fields measured at the ^{119}Sn nucleus by the Mössbauer effect. *d*) Thermal behaviour of different magnetic moments on the manganese atoms. The full circles show the $\text{Mn}_{1,2}$ moments in the T_1^+ and T_1^- phases. At low temperatures they are the sum of a sinusoidal ($\sim$) and a non-colinear ($-$) component. The crosses represent the behaviour of the Mn_3 moment in these phases. Triangles are used in the cubic triangular antiferromagnetic phase for $\text{Mn}_{1,2,3}$.

2. Magnetic ordering. — Between T_3 and T_c the magnetic configuration is colinear; we measure at 387 K per atom : $M_1 = M_2 = 1.3 \mu_B$ for Mn at $0 \frac{1}{2} \frac{1}{2}$ and $\frac{1}{2} 0 \frac{1}{2}$ and (antiparallel) $M_3 \simeq 2.6 \mu_B$ for Mn at $\frac{1}{2} \frac{1}{2} 0$. We cannot determine the direction of the easy axis of magnetization; in the group $P4/\text{mm}$, the group theoretical analysis authorizes either $[001]$ in the irreducible representation Γ_g^2 or $[110]$ in Γ_g^5 . The response of the neutron diffraction data to vertical magnetic fields is also negative.

Between T_2 and T_3 the compound shows a triangular antiferromagnetic ordering. In the (111) plane we observe a rotation of the manganese spins between modes belonging to the Γ_g^5 and Γ_g^4 cubic irreducible representations, respectively. Simultaneously a very weak ferromagnetic component arises along the $[111]$ axis. Previously such a process had been encountered and analyzed in Mn_3NiN and Mn_3AgN [3, 4]. To explain the spin reorientation we write a phenomenological hamiltonian $H_m = H_a + H_e$ where H_a is the magneto-crystalline energy in the (111) plane and H_e the anisotropic exchange energy. The thermal variations of anisotropic exchange and magneto-crystalline coefficients K_i entail such a phenomenon. In figure 2 we have plotted the thermal variations of the magnetic moment of manganese as determined

FIG. 2. — By neutron diffraction we measure ϕ , the rotation of the triangular arrangement in the (111) plane, and we report also the magnetic moment on manganese. The weak magnetization (w.m.) is represented by heavy circles.

by neutron diffraction, of the weak magnetization and finally of ϕ and $\sin \phi$ where ϕ is the angle of the spin rotation in the (111) plane. The proportionality between the weak magnetization and $\sin \phi$ confirms the results of the hamiltonian minimization with respect to ϕ [3].

At low temperature neutron diffraction patterns show a complex magnetic ordering which could be resolved with the D_{1B} high resolution multi-counter of the *Institut Laue Langevin*. The magnetic ordering has two components : an α -component which is colinear along $[001]$, sinusoidal of long periodicity, on the $\text{Mn}_{1,2}$ spins, a β -component which is non colinear, nearly antiferromagnetic in the (001) plane on the $\text{Mn}_{1,2,3}$ spins. These components exist in the two T_1^+ phases but with different values. From the group theoretical analysis of the G_k group $P4/\text{mm}$ we derive a model in the irreducible representation Γ^4 for the β -component and Γ^5 for the α -component. The models are described in figure 3. The magnetic wave-vector $k = [0, 0, k_z]$ of the sinusoidal component changes with temperature. Figure 4 shows this thermal variation and those of some magnetic intensities. We can see that the important variation of the hyperfine fields at the ^{119}Sn nucleus (Fig. 1c) begin-

FIG. 3. — Low temperature magnetic ordering determined at 50 K ($k_z \approx 0.25$) left-hand side and at 217 K ($k_z \approx 0.15$) (right-hand side).

ning at 80 K is followed at 120 K by a sharp decrease of k_z and at $T_{t1} = 186$ K, by the crystallographic transition $T_1^+ \rightarrow (T_1^+)^-$. However the unit cell volume varies continuously, increasing slowly with temperature. Figure 1d represents the thermal variation of the magnetic moment of the manganese atoms. If we assume that an electron transfer is responsible for the hyperfine field behaviour and for the decrease of k_z and c/a , the effect is mainly visible on the Mn_1 and Mn_2 atoms. Indeed knowing the magnetic structure, the Mn_3 environment of Sn atoms cannot give rise to two kinds of ^{119}Sn hyperfine fields; this is only possible if there is a sinusoidal component

FIG. 4. — Thermal behaviour of k_z and some magnetic intensities.

and if this spin density wave has no maxima on the $\text{Mn}_{1,2}$ atoms themselves. According to figure 1d the β -component varies continuously with temperature; this is not the case for the variation of the α -component which decreases abruptly at T_{t1} . In the entire range of temperature studied the shortest distances Mn-Sn correspond to a nearly continuous decrease of the magnetic moment of manganese atoms (Fig. 1d).

According to the band model proposed by Jardin and Labbé [5] there is a very sharp peak near the Fermi level in the density of states. This singularity could explain the nature of the structural phase transitions produced by a Jahn-Teller type effect; the relative positions of subbands and also the magnetic moment of manganese change consequently probably by a $s \leftrightarrow d$ electron transfer.

In conclusion we assume that in the Mn_3MX series indirect exchange interactions by means of itinerant electrons are very important if the metal M is responsible for a large contribution to the band conduction. This is the case with $\text{M} = \text{Sn}$ which has a high valency and the main influence of the temperature is to reduce this band effect. We observe similar transformations in solid solutions of metallic perovskite-like compounds when the valence number of M changes [2]; crystallographic and magnetic properties of the compounds change simultaneously.

References

- [1] FISHER, G., MEYER, A., *Solid State Commun.* **16** (1975) 335.
- [2] FRUCHART, D., *Doct. Etat Thesis-Univ. of Grenoble* (1976).
- [3] BERTAUT, E. F., FRUCHART, D., *Int. J. Mag.* **2** (1972) 259.
- [4] FRUCHART, D., BERTAUT, E. F., FRUCHART, E., BARBERON, M., LORTHIOIR, G., FRUCHART, R., *Proc. Int. Conf. on Magnetism, Moscow, IV* (1973) 572.
- [5] JARDIN, J. P., LABBÉ, J., *J. Physique* **36** (1975) 1317.