Antiferromagnetic properties of MnGa2Se4-α

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Antiferromagnetic properties of $MnGa_2Se_4$-α

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Résumé. — On a préparé par transport en phase vapeur des monocristaux du composé ternaire $MnGa_2Se_4$-α. Les mesures de susceptibilité et d'aimantation établissent que ce composé s'ordonne antiferromagnétiquement au-dessous de 7 K. La température de Curie-Weiss est de -23 ± 2 K ; le moment effectif par manganèse, de $6{,}0 \pm 0{,}1\ \mu_B$ correspond à des ions de Mn^{2+}. Les mesures de chaleur spécifique établissent que la transition est du second ordre et que la température de Néel est $T_N = 6{,}4 \pm 0{,}1$ K ; l'entropie de la transition est aussi en bon accord avec des moments magnétiques correspondant à Mn^{2+}. La variation thermique de la largeur de raie RPE et les courbes de chaleur spécifique indiquent que l'ordre magnétique à courte distance persiste à des températures bien supérieures à T_N. Les diagrammes de diffraction neutronique sur poudre sont en accord en ce qui concerne la structure cristallographique avec des résultats antérieurs obtenus aux rayons X ; de plus, ils établissent que les cations Mn et Ga sont bien ordonnés sur les sites tétraédriques ; à basse température, plusieurs réflexions magnétiques apparaissent. On propose un type possible de structure magnétique. On montre aussi que les couplages magnétiques dus au super-superéchange à travers les liaisons Mn-Se-Ga-Se-Mn sont de l'ordre de 0,1 K à 0,5 K.

Abstract. — Single crystals of the ternary tetragonal manganese chalcogenide $MnGa_2Se_4$-α have been grown by the vapour phase transport technique. Magnetic susceptibility and magnetization measurements establish that $MnGa_2Se_4$-α orders antiferromagnetically below 7 K. The Curie-Weiss temperature is found to be -23 ± 2 K ; the effective magnetic moment per Mn of $6.0 \pm 0.1\ \mu_B$ is consistent with Mn^{2+} ions. The value of the Néel temperature as obtained by specific heat data is $T_N = 6.4 \pm 0.1$ K. The transition is second order with an entropy well accounted for by Mn^{2+} ions. Both the temperature dependence of the EPR linewidth and the specific heat data show that short-range order persists at temperatures much higher than T_N. Powder neutron diffraction data have been collected at several temperatures ; they are consistent with previous X-ray studies and further establish that the cations are well ordered on the tetrahedral sites ; several magnetic reflections are found on the low-temperature spectra ; a possible type of magnetic ordering is proposed. Exchange integrals, involving super-superexchange through Mn-Se-Ga-Se-Mn bonds are estimated to be in the range 0.1 K to 0.5 K.

1. **Introduction.** — $MnGa_2Se_4$ belongs to the series of the ternary manganese chalcogenides of general formula MnA_2X_4 with X being S, Se or Te and A a trivalent metal (Al, Ga or In). Among this family, the crystal structure and the magnetic properties of the sulfide have been recently studied [1] ; two phases, a monoclinic phase, $MnGa_2S_4$-α, and an orthorhombic phase, $MnGa_2S_4$-β, have been prepared and found antiferromagnetic below 23.5 K and 11 K respectively. Up to now, the physical properties of the selenide had never been studied. $MnGa_2Se_4$ powder had been first synthetized in 1976 [2]. As for $MnGa_2S_4$, there are two phases, a low temperature α-phase and a high temperature orthorhombic β-phase [3].

The crystal structure of $MnGa_2Se_4$-α has been found tetragonal, possibly isomorphous with $CdGa_2S_4$, space group $I\bar{4}$, with two chemical formulas per unit cell [2]. The proposed crystal structure is shown in figure 1 ; the cations would be ordered on sites with Se tetrahedral environment. However, one should note that these previous data have been obtained on powder, by X-rays and that the X-ray form factors of Mn and Ga are close to each other, so that the ordering of the cations cannot be determined with a great accuracy. On the contrary, the neutron Fermi lengths are clearly different (-0.37×10^{-12} cm for Mn and $+0.80 \times 10^{-12}$ cm for Ga), so that structural neutron studies could be valuable for this compound.

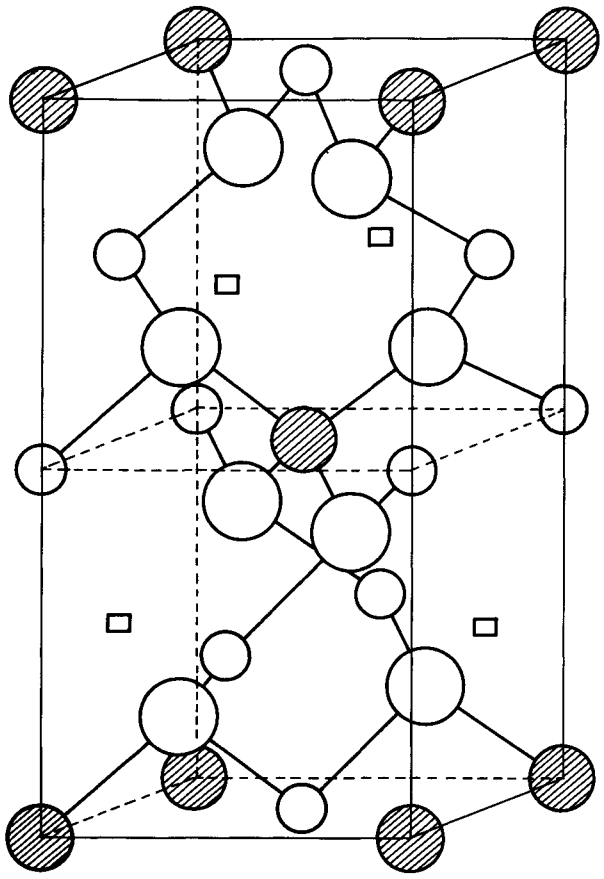

Fig. 1. — Crystallographic structure of $MnGa_2Se_4$-α ▨ Mn ○ Ga ◯ S. The cell is centred tetragonal with two Mn per unit cell (it is shown with the origin on a Mn).

X-ray pattern characteristic of the single phase $MnGa_2Se_4$-α.

As the phase diagram of MnSe-Ga_2Se_3 shows a solid-solid transformation at 924 °C, the single crystals cannot be grown by fusion techniques. We have therefore used the vapour phase transport method although previous attempts had been unsuccessful [2]. Single crystals have been obtained from $MnGa_2Se_4$-α powder with I_2 as transport agent and with a slight excess of Se, in a two-zone furnace with a temperature gradient from 800 °C to 720 °C. The crystals are triangular-shaped needles, orange transparent, typically $3 \times 0.5 \times 0.5$ mm^3; figure 2 shows the orientation of the needles with respect to the crystal axis; the cell parameters, obtained by X-ray patterns are identical to those measured on the starting powder.

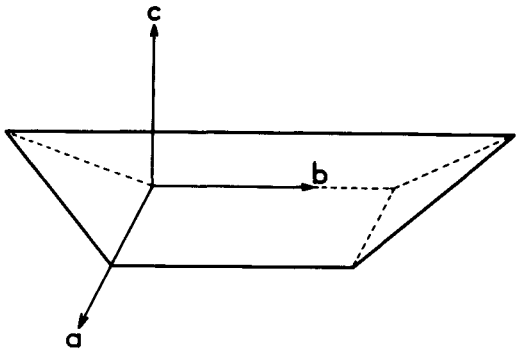

Fig. 2. — Typical shape of the $MnGa_2Se_4$-α single crystals.

We report in this article the preparation of $MnGa_2Se_4$-α and their physical properties. The experimental techniques are described in section 2. The results of magnetization, electron paramagnetic resonance and specific heat measurements as well as neutron studies are reported in section 3. In section 4, we discuss the magnetic properties and the nature of the long-range antiferromagnetic order at low temperature; a possible, but not exclusive, type of magnetic order and approximate values of the exchange integrals are proposed.

2. **Experimental techniques.** — The starting materials for the powder synthesis are Mn, Ga and Se with purities of 99.98 %, 99.99 % and 99.995 %, respectively. The manganese particles are first cleaned with nitric acid, rinsed in distilled water and dried under vacuum. A stoichiometric mixture of the elements is progressively heated up to 900 °C in an evacuated silica cell, kept for one day at 900 °C then slowly cooled down to room temperature; the resulting product is an inhomogeneous material, containing both tetragonal $MnGa_2Se_4\alpha$ and the binary selenides MnSe and Ga_2Se_3. This mixture is then carefully crushed and heated at 800 °C for one week; the final powder is brown-orange and shows an

Magnetic measurements have been performed between 4.2 K and 300 K with a vibrating sample magnetometer, Foner type, equipped with a superconducting coil providing a maximum field of 60 kG. Electron paramagnetic resonance spectra have been obtained with a Thomson-CSF spectrometer at a frequency of 9 GHz, between 7 K and 300 K. The specific heat has been measured on small single crystals between 2 K and 140 K with a microcalorimeter using a relaxation technique as described elsewhere [4].

Neutron powder diffraction experiments have been performed on the DN5 diffractometer of Siloe Reactor at Centre d'Etudes Nucléaires de Grenoble using a wavelength of 1.61 ± 0.01 Å, provided by a germanium monochromator.

3. **Results.** — The reciprocal magnetic susceptibility $1/\chi$ measured on powder is shown *vs.* temperature in figure 3 ; it follows a Curie-Weiss law $\chi = C/T - \theta$ between 12 K and 300 K with a Curie constant C of 4.5 ± 0.1 emu/mole and a Curie-Weiss temperature θ of − 23 ± 2 K. The value of C corresponds to an effective magnetic moment per Mn of 6.0 ± 0.1 μ_B consistent with the Mn^{2+} free ion value (electronic configuration $3d^5$, $S = 5/2$, $\mu_{eff} = 5.92\ \mu_B$).

Single crystals data are shown on figure 4 for the

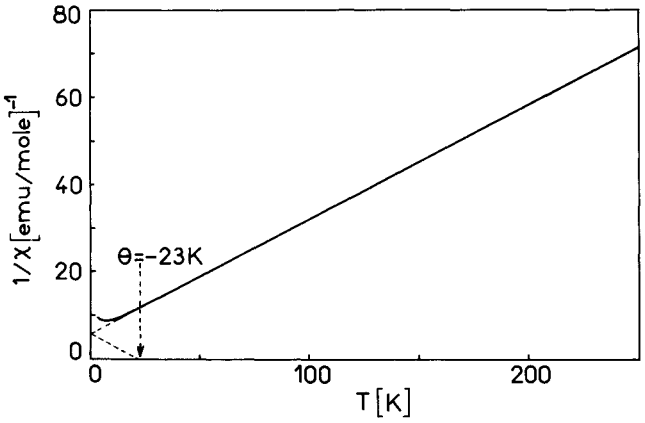

Fig. 3. — Reciprocal magnetic susceptibility measured on powder *vs.* temperature.

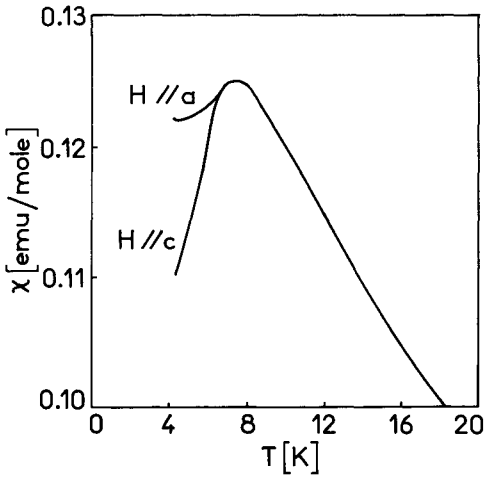

Fig. 4. — Susceptibility measured on a single crystal *vs.* temperature.

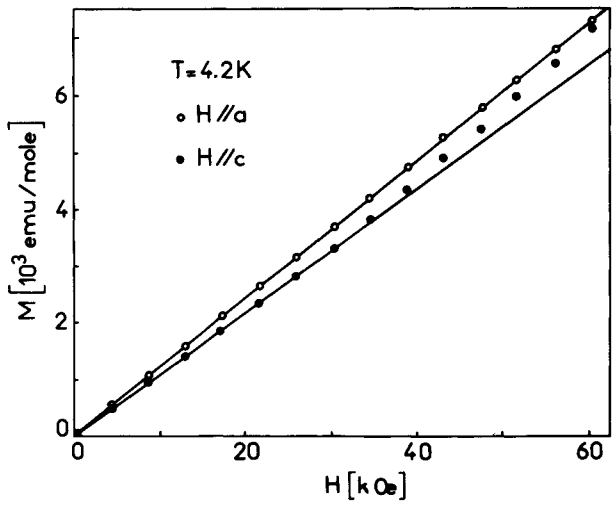

Fig. 5. — Magnetization *vs.* magnetic field at $T < T_N$ (T = 4.2 K).

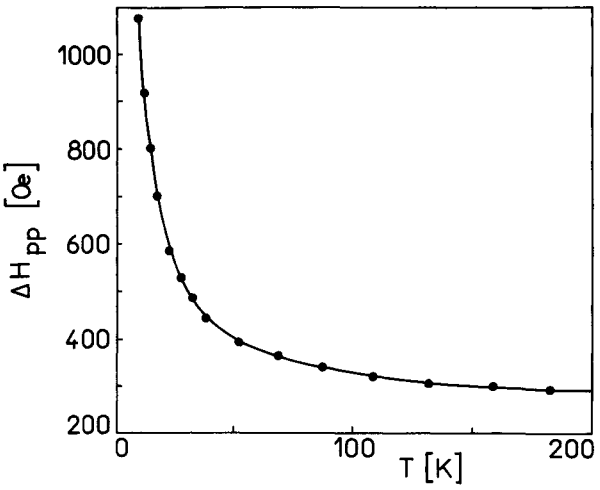

Fig. 6. — EPR peak-to-peak linewidth *vs.* temperature.

low temperatures; the susceptibility exhibits a broad peak centred at 7 ± 0.5 K; below ~ 6.2 K, it is strongly anisotropic, with a slow decrease of χ along the *a*-axis and a steep decrease along the *c*-axis. This behaviour is characteristic of an antiferromagnet with a Néel temperature close to 7 K.

The magnetization M has been measured *vs.* field at 4.2 K in fields up to 60 kG (Fig. 5); while the curve $M(H)$ is always linear for $H//a$, it shows a slight deviation from linearity for $H // c$ above ~ 30 kOe; this is also characteristic of an antiferromagnet.

For $T > T_N$, the EPR spectra consist of a single Lorentzian line, with a *g*-value of 2.0; the peak to peak linewidth is plotted *vs.* T in figure 6; it is found to be ~ 300 Oe at 300 K and increases with decreasing temperature, steeply below ~ 20 K; it seems to diverge close to 7 K (the lowest temperature obtained in the available spectrometer).

The specific heat has been measured at low tempe-

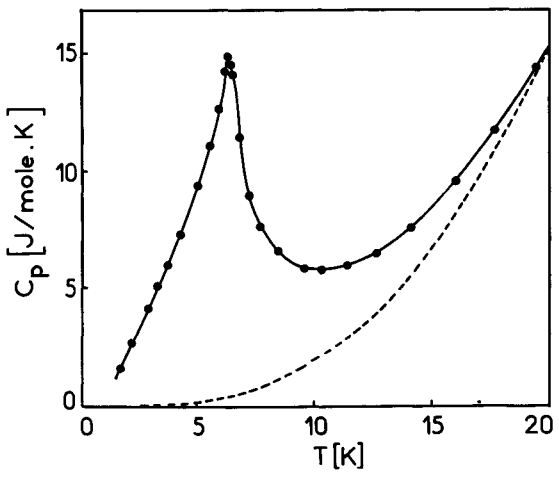

Fig. 7. — Specific heat obtained on a single crystal of 7.23 mg *vs.* temperature. ● Experimental data; - - - Estimated lattice specific heat.

rature on a small single crystal (7.23 mg) (Fig. 7); it shows a sharp peak, with a maximum at

$$T = 6.4 \pm 0.1 \text{ K},$$

clearly related to the antiferromagnetic transition.

Powder neutron data have been collected at 300 K, 77 K, 15 K, 4.2 K and 3 K. Figures 8*a* and 8*b* show the spectra obtained at 300 K and 4.2 K, respectively; extra magnetic lines are clearly seen on the 4.2 K spectrum.

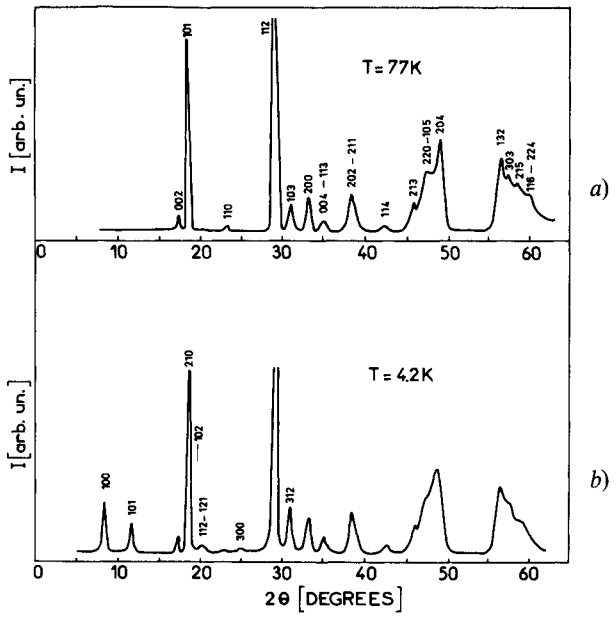

Fig. 8. — Neutron powder diffractograms (*a*) $T = 77$ K; (*b*) $T = 4.2$ K. Only the magnetic reflections or those including a magnetic contribution are indexed in the magnetic cell ($2a\ 2a\ c$).

3.1 STRUCTURAL REFINEMENT. — The lattice parameters at 300 K are found to be : $a = 5.686(6)$ Å, $c = 10.798(6)$ Å, slightly different from the values obtained with powder X-ray data ($a = 5.676(2)$ Å and $c = 10.760(3)$ Å, in Ref. [2]). No significative change of these parameters is found at 77 K.

Table I shows the measured and calculated intensities for the first 24 reflections at 77 K. The structure has been refined with these 24 reflections with the assumption that the space group was $I\bar{4}$; an *R*-factor of 0.020 was found; no more symmetrical space group is consistent with the data. The position parameters of the Se (8g), (given in the X-ray International Table unit cell with the origin on Ga(1)), were found to be :

$$x_{Se} = 0.251(3), \quad y_{Se} = 0.275(6), \quad z_{Se} = 0.117(1)$$

roughly consistent with the data of reference [2] ($x_{Se} = 0.244, y_{Se} = 0.265, z_{Se} = 0.117$).

The cations are found ordered on the special positions : 2 Ga(1) on 2*a*, 2 Ga(2) on 2*c* and 2 Mn on 2*d*. Only the Mn site occupation factor allows a slight deviation from stoichiometry (3 %) which could correspond to a substitution by Ga atoms.

Table I. — *Powder neutron data, observed* I_o *and calculated* I_c *(in barns) intensities at* 77 K.

$h\,k\,l$	I_o	I_c
0 0 2	3.27	3.25
1 0 1	54.12	54.05
1 1 0	2.13	1.77
1 1 2	331.00	331.20
1 0 3	42.85	41.90
2 0 0	63.20	63.30
0 0 4, 1 1 3	26.25	26.30
2 0 2, 2 1 1, 2 $\bar{1}$ 1	107.25	110.35
1 1 4	18.70	12.70
1 2 3, 1 $\bar{2}$ 3, 1 0 5, 2 2 0, 2 0 4	836.40	820.60
1 3 2, 1 $\bar{3}$ 2, 3 0 3, 2 1 5, 2 $\bar{1}$ 5, 1 1 6, 2 2 4	942.50	962.30

These data corroborate the X-ray analysis given in [2] and that $MnGa_2Se_4$ is isomorphous with $CdGa_2S_4$.

In order to study the magnetic structure at low temperature, data were also collected at 4.2 K with $\lambda = 2.47$ Å; the tetragonal lattice parameters obtained are : $a = 5.656(5)$ Å, $c = 10.765(5)$ Å. No lattice distortion at low temperature could be detected with the corresponding refinement.

3.2 MAGNETIC STRUCTURE. — The magnetic reflections (Fig. 8*b*) can be indexed with the propagation vector *k*, either [1/2 0 0] or [1/2 1/2 0]. Since no lowering of the lattice symmetry could be detected below the ordering temperature, we have chosen the propagation vector [(1/2 1/2 0)] which allows more general and complex magnetic arrangements. The magnetic cell therefore contains eight magnetic atoms.

Let us label the spins in the magnetic cell :

S_1 on	0	0	0	S_5	1/4	1/4	1/2
S_2	1/2	0	0	S_6	3/4	1/4	1/2
S_3	0	1/2	0	S_7	1/4	3/4	1/2
S_4	1/2	1/2	0	S_8	3/4	3/4	1/2.

The extinction rules for the magnetic reflections lead for the components $S_{i\perp}$ of the spin S_i in the **a**, **b**

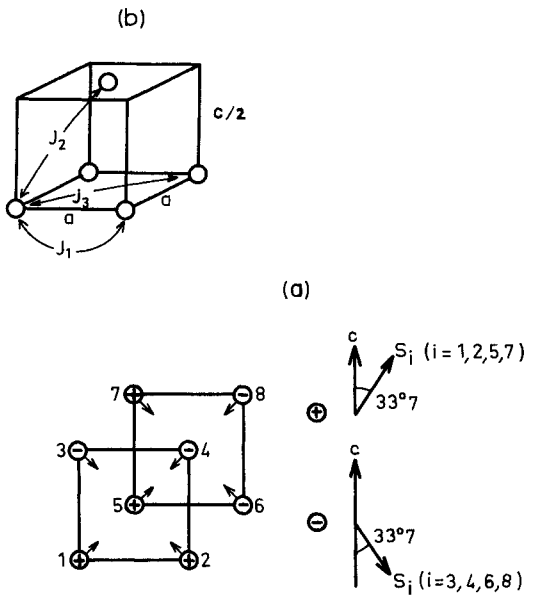

Fig. 9. — *a*) Possible non-collinear magnetic structure. The spins make an angle of 33.7° with *c*; *b*) Scheme showing the three exchange interactions.

plane to the following relations :

$$S_{1\perp} = -S_{4\perp} \qquad S_{2\perp} = -S_{3\perp}$$
$$S_{5\perp} = -S_{8\perp} \qquad S_{6\perp} = -S_{7\perp}.$$

This set of relations derived from powder sample diffraction does not allow a unique determination of the magnetic structure and different collinear and non-collinear arrangements lead to the same calculated values of the magnetic intensities. Quite a similar situation and comparable types of arrangements have been described by M. Wintenberger on the compound Cu_2FeGeS_4 (space group $I\bar{4}2m$) [5]. In our case, the easy axis in the (001) plane may be either [100] or [110], but the angle between the spins and the c-axis is found to be roughly $\phi = 33.7°$. Figure 9 shows however one of the possible types of ordering for the S_i components, with 90° couplings between each other. The *z*-components, positive or negative, are also indicated.

The values of the magnetic moment, deduced from the data at 4.2 K and 3 K are :

$$\mu\,(4.2\text{ K}) = 3.62 \pm 0.15\ \mu_B$$
$$\mu\,(3\text{ K}) = 4.50 \pm 0.15\ \mu_B.$$

Assuming a Brillouin curve with $S = 5/2$ for $\mu(T)$, this corresponds, with a Néel temperature close to 7 K, to a value extrapolated to 0 K : $\mu(0\text{ K}) = 4.8\ \mu_B$; this is roughly consistent with the values of $5\ \mu_B$ expected for Mn^{2+}.

Table II shows the measured magnetic intensities compared with the values calculated with the configuration of figure 9; the agreement is satisfactory. However, neutron diffraction performed on a single crystal would be necessary in order to determine uniquely the magnetic structure.

Table II. — *Magnetic intensities observed* (I_o) *at* 4.2 K *and calculated* (I_c) *using* $\mu = 3.62\ \mu_B$ *with the configuration of figure* 9 (2*a*, 2*a*, *c unit cell*).

h k l	I_o	I_c
0 0 1	0.0	0.0
1 0 0	35.90	31.35
1 1 0	0.0	0.0
1 0 1	32.80	39.25
1 1 1	0.0	0.0
2 0 0	0.0	0.0
0 0 2	0.0	0.0
2 1 0	34.85	39.60
1 0 2	27.85	24.60
1 1 2 / 1 2 1	66.55	68.35
3 0 0	30.05	23.30
3 1 0	0.0	0.0
3 1 2	55.75	50.15

4. **Discussion.** — All the data obtained on $MnGa_2Se_4$-α are clearly consistent with a long-range antiferromagnetic ordering taking place below 7 K.

The temperature of the maximum of the specific heat is found to be slightly lower than that of the susceptibility; this result is usual and well accounted for by theories taking into account the existence of short-range order above the peak of $C_p(T)$ [6, 7]. The Néel temperature is given by the maximum of C_p and should correspond to the maximum of the temperature derivative of the parallel susceptibility. In our case, both data establish that the Néel temperature is $T_N = 6.4 \pm 0.1$ K.

In order to analyse the curve $C_p(T)$ and the entropy of the magnetic transition, one must first evaluate the lattice contribution to the specific heat; this could be done if the low temperature specific heat of a non magnetic isomorphous compound was known; this does not seem to be the case. We have therefore assumed in a rough approximation, that the magnetic contribution is negligible at $T \sim 20$ K and that the Debye law is well obeyed at this temperature; the Debye temperature is then found to be $\theta_D \simeq 190$ K; the lattice specific heat estimated by this method is shown on Figure 7. The magnetic entropy can then be evaluated from the two curves of figure 7 and is found to be $\Delta S_{magn} \simeq 13$ J/mole K; this is consistent with the theoretical value :

$$\Delta S_{magn} = R\,\text{Log}\,(2S + 1) =$$
$$= 14.9\text{ J/mole K for } Mn^{2+}(S = 5/2)$$

taking into account the large uncertainty on the lattice contribution.

The specific heat curve indicates that the transition

is close to a lambda-type transition and therefore second order. However, one may evaluate that approximately 30 % of the magnetic entropy is gained above the Néel temperature; this shows that short-range order persists at temperatures much higher than the ordering temperature.

The EPR line, with a g-value of 2.00 is consistent with Mn^{2+} ions. At room temperature, the line is exchange-narrowed; the progressive increase of the linewidth below 300 K is consistent with three-dimensional antiferromagnetic interactions [9, 10]. The steep broadening below $\sim$ 50 K is due to the critical fluctuations above T_N. It also indicates that short-range order persists at temperatures much higher than the Néel temperature, as shown by the specific heat data.

The magnetic couplings in $MnGa_2Se_4\alpha$ are super-superexchange interactions through both the Ga cations and the Se in zigzag bonds Mn-Se-Ga-Se-Mn. From the EPR linewidth at room temperature, one may estimate the average value J of the exchange integrals; the exchange narrowed width is expected to be [8] :

$$\Delta H_{1/2} = \frac{10}{3} \frac{\Delta H_{dip}^2}{H_{exch}}$$

where ΔH_{dip} would be the linewidth due to dipolar couplings and H_{exch} the exchange field; the average dipolar field in $MnGa_2Se_4$-α is found to be $\sim$ 710 Oe; with a peak-to-peak linewidth of 270 Oe at 300 K, the exchange field is then of the order of 3.6 kOe. This corresponds to an approximate value for $\langle J \rangle$ of 0.5 K.

In a first approximation, one may consider three types of Mn-Mn exchange interactions, J_1 along the a-axis, between the corner spins (Mn-Mn distance of 5.7 Å), J_2 along the [111] direction between the corner and body centre ones (Mn-Mn = 6.7 Å) and J_3 along [110] between the corner ones (Mn-Mn = 8.0 Å) (Fig. 9). Considering the experimental values of the Curie-Weiss and Néel temperatures and the stability conditions of the magnetic structure, one may obtain more information on the signs and values of these exchange integrals [11, 12, 13]. This has been done in [11] and [12] for rutile-type tetragonal lattices, but not for the $MnGa_2Se_4$-α-type lattice.

In the molecular field theory, for the centred quadratic lattice of $MnGa_2Se_4$-α, the Curie-Weiss temperature is expected to be :

$$\theta = \tfrac{2}{3} S(S+1)(4J_1 + 8J_2 + 4J_3)$$

which corresponds to :

$$J_1 + 2J_2 + J_3 \sim -1\,\mathrm{K}\,.$$

By performing a Fourier transform on the exchange hamiltonian, one defines the quantity :

$$\xi(\mathbf{k}) = \sum_i J_i \exp i(\mathbf{k}.\mathbf{R}_i)$$

where $\mathbf{k}(hkl)$ is a reciprocal vector and $\mathbf{R}_i$ the position of the relevant magnetic atom in the chemical cell [11]. In the case of $MnGa_2Se_4$-α, this leads to :

$$\xi(k) = 2J_1(\cos 2\pi h + \cos 2\pi k) + 8J_2 \cos \pi h \cos \pi k \cos \pi l + 4J_3 \cos 2\pi h \cos 2\pi k\,.$$

If $\mathbf{k}_0$ is the propagation vector of the magnetic structure, it may be shown that :

$$\xi(k_0) = \frac{3}{2S(S+1)} kT_N\,.$$

Using the neutron results for $\mathbf{k}_0$, [1/2, 1/2, 0], one then obtains :

$$\xi(\mathbf{k}_0) = 4(J_3 - J_1)$$

and

$$J_3 - J_1 = \frac{3}{70} T_N \simeq 0.3\,\mathrm{K}\,.$$

It is not possible in this context to obtain an additional equation which would allow us to obtain the three exchange integrals. However, from the stability conditions which assign $\mathbf{k}_0$ to be the reciprocal vector which maximizes $\xi(\mathbf{k})$, one derives several inequations; in our case, these are :

$$J_2 > J_1 - 2J_3 \quad \text{and} \quad J_1 - 2J_3 < 0\,.$$

On the other hand, the possible magnetic configurations allowed by the neutron data establish that :

$$J_3 < 0\,.$$

One deduces : $J_1 < 0$ and $|J_1| > 2|J_3|$.

This agrees with $J_3 - J_1 \simeq 0.3$ K and indicates that :

$$|J_3| \quad \text{and} \quad |J_1|/2 < 0.3\,\mathrm{K}\,.$$

All these considerations are consistent with exchange interactions which are in the range 0.1 K-0.5 K. One should point out that these interactions involve four bonds through the Ga and Se between the magnetic ions.

The orientation of the spins at 33.7° of the c-axis (54.3° of the ab plane) is connected to the magnetic anisotropy. For Mn^{2+} ions, in S-states, the single-ion anisotropy must be negligible and the anisotropy should very likely be attributed to the dipolar couplings. One may note that the spin orientation involves roughly the magic angle $\theta_c = 54.7°$ characteristic of the dipolar couplings ($3\cos^2\theta_c - 1 = 0$). Further investigations would be necessary to account for this point.

5. **Conclusion.** — We have reported in this article a rather complete study of a ternary Mn compound,

$MnGa_2Se_4$-α, including structural, magnetization, EPR and specific heat data. This is done, to our knowledge, for the first time in this class of compounds. We have established that $MnGa_2Se_4$-α is an antiferromagnet with a Néel temperature of 6.4 K. We have shown that indirect superexchange integrals which involve four bonds between the magnetic ions through another cation and a chalcogen are in the range 0.1-0.5 K. A possible type of magnetic ordering is also proposed. Single crystal neutron studies and therefore the growth of crystals of a larger size, would now be necessary in order to settle the magnetic structure.

References

[1] RIMET, R., BUDER, R., SCHLENKER, C., ROQUES, R. and ZANCHETTA, J. V., *Solid State Commun.* **37** (1981) 693.

RIMET, R., Thèse de doctorat d'état. Université Scientifique et Médicale de Grenoble (1982).

[2] RANGE, K. J. and HUBNER, H. J., *Z. Naturforsch.* **31b** (1976) 886.

[3] PARDO, M. P. and FLAHAUT, J., *Mat. Res. Bull.* **13** (1978) 1231.

[4] HARPER, J. M. E., GEBALLE, T. H. and DI SALVO, F. J., *Phys. Rev.* **B 15** (1977) 2943.

[5] WINTENBERGER, M., *Mat. Res. Bull.* **14** (1979) 1195.

[6] FISHER, M. E., *Philos. Mag.* **7** (1962) 1731.

[7] DE JONGH, L. J. and MIEDEMA, A. R., in *Experiments on simple magnetic models*, Ed. Taylor and Francis, London (1974).

[8] ANDERSON, P. W. and WEISS, P. R., *Rev. Mod. Phys.* **25** (1953) 269.

[9] HUBER, D. L., *Phys. Rev.* **B 6** (1972) 3180.

[10] RICHARDS, P. M., in *Local properties near phase transitions*, Ed. Muller K. A. and Rigamonti P. (North Holland) 1976, p. 539.

[11] VILLAIN, J., *J. Phys. Chem. Solids* **11** (1959) 303.

[12] YOSHIMORI, A., *J. Phys. Soc. Japan* **14** (1959) 807.

[13] BERTAUT, E. F., *J. Phys. Chem. Solids* **21** (1961) 256.