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NEUTRON DIFFRACTION STUDY OF Mn_3Ga

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The crystal and magnetic structures have been investigated by neutron diffraction in $Mn_{2.85}Ga_{1.15}$. The high temperature quenched DO_{19} phase has a triangular antiferromagnetic structure with magnetic moments $\mu_{Mn} = 2.4 \pm 0.2 \mu_B$ lying in the basal plane. A slight distortion of this configuration results in a weak ferromagnetism. The Néel temperature is $470 \pm 10°K$.

On annealing at 750°K a new tetragonal DO_{22} structure is observed. This phase is ferrimagnetic with magnetic moments $\mu_I = 2.8 \pm 0.3$ and $\mu_{II} = 1.6 \pm 0.2 \mu_B$ pointing in the direction of the tetragonal axis c. T_c is higher than the temperature of the tetragonal–hexagonal transformation which starts at 770°K.

VERY FEW data have been reported on the magnetic properties of the Mn–Ga system. In the phase diagram established from X-ray diffraction measurements by Meissner *et al.*[1] several intermetallic phases can be found but their magnetic properties are not sufficiently specified. It seemed of interest to start a neutron diffraction study of the system for determining the magnetic structures. Owing to the negative scattering amplitude of Mn it was expected to get also some new information on the possible atomic ordering. As part of this program, the crystal and magnetic structures of the Mn_3Ga phase were investigated.

The high temperature phase of Mn_3Ga can be quenched from 800°C as a single phase only at Ga-rich compositions. It is of ordered hexagonal DO_{19} type according to Tsuboya and Sugihara[2] but it is described as a hexagonal close-packed structure in the phase diagram mentioned above.[1] From magnetic susceptibility measurements ferrimagnetism with $T_c = 470°K$ was assumed.[2]

A sample of $Mn_{2.85}Ga_{1.15}$ composition was prepared by melting the metals of 99.9 per cent purity. The ingot was powdered then annealed at 800°C in an evacuated quartz tube and quenched into water. The composition was checked by chemical analysis. X-ray diffraction showed a single DO_{19} type hexagonal phase with $a = 5.36_3$ Å, $c = 4.32_7$ Å and $c/a = 0.807$. The magnetic measurements indicated a weak ferromagnetism with $T_c = 470 \pm 10°K$ and spontaneous magnetization $M_S = 0.015 \mu_B$/Mn atom at 300°K.

As seen in Table 1, the neutron diffraction intensities measured at 490°K are in good agreement with those calculated for the DO_{19} type crystal structure with the ideal value of the atomic position parameter $x = 5/6$ and assuming a random distribution of the excess Ga atoms at the Mn sites. The neutron diffraction patterns taken at 6°, 77° and 300°K have no extra reflections but show magnetic contributions to the nuclear superreflections, thus suggest an antiferromagnetic phase having the same unit cell as the crystallographic structure. The observed neutron intensities can be described by the triangular antiferromagnetic model of Fig. 1. with magnetic moments lying in the hexagonal basal plane at an angle of 120° from one another. The angle ϕ between the magnetic moment on site 1 and the axis x was found to be 45° with $\mu_{Mn} = 2.4 \pm 0.2 \mu_B$ at

Table 1. Neutron intensities measured at 300° and 490°K and calculated for the triangular antiferromagnetic structure in hexagonal DO_{19} type $Mn_{2.85}Ga_{1.15}$. The values are given in barns.

hkl	$F^2_{calculated}$ magnetic	nuclear	total	$F^2_{observed}$ 300°K	490°K
100	0.56	1.05	1.61	1.55±0.20	1.09±0.10
001	0	0	0	<0.30	<0.30
101	1.94	3.16	5.10	5.26±0.40	3.42±0.30
110	1.43	4.21	5.64	5.95±0.30	4.21±0.20
200	0	0.04	0.04	<0.30	<0.30
111	0	0	0	<0.30	<0.30
002	0	0.16	0.16	<0.30	<0.30
201	0	0.12	0.12	<0.30	<0.30
102	0.37	1.05	1.42	1.20±0.30	0.95±0.10
210	0.14	1.05	1.19	1.19±0.30	1.00±0.10
112	0.75	4.21	4.96	5.20±0.30	4.47±0.30
211	0.36	3.16	3.52	3.67±0.20	2.95±0.30

300°K, the intensities calculated with these values are in good agreement with those measured at 300°K, as seen in Table 1. For the calculated values the experimental form factor of Mn^3 was used.

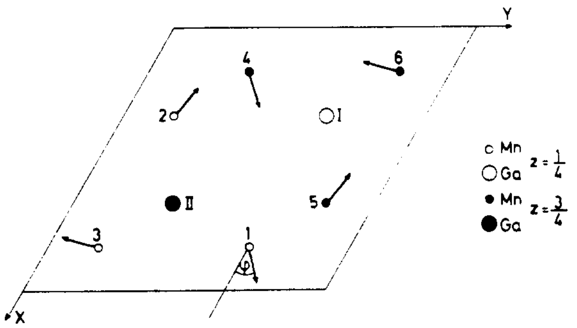

FIG. 1. Projection of the DO_{19} type unit cell on the basal plane (00.1). The triangular antiferromagnetic structure is illustrated.

The magnetic structure remains unchanged at 77° and 6°K. The temperature dependence of the magnetic intensities yields T_N = 460 ± 10°K which coincides with the Curie temperature of the weak ferromagnetism obtained from the magnetic measurements.

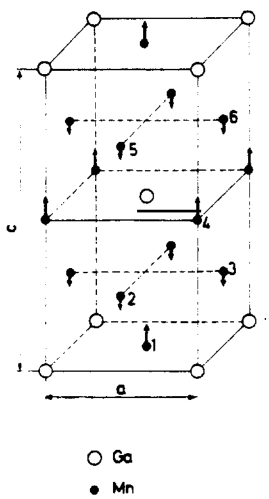

FIG. 2. Crystal and magnetic structure of the tetragonal phase of $Mn_{2.85}Ga_{1.15}$.

On annealing the sample at 750°K for a week a structural change takes place, the hexagonal DO_{19} type transforms into the tetragonal DO_{22} type structure shown in Fig. 2. The latter could not be obtained as a single phase, it is contaminated by the residual hexagonal phase. The values of the lattice parameter are a = 3.90_1 Å, c = 7.12_0 Å and c/a = 1.824. The ferromagnetism of the tetragonal phase is stronger than that of the hexagonal phase.

The neutron reflections of the tetragonal phase contain both nuclear and magnetic components. The measured intensities can be explained by a DO_{22} type crystal structure with an atomic long-range order parameter $S = 0.75$, assuming the ferrimagnetic structure shown in Fig. 2 in which the magnetic moments μ_I at sites numbered 1 and 4 are larger than and antiparallel to μ_{II} at the sites 2, 3, 5 and 6. As inferred from the absence of magnetic contribution to the reflection (002), the angle of the magnetic moments to the tetragonal axis c is 0°. The measured intensities in this two-phase alloy do not permit an unambiguous determination of the magnetic structure, the above model with $\mu_I = 2.8 \pm 0.3$ and $\mu_{II} = 1.6 \pm 0.2 \mu_B$ gives, however, a good agreement between the observed and calculated intensities at both 6° and 300°K. The Curie point could not be determined since it lies higher than the temperature of the tetragonal–hexagonal transformation which starts at about 770°K.

The low temperature DO_{22} type phase is probably the same as the face-centred tetragonal phase observed above 30 at. % Ga concentrations by Meissner *et al.*[1] and that described as a ferrimagnetic CuAu type phase by Tsuboya and Sugihara.[4] The negative neutron scattering amplitude of Mn made it possible in the present study to observe the superreflections associated with the DO_{22} type superlattice.

In the hexagonal DO_{19} type Mn_3Ge and Mn_3Sn alloys Kouvel and Kasper[5] observed a triangular antiferromagnetic configuration similar to that found in the hexagonal phase of Mn_3Ga. However, the magnetic moments lie in a plane perpendicular to the basal plane in Mn_3Ge and Mn_3Sn while in Mn_3Ga they are in the basal plane. The observed weak ferromagnetism implies a slight distortion in the triangular configuration of the magnetic moments. The magnetic structures for both the hexagonal and tetragonal phases suggest a dominant nearest neighbour direct interaction between the Mn atoms.

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Les structures cristallines et magnétiques de $Mn_{2.85}Ga_{1.15}$ ont été étudié par la diffraction neutronique. La phase DO_{19} trempée de haute température montre une structure triangulaire antiferromagnétique avec des moments $\mu_{Mn} = 2.4 \pm 0.2 \mu_B$ dans le plan de base. Une déformation legère de cette configuration donne un faible ferromagnétisme. Le point de Néel est à 470 ± 10°K.

Après un recuit à 750°K on a observé une phase quadratique de type DO_{22}. Cette phase est ferrimagnétique avec des moments $\mu_I = 2.8 \pm 0.3$ et $\mu_{II} = 1.6 \pm 0.2 \mu_B$ dans la direction de l' axe quadratique c. Le point T_c est plus élevé que la température de la transformation quadratique–hexagonale qui commence à 770°K.