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LOW-TEMPERATURE MAGNETIC TRANSITION IN Mn_3Ge_2

I. G. Fakidov, N. P. Grazhdankina,
R. I. Zainullina, A. M. Burkhanov,
and Yu. S. Bersenev

Institute of Metal Physics, Academy of Sciences of the USSR, Sverdlovsk

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The effect of high pressure (up to 10,000 atm) and strong magnetic fields (up to 300 kOe) on the low-temperature magnetic transition $\Theta_1 = 158°K$ in Mn_3Ge_2 is investigated. The elastic properties of this compound were determined and dilatometric data were measured within the temperature interval 77 to 380°K. The Θ_1 magnetic transition is accompanied by compression of the crystal lattice; the signs of the $d\Theta_1/dP$ and $d\Theta_1/dH$ effects are negative. The possibility of applying the exchange-inversion theory of C. Kittel to explain the Θ_1 magnetic phase transition in Mn_3Ge_2 is considered.

The presence of two magnetic transitions in Mn_3Ge_2 has been first reported by Fakidov, Grazhdankina, and Novogrusskii [1], who noted that this compound is ferromagnetic between two temperature limits Θ_1 and Θ_2. The low-temperature transition $\Theta_1 = 153°K$ was later found to be a first-order magnetic phase transition which is associated with an abrupt onset of magnetization [2] and liberation of latent heat [3]. Further heating leads to the disappearance of magnetization of the point $\Theta_2 = 283°K$ that is also quite abrupt [the $\sigma(T)$ curve is cut off at a σ that is approximately equal to one half the maximum value] [2].

M. Shimizu [4] made an attempt to explain magnetic transitions in Mn_3Ge_2 with the aid of the band model of ferromagnetism. He assumed that the transitions Θ_1 and Θ_2 are associated with a disruption of the spin order and belong to magnetic transitions of the ferromagnetism-paramagnetism kind. Analyzing the dependence of kinetic and exchange energy on spontaneous magnetization of the collective-electron system, Shimizu proved that for an energy band with an arbitrary dispersion law there can exist conditions (depending on the Fermi level position) in which the system is paramagnetic at low and high temperatures and ferromagnetic within a certain intermediate interval of temperatures Θ_1-Θ_2. Both the onset and the disappearance of ferromagnetism at the limits of this interval should be first-order phase transitions.

Subsequent investigation of the magnetic properties of Mn_3Ge_2 raised some doubts as to the applicability of this magnetic transition mechanism to the given compound. Measurements made with a grain-oriented Mn_3Ge_2 sample [5] proved that the magnetic properties of this compound resemble very closely the behavior of antiferromagnets with weak ferromagnetism so that the transition can be treated as a Morin-point transition due to spontaneous reorientation of spins with respect to the crystallographic axes. As is well known, this class of magnetic transitions has been explained by Dzyaloshinskii [6] with the aid of the Landau theory for phase transitions. It could thus be assumed that the first-order magnetic phase transition at Θ_1 is associated with a change of magnetic symmetry of Mn_3Ge_2 and that the weak ferromagnetism of this compound is due to a displacement of the magnetic moments of the antiferromagnet sublattices through a small angle from strict antiparallelism.

In [7] the magnetic transition Θ_1 in Mn_3Ge_2 is treated as a transition due to an exchange inversion of the antiferromagnetism-ferromagnetism kind and is analyzed on the basis of the Kittel thermodynamic theory [8]. However, the available data on the low-temperature transition in Mn_3Ge_2 are far from being complete; in particular, little is known about the elastic properties of this compound and its thermal expansion and about the dependence of Θ_1 on high pressure. As is well known (see, e.g.,

[9]), these characteristics must be known in order to test the applicability of the theories based on exchange-inversion models to magnetic phase transitions.

Accordingly, we set out to investigate the effect of high pressure and strong magnetic fields on the low-temperature transition in Mn_3Ge_2, to determine its elastic properties, and to take dilatometric measurements in a wide temperature interval.

1. SAMPLES AND MEASURING TECHNIQUES

The measurements were conducted with polycrystalline Mn–Ge alloy samples containing 60-70 at.% of Ge. According to phase diagrams [10], alloys of such a chemical composition contain Ge and an eutectic consisting of Mn_3Ge_2 and Ge. The use of alloys with a high content of Ge has been dictated by the following reasons. Since Mn_3Ge_2 is formed by means of a peritectic transition from Mn_5Ge_3 and an alloy containing 50.5 at.% of Ge, it is very difficult to obtain in a pure form. At the same time, since Mn_5Ge_3 is strongly ferromagnetic, even a very small addition of the Mn_5Ge_3 phase affects the magnetic properties of the alloy as a whole. The hazard of Mn_5Ge_3 contamination is greatly reduced by preparing alloys with a large content of Ge. Microstructure analysis of the investigated alloys indicated the presence of two phases only: the chemical compound Mn_3Ge_2 and Ge. The preparation technique and the purity of the starting materials are the same as those described in [2].

The high-pressure magnetization has been measured with a pendulum magnetic balance and a miniature high-pressure chamber made of VT3-1 titanium alloy [11]. The pressure transfer medium was a 50% mixture of transformer oil and isopentane. The weight of the samples was 228 mg and their linear dimensions did not exceed 6.3 mm.

Magnetic measurements in pulsed magnetic fields were made by the Faraday method using a piezoelectric torsion balance described in [12]. The balance was calibrated by comparing the relative magnetization intensity σ measured under pulse conditions with σ obtained in static measurements.

Thermal expansion of Mn_3Ge_2 was measured with a quartz dilatometer having a clock-type indicator with minimum scale division of 0.001 mm. The heating and cooling rate did not exceed 1 deg $\cdot$ min^{-1}. In dilatometric measurements and for investigation of the elastic properties we used samples 42 mm long and 3 mm in diameter. The elastic moduli – Young's modulus E and the shear modulus G – were measured by the "composite vibrator" method with quartz-crystal excitation at frequencies of about 38 and 26 kHz respectively. The obtained values of E and G made it possible to calculate the Poisson ratio $\mu = (E/2G) - 1$ and the compressibility $\varkappa = 3(1 - 2\mu)/E$.

2. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of the relative elongation $\Delta L/L$ and of the thermal expansion coefficient α of Mn_3Ge_2 plotted in the course of heating. In the region of magnetic transition temperatures $\Theta_1 = 158$ and $\Theta_2 = 264$°K the $(\Delta L/L)$ curve shows sharp discontinuities and the $\alpha(T)$ curve, deep minima. Such changes are characteristic of first-order magnetic phase transitions and their origin is due to changes in the magnetic state taking place at the temperatures Θ_1 and Θ_2. Figure 1 indicates that magnetic transitions taking place with rising temperature at the point Θ_1 are associated with constriction of the crystal lattice, the volume change being equal to $\Delta V/V = 3\Delta L/L = (1 \pm 0.1) \cdot 10^{-4}$. In the temperature regions $T < \Theta_1$, $\Theta_1 < T < \Theta_2$, and $T > \Theta_2$ the thermal expansion coefficients are nearly constant and are equal respectively to $\alpha_1 = (9 \pm 1) \cdot 10^{-6}$, $\alpha_2 = (12 \pm 1) \cdot 10^{-6}$, and $\alpha_p = (13 \pm 1) \cdot 10^{-6}$ deg^{-1}.

Figure 2 shows the temperature dependence of Young's modulus E, the shear modulus G, and the compressibility $\varkappa$. The temperature dependence of Young's modulus E plotted during heating (and cooling) approximately repeats the temperature dependence G(T); their shape is quite involved but they do not exhibit characteristic minima at the points Θ_1 and Θ_2 that usually correspond to magnetic transitions. Of special interest is the ab-

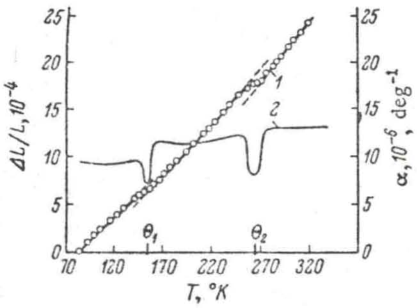

Fig. 1. Temperature dependence of relative elongation $\Delta L/L$ (1) and thermal expansion coefficient α (2) of Mn_3Ge_2.

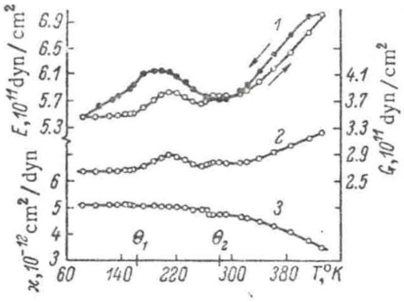

Fig. 2. Temperature dependence of Young's modulus E (1), shear modulus G (2), and compressibility $\varkappa$ (3) of Mn_3Ge_2.

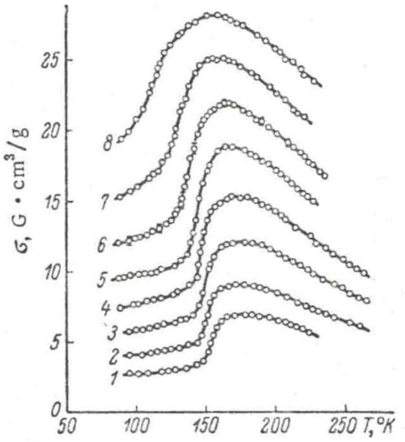

Fig. 3. Temperature dependence of magnetization of Mn_3Ge_2; field in kOe: 1) 20; 2) 30; 3) 40; 4) 50; 5) 60; 6) 80; 7) 100; 8) 130.

normal behavior of E and G in the paramagnetic region with rising temperature and the low values of the Poisson ratio in magnetically ordered states. In the Θ_1 magnetic transition region the Poisson ratio of Mn_3Ge_2 is 0.030.

Figure 3, which shows the temperature dependence of specific magnetization σ in fields from 20 to 130 kOe, indicates that the sharp rise in σ corresponding to the low-temperature magnetic transition in Mn_3Ge_2 is field-dependent and shifts to lower temperatures with increasing H. Using the temperature and field dependence data of magnetization we have plotted Θ_1 as a function of the external magnetic field intensity. Figure 4, in which Θ_1 has been plotted as a function of H from our data and from the data of [7] and [13], shows that the experimental data do not agree. Moreover, our measurements do not confirm the presence of a magnetization discontinuity at $T < 100°K$ in strong magnetic fields, which has been reported in [13].

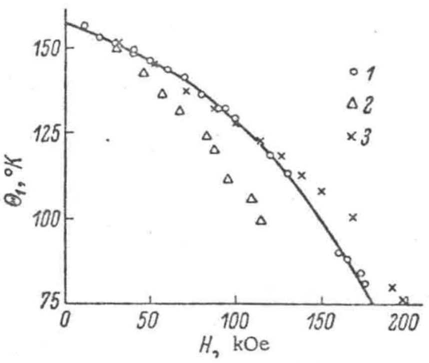

Fig. 4. Magnetic transition temperature Θ_1 as a function of external magnetic field intensity: 1) our data; 2) data of [7]; 3) data of [13].

As seen in Fig. 4, the dependence of Θ_1 on H is nonlinear and can be represented as $\Theta_1 = a - bH + cH^2 - dH^3$, where the numerical values of the coefficients have been determined by the method of least squares as $a = 158.2$, $b = 0.240$, $c = 0.357 \cdot 10^{-3}$, and $d = 0.921 \cdot 10^{-5}$. The derivative $d\Theta_1/dH$ is (at H = 0) equal to

$$\frac{d\Theta_1}{dH} = -(2.4 \pm 0.2) \cdot 10^{-4} \text{ deg/Oe}.$$

The effect of pressure on the low-temperature magnetic transition in Mn_3Ge_2 has been determined by measuring the temperature dependence of magnetization at atmospheric pressure and at a pressure of 10,000 atm in fields of 3, 6, 9, 12, and 15 kOe. As an example, Fig. 5 shows $\sigma(T)$ curves plotted during heating and cooling in 6- and 15-kOe fields. The curves indicate that at a pressure of 9700 atm (dashed curves) the magnetic transition temperature shifts by 3° in the low-temperature direction so that

$$\frac{d\Theta_1}{dP} \simeq -0.3 \cdot 10^{-3} \text{ deg/atm}.$$

It should be noted that the results of measurements taken in rising and falling temperatures are not the same, i.e., a hysteresis is observed whose width decreases with a decreasing rate of $\sigma(T)$ measurements. The magnetic transition temperature obtained in very slow measurements, i.e., under nearly equilibrium conditions, is equal to 158°K.

Table 1 lists thermodynamic data characterizing the low-temperature magnetic transition in Mn_3Ge_2. The transition entropy ΔS and latent heat ΔQ were calculated from the Clausius-Clapeyron equation. The two forms $\Delta S_1 = -\Delta\sigma_S(dH/dT)_P$ and $\Delta S_2 = \Delta V(dP/dT)_H$ of this equation were used. $\Delta\sigma_S$ has been determined from the temperature dependence of spontaneous magnetization $\sigma_S(T)$. For this purpose we have used the results of measurements of magnetization isotherms that had the form

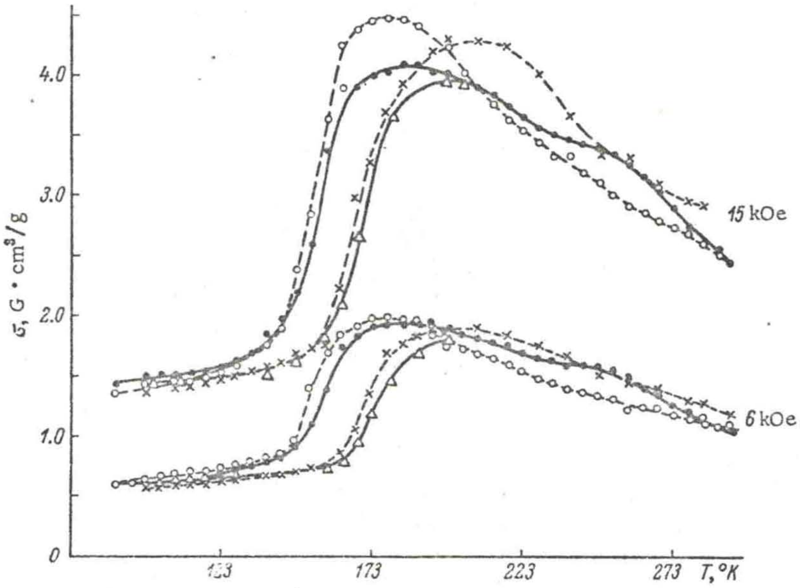

Fig. 5. Temperature dependence of magnetization of Mn_3Ge_2 alloy at atmospheric pressure (solid curves) and at 9700 atm (dashed curves).

TABLE 1. Thermodynamic Data Characterizing the Low-Temperature Transition in Mn_3Ge_2

Θ_1, °K	ΔV, cm³/g	$\Delta\sigma_s$, G·cm³/g	ΔS, ergs/g·deg	ΔQ, cal/g
158	$-1.55 \cdot 10^{-5}$	2.0	$0.8 \cdot 10^4$ $5.0 \cdot 10^4$	0.030 0.190

$\sigma = \sigma_S + \chi H$; extrapolation of the obtained lines to a zero field made it possible to determined σ_S. These values were then corrected for the Mn_3Ge_2 phase content since, as noted above, our samples were an eutectic of Mn_3Ge_2 and Ge. The change in specific volume ΔV has been found from dilatometric data and the sample density $\rho = 6.44$ g/cm³ measured by hydrostatic weighing.

As seen in Table 1 the change in entropy $\Delta S_1 = 0.8 \cdot 10^4$ ergs/g·deg calculated from magnetic measurements differs considerably from $\Delta S_2 = 5.0 \cdot 10^4$ ergs/g·deg found from the shift of Θ_1 with pressure and from the change in volume at the point of transition. Consequently, the obtained data are suitable only for a qualitative comparison with the Kittel theory, which is based on the exchange-inversion mechanism [8].

This theory states that the change of magnetic transition temperature with pressure depends on Young's modulus and on the thermal expansion coefficient in the paramagnetic temperature intervals:

$$\frac{d\Theta}{dP} = \frac{1}{E\alpha_p}.$$

Our experimental data give Young's modulus of Mn_3Ge_2 as $5.50 \cdot 10^{11}$ dyn/cm² whereas the Kittel equation gives $E = 2.5 \cdot 10^{14}$ dyn/cm²; the sign of $d\Theta_1/dP$ also does not agree with theoretical conclusions. As was already mentioned, the magnetic transition in Mn_3Ge_2 which takes place at the point Θ_1 with rising remperature is accompanied by constriction of the crystal lattice, whereas the theory [10] predicts lattice expansion in the case of an AF → F transition. The change in lattice parameter in the AF → F transition is determined by

$$\Delta a = a_F - a_{AF} = \frac{2\rho}{R} M^2,$$

where ρ is the rate of change of the exchange interaction as a function of interatomic spacing, $R = E/a^2$, and M is the sublattice magnetization. This expression makes it clear that the sign of Δa is governed by the sign of ρ, i.e., by the sign of the derivative of the change of magnetic transition temperature with pressure. It should be mentioned in this connection that the negative sign of the $d\Theta_1/dH$ effect observed experimentally also does not agree with the Kittel expression

$$\frac{d\Theta}{dH} = -\frac{1}{\rho M}\left(\frac{\partial a}{\partial T}\right)_P.$$

The exchange-inversion theory of C. Kittel has been further expanded in [14]. The entropy change

ΔS at the Θ_1 transition calculated from the Jarrett expression

$$\Delta S = -E\frac{\Delta c}{c}\alpha_p = 38.9\,\text{ergs/g}\cdot\text{deg}$$

differs by three orders of magnitude from experimental data (see Table 1). Such a large difference between theory and experiment is evidently due to the fact that the low-temperature magnetic transition in Mn_3Ge_2 does not belong to the AF → F type and is not associated with exchange inversion. The transition at point Θ_1 is possibly caused by spontaneous reorientation of the antiferromagnetic vector relative to the crystallographic axes and belongs to magnetic transitions of the Morin-point kind.

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