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Magnetic Transformations in the $Mn_2Ge_ySb_{1-y}$ System in Strong Magnetic Fields under High Pressure

By

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At temperature changes some magnetic phase transformations are observed in the $Mn_2Ge_y Sb_{1-y}$ system, which are accompanied by magnetic structure changes. The main characteristics of such transformations, magnetization change, change of the entropy of the spin system, and transition heat, were determined on the basis of magnetic measurements over a wide range of magnetic fields. The effect of pressure on the magnetic transformation temperature was also studied. An analysis of the experimental results is made on the basis of Kittel's exchange inversion theory.

Bei Temperaturänderungen werden einige magnetische Phasentransformationen im System $Mn_2Ge_ySb_{1-y}$ beobachtet, die von magnetischen Strukturänderungen begleitet sind. Die Hauptcharakteristiken solcher Transformationen, Magnetisierungsänderungen, Änderungen der Entropie des Spinsystems und Übergangswärme, werden auf der Grundlage magnetischer Messungen in einem großen Magnetfeldbereich bestimmt. Der Einfluß von Druck auf die magnetische Transformationstemperatur wurde ebenfalls untersucht. Eine Analyse der experimentellen Ergebnisse wird auf der Grundlage der Kittelschen Austauschinversionstheorie durchgeführt.

1. Introduction

In the $Mn_2Ge_ySb_{1-y}$ system there were observed two phase transitions of the first kind, at which the lattice symmetry did not change. These are a transition from the ferrimagnetic structure (FM) to the spiral one (SP) and from the spiral to the antiferromagnetic structure (AF) [1]. Furthermore at nitrogen temperature one more magnetic transformation was observed which is connected with a lattice symmetry change [2]. As a result of this transformation the rigid collinearity of sublattice magnetizations is distorted and a transition into the weak ferromagnetic state (FMS) is observed. For the description of magnetic transformations associated with the exchange interaction inversion Kittel developed a thermodynamic theory, supposing that the molecular field constant α, presenting interlattice interaction, depends on temperature and hence on the lattice parameter C. Assuming a linear dependence of exchange interaction on lattice parameter, it is possible to write

$$E_{\mathrm{ex}} = -\frac{\partial \alpha}{\partial C}(C - C_{\mathrm{k}})\, M_{\mathrm{A}} M_{\mathrm{B}}\,, \tag{1}$$

where C_{k} is a lattice parameter corresponding to the exchange interaction inversion. It was expected than, that the magnetizations of sublattices M_{A} and M_{B} were equal and did not depend neither on C nor on temperature. Using such a form of the exchange energy in the expression for the thermodynamic potential, Kittel obtained relations connecting physical quantities which define the system state. Applying these relations, it is possible, on the basis of a study of magnetic transformations in the system in the presence of strong magnetic field, to calculate the temperature coefficient of $(\partial T_k/\partial P)$ and to compare the calculated value with the experimental one. It would directly allow to judge about the application of Kittel's theory to the description of magnetic transformation in the $Mn_2Ge_ySb_{1-y}$ system under pressure. Such a comparison is given in our paper.

2. Measurements and Samples

Investigations were carried out on polycrystalline samples of the $Mn_2Ge_ySb_{1-y}$ system with composition $y = 0.04$, 0.08, 0.12, 0.16, and 0.20. Magnetic measurements were performed in pulse magnetic fields up to 300 kOe in the temperature range from 77 to 450 °K. The measurement technique and sample preparation were the same as in paper [1]. The shift of transition temperature with pressure was studied by the electrical resistance anomaly at the phase transition point. The samples were placed in a high-pressure bomb where measurements were performed at pressures up to 15 katm and in the temperature range 77 to 450 °K. Pressure was measured with a manganin manometer using methods described in [3].

3. Results of Measurements

From the numerous compositions of the system studied we use only data obtained on samples with $y = 0.08$, 0.12, 0.16, and 0.20 which we consider to be of interest.

Fig. 1 shows the temperature dependence of magnetization for samples of $Mn_2Ge_{0.16}Sb_{0.84}$ composition obtained in fields of 53, 106, and 212 kOe. At low temperatures the magnetization is very low and practically does not depend on temperature, which is characteristic of the antiferromagnetic state.

With temperature increase a transition is observed first into the spiral state and then into the ferrimagnetic one. Increase in the magnetic field strength shifts both transitions to the low-temperature region. The magnetization values 17.3 e.m.u./g at 340 °K, 16.1 e.m.u./g at 360 °K, and 14.5 e.m.u./g at 365 °K

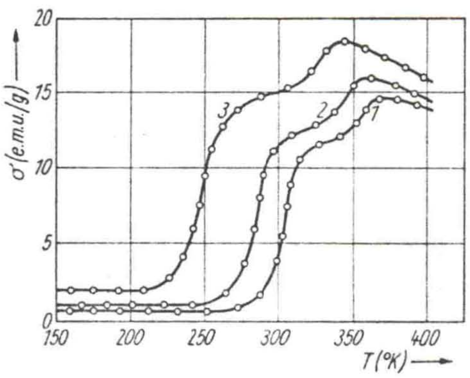

Fig. 1. Temperature dependence of the magnetization of $Mn_2Ge_{0.16}Sb_{0.84}$ samples in magnetic fields of different strength. (1) $H = 53$ kOe, (2) $H = 106$ kOe, and (3) $H = 212$ kOe

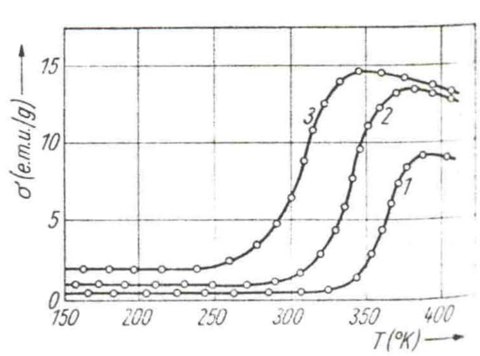

Fig. 2. Temperature dependence of magnetizations in $Mn_2Ge_{0.20}Sb_{0.80}$ samples in magnetic fields of different strength. (1) $H = 27$ kOe, (2) $H = 100$ kOe, and (3) $H = 240$ kOe

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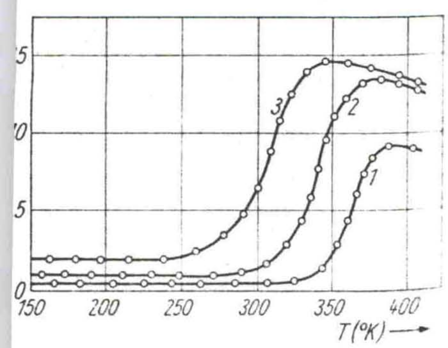

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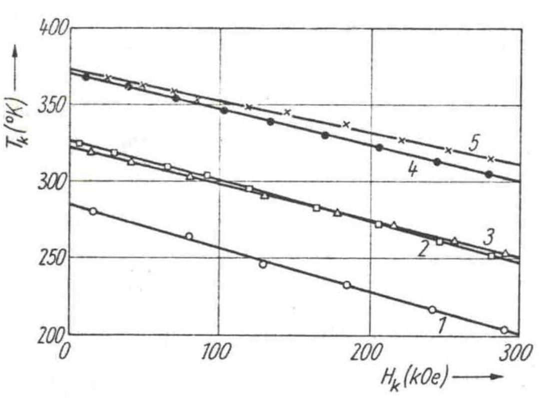
Fig. 3. Transition temperature dependence on magnetic field strength for different samples of the system. (1) AF–SP, $y = 0.12$; (2) AF–SP, $y = 0.16$; (3) AF–FM, $y = 0.12$; (4) AF–FM, $y = 0.20$; (5) AF–FM, $y = 0.16$



are close to the magnetization saturation of Mn_2Sb at the same temperatures [4]. Similar dependences are also observed for $Mn_2Ge_{0.12}Sn_{0.88}$ samples, in which both AF–SP and SP–FM consecutive transitions were found with temperature change. For $Mn_2Ge_{0.2}Sb_{0.8}$ samples a different behaviour is observed. Fig. 2 shows the temperature dependence of magnetization measured in one of the samples with the above mentioned composition at different values of magnetic field strength. At low temperatures here too the AF structure is realized, but with temperature increase the transition to the FM structure is observed, but no SP structure is found. With field increase the transition temperature is decreased and the magnetization in the FM state is consistent with data obtained for Mn_2Sb. Fig. 3 is expected to be a kind of generalization of the strong magnetic field effect on the transition temperature, where the $T_k(H_k)$ dependence is shown for different transitions. The dependences 1 and 2 correspond to AF–SP transitions, the remaining ones to AF–FM transitions. Fig. 3 vividly depicts all dependences as linear ones which little differ in their slope. The temperature for a phase transition of first kind must depend not only on magnetic field strength but also on pressure. Our measurements showed that with pressure increase the transition temperature rose both for the AF–FM transition and the SP–FM one. The temperature dependences of the electrical resistivity of $Mn_2Ge_{0.08}Sb_{0.92}$ are shown in Fig. 4. These dependences were obtained at different pressure. As is seen from Fig. 4, with pressure increase the SP–FM transition temperature is shifted into the high-temperature region.

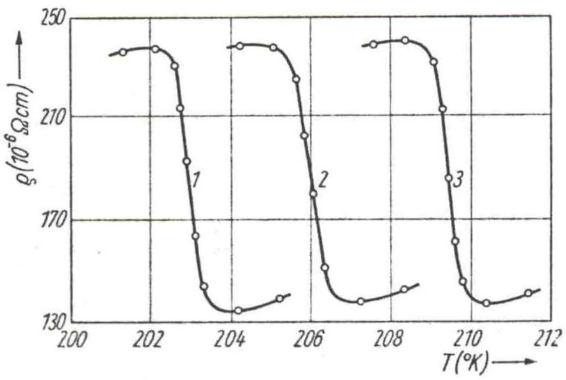


Fig. 4. Pressure influence on the temperature dependence of the electrical resistivity of $Mn_2Ge_{0.08}Sb_{0.92}$. (1) $P = 1.3$ katm, (2) 3 katm, and (3) 6.5 katm

4. Discussion

Kittel's theory was repeatedly used for the explanation of the magnetic field influence on the AF–FM-type transition temperature. In this case the fulfilment of the basic conclusion for this theory was experimentally verified. It may be possibly written as

$$\frac{M^2}{\Delta C} = \text{const}\,, \tag{2}$$

where M is the sublattice magnetization, ΔC the lattice parameter change accompanied by the transition.

At present one can consider it proved that condition (2) is fulfilled in the $Mn_{2-x}Cr_xSb$ system [5]. This is also true for the $Mn_2Ge_ySb_{1-y}$ system as evidenced by the experimental results reported by us. Thus Kittel's theory quite satisfactorily describes the magnetic field influence on the transition temperature, which is accompanied by an exchange interaction inversion. But it is not clear how this theory is applicable to the description of the pressure influence on the transition temperature. This subject must be solved separately for each investigated system as in theory it is assumed that with transition the lattice parameter changes only along the c-axis, while in reality any other lattice parameter may change. We consider the verification of the theory logically justified, when the calculated value $(\partial T_k/\partial P)$ is comparable with the measured one.

The temperature dependence of T_k on pressure, in accordance with Kittel's theory, is described by the following expression:

$$\frac{\partial T_k}{\partial P} = \frac{C}{\gamma}\,\frac{\partial C_T}{\partial T}\,, \tag{3}$$

where γ is the Young modulus, $(\partial C_T/\partial T)$ the thermal expansion coefficient of the crystal cell along the c-axis.

In order to use expression (3) for calculations one has to make use of two relations obtained in Kittel's work [6]:

$$\frac{M^2}{\Delta C} = \frac{\gamma}{2\,C^2}\,\frac{\partial \alpha}{\partial C} \tag{4}$$

and

$$\Delta S = 2\,\frac{\partial \alpha}{\partial C}\,\frac{\partial C_T}{\partial T}\,M^2\,. \tag{5}$$

Thus for calculation of $(\partial T_k/\partial P)$ it is necessary to know the entropy change ΔS of transition, the sublattice magnetization M, and the lattice parameter change ΔC at transition. The value of ΔC is to be found from X-ray diffraction investigations, the remaining quantities can be found from magnetic measurements in strong magnetic fields.

A thermodynamical analysis of phase transitions of the first kind gives the following transition temperature dependence on magnetic field strength [7]:

$$T_k = T_{k0} - \frac{H\,\Delta\sigma}{\Delta S}\,, \tag{6}$$

Table 1

Composition	Transition	T_{k0} (°K)	σ_s (e.m.u./g)	$\partial H_k/\partial T$ (Oe/deg)	ΔS (erg/g deg)	ΔQ (cal/g)
$Mn_2Ge_{0.12}Sb_{0.88}$	AF–SP	285	16.4	3.57×10^3	5.84×10^4	0.4
	AF–FM	324	23.2	3.96×10^3	$9.2\ \times10^4$	0.71
$Mn_2Ge_{0.16}Sb_{0.84}$	AF–SP	327	10.8	3.23×10^3	$3.5\ \times10^4$	0.27
	AF–FM	372	13.1	4.41×10^3	5.78×10^4	0.513
$Mn_2Ge_{0.20}Sb_{0.80}$	AF–FM	370	7.1	4.28×10^3	3.04×10^4	0.269

where T_{k0} is the transition temperature without magnetic field, $\Delta\sigma$ the sublattice magnetization change, ΔS the change of entropy of the spin system at transition.

From the temperature dependence of magnetization, $\sigma(T)$, measured in strong magnetic field, it is possible to define $\Delta\sigma$, and from the experimental dependence $T_k(H_k)$ it is easy to find $(\partial H_k/\partial T_k)$. Then on the basis of (6) it is possible to calculate the entropy change and transition heat. We have performed such calculations for all investigated samples. Table 1 gives the calculated results for three compositions in which all magnetic transformations peculiar to the $Mn_2Ge_ySb_{1-y}$ system are observed. Using the results given in Table 1 and the X-ray diffraction investigations of the $Mn_2Ge_ySb_{1-y}$ system [8], we have for $Mn_2Ge_{0.12}Sb_{0.88}$

$$\frac{M^2}{\Delta C} = 3.8\times10^5\,\mathrm{G^2/Å}\,.$$

Then using $\gamma = 2\times10^{12}\ \mathrm{cm^{-1}\,g\,s^2}$ [5] it is possible on the basis of (4) to calculate

$$\frac{\partial\alpha}{\partial C} = 5.9\times10^4\ \mathrm{erg/G^2\,Å}\,.$$

Now on the basis of (5) we can define a thermal expansion coefficient of the lattice, $(\partial C_T/\partial T) = 7.7\times10^{-4}$ Å/deg, and calculate using (3) the coefficient $(\partial T_k/\partial P)$. For $Mn_2Ge_{0.12}Sb_{0.88}$ we obtain

$$\frac{\partial T_k}{\partial P} = 4.25\ \mathrm{deg/katm}\,.$$

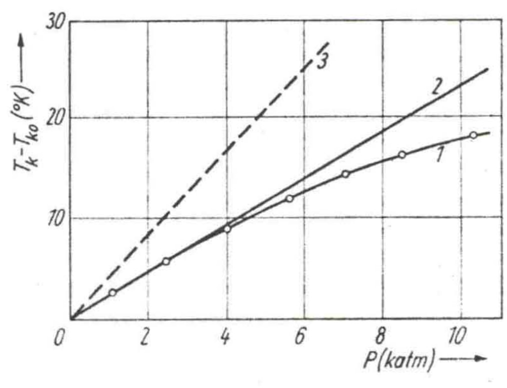


Fig. 5. Comparison of experimental and calculated dependences of pressure influence on the shift of the transition temperature in $Mn_2Ge_{0.12}Sb_{0.88}$. Curve 1 is an experimental one, curve 2 is the tangent to the experimental dependence, and curve 3 is the calculated dependence

Fig. 5 exhibits the experimental dependence of transition temperature change on pressure in a $Mn_2Ge_{0.12}Sb_{0.88}$ sample (curve 1), plotted by us on the basis of curves analogous those given in Fig. 4. It is possible to show that the $T_k(P)$ dependence must be linear only at low pressures, so deviations of the experimental dependence 1 from slope 2 are readily explained. In Fig. 4 the calculated dependence is shown by the dotted line 3; its slope essentially differs from the experimental value $(\partial T_k/\partial P) = 2.3$ deg/katm at $T = 324$ °K. A similar discrepancy was also observed in the $Mn_{2-x}Cr_xSb$ system [9, 10]. It is appropriate to assume that these deviations are caused by the fact that in Kittel's theory only the change along one crystallographic axis with transition is considered, while in reality, as is shown by X-ray investigations of the $Mn_{2-x}Cr_xSb$ system [9], AF–FM transitions are accompanied not only with an increase of the parameter C, but with a decrease of the parameter a. Thus the crystal cell volume change at transition of the AF–FM type will be little less than it was assumed in Kittel's theory. This must result in a decrease of the coefficient $(\partial T_k/\partial P)$. We have no values for the $Mn_2Ge_ySb_{1-y}$ system, but if for estimates one uses a value obtained for the $Mn_{2-x}Cr_xSb$ system, the calculated value of $(\partial T_k/\partial P)$ would be 2.47 deg/katm. This value is close to the experimental one of 2.3 deg/katm, obtained for $Mn_2Ge_{0.12}Sb_{0.88}$.

Thus the magnetic transition in the $Mn_2Ge_ySb_{1-y}$ system under high pressure at room temperature cannot be described by Kittel's theory without corrections due to the change of unit cell parameters along different axes.

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