THE EFFECT OF HYDROSTATIC PRESSURE ON THE CURIE TEMPERATURE OF MANGANESE MONOPHOSPHIDE

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The transverse galvanomagnetic effect of $\Delta R/R$ in MnP is measured at hydrostatic pressures up to 12,300 kg/cm^2. The compressibility and temperature dependence of the thermal expansion coefficient are measured. The shift of the Curie point Θ_f due to hydrostatic compression is determined on the basis of the anomalous variation of $\Delta R/R$ in the region of the magnetic transformation; $d\Theta_f/dP = -(1.14 \pm 0.07) \times 10^{-3}$ deg-cm^2/kg. Possible explanations of the differences of the signs of the $d\Theta_f/dP$ effect measured under hydrostatic compression of polycrystalline samples and under unilateral compression of single crystals of MnP[5] are discussed.

INTRODUCTION

THE compound manganese monophosphide MnP has two magnetic transformations: at $T_S = 50^\circ$K a transition takes place from the antiferromagnetic to the ferromagnetic state which is destroyed on further increasing the temperature at the Curie point $\Theta_f = 291.5^\circ$K.[1] The crystal structure of this compound has orthorhombic Pbnm symmetry with orthorhombic axes $a > b > c$. This structure is obtained when a hexagonal NiAs-type lattice is somewhat distorted with the orthorhombic c axis corresponding to the hexagonal axis of the NiAs structure. On the basis of magnetic measurements it was established that MnP belongs to the class of metamagnetic compounds, since the antiferromagnetic ordering at low temperatures is destroyed by relatively weak external fields of 2.3 and 5 kOe when the magnetic field is directed along the easy magnetization axes c and b. Neutron diffraction investigations[2,3] carried out at 4.2°K established the fact that in the orthorhombic MnP lattice the magnetic moments lying in the bc plane are ordered ferromagnetically but they are canted relative to the adjacent planes by an angle $\varphi = 20^\circ$ producing a helix-like spin configuration. The presence of a helicoidal magnetic structure in MnP, as well as the exchange-inversion transition at $T_S = 50^\circ$K makes it possible to assume that in this compound there coexist simultaneously different types of exchange interactions which differ from one another both in magnitude and sign. Goodenough[4] proposed on the basis of the narrow 3d-band model a scheme of electron energy levels of MnP and made assumptions as to the magnitudes and signs of the exchange interactions and their change with interatomic distance.

As is well known, the most direct experimental determination of the variation of exchange interactions with the volume is the investigation of the effect of high pressure on the temperature of the magnetic transformations T_S and Θ_f. Such measurements were carried out by Hirahara, Suzuki, and Matsumura[5] on single crystals of MnP under uniaxial compression along three different crystallographic axes (a, b, and c). From the data obtained in[5] it was possible to conclude that a decrease of the interatomic distances in MnP should lead to an increase of ferromagnetic interactions and consequently also to a higher Curie point. This contradicts the results of our measurements of the shift of the Curie temperature of MnP under the influence of hydrostatic pressure; the main discrepancy consists in the lack of correspondence of the signs of the $d\Theta_f/dP$ effect, since under hydrostatic pressure Θ_f does not increase, as one would expect in accordance with[5], but decreases.

In this paper we present the results of an investigation of the effect of high hydrostatic pressure (up to 12,300 kg/cm^2) on the Curie temperature of MnP. The measured $d\Theta_f/dP$ effect was checked by means of the thermodynamic Ehrenfest relation of second-order phase transitions; to this end we carried out measurements of the thermal expansion coefficient of MnP in the temperature region of Θ_f.

RESULTS OF THE MEASUREMENTS AND THEIR DISCUSSION

1. The effect of pressure on the Curie temperature was determined on the basis of measurements of temperature dependences of the transverse galvanomagnetic effect $\Delta R/R$. The sample was hydrostatically compressed in a chamber constructed of high-strength austenitic steel; the pressure in it was produced with the aid of a compressor system of L. F. Vereshchagin and a pressure booster which made it possible to obtain maximum pressures up to 14,000 kg/cm^2; a mixture of transformer oil and isopentane served as the pressure transmitting medium. The methods of measuring the galvanomagnetic effect, the temperature, and the pressure were analogous to those described by us previously.[6]

2. The isotherms of the galvanomagnetic effect $\Delta R/R = f(H)$ were measured at six different pressures: atmospheric, 2800, 5100, 8000, 8900 and 12,300 kg/cm^2. Figure 1 shows, as an example, the results of the measurement of $\Delta R/R$ as a function of H at a pressure of 8000 kg/cm^2. On the basis of the obtained isotherms we plotted $\Delta R/R = f(T)$ curves characterizing the temperature dependence of the galvanomagnetic effect, and from

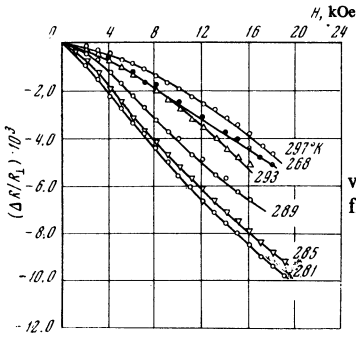

FIG. 1. Isotherms of the variation of $\Delta R/R$ in a magnetic field at a pressure of 8000 kg/cm³.

the shift of the minimum of these curves we determined the change of the Curie temperature with pressure. Figure 2 shows the dependences of $\Delta R/R$ on T for various values of the magnetic field strength measured at atmospheric pressure (dashed curve) and at a pressure of 8000 kg/cm². It is seen from these graphs that hydrostatic compression leads to a decrease of the Curie temperature.

It must be noted that the results of the measurements of the galvanomagnetic effect at high pressures are in good agreement with the characteristic dependences of the even effects belonging to the region of the paraprocess. Figure 3 presents, as an example, a comparison of the $\Delta R/R = aH^{2/3}$ dependence at atmospheric pressure (curve 1) and at P = 8000 kg/cm² (curve 2). Allowing for the strong temperature dependence of the galvanomagnetic effect, the values of $\Delta R/R$ are given for equal values of the reduced temperatures $T/\Theta_f = 0.995$. As is seen from the graphs, in both instances $\Delta R/R$ depends linearly on $H^{2/3}$; the slope of the straight lines characterizing the intensity of the paraprocess increases with increasing pressure, whereas the magnitude of the spontaneous galvanomagnetic effect ($\Delta R/R$ for H = 0) remains unchanged. Hence one can assume that hydrostatic compression (within the range of pressures which we employed) does not lead to appreciable changes of the spontaneous magnetization of MnP, and the change of the magnetic properties of this compound under pressure is basically determined by a shift of the Curie point. The increase of the intensity of the paraprocess under hydrostatic compression is a completely natural consequence of the negative $d\Theta_f/dP$ effect.

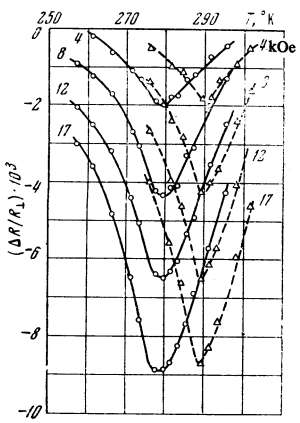

FIG. 2. Temperature dependences of the galvonomagnetic effect for various values of the magnetic field strength. The dashed curves were obtained at atmospheric pressure, the solid curves – at a pressure of 8000 kg/cm².

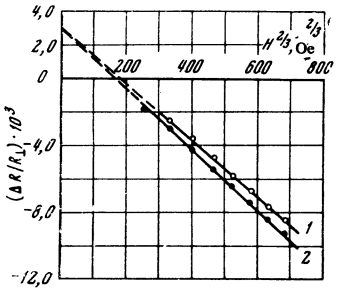

FIG. 3. The dependence of $\Delta R/R$ on $H^{2/3}$: curve 1 – at atmospheric pressure, curve 2 – at P = 8000 kg/cm².

Figure 4 shows the change of the Curie temperature as a function of pressure; it is seen from the figure that Θ_f decreases linearly with increasing pressure:

$$d\Theta_f / dP = -(1{,}14 \pm 0{,}07)\cdot 10^{-3} \text{ deg-cm}^2/\text{kg}$$

Having measured the compressibility of MnP, $\kappa = (1.58 \pm 0.04) \times 10^{-12}$ cm²/dyne, it was possible to determine the relative change of the Curie temperature with the volume; this turned out to be $\Theta_f^{-1} d\Theta_f/dV = 2.5$.

In order to check the measured value of $d\Theta_f/dP$, we investigated the thermal expansion anomaly $\Delta\alpha$ in MnP in the vicinity of the Curie temperature. This made it possible to determine $d\Theta_f/dP$ by an independent method with the aid of the Ehrenfest relation $d\Theta_f/dP = V\Theta_f \Delta\alpha/\Delta C_p$. The thermal expansion of MnP was investigated by a tensometric method. Figure 5 shows the curve of the temperature dependence of the relative elongation $\Delta L/L$ from which values of the thermal expansion coefficient $\alpha = \Delta L/L_0 \Delta T$ were calculated by graphical differentiation. Substituting in the Ehrenfest formula the obtained value $\Delta\alpha_V = -2.2 \times 10^{-5}$ deg^{-1} and the data of Krasovskiĭ and Fakidov[7] on the change of the specific heat at the magnetic transition $\Delta C_p = 2.15$ cal/deg-mole, we obtained[1)] $d\Theta_f/dP = 1.05 \times 10^{-3}$ deg-cm²/kg which agrees within experimental error with the value of $d\Theta_f/dP$ determined on the basis of direct measurements of the shift of Θ_f under pressure.

3. From our point of view, the following two facts are most important in comparing the results of our experiments carried out under hydrostatic compression of polycrystalline samples with the results of the investigation of the uniaxial compression of single crystals of MnP.[5]

First, one observes a very strong influence of the various conditions of compression on the effect of the shift of the Curie temperature with pressure. Evidence for this is the large difference in the absolute values of $d\Theta_f/dP$ obtained in compressing a single crystal along

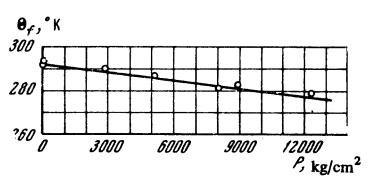

FIG. 4. The shift of the Curie point of MnP with hydrostatic pressure.

[1)] In calculating the molar volume V the density of MnP was taken in accordance with x-ray data [8] to be 5.77 g/cm³.

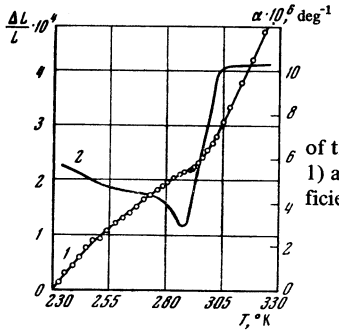

FIG. 5. Temperature dependences of the relative elongation ΔL/L (curve 1) and of the thermal expansion coefficient α(curve 2).

the a and c axes, as well as the entirely different nature of the $\Theta_f(P)$ dependence under hydrostatic pressure. Thus, for example, the derivatives in compressing a single crystal along the a and c axes respectively are: $d\Theta_f/dP_a \approx 34 \times 10^{-3}$ deg/atm and $d\Theta_f/dP_c \approx 1 \times 10^{-3}$ deg/atm, i.e. they differ by an order of magnitude and under hydrostatic pressure the derivative $d\Theta_f/dP$ is negative. Obviously the reason of such a discrepancy is the plastic deformation of the sample taking place under uniaxial compression.

Secondly, the shift of the temperature T_S of the antiferromagnetism $\rightleftarrows$ ferromagnetism transition under pressure is only determined by the change of the interatomic distances, since the change in the temperature of the exchange inversion dT_S/dP has practically the same value in compressing the single crystal along different crystallographic directions: $dT_S/dP_a \approx 6 \times 10^{-3}$ deg/atm and $dT_S/dP_c \approx 5 \times 10^{-3}$ deg/atm. In this connection it can be expected that under hydrostatic compression the sign of the dT_S/dP effect and its magnitude will be close to those obtained in[5].

Starting with the available experimental data, let us consider the changes of the exchange interactions of MnP caused by the decrease of the interatomic distances. Taking into account the helicoidal magnetic structure of MnP at low temperatures, one can explain the variation of Θ_f and T_S with pressure as follows. If it is assumed that the value of Θ_f is determined by the largest exchange interaction existing in this crystal, then the decrease of the distances between the manganese atoms lying in the ferromagnetically ordered bc planes should lead to a decrease in the positive interaction, because Θ_f decreases with increasing pressure. At the same time, the decrease of the distances between the bc planes resulting from the pressure leads to an enhancement of the negative antiferromagnetic interactions, because the temperature of the exchange inversion increases with increasing compression. With this it can be assumed that the mechanisms of ferro- and antiferromagnetic interactions in this compound are of a different nature. The basis of such an assumption is the experimentally established fact of the strong influence of the plastic deformation on the effect of the shifting of the Curie point with pressure.

The question arises why the plastic deformation connected with uniaxial compression does not exert any influence on the temperature of the exchange inversion T_S. It appears to us that a possible reason for this phenomenon can be the presence in MnP of both localized and collectivized 3d electrons which in turn results in the existence of various exchange mechanisms. In such a case one can treat the antiferromagnetic interaction (along the a axis) as an indirect exchange between the localized 3d electrons of the manganese ions with the active participation of the nonmagnetic phosphorus ions. This interaction is basically determined by the degree of overlap of the electron orbits and here the plastic deformation of the sample should apparently be of little significance. One can assume that the ferromagnetic interaction, unlike the indirect antiferromagnetic exchange, is basically due to the collectivized electrons and is determined by the state of the electrons near the Fermi surface. Therefore any plastic deformation which gives rise to a change of the density of states or distorts the shape of the Fermi surface should lead to changes of the Curie temperature. It is perfectly clear that to check the correctness of these ideas further experimental investigations, and in particular a study of the effect of hydrostatic compression on the temperature of the exchange inversion T_S, are essential.

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