EFFECT OF PRESSURE ON MAGNETIC TRANSFORMATIONS IN MANGANESE ARSENIDE

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Submitted to JETP editor May 24, 1966

J. Exptl. Theoret. Phys. (U.S.S.R.) **51**, 1052–1058 (October, 1966)

The effect of pressures P up to 10 000 kg/cm^2 on the magnetic transformation temperature of manganese arsenide is investigated, the normal value being $\Theta_1 = 314°$ K. Hydrostatic pressures $P < 2500$ kg/cm^2 shift Θ_1 towards lower temperatures. The magnitude of the effect is $d\Theta_1/dP = -(16.0 \pm 0.3) \times 10^{-3}$ deg kg^{-1} cm^2. In the temperature range 250–270° K, pressures above 2500 kg/cm^2 produce a different phase transition, the temperature of which strongly decreases with growth of P: $dT_k/dP = -(34 \pm 7) \times 10^{-3}$ deg kg^{-1} cm^2. In this case hydrostatic pressure leads to the formation of a new modification of manganese arsenide which apparently is ordered antiferromagnetically at low temperatures. The Néel temperature of the MnAs high-pressure phase grows with the temperature, $d\Theta_N/dP = (2.22 \pm 0.07) \times 10^{-3}$ deg kg^{-1} cm^2.

INTRODUCTION

A LARGE number of experimental[1-3] and theoretical[4,5] papers have been devoted to the investigation of the magnetic transformations of manganese arsenide; nevertheless, the nature of these transformations still remains unclear. The main premise of these theoretical papers was the assumption of a strong dependence of the exchange integrals on the interatomic spacing in MnAs. This hypothesis was confirmed in an experiment on the investigation of the effect of hydrostatic compression on the temperature of the magnetic transformation Θ_1; however, the absolute values of $d\Theta_1/dP$ obtained by means of magnetic[6] and electrical[7] measurements differ strongly from each other. In order to elucidate the reasons for this large discrepancy in $d\Theta_1/dP$, it was of interest to repeat these investigations over a wide interval of temperature and pressure.

In this paper we present the results of an experimental investigation of the effect of hydrostatic pressure on the temperature of the magnetic transformation Θ_1 in MnAs. The measurements were carried out in the temperature region from 77 to 400° K and using pressures up to 10 000 kg/cm^2. It was found that the shift of Θ_1 with pressure could be investigated only in the region of low pressures up to 2500 kg/cm^2. Higher pressure produces another phase transition, associated with the formation of a new modification of MnAs. The features of this new, pressure-induced transformation were investigated.

MEASUREMENT METHOD

The temperature Θ_1 was determined by means of both magnetic and electrical measurements, which were carried out in two different high-pressure chambers.

The electrical resistance of MnAs was measured under conditions of uniform hydrostatic compression of the sample. The pressure in the chamber was produced with the compressor of A. Ph. Vereshchagin's system and a multiplier, which permitted maximum pressures of up to 10 000 kg/cm^2 to be obtained. The pressure-conveying medium was a mixture of transformer oil and isopentane. As preliminary experiments showed, this mixture did not solidify at 10 000 kg/cm^2 down to temperatures near $-25°$ C. In this interval of temperature and pressure, isothermal and isobaric measurement cycles of the electrical resistance of MnAs were carried out. The chamber was provided with a 7-port closure, which permitted placing into the chamber, besides the sample, a copper-constantan thermocouple and a manganin resistance manometer. The measurements were carried out at constant current by the usual compensation method.

The high-pressure chamber for the magnetic measurements, as well as the method of pressure production, was similar to that described by Itskevich.[8] In this case, at low temperatures the sample was under the condition of quasihydrostatic pressure, since the mixture of transformer oil and kerosene which was used as the pressure-convey-

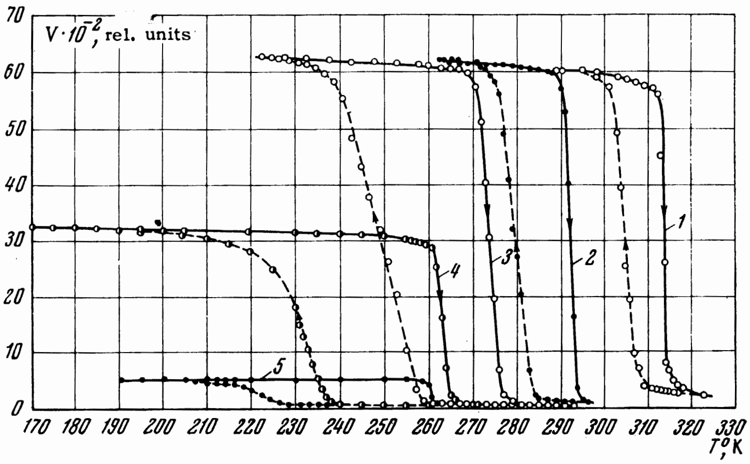


FIG. 1. Temperature dependence of the emf induced in the measuring coil (in relative units) at various pressures: 1 – atmospheric pressure; 2 – P = 1400 kg/cm²; 3 – P = 2350 kg/cm²; 4 – P = kg/cm²; 5 – P = 2970 kg/cm². The solid curves were obtained during warming of the sample, the dashed curves, during cooling.

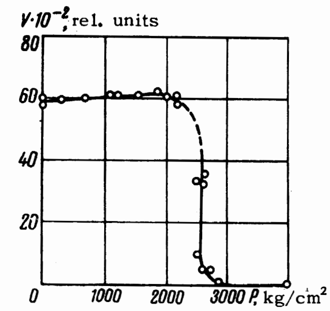
ing medium completely solidified. Upon lowering of the temperature the pressure in the chamber decreased in a non-monotonic manner. The maximum decrease of from 33 to 45% occurred in the temperature 150–170° K; upon further cooling to 77° K, the pressure in the chamber increased. This circumstance lowered the accuracy of the determination of $d\Theta_1/dP$, since the temperature of the transition Θ_1 was fixed not at a constant pressure P, but in an interval $\Delta P \approx 50$ kg/cm², characterizing the difference between the beginning and end of the magnetic transformation.

The determination of Θ_1 was made by an induction method. The measuring coil consisted of two sections so arranged that in the absence of a sample but in the presence of a coaxial alternating magnetic field from the primary coil, the signals from the two sections cancelled out. The sample, in the form of a cylinder 5 mm in diameter and 8 mm long, was placed in one of the sections of the measuring coil, and measurements were made of the emf induced in this winding. The measurements were made with a 28IM measuring amplifier; the alternating magnetic field was at a frequency of about 3 kHz. The temperature of the magnetic transformation was determined from the sharp jump in the induced emf vs. temperature curves measured at different pressures.

RESULTS AND DISCUSSION

Figure 1 shows the most characteristic curves of the temperature dependence of the emf induced in the measuring coil, obtained at different pressures. From these graphs it is clear that at atmospheric pressure the temperature Θ_1 is 314° K and decreases markedly with increasing pressure. Measurements carried out at increasing and decreasing temperature do not give identical results —there is a hysteresis, the width of which in-

FIG. 2. Dependence of the induced emf on pressure for the same values of the reduced temperature $T/\Theta_1 = 0.948$.



creases with increasing pressure. If this width is 6° at atmospheric pressure, it becomes about 27° at P = 2000 kg/cm². In all cases the reverse transition, i.e., the transformation observed upon cooling the sample, occurs at a lower temperature and has a less distinct character. It is significant that in the region of low pressures (curves 1, 2, and 3), hydrostatic compression of the sample leads only to a shift of the V(T) curves toward lower temperatures without a change in the magnitude of the emf V and the shape of its temperature dependence. At pressures above 2700 kg/cm² (curves 5 and 6), there occurs not only a shift in Θ_1, but also a sharp decrease in V, which is due to a change in the character of the magnetic transition itself in this pressure region.

Figure 2 illustrates the dependence of the induced emf on pressure, measured in the ferromagnetic region and at the same reduced temperatures $T/\Theta_1 = 0.948$. From the V(P) curve it is seen that when $P < 2200$ kg/cm² the induced emf is large and does not change noticeably with pressure. In the interval 2500 to 2700 kg/cm² the value of V decreases sharply and with further increase in pressure approaches the value of induction of the empty coils.[1)] Thus, the curve V(P)

[1)]The last two points on this curve (P = 2900 and 4000 kg/cm²) were measured at T = 285°K.

also indicates the presence of two regions of pressure in which the phase transitions have an essentially different character.

In the low-temperature region the principal effect of hydrostatic pressure is a shift of the temperature of the magnetic transformation Θ_1. The magnitude of this effect is

$$d\Theta_1 / dP = -(16.0 \pm 0.3) \cdot 10^{-3} \text{ deg kg}^{-1}\text{ cm}^2$$

It may be assumed that a strong decrease in the exchange interaction is evidently not accompanied by a marked change in the spontaneous magnetization of MnAs. The transformation in the interval 2500 to 2700 kg/cm^2 is associated with the formation under pressure of a nonmagnetic modification of manganese arsenide. The temperature of this transformation T_c decreases very rapidly with increasing P:

$$dT_c / dP = -(34 \pm 7) \cdot 10^{-3} \text{ deg kg}^{-1}\text{ cm}^2$$

The formation under pressure of a new modification of MnAs is confirmed by the data we obtained in the region of higher pressures up to 10 000 kg/cm^2. In Fig. 3 is shown the temperature dependence of the induced emf (curve 1), measured at an initial pressure of 9400 kg/cm^2. From this curve it is seen that at high pressures the absolute values of the induced emf are small; cooling to 100°K does not lead to the sharp increase in V associated with the emergence of a ferromagnetic state of the sample, as was observed at low pressures (Fig. 1, curves 1, 2, and 3). However, in the region of 240°K there is a distinct maximum, which may be due to a magnetic transformation of the high-pressure phase of MnAs. The form of the obtained V(T) curve closely resembles the behavior of antiferromagnets near the Néel temperature.

In order to check whether the maximum at 240°K was connected with some kind of secondary phenomenon or with the experimental method itself, controlled measurements using repeated cycles of cooling and warming were carried out; they showed that the V(T) curves were highly reproducible. In addition, the temperature dependence of the induced emf of the empty coils was measured (see Fig. 3, curve 3; the same figure shows how the pressure varies in this temperature interval—curve 2). It is clear from these curves that the maximum in the V(T) curve is characteristic of the sample and cannot be due to decompensation of the measuring coils as a consequence of pressure variations in the cooling process. It was also necessary to keep in mind that the inductance of the measuring coil changes not only with sample magnetization, but also with changes in its volume and electrical resistance.[9] In this connection, measurements were made of the electrical resistance of the MnAs in this temperature and pressure interval, on the basis of which it was concluded that the observed transformation is due principally to a change in the magnetic state of MnAs.

Measurements made at other initial pressures (from 4700 to 10 100 kg/cm^2) showed very good reproducibility of the general character of the V(T) curves; however, the maxima of these curves were shifted with increasing pressure toward higher temperatures. If it is assumed that the observed magnetic transformation of the high-pressure phase of MnAs is caused by the appearance of antiferromagnetic ordering, then the shift of the maximum of the V(T) curve with pressure can be connected with a change in the Néel temperature with pressure. The magnitude of this effect is

$$d\Theta_N / dP = (2.22 \pm 0.07) \cdot 10^{-3} \text{ deg kg}^{-1}\text{ cm}^2$$

Figures 4, 5, and 6 show the results of an investigation of the effect of hydrostatic pressure on the electrical resistance of MnAs. Figure 4 gives curves of R(P) measured in the neighborhood of Θ_1. The isotherms of resistance were taken during two pressure cycles: at T = 292°K direct and re-

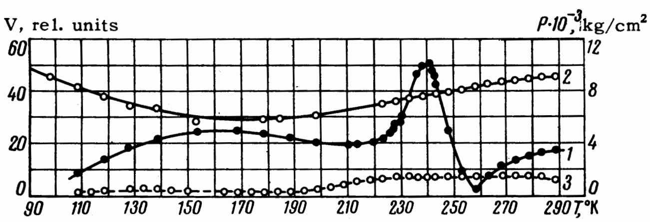


FIG. 3. Temperature dependence of the induced emf at an initial pressure of 9400 kg/cm^2. Curve 1—measuring coil with sample; curve 3—without sample. Curve 2—pressure variation in the chamber as the temperature is lowered.

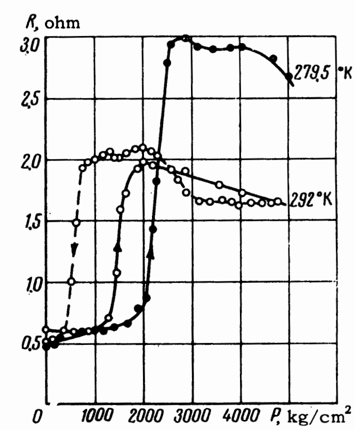


FIG. 4. Pressure dependence of the electrical resistance of MnAs, measured in the neighborhood of the magnetic transformation temperature Θ_1.

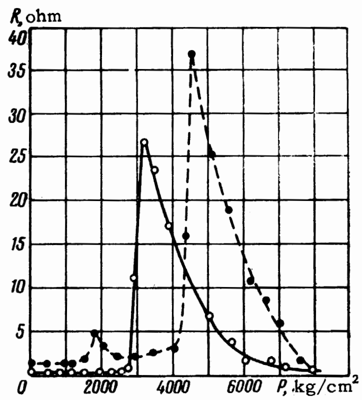


FIG. 5. Pressure dependence of the electrical resistance of MnAs, measured in the neighborhood of the transition temperature T_c.

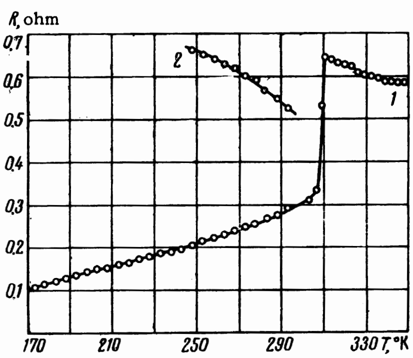


FIG. 6. Temperature dependence of the electrical resistance of MnAs. Curve 1—at atmospheric pressure; curve 2—at P = 8000 kg/cm².

verse R(P) curves were measured, whereas at T = 279.5 °K the measurements were made only with increasing pressure. From these graphs it is seen that as the pressure increases there takes place at 1400 and 2200 kg/cm² an increase in electrical resistance that is just as sharp as the jump in electrical resistance during the Θ_1 transition due to changing temperature at atmospheric pressure (Fig. 6, curve 1). These jumps in the R(P) and R(T) curves respectively define a "pressure transition" and a "temperature transition" and are identical in magnitude. In both cases the destruction of ferromagnetic ordering is accompanied by a several-fold increase in resistance irrespective of whether the disordering is caused by temperature or pressure. The observed difference in the curves of Fig. 4 between the direct and reverse R(P) curves indicates a hysteresis of the "pressure transition," the reverse transformation taking place at lower P.

The R(P) curves measured near the transition temperature T_c have a quite different character. Figure 5 shows the change in resistance as a function of pressure, measured at 268 °K. It is seen that as the pressure is increased (solid curve) up to 2700 kg/cm² there is very little change in electrical resistance. However, in the region of pressures 2800 to 3200 kg/cm² R increases almost 30 times, after which the resistance fails and approaches its initial value at P = 8000 kg/cm². As the pressure is lowered (dashed curve) the shape of the R(P) curve is reproduced; however, the reverse transformation sets in at higher P. In the pressure interval 2500 to 1800 kg/cm² the resistance increases again, which is associated with the Θ_1 magnetic transformation. Thus, these data also indicate the presence of two types of magnetic phase transitions evoked by pressure. In this connection it is interesting to note the different character of the temperature dependences of the electrical resistance of the modification of MnAs obtained at high pressure and of normal MnAs measured at atmospheric pressure (Fig. 6).

As a result of these measurements a P,T-diagram of the magnetic phase transformations in MnAs was obtained for the temperature interval 230 to 315 °K and for pressures up to 10 000 kg/cm². In Fig. 7 are shown the variation with pressure of the temperature of the magnetic transformation Θ_1 (curve 1), the transition temperature T_c (curve 2), and the Néel point of the high-pressure phase (curve 3); these data were obtained as the sample was warmed. In the same figure the results of a measurement of Θ_1 during cooling of the sample (dashed curve) are presented. Owing to the diffuse character of the reverse transitions, the dashed curve was determined with high error. Only the data obtained for the direct transitions Θ_1 and T_c were subjected to treatment and analysis. The magnitude of $d\Theta_1/dP$ was determined by the method of least squares, and the magnitudes of dT_c/dP and $d\Theta_N/P$ were calculated

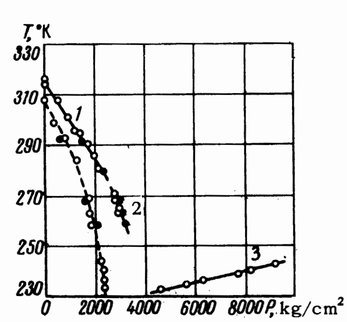


FIG. 7. Phase diagram for MnAs. Curve 1—change with pressure of the magnetic transformation temperature Θ_1; 2—change of the transition temperature T_c; 3—change of the Néel point of the high-pressure phase. Dashed curve obtained during sample cooling. ○—points obtained by magnetic measurements, ●—by electrical measurements.

respectively as $\Sigma\Delta T/\Sigma P$ and $\Sigma\Delta\Theta_N/P$. From the graphs it is seen that all three temperatures, Θ_1, T_C, and Θ_N vary linearly with pressure, Θ_1 and T_C decreasing with increasing P and Θ_N increasing.

Our result $d\Theta_1/dP = -(16.0 \pm 0.3) \times 10^{-3}$ deg kg^{-1} cm^2 does not agree with the data of other authors. On the basis of measurements of the magnetization of MnAs as a function of pressure, Rodbell[6] obtained the value -12×10^{-3} deg kg^{-1} cm^2. The measurements were performed near the temperature Θ_1 and pressures up to 1500 kg/cm^2. Rather recently a paper was published by several authors[7] in which the shift of Θ_1 with pressure was determined by means of electrical measurements carried out in the region of temperature 273 to 325° K and of pressure up to 5000 kg/cm^2. In this case a larger value was obtained: $d\Theta_1/dP = -(17.5 \pm 0.5) \times 10^{-3}$ deg kg^{-1} cm^2. It should be mentioned that the character of the anomalies'''' and the magnitudes of the jumps in resistance in the Θ_1 transition regions agree with our data.

In conclusion we remark that our results indicate a complete identity of the values of the temperatures and pressures of the magnetic transitions as determined by different methods. Of greatest significance from our point of view is the break in the line of points of the magnetic transformation Θ_1 in the P,T-plane in the pressure interval 2400 to 2600 kg/cm^2. We associate this phenomenon with the appearance of a new phase transition evoked by the uniform compression of MnAs. Further research is needed to elucidate the nature of this transition, especially x-ray investigations. Determination of the crystal structure of the high-pressure phase of MnAs will permit us to find out whether this transition is a polymorphic transformation or if it indeed belongs to the class of electronic transitions that occur without a change in the symmetry of the crystalline lattice. Such a possibility for MnAs is not excluded, since available experimental data[10] indicate that the energy levels of the 3d, 4s, and 4p electrons are near each other, and high pressure may stimulate mutual electronic transitions due to a change in the overlap of the energy bands.

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Translated by L. M. Matarrese
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