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THE MAGNETIZATION AND MAGNETOCALORIC EFFECT OF MANGANESE PHOSPHIDE

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The magnetocaloric effect and magnetization of manganese phosphide (MnP) were investigated at various field strengths in the temperature region of magnetic transformations. As contrasted with Guillaud, we found that the magnetic transformation temperature was not dependent on the magnetic field strength. The character of the dependence of magnetocaloric effect on the temperature and magnetic field strength and also the temperature dependence of the spontaneous magnetization indicate the existence of a Curie point at 22° C.

The results obtained are discussed from the viewpoint of the s-d exchange model of ferromagnetism.

INTRODUCTION

GUILLAUD'S[1] measurements have shown that the temperature dependence of the magnetization of the monophosphide of manganese (MnP) follows a T^2 law at low temperatures. The saturation magnetization is not large and the magnetic moment per atom of manganese comes to $1.2\ \mu_B$. On the basis of these data, Guillaud suggests the existence in manganese phosphide of an anti-ferromagnetic interaction between the manganese atoms. He breaks down the crystal lattice of MnP into two sub-lattices one of which consists of the Mn_I atoms with electron state $3d^7$, and the other consisting of Mn_{II} in a $3d^5 4s^2$ state. The magnetic moments of the Mn_I atoms, equal to $3\ \mu_B$, are oriented antiparallel to the moments of Mn_{II} with value $5\ \mu_B$. As a result of such an orientation the magnetic moments of the manganese atoms in various electronic states provide a resultant moment equal to $1\ \mu_B$ per atom. The temperature of magnetic transformation Θ_f found by Guillaud is equal to 25° C. By his assertion, the magnitude of Θ_f is strongly dependent on the intensity of the external magnetic field.[2,3]

Measurements carried out by us on the temperature dependence of the electrical resistivity of MnP show that the curve of the function $\rho = \rho(t)$ has a singular point at 22° C. The character of the singular point is analogous to the kind which usually occurs in ferromagnetic substances at the transition through the Curie point. Moreover, measurements of the effect of the magnetic field on the resistance of the same compound have confirmed the assumed presence of a second-order phase transformation in the vicinity of $t = 22°$ C (Curie point), which followed from measurements of the electrical conductivity. However, a definite conclusion about the character of the magnetic transformation could only have been made on the basis of an investigation of the magnetocaloric effect in MnP.

Altogether, the measurements of the magnetocaloric effect, when considered with the measurements of the magnetization isotherms, make it possible to establish the temperature dependence of spontaneous magnetization in the vicinity of the magnetic transformation.

PREPARATION OF SAMPLE AND METHOD OF MEASUREMENT

As raw materials for obtaining manganese phosphide we used red phosphorus and manganese obtained electrolytically by sublimation in vacuo. The mixture of manganese and phosphorus powders was mixed in a quartz vessel which was then pumped down in a vacuum system to a pressure of 10^{-6} mm of Hg.

To obtain a sufficiently uniform alloy the vessel was kept in an oven at 650° C for 50 hours. The alloy was allowed to cool down with the oven. From the alloy thus obtained a sample was prepared in the shape of an ellipsoid with axes equal to 12 and 6 mm respectively. The sample was cemented to a thin glass rod which was held inside a silvered glass tube. The latter was placed into a copper chamber over which thermostatically controlled water was allowed to circulate, and it was held between the poles of an electromagnet. Measurements of the heat effect, Δt, were carried out in vacuum at a pressure of 10^{-4} mm Hg., which was attained by means of an adsorption type pump in which activated charcoal was used as the adsorbent.

For the measurement of temperature, as well as the change in temperature during magnetization and demagnetization of the sample, a thermistor with a time constant of the order of hundredths of a second was used. The thermistor was inserted into the sample, approximately down to the middle, through a hole 0.8 mm in diameter. A magnetic field of intensity up to 20,000 oersteds showed no effect on the thermistor resistance. The thermistor was calibrated at temperatures of 0.2 and 100° C. The parameters of the thermistor were $R\ (0°\,C) = 4736\,\Omega$ and $B = 2409°\,K$. The resistance-temperature coefficient for the thermistor at room temperature (20° C) was $\alpha = 2.8\%/°C$. The thermistor resistance was measured with an MTV bridge to an accuracy of 0.02 ohms. The temperature stability of the sample was not less than 0.001°. The sensitivity of the measuring equipment changed with the sample temperature because of the nonlinearity of the thermistor temperature coefficient, and was not less than 0.001° per mm.

The use of a thermistor for the measurement of the magnetocaloric effect has some advantages over the measurement of small temperatures Δt by means of thermocouples. In addition to the considerable increase in sensitivity of the measuring equipment obtained by the use of a thermistor, its use in a bridge circuit makes it possible to eliminate the ballistic throw which always occurs when thermocouples are used.

The magnitude of the heat effect, Δt, was measured both during magnetization of the sample and during demagnetization. The change in sample temperature during magnetization was always very closely equal to the change in temperature of the sample during demagnetization.

Measurements of the magnetization isotherms were carried out on the same sample in the vicinity of the Curie point. These measurements were obtained ballistically. The sample was magnetized in the field of an electromagnet and then was pulled out of the search coil through a hole in one of the magnet pole shoes.

The magnetization of the sample was computed from the formula

$$\sigma = \frac{C\alpha}{Sn\,(4\pi - N)},$$

where σ is the magnetization, C is the value for one galvanometer division in maxwells/mm, α is the deflection in mm, S is the sample cross section area in cm^2, n is the number of turns in the search coil, and N is the demagnetizing factor.

DISCUSSION OF RESULTS

We have investigated the dependence of the magnitude of the magnetocaloric effect on the intensity of magnetic field at various temperatures in the vicinity of the temperature of magnetic transformation, along with investigating the magnetization isotherms for a sample of MnP. Figure 1 depicts the magnitude of the Δt effect as a function of the sample temperature. As is evident, all the curves have a maximum near 22° C. The position of this maximum along the axis of temperatures is independent of the magnitude of magnetic field intensity. This temperature is the Curie point for the manganese monophosphide investigated by us. The strong dependence of the Curie point on the magnetic field intensity noted by Guillaud was not found by us either in the investigation of the magnetocaloric effect or when we studied the influence of magnetic field on the electrical resistance of a whole series of manganese alloys with various amounts of phosphorus.

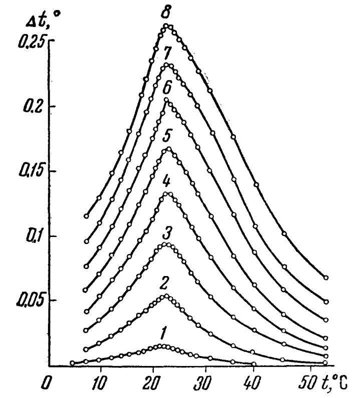

FIG. 1. Temperature dependence of the magnetocaloric effect, Δt, for various magnetic field intensities: 1 – at 1000, 2 – 3000, 3 – 5000, 4 – 7000, 5 – 9000, 6 – 11,000, 7 – 13,000, and 8 – 15,000 oersteds.

Figure 2 shows the dependence of the temperature effect, Δt, on the square of the magnetization. As is well known,[4,5] by extrapolating the linear portions of these curves we can determine the magnitude of the spontaneous magnetization at a given temperature. It should be pointed out that the extent of the linear portion of these curves is rapidly shortened with a reduction in temperature, which complicates the process of extrapolation. For this reason, to obtain sufficiently accurate values of spontaneous magnetization at lower temperatures, it is necessary to use field strengths of the order of 20,000 oersteds which were not available to us.

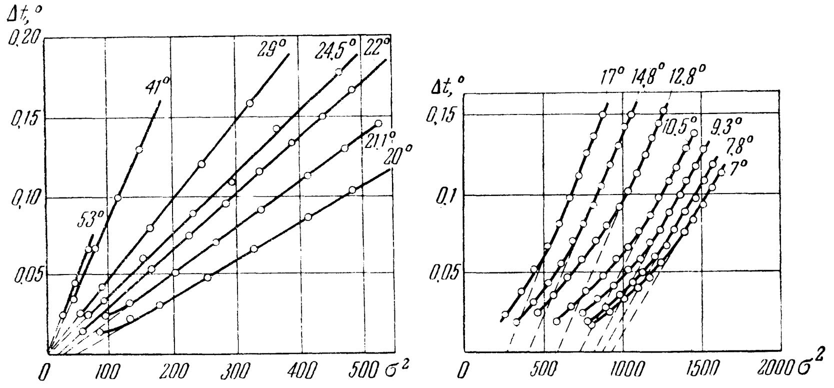

FIG. 2. Dependence of magnetocaloric effect, Δt, on the square of the magnetization at various temperatures.

The value of the spontaneous magnetization σ_s was determined from the curves of the magnetocaloric effect, Δt, as a function of the square of the magnetization σ^2, which were obtained at various temperatures above and below the Curie point (see Fig. 2). Curve 1 in Fig. 3 depicts the temperature as a function of the spontaneous magnetization σ_s. The value of σ_0 for manganese phosphide MnP is taken from Guillaud's paper.[1]

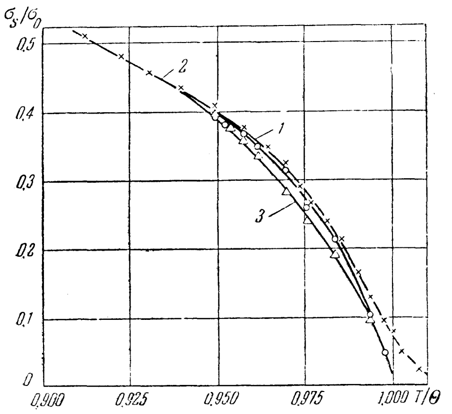

FIG. 3. Spontaneous magnetization as a function of temperature. Curve 1 – from magnetocaloric effect data, 2 – from the data of "line of equal magnetization," 3 – by the method of "thermodynamic coefficients."

The temperature dependence of the spontaneous magnetization can also be determined by working over the data obtained from the magnetization isotherms in the vicinity of the paraprocess. Firstly, the temperature dependence of σ_s may be determined by extrapolating the isotherms of the true magnetization down to zero magnetic field, H = 0, and also by the method proposed by Weiss and Forrer, called the method of " line of equal magnetization." The results of analyzing the curve of true magnetization by the "line of equal magnetization" method are given in curve 2 of Fig. 3.

Belov[6-8] has recently used the "method of thermodynamic coefficients" to investigate the temperature dependence of the spontaneous magnetization for a whole series of ferromagnetic alloys and ferrites. This method is based on the analysis of the curves of true magnetization by means of the thermodynamic equation

$$H = a\sigma + b\sigma^3, \tag{1}$$

where a and b are thermodynamic coefficients. This equation, at a value of H = 0, provides an expression for the spontaneous magnetization in the vicinity of a Curie point from the relation $\sigma_s^2 = -a/b$. This method makes it possible to determine the Curie point as well, if we take a = 0 at $T = \Theta_f$.

The results of working over the data of measurements of the MnP magnetization by Belov's method are shown in curve 3 of Fig. 3. It is worth noting the rather good coincidence of the curves for σ_s/σ_0, obtained by three different methods. A comparison of these curves indicates that curves 1 and 3, obtained by magnetocaloric-effect measurements and by the method of "thermodynamic coefficients" both drop off sharply to the temperature axis, whereas curve 2 obtained by the method of "line of equal slope" drops off more smoothly. As curve 2 drops off it forms a "tail" of spontaneous magnetization. This "tail" is rather short (on the order of 20) for manganese phosphides. For temperatures higher than 42° C, the magnetization isotherms appear as straight lines.

The Curie temperature determined by the method of "thermodynamic coefficients" is equal to 21.1° C; this corresponds to the value of Curie temperature obtained from the magnetocaloric effect.

It thus becomes evident that the magnetization of manganese phosphide for the para process region near the Curie point is quite satisfactorily described by the thermodynamic relation (1).

The quantity ξ which appears in the well known formula

$$(\sigma_s/\sigma_0)^2 = \xi(1 - T/\Theta).$$

is of considerable importance for an understanding of the character of the magnetic transformation in the vicinity of the Curie temperature.

Vlasov and Vonsovskiĭ have shown, on the basis of the s-d exchange model,[10] that $\xi > 3$ for metallic ferromagnetic substances. For ferrites $\xi < 3$, according to the computation carried out by Vlasov. The results of our measurements given in Fig. 4 lead to a value $\xi = 3.4$, according to the data for the magnetocaloric effect (curve 1), and $\xi = 3.0$ according to the data obtained when using the method of "line of equal magnetization" (curve 2), i.e., the values of ξ are close to those obtained from the "quasi-classical" theory of ferromagnetism. We must therefore conclude that from the paramagnetic standpoint manganese phosphide resembles the metallic ferromagnetic materials more closely than it does the ferrites.

It should be emphasized that in the paramagnetic region, according to the data of reference 11 and from our measurements, the susceptibility follows the Curie-Weiss law and does not have the hyperbolic form characteristic of ferromagnetic substances. This makes it possible to suppose that the manganese phosphide, MnP, is possibly ferromagnetic, and not ferrimagnetic as was proposed by Guillaud.

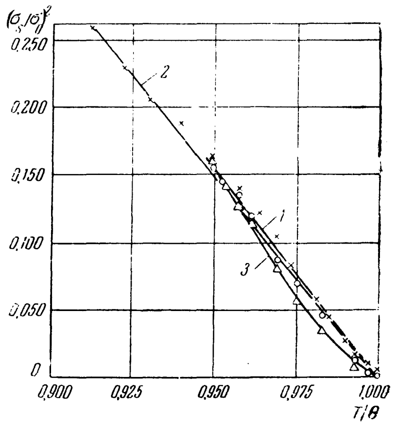

FIG. 4. Square of spontaneous magnetization as a function of temperature. Experimental point designation corresponds to Fig. 3.

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