SHIFT OF THE CURIE TEMPERATURE BY HYDROSTATIC COMPRESSION OF MANGANESE AND COBALT FLUORIDES

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The shift of the Curie temperature in the antiferromagnetics MnF_2 and CoF_2, under the influence of hydrostatic compression, has been determined for polycrystalline specimens by measurement of the magnetic susceptibility and of the change of the coefficients of linear expansion at the transition temperatures. For MnF_2 the shift is $(1.5 \pm 0.2)°$ at pressure (1900 ± 100) atmos; for CoF_2 no shift was observed. The antiferromagnetic transition temperatures are respectively 68 and 39° K.

INTRODUCTION

THE change of the Curie temperature of ferromagnetics under the influence of hydrostatic compression has been investigated repeatedly (cf., for example, the bibliography in the work of Patrick[1]). The effect of hydrostatic compression on the antiferromagnetic manganese telluride (an intermetallic compound) was studied by Grazhdankina[2] at room temperature. The amount of the shift of Curie temperature for antiferromagnetic substances appeared to be much larger than for ferromagnetics. It seemed interesting to investigate the change of Curie temperature for typical antiferromagnetic substances, for example ionic crystals.

To this end, measurements of the shift of Curie temperature of MnF_2 and CoF_2, under the influence of hydrostatic compression, were undertaken by two methods: by a shift of the magnetic susceptibility curve, and by calculation by means of the relation, known from thermodynamics,[3]

$$dT / dp = 3VT\Delta\alpha / \Delta c_p, \qquad (1)$$

where $\Delta\alpha$ and Δc_p are respectively the jump in the coefficient of thermal expansion and the jump in the specific heat at constant pressure at the transition point.

The measurements were made on polycrystalline specimens of manganese fluoride and of cobalt fluoride. The antiferromagnetism of MnF_2 was discovered by Bizette and Tsai.[4] Its antiferromagnetic transition temperature is 68° K. The antiferromagnetism of CoF_2 was established by Erickson.[5] The antiferromagnetic transition temperature is 38° K.[6]

METHOD

The measurements of magnetic susceptibility were made by Faraday's method, with balance and cryostat like those described in the work of Borovik-Romanov and Kreĭnes.[7] There was a change in construction in that the pulling of the balance was accomplished with a tungsten filament of diameter 0.2 mm. Consequently the balance could stand a load of the order of 20 grams. Furthermore there was introduced a zero corrector, consisting of a tungsten filament of diameter 0.1 mm bent to U shape. One end of it was fastened to the beam of the balance, the other was brought out of the vacuum jar through a sylphon seal.

The apparatus permitted measurements from 300° K to 10° K. The temperature measurement was made by means of a copper-constantan thermocouple, which was calibrated by comparison with a platinum resistance thermometer over the whole temperature range from 20 to 300° K. To increase the accuracy of the temperature determination, the "cold" junctions of the thermocouple were placed in an ampoule held at the triple point of water. The precision of the temperature measurement was estimated as ± 0.2° at hydrogen temperatures and ± 0.1° at nitrogen. The pressure was produced by the method of Lazarev,[8] with ice in a bomb. The bomb was manufactured of beryllium bronze with subsequent heat treatment. The pressure created was of the order of 1900 ± 100 kg/cm^2.

The specimens were made from a powder of "chemically pure" grade. To remove sorbed water, the powder was dried in a vacuum by heating to 150° C. The dried powder was pressed under a pressure of about 15000 atm to cylindrical specimens of diameter about 2.5 mm and length 4 mm. To protect the specimen from the effect of water, its surface was coated with several layers of BF-4 gum, which was subsequently polymerized. It was established that the coating of the specimen with gum did not change the temperature dependence of the magnetic susceptibility $\chi(T)$.

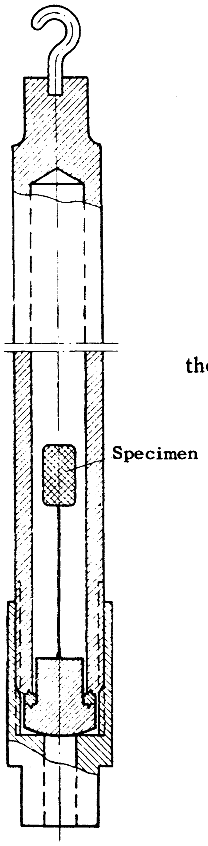

FIG. 1. Schematic sketch of the bomb with the specimen.

The specimen prepared by this method was placed in the bomb (Fig. 1). The bomb with the specimen was suspended on the balance. Three series of measurements were made on each fluoride. The magnetic susceptibility of the specimen was measured in the bomb without pressure, then with pressure, and again without pressure, to verify the absence of irreversible changes in the specimen. The repeated measurements without pressure gave values of the magnetic susceptibility in agreement with the initial values.

The measurements were made on two specimens of manganese fluoride and three of cobalt fluoride. The error of the relative measurements of susceptibility was less than ±1%. In the calculation of the value of the magnetic susceptibility of the specimens, a correction was introduced for the susceptibility of the bomb and the water. At the antiferromagnetic transition temperature it amounts to 2.5% of the susceptibility of the MnF_2 specimen and 10% of the susceptibility of the CoF_2 specimen.

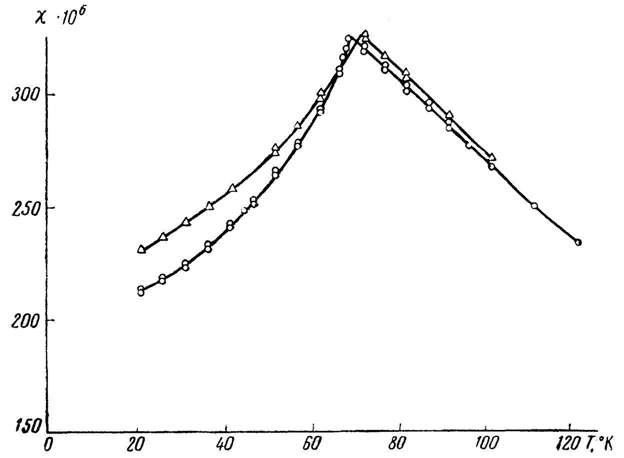

FIG. 2. Dependence of the magnetic susceptibility on temperature for MnF_2: Δ – with pressure; o – without pressure.

All the basic measurements were made in a field of about 3500 oe.

To determine the shift of the Curie temperature from the relation (1), it is necessary to know the values of the jumps in specific heat and in the coefficient of thermal expansion, Δc_p and $\Delta\alpha$. The value of Δc_p is known from specific heat measurements with manganous fluoride and cobaltous fluoride.[9] The coefficients of linear expansion of these substances had not been measured previously. We made a measurement of the coefficients of thermal expansion in the temperature range from 22 to 200°K for MnF_2 and from 22 to about 130°K for CoF_2, on a low-temperature dilatometer of Strelkov's design.[10] The specimen was made by the same method as for the magnetic susceptibility measurement, except that it was not coated with the layer of gum. It was a cylinder of diameter 5 mm and length 9 mm.

RESULTS

Measurements on MnF_2. The curves in Fig. 2 show the dependence of the magnetic susceptibility of manganese fluoride on temperature with and without pressure. The curves in the absence of pressure coincide with the $\chi(T)$ curves for unpressed powder (the values of χ corresponding to this curve were obtained on the same specimen before application of the pressure and after release of the pressure). The branches of the curve above the antiferromagnetic transition temperature are displaced parallel to one another. The left branches of the curve, corresponding to manganese fluoride in the antiferromagnetic state, are very different. The curve corresponding to the measurement under pressure is higher. We have not found a satisfactory explanation of this phenomenon.

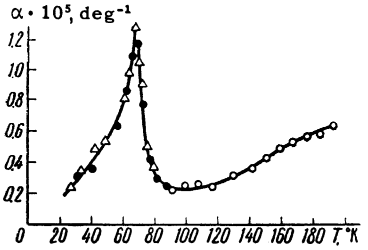

FIG. 3. Dependence of the coefficient of linear expansion on temperature for MnF_2: Δ – for specimen no. 1 in a hydrogen bath; • – for specimen no. 2 in a hydrogen bath; o – for specimen no. 2 in a nitrogen bath.

It is evident from comparison of the curves that the shift of the Curie temperature under the influence of hydrostatic compression (at pressure of 1900 ± 100 kg/cm^2) amounts to $(1.5 \pm 0.2)°$, or $dT/dp = (0.8 \pm 0.1) \times 10^{-3}$ deg/(kg/cm^2).

The antiferromagnetic transition temperature is 68°K. Figure 3 shows the dependence on temperature of the linear coefficient of expansion. The measurements were made on two specimens: on specimen No. 1 in a hydrogen bath, and on specimen No. 2 in hydrogen and nitrogen baths. The antiferromagnetic transition temperature from measurements of the coefficient of expansion can be taken as 67.5°. For the jump of the coefficient of thermal expansion, the value 1.2×10^{-5} deg^{-1} was obtained.

The value of the jump of specific heat, Δc_p, was determined from the measurements of Adams and Stout[9] and was equal to 2.4 cal/mole-deg.

For MnF_2, the calculated value of dT/dp according to formula (1) was equal to $+0.78 \times 10^{-3}$ deg/(kg/cm^2).

Measurements on CoF_2. Magnetic susceptibility measurements were made on three specimens of CoF_2. Within the limits of error, no shift of the $\chi(T)$ curves with pressure was observed. The antiferromagnetic transition temperature is 39.0°. The left branch of the $\chi(T)$ curve corresponding to the measurements under pressure is above the curve without pressure, as was the case also for MnF_2.

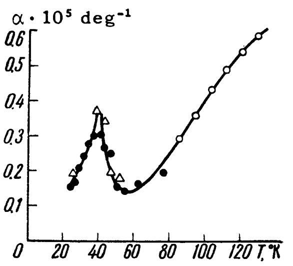

FIG. 4. Dependence of the coefficient of linear expansion on temperature for CoF_2. The symbols are the same as in Fig. 3.

Figure 4 shows the dependence of the linear coefficient of expansion on temperature, measured on two specimens. The antiferromagnetic transition temperature from measurements of the coefficient of expansion is 40.0°. The value obtained for the jump of the coefficient of thermal expansion for CoF_2 was 0.2×10^{-5} deg^{-1}.

The value of the jump of specific heat, Δc_p, was also determined from the measurements of Adams and Stout[9] and corresponds to 3 cal/mole-deg.

For CoF_2 the calculated value of dT/dp was equal to 0.09×10^{-3} deg/(kg/cm^2), at pressure (1900 ± 100) kg/cm^2. The shift should be +0.2, i.e., of the order of the error in the temperature measurement, and could scarcely be observed with our apparatus.

DISCUSSION OF RESULTS

It must be mentioned that the values of the antiferromagnetic transition temperatures of MnF_2 and CoF_2 determined by the two methods differ by 2°. This difference occurs for both salts. The discrepancy exceeds the error of the temperature measurements in either of the methods; it can be attributed to a difference in the thermocouple calibrations.

In the measurement of the coefficients of thermal expansion near the Curie point, larger anomalies were observed.

TABLE I

Substance	Curie temperature, °K	$10^6\ \Delta\alpha$, deg^{-1}
MnO	122	50 [11]
CoO	293	12 [11]
FeO	193	25 [11]
MnF_2	68	12
MnTe	310	4 [12]
CoF_2	39	2

Table I gives approximate values of the jumps in the coefficient of thermal expansion, $\Delta\alpha$, at the antiferromagnetic transitions. The values of $\Delta\alpha$ for MnF_2 are of the same order as for other antiferromagnetics, such as MnO, CoO, and FeO. The value of $\Delta\alpha$ for CoF_2 is much smaller.

It should be mentioned that in the measurements of the magnetic susceptibility of the fluoride specimens at various fields under pressure, starting at 300 oe, we observed no deviation from linearity in the dependence of magnetic moment on field, such as would correspond to a piezomagnetic effect.[13,14] This may be attributed to the fact that we used polycrystalline specimens and a hydrostatic compressive strain. Under these conditions, piezomagnetism could be observed only in the case of large elastic anisotropy in MnF_2 and CoF_2.

For comparison of our results on the shift of the Curie temperature under hydrostatic compression, we present Table II.

TABLE II

Specimens	Curie temperature	
	°K	deg/1000 atmos
Co	1393	0±0.1 [1]
Fe	843	0±0.1 [1]
Ni	633	+0.35±0.02 [15]
MnTe	310	+2±0.4 [2]
MnF_2	68	+0.73±0.1
CoF_2	39	0±0.1

It is evident that for MnF_2 the shift is larger than in ferromagnetics, and that in CoF_2 it is of the same order as in ferromagnetics.

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