Observation of the magnetic compensation points in the spinel ferrites $MnFe_{2-x}Cr_xO_4$

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We measured the temperature dependences of the magnetocaloric effect in the system of substituted spinel ferrites $MnFe_{2-x}Cr_xO_4$ at $0 \leq x \leq 1.6$. In the composition with $x = 1.085$ we observed a compensation point whose onset is attributed to the existence of a temperature dependence of the local noncollinearity angles in the arrangements of the magnetic moments of the Fe^{3+} and Cr^{3+} ions, which are statistically distributed in the octahedral B sublattice.

The system of substituted spinel ferrites $MnFe_{2-x}Cr_xO_4$ has attracted the interest of researchers for many years [1-3], since the ferrites of this system have many interesting features: they have an anomalous dependence of the magnetic moment on the substitution at 0°K, they have a large paraprocess susceptibility, etc.

The cause of the anomalous properties of these ferrites is the presence in them, at definite substitutions and in a definite temperature range, of intersublattice and intrasublattice exchange interactions of comparable magnitude, as a result of which some of the magnetic moments of the Fe^{3+} and Cr^{3+} ions in the octahedral sublattice deviate from the collinear arrangement[1)] [1-3]. No noncollinear arrangement of the magnetic moments of the ions was observed in this system of ferrites by neutron diffraction[4]. Recently, however, nuclear γ resonance[3] has revealed noncollinear arrangements of both the Fe^{3+} and the Cr^{3+} ions in the octahedral sublattice B. These deviations from collinearity have a local character, and the noncollinearity angle θ_i for the Fe^{3+} (or Cr^{3+}) ions depends on the number of neighbors i $(0 \leq i \leq 6)$ of the Cr^{3+} (or Fe^{3+}) ions.

It was established in[3] that at $i = 6$ (and also at $i = 5$ for Cr^{3+} ions) the noncollinearity angle is $\theta_6 = 180°$, i.e., the magnetic moment of the ion is directed even opposite to the magnetic moment of the B sublattice. Inasmuch as the Fe^{3+} and Cr^{3+} ions are statistically distributed over the octahedral voids and have different surroundings, the local noncollinearity angles θ_i are also statistically distributed in the lattice. The presence of such statistically-distributed noncollinear magnetic moments of the Fe^{3+} and Cr^{3+} ions can explain the anomalous properties of the spinels of this system of ferrites. Indeed, if the magnetic moments of the Fe^{3+} and Cr^{3+} are canted relative to each other, the magnetic moment of the octahedral sublattice at 0°K is smaller than it should be in accordance with the Neél theory, which in turn can explain also the anomalous dependence of the magnetic moment on the degree of substitution x. The presence of statistically distributed angles in the arrangement of the magnetic moments can explain also the high value of the paraprocess susceptibility.

The existence of such angular configurations leads in these materials to the appearance of a unique compensation point. It is known that usually the compensation point appears in ferrimagnets that have not less than two magnetic sublattices with different temperature dependences of the sublattice magnetic moments, and the larger sublattice magnetic moment having a stronger temperature dependence, whereas the smaller has a smaller temperature dependence. A consequence of this phenomena is the appearance of a temperature T_c at which the magnetic moments of the sublattices become equal.

In the spinels $MnFe_{2-x}Cr_xO_4$, the presence of angular configurations and of a temperature dependence of the noncollinearity angle θ_i[3], due to the fact that the intrasublattice interactions decrease more rapidly with increasing temperature than the intersublattice interactions, can lead to the appearance of a compensation temperature at which magnetizations of sublattices A and B become equal. The existence of such a compensation temperature was indirectly deduced in[3] from the fact that the magnetization of the ferrite $MnFeCrO_4$ $(x = 1)$ turned out to be directed along the A sublattice at 120°K, and along the B sublattice at 296°K. According to that reference, the temperature T_c for the ferrites with $x = 1$ should lie in the interval $120° < T < 296°$K. In an earlier investigation of the magnetocaloric effect (ΔT effect) we have established[5,6] that the ΔT effect changes sign at the compensation point T_c. We have also established[7,8] that the magnetocaloric ΔT effect is a very sensitive characteristic of the magnetic behavior of a ferrimagnet and makes it possible to trace the singularities of the magnetic behavior of substituted systems[8,9].

In the present study we investigated the magnetocaloric ΔT effect in the system of spinels $MnFe_{2-x}Cr_xO_4$ in the temperature interval from 78 to 600°K for compositions with x = 0, 0.125, 0.5, 1.085, 1.25, 1.4, and 1.6. The samples were produced by the usual ceramic technology, were single-phase, had lattice parameters close to the published data, and Curie temperatures Θ_f, determined from the maximum of ΔT at the point Θ_f, which agreed sufficiently well with the data of Gorther[1] (Fig. 1).

Figure 2 shows the temperature dependence of the magnetocaloric ΔT effect for all samples of the system. All the investigated samples have at the Curie point a clearly pronounced maximum $(\max \Delta T)_{\Theta f}$, the value of which depends on the degree of substitution.

We have previously established[5,6] that in ferrimagnets, in individual sublattices coupled by negative exchange interaction, depending on the orientation of the sublattice magnetic moment relative to the external field H and the effective exchange field H_{eff}, two different types of the paraprocess can exist, ferromag-

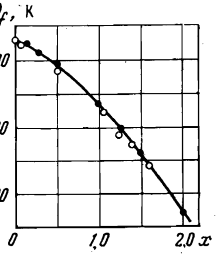

FIG. 1. Dependence of the Curie temperature of ferrites of the $MnFe_{2-x}Cr_xO_4$ system on x: ●—Gorther's data [1], ○—our data.

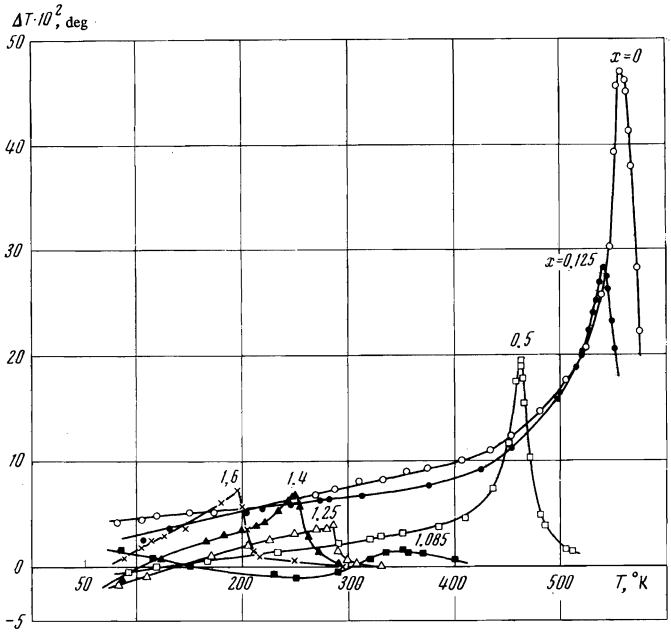

FIG. 2. Temperature dependence of the magnetocaloric effect for ferrites of the system $MnFe_{2-x}Cr_xO_4$.

netic and antiferromagnetic. The paraprocess of the ferromagnetic type occurs when H and H_{eff} have the same direction, and then the external field enhances the magnetic order in the sublattice, this being accompanied by a release of heat ($\Delta T_{sub} > 0$). A paraprocess of the antiferromagnetic type occurs at oppositely directed H and H_{eff}. In this case, the external field decreases the magnetic order in the sublattice, this being accompanied by absorption of heat by the spin system and consequently by cooling of the sample ($\Delta T_{sub} < 0$). We have thus established that the ferromagnetic and antiferromagnetic paraprocesses make contributions of opposite signs to the magnetocaloric effect ([5,6], and also[8]). Since the magnetic moments of the sublattices A and B are coupled by negative exchange interaction and both types of paraprocess are realized in the spinels simultaneously, the sign of the summary magnetocaloric effect is determined by the more intense of the paraprocesses[8,9].

In the samples of the system investigated by us, with x = 0, 0.125, and 0.5, the magnetic moment of the B sublattice at 0°K exceeded the magnetic moment of the A sublattice[1], and consequently in the entire temperature interval investigated by us, the external field aligns the magnetic moment of the sublattice B in which a paraprocess of the ordinary ferromagnetic type is observed and makes a positive contribution to the summary ΔT effect. For these compositions, the paraprocess in the sublattice A, the magnetic moment of which is opposite to the external field, will be of the antiferromagnetic type, making a negative contribution to ΔT. Consequently $\Delta T_B > 0$ and $\Delta T_A < 0$ for these samples. The summary (measured) ΔT effect, as seen from Fig. 2, is positive for the samples with x = 0 and 0.125 in the entire investigated temperature interval, thus indicating that the more intense paraprocess takes place in the B sublattice and that $|\Delta T_B| > |\Delta T_A|$.

This behavior of the ΔT(T) curves, which is the "ordinary" one for ferromagnets, agrees also with the "ordinary" Weiss temperature dependence of the magnetization I(T). Indeed, the temperature dependence of the magnetocaloric effect which is uniquely connected with the derivative $\partial I/\partial T$, inasmuch as

$$dT = -\frac{T}{C_{p,H}}\left(\frac{\partial I}{\partial T}\right)_H dH,$$

should characterize also the temperature dependence of the magnetization. At the compensation point, where the derivative $\partial I/\partial T$ reverses sign, the ΔT effect also reverses sign. Consequently, the reversal of the sign of the magnetocaloric effect ΔT, from positive to negative, with increasing temperature corresponds to a compensation temperature T_c whose value can be determined both from the I(T) curve and from the ΔT(T) curve. Analogously, the position of the Curie point Θ_f can also be determined by different methods, particularly from the maximum of ΔT at the Curie point.

An analysis of the behavior of the ΔT(T) curves enables us to draw the following conclusions: For the sample with x = 0.5 we have observed in the 140°K region changes in the sign of the ΔT effect. On the one hand, this indicates that the temperature dependence of the magnetization differs for this sample from the usual Weiss type, and is represented by a curve of the Néel p-type. Indeed, it is seen from Fig. 2 that in the region 78–140°K the ΔT effect for this sample, while remaining negative, decreases in magnitude, corresponding to a growth of the magnetization with increasing temperature (see the formula for dT). The anomalous I(T) curve of the sample with x = 0.5 can be attributed to the presence of angles whose magnitude changes with increasing temperature in the arrangement of the magnetic moments of the Fe^{3+} and Cr^{3+} ions in the sublattice B[1,3]. The growth of the magnetization with increasing temperature in this region is obviously evidence of an increase in the magnetic moment of the sublattice B, which occurs as a result of the decrease in the angles between the magnetic moments of the Fe^{3+} and Cr^{3+} ions.

On the other hand, the fact that the ΔT effect goes through zero in 140°K indicates that the intensities of the paraprocesses of the ferromagnetic and antiferromagnetic types in the sublattices A and B are the same at this temperature, and their contributions to the summary ΔT effect cancel each other.

The shape of the ΔT(T) curve of the sample with x = 1.085 indicates that this sample has a compensation temperature T_c = 150°K. At this temperature, the sign of ΔT(T) of this sample reverses with increasing temperature, from positive to negative, and this corresponds, as described above, to the compensation point.

According to Gorther[1], the magnetic moment of a ferrite with x = 1 at 0°K is directed along the A sublattice, which is stronger at low temperatures. The weakening of the B sublattice with increasing substitution x can be attributed to the presence of statistically distributed noncollinearity angles θ_i in the arrangement of the magnetic moments of the Fe^{3+} and Cr^{3+} ions in this sublattice[3]. On the other hand, the presence of a compensation point indicates that, starting with $T = 150^\circ K$, the sublattice B becomes stronger. The results of our measurements confirm the data of[3], namely that the magnetization of the ferrite M and $FeCrO_4$ is directed along the A sublattice at 120°K and along the B sublattice at 296°K. The presence of a such peculiar compensation temperature is due to the temperature dependence of the noncollinearity angles θ_i and the arrangement of the magnetic moments. With increasing temperature, the intrasublattice interactions seem to decrease more rapidly than the intersublattice ones, and this leads to a decrease in the noncollinearity angles θ_i and hence to an increase of the magnetic moment of the B sublattice. At temperature $T > 150^\circ K$, the ferrite magnetization is directed along the B sublattice, which becomes stronger starting with $T = 150^\circ$, owing to the decrease of the noncollinearity angles θ_i, as a result of which its magnetic moment becomes aligned with the external field, whereas the magnetic moment of the A sublattice is opposite that of the external field. Consequently, starting with $T_c = 150^\circ K$, the external field increases the magnetic order in the B sublattice (paraprocess of the ferromagnetic type, with a contribution $\Delta T_B > 0$) and decreases the magnetic order in the sublattice A (antiferromagnetic-type paraprocess, with contribution $\Delta T_A < 0$).

For the sample with x = 1.085, the negative sign of the ΔT effect and the temperature region from 150 to 300°K is due to the larger contribution of ΔT_A ($|\Delta T_A| > |\Delta T_B|$). At 350°K the contributions ΔT_A and ΔT_B are equal to each other, the ΔT effect goes through zero again and becomes positive (above 350°K we have $|\Delta T_B| > |\Delta T_A|$). In the region of the Curie temperature (350°K) there is a smeared maximum of the ΔT effect. The smearing of the transition in this case is evidence of a weakening of the intersublattice exchange interaction, due to replacement of the Fe^3 (B) ions by Cr^{3+} (B) ions; this is also evidenced by the decrease in the value of Θ_f and by the data of[3].

In samples with larger chromium content (x = 1.25, 1.4, and 1.6), the inclination angles of the magnetic moments of the Fe^{3+} and Cr^{3+} ions play an even more important role. It is known[1] that at $x > 0.8$ and 0°K the magnetic moment of the ferrite is directed along the A sublattice, which is the stronger one. Consequently, the contribution ΔT_A at 0°K should be positive for these compositions. If the noncollinearity angles θ_i would not decrease with increasing temperature then the sublattice A would remain the stronger one up to the Curie point, and the ΔT effect would be positive up to $T = \Theta_f$. However, the sign of ΔT for the sample with x = 1.25 is negative at $T < 137^\circ K$, which indicates that the unusual compensation temperature due to the presence of $\theta_i(T)$ lies below 78°K, in full agreement with the data of[3]. According to[3], in the temperature interval investigated by us the sublattice B is already the stronger one in this compound. The similar course of the $\Delta T(T)$ plots for the samples with x = 1.4 and 1.6 allows us to assume that their compensation temperature resulting from the temperature dependence of the noncollinearity angle also lies below 78°K.

In the temperature range 78—300°K, where the intrasublattice interactions are already somewhat weakened, the presence of noncollinearity angles θ_i in the arrangements of the magnetic moments of the Fe^{3+} and Cr^{3+} in the B sublattices should make an additional contribution to the paraprocess, since the external field, which tends to align the magnetic moments of these ions along the field, decreases the angles θ_i thereby increasing the contribution of the B sublattice to the paraprocess and, consequently the contribution ΔT_B to the summary ΔT effect ($\Delta T_B > 0$). Therefore as the substitution x is increased the intensity of the paraprocess in the sublattice B should increase, and the $\Delta T(T)$ curves for the samples with $x > 1.25$ should lie higher, as is observed in experiment (see Fig. 2).

It should be noted in conclusion that the magnetocaloric effect is such a sensitive characteristic of the magnetic behavior of ferrimagnets, that it makes it possible to observe the unusual compensation temperature resulting from the existence of a temperature dependence of local noncollinearity angles in the arrangement of the magnetic moments, something quite difficult to observe by other methods.

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1)In this case a noncollinear arrangement of the magnetic moments of the Fe^{3+} and Cr^{3+} ions corresponds to the minimum of the interaction energy.

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