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Investigation of "Sublattice" Magnetocaloric Effects in Substituted Gadolinium Iron Garnets

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A study is made of the temperature dependence of the magnetocaloric effect ΔT in the system of garnets $Gd_3Ga_xFe_{5-x}O_{12}$ for $0 \le x \le 1.5$. It is shown that the peculiarities in the behavior of ΔT—a sharp increase in the nitrogen-temperature region, cooling on magnetization, and the maxima of ΔT at the Curie point—can be explained with the aid of the concepts of paraprocesses of ferro- and of antiferromagnetic types in separate sublattices.

In the three-sublattice iron garnets $R_3Fe_5O_{12}$ the paraprocess is of a complicated nature, because the a, d, and c sublattices make their individual contributions to the paraprocess. In the present paper, measurements of the magnetocaloric effect (ΔT-effect) will be applied to the study of the complicated paraprocess in these ferrites.

Depending on the orientation of the magnetic moment of the sublattice with respect to the external field H_{ext} and the effective exchange field H_{eff}, two different types of paraprocess may occur in a sublattice:[1,2] a paraprocess of ferromagnetic type (when H_{ext} and H_{eff} are in the same direction), in which the external field increases the magnetic order in the sublattice, a change that is accompanied by a liberation of heat ($\Delta T > 0$); and a paraprocess of antiferromagnetic type (occurring when H_{ext} and H_{eff} are in opposite directions), in which the external field decreases the magnetic order in the sublattice, a change that is accompanied by an absorption of heat by the spin system and, consequently, a cooling of the specimen ($\Delta T < 0$). Because the magnetic moments of the sublattices in garnets are coupled by negative exchange interaction, both types of paraprocess occur in different sublattices simultaneously. The sign of the resultant magnetocaloric effect is determined by the contribution of the more intense of the paraprocesses.

Paraprocesses of ferro- and antiferromagnetic types can be observed in the same sublattice in different ranges of temperature. We showed earlier that in iron garnets of heavy rare-earth elements possessing a compensation temperature T_c, in the range $T < T_c$ — where, as is well known, the magnetic moment of the rare-earth sublattice c is the largest and consequently orients itself along the direction of the external field—a paraprocess of ferromagnetic type occurs in the rare-earth sublattice; but in the range $T > T_c$ a paraprocess of antiferromagnetic type is observed in the same sublattice, since in this range of temperature the magnetic moment of the sublattice c (as the smaller in magnitude) orients itself opposite to the external field.[1-3] The magnitude of the magnetic moment of a sublattice can also be changed by introducing nonmagnetic ions into it.

In order to study the complicated magnetocaloric effect and the complicated paraprocess responsible for it in three-sublattice iron garnets, we prepared and studied the system of garnets $Gd_3Ga_xFe_{5-x}O_{12}$, where x = 0, 0.15, 0.3, 0.4, 0.6, 0.9, 1.2, and 1.5, in which nonmagnetic Ga^{3+} ions were introduced instead of Fe^{3+} ions in the d sublattice.[4-6] The lattice of Gd^{3+} ions remained unchanged. Such a substitution led to a weakening of the exchange interaction between the a and d sublattices, which is the strongest in iron garnets. Measurements of the ΔT-effect were made on polycrystalline specimens in the temperature interval from 78 to 600°K, in a field of 16 kOe, by the method described in [1].

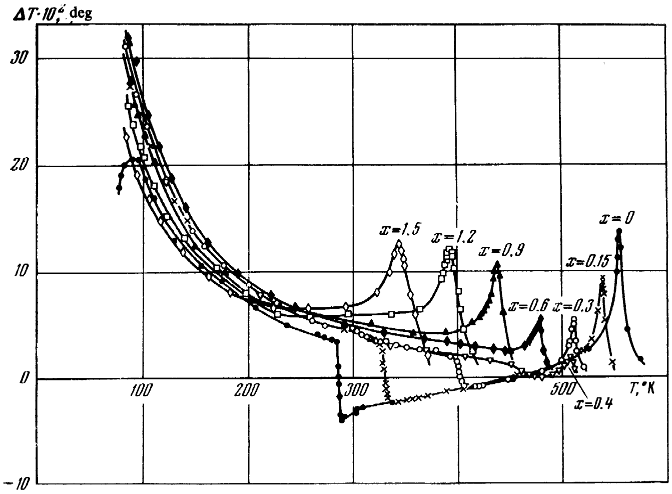

FIG. 1. Temperature dependence of the magnetocaloric effect ΔT for the system of substituted garnets $Gd_3Ga_xFe_{5-x}O_{12}$, where x = 0 to 1.5.

Figure 1 shows the results of the measurements. The general character of the temperature dependence of the ΔT-effect for the substituted garnets with x = 0.15 and 0.3 is similar to that for the specimen with x = 0. In garnets of these three compositions, the resultant magnetocaloric effect is positive in the low-temperature range (for $T < T_c$); a change of sign of the ΔT-effect occurs at the compensation point; then, with increase of temperature, the ΔT-effect passes through zero and becomes positive, and a maximum of the magnetocaloric effect is observed in the neighborhood of the Curie point. The difference in the behavior of the ΔT-effect for the compositions with x = 0.15 and 0.3, as compared with the specimens with x = 0, consists in the fact that in the low-temperature range for these compositions we do not observe a maximum of the ΔT-effect, corresponding to a low-temperature point (T_l), and in the fact that with increase of x the compensation temperature increases, the Curie temperature decreases, and the maximum of the ΔT-effect at the Curie point becomes smaller. Such a behavior of the ΔT-effect we explain as follows.

In the temperature range $T < T_c$, the orientations of

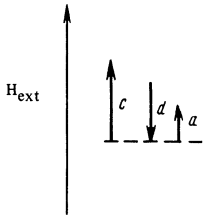

FIG. 2. Vector diagram of the orientation of magnetic moments of the sublattices of iron garnets for $T < T_c$.

the sublattice magnetic moments and their magnitudes are shown in Fig. 2.[1] The external field will increase the magnetic order in sublattices c and a and will decrease it in sublattice d. Consequently, in this temperature range a paraprocess of ferromagnetic type will be observed in sublattices c and a, and the magnetocaloric effects accompanying these paraprocesses in sublattices c and a will be positive. In sublattice d, a paraprocess of antiferromagnetic type will be observed, and the ΔT-effect accompanying it will be negative. But in the Gd iron garnet with x = 0, in the iron sublattices a and d, coupled by strong negative exchange interaction, the paraprocess far from the Curie temperature is small. Consequently, the largest contribution to the magnetocaloric effect in the range $T < T_c$ will be made by the paraprocess of ferromagnetic type in sublattice c, and this determines the sign and behavior of the resultant ΔT-effect.

The maximum of the ΔT-effect in the 100°K region, observed in the iron garnet with x = 0, corresponds to the so-called low-temperature point T_l [9]—a peculiar Curie point of the rare-earth sublattice, which is in the biasing field of the iron sublattices a and d. In the specimens with x = 0.15 and 0.3, the substitution causes a diminution of the magnetic moment of sublattice d and consequently of the d-a and d-c exchange interactions and leads to the result that the low-temperature points T_l of these compositions, because of weakening of the effective field $H_{\text{eff}}^{(c-ad)}$, are displaced toward lower temperatures (below 78°K), and therefore we did not observe the maxima of the ΔT-effect corresponding to T_l. The weakening of sublattice d (that is, the diminution of its magnetic moment) leads to the result that the negative contribution to the ΔT-effect by the paraprocess of antiferromagnetic type in sublattice d will decrease, while the positive contribution to the ΔT-effect, because of the slight increase of intensity of the paraprocess of ferromagnetic type in sublattices c and a, increases somewhat. This should lead to an increase of ΔT (for T = const) with increase of the substitution, as was in fact observed (see Fig. 1, temperature range ~100°K).

On rise of temperature, the magnitude of the magnetocaloric effect decreases; and at the compensation point, the ΔT-effect, abruptly changing its sign, becomes negative for compositions with x = 0, 0.15, and 0.3. We explain the occurrence of cooling upon magnetization by the fact that in the range $T > T_c$, in the rare-earth sublattice c there is observed a strong paraprocess of antiferromagnetic type ($\Delta T_c < 0$). The external field decreases the magnetic order in sublattices c and a; that is, it increases the magnetic part of the entropy; but the contribution from the paraprocess in sublattice a is still small ($\Delta T_a \ll \Delta T_c$). In this temperature range, a paraprocess of ferromagnetic type is observed in sublattice d ($\Delta T_d > 0$). On increase of temperature, the strength of the paraprocess increases in the iron sublattices, and primarily in the stronger sublattice d; this leads to an increase of the positive contribution to the magnetocaloric effect from ΔT_d, and this in turn leads to the result that in the 460°K region the resultant magnetocaloric effect of the garnet again goes through zero (for compositions with x = 0, 0.15, and 0.3). The presence of such a peculiar temperature of magnetocaloric-effect compensation, at which the contributions from paraprocesses of ferro- and antiferromagnetic types are equal, is proof of the existence of sublattice contributions of different signs. Then ΔT becomes positive and increases rapidly with approach to the Curie temperature, because of the occurrence of a strong paraprocess of ferromagnetic type in sublattice d. At the Curie point there is observed in all specimens a positive maximum of the magnetocaloric effect.

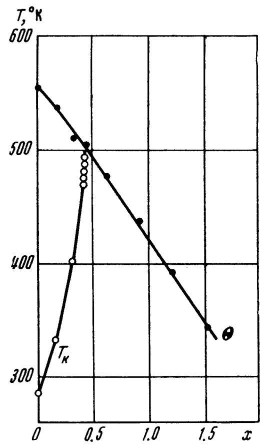

FIG. 3. Dependence of Curie temperature Θ and of compensation temperature T_c on composition for the system of garnets $Gd_3Ga_xFe_{5-x}O_{12}$.

The observed decrease of the Curie temperature with increase of the compensation temperature of the garnets, on increase of the substitution x, gives evidence both of the weakening of the strongest exchange interaction, between sublattices a and d, and of the diminution of the magnetic moment of the resultant sublattice a-d. It is obvious that when there is simultaneous lowering of the Curie point and raising of the compensation point with substitution (see Fig. 3), there must exist a composition (x = 0.42) for which the compensation point coincides with the Curie point. We investigated a specimen with x = 0.4, for which there was observed a whole "compensation range" of the magnetocaloric effect (see Figs. 1 and 3).

We shall also consider how the magnetocaloric effect in the Curie-temperature region changes on substitution. On increase of the substitution x from 0 to 0.4, the magnitude of the maximum of the magnetocaloric effect in the Curie-point region, $(\Delta T)_\Theta$, decreases (see Fig. 1). Such a decrease of the magnitude of $(\Delta T)_\Theta$ we explain as follows. As was established earlier,[2] $(\Delta T)_\Theta$ for all rare-earth ferrite garnets is smaller than for yttrium garnet. The smaller value of $(\Delta T)_\Theta$ in rare-earth ferrites is due to the fact that in them there occur in the Curie-point region both a paraprocess of ferromagnetic type in the sublattice d, which makes a positive contri-

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[1] Here we consider magnetic fields $H < H_{ci}$ [7,8], for which noncollinear spin structures do not occur and the magnetic moments of the sublattices are collinear.

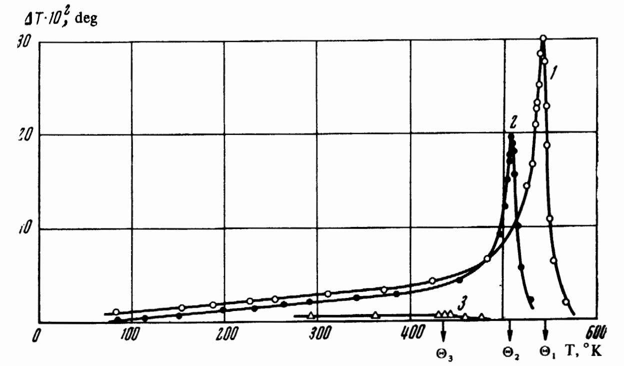

FIG. 4. Temperature dependence of the magnetocaloric effect ΔT for substituted yttrium garnets: curve 1, $Y_3Fe_5O_{12}$; curve 2, $Y_3Ga_{0.3}Fe_{4.7}O_{12}$; curve 3, $\{Y_{2.5}Na_{0.5}\}\ Fe_4GeO_{12}$.

bution to the resultant ΔT-effect, and also a paraprocess of antiferromagnetic type in sublattices c and a, which makes a negative contribution to the ΔT-effect. In substituted iron garnets of compositions $x = 0.15$, 0.3, and 0.4, the negative contribution from the rare-earth sublattice and from the sublattice a does not change, since the sublattice a and the sublattice of Gd ions have not been weakened,[2] whereas the positive contribution to ΔT from the paraprocess of ferromagnetic type in sublattice d decreases because of its weakening. The weakening of sublattice d and the consequent weakening of the a-d exchange interaction lead also to some strengthening of the paraprocess of antiferromagnetic type in sublattice a, and this increases the negative contribution to the resultant magnetocaloric effect of the garnet and consequently decreases still further the magnitude of $\max(\Delta T)_\Theta$.

Thus in consequence of the weakening of sublattice d, there is a diminution of the magnitude of the resultant maximum of the magnetocaloric effect at the Curie point. To verify the correctness of this proposition, we prepared a specimen of the composition $Y_3Ga_{0.3}Fe_{4.7}O_{12}$ ($x = 0.3$), for which the contribution to the ΔT-effect from the rare-earth sublattice was zero. Investigations of the ΔT-effect carried out on this specimen showed that on replacement of the iron ions in sublattice d by Ga^{3+} ions, there actually occurs a decrease of the value of $(\Delta T)_\Theta$ as compared with the $(\Delta T)_\Theta$ of the unsubstituted iron garnet $Y_3Fe_5O_{12}$ (see Fig. 4); this supports the correctness of our proposition.

For the compositions with $x = 0.6$, 0.9, 1.2, and 1.5, the compensation point is absent; this is evidence that the magnetic moment of the rare-earth sublattice c, over the whole temperature interval—from nitrogen temperature to the Curie point—is larger than the resultant magnetic moment of the iron sublattices a and d. As a result, on application of an external magnetic field the magnetic moment of sublattices a and c orients itself along its direction over the whole temperature interval. This in its turn leads to the result that for these compositions, over the whole temperature range, a paraprocess of ferromagnetic type occurs in the rare-earth sublattice c and in the iron sublattice a, a paraprocess of antiferromagnetic type in the iron sublattice d. Consequently the value of $(\Delta T)_\Theta$ is determined for $x = 0.6$ by the positive contribution to ΔT from the paraprocess of ferromagnetic type in the sublattices c and a; the positive contribution to the ΔT-effect is larger than the negative contribution from the paraprocess of antiferromagnetic type in the weakened sublattice d of iron ions, since $\Delta T > 0$. On weakening of the d-sublattice with increase of x, the negative contribution to the ΔT-effect should diminish, and this should lead to an increase of $(\Delta T)_\Theta$. Actually, at substitutions $x = 0.9$ and 1.2 there is observed some increase of the value of $(\Delta T)_\Theta$ as compared with $(\Delta T)_\Theta$ for $x = 0.6$ (see Fig. 1).

According to [4,11,12], in substituted Y iron garnets at certain values of x, depending on the substituting ion, there is observed a compensation of the magnetic moments of the iron ions in sublattices a and d. In particular, compensation of the magnetic moments in the case of replacement of Fe^{3+} ions by Ge^{4+} ions is observed at an x close to unity; and in the case of replacement of Fe^{3+} ions by Ga^{3+} ions, at $x = 1.25$ to 1.30.

Our investigation of the temperature dependence of the magnetocaloric effect for the garnet $\{Y_{2.5}Na_{0.5}\}\ Fe_4GeO_{12}$ ($x = 1$) showed that for this specimen, the magnetocaloric effect at the Curie point, $(\Delta T)_\Theta$, is very small (see Fig. 4). This gives us justification for concluding that in yttrium iron garnet with gallium substituted, the magnetocaloric effect for compositions with substitutions $x = 1.25$ to 1.30, at which compensation of the magnetic moments of sublattices a and d occurs, is also very small because of compensation of paraprocesses of ferro- and antiferromagnetic types in these sublattices. Consequently, the value of $(\Delta T)_\Theta$ for the specimen of $Gd_3Ga_{1.2}Fe_{3.8}O_{12}$ ($x = 1.2$) is almost completely determined by the positive contribution from the paraprocess of ferromagnetic type in the rare-earth sublattice.

On further increase of the substitution ($x = 1.5$), the value of $(\Delta T)_\Theta$ continues to increase (see Fig. 1); we explain this for the composition with $x = 1.5$ by the presence of an additional positive contribution to the resultant ΔT-effect from the paraprocess of ferromagnetic type observed at this composition in the sublattice a, whose magnetic moment is oriented along the magnetic moment of sublattice c and consequently along the direction of the external field.

The presence of an increase of $(\Delta T)_\Theta$ at those substitutions at which the magnetic moment of sublattice a dominates over the magnetic moment of sublattice d[6] is evidence in favor of the proposition that the magnetic moments of sublattices a and c coincide in direction.

Our investigations permit us to conclude that the magnetocaloric effect is very sensitive in iron garnets to a change of the magnetic state of the sublattices, of their magnetic entropy, or of the sublattice exchange interactions. The fact that paraprocesses of different types, occurring in individual sublattices of ferromagnets, make contributions of different signs to the magnetocaloric effect makes it expedient to apply measurements of the ΔT-effect to the study of the magnetic state of substituted iron garnets.

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[2] According to[10], the magnetic moment of the Gd sublattice does not change under such substitutions in the d sublattice.

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