Cluster character of antiferromagnetic ordering in garnets

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Measurements of the heat capacity of garnets containing two types of $3d$ ions in one (octahedral) or two (octa- and dodecahedral) sublattices shows that an antiferromagnetic ordered state of the cluster type is realized in these compounds.

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The garnet-structure singularities due to the existence of three types of sites (sublattices)—dodecahedral $\{c\}$, octahedral $[a]$, and tetrahedral (d)—and the possibility of isomorphic substitution of certain atoms by others give rise to a large diversity of the magnetic properties of these compounds. Detailed investigations have by now been carried out of the rare-earth iron garnets, the ferrimagnetism of which is determined by the strong ($T_c \approx 550$ K) a-d interaction, and the so called "single-sublattice" garnets, in which weak exchange interactions of $3d$ or $4f$ ions in one of the sublattices causes antiferromagnetic ordering at temperatures on the order of 15 K.

The least investigated interaction in garnets is the c-a exchange interaction. Bozorth and Geller,[1] in an investigation of the magnetic susceptibility of the garnet $\{Mn_3^{2+}\}[Fe_2^{3+}](Ge_3)_{012}$ (MnFeG), obtained a rather unexpected result: the compound exhibits antiferromagnetic properties below 10 K, although according to the Neel model one should expect ferrimagnetism with a spontaneous moment $M_S = 3M_c - 2M_a = 5\mu_B$.

To obtain more detailed information on the character of the magnetic order

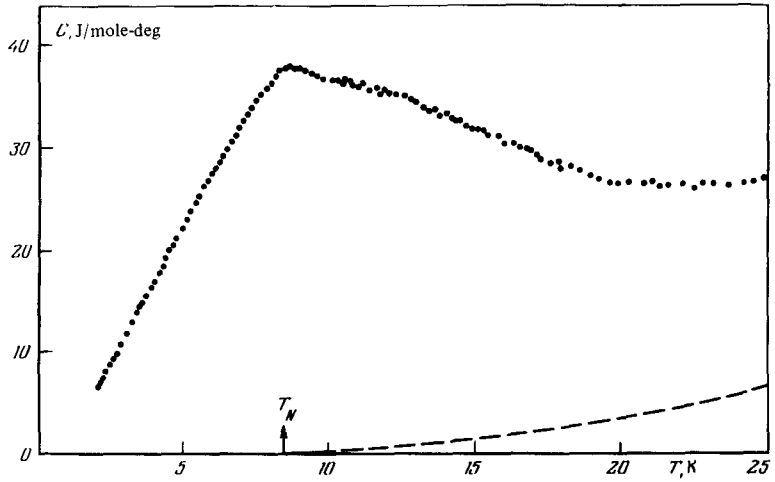

FIG. 1. Heat capacity of the garnet $Mn_3Fe_4Ge_3O_{12}$ (points). The dashed curve shows the contribution of the lattice heat capacity.

in MnFeG, we measured, by the vacuum calorimeter method,[2] the heat capacity of a polycrystalline sample in the temperature interval 2—25 K. The phase composition of the garnet was monitored with an x-ray diffractometer. The contents of the impurity phases did not exceed 1.5%.

The magnetic susceptibility of MnFeG measured by us exhibits the usual behavior of antiferromagnetic garnets with 3*d* ions, namely, satisfaction of the Curie—Weiss law in the interval 15—100 K and a weak $\chi(T)$ dependence below 10 K, in qualitative agreement with the data of[1].

The results of the measurements of the heat capacity of MnFeG are shown in Fig. 1. Figure 1 shows also the heat capacity of the lattice, calculated from the data for the diamagnetic garnet $Cd_3Ga_2Ge_3O_{12}$. The temperature dependence of the heat capacity of MnFeG, in contrast to that of the single-sublattice gargets $Mn_3Al_2Ge_3O_{12}$ (MnAlG)[3] and $Ga_3Fe_2Ge_3O_{12}$ (CaFeG),[4] does not show the λ-anomaly typical of second-order phase transitions. Below $T_N \approx 8.5$ K, the heat capacity of MnFeG varies practically linearly with the temperature and decreases quite slowly in the region $T \gg T_N$. This behavior of the magnetic heat capacity is typical of the so called spin glasses and of systems with magnetic clusters (see, e.g., the review[5]). The possible appearance of clusters in substituted ferrimagnet-garnet was discussed in[6]. It appears that in the case of MnFeG the cluster character of the magnetic ordering is caused by the approximate equality of the intra- and intrasublattice exchange interaction ($J_{cc} \approx J_{ca} \approx J_{aa}$), as is evidenced by the values of T_N of the garnets MnAlG (5.54 K),[3] GaFeG (12.2 K),[4] and MnFeG (8.5 K). It can also be assumed that the character of the magnetic order in MnFeG is strongly influenced by the difference in the magnetic structures of the "initial" single-sublattice garnets: according to neutron-diffraction data, MnAlG has a propagation vector $\mathbf{k}=0$,[7] while the structure of GaFeG is characterized by $\mathbf{k}=(111)$.[8]

To verify the foregoing assumptions, we investigated the garnet system

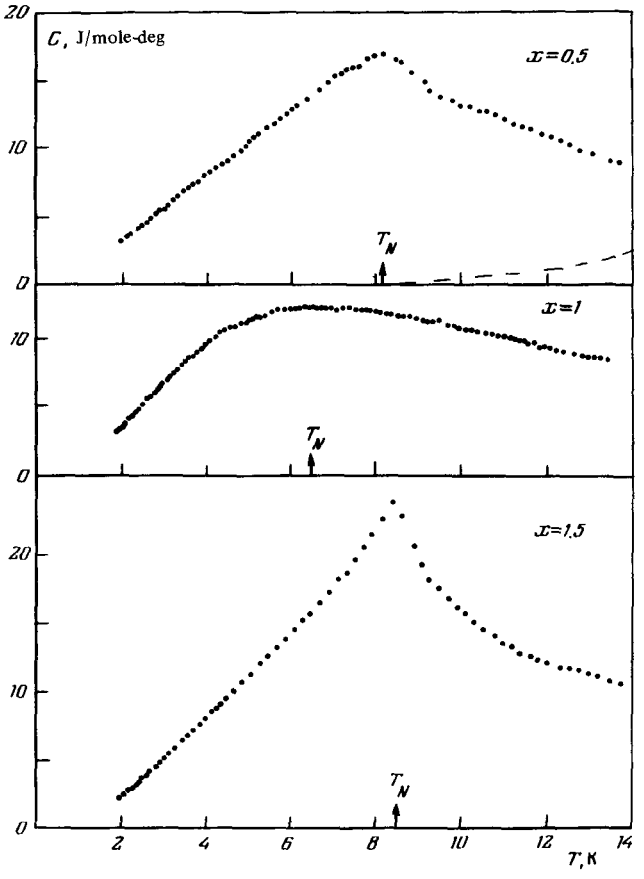

FIG. 2. Heat capacity of the garnets $Ca_3Fe_xCr_{2-x}Ge_3O_{12}$, dashed curve—heat capacity of the lattice.

$Ga_3Fe_xCr_{2-x}Ge_3O_{12}$ ($x = 0.5; 1.0; 1.5$), in which the ions Cr^{3+} and Fe^{3+} are in the same magnetic sublattice. According to the data of[4,9], for the limiting compositions of this system ($x = 0$ and 2.0), the integrals of the exchange interactions of the octahedral ions Cr^{3+} and Fe^{3+} practically coincide, while the magnetic moments of CaCrG and GaFeG below T_N are directed respectively along the axes ⟨100⟩ ($K_1 > 0$) and ⟨111⟩ ($K_1 < 0$).[10] In the CaCrG magnetic structure $\mathbf{k} = 0$.

Figure 2 shows the measured heat capacity of the system CaFeCrG. The $C(T)$ plot for the composition with $x = 1.0$ [1)] reveals the same singularities as for MnFeG. The magnetic susceptibility of the garnets GaFeCrG in the interval 10—100 K follows the Curie—Weiss law with negative Θ_p. Below 10 K, is independent of temperature. However, whereas at $x = 0$ and 2.0 the effective magnetic moment coincides with the theoretical values $s_{Fe} = \frac{5}{2}$ and $s_{Cr} = \frac{3}{2}$, in the case of samples with intermediate compositions no such correspondence is observed. Thus, for the garnet with $x = 1.0$ experiment yields $s_{eff} = 1.84$ as against the calculated 2.05.

According to the experimental data on the heat capacity of spin glasses,[11] below the magnetic-ordering temperature, as a rule, approximately $\frac{1}{3}$ of the total magnetic entropy of the system is realized. For Heisenberg magnets with long-range magnetic order the entropy change $\Delta S|_0^{T_N}$ amounts to ~ 80%,[12] in good agreement with the results for single-sublattice antiferromagnetic garnets.[13] For the sample $Ca_3Fe_{1.0}Cr_{1.0}Ge_3O_{13}$ we obtain

$$\Delta S|_0^{T_N} = 0.47R[\tfrac{1}{2}\ln(2s_{Fe}+1) + \tfrac{1}{2}\ln(2s_{Cr}+1)],$$

i.e., 47% of $\Delta S|_0^{\infty}$, while for MnFeG $-\Delta S|_0^{T_N} = 0.42\Delta S|_0^{\infty}$. The presented values of $\Delta S|_0^{T_N}$ and the character of the $C(T)$ dependence attest to the preservation of the short-range magnetic order in MnFeG and $Ga_3Fe_{1,0}Cr_{1,0}Ge_3O_{12}$ in the region $T > T_N$. As to the heat capacity of the samples with $x = 0.5$ and 1.5, its temperature dependence (Fig. 2) obviously corresponds to a transition state from an antiferromagnetic with long-range magnetic order to a cluster ordering.

Thus, in garnets with weak exchange interactions there can apparently be realized a magnetic order of the cluster type. The possibility of such an order is quite realistic for substituted and magnetically-diluted ferrimagnetic garnet systems.

[1)]We investigated two samples shown by x rays to be single-phase, but with different widths of the diffraction lines on the x-ray patterns, and consequently with different homogeneities in the distributions of Fe^{3+} and Cr^{3+} over the octahedral lattice sites. The measurements of the heat capacity yielded practically identical results.

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