Quasi-one-dimensional nature of magnetic ordering due to the cooperative Jahn-Teller effect in the garnet $NaCa_2Cu_2V_3O_{12}$ (CuVG)

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Based on the results of measurements of the magnetic properties and heat capacity of CuVG, it is concluded that quasi-one-dimensional antiferromagnetic ordering, whose microscopic mechanism is related to antiferrodistortional ordering of the orbitals of Cu ions as a result of the cooperative Jahn-Teller effect (CJTE), arises in this compound at $T \sim 10$ K.

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Among antiferromagnetic (AF) garnet with 3d ions,[1] CuVG, in which the Cu ions with and E_g electronic ground state occupy the octahedral positions, is distinguishd by its unusual magnetic properties. According to data in Ref. 2, the magnetic ordering temperature of CuVG is $T_N = 0.2$ K, while the characteristic temperature θ_p in the Curie-Weiss law is 25 K; near 10 K, the magnetic part of the heat capacity of CuVG exhibits a diffuse maximum; the change in magnetization in an external magnetic field at liquid-helium temperatures differs from the behavior of a parametric material with noninteracting Cu ions.

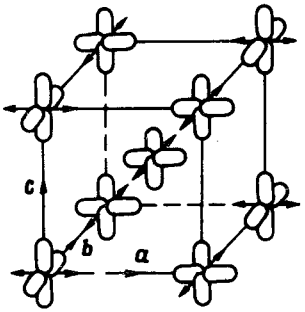

FIG. 1. Ordering of half-filled hole orbitals $d_{z^2-y^2}$ and $d_{z^2-x^2}$ of Cu ions in CuVG, arising with CJTE. The arrows denote the tetragonal axes of the elongated octahedra.

It is shown in Ref. 3 that the CJTE arises in CuVG at 250 K, giving rise to tetragonal distortion of the lattice $(c/a-1) = -15\times10^{-3}$. From an analysis of the energy of interaction of JT centers in the bcc garnet lattice, it follows that with CJTE, an antiferrodistortional ordering of the orbitals of Cu ions, shown schematically in Fig. 1, is realized in this garnet. The anisotropic nature of the ordering of half-filled hole orbitals $d_{z^2-x^2}$ and $d_{z^2-y^2}$ in CuVG leads to the appearance of strong AF exchange along the tetragonal axis c and much weaker exchange interaction along the a and b axes of the crystal. This gives a basis for conjecturing that the magnetic properties of CuVG could be related to the one-dimensional nature of AF ordering of Cu ions at low temperatures. In this paper, we present experimental data confirming this proposition.

Figure 2 shows the results of measurements of the heat capacity of a polycrystalline specimen of CuVG at temperatures $T > T_N$. Taking into account the contribution of the heat capacity of the lattice (the measurements were made for an isomorphic specimen not containing magnetic ions), the experimental dependence $C_{\max}(T)$ of CuVG is close to the theoretical curve constructed using the results of numerical

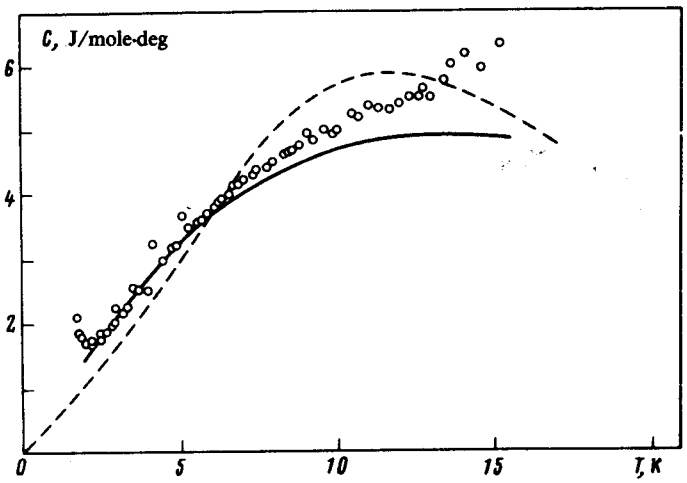

FIG. 2. Heat capacity of CuVG. O—Experimental points; —— magnetic heat capacity obtained after substracting the lattice contribution; – – – theoretical heat capacity of a one-dimentional antiferromagnet with $|J| = 12$ K.

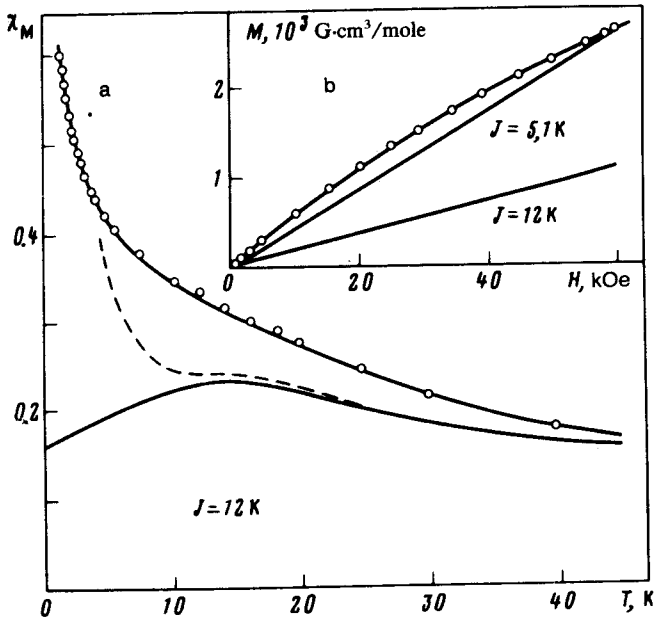

FIG. 3. Molar susceptibility $\chi_M(a)$ and magnetization M at $T = 1.7$ K (b) of CuVG. O—Experimental points; – – – – – the calculation for an infinite AF chain; ——— – – the calculation for chains consisting of five spins.

calculations by Bonner and Fisher.[4] According to Ref. 4, $C_{\max}(T)$ of a one-dimensional AF has a diffuse maximum of 5.8 J/mole·K (scaled to the two Cu ions in the CuVG molecule) at a temperature $T_c^{\max} = 0.962|J|/k$, where J is the exchange interaction of the nearest neighbors in the chain. We obtained the best agreement between the experimental data and the theoretical model[4] for the value $|J| = 12$ K (Fig. 2). In this model, the low-temperature transition with $T_N = 0.2$ K in CuVG corresponds to the appearance of three-dimensional ordering due to weak exchange interaction $|J'|$ between chains. From the quantity T_N, using Oguchi's calculations,[5] it is easy to obtain the estimate $|J'|:|J'/J| \cong 1.2\times 10^4$ and $|J'| \cong 1.4\times 10^{-3}$ K.

Figure 3 illustrates the behavior of the magnetization (M) and of the magnetic susceptibility (χ) of CuVG. It is evident that the dependence $\chi(T)$, which is close to that calculated theoretically for one-dimensional AF[4] at high temperatures, exhibits a considerable growth instead of the smeared peak at $T \sim 1.28|J|/k$ at liquid-helium temperatures. At the same time, the experimental curve $M(H)$ (Fig. 3b) follows the theoretical dependence with $|J| = 5.1$ K, i.e., it does not correspond to J determined from the heat capacity.

In our opinion, the observed disagreeement between the magnetic properties of CuVG and the results of theoretical calculations for one-dimensional AF is related to two features of the orbital structure of this garnet, shown in Fig. 1. First of all, in contrast to the "classical" one-dimensional magnet $KCuF_3$,[6] in CuVG there is an exchange interaction with eight Cu ions situated along the directions ⟨111⟩ of the weakly distorted bcc garnet lattice. In the absence of a magnetic field, this interaction

can be ignored, since the molecular field from the nearest neighbors at the central ion is zero due to the existence of short-range AF order in chains. In a sufficiently strong external magnetic field, however, it can have a considerable effect on the magnetic behavior of CuVG. Second, as investigations of the elastic properties show,[7] CuVG exhibits a local breakdown of CJTE, leading to the formation of chains of Cu ions with different lengths. This process, in its turn, makes a superparamagnetic contribution to the dependence $\chi(T)$ and $M(H)$ at low temperatures and smears the peak in the heat capacity. Figure 3 shows the theoretical curve $\chi(T)$ for one-dimensional chains consisting of five ions bound by the interaction $|J| = 12$ K (according to the data of Ref. 4).

Thus the physical properties that characterize the magnetic ordering in the Jahn-Teller garnet CuVG ($T_N/\theta_p \cong 0.01$, the dependences $C_{\max}(T)$, $M(H)$, etc.] are explained qualitatively under the assumption that there is one-dimensional ordering of Cu ions at $T \sim 10$ K. The disagreement with the theoretical calculations, within the framework of a simple model of one-dimensional AF,[4] is apparently related to the peculiarities of the ordering of orbitals in CuVG and, from this point of view, it would be interesting to study it further.

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