Observation of Dzyaloshinskiĭ interaction in three-nucleus clusters of copper (II)

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We investigated the magnetic susceptibility of the three-nucleus compound $[Cu_3(C_6H_5N_2O)_3(OH)]SO_4 \cdot 10.5H_2O$ in the temperature interval 4.2–11 °K and at magnetic fields 0–50 kOe. We show that allowance for the antisymmetrical interaction leads to good agreement between theory and experiment.

We report here an attempt to determine directly the antisymmetrical (AS) interaction parameter first introduced by Dzyaloshinskiĭ[1,11] and Moria.[2] The investigated objects were $[Cu_3(C_6H_5N_2O)_3(OH)]SO_4 \cdot 10.5\ H_2O$ crystals, the structure elements of which are three-nucleus clusters of copper (II).[3] The considerations dictating the choice of the objects will be advanced later on. Measurement of the magnetic susceptibility $\chi(T)$ at high temperatures ($T > 105$ °K)[3] has shown that the Cu(II) ions are coupled by exchange interaction of the antiferromagnetic type

$$\hat{H}_0 = I_0(\hat{S}_1\hat{S}_2 + \hat{S}_1\hat{S}_3 + \hat{S}_2\hat{S}_3),\ I_0 \approx 300\ \text{cm}^{-1}. \tag{1}$$

Within the framework of the Heisenberg Hamiltonian (1), the ground state is a quadruplet with total spin $S = 1/2$ and intermediate spins $S' = 0, 1$. The point group D_3 of the Hamiltonian (1) does not admit of fourfold degeneracy. A determination of the permutation symmetry of the spin functions with $S = 1/2$ ($S' = 0$ and 1) and the construction of dual Young patterns for the coordinate components of the corresponding Heitler-London states leads to the conclusion that the Heisenberg quadruplet $2D^{1/2}$ corresponds to the orbital doublet ^2E of the trigonal group in the Heither-London scheme.[4] A determination of the nature of the "unphysical" degeneracy shows that the isotropic exchange forms do not lift the degeneracy of the ground state. In fact, an active role in the orbital doublet of the trigonal group, in first-order perturbation theory, is played by the spin-orbit interaction (SOI), which splits this doublet into two Kramers doublets $(A_1 + A_2) + E$. The performed group-theoretical classification of the exchange multiplets allows us to state that the AS interaction, being the effective spin equivalent of the SOI, splits the ground state. The splitting of the levels is typical of multinuclear systems and distinguishes them from the widely investigated two-nucleus systems, in which the AS exchange leads to small shifts of the multiplets. It is precisely for this reason that we chose three-nucleus clusters as the object of investigation. The most general expression for the AS interaction operator is

$$\hat{H}_{AC} = \sum_{ij} \bar{D}_{ij}[\bar{S}_i \times \bar{S}_j], \tag{2}$$

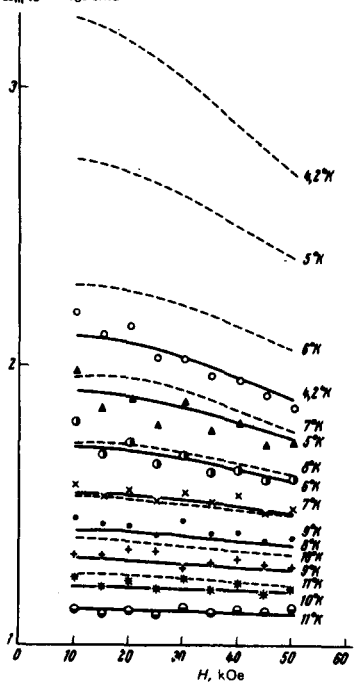
where $D_{ij} = -D_{ji}$ are vector coefficients, while i and j label the paramagnetic ions. It can be shown that for a trigonal three-nucleus system expression (2) can be reduced to the form

$$\hat{H}_{AC} = D_z \sum_{ij} [\bar{S}_i \times \bar{S}_j]_z, \tag{3}$$

where $D_z = D\,1,2,z + D\,2,3,z + D\,3,1,z$. According to Moria's estimate,[2] $D_z = (\Delta g/g_e)Z$. Since the SOI is large for the CU(II) ions ($\lambda \approx 830\ \text{cm}^{-1}$), and the isotropic exchange is considerable for Cu_3 clusters, the AS exchange can be observed in a region of not too low temperatures. Diagonalization of (3) with allowance for the Zeeman interaction leads to the following result for the ground state

$$E = \pm 1/2[(g\beta H)^2 + D_z^2 \pm 2D_z g\beta H\cos\nu]^{1/2}, \tag{4}$$

where β is the Bohr magneton, g is the Lande factor of the Cu(II) ion in the local crystal field, and $H_z = H\cos\theta$ ($z \parallel C_3$). Unlike the isotropic model (1), the spectrum (3) contains, in accord with the general considerations developed above, zero splitting and is essentially anisotropic. The indicated singularities, and particularly the radical deviation from the spectrum of the Hamiltonian (1) at $H \parallel C_2$, lead to low-temperature



Temperature and field dependences of the molar magnetic susceptibility χ_m of the $[Cu_3(C_6H_5NO)_3(OH)]\,SO_4 \cdot 10.\,5H_2O$ crystals per copper ion. Experimental data: ○—4.2 °K, ▲—5 °K, ◑—6 °K, ×—7 °K, ●—8 °K, +—9 °K, ✱—10 °K, ◒— °K.

singularities of the magnetic behavior of the crystals. A new effect is also the peculiar field dependence of the indicated characteristics.

To verify the theoretical conclusions, we have investigated the magnetic susceptibility of the crystals in the temperature interval 4.2—11 °K and in fields 0—50 kOe. The measurements were made with a vibration magnetometer constructed at the Institute of Physics Problems of the USSR Academy of Sciences.[5] The figure shows the theoretical $\chi(T) = M/H$ curves for the simple model (1) (dashed), which can be seen to deviate strongly from the experimental data on the temperature and field dependences at low temperatures, when the Curie-Weiss law does not hold. The high-temperature is reached already at $T = 10$—11 °K; the field dependence of $\chi(T)$ vanishes in this case, but the numerical values also deviate strongly from experiment at all reasonable values of the g-factors. It is seen from (4) that the AS interaction of weak and intermediate fields $g\beta H \sim D_z$. The magnetic moment of the system therefore turns out to be suppressed by the AS interaction, thereby qualitatively explaining the discrepancy between the experimental data and the isotropic model, which leads to a linear behavior of the levels regardless of the field orientation. The turning on of the AS interaction in the Hamiltonian (1) leads to a practically complete agreement between the theory (solid lines) and experiment, at $D_z = 12$ cm^{-1} and $g = 2.1$, in the entire considered range of temperature and fields. Since we used polycrystalline samples, we compared with the experiments the value of $\chi(T)$ averaged over the field orientation and calculated with the BESM-4M computer. The obtained value of the AS interaction parameter agrees well with Moria's estimate,[2] according to which $D_z = (0.1/2) \times 300$ cm^{-1} $= 15$ cm^{-1}. Thus, the experimental investigation allows us to state that the theoretically predicted effects of the AS interaction have been observed in the $[Cu_3(C_6H_5N_2O)_3(OH)]SO_4 \cdot 10.\,5H_2O$ crystals.

A generalization of the developed theory to include a larger class of systems having a distorted (rhombic) configuration leads to the conclusion that the AS interaction is suppressed by static distortions. In the limiting case of strong distortions, the AS interaction is completely suppressed, and the system is described by an isotropic Heisenberg Hamiltonian, so that the magnetic moment is unquenched and assumes a value corresponding to the spin of the ground state. To the contrary, at large distortions, the AS interaction suppresses as before the magnetic moment, and the system, being geometrically distorted, remains trigonal from the point of view of its magnetic properties.

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