Effect of Short Range Order on the Magnetic Properties of Copper Tungstate

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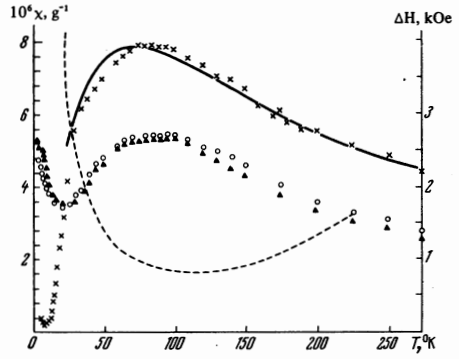
The temperature dependence of the magnetic susceptibility and the EPR spectrum are measured in a $CuWO_4$ single crystal. The measurements indicate that short-range exchange interactions contribute significantly to the magnetic properties of the compound. One result of this, in particular, is the presence of a broad maximum on the $\chi(T)$ curves above the Neel point ($T_N = 24° \pm 1°$). The value of the antiferromagnetic exchange integral, $J = 30°K$, is determined from the EPR specturm of Cu^{2+} exchange-coupled pairs. The experimental results can be described by a theory which takes into account the presence of short-range order.

MONOCLINIC tungstates of divalent ions of the iron group are convenient objects for the study of the singularities of the magnetic properties of antiferromagnets due to low symmetry of the crystal lattice. An investigation of the magnetic susceptibility and of the resonant frequencies of the tungstates of cobalt and manganese[1,2] has made it possible, in particular, to show that an appreciable contribution to the energy of the magnetic anisotropy of these antiferromagnets is made by single-ion crystallographic anisotropy. The study of $CuWO_4$, the magnetic structure of which is analogous to that of $CoWO_4$, makes it possible to determine the singularities of the magnetic properties of tungstates, due to the specific arrangement of the paramagnetic ions in their crystal lattice. The ground state of the Cu^{2+} ion is almost a pure spin state with $S = 1/2$, and this simplifies the theoretical analysis.

In the temperature interval 4.2–300°K, we have measured the extremal values of the magnetic susceptibility χ_i along the three magnetic axes x, y, and z of the crystal, the EPR spectrum of copper tungstate and of zinc tungstate with admixture of Cu^{2+} ions at concentrations 0.5–10%. The measurements of χ_i were made with a setup similar to that described in[3], and the measurements of the EPR spectra were made with a radiospectrometer for the 70×10^3 MHz band. The $ZnWO_4 + Cu^{2+}$ crystals were grown from the melt by the Czochralski method, and the $CuWO_4$ single crystals were grown by the Czochralski method and also from the solution in a melt of sodium tungstate by slow cooling. The results of the investigation of the magnetic and resonant properties of the $CuWO_4$ grown by the different methods turn out to be similar.

The temperature dependence of the magnetic susceptibility of the copper tungstate is shown in the figure. As seen from the figure, in the entire investigated temperature interval, the susceptibilities measured along the magnetic axes x, y, and z are different. Attention is called to the presence of a broad maximum on the $\chi(T)$ curves in the temperature region 70–90°K. Van Uitert and co-workers, who measured the magnetic susceptibility of $CuWO_4$ at an arbitrary orientation of the sample, determined from this maximum the Neel temperature of the copper tungstate T_N and found it to be 90°K[4].

In the interval from room temperature to ~100°K, the magnetic susceptibility follows the Curie-Weiss law with a Curie temperature $\Theta_C = -180°K$, the value of which agrees well with the $\Theta_C = -170°K$ obtained in



Temperature dependences of the magnetic susceptibilities (the solid curve was calculated from formula (1) at $g_z = 2.39$, $J = 30°K$, $J' = 0$, and $z = 6$; the points are experimental: X–χ_z; O–χ_y; ▲–χ_x). The dashed curve is the temperature dependence of the EPR spectrum of copper tungstate.

in[4]. Our measurements of the temperature dependence of the EPR spectrum of copper tungstate, however, cast doubts on the reliability of the Neel temperature determined in[4]. As seen from the figure, which shows the temperature dependence of the half-width ΔH of the EPR line of $CuWO_4$, the EPR spectrum can be observed down to a temperature ~ 24°K. Cooling the sample from room temperature to ~90°K leads to a certain narrowing of the EPR line, owing to the natural decrease of the contribution made to its width by the spin-lattice relaxation. With further lowering of the temperature, the EPR line width increases particularly noticeably on approaching 24°K, below which no EPR can be observed.

Such an anomalous behavior of the EPR line width with decreasing temperature is typical of magnetically concentrated crystals in the vicinity of the magnetic-ordering temperature. The vanishing of the EPR line for a number of antiferromagnets at $T = T_N$ was first noted in[5]. The Neel point of $CuWO_4$, determined by us from the vanishing of the EPR spectrum, turned out to be $24 \pm 1°K$. The establishment of magnetic order at 24°K is much less pronounced on the $\chi(T)$ plot, but it is seen from the figure that the $\chi_x(T)$ dependence experiences a noticeable kink in the region of this temperature.

Let us discuss our results. The presence of a magnetic-susceptibility maximum at temperatures above the Neel point was noted earlier for certain other antiferromagnets, for example $CuF_2 \cdot 2H_2O$ ($T_N = 10.9°K$, $T_{max} = 28°K$)[6], and was attributed to the appreciable

role of the short-range exchange interaction. A theory of the magnetic properties of such antiferromagnets was developed within the framework of the spin vector model in[7]. According to this theory, the occurrence of a maximum on the paramagnetic part of the susceptibility is evidence of establishment of a short-range magnetic order in the system of magnetic ions.

The theory yields the following temperature dependence for the susceptibility above the Neel point[7]

$$\chi = N\mu_B^2 g^2 \frac{S(S+1)}{3kT}\left[1+\frac{z}{4}(e^{2J/kT}-1)-\frac{z'}{4}(1-e^{2J'/kT})\right]^{-1}; \quad (1)$$

where N is the number of magnetic ions with spin S in the system, μ_B is the Bohr magneton, g is the g-factor, J, J′ and z, z′ are respectively the values of the antiferromagnetic and ferromagnetic exchange integrals and the numbers of the nearest neighbors coupled with the central ion by antiferromagnetic and ferromagnetic exchange interaction. J and J′ have positive sign.

An estimate of the exchange integral J can be obtained from the results of our measurements of the EPR spectra of the $ZnWO_4 + Cu^{2+}$ crystals containing 0.5—10% copper. Besides the lines of the individual Cu^{2+} ions, the EPR spectrum of which was investigated in detail in[8], additional groups of lines are observed in samples with copper concentration exceeding 0.5%, and are particularly strongly pronounced when the external field H is oriented parallel to the magnetic axis x. (In analogy with the $CuWO_4$ case, we have denoted by x the magnetic axis that lies in the plane ac of the $ZnWO_4 + Cu^{2+}$ crystal, corresponding to the smaller value of the g factor. This symbol differs from that used in[8].) Their positions in the spectrum correspond at $H \parallel x$ to the following values of the g factors: $g_1 = 2.097$, $g_2 = 2.058$, $g_3 = 2.039$, $g_4 = 2.011$, and $g_5 = 1.980$, whereas the g-factor of an individual Cu^{2+} ion is 2.001. The well resolved hyperfine structure of seven lines with an hfs constant equal to $A = (36-40) \times 10^{-4}$ cm^{-1}, i.e., amounting approximately to half its value for a single ion, $A_x = 76.5 \times 10^{-4}$ cm^{-1}, and also the ratio of the intensities of the hfs lines in the group, proportional to 1 : 2 : 3 : 4 : 3 : 2 : 1, enables us to identify these line groups with the spectra of the exchange-coupled Cu^{2+} ion pairs. From the temperature dependence of the intensity of these lines it follows that the sign of the exchange integral is antiferromagnetic for the lines 1, 3, 4, and 5 and ferromagnetic for the line 2. An analysis of the temperature dependence of the line intensities of the antiferromagnetic pairs, with allowance for the correction for the spin-lattice relaxation, estimated from the behavior of the line of the single ion with changing temperature, has shown that the lines 1, 3, 4, and 5 correspond approximately to the same value of the exchange integral, $J \approx 30°K$. Unfortunately, it is impossible to determine the ferromagnetic exchange integral J′ from our experimental results. In principle, J′ can be estimated from the shift of the g-factor of the ferromagnetic pair relative to the g-factor of the single ion, but for such an estimate it is necessary to know the positions of the excited energy levels, concerning which there is no information.

As follows from an analysis of the magnetic structure of copper tungstate, determined from neutron scattering[9], the parameters b and c of the magnetic structure of $CuWO_4$ are the same as for the crystal-chemical cell, and the parameter a of the magnetic cell is twice as large as for the crystal-chemical cell. The magnetic ordering occurs in such a way that the Cu^{2+} ion becomes aligned ferromagnetically in planes parallel to bc, and antiferromagnetically in the direction of a. The distance from each Cu^{2+} ion to the two nearest neighbors in a direction close to b is much smaller in the ferromagnetic plane bc than the distance to the ions in the direction c. We can therefore assume for the number of ferromagnetic neighbors $z' = 2$. At the same time, judging from the distances along the directions close to a, the number of nearest antiferromagnetic neighbors is $z = 6$. At such values of z and z′, the contribution of the ferromagnetic exchange interaction to the magnetic susceptibility, described by expression (1), is small, and in first approximation we can attempt to calculate χ by assuming $J' = 0$. The calculated temperature dependence of the paramagnetic susceptibility χ_Z for single crystals $CuWO_4$, using expression (1) with $z = 6$, $J = 30°K$, $J' = 0$, and $g_Z = 2.39$, the latter being experimentally determined from the EPR spectrum of $CuWO_4$, are shown in the figure.

An attempt to determine the value of the ferromagnetic integral J′ by calculating the $\chi(T)$ dependence for different values of J′ from expression (1) and obtaining best agreement with experiment, turned out to be unsuccessful, since variation of J′ has little effect on the susceptibility. Thus, the difference between the susceptibilities calculated at $J' = 0$ and at $J' = 30°K$ (which is equal to the value of the antiferromagnetic exchange integral J) amounts to several per cent, so that the reliability with which J′ is determined by this method is low.

Thus, the singularities of the temperature dependence of the magnetic susceptibility of copper tungstate are due to the appreciable predominance of exchange interaction between the nearest neighboring Cu^{2+} ions over the interaction with the more remote neighbors. The presence of a maximum of magnetic susceptibility at temperatures 70--90°K, and also the broadening of the EPR line below these temperatures, indicates that the occurrence of short-range magnetic order in the Cu^{2+} system of copper tungstate occurs already at a temperature ~90°K, whereas the transition of $CuWO_4$ into the antiferromagnetic state, i.e., the establishment of long-range magnetic order, occurs at a much lower temperature ~ 24°K. Obviously, this difference between the short- and long-range exchange interaction is connected with the specific nature of the exchange coupling of the Cu^{2+} magnetic ions in the tungstate lattice.

[1]A. I. Zvyagin and E. N. Khats'ko, Fiz. Tverd. Tela **12**, 314 (1970) [Sov. Phys.-Solid State **12**, 258 (1970)].
[2]V. A. Moiseev, A. I. Zvyagin, and N. M. Nesterenko, Fiz. Tverd. Tela **12**, 1551 (1970) [Sov. Phys.-Solid State **12**, 1222 (1970)].
[3]I. V. Svechkarev, Prib. Tekh. Eksp. (4), 142 (1963).
[4]L. G. Van Uitert, R. G. Sherwood, H. G. Williams, I. I. Rubin, and W. A. Bonner, J. Phys. Chem. Solids **25**, 1447 (1964).
[5]T. Okamura, J. Torizuka, and J. Kojima, Phys. Rev. **82**, 285 (1951).
[6]S. Tazawa, K. Nagata, and M. Date, J. Phys. Soc. Jap. **20**, 181 (1965).

[7]O. Nagai, J. Phys. Soc. Jap. **18,** 510 (1963).
[8]A. A. Galkin, A. D. Prokhorov, G. A. Tsintsadze, and V. A. Shapovalov, Dokl. Akad. Nauk SSSR **173,** 309 (1967) [Sov. Phys.-Dokl. **12,** 236 (1967)]; Z. Sroubek, Zdauský, J. Chem. Phys. **44,** 3078 (1966); A. A. Bugaĭ, M. F. Deigen, V. O. Oganesyan, and M. V. Pashkovskii, Fiz. Tverd. Tela **9,** 352 (1967) [Sov. Phys.-Solid State **9,** 266 (1967)]; K. J. Riggs and R. J. Standley, Journal of Phys. (Proc. Phys. Soc. C) **2,** 992 (1969).
[9]H. Weitzel, Solid State Commun. **8,** 2071 (1970).

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