EFFECT OF SHORT-RANGE MAGNETIC ORDER ON THE TEMPERATURE DEPENDENCE OF THE COPPER TUNGSTATE EPR LINE WIDTH

A. G. ANDERS and A. I. ZVYAGIN

Physico-technical Institute of Low Temperatures, Ukrainian Academy of Sciences

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The EPR spectrum of the antiferromagnetic substance $CuWO_4$ which is characterized by strong short-range exchange interaction is measured at temperatures ranging from the Neel point $T_N = 23\,^\circ K$ to $300^\circ K$. Broadening of the resonance line in the high temperature region is due to spin-lattice relaxation processes. With approach to T_N line broadening in the low temperature region is ascribed to critical fluctuations in the spin system. The existing theory of resonance line width does not yield a sufficiently good description of the temperature behavior of the $CuWO_4$ EPR spectrum since in this theory short-range exchange interaction, which is the major contribution to the broadening mechanism, is not considered.

AN appreciable contribution to the EPR line width of magnetically concentrated crystal is made by spin-spin interactions. Investigations of the EPR spectrum and of the temperature dependence of the line width make it possible to estimate the magnitude and character of these interactions, and to trace the features of the behavior of such systems in the magnetic ordering point. A number of recent theoretical and experimental papers are devoted to this question. It should be noted that the existing theory of temperature broadening of a resonance line has been constructed for crystals with high symmetry[1,2], and furthermore it does not seem to describe sufficiently well the experimental data in cases when exchange interaction of short-range order plays an important role in the spin-spin interactions[3]. At the same time, the temperature dependence of the EPR line width in crystals with short-range magnetic order in the temperature region of the magnetic ordering has not yet been sufficiently well studied. Yet, judging from the anomalous character of the temperature variation of the magnetic susceptibility, when the temperature of the maximum on the $\chi(T)$ curve greatly differs from the Neel point T_N and the Curie temperature in the Curie-Weiss law exceeds by several times the Neel temperature T_N, one should expect in these crystals singularities also in the temperature dependence of the EPR line width when the temperature drops to the Neel point.

In a preceding paper, devoted to an investigation of the magnetic properties of antiferromagnetic opper tungstate[4], it was shown that their behavior is determined to a considerable degree by short-range order exchange interaction. Characteristic singularities inherent in such systems appeared in the temperature dependence of the magnetic susceptibility. $CuWO_4$ has a Neel temperature $T_N = 23^\circ K$ and a Curie temperature $\Theta_c = -170^\circ K$, while the maximum of the $\chi(T)$ occurs at $T_{max} = 90^\circ K$. The present paper is devoted to a study of the temperature dependence of the EPR spectrum of this crystal from room temperature to T_N.

The symmetry of the crystal structure of $CuWO_4$ is triclinic, the space group is $P\bar{1}$[5], and the unit cell contains two paramagnetic ions in equivalent positions. Its parameters are

$$a = 4.70\,\text{Å},\quad b = 5.84\,\text{Å},\quad c = 4.88\,\text{Å},$$
$$\alpha = 91.7^\circ,\quad \beta = 92.4^\circ,\quad \gamma = 82.8^\circ.$$

The structure of lead tungstate is quite similar to that of monoclinic tungstates. The paramagnetic ions are arranged in layers parallel to the ab plane, and each layer consists of zigzag-like chains. The local environment of the CU^{2+} ion is a distorted oxygen octahedron. A neutron-diffraction investigation of the magnetic structure has shown that $CuWO_4$ is an antiferromagnet with magnetic-cell dimensions (2a, b, c). The magnetic moments lie in the ac plane[6].

The $CuWO_4$ single crystals were grown from a solution in molten Na_2WO_4. The measurements were performed mainly at ~75 GHz, and the results obtained at ~30 GHz were similar. To obtain a wide temperature interval, we used a cryostat similar to that described in[7]. The temperature was measured with a carbon resistance thermometer in the lower part of the interval, and with a copper-constantan thermocouple in the range from nitrogen to room temperature.

The EPR spectrum of $CuWO_4$ is single line with a somewhat anisotropic g-factor, the extremal values of which along the axis x, y, and z are shown in the table. The x axis lies in the ac plane and coincides with the crystallographic direction c, while the y and z axes are inclined to the ac plane by $45 \pm 5^\circ$. The temperature dependence of the $CuWO_4$ EPR line width, determined from the half-intensity value, is shown in Fig. 1.

Owing to the appreciable line width and the limited range of attainable magnetic fields, it was impossible to perform a complete analysis of the line shape by the linear anamorphosis method. We therefore restricted the examination of the "wings" of the lines only to the weak-field section, whereas the central part of the line was analyzed completely. It was established that at temperatures from room to $30^\circ K$ the line has a Lorentz shape at the center and a Gaussian shape on the wing.

Axis	g	ΔH_0, Oe	$\alpha \cdot 10^8$, Oe/deg^2	ΔH_∞, Oe	n
x	2.07	760	8	930	0.83
y	2.06	820	5.7	860	0.84
z	2.39	1520	5	1440	0.81

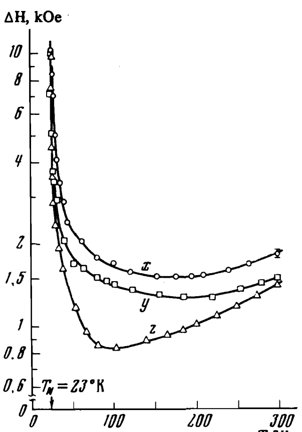

FIG. 1. Temperature dependence of the EPR line width of $CuWO_4$.

For temperature below 30°K, the analysis of the line shape is made difficult by the sharp decrease of its peak intensity.

As seen from Fig. 1, the temperature dependence of the EPR line width $\Delta H(T)$ can be divided into two sections, the high-temperature region where ΔH decreases with decreasing temperature, and the low-temperature region where ΔH increases up to T_N, at which the line becomes too broad to be observable. The experimental curves in the region $T > 150°K$ can be approximated by the expression

$$\Delta H_i = \Delta H_{0i} + \alpha_i T^2, \qquad (1)$$

where i = x, y, z. The second term apparently characterizes the decrease of the spin-lattice relaxation time with decreasing temperature. Such a dependence is typical of the Kronig—Van Vleck relaxation mechanism in the region above the Debye temperature Θ_D, where two-phonon scattering processes play an important role[8]. Judging from the measured phonon spectra of the iron-group tungstates, the Debye temperature of these crystals lies in the range 100—200°K[9], so that our assumption concerning the type of spin-lattice relaxation mechanism is obviously reasonable. The experimental values of ΔH_{0i} and α_i are listed in the table.

In the temperature region below ~150°K, an appreciable increase of the resonance line width is observed with decreasing temperature. The contribution of the spin-lattice relaxation to the line width is quite small in this region. The line has the Lorentz shape characteristic of exchange narrowing at the center, and a Gaussian shape on the wing. Such a shape is typical of the case when the exchange line narrowing mechanism operates. We have attempted to estimate the EPR line width due to pure dipole-dipole interactions of the copper ions, using for this purpose, the method described in[10]. To simplify the calculation we have neglected the deviations of the cell from orthorhombic. The calculated values of the line width, assuming a Gaussian shape, greatly exceeds the observed values[1)]. This is also evidence of the exchange narrowing of the EPR line in copper tungstate[11].

As T_N is approached, the $CuWO_4$ EPR line broadening becomes particularly strong. Usually such behavior of the resonace line is attributed to critical short-range order fluctuations in the spin system. Mori and Kawasaki[2] has shown that for a uniaxial antiferromagnet the dependence of the line width on the temperature near the Neel point is

$$\Delta H = \Delta H_\infty \left(\frac{T - T_N}{T}\right)^{-3/4}, \qquad (2)$$

where ΔH_∞ is the line width at $T \gg T_N$. It is assumed here that the exchange narrowing of the line is still sufficiently effective and the line has a Lorentz shape. The temperature range where short-range order appears is usually $1.05T_N < T < 1.5T_N$. However, many theoretical and experimental results for crystals with different symmetries and with different types of magnetic ordering show a considerable scatter of both the temperature range of the critical broadening and the exponent of the temperature factor in (2)[12-17].

We have attempted to represent the temperature dependence of the $CuWO_4$ line width, as T_N is approached, in the form

$$\Delta H_i(T) = \Delta H_{\infty i}\left(\frac{T - T_N}{T}\right)^{-n}.$$

The results of the approximation are given in the table, and the functions $\Delta H_i(T)$ themselves are plotted in Fig. 2 in a logarithmic scale. The obtained values of $\Delta H_{\infty i}$ are in good agreement with the values of ΔH_{0i} obtained from an analysis of the high-temperature region of $\Delta H(T)$. It should be noted that an appreciable increase in the width of the resonance line with decreasing temperature begins in $CuWO_4$ starting with ~90—100°K, i.e., with the temperature corresponding to the $\chi(T)$ maximum determined by the short-range magnetic order in the system.

Mori[1] investigated the temperature behavior of the damping constant of the transverse component of the magnetic moment and the associated width of the resonance line as applied to the uniaxial antiferromagnet MnF_2. The expression obtained for $\Delta H(T)$ at $T > T_N$ is

$$\Delta H = \Delta H_\infty C \xi^{3/2} / T\chi_\perp, \qquad (3)$$

where C is the Curie-Weiss constant and $\chi_\perp$ is the magnetic susceptibility in the direction perpendicular to the anisotropy axis. The quantity 3ξ is equal to the ratio of the fourth moment to the square of the second moment of the temporal correlation function, and depends in a complicated manner on the temperature and on the dimensions of the short-range order region. According to theory, $\xi > 1$. A relation of the type (3) describes well the experimental results for MnF_2 in the temperature region $1.02 < T/T_N < 1.25$.

If it is assumed that the Mori theory is applicable also to the case of $CuWO_4$, we can attempt to determine empirically the constant ξ, since a direct calcu-

[1)] For example, for the x direction, which coincides with the crystallographic c axis, the calculated line width is ~5 kOe, whereas the observed value without allowance for spin-lattice broadening is ΔH_{0x} = 760 Oe.

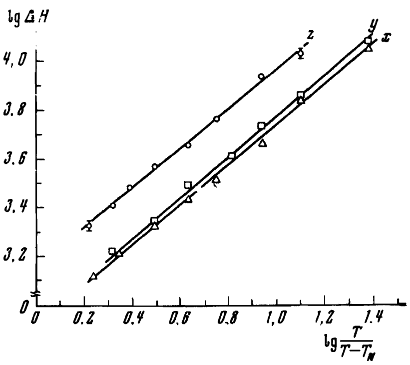

Fig. 2. Temperature dependence of EPR line width when the temperature decreases to T_N.

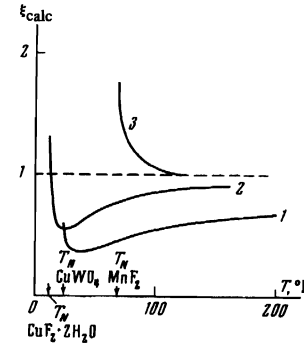

FIG. 3. Temperature dependence of the parameter ξ_{calc} for $CuWO_4$ (curve 1), $CuF_2 \cdot 2H_2O$ (curve 2), and MnF_2 (curve 3).

sion for ξ contains parameters that cannot be determined explicitly. Using (3), we can obtain

$$\xi_{calc} = \left(\frac{T\chi_\perp}{C}\right)^{1/2}\left(\frac{\Delta H}{\Delta H_\infty}\right)^{1/2}. \tag{4}$$

All the quantities in the right-hand side of this expression were determined experimentally; ΔH includes the high-temperature relaxation correction in accordance with (1). The relation calculated from (4) is plotted in Fig. 3, which shows for comparison $\xi_{calc}(T)$ for MnF_2. As seen from the plot, $\xi_{calc} < 1$ for $CuWO_4$ in the entire range of temperatures. This is a natural consequence of the "anomalous" temperature behavior of the magnetic susceptibility, which has a maximum that does not coincide with the Neel point and corresponds to the appearance of short-range magnetic order in this system in a wide temperature interval.

Apparently, the Mori theory does not describe sufficiently well systems with short-range order and with rhombic symmetry of the crystal field. The fact that the $CuWO_4$ symmetry is rhombic and not tetragonal as in the case of MnF_2 is probably not very important, since a similar dependence of $\xi_{calc}(T)$ can be traced for antiferromagnets with a noticeable short-range order, but with different symmetry and type of magnetic ordering. By way of example, Fig. 3 shows a plot of $\xi_{calc}(T)$ for $CuF_2 \cdot 2H_2O$, which has a crystal field of axial symmetry.

The biaxial antiferromagnet $CuF_2 \cdot 2H_2O$ is characterized by a strong exchange interaction in the antiferromagnetic layers, and reveals a broad maximum of $\chi(T)$, due to short-range order[13], in the region $T \approx 2T_N$. For this compound we also have $\xi_{calc} \ll 1$. A similar behavior of $\xi_{calc}(T)$ is observed also for the "one-dimensional" antiferromagnets $KCuF_3$[3,16] and $CsMnCl_3 \cdot 2H_2O$[17]. In these crystals, the magnetic ions form linear antiferromagnetic chains coupled by a relatively weak exchange ferromagnetic interaction. Apparently, such a $\xi(T)$ dependence can be expected also for a large number of antiferromagnetic systems, in which, judging from the measurements of $\chi(T)$, there is short-range order[14,18], but there are still no resonance measurement results.

As is well known, short-range order effects become most clearly manifest when the magnetic ordering has a chain-like or a planar character, i.e., when the interaction in the chain or in the layer exceeds the interaction between them. $CuWO_4$ is apparently close to being such a crystal. When considering the temperature behavior in the region adjacent to the critical temperature, such systems are quite strongly influenced by anisotropy, since (see[19]) one-dimensional and two-dimensional isotropic magnets cannot become ordered at a finite temperature. In addition, a noticeable role can be played also by the fact that the magnitude and radius of the spin correlation function for one-dimensional and two-dimensional magnetic crystals are quite large in the paramagnetic phase. The correlation radius L_c, which was studied by Lines[20] for a quadratically-layered antiferromagnet, reaches values exceeding the lattice parameter in a wide range of temperatures. The spin correlation function remains sufficiently large at $T > T_N$, as is confirmed by experiments on neutron scattering by spin waves[21]. These effects may exert an influence on the character of variation of width of the resonance line of the magnet with short-range order when the magnetic-ordering point is approached.

Thus $CuWO_4$, like other compounds with noticeable short-range magnetic order, is characterized by a broad temperature interval adjacent to the phase-transition point, in which a broadening of the resonance line is observed ($\sim 3-4T_N$). This is evidence that the establishment of short-range order is the main cause of the change in the EPR line width. At the same time, the theory of line width, developed for antiferromagnets that are not characterized by a predominant exchange interaction of short-range order, does not describe sufficiently well the peculiarities of the behavior of the EPR spectrum of $CuWO_4$, and should be improved.

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