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THE MAGNETIC RESONANCE IN YTTRIUM AND GADOLINIUM ORTHOCHROMITES NEAR THE PHASE TRANSITIONS AND UP TO 700 K

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EPR linewidth measurements in $YCrO_3$ and $GdCrO_3$ are reported in the temperature range from the Neel temperature T_N up to 700 K. It was shown, that the behaviour of EPR linewidth in the region near T_N cannot be explained by existing theories. The discrepancies are believed due to inadequate decoupling of the four-spin correlation function used in the theories. High temperature behaviour of EPR linewidth in orthochromites is explained in terms of exchange narrowing processes. The influence of thermal lattice expansion on EPR linewidth is proposed to explain the origin of the linear term in $\Delta H(T)$.

Recent experimental studies of the electron paramagnetic resonance (EPR) linewidth in ferromagnets [1–8] as well as in antiferromagnets [9–18] in the paramagnetic region have shown that the anisotropy plays a fundamental role in the nature of the anomalous behaviour observed near the critical temperature. For example in uniaxial antiferromagnets MnF_2 [9] and $NiCl_2$ [16] the EPR line broadens as $T \to T_N$ whereas in the cubic antiferromagnets $RbMnF_3$ [17] and $KMnF_3$ [18] and in the cubic ferromagnet EuO [2] the EPR line narrows slighty in the critical region. The critical-point anomalies in the EPR linewidth have been discussed by Tomita and Kawasaki [19]. A more consistent theory of the analysed phenomena was given by Huber [10], who showed that anomalies in the EPR linewidth arise from a coupling between the fluctuations in the total magnetization and the long wavelength fluctuations in the order parameter. This coupling is induced by anisotropic terms in the Hamiltonian. According to the theoretical works mentioned above, Hamiltonian of the system can be written in the following form:

$$\mathscr{H} = -\frac{1}{N}\sum_q J(q)\vec{S}(q)\vec{S}(-q)+\frac{1}{N}\sum_q S_i(q)D_{ij}(q)S_j(-q), \tag{1}$$

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where N is the number of spins and sum on q is taken over the Brillouin zone associated with the magnetic lattice; $S_i(q)$ is the Fourier transform of the spin operator; $J(q)$ and $D(q)$ are the Fourier transforms of the exchange interaction and anisotropy tensor, respectively. The relaxation time $T_{2\alpha}$, for the fluctuations of the $S_\alpha(0)$ is given by

$$T_{2\alpha}^{-1} = \frac{g^2\beta^2}{\chi_\alpha(0)} \int_0^\infty dt\{\dot{S}_\alpha(0, t), \dot{S}_\alpha(0)\}, \tag{2}$$

where $\dot{S} = (i/\hbar)\,[S, \mathscr{H}]$ and $\{\ldots\}$ denotes a relaxation function; $\chi_\alpha(0)$ is the uniform field susceptibility in the α-direction. The main contribution to the $T_{2\alpha}$ comes from the region of the Brillouin zone with $q \approx 0$ — for ferromagnets, and with $q \approx K_0$ (K_0 — the superlattice vector for the ordered state) — for antiferromagnets. If one assumes that the contribution from the rest of the zone varies slowly with temperature, then near the transition temperature one has

$$T_2^{-1}(T) = T_2^{-1}(\infty)+\Delta(T_2^{-1}(T)), \tag{3}$$

where $T_2(\infty)$ is the relaxation time for the high-temperature limit.

Thus, the EPR linewidth ΔH has the following form:

$$\Delta H = \Delta H(\infty)+\Delta H(T), \tag{4}$$

where $\Delta H(\infty)$ is the limiting value of the linewidth at high temperatures. If the four-spin functions in (2) are factorized into products of two-spin correlation functions (functional form of which is taken identical as for a completely isotropic spin system) then the following behaviour is predicted

$$\Delta H(T) \sim (T-T_N)^{-5/3} \tag{5}$$

for antiferromagnets, and

$$\Delta H(T) \sim (T-T_c)^{-7/3} \tag{6}$$

for ferromagnets.

The main purpose of this paper is to study experimentally much more complicated systems than described above, namely orthochromites. Until now there is no data in literature on EPR linewidth of orthochromites near the transition temperature. Two compounds have been investigated: $YCrO_3$ and $GdCrO_3$. For comparison some measurements on orthoaluminate $GdAlO_3$ will be reported.

Orthochromites (and orthoaluminates) crystallize in an orthorhombically distorted perovskite structure — space group D_{2h}^{16}. Transition temperatures for $YCrO_3$, $GdCrO_3$ and $GdAlO_3$ are equal to 141 K, 166 K and 3.5 K, respectively.

The analysed system has two characteristics:

1) In ordered state orthochromites are weak ferromagnets, this means antiferromagnets with canting of spins. For such systems antisymmetric (Dzialoshinski–Moriya) exchange interactions must be included in Hamiltonian (1), which are the same order of magnitude as the anisotropic-symmetric exchange interactions and single-ion anisotropy.

2) There are compounds with like spins ($YCrO_3$ and $GdAlO_3$) and with unlike spins ($GdCrO_3$). By studying the properties of these two groups of materials it is possible to obtain information about the exchange interactions.

The EPR measurements were performed in the X-band, in the temperature range 130 to 700 K. The single crystal samples of $YCrO_3$, $GdCrO_3$ and $GdAlO_3$ were grown by the flux method.

Single lines with $g \approx 2$ were observed in both orthochromites in the temperature region from T_{N1} (temperature of Cr^{3+} ions ordering) to 700 K, as well as in gadolinium orthoaluminate measured for comparison with orthochromites but only at room temperature. Contrary to the results given in [20–22], no resonance line below T_{N1} in $GdCrO_3$ was observed. The intensity of the resonance line in $GdCrO_3$ was only few times greater than the intensity of the resonance line in $YCrO_3$ which does not agree with the rate of these intensites reported in [21]. These differences are not clear for us and probably result from some extra admixtures in the sample material investigated in [20–22]. Investigating the dependence of the resonance line-width on temperature we stated that in the range from T_N to 700 K the line-width can be presented in a form similar to (4):

$$\Delta H(T) = \Delta H_0 + C \cdot \left(\frac{T}{T_{N1}} - 1\right)^{-P} - K(T - T_{N1}). \qquad (7)$$

The best fit of the above relation with the experiment was reached for the values of parameters given in Table I. The results of measurements are presented in Fig. 1. The solid lines correspond to $\Delta H(T)$ calculated from the above relation with appropriate parameters (see Table I).

TABLE I

Parameters of Eq. (7) describing the relation of EPR linewidth vs temperature

	$YCrO_3$	$GdCrO_3$
T_{N1} [K]	140.6	166
H_0 [mT]	45	61.5
C [mT]	0.7	51.2
P	0.9	0.32
K [mT/K]	0.015	0.09

It follows from Table I that in the critical region the temperature dependence of linewidth in orthochromites cannot be described by the existing theory. The critical exponent of 5/3 (Eq. (5)), which is based on the RPA approximation of decoupling the four-spin functions into products of isotropic two-spin functions is larger than the measured values for $YCrO_3$ and $GdCrO_3$. It is possible that such a discrepancy is connected with the assumption of the isotropy of two-spin functions. Another explanation of this discrepancy is that the decoupling of the four-spin functions into products of two-spin functions using RPA approximation is inadequate.

It results from our experimental data (see Fig. 1) that for $T \gg T_N$.

$$\frac{\Delta H_{\mathrm{GdCrO_3}}}{\Delta H_{\mathrm{YCrO_3}}} = 2.8, \quad \frac{\Delta H_{\mathrm{GdAlO_3}}}{\Delta H_{\mathrm{YCrO_3}}} = 7.8. \tag{8}$$

Such results may be qualitatively understood on the basis of the exchange narrowing of EPR lines in insulators [23, 24]. The following relation for the observed linewidth ΔH in the temperature range above the critical fluctuations is expected (extreme narrowing):

$$\Delta H = c\,\frac{H_d^2}{H_e}, \quad (H_d \ll H_e). \tag{9}$$

H_d^2 means the second order of the EPR line in the case where only dipole-dipole interaction is considered. The "exchange field" H_e takes into consideration the exchange interaction between magnetic moments; c is a numerical factor (for the cubic environment $c = 1$ for $H_e \ll H$ and $c = \frac{10}{3}$ for $H_e \gg H$). For the studied crystals factor c is unknown, therefore it is impossible to carry out in detail the comparison of the theory with experimental data. But it may be seen that qualitatively Eq. (9) describes satisfactorily the relations between the linewidth for investigated crystals.

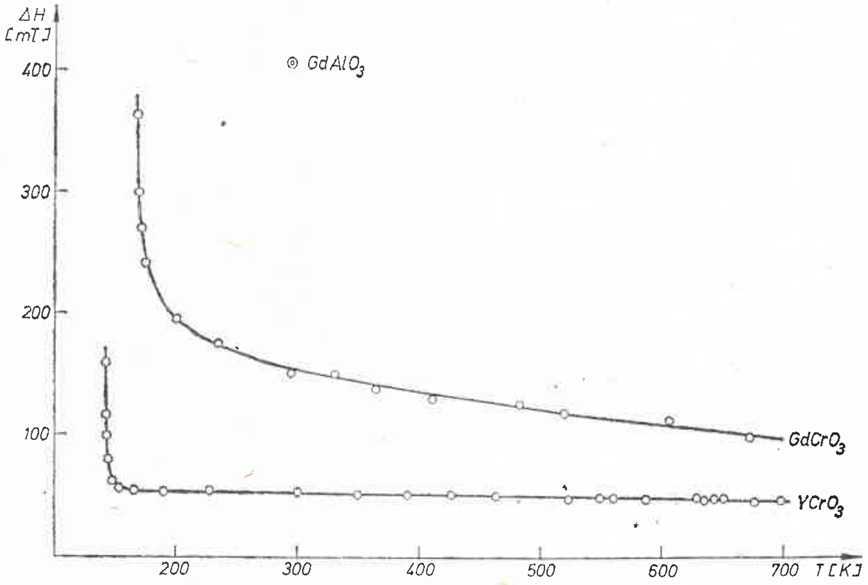

Fig. 1

For explanation of the linear term in the experimental relation $\Delta H(T)$ (see Eq. (7)) two mechanisms have been propsed in the literature [3, 25]. In [3] a term proportional to T arises from the spin-lattice interactions. In [25] the origin of the linear temperature dependence has been attributed to phonon modulation of the Dzialoshinsky–Moriya interaction. Unfortunately, it can be shown that for both proposed mechanisms $\partial(\Delta H)/\partial T > 0$. Therefore the only explanation of the observed experimentally linear dependence of $\Delta H(T)$ with negative slope have to be connected with the thermal lattice expansion. If $H_e \sim r^{-n}$ (r — distance between magnetic ions) then from (9) $\Delta H \sim r^{-6+n}$ and negative slope can be obtained for $n < 6$. To prove the above assumption it is necessary to perform the investigation of H_e as a function of temperature or hydrostatic pressure.

The results of our EPR measurements can be summarized as follows: 1) The behaviour of EPR linewidth near critical points in weak ferromagnets (orthochromites) cannot be explained by existing theories. 2) The behaviour of EPR linewidth of orthochromites in the high-temperature region $T \gg T_N$ can be satisfactorily explained by taking into account exchange narrowing process as well as the contribution connected with thermal lattice expansion.

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