this is the case only as long as the line width remains constant, being determined by the inhomogeneity of the field. With further increases in N the line width goes beyond the limits imposed by the inhomogeneity of the field, causing a reduction in χ''_{max}. An analysis of the curves using the Bloch equation[6] leads to the conclusion that relaxation of deuterium nuclei in paramagnetic solutions is characterized by the condition $T_1/T_2 \gg 1$ (T_2 is the transverse relaxation time) where the values of T_1/T_2 for the various ions fall in the following order: $(T_1/T_2)_{Cu^{++}} > (T_1/T_2)_{Cr^{+++}} > (T_1/T_2)_{Fe^{+++}} > (T_1/T_2)_{Mn^{++}}$.

These experimental data indicate that the line broadening is due to the displacement of the spin levels of the nuclei by virtue of the interaction of the quadrupole moment of the deuteron with the gradient of the electric field set up by the paramagnetic ion. In this case T_1/T_2 should be approximately proportional to the ratio e^2/μ^2 where e is the charge of the magnetic ion and μ the magnetic moment of the ion. This relation is actually observed in the experiments. In descending order the ratio e^2/μ^2 for the various ions is as follows:

$$(2^2/2^2)_{Cu^{++}} > (3^2/3.8^2)_{Cr^{+++}} > (3^2/5.9^2)_{Fe^{+++}} > (2^2/5.9^2)_{Mn^{++}}.$$

The T_1/T_2 ratios are in exactly the same order (cf. above). If the spin levels of the nuclei are equidistant while the probability for $\Delta m = \pm 1$ transitions is proportional to γ^2, using the general expression for the relaxation time T_1,[7] the expression given in (1) results if we take the value $\alpha = 2$. The values found in the present work ($\alpha \sim 4.2$ for solutions containing Cr^{+++}, Fe^{+++} and Cu^{++}) would also seem to be explained by the existence of unresolved quadrupole structure in the deuteron lines.

Since the anomaly associated with manganese solutions ($\alpha \sim 6.8$) is not observed in complex ions, it is probably due to the nature of the hydration of the Mn^{++} ions in D_2O. It may be assumed that the bonding of the water molecules in the hydrate shell with the paramagnetic ion is slightly covalent. An exception is the $Mn(D_2O)_X^{++}$ ion in which the binding is purely electrovalent. The absence of a covalent bond tends to reduce the magnetic interaction between the neutral ion and the deuterium nuclei in the first coordination sphere, thus increasing T_1.

*EDTA ions are ions of ethylene diamine tetra acetic acid. The EDTA ions form stable complex compounds with a stochiometric ratio of 1:1 with metal ions; the EDTA particle replaces several water molecules in the internal coordination sphere of the central ion.[5]

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ANISOTROPY IN MAGNETIC SUSCEPTIBILITY AND DEPENDENCE OF HEAT CAPACITY ON FIELD DIRECTION IN AN ANTIFERROMAGNET

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1. It is well known that in a magnetic field H smaller than some threshold value H_0 the spin wave energy spectrum in a uniaxial antiferromagnet exhibits a marked anisotropy.[1] Thus, for example, if the characteristic antiferromagnetism direction is along the z axis, in the case $\mathbf{H} \parallel z$ the energies of the two types of spin waves depend on H and the wave vector $\mathbf{k}$ as follows:[2]

$$\varepsilon_k^{(1,2)} = \sqrt{(\mu H_0)^2 + I^2k^2} \pm \mu H, \qquad (1)$$

while in the case $\mathbf{H} \perp z$:[3]

$$\varepsilon_k^{(1)} = \sqrt{(\mu H_0)^2 + I^2k^2}, \quad \varepsilon_k^{(2)} = \sqrt{\mu^2(H^2 + H_0^2) + I^2k^2}. \qquad (2)$$

Here $\mu = ge\hbar/2mc$, $H_0 = M_0\sqrt{J_1(K_1 - K)}$, M_0 is the maximum possible magnetization for the given antiferromagnet, J_1, I, K and K_1 are the constants in the exchange and anisotropy interactions.* It is characteristic that in these two cases the ground states of the antiferromagnet are also considerably different: in the case $\mathbf{H} \parallel z$ the antifer-

romagnetism direction $\Delta \parallel \mathbf{H}$ (i.e., this direction corresponds with the natural direction of z) where for $T = 0$, $M_{1z} = -M_{2z} = \frac{1}{2}M_0$ and $\chi_z^{\parallel} = 0$;† while for $\mathbf{H} \perp z$, $\Delta \perp \mathbf{H}$ (although $\Delta \parallel z$) where for $T = 0$ and $H \parallel y$, $M_{1y} = M_{2y} = M_0H/2H_e$ and $\chi_y^{\perp} = H/H_e$ where $H_e = M_0(J_1 + K_1 - K)$.

Until recently, however, no calculations have been made of the spin wave spectra for the case $\mathbf{H} \parallel z$ and $H > H_0$ in which in the ground state $\Delta \perp \mathbf{H}$, $M_{1z} = M_{2z} = M_0H/2H_e$ and $\chi_z^{\perp}H/H_e$ where $H_e = M_0(J_1 + K_1 + K)$. This calculation has been carried out by Irkhin and the author.[4] The results are as follows:‡

$$\varepsilon_k^{(1)} = Ik, \quad \varepsilon_k^{(2)} = \sqrt{\mu^2 (H^2 - H_0^2) + I^2k^2}. \qquad (3)$$

A comparison of Eqs. (2) and (3) indicates that the difference in the spectra in the cases $\mathbf{H} \parallel z$ and $\mathbf{H} \perp z$ remains after rotation of Δ into a position perpendicular to the $\mathbf{H}$ field (for $H > H_0$), although the ground states corresponding to (2) and (3) are similar. It is noteworthy that according to (3) one of the branches of the spectrum does not have a break.

In the present work we report on several new results which have been obtained in a calculation of the temperature dependence of the susceptibility χ and heat capacity of the spin waves C from an analysis of all three states listed above. The results apply only for those limiting cases in which the effects which are of interest are most marked.

2. With $\Delta\chi = \chi_T - \chi_0$:

a) $H < H_0$, $\mu H \ll \varkappa T$: $\Delta\chi_z^{\parallel} \approx -4\Delta\chi_y^{\perp} \approx \alpha T^2$, $\alpha = (\mu\varkappa)^2/3I^3$.

b) $H > H_0$, $\mu\sqrt{H^2 - H_0^2} \ll \varkappa T \ll \mu H_0$: $4\Delta\chi_z^{\perp} \approx -\alpha T^2$; $\Delta\chi_y^{\perp} \approx 0$.

c) $H > H_0$, $\mu\sqrt{H^2 - H_0^2} \gg \varkappa T$: $\Delta\chi_z^{\perp} \approx 0$; $\Delta\chi_y^{\perp} \approx 0$.

The list of formulas given above allows a theoretical explanation of the anisotropy in the temperature dependence of the susceptibility at fields near threshold H_0 observed by van den Handel et al.[7] (our results apply only to the low-temperature region).

3. For C we present the results which apply when $\varkappa T \ll \mu H_0$, in which case there is a marked dependence of spin heat capacity on the magnitude and direction of the field:

a) $H < H_0$, $\mu_i(H_0 - H) \gg \varkappa T$: $C_z^{\parallel} \approx 0$; $C_y^{\perp} \approx 0$.

b) $H < H_0$, $\mu(H_0 - H) \ll \varkappa T$: $C_z^{\parallel} \approx a_1 T^{3/2}$; $C_y^{\perp} \approx 0$.

c) $H > H_0$, $\mu\sqrt{H^2 - H_0^2} \ll \varkappa T$: $C_z^{\perp} \approx aT^3$; $C_y^{\perp} \approx 0$.

d) $H > H_0$, $\mu\sqrt{H^2 - H_0^2} \gg \varkappa T$: $C_z^{\perp} \approx \frac{1}{2}aT^3$; $C_y^{\perp} \approx 0$;

$a = (4\pi^2/15)\varkappa(\varkappa/I)^3$, $a_1 = 15(2\mu H_0\varkappa)^{3/2}\varkappa/32\pi^{3/2}I^3$.

From the examples which have been considered it is apparent that in a uniaxial single crystal the spin heat capacity and its temperature dependence are both functions of the magnitude of the field $\mathbf{H}$[6] [for example in the transition from condition (a) to (b), (c), and (d)] as well as the direction of the crystal axis with respect to the fixed field $\mathbf{H}$ [for example in rotation of the crystal axis through 90° from the position $\mathbf{H} \perp z$ into the position $\mathbf{H} \perp z$ in cases (b), (c) and (d)]. The last result means that if the spin heat capacity comprises a significant part of the total heat capacity of the antiferromagnet, adiabatic rotation of the crystal about an axis which lies in the base plane should result in a noticeable change in the temperature of the sample.

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*$J_1 > 0$ and $K_1 - K > 0$ since these are the conditions for the existence of antiferromagnetism with natural direction along the z axis.

†The lower sign denotes the direction of the magnetizing field $\mathbf{H}$ while the upper sign denotes the mutual orientation of Δ and $\mathbf{H}$.

‡The application of the phenomenological analysis[5] makes it possible to find the spin wave spectrum for the antiferromagnet for any magnitude and arbitrary direction of $\mathbf{H}$.[4] The approximate formulas used here (1)–(3) are valid only when $H \ll H_e$ $H \ll H_e'$. A phenomenological theory of antiferromagnetism has also been developed by Kaganov and Tsukernik.[6] However, the spectrum for the case $\mathbf{H} \parallel z$, and $H > H_0$ has not been studied by these authors.

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