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Magnetic interactions in $CoBr_2{\cdot}6H_2O$

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High-precision measurements of the heat capacity of $CoBr_2{\cdot}6H_2O$ were performed between 1.2 and 11 K. A fit of the high-temperature magnetic specific heat to the high-temperature-series expansion for a two-dimensional XY antiferromagnet yielded $J/k = -2.5$ K. A combination with antiferromagnetic-resonance results gave $J_{1xx} = -2.4$ K, $J_{1yy} = -2.3$ K, $J_{1zz} = -0.3$ K for the intersublattice interaction and $J_{2xx} = -0.5$ K, $J_{2yy} = -0.5$ K, and $J_{2zz} = -0.07$ K for the intrasublattice interaction. A calculation of the Curie constant, the perpendicular susceptibility, and the paramagnetic phase transition based upon these values gave satisfactory agreement with the experimental data. From the critical entropy (57%), as well as the critical behavior of the sublattice magnetization ($\beta = 0.31$), a somewhat bidimensional character could be concluded. The effect of deuteration will be briefly considered.

INTRODUCTION

In the last decade a considerable number of papers have been devoted to the magnetic state of $CoBr_2 \cdot 6H_2O$ and $CoCl_2 \cdot 6H_2O$. Although most of the experimental data are obtained on the chlorine compound, the majority of the results seem to apply, at least qualitatively, to the bromine isomorph also. In general, the experimental evidence indicates that this compound can be described as a two-dimensional antiferromagnet in which the dominant interactions are of the planar type (two-dimensional XY model). The experimental evidence concerning the bromine compound is, however, rather fragmentary. Forstat *et al.*[1] reported more or less preliminary specific-heat data while Garber[2] performed some susceptibility measurements. Murray and Wessel[3] studied the antiferromagnetic resonance (AFMR). The phase diagram was reported by McElearny *et al.*,[4] and recently by Metselaar and De Klerk.[5] Bromine resonance was reported by Rama Rao *et al.*,[6] and anomalous magnetic behavior upon deuteration was published by Hijmans *et al.*[7] In view of the fact that $CoBr_2 \cdot 6H_2O$ is one of the few substances that might behave as a two-dimensional XY antiferromagnet, we thought it worthwhile to continue our research on this compound. In this paper we wish to report detailed specific-heat measurements in the region from 1.2 to 11 K, including the critical behavior near the ordering temperature. The data in the paramagnetic state will be interpreted with high-temperature expansions and the relevant results will be compared with the AFMR and susceptibility data.

CRYSTALLOGRAPHIC AND MAGNETIC STRUCTURE

$CoBr_2 \cdot 6H_2O$ is assumed to be isostructural with $CoCl_2 \cdot 6H_2O$.[8-10] The structure can be described as monoclinic with space group $C2/m$. The unit cell with dimensions $a = 11.00$ Å, $b = 7.16$ Å, $c = 6.90$ Å and $\beta = 124°$ contains two formula units. The Br-Co-Br axis of the isolated $CoBr_2O_4$ cluster is situated in the ac plane at an angle of about 10° from the a^* axis, (perpendicular to c) towards the a axis. The schematical spatial arrangement of the clusters is shown in Fig. 1.

In general, both dipolar and exchange interactions will contribute to the coupling between Co^{2+} ions. However, in the case of nearest-neighbor interactions, the dipolar contribution may often be neglected since, in general, it is very small compared to the exchange interaction. The nearest-neighbor interaction between two Co^{2+} ions in the face-centered ab plane (denoted by J_1 in Fig. 1) involves exchange paths like Co-Br-Br-Co and Co-Br-H-O-Co. The exchange contribution to the coupling J_2 between adjacent Co^{2+} ions along the b axis involves links like Co-O-H-H-O-Co, and will presumably be smaller.[11] It seems likely that, in view of the large interatomic distance between adjacent Co^{2+} ions along the a axis (11.00 Å), the interaction J_3 may be considered as relatively small. The cou-

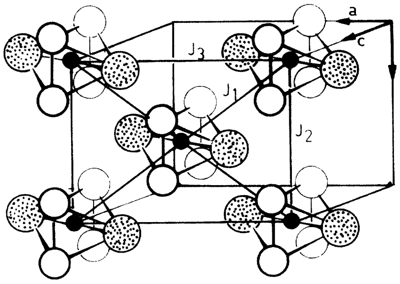

FIG. 1. Schematic drawing of the spatial arrangement of the $CoBr_2O_4$ clusters. To avoid confusion only the front layer is shown. J_1, J_2, and J_3 are the conjectured exchange interactions. Cobalt atoms are small and black, bromine atoms are shaded and oxygen atoms are drawn as open circles. Some water molecules are not shown.

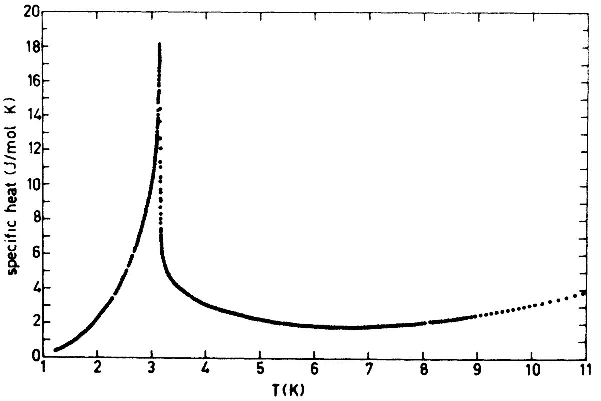

FIG. 2. Molar specific heat of $CoBr_2 \cdot 6H_2O$.

pling between the *ab* layers in the *c* direction is expected to be very weak,[10,11] which is also indicated by the experimental evidence obtained from measurements on the deuterated compound.[7]

We wish to note that from the magnetic space group $C2'/m'$ (Ref. 3, 10) for $CoBr_2 \cdot 6H_2O$ it follows that both J_2 and J_3 contribute to the intrasublattice interaction. From AFMR experiments it was inferred[3] that this interaction is rather small compared to the interaction J_1 between the two sublattices. This supports the assumptions concerning the relative magnitude of J_1, J_2, and J_3, that are conjectured from arguments based upon the geometrical arrangement of the different ions in the crystal.

SPECIFIC HEAT

High-precision heat-capacity measurements were performed on a sample consisting of 33.038 g of small crystals of $CoBr_2 \cdot 6H_2O$ (average dimension 5 mm). The specimen was sealed inside a simple vacuum calorimeter of conventional design together with a little ^{3}He exchange gas. Temperatures were obtained from a calibrated germanium thermometer, that was measured with an audio frequency resistance bridge using synchronuous detection.

The specific-heat data between 1.2 and 11 K are shown in Fig. 2; the data in the immediate neighborhood of the ordering temperature ($T_N = 3.150 \pm 0.005$ K) are given in greater detail in Fig. 3. Between 4.5 and 11 K our data are very well represented by the equation $C/R = AT^3 + BT^{-2}$ with $A = 3.158 \times 10^{-4}$ K^{-3} and $B = 5.768$ K^2. The relative rms error of the fit was less than 3×10^{-3}. We used the inferred value of A to substract the lattice contribution from the measured specific heat. The total magnetic entropy increase was found to be $0.690R$, which agrees within 0.4% with the theoretical value for a $s = \frac{1}{2}$ system. An amount of $0.393R$ (57%) was gained below the ordering temperature.

Figure 4 shows a plot of C vs $\ln|T - T_N|$ for $T_N = 3.150$ K. With this choice for T_N, the heat capacity near the transition point satisfies the equations $C/R = 0.6 - 0.27 \ln(T_N - T)$ and $C/R = -0.4 - 0.27 \ln(T - T_N)$ for $T < T_N$ and $T > T_N$, respectively. These equations describe the dashed curves in Fig. 3. Qualitatively, this behavior is the same as observed in the specific heat of $CoCl_2 \cdot 6H_2O$.

We note that for both the chlorine and the bromine compound the value of T_N that gives the best fit is a few millekelvin higher than the temperature that corresponds with the maximum of the specific heat. This is most likely explained by the significant rounding of the peak, that has been assumed to be mainly due to crystal imperfections[12] which may give rise to a small difference in the local exchange interactions.

A logarithmic singularity in the specific heat at the ordering temperature is displayed by the two-dimensional Ising model.[13] It is not quite clear whether the ordering of a three-dimensional Ising model may be described by a logarithmic or a power-law behavior,[14-16] although more recent calculations seem to favor a power-law behavior with a critical exponent $\beta = \frac{1}{8}$.[29] On the other hand, calculations based upon high-temperature-series expansions indicate that the two-dimensional *XY* model does not show any singularity in the specific heat.[25,26] The nature of the ordering of a three-dimensional *XY* model might be analoguous to the transition in a lattice of planar dipoles, that has been shown to be equivalent to the phase transition in a Bose fluid.[17] If the analogy holds, the singularity in the specific heat will be qualitatively similar to the λ transition in ^{4}He, that has been observed to display a logarithmic behavior.[18]

SUSCEPTIBILITY

Static susceptibility measurements were performed with the Faraday balance method on several

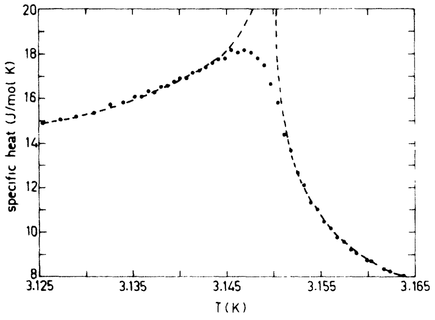

FIG. 3. The heat capacity of $CoBr_2 \cdot 6H_2O$ in the immediate neighborhood of the ordering temperature. The dashed curves correspond to the drawn lines in Fig. 4.

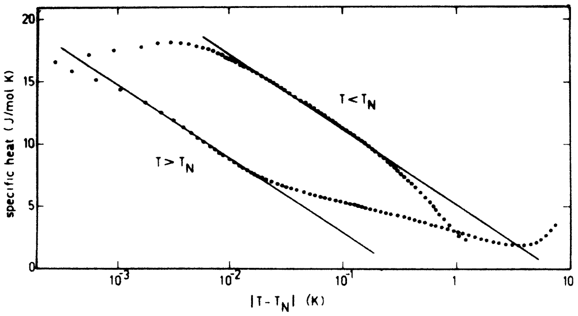

FIG. 4. The heat capacity of $CoBr_2 \cdot 6H_2O$ plotted vs $\ln|T-T_N|$. The drawn lines represent the equations $C/R = 0.6 - 0.27 \ln|T-T_N|$ and $C/R = -0.4 - 0.27 \ln|T-T_N|$ for $T<T_N$ and $T>T_N$, respectively.

single crystals at liquid helium, hydrogen, and nitrogen temperatures. The crystals were oriented using x-ray diffraction. A detailed interpretation of the measurements will be given elsewhere; we will only present some preliminary results that are of particular interest here. Rotation diagrams in the *ac* plane, at various temperatures in the paramagnetic region, revealed a very high anisotropy, and have shown minima at about 9° from the a^* axis towards the *a* axis. This direction must be noted to coincide with the direction of the Br-Co-Br axis of the $CoBr_2O_4$ cluster, within the possible error of orientation after the crystal has been mounted (a few degrees). The position of both the minima and the maxima did not change in the entire paramagnetic region (up to 80 K) within our experimental resolution, which was better than 0.2°. Measurements of the spin-flop transition in the ordered state, as a function of angle in the *ac* plane, revealed that the preferred direction of spin alignment ("easy" axis) coincides with the direction of the maxima mentioned above.

From susceptibility measurements at hydrogen temperatures along the c_1 and a_1 axis (the position of the maxima and minima, respectively) we inferred the values

$$g_{c_1} = 5.3, \quad \theta_{c_1} = -4.4 \text{ K}$$

$$g_{a_1} = 2.15, \quad \theta_{a_1} = -1.5 \text{ K}.$$

These results agree fairly well with the values obtained by Murray and Wessel[3] from data along the *c* and a^* axis. The inferred θ values, however, should be regarded as approximate, since the susceptibility data can be fitted to a Curie-Weiss law only in this rather limited temperature range. Some consideration of this fact will be given in the following chapter.

EXCHANGE INTERACTIONS

The most direct method of interpreting the specific-heat data would be to confront them with the calculated magnetic specific heat of a pure two-dimensional square lattice with *XY* interaction as reported by Betts *et al.*[26] A good fit was obtained in the temperature region $3.5 \text{ K} < T < 11 \text{ K}$ with $J/k = -2.54$ K. However, this agreement seems rather fortuitous in view of the fact that the series seems to diverge at $kT/|J| = 1.8$. Therefore we quote as our result the fit for $4.1 \text{ K} < T < 11 \text{ K}$ which yielded $J/k = -2.50$ K.

The procedure outlined above imposes the conditions $J_{xx} = J_{yy}$, $J_{zz} = 0$ and assumes a pure square lattice ($J_2 = 0$). Although, qualitatively, these conditions may be reasonably satisfied in this case, we felt that the available data enable one to perform a more detailed investigation without using the, in a sense, simplifications mentioned above. The remaining part of this section will be devoted to this subject.

AFMR results, in compounds with a relatively high anisotropy, such as $CoBr_2 \cdot 6H_2O$, are usually interpreted with the theory developed by Date.[19] Within the framework of this theory, the energy of a two-sublattice antiferromagnet can be written as

$$E = \vec{M}_+ \overleftrightarrow{A} \vec{M}_- + \tfrac{1}{2} (\vec{M}_+ \overleftrightarrow{\Gamma} \vec{M}_+ + \vec{M}_- \overleftrightarrow{\Gamma} \vec{M}_-), \qquad (1)$$

where $\vec{M}_+$ and $\vec{M}_-$ represent the *modified* magnetizations of the + and − sublattices, respectively ($\vec{M}_{\pm,modified} = 2\overleftrightarrow{g}^{-1} \vec{M}_{\pm,real}$).

Consider the Hamiltonian

$$\mathcal{H} = -2 \sum_{\langle ij \rangle} \vec{s}_i \overleftrightarrow{J}_{ij} \vec{s}_j, \qquad (2)$$

where the $\vec{s}_i$ are the effective spins of the Co^{2+} ions, and the summation runs over all pairs $\langle ij \rangle$ in the crystal. It is possible to express the microscopic interaction tensors $\overleftrightarrow{J}_{ij}$ in the molecular-field parameters $\overleftrightarrow{A}$ and $\overleftrightarrow{\Gamma}$, given the characteristic properties of this compound. First of all, we assume that dipolar interactions are sufficiently weak, in which case we only need to consider exchange interactions between nearest and next-nearest neighbors. In that case the procedure is rather straightforward, provided that the principal axes of the exchange tensors $\overleftrightarrow{J}_{ij}$ coincide. Some consideration of this fact will be given later.

Given the magnetic space group $C2'/m'$,[3,10] and the fact that all Co^{2+} ions are equivalent, we assume that each Co^{2+} ion interacts with four nearest neighbors on a different sublattice through an interaction $\overleftrightarrow{J}_1$ (see Fig. 1), and with two nearest neighbors on the same sublattice through an interaction $\overleftrightarrow{J}_2$. In view of the conjectured relative magnitude of the interactions, both the next-nearest-neighbor interaction $\overleftrightarrow{J}_3$ and the coupling between the *ab* layers in the *c* direction will be neglected in the following calculation.

The Hamiltonian for a spin *i* on the + or − sublattice can be written as

$$\mathcal{H}_{i\pm} = -2\vec{s}_{i\pm} \cdot \sum_{i\neq j} \overleftrightarrow{J}_{ij}\, \vec{s}_j \,.$$

Within the model we adopted, and within the molecular field approximation, this can be reduced to

$$\mathcal{H}_{i\pm} = -\vec{s}_{i\pm} \cdot \left(8\overleftrightarrow{J}_1 \langle \vec{s}_{j\mp}\rangle + 4\overleftrightarrow{J}_2 \langle \vec{s}_{j\pm}\rangle\right). \tag{3}$$

The $\langle \vec{s}_j \rangle$ are related to the modified sublattice magnetizations $\vec{M}_{\pm,\mathrm{mod}}$ by

$$\vec{M}_{\pm,\mathrm{mod}} = 2\overleftrightarrow{g}^{-1}(N/2)\overleftrightarrow{g}\,\mu_B \langle \vec{s}_\pm \rangle = N\mu_B \langle \vec{s}_\pm \rangle \,,$$

which gives for the Hamiltonian (3):

$$\mathcal{H}_{i\pm} = -\vec{s}_{i\pm} \cdot \left[(8\overleftrightarrow{J}_1/N\mu_B)\vec{M}_\mp + (4\overleftrightarrow{J}_2/N\mu_B)\vec{M}_\pm\right].$$

The modified effective fields $\vec{H}_{e\pm}$ acting on $\vec{M}_\pm$, respectively, can now be obtained from

$$\vec{H}_{e\pm} = (8\overleftrightarrow{J}_1/2N\mu_B^2)\vec{M}_\mp + (4\overleftrightarrow{J}_2/2N\mu_B^2)\vec{M}_\pm \,.$$

This yields an energy density identical to (1) if we choose

$$\overleftrightarrow{A} = -4\overleftrightarrow{J}_1/N\mu_B^2 \,; \quad \overleftrightarrow{\Gamma} = -2\overleftrightarrow{J}_2/N\mu_B^2 \,. \tag{4}$$

Qualitative information about the $\overleftrightarrow{A}$ and $\overleftrightarrow{\Gamma}$ tensors can be obtained from AFMR experiments[3,19] while susceptibility and specific-heat data may give additive information about the interactions $\overleftrightarrow{J}_1$ and $\overleftrightarrow{J}_2$.

AFMR experiments were performed by Murray and Wessel[3] who fitted their data to the generalized theory developed by Date.[19] They found the best agreement between theory and experiment for

$$A_{xx} = 712A, \quad A_{yy} = 680A, \quad A_{zz} = 108A \,,$$

while their results indicate that the second interaction $\overleftrightarrow{\Gamma}$ is smaller by one order of magnitude. The principal axes of the $\overleftrightarrow{A}$, $\overleftrightarrow{\Gamma}$, and $\overleftrightarrow{g}$ tensors were reported to coincide within experimental accuracy, a fact that has also been inferred to occur in $CoCl_2 \cdot 6H_2O$.[19] One may readily assert that the molecular-field approximation used in the interpretation of this experiment does affect the magnitude of the $\overleftrightarrow{A}$ and $\overleftrightarrow{\Gamma}$ tensors rather than the ratio of their components. Therefore we thought it worthwhile to combine the AFMR results with the high-temperature expansion of the specific heat, in order to obtain a quantitative estimate of the microscopic interaction parameters.

The high-temperature series expansion for the specific heat C of a system of spins, whose interactions can be described by the Hamiltonian (2), yields for the coefficient of T^{-2} the relation[20]

$$CT^2/R = \frac{2s^2(s+1)^2}{9} \sum_\alpha \sum_\beta \sum_{j\neq i} (J_{ij\alpha\beta}/k)^2 \,; \qquad \alpha, \beta = x, y, z. \tag{5}$$

This equation holds for general lattice and general spin. Within the model we adopted for $CoBr_2 \cdot 6H_2O$, this expression can be written as

$$CT^2/R = \frac{1}{2}\sum_\alpha \left(\frac{J_{1\alpha\alpha}}{k}\right)^2 + \frac{1}{4}\sum_\alpha \left(\frac{J_{2\alpha\alpha}}{k}\right)^2 , \tag{6}$$

where the summation α runs over the principal axes of the $\overleftrightarrow{J}$ tensors.

Values for $J_{1\alpha\alpha}$ and $J_{2\alpha\alpha}$ may now be obtained by substitution of the AFMR data using Eq. 4, assuming that both interactions have roughly the same anisotropy. Given the fact that all Co^{2+} ions in $CoBr_2 \cdot 6H_2O$ are equivalent, this assertion will be correct if dipolar interactions are sufficiently small and exchange interactions between "real" spins are assumed to be isotropic. In that case, the Hamiltonian of a pair of Co^{2+} ions can be written as[21]

$$\mathcal{H}_{ij} = V_{\mathrm{cryst},i} + V_{\mathrm{cryst},j} - \lambda\vec{L}_i\vec{S}_i - \lambda\vec{L}_j\vec{S}_j - 2\overleftrightarrow{J}^1_{ij}\vec{S}_i\vec{S}_j \,, \tag{7}$$

and the exchange tensor $\overleftrightarrow{J}_{ij}$ connecting a pair of effective $s = \frac{1}{2}$ spins can be obtained from the components of the ground-state eigenvectors.[22] As long as $\overleftrightarrow{J}^1_{ij}$ may be treated as a perturbation, the anisotropy of $\overleftrightarrow{J}_{ij}$ will be a function of the spin-orbit coupling λ and the crystal field V only, and therefore independent of i and j. The addition of a small Zeeman term to this Hamiltonian shows that identical arguments are applicable to the anisotropy of the "effective" $\overleftrightarrow{g}$ tensor. This leads us to the conclusion that within this model the principal axes of the $\overleftrightarrow{J}_{ij}$ and $\overleftrightarrow{g}$ tensors have to coincide and that their direction will be mainly determined by the local environment of the Co^{2+} ions. Since the b or *diad* axis has to be a principal axis, the experimental evidence inferred from our susceptibility measurements in the *ac* plane strongly supports this conclusion.

Substitution of the reported AFMR results and the value $CT^2/R = 5.768\ \mathrm{K}^2$, which we inferred from our specific-heat data, yields

$$J_{1xx}/k = -2.4\ \mathrm{K}, \quad J_{1yy}/k = -2.3\ \mathrm{K}, \quad J_{1zz}/k = -0.3\ \mathrm{K}.$$

The principal axes x, y, and z are assumed to coincide with the c_1, b, and a_1 axes, respectively.

In general the values of $\overleftrightarrow{\Gamma}$ determined from resonance experiments appear to be subject to considerable scatter. However, one should note that (6) contains a sum of squares of the interaction parameters, which implies that the values we inferred for the interaction $\overleftrightarrow{J}_1$ will not be significantly altered if we neglect the apparently small interactions represented by $\overleftrightarrow{J}_2$ or $\overleftrightarrow{\Gamma}$. If we assume the values for the anisotropic part of $\overleftrightarrow{\Gamma}$ reported by Murray and Wessel[3] to be approximately correct, we obtain an antiferromagnetic interaction $\overleftrightarrow{J}_2$ given by

$$J_{2xx}/k = -0.5\ \mathrm{K}, \quad J_{2yy}/k = -0.5\ \mathrm{K}, \quad J_{2zz} = -0.07\ \mathrm{K}.$$

One might substitute the obtained values for the microscopic interaction parameters in the expression for $\overleftrightarrow{\theta}$ derived from the first two terms in the high-temperature series expansion of the susceptibility.[20] For this case this would give

$$\theta_{a_1} = -0.9\ \text{K}, \quad \theta_b = -5.6\ \text{K}, \quad \theta_{c_1} = -5.8\ \text{K}.$$

The discrepancy with the experimental values inferred from measurements at liquid hydrogen temperatures is mainly due to the significant contribution of higher-order terms in the series expansion of the susceptibility. This was checked by calculations based upon the particular model we adopted,[23] which also showed that in the specific-heat series the contribution of higher-order terms is relatively small. This most likely explains the very good fit of the experimental specific-heat data between 4.5 and 11 K to only a T^3 and a T^{-2} term.

The possibility of determing experimental θ values from susceptibility measurements at higher temperatures was precluded by the proximity of the next Co^{2+} doublet, as this gave rise to a considerable deviation of the data at nitrogen temperatures from the expected behavior of an $s = \frac{1}{2}$ system. A study on the influence of both the crystal field at the Co^{2+} sites and the spin-orbit coupling on the high-temperature susceptibility is in progress, but the results will not be discussed in detail in the present paper.

The perpendicular suceptibility of an ordered system described by (1) can be easily calculated from the torque balance equation. If the spins point in the α direction, the susceptibility in the β direction is given by

$$\chi_\beta^\alpha = g_\beta^2 / 2(A_\alpha + A_\beta - \Gamma_\alpha + \Gamma_\beta), \quad \alpha \neq \beta. \tag{8}$$

In this expression, α and β are the directions of the principal axes of both the $\overleftrightarrow{A}$ and $\overleftrightarrow{\Gamma}$ tensors. If we substitute the values for $\overleftrightarrow{A}$ and $\overleftrightarrow{\Gamma}$, as can be inferred from $\overleftrightarrow{J}_1$ and $\overleftrightarrow{J}_2$ by (4), we obtain $\chi_b^c = 0.75 \times 10^{-3}$ emu/g and $\chi_{a_1}^{c_1} = 0.26 \times 10^{-3}$ emu/g.

There is a fair agreement with the measurements reported by Garber[2] that yielded $\chi_b^c = 0.7 \times 10^{-3}$ emu/g and $\chi_a^c = 0.2 \times 10^{-3}$ emu/g, except from the fact that the calculated values are systematically too high. This may be explained by the existence of a spin reduction, which indeed has been observed to be rather important in this compound.[24,30] In general, spin reduction will give rise to an experimental susceptibility that is smaller than the molecular field value, at least at magnetic fields that are low compared to the saturation value.

Since near saturation the spin reduction will be zero, one is tempted to use the molecular-field approximation to obtain values for the field H_p at which (at $T = 0$) a transition to the paramagnetic state occurs. From the torque balance equation one may calculate:

$$H_p = (4M/g_\beta^2)(A_\alpha + A_\beta - \Gamma_\alpha + \Gamma_\beta), \tag{9}$$

if the spins originally point in the α direction and the magnetic field is applied in the β direction. M is the magnitude of the "real" sublattice magnetization defined by $M = \frac{1}{2} N g_\beta \mu_\beta \langle S \rangle$.

Substitution of our values of $\overleftrightarrow{J}_1$ and $\overleftrightarrow{J}_2$ using Eq. (4) yields $H_p = 53$ kG if the magnetic field is applied along the b or c_1 axis. This agrees very well with the experimental value 55 kG inferred by Metselaar[24] from measurements along the crystallographic b and c axes.

The obtained values of the $\overleftrightarrow{J}$ tensors clearly indicate that the character of the interactions is highly XY like. Secondly, the dominant interactions are assumed to act only between ions in the ab layers. This brings about the question whether $CoBr_2 \cdot 6H_2O$ might be adequately described by a two-dimensional XY model. Theoretical calculations by Betts *et al.*[25,26] on several XY models reveal, for the fcc lattice and the triangular lattice, a critical entropy of 0.52 and 0.27R, respectively. The two-dimensional model, however, does not show any singularity in the specific heat. We are inclined to believe that this compound may be approximated by a square lattice rather than a triangular lattice, as can be seen from the geometry of the interactions and the relative magnitude of $\overleftrightarrow{J}_1$ and $\overleftrightarrow{J}_2$. For the Ising model, however, it has been shown that the critical entropy mainly depends on the lattice dimensionality, while the dependence on the detailed lattice structure seems to be rather small.[27,28] Although calculations on the XY model are less extensive, the available evidence strongly suggests that the critical entropy will show the same tendency. The value 0.39R inferred from our specific-heat measurements, therefore, could indicate a dimensionality of the interactions between the pure

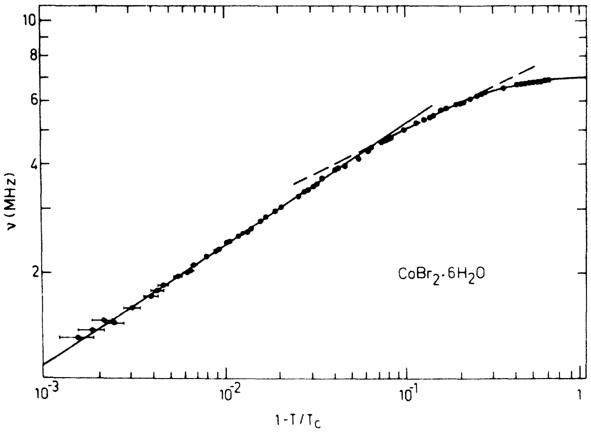

FIG. 5. The logarithm of a proton NMR frequency ν plotted vs $\ln(1 - T/T_N)$ for $CoBr_2 \cdot 6H_2O$. The slope of the drawn line corresponds to a critical exponent $\beta = 0.31 \pm 0.02$. The dashed line can be compared with earlier results on $CoCl_2 \cdot 6H_2O$.

two- and three-dimensional case.

Additional information about the dimensionality may be obtained from the critical behavior of the sublattice magnetization. Van der Lugt and Poulis[31] measured the sublattice magnetization of the isostructural $CoCl_2 \cdot 6H_2O$ by means of a proton NMR technique, and from their data a critical exponent $\beta = 0.18$ was inferred.[32] However, their experiments did not extend nearer to T_N than $1 - T/T_N \simeq 0.04$. As this still may be outside the critical region, we thought it worthwhile to investigate the behavior of the sublattice magnetization of both $CoCl_2 \cdot 6H_2O$ and $CoBr_2 \cdot 6H_2O$ for $1 - T/T_N < 0.04$. Since the results for both compounds are very similar, we will only present data on the bromine compound. Figure 5 shows a double-logarithmic plot of a proton NMR frequency ν vs $1 - T/T_N$. The critical exponent β is given by the slope of the drawn line, which corresponds to $\beta = 0.31 \pm 0.02$ in the range $2\times10^{-3} < 1 - T/T_N < 0.06$. The dashed line can be compared with the observations of Van der Lugt and Poulis on the chlorine compound.

In view of the fact that most of the calculations on the critical behavior, which are based upon high-temperature expansions, are restricted to the ferromagnetic case, it is surprising that both the critical exponent $\alpha = 0$ for the specific heat and the critical exponent $\beta = \frac{1}{3}$ for the sublattice magnetization in the range $2\times10^{-3} < 1 - T/T_N < 0.06$ agree with the predictions for the three-dimensional XY model.[33] Whether the change in the derivative of the logarithmic plot at $1 - T^*/T_N \simeq 0.06$ is indicative of a change of critical behavior from two- to three-dimensionality, as suggested by several authors,[32,34–36] is open for discussion, especially in view of the range of temperatures from which the (two-dimensional) exponent $\beta = 0.18$ is obtained. In view of the reported data we feel confident to state that the ordering phenomena at $T_N = 3.150$ K is largely three dimensional in nature. If one accepts the change in derivative at $1 - T^*/T_N \simeq 0.06$ as physically meaningful in this compound, this would imply a rather small value of the interlayer interaction indeed.

DEUTERATION

Both $CoCl_2 \cdot 6H_2O$ and $CoBr_2 \cdot 6H_2O$ have been extensively studied in our laboratory by resonance techniques.[6,7] As a part of our study on the deuterated compound, specific-heat measurements were performed on 36.020 g of small crystals of $CoBr_2 \cdot 6D_2O$, grown from a saturated solution of $CoBr_2$ in 98-at.% D_2O. Because the results appeared to be very similar to those obtained on the hydrated compound they will only be discussed very briefly.

The onset of long-range order occurs at $T_N = 3.225 \pm 0.005$ K, while the lattice contribution to the measured specific heat is equal to the lattice contribution in the hydrated compound within our experimental accuracy. The high-temperature magnetic specific heat satisfies the equation $C_{magn}T^2/R = 5.557\ K^2$ which corresponds to a decrease of about 3% compared with the hydrated compound. One should note that an explanation of the effect of deuteration by the available theories[37,38] is ruled out by the reported change of the crystallographic structure going from the hydrated to the completely deuterated case. It was inferred[7] that deuteration of this compound causes a doubling of both the crystallographic and the magnetic unit cell in the c direction, while the ordering of the spins in the ab layers remains antiferromagnetic.

AFMR experiments performed by Hijmans *et al.*[7] reveal that deuteration causes an increase of about 50% of both the spin-flop field and the zero-field resonance frequency. As can be seen from the formulas worked out by Date[19] this implies an increase of the anisotropy in the "easy" $(a_1 b)$ plane, within our model proportional to $A_{xx} - A_{yy}$ or $J_{1xx} - J_{1yy}$. Because in the hydrated compound the easy-plane anisotropy is about 5%, it follows that an increase to about 7.5% will be sufficient to explain the AFMR data. One may readily assert that such a small change will hardly affect the magnitude of the interactions, which is consistent with the relatively small effect of deuteration upon both the ordering temperature and the high-temperature magnetic specific heat.

In the hydrated compound the four oxygen atoms of the $CoBr_2O_4$ cluster are arranged in a nearly square rectangle and form an "easy" plane perpendicular to the Br-Co-Br axis. Within our experimental accuracy the preferred direction of spin alignment is situated in this plane in a direction perpendicular to the b axis. We wish to note that the proposed crystallographic space group $C2/c$ for the deuterated compound admits a (perhaps very small) departure of the arrangement of the oxygen atoms from the original rectangular symmetry. Because even a very small rearrangement might probably be sufficient to explain both the increase of the anisotropy and the canted spin structure in the deuterated compound, part of our research will be continued in this direction.

Note added in proof. Recently L. J. de Jongh (private communication) has fitted the susceptibility results in the region $1.5 < kT/|J| < 5$ to the high-temperature-series expansion of a quadratic $s = \frac{1}{2}$ XY model developed by D. D. Betts and D. J. Austen. His result $J/k = -2.45$ K is in good agreement with the value inferred from our specific-heat data.

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