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# Crystal-field effects and high-temperature susceptibility of $CoBr_2 \cdot 6H_2O$

J.P.A.M. Hijmans, Q.A.G. van Vlimmeren, and W.J.M. de Jonge
*Department of Physics, Eindhoven University of Technology, Eindhoven, The Netherlands*

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The susceptibility of $CoBr_2 \cdot 6H_2O$ has been measured between 1 and 120 K along all principal axes. The data have been interpreted in terms of the two-dimensional *XY* model and its extension to an uniaxial model for the exchange interactions. The influence of the excited doublet states has been accounted for by means of a crystal-field calculation. It is shown that a consistent set of both crystal field and magnetic parameters quantitatively explains the susceptibility for all three principal directions.

## I. INTRODUCTION

The magnetic behavior of $CoCl_2 \cdot 6H_2O$ and $CoBr_2 \cdot 6H_2O$ has been the subject of a considerable number of both experimental and theoretical studies. The majority of these papers deal with $CoCl_2 \cdot 6H_2O$, however, most of the qualitative results seem to apply to both substances. The studies include specific-heat measurements,[1,2] nuclear magnetic resonance,[3] antiferromagnetic resonance,[4,5] susceptibility measurements,[5-7] and calculations of the ground state of the $Co^{2+}$ ion.[8] In general the experimental evidence indicates that these compounds can be fairly well approximated as two-dimensional antiferromagnets in which the dominant interactions are of the planar type (two-dimensional *XY* model).

In foregoing papers[9,10] we reported the magnetic structure, the anomalous behavior of $CoBr_2 \cdot 6H_2O$ upon deuteration, and an analysis of the specific heat combined with antiferromagnetic-resonance results. Recently, Metselaar *et al.*[11] reported a comparison of the specific-heat and susceptibility results with the two-dimensional *XY* model. A nice agreement was obtained for the zero-field susceptibilities $\chi_x$ and $\chi_y$ in the temperature region $1.4 < |kT/J| < 6$. However, it is clear that this simple model does not account for the nonzero $\chi_z$ and the influence of the excited doublet states. Apart from the direct contribution to the susceptibility at higher temperatures, these excited levels will also give rise to a substantial van Vleck contribution. In this paper we will present the susceptibility data up to 120 K and we will show that a consistent set of both crystal-field and magnetic parameters quantitatively explains the susceptibility for all three principal directions.

In Sec. II we will review the crystallographic and magnetic properties of $CoBr_2 \cdot 6H_2O$. Section III will be devoted to the theoretical outline of the procedure. The experimental results will be presented in Sec. IV, whereas we will discuss the results in Sec. V.

## II. CRYSTALLOGRAPHIC STRUCTURE AND MAGNETIC INTERACTIONS

$CoBr_2 \cdot 6H_2O$ is assumed to be isostructural with $CoCl_2 \cdot 6H_2O$.[12] This assumption is recently corroborated by high-resolution powder neutron diffraction experiments.[13] The room-temperature structure can be described as monoclinic with space group $C2/m$. The unit cell with dimensions $a = 11.03$ Å, $b = 7.18$ Å, $c = 6.91$ Å, and $\beta = 124.7°$ contains two formula units. The spatial arrangement of the $[CoBr_2O_4]$ clusters is shown in Fig. 1(a). All the clusters are equivalent and can be described as distorted octahedra. The basal plane contains the four $H_2O$ molecules (*XY* plane). The Br-Co-Br axis is almost perpendicular to that plane and is slightly elongated [Fig. 1(b)]. From a configuration like this one may expect a crystal field on the magnetic ion with rather strong tetragonal components besides the main term of cubic symmetry. The combined effect of such a crystal field and the spin-orbit coupling results in a splitting of the free-ion $^4F$ state in a number of levels of which six Kramers doublets are the lowest, as is sketched in Fig. 2. In general it is assumed that, at low temperatures, only the lowest doublet is populated. In that case a description in terms of a fictitious spin $S' = \frac{1}{2}$, with anisotropic exchange parameters and *g* values, is sufficient to characterize the magnetic behavior. With the exception of Uryu *et al.*[8] so far the data have been interpreted in terms of this fictitious spin formalism. A detailed survey of the results can be found elsewhere.[11] The major conclusion is that the magnetic behavior of $CoBr_2 \cdot 6H_2O$ at low temperatures can be satisfactorily explained on the basis of a $S' = \frac{1}{2}$ system with an exchange interaction of the *XY* type ($J_x = J_y = J$, $J_z = 0$). This fact is most clearly demonstrated by the values of $g_x \simeq g_y \simeq 5.0$ and $g_z \simeq 2.2$. If one neglects orbital contributions this would yield $J_x \simeq J_y$ and $J_z / J_x \simeq 0.25$. The quantitative results, however, should be judged with care because, in general, they are obtained from

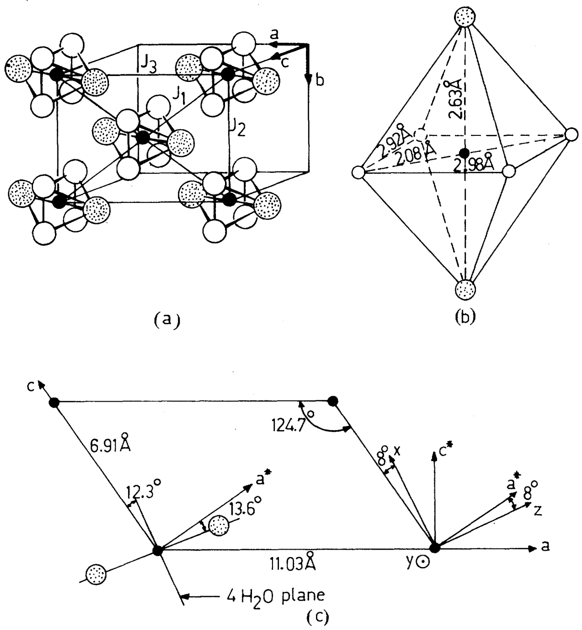

FIG. 1. Details of the crystal structure of $CoBr_2 \cdot 6H_2O$. Cobalt atoms are small and black, bromine atoms are shaded, and oxygen atoms are drawn as open circles. (a) The face-centered arrangement of the $[CoBr_2O_4]$ clusters in the *ab* plane. (b) Some distances within the $[CoBr_2O_4]$ cluster. (c) Sketch of the *ac* plane also showing the principal axes *x*, *y*, and *z* of the susceptibility tensor ($\vec{a}^* \perp \vec{c}$, $\vec{c}^* \perp \vec{a}$).

interpretations imposing a simple model behavior, which will not completely be satisfied.

The dimensionality of the magnetic system has been discussed by Hasêda.[14] There are two features which are of importance, i.e., the interactions in the centered *a-b* plane and the interactions between the planes. As is shown in Fig. 1(a), one can distinguish a number of possible intralayer interactions. Analyzing the nature of the exchange paths, Hasêda concluded that $J_2$ and $J_3$ probably would be small. Kopinga *et al.*[10] obtained the value $2(J_2+J_3) \simeq 1.0$ K compared with $4J_1 = 9.4$ K. The interlayer exchange interaction was estimated by Hasêda[14] to range between 0.01 and 0.1 K. Experimentally, the lower dimensionality gives rise to a rather high amount of short-range order apparent above the antiferromagnetic ordering temperature $T_N$. The lower dimensionality is also indicated by the rather independent behavior of the magnetic moments in successive layers in the deuterated compound[9,15] below $T_N$. In view of this we will assume in this paper that the magnetic behavior in the paramagnetic region can be described by one interaction $J_1$ between nearest neighbors in the *a-b* plane, which results in the so-called square lattice for the magnetic ions.

## III. THEORY

The ground state of the free $Co^{2+}$ ion is a $^4F$ state ($L=3$, $S=\frac{3}{2}$). Using the method of operator equivalents, the combined effect of a crystal field of orthorhombic symmetry and spin-orbit coupling can be written

$$\mathcal{H} = \tfrac{1}{2}(C_0^4+C_4^4)\left[\tfrac{1}{15}T_0^4+\tfrac{1}{6}(T_4^4+T_{-4}^4)\right]+\tfrac{1}{2}(C_0^4-C_4^4)\left[\tfrac{1}{15}T_0^4-\tfrac{1}{6}(T_4^4+T_{-4}^4)\right]+\tfrac{1}{3}C_0^2T_0^2+\tfrac{1}{12}C_2^4(T_2^4+T_{-2}^4)+\tfrac{1}{2}C_2^2(T_2^2+T_{-2}^2)+\lambda\vec{L}\cdot\vec{S}, \tag{1}$$

where

$$T_0^4 = 35L_z^4-335L_z^2+360\,,\quad T_{\pm4}^4 = L_\pm^4\,,\quad T_{\pm2}^4 = (7L_z^2-17)L_\pm^2+L_\pm^2(7L_z^2-17)\,,\quad T_0^2 = 3L_z^2-12\,,\quad T_{\pm2}^2 = L_\pm^2\,.$$

In this Hamiltonian the first term represents the cubic field, the next two terms represent the tetragonal field components, and the fourth and the fifth terms the orthorhombic field components. In the last term λ is the spin-orbit coupling constant. The *z* axis is chosen along the tetragonal axis.

In a crystal field of cubic symmetry the free ion $^4F$ states splits into two orbital triplets $\Gamma_5$ and $\Gamma_4$, and one orbital singlet $\Gamma_2$, with $\Gamma_4$ lowest (Fig. 2). The energy gap between this level and the first excited state $\Gamma_5$ is, according to Papallardo,[16] about 11 000 K. For the present we will restrict our attention to the lowest state $\Gamma_4$. A suitable set of orbital basis functions for this ground state is given by the following combinations of angular momentum functions $|M_L\rangle$ with $L=3$:

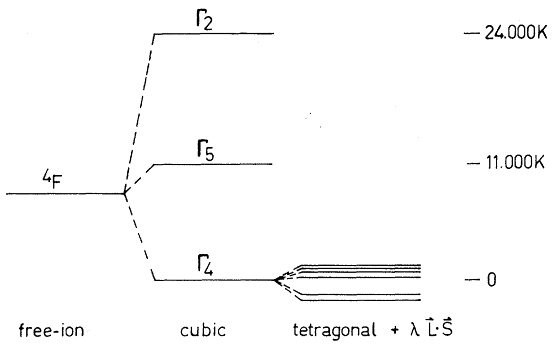

FIG. 2. Splitting of the $Co^{2+}$ free ion ground state by a crystal field with tetragonal deviations from cubic symmetry. The energy scale applies to $CoBr_2 \cdot 6H_2O$ (Ref. 16).

$$
\begin{aligned}
|\alpha_1\rangle &= |0\rangle ,\\
|\alpha_2\rangle &= \tfrac{1}{4}(\sqrt{10}\,|3\rangle + \sqrt{6}\,|-1\rangle) ,\\
|\alpha_3\rangle &= \tfrac{1}{4}(\sqrt{10}\,|-3\rangle + \sqrt{6}\,|1\rangle) .
\end{aligned}
\tag{2}
$$

These orbital states still have a fourfold spin degeneracy. The action of the tetragonal field, the orthorhombic field, and the spin-orbit coupling will partially remove this degeneracy and leads to a splitting into six Kramers doublets. A convenient set of product basis functions $|\alpha_i, M_S\rangle$ can be found in

$$
\begin{aligned}
&|1\rangle = |\alpha_1, +\tfrac{3}{2}\rangle , \quad |1'\rangle = |\alpha_1, -\tfrac{3}{2}\rangle ,\\
&|2\rangle = |\alpha_1, -\tfrac{1}{2}\rangle , \quad |2'\rangle = |\alpha_1, +\tfrac{1}{2}\rangle ,\\
&|3\rangle = |\alpha_2, -\tfrac{3}{2}\rangle , \quad |3'\rangle = |\alpha_3, +\tfrac{3}{2}\rangle ,\\
&|4\rangle = |\alpha_2, +\tfrac{1}{2}\rangle , \quad |4'\rangle = |\alpha_3, -\tfrac{1}{2}\rangle ,\\
&|5\rangle = |\alpha_3, +\tfrac{1}{2}\rangle , \quad |5'\rangle = |\alpha_2, -\tfrac{1}{2}\rangle ,\\
&|6\rangle = |\alpha_3, -\tfrac{3}{2}\rangle , \quad |6'\rangle = |\alpha_2, +\tfrac{3}{2}\rangle .
\end{aligned}
\tag{3}
$$

On this basis the Hamiltonian Eq. (1) factorizes into two identical blocks. The submatrix on the basis $|1\rangle - |6\rangle$ (or on the basis $|1'\rangle - |6'\rangle$) is, apart from a constant diagonal contribution $10C_4^4 + 14C_0^4$,

$$
\begin{pmatrix}
2C_{ax} & 0 & 0 & 0 & \Lambda\sqrt{6} & 0\\
0 & 2C_{ax} & 0 & 2\Lambda\sqrt{2} & 0 & \Lambda\sqrt{6}\\
0 & 0 & -C_{ax}-3\Lambda & 0 & 0 & C_{or}\\
0 & 2\Lambda\sqrt{2} & 0 & -C_{ax}+\Lambda & C_{or} & 0\\
\Lambda\sqrt{6} & 0 & 0 & C_{or} & -C_{ax}-\Lambda & 0\\
0 & \Lambda\sqrt{6} & C_{or} & 0 & 0 & -C_{ax}+3\Lambda
\end{pmatrix}
\tag{4}
$$

The constants $C_{ax}$, $C_{or}$, and $\Lambda$ stand for

$$
C_{ax} = 5C_0^4 - 5C_4^4 - 2C_0^2 , \quad C_{or} = 15C_2^4 + 6C_2^2 ,
$$
$$
\Lambda = \tfrac{3}{4}\lambda . \tag{5}
$$

Diagonalization for given values of $C_{ax}$, $C_{or}$, and $\lambda$ yields the eigenvalues $E_{j,i}^0$, where $i = 1, 2$ denotes the double degeneracy arising from the existence of the two identical blocks mentioned before. It should be noted that more elaborate calculations, which involve for instance ${}^4P$-${}^4F$ mixing under the action of the cubic field, result in the same matrix Eq. (4) accompanied by more complicated definitions Eqs. (3) and (5). Because we will consider $C_{ax}$, $C_{or}$, and $\lambda$ as adjustable parameters we do not go into such details.

In order to obtain the zero-field susceptibility we have to calculate the effect of a perturbation of the form

$$
\mathcal{H}_{\text{Zeeman}} = \mu_B (k_0 L_\alpha + 2S_\alpha) H_\alpha , \tag{6}
$$

where $\mu_B$ is the Bohr magneton, $k_0$ is a constant called the orbital reduction factor, which we will discuss later on, and the subscript $\alpha$ denotes $x$, $y$ or $z$.

The perturbed energy levels can be written

$$
\begin{aligned}
E_{j,1} &= E_j^0 + f_j H + s_j H^2 + \cdots ,\\
E_{j,2} &= E_j^0 - f_j H + s_j H^2 + \cdots ,
\end{aligned}
\tag{7}
$$

where $f_j$ and $s_j$ follow from perturbation theory. The doublet $g$ values are found from $g_j = 2f_j/\mu_B$ and they depend on the orientation of the magnetic field. The spin-only $g$ values, $g_S$, are found by inserting $k_0 = 0$ in Eq. (6). From thermodynamics it follows that

$$
\chi = -\left(\frac{\partial^2 G}{\partial H^2}\right)_{H=0} , \tag{8}
$$

where

$$
G = -kT \ln Z \tag{9}
$$

and

$$
Z = \sum_{j,\alpha} e^{-E_{j,\alpha}/kT} . \tag{10}
$$

Inserting Eqs. (10) and (9) into Eq. (8) we obtain for the susceptibility per spin

$$
\chi = \frac{1}{Z_0^d} \sum_j \frac{f_j}{kT} e^{-E_j^0/kT} - \frac{1}{Z_0^d} \sum_j 2s_j e^{-E_j^0/kT} , \tag{11}
$$

with

$$
Z_0^d = \sum_j e^{-E_j^0/kT} .
$$

The first term in Eq. (11) can be considered as a Curie-like susceptibility, whereas the second term is known as the Van Vleck contribution $\chi_{VV}$.

So far we have not considered the exchange interaction between neighboring ions. In view of the fact that the splitting between the ground-state doublet and the first exited doublet is of the order of 100 K and the exchange energy is at least one order of magnitude smaller, it seems reasonable to assume that the introduction of this interaction and thus the conversion of discrete levels into narrow bands does not seriously modify the energy-level scheme. Moreover, the exchange contribution can conveniently be calculated within the ground-state doublet adapting a fictitious $S'=\frac{1}{2}$ formalism and using the anisotropic $g$ values obtained from the crystal-field calculations outlined before. Although the fictitious spin formalism (which implies that only the ground state is populated) does not hold at temperatures comparable with the doublet-doublet splitting, the contribution of the exchange interaction at those temperatures is already negligible. One must bear in mind that we are referring to the contribution which depends on the interaction $J$ and not to the paramagnetic term which is already contained in Eq. (11).

The interaction between neighboring spins can be written

$$\mathcal{H}_{\mathrm{exch}} = -2\sum_{i<j}\left(J_x S_i^x S_j^x + J_y S_i^y S_j^y + J_z S_i^z S_j^z\right) . \qquad (12)$$

In our case we assume that the principal axis $x$, $y$, $z$ of the exchange tensor $J$ coincide with the crystal-field axis, an assumption which is almost exact if dipolar interactions are small and the exchange between real spins is isotropic. The contribution of Eq. (12) to the susceptibility is not known to a sufficient degree of accuracy, therefore we have to adopt simplifications which transform Eq. (12) into a "model" Hamiltonian from which the contribution is known in certain approximations. In this paper we will use for the susceptibility along $x$ or $y$ directions (respectively, $\chi_x$, $\chi_y$) the high-temperature series expansion (HTE) of the pure $XY$ model on a square lattice for which

$$\mathcal{H}'_{\mathrm{exch}} = -2J_{xy}\sum_{i<j}\left(S_i^x S_j^x + S_i^y S_j^y\right) , \qquad (13)$$

where $J_{xy}=J_x=J_y$. For the susceptibility in the $z$ direction ($\chi_z$) we will use the HTE of a uniaxial model, also on a square lattice, in which

$$\mathcal{H}''_{\mathrm{exch}} = -2\sum_{i<j}\left[J_z S_i^z S_j^z + J_{xy}\left(S_i^x S_j^x + S_i^y S_j^y\right)\right] . \qquad (14)$$

For $\chi_x$ and $\chi_y$ de Jongh *et al.*[6] reported a formula equivalent with

$$\chi_\alpha T/C_\alpha = 1 + 2K + \tfrac{8}{3}K^2 + \tfrac{19}{6}K^3 + \tfrac{101}{30}K^4 + \tfrac{1223}{360}K^5 + \tfrac{1709}{504}K^6 + \tfrac{3799}{1120}K^7 + \tfrac{15619}{5040}K^8 + \tfrac{330019}{120960}K^9 , \qquad (15)$$

where $C_\alpha = Ng_\alpha^2\mu_B^2/4$, $K=J_{xy}/kT$, and $\alpha$ denotes $x$ or $y$. Note that in Ref. 6, $K$ is defined as $|J_{xy}|/kT$ which implies a sign reversal of the odd terms in the series Eq. (15).

From the average of the Padé approximants of Eq. (15) we obtained the following mathematical expression which is valid for negative $K$ up to $|K| = 0.8$ with an error $< 2\%$:

$$\chi_\alpha T/C_\alpha = \left(1-\tfrac{9}{10}K\right)^{-3/2}\left(1+0.6500K+0.2704K^2 + 0.2197K^3 + 0.0082K^4 - 0.0267K^5 + 0.0300K^6 + 0.0462K^7\right) . \qquad (16)$$

We calculated $\chi_z$ for an exchange interaction according to Eq. (14) by the finite cluster expansions method.[17] The results agree completely with those reported by Obakata *et al.*,[18]

$$\frac{\chi_z T}{C_z} = 1 + \sum_{n=1}^{7}\frac{1}{n!}\left(\frac{1}{kT}\right)^n \sum_{j=0}^{[\frac{1}{2}n]} (-1)^j C_{nj} J_z^{n-2j} J_{xy}^{2j} \qquad (17)$$

with $C_z = \frac{1}{4}N g_z^2 \mu_B^2$ and $[\frac{1}{2}n]$ denoting $\frac{1}{2}n$ if $n$ is even and $\frac{1}{2}(n-1)$ if $n$ is odd. The coefficients $C_{nj}$ are given in Table I. From the calculated Padé approximants it showed that for $J_z/J_{xy} < 0.25$ the expression can be used up to $|K| = 0.5$ (error $< 1\%$).

## IV. EXPERIMENTAL RESULTS

The susceptibility was measured in the temperature range from 1 to 120 K along the $x$, $y$, and $z$ principal axes defined in Fig. 1(c). The majority of the data points were obtained by a dynamical mutual inductance method, which is described elsewhere.[19] The measuring device was constructed in such a way that the crystal could be rotated and also could be moved out of the coil system in order to correct for an empty apparatus effect. Furthermore, the temperature of the sample could be raised by approximately 15 K above the bath temperature by means of a simple heatshield. Using helium, hydrogen, and nitrogen the temperature ranges 1–35 K and 50–95 K could be covered. Temperature measurements were made with a calibrated germanium thermometer. In the temperature ranges 1–5 K, 14–20 K, 65–77 K, and at 116 K the data were supplemented with absolute static values for $\chi$ obtained with a Faraday balance. The results are shown in Figs. 3 and 4. After correction for diamagnetism ($-5\times10^{-7}$ emu/g), the temperature dependences of $\chi_x$ and $\chi_y$ ($3.5 < T < 120$ K) and $\chi_z$ ($5 < T < 120$ K) were simultaneously fitted to a combination of expressions (11) and (16), and Eq. (17), respectively, with $\lambda$, $C_{\mathrm{ax}}$, $C_{\mathrm{or}}$, $J_{xy}$, and $J_z$ as variables. It should be noted that the first term in

TABLE I. Numerical value of the coefficients $C_{nj}$ occurring in the high-temperature series for $\chi_z$ given in Eq. (17).

| $n$ \ $j$ | 0 | 1 | 2 | 3 |
|---|---|---|---|---|
| 1 | 2 | | | |
| 2 | 6 | 2 | | |
| 3 | 26 | 18 | | |
| 4 | 138 | 132 | 20 | |
| 5 | 902 | 1 110 | 350 | |
| 6 | 6 876 | 10 194 | 4 143 | 458 |
| 7 | 60 566 | 105 630 | 54 838 | 11 396 |

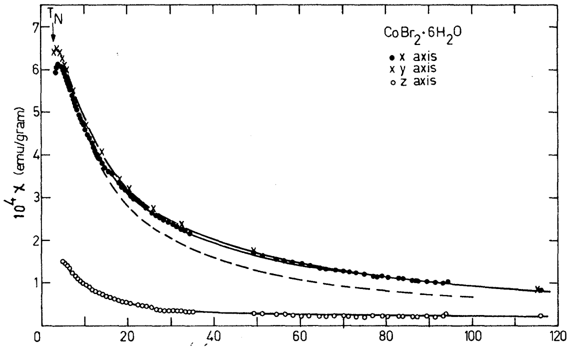

FIG. 3. Susceptibilities of $CoBr_2 \cdot 6H_2O$ vs temperature. For the $y$ axis only part of the data is shown. The fully drawn curves are calculated with $k_0 = 0.90$, $C_{ax} = -815$ K, $C_{or} = 26$ K, $\lambda = -284$ K, $J_{xy} = -2.37$ K, and $J_z = -0.7$ K. The dashed curve represents the extension of the fit for the $x$ axis obtained by de Jongh *et al.* (Ref. 6).

Eqs. (15) and (17) has to be omitted because it is already contained in Eq. (11). This procedure was performed with different values of the orbital reduction factor $k_0$ defined in Eq. (6). The influence of this factor on the obtained best-fit magnetic parameters was very small and well within the estimated uncertainty. The deviation between the data points and the calculated points was in all cases comparable with the estimated error in the data points. The resulting magnetic parameters for the ground state are tabulated in Table II.

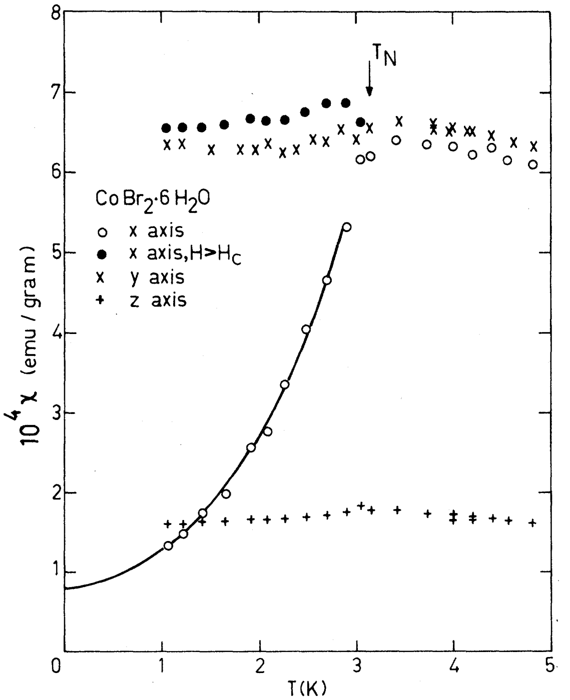

FIG. 4. Static susceptibilities of $CoBr_2 \cdot 6H_2O$ below $T = 5$ K. The drawn curve is used to extrapolate the parallel susceptibility in the ordered state to $T = 0$ K as described in the text.

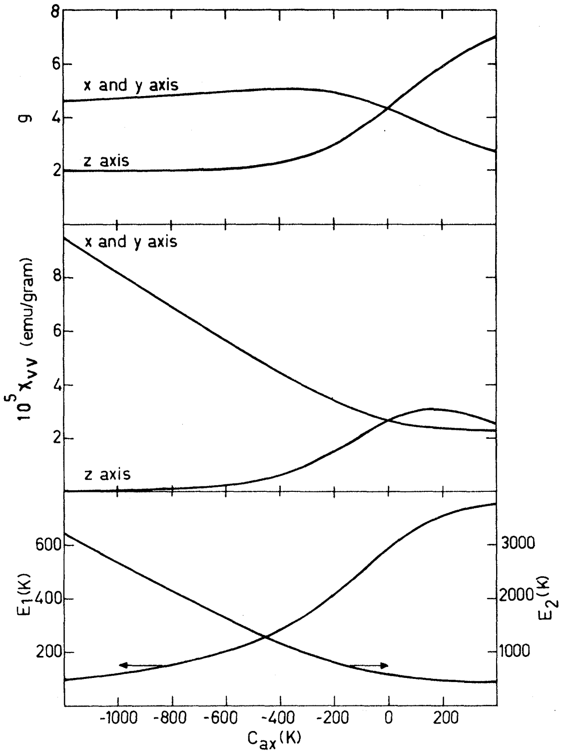

FIG. 5. Various dependences on $C_{ax}$ calculated with $k_0 = 1$, $C_{or} = 0$ K, and $\lambda = -260$ K. From top to bottom: the $g$ values, the value of the Van Vleck contribution $\chi_{VV}$ for $T \to 0$ K, and the energies of the first and second excited doublet state measured from the ground state.

In Table III the best-fit crystal-field parameters are tabulated as a function of the orbital reduction factor $k_0$ and in Fig. 5 several quantities are plotted as a function of $C_{ax}$. It can be seen that the tetragonal distortion and the spin-orbit coupling are rather sensitive to a change of $k_0$. This leaves, however, the lowest doublet-doublet splitting ($E_1$) almost unaffected. This, combined with the fact that the splitting of the doublets reflects the strong axial field such that there is a large energy gap between the two lowest doublets and the center of the

TABLE III. Best-fit crystal-field parameters as a function of the orbital reduction factor $k_0$. Also given are the resulting values of $E_1$, $E_g$ (see text), and the overall width $\Delta E$ of the four highest doublet energies.

| $k_0$ | $C_{ax}$ (K) | $C_{or}$ (K) | $\lambda$ (K) | $E_1$ (K) | $E_g$ (K) | $\Delta E$ (K) |
|---|---|---|---|---|---|---|
| 1.00 | −1140 | 34 | −336 | 177 | 3790 | 1430 |
| 0.95 | −970 | 30 | −312 | 177 | 3290 | 1310 |
| 0.90 | −815 | 26 | −284 | 177 | 2810 | 1190 |
| 0.85 | −680 | 22 | −256 | 173 | 2390 | 1060 |

TABLE II. Best-fit magnetic parameters and related quantities for the ground state. For $\chi_{VV}$ the temperature-independent value below 35 K is given.

| Quantity | This work | Literature | Quantity | This work |
|---|---|---|---|---|
| $J_{xy}$ (K) | $-2.37 \pm 0.05$ | $-2.5$ [a]<br>$-2.45 \pm 0.1$ [b] | $\chi_{VV\,x,y}$ (emu/g) | $(6 \pm 1) \times 10^{-5}$ |
| $J_z$ (K) | $-0.7 \pm 0.1$ | $-0.3$ [a]<br>$-0.4 \pm 0.1$ [c] | $\chi_{VV\,z}$ (emu/g) | $(1.2 \pm 0.5) \times 10^{-6}$ |
| $g_x$ | $4.70 \pm 0.05$ | $5.1$ [d]<br>$5.0 \pm 0.1$ [b] | $g_{Sx}$ | $3.90 \pm 0.05$ |
| $g_y$ | $4.82 \pm 0.05$ | $5.0$ [d]<br>$5.0 \pm 0.1$ [b] | $g_{Sy}$ | $3.99 \pm 0.05$ |
| $g_z$ | $2.02 \pm 0.05$ | $2.2$ [d] | $g_{Sz}$ | $2.01 \pm 0.05$ |

[a] Reference 10.
[b] Reference 6.
[c] Reference 11.
[d] Reference 5.

four others ($E_g$), explains why in the temperature range we studied the magnetic parameters are only slightly affected by the reduction factor $k_0$.

## V. DISCUSSION

In Table II some results for the magnetic parameters from previous sources are also given. The main reason for the discrepancy, in particular for the $g$ values, can be found in the Van Vleck contribution. According to our calculations this contribution amounts to ~10% of the total experimental susceptibility in the temperature region between 3.5 and 15 K, studied by previous authors.[11] As a check on this number we extrapolated the $\chi_{\parallel} = \chi_x$ in the ordered state to $T = 0$ K, taking into account that, according to spin-wave theory,[20] the low-temperature expansion of $\chi$ does not contain a linear term in $T$. This extrapolation is shown in Fig. 4 and results in $\chi_{VV\,x} = (8 \mp 1) \times 10^{-5}$ emu/g, which value may be compared with the calculated $\chi_{VV\,x,y} = (6 \mp 1) \times 10^{-5}$ emu/g. To demonstrate the influence of this and other crystal-field effects we have reproduced the theoretical fit obtained by de Jongh *et al.*[6] from the temperature dependence of $\chi_{x,y}$ below $T = 15$ K, in Fig. 3.

The comparison in Table II also shows that the ratio $J_z/J_{xy}$ is substantially higher than estimated before.[10,11] The reason for this is that former estimates were obtained from the anisotropy in the $g$ tensor, neglecting orbital contributions. The orbital contribution to $g_z$ is rather small, but to $g_{x,y}$ it is substantial. This tends to change the exchange anisotropy drastically. In our case, we obtain $(g_{S\,z}/g_{S\,x})^2 = 0.27 \mp 0.02$ and, independently, $J_z/J_{xy} = 0.29 \mp 0.04$, which is in rather fair agreement.

It was our aim to interpret the susceptibility data with a minimum of conditions imposed upon the system. We could not obtain, however, direct information about $J_x$ and $J_y$ separately because in our procedure we were limited by the available solutions of model Hamiltonians, and had to assume $J_x = J_y$. The quoted value for $J_{xy}$ should therefore be considered as an average of $J_x$ and $J_y$. If one adapts the view that $J_x/J_y = (g_{Sx}/g_{S\,y})^2$ we arrive at $J_x/J_y = 0.98$, which confirms the conjecture $J_x = J_y$.

As we noted before the crystal-field parameters, tabulated in Table III, reflect the strong axial symmetry. Comparison of these data with those obtained by Uryu *et al.*[8] in their calculation of the Schottky anomaly in the specific heat, is hampered by the fact that they have chosen the $z$ axis of the system along the $b$ axis. In their treatment the axial symmetry around the Br-Co-Br axis is purely accidental and is caused by the combination of a tetragonal term and an orthorhombic term which are of roughly the same order of magnitude. The energy levels were obtained with an assumed fixed spin-orbit coupling of $-140$ cm$^{-1}$ ($-201$ K) and are quite different from our results. One should, however, bear in mind that their results were obtained from a rather qualitative comparison with experimental data which exhibit rather large uncertainties.

In Eq. (6) we introduced the orbital reduction factor $k_0$. Formally this type of factor is defined by[21]

$$k_{ij} = \langle \psi_i | \vec{1} | \psi_j \rangle / \langle d_i | \vec{1} | d_j \rangle \ ,$$

where $\vec{1}$ is the one-electron orbital angular momentum operator, the $\psi$'s are the molecular orbitals of the cluster, and the $d$'s are the corresponding $3d$ orbitals. Now the reduction depends on magnitude and origin of the spin density transferred to the ligand. In typical cases $k_0$ varies from ~ 0.8 to 1.0 for transition-metal ions in complex salts. This range has been chosen for Table III. Smaller $k_0$ values give rise to a slightly worse fit to the susceptibility data. As we noted before, the best-fit tetragonal term and the spin-orbit coupling are rather sensitive to $k_0$. As there is no significant change in the quality of the fit we have no way to decide about these values. As far as the spin-orbit coupling is concerned, the values of $\lambda$ in Table III are, on the average, in absolute value higher than the free-ion value $-260$ K. Owing to the covalency in the bonding of the central ion with the ligands and the spin-orbit coupling on the ligand a modification of the free-ion value can be anticipated. Typically in the transition-metal complexes studied so far, this amounts to a reduction of the free-ion value. However, as pointed out by Owen and Thornley,[21] this strongly depends on the symmetry of the bond and the ligand ion. More specifically they state that heavy ligands (with large spin-orbit coupling), such as $Br^-$, might give an effective $|\lambda|$ greater than the free-ion value. Though the value of $|\lambda|$ in this case is rather high on the average it does not seem to be inconsistent with theoretical predictions. Moreover, the experimental values reported in $Co^{++}$ salts seem to be restricted to cubic cases, while we are dealing with a strong tetragonal distortion.

## VI. ACKNOWLEDGMENTS

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