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Spin canting in $RbCoCl_3 \cdot 2H_2O$, a Dzyaloshinsky-Moriya linear chain magnet

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Heat-capacity and magnetic-susceptibility measurements at low temperatures on single crystals of $RbCoCl_3 \cdot 2H_2O$ are described here which indicate that this material is the first reported example of a magnet which can be formally described as having a primarily one-dimensional Dzyaloshinsky-Moriya-like character. Although the compound is not isomorphic to its Cs analog, there are some similarities in their magnetic behavior. Specifically, $RbCoCl_3 \cdot 2H_2O$ magnetically orders at $T_N = 2.94 \pm 0.01$ K and displays spin canting with an unusual amount of anisotropy observed in the single-crystal paramagnetic susceptibilities. The data have been fit using a linear-chain model in which the symmetric part of the intrachain spin-spin interaction is relatively small compared to the Dzyaloshinsky-Moriya antisymmetric contribution. Although the model does not result in unique predictions for the exchange parameters, the present data can be described with symmetric and antisymmetric exchange parameters of $J/k = 0$ and $|D/k| = 59$ K, respectively. The spectroscopic splitting parameters of $g_a = 4.12$ and $g_{c'} = 5.2$ have also been determined from the fits. The results are consistent with the presence of only two sublattices which are severely canted with respect to each other. The spins apparently lie in the bc' plane and the angle between the sublattices approaches 90°.

I. INTRODUCTION

Recently there has been widened interest in the study of lower-dimensional magnetic systems.[1] This interest is a result of the existence of many theoretical descriptions of the behavior of such systems coupled with the recent discovery of many compounds which can be approximately described as being lower-dimensional in character. Two of the best-characterized one-dimensional materials, tetramethylammonium-manganese-trichloride[2,3] and $CsMnCl_3 \cdot 2H_2O$,[4–6] are describable by spin-$\frac{5}{2}$ isotropic Heisenberg Hamiltonians, and have been useful testing grounds for many aspects of the theory. The study of systems describable by anisotropic Hamiltonians should, likewise, contribute to the understanding of magnetic exchange effects in insulators. The logical choices for such studies are compounds containing Co^{2+}, since such materials generally exhibit highly anisotropic behavior at low temperatures. Indeed, highly interesting behavior has been shown by two of the best-characterized lower-dimensional cobalt compounds studied to date: $CsCoCl_3 \cdot 2H_2O$,[7–11] which is isomorphic to the analogous Mn^{2+} compound mentioned above, and $[(CH_3)_3NH]CoCl_3 \cdot 2H_2O$,[12–14] which is also a member of a widely studied isomorphic series.[15–19] The former compound has been described as consisting of Ising-like spins antiferromagnetically coupled into linear chains which are weakly coupled. In addition, the presence of antisymmetric exchange interactions results in spin canting in that material. Likewise, the latter material consists of weakly coupled Ising-like linear chains with, however, ferromagnetic intrachain coupling. Similarly, spin canting is observed in that material also. The magnetic field behavior of both compounds is also quite interesting. The studies indicate that $[(CH_3)_3NH]CoCl_3 \cdot 2H_2O$ is a metamagnet with a critical field of only 64 Oe! Metamagnetic behavior with a critical field of 2900 Oe has also been observed in $CsCoCl_3 \cdot 2H_2O$.

Clearly, the availability of other highly anisotropic spin-$\frac{1}{2}$ linear-chain systems for study is desirable, and thus an attempt was made to extend the isomorphic series to which $CsCoCl_3 \cdot 2H_2O$ belongs by synthesizing an analogous compound, $RbCoCl_3 \cdot 2H_3O$. As it turns out, the two compounds are not isomorphic, but nevertheless the Rb analog exhibits interesting behavior and the results reported here give evidence that it appears to be the first example of a Dzyaloshinsky-Moriya–like lower-dimensional magnet, that is, a magnet which consists of weakly interacting linear chains with intrachain exchange which is formally predominantly antisymmetric. After this work was completed, a short report[20] of a study of the ordered state of this compound appeared indicating that the field behavior of this material may be complex. The few details of the compound's characteristics given in that report are completely consistent with the present work.

II. EXPERIMENTAL

Single crystals of $RbCoCl_3 \cdot 2H_2O$ were grown by slowly evaporating a room-temperature aqueous solution of reagent-grade RbCl and $CoCl_2 \cdot 6H_2O$ (molar ratio of 1:4.44). Commercial chemical analysis gave Rb : 28.1%, Co : 20.1%, Cl : 37.7%, and H : 1.19%. The theoretical values are Rb : 29.8%, Co : 20.6%, Cl : 37.1%, and H : 1.40%. The agreement is satisfactory. The crystals grow as prisms elongated along [001], bounded by {100} and {110}, and truncated by {001}. They easily cleave parallel to (100). X-ray precession photos of a small crystal showed monoclinic symmetry, space group $C_{2/c}$ (centrosymmetric) or C_c (noncentrosymmetric). The lattice parameters determined from the photos are $\beta = 118.3(1)°$, $a = 15.67(6)$ Å, $b = 5.60(3)$ Å, and $c = 8.72(3)$ Å. The experimentally measured density, 2.7 g/cm^3, compares reasonably well with that calculated using the above parameters and four molecules per unit cell, 2.83 g/cm^3. The above cell parameters are in agreement with those recently reported[21] for $RbCoCl_3 \cdot 2H_2O$ in a short paper on its crystal structure. The correct space group was found to be $C_{2/c}$.

Magnetic-susceptibility measurements from 1.5 to 30 K were made using a low-frequency mutual-inductance technique described elsewhere.[22] The measurements were made in near-zero field (less than 5 Oe) and temperatures were generally held stable to within at least 0.02 K for each data point. To obtain the principal axes susceptibilities, measurements were made along the b axis as well as in several directions within the ac plane. The principal axes in the ac plane were determined by finding the two orthogonal orientations where the anisotropy was a maximum. The minimum values of the susceptibility in the ac plane occur nearly along the a axis in a direction which can be described as being 2° away from the a axis and 120° away from the c axis. The maximum values in the ac plane occur in a direction perpendicular to that direction. For convenience, these directions will be termed the a and c' axes, respectively. The b axis orientation was ensured to be highly accurate because of the crystal morphology; the orientations within the ac plane may be uncertain within 1° or 2° . Because of the high degree of anisotropy, it was necessary to use two different crystals for the measurements. For data measured parallel to the c' axis, a crystal weighing 0.0014 g was used, while the a- and b-axes data were obtained with a single crystal weighing 0.52 g.

Heat-capacity data between 2 and 25 K were obtained on a single crystal weighing 5.6 g. Measurements were made using apparatus and a standard heat-pulse technique which have been described elsewhere.[22] Temperature measurements in both the heat-capacity and susceptibility experiments were measured with commercially calibrated germanium resistance thermometers.

III. STRUCTURAL DETAILS

As reported in the structural analysis,[21] $RbCoCl_3 \cdot 2H_2O$ is composed of *trans*-$[CoCl_4(H_2 0)_2]$ octahedra which share corner chlorines to form infinite linear chains along the c axis. Although the structural study did not locate the hydrogen atoms, a reasonable guess as to the presence of any hydrogen bonding can be made by considering whether any chlorine atoms are within about 3.2 Å of a given oxygen atom, since that separation distance is about what would be expected when a water hydrogen is hydrogen bonded to a chlorine. Furthermore, if any such distances are consistent with approximate tetrahedral bonding angles about the oxygen, the likelihood that the supposed hydrogen bonds exist is very high. Such an analysis of the atomic positions reported for $RbCoCl_3 \cdot 2H_2O$ leads to the hypothesis that hydrogen bonds link the chains together into layers in the crystallographic b direction as well as also further bridge cobalt octahedra within a given chain. These layers of cobalt octahedra are separated from each other by layers of rubidium ions. The easy cleavage in the bc plane is supporting evidence for the proposed hydrogen bonds.

A projection of a portion of a cobalt-octahedra layer onto the bc plane is shown in Fig. 1. A projection of

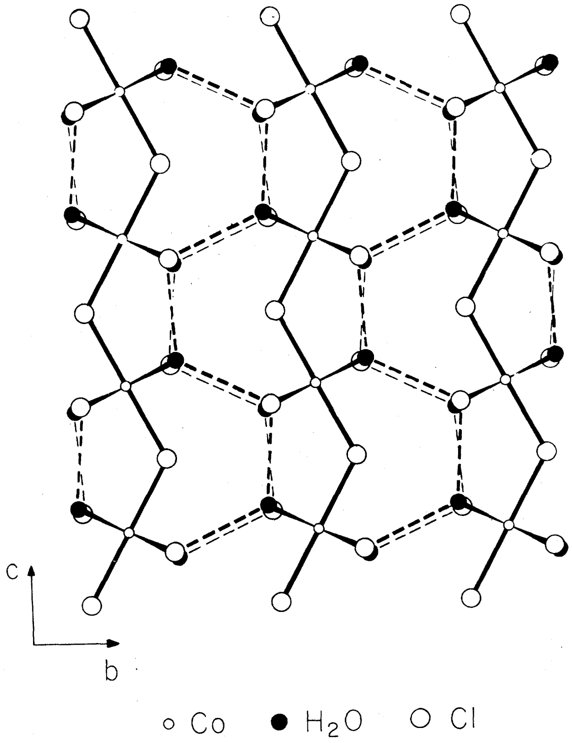

FIG. 1. Projection onto the bc plane of a cobalt-containing layer of $RbCoCl_3 \cdot 2H_2O$. Hydrogen bonds are shown as dashed lines here as well as in Figs. 2 and 3.

the structure along the *b* axis is given in Fig. 2, and Fig. 3 shows the *c*-axis projection of an approximately 5-Å-thick section of the structure taken parallel to the *ab* plane. The chainar-planar nature of the compound is evident from the figures.

It is important to point out that the structure of the present compound is significantly different from either of the structures of the two cobalt linear-chain materials mentioned earlier. In all three compounds hydrogen bonds tie chains together into layers, but more importantly, in contrast to the singly bridged *trans*-[$CoCl_4$ $(H_2O)_2$] octahedra found in $RbCoCl_3 \cdot 2H_2O$, the chains in $CsCoCl_3 \cdot 2H_2O$ consist of singly bridged *cis*-[$CoCl_4(H_2O)_2$] octahedra, while those in [$(CH_3)_3NH$]$CoCl_3 \cdot 2H_2O$ contain doubly bridged *trans*-[$CoCl_4(H_2O)_2$] octahedra.

IV. RESULTS

The heat-capacity results shown in Fig. 4 indicate the presence of a second-order transition. Careful examination of the data shows the transition temperature to be $T_N = 2.94 \pm 0.01$ K.

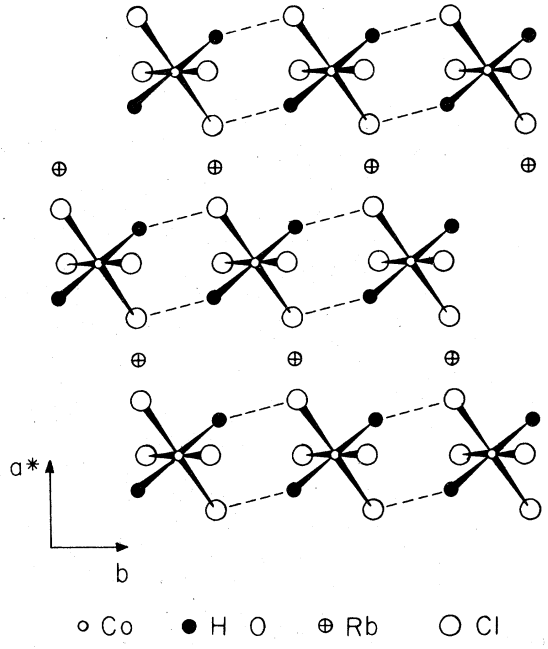

FIG. 3. Projection along the *c* axis of a 5-Å-thick section of the structure of $RbCoCl_3 \cdot 2H_2O$ taken parallel to the *ab* plane. Hydrogen bonds more or less parallel to the *c* axis are not shown.

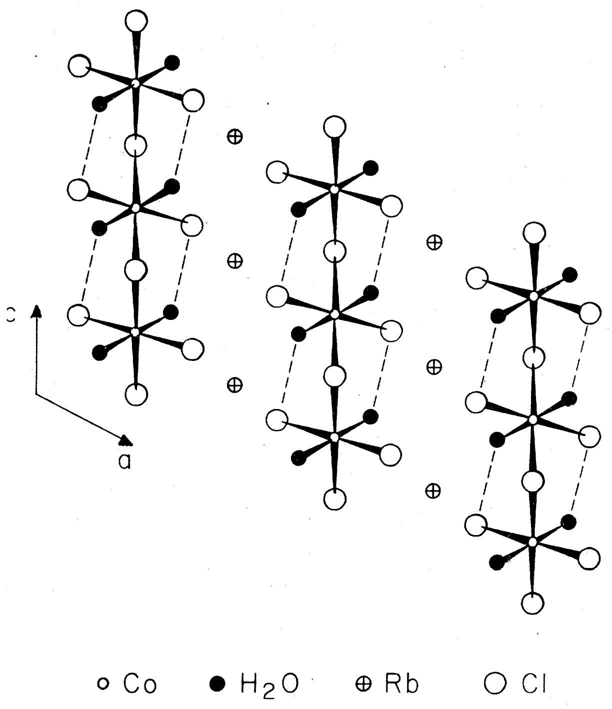

FIG. 2. Projection of the structure of $RbCoCl_3 \cdot 2H_2O$ along the *b* axis. Hydrogen bonds more or less parallel to the *b* axis are not shown.

The results of the principal axes susceptibility measurements are shown in Figs. 5 and 6. A high degree of anisotropy is clearly evident: although χ_b is only about two times larger than χ_a over most of the measured region, at 3.01 K, $\chi_{c'}$ reaches a peak value of 20.4 emu/mole which is approximately 500 times larger than χ_a at that temperature. Just below 3 K, $\chi_{c'}$ abruptly decreases with decreasing temperature so that at 1.5 K the anisotropy is reduced by a factor of 10. The strong effect of $\chi_{c'}$ on measurements made in the *ac* plane can be seen in Fig. 7, which shows the results of measurements along the a^* axis (the axis in the *ac* plane perpendicular to the *c* axis).

Although the χ_a and χ_b data are for the most part unusually featureless, there are some characteristics worthy of note. There is, in fact, a very slight maximum in the χ_a data at about 18 K. In addition, there is a small spike at 3 K which results from a very slight misalignment of the crystal away from the principal axis. At the lowest temperature, χ_a appears to approach a constant value. Similar to the behavior of χ_a, a local maximum in the χ_b data is observed at about 14 K. Below 10 K, however, a behavior is observed which is reminiscent of the behavior of the parallel susceptibility of an antiferromagnet: χ_b rises, with decreasing temperature, to a maximum at 3.5 K and then decreases, passing through an inflection point at about 3 K. However, unlike the parallel susceptibility of a simple antiferromagnet, χ_b does not approach zero at 0 K, but appears to level off at a nonzero value. It is important to note that at low temperatures $\chi_{c'}$ also appears to level off, but at an

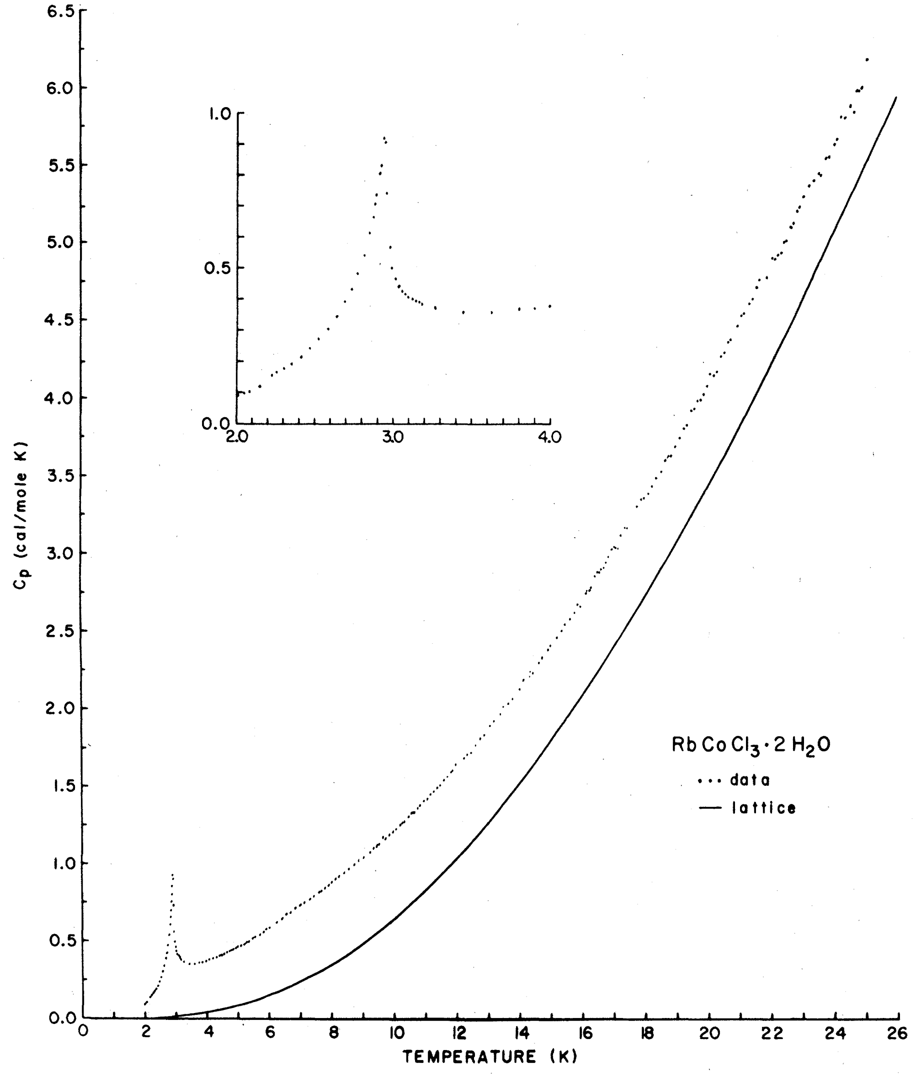

FIG. 4. Measured heat capacity of $\mathrm{RbCoCl_3 \cdot 2H_2O}$. The solid curve is the lattice behavior determined from the fits.

unusually high value of 2–3 emu/mole. Thus, none of the principal axes measurements give any evidence of an easy axis.

The susceptibility data supply further evidence that there is a transition near 3 K. There is an inflection point near that temperature in the χ_b data, as well as one at 2.975 ±0.015 K in the $\chi_{c'}$ data. This latter value is identical to the inflection point observed in the data in the ordered-state study[20] and interpreted as the transition temperature, as is sometimes possible.[23] However, as can be seen from the expanded view of the $\chi_{c'}$ data shown in Fig. 8, there is also some sort of anomalous behavior between 2.82 and 2.94 K in the $\chi_{c'}$ data. Because of this behavior the susceptibility results do not appear to determine unambiguously the transition temperature and it thus seems appropriate to consider the transition temperature determined from the heat-capacity results to be the correct value.

It is both interesting and useful to compare the present data to those reported for $\mathrm{CsCoCl_3 \cdot 2H_2O}$ (Refs. 7 and 11) and $\mathrm{[(CH_3)_3NH]CoCl_3 \cdot 2H_2O}$.[12] The general susceptibility behavior reported for $\mathrm{CsCoCl_3 \cdot 2H_2O}$ is similar to that observed for $\mathrm{RbCoCl_3 \cdot 2H_2O}$: the susceptibility along two of the crystallographic axes is small and nearly constant, while the susceptibility parallel to the third axis exhibits a sharp peak near that compound's transition temperature, reaching a peak value of about 0.7 emu/mole, a much smaller value than the peak value reported here. On the other hand, the susceptibility of $\mathrm{[(CH_3)_3NH]CoCl_3 \cdot 2H_2O}$ is relatively different, with the susceptibility along two axes exhibiting sharp

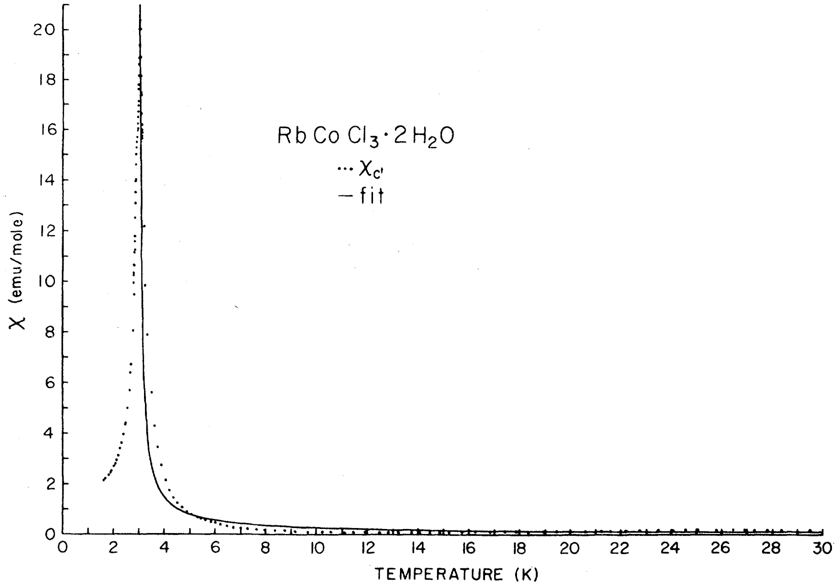

FIG. 5. Magnetic susceptibility of $RbCoCl_3 \cdot 2H_2O$ measured parallel to the c' axis. The solid curve is the prediction of Moriya's molecular-field model for a canted spin system.

peaks and the susceptibility along the third axis being small and nearly constant. The maximum peak susceptibility value observed for one of those peaks is about $2\frac{1}{2}$ times larger than that observed in the present case. However, the maximum value of the other peak is quite near that reported here.

The present heat-capacity results are also more like those found for $CsCoCl_3 \cdot 2H_2O$. The heat capacities of both materials exhibit small sharp anomalies near 3 K. Above the transition in both compounds the heat capacity rises almost immediately with increasing temperature. The heat capacity of $[(CH_3)_3NH]CoCl_3 \cdot 2H_2O$ is relatively different: a sharp anomaly roughly five times larger than those in the other compounds occurs near 4 K at that material's transition temperature. Above the transition the heat capacity is essentially constant for nearly 2 K before beginning to rise in a more or less T^2-type behavior.

V. ANALYSIS

A. General approach

Although it is similar to the other Co^{2+} compounds in some ways, $RbCoCl_3 \cdot 2H_2O$ clearly has a character of its own and an analysis of its behavior can, at best, only make use of the insights gained in the previous studies. Thus an analysis of the results presented here best begins by first considering the data set which displays the most features which vary greatly as a function of temperature. Theoretical fits to such data should be far less ambiguous than fits to more featureless data.

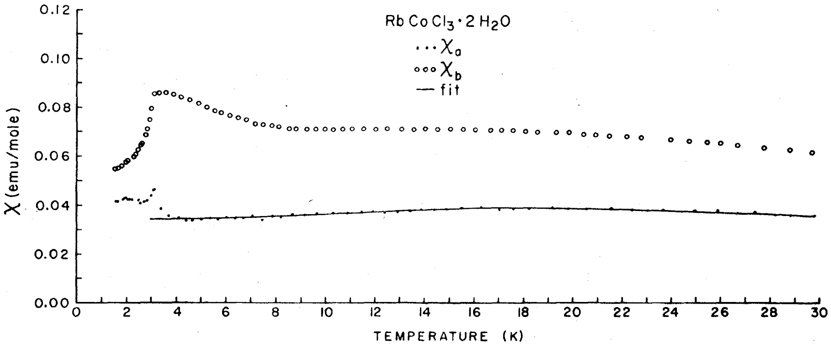

FIG. 6. Magnetic susceptibility of $RbCoCl_3 \cdot 2H_2O$ measured parallel to the a and b axes. The solid curve is the theoretical prediction for χ_z of a Dzyaloshinsky-Moriya linear chain.

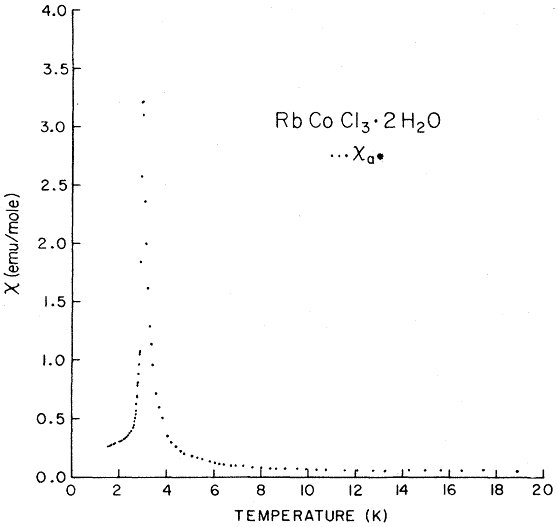

FIG. 7. Magnetic susceptibility of $RbCoCl_3 \cdot 2H_2O$ measured parallel to the a^* axis.

B. $\chi_{c'}$ fit

Thus the key to understanding the behavior of $RbCoCl_3 \cdot 2H_2O$ lies in a proper interpretation of the behavior of $\chi_{c'}$. In the $[(CH_3)_3NH]CoCl_3 \cdot 2H_2O$ study, two different phenomena were found capable of producing such behavior. If the susceptibility of an Ising linear-chain system with ferromagnetic intrachain exchange is measured parallel to the easy axis, then behavior qualitatively similar to that of $\chi_{c'}$ results. The theoretical susceptibility is given by[24]

$$\chi_{\parallel} = (Ng^2\mu_B^2/4kT)\exp(2J/kT) \ , \tag{1}$$

where the spin Hamiltonian is $H = -4J\sum_i S_{iz}S_{jz}$. A reasonable fit to the $\chi_{c'}$ data above about 3.5 K can be achieved using $g_{c'} = 2.2$ and $J/k = 6.0$ K with Eq. (1). However, below that temperature the fitted curve does not rise as sharply as the data do. In addition, neither χ_a nor χ_b can be fit using that value of J/k with the theoretical prediction for the perpendicular susceptibility of an Ising linear chain. Thus one must conclude that Eq. (1) is not applicable to $RbCoCl_3 \cdot 2H_2O$.

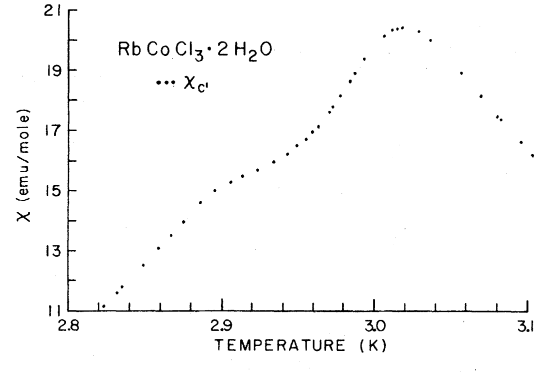

FIG. 8. Expanded view of the c-axis susceptibility of $RbCoCl_3 \cdot 2H_2O$ near the transition.

The other alternative, suggested by the previous studies, is that spin canting occurs in $RbCoCl_3 \cdot 2H_2O$, thus giving rise to weak ferromagnetism which can result in behavior similar to that observed for $\chi_{c'}$. Dzyaloshinsky[25] and Moriya[26] have shown that spin canting can result from antisymmetric spin exchange of the form $\vec{D} \cdot (\vec{S}_i \times \vec{S}_j)$. Including such a term along with an isotropic spin exchange term and a Zeeman contribution, Moriya has considered the Hamiltonian[26]

$$H = \sum_{i,j} [-2J\vec{S}_i \cdot \vec{S}_j + D(S_{ix}S_{jy} - S_{iy}S_{jx})] + g\mu_B\vec{H} \cdot \sum_i \vec{S}_i \ . \tag{2}$$

Assuming that the easy axis lies in the xy plane and using a molecular field approximation, he found that for a spin-S linear-chain system when $\vec{H}$ is in the xy plane and parallel to the direction of the weak moment, the susceptibility should be given by

$$\chi_{xy} = \frac{Ng_{xy}^2\mu_B^2 S(S+1)}{3k(T+T_N)} \frac{T-T_0}{T-T_N} \ , \tag{3}$$

where g_{xy} is the g value for the direction parallel to $\vec{H}$,

$$T_0 = (-4J/3k)S(S+1) \ , \tag{4}$$

and where the transition temperature is given by

$$T_N = \pm T_0[1 + (D/2J)^2]^{1/2} \ . \tag{5}$$

The positive sign in Eq. (5) is used for antiferromagnetic exchange and the negative sign is for ferromagnetic exchange. It is well known that molecular field approximations predict transition temperatures poorly, so when Moriya's results are used to fit experimental data, it is best to build in the correct transition temperature by inserting it in Eqs. (3) and (5) and then use those equations to fit the data.

It turns out that Eqs. (3) and (5) are, indeed, quite capable of reasonably describing $\chi_{c'}$. Interestingly, it turns out that essentially equivalent fits may be obtained by using either sign in Eq. (5): large values of $D/2J$ with the positive sign, or small values of $D/2J$ with the negative sign. The implication of the case of small values of $D/2J$ is that the exchange is primarily symmetric and ferromagnetic, with the spins essentially aligned along a direction perpendicular to the c' axis. If so, Eq. (1), with $J > 0$, should apply to some orientation in the ab plane. Because χ_a and χ_b are principal axes susceptibilities, and because Eq. (1) with $J > 0$ results in susceptibilities much larger than either χ_a or χ_b, this case is clearly not applicable. Thus the remaining case of large values of $D/2J$ must be considered to be the appropriate way to interpret the data. A typical curve resulting from such a fit with the values $g_{c'} = 5.24$ and $|D/2J| = 60$ is shown in Fig. 5. The curve does not match the data within the experimental uncertainties, and there are consistent deviations of the fitted curve from the data, but nevertheless the fit should be considered acceptable since a relatively wide range of experimental values can be reasonably described with a simple molecular field approach. Furthermore, demagnetization effects have been ignored and undoubtedly they have some influence on the data. It is important to note that the fitted curve is not very sensitive to the value of $D/2J$ and essentially equivalent curves may be obtained using slightly different values of $g_{c'}$ with any large value of $|D/2J|$.

C. χ_a fit

Obviously the $\chi_{c'}$ fit gains credence if the χ_a and χ_b data are describable with a consistent model. Thus the susceptibility resulting from Eq. (2) for $\vec{H}$ parallel to the z axis must be compared to either the χ_a or χ_b data. According to Moriya,[26] that susceptibility should follow a Curie-Weiss law. Fortunately, an exact solution of a Hamiltonian very similar to Eq. (2) has been given by Siskens, Capel, and Gaemers,[27,28] who have considered the one-dimensional anisotropic XY model with antisymmetric nearest-neighbor interactions in the presence of a magnetic field parallel to the z axis. The Hamiltonian they used is

$$H = \sum_{i,j} [(1+\gamma) S_{ix}S_{jx} + (1-\gamma) S_{iy}S_{jy} + \Delta(S_{ix}S_{jy} - S_{iy}S_{jx}) - BS_{jz}] , \tag{6}$$

where the summation is over nearest neighbors of a linear chain. The case $\gamma = 0$ is equivalent to the symmetric part of the spin-spin interaction in Eq. (2) being considered to be XY-like in nature. That interaction being Ising-like in nature corresponds to the case $\gamma = 1$ in Eq. (6).

Actually, it is more appropriate to consider a slight modification of the Hamiltonian given by Eq. (6), one that is more consistent with the details of the Hamiltonian of Eq. (2), regardless of the details of the symmetric part of the spin-spin interaction. The exchange interaction part of the modified Hamiltonian is given by

$$H = \sum_{i,j} \left\{ -2J \left[S_{ix}S_{jx} + \left[\frac{1-\gamma}{1+\gamma} \right] S_{iy}S_{jy} \right] + D(S_{ix}S_{jy} - S_{iy}S_{jx}) \right\} . \tag{7}$$

Clearly the Hamiltonian of Eq. (6) is simply related to that of Eq. (7) by a factor of $-(1+\gamma)/2J$. Thus, it is relatively straightforward to transform the results reported for Eq. (6) to ones valid for Eq. (7). The z-axis susceptibility is then given by

$$\chi_z = \chi_1 + \chi_2 , \tag{8}$$

where

$$\chi_1 = \frac{N g_z^2 \mu_B^2}{8\pi J} \frac{\gamma^2}{1+\gamma} \times \int_0^{2\pi} \frac{\sin^2(\omega)\tanh(KR)}{r^3} d\omega , \tag{9}$$

$$\chi_2 = \frac{N g_z^2 \mu_B^2}{8\pi kT} \int_0^{2\pi} \frac{\cos^2(\omega)}{r^2 \cosh^2(KR)} d\omega , \tag{10}$$

$$K = J/[(1+\gamma)kT] , \tag{11}$$

$$r^2 = \cos^2(\omega) + \gamma^2 \sin^2(\omega) , \tag{12}$$

and

$$R = r + (1+\gamma)(D/2J)\sin(\omega) . \tag{13}$$

These equations are consistent with the previously reported results for the Ising ($\gamma = 1$) and XY ($\gamma = 0$) models.[24,29] For example, when $\gamma = 0$, χ_z reduces to the solution for χ_z of the XY model given by Katsura.[29] Several features of the equations should be pointed out. As pointed out by Siskens, Capel and Gaemers, the magnetization calculated using the Hamiltonian of Eq. (6) is even in Δ. Therefore χ_z must also be even in Δ and thus the sign of D cannot be determined from fits using Eq. (8). Similarly, χ_z is independent of the sign of J, as can be seen by noting that Eqs. (9) and (10) are even functions of K and that the sign of J in Eq. (13) is obviously unimportant since χ_z is independent of the sign of D. Another important feature of χ_z is its behavior for large values of $D/2J$. For large values of $D/2J$, the argument of the hyperbolic function, KR, essentially becomes independent of γ, so that the details of the symmetric part of the spin-spin interaction become unimportant. (Clearly, in the limit $J = 0$ the value of γ cannot influence the results since it no longer appears in the Hamiltonian.) Furthermore, numerical studies of χ_z show that the contribution of χ_1 to χ_z becomes less important the larger $D/2J$ is. Also, for large fixed $D/2J$ values, χ_1 obviously becomes less important the larger J is. Thus, for $D/2J > 3$ and $J/k = 3$ K, for example, χ_z differs by not much more than a few percent from χ_2 and is more or less independent of γ. For $D/2J$ approaching infinity, χ_z approaches χ_2. Actually, this result can be seen from the work of Siskens, Capel, and Gaemers. Besides considering the Hamiltonian of Eq. (6), they also considered one in which there was no symmetric exchange term at all, in other words, one equivalent to that of Eq. (7) with $J = 0$. [Of course, $J = 0$ in Eq. (7) corresponds to the case $D/2J = \infty$.] Although they did not note it, the susceptibility they derived in that case is equivalent to χ_2, with $J = 0$, in agreement with the above deductions regarding the behavior of χ_z for large $D/2J$. Siskens, Capel, and Gaemers did note that the antisymmetric spin-spin coupling (Dzyaloshinsky-Moriya coupling), if strong enough, predominates the antiferromagnetic ordering and the above observations support that statement. Thus an interesting aspect of the behavior χ_z is that pure Dzyaloshinsky-Moriya coupling gives z-axis susceptibility behavior identical to that of the XY model.

So, although when Eq. (8) is used to fit data there are actually four variables, g_z, γ, D and J, if $D/2J$ is large there are effectively only two. When Eq. (8) is used to fit χ_a the values $g_a = 4.15$, $|J/k| = 3.00$ K, and $|D/k| = 59.7$ K result, with the fit being essentially independent of γ. However, as would be expected from the previous discussion of the behavior of Eq. (8), an equivalently good fit which is actually slightly better is obtained for $g_a = 4.12$, $|D/k| = 59.2$ K, and $J = 0$ (pure Dzyaloshinsky-Moriya coupling). This fit is shown in Fig. 6 and is seen to describe the data nearly perfectly from 4 to 30 K. In fact, for that region the fitted curve matches the data completely within the experimental uncertainty.

It is interesting to note that the behavior of χ_a is not too different from that of the perpendicular susceptibility of an Ising linear-chain magnet and that, taken alone, the use of that model to describe the data could lead to erroneous results. For example, an almost reasonable fit of the χ_a data can be obtained using $g = 3.87$ and $|J/k| = 21.0$ K with that model such that the data are matched within 4% between 4 and 30 K. However, the fitted curve's maximum is approximately 4 K below the maximum of the data and there are consistent deviations of the data from the fitted curve. Such an exact model should be expected to give better results. More important, the magnitude of the measured heat capacity between 4 and 8 K is smaller than possible in that region if the system behaves as an Ising linear-chain magnet with $|J/k| = 21$ K.

D. Heat-capacity fit

Further support for the Dzyaloshinsky-Moriya-like linear-chain model used to fit the susceptibility data is given by the heat-capacity behavior, as the analysis below will show. The first problem in the analysis of the heat capacity of a magnetic system is that a reasonable estimate for the lattice contribution must be obtained. Often the lattice behavior is assumed to follow a T^3 behavior. In other cases, nonmagnetic isomorphic materials have been used in conjunction with corresponding states procedures to obtain estimates for lattice contributions.[12,30,31] Unfortunately, in the present case a nonmagnetic compound with the stoichiometry $AMX_3 \cdot 2H_2O$ (A is an alkali metal, M is a nonmagnetic metal, and X is a halide) has not been found yet, even though many workers have searched for such a material because of the interest in $CsCoCl_3 \cdot 2H_2O$ and its Mn^{2+} isomorph. Furthermore, assumption of a T^3-type behavior in the present case is hazardous at best. The Mn^{2+} isomorph of $CsCoCl_3 \cdot 2H_2O$ has been shown to have a lattice which follows a two-dimensional Debye law[6]; each of the lattices of $[(CH_3)_3NH]CoCl_3 \cdot 2H_2O$ and its isomorphs[12,18] has similarly been found to have a temperature dependence closer to T^2 rather than T^3. All of those compounds contain easy cleavage planes which correspond to crystallographic planes of linear chains linked together by hydrogen bonds. Since $RbCoCl_3 \cdot 2H_2O$ similarly contains such planes and since its stoichiometry is similar, it is not unreasonable to expect its lattice behavior to be similar. It is thus appropriate to determine whether the heat capacity data are describable by the Dzyaloshinsky-Moriya linear-chain model in conjunction with a lattice given by a two-dimensional Debye law.

To obtain the prediction of the Dzyaloshinsky-Moriya-like linear-chain model for the magnetic contribution to the heat capacity, it is again necessary to transform the results given by Siskens, Capel, and Gaemers for the Hamiltonian of Eq. (6) to ones valid for the Hamiltonian of Eq. (7). The resulting heat capacity equation is

$$C_{\mathrm{MAG}} = \frac{Nk}{2\pi} \int_{-\pi}^{\pi} \frac{(KR)^2}{\cosh^2(KR)}\, d\omega \ , \tag{14}$$

where K and R are given in Eqs. (11)–(13). Just as for the susceptibility results previously discussed, this equation is consistent with the reported results for the Ising and XY models,[29,32] as well as also being independent of the signs of D and J. Additionally, again similar to the susceptibility results, Eq. (14) is essentially independent of the value of γ for large $D/2J$ values and approaches the behavior found by Siskens, Capel, and Gaemers for the pure Dzyaloshinsky-Moriya linear chain, which can be obtained from Eq. (14) by using $J = 0$. As with the susceptibility results, that behavior turns out to be identical to the behavior found for the XY model.[29]

The model chosen to represent the lattice contribution to the heat capacity is similar to the model of Tarasov[33] used in the study of $CsMnCl_3 \cdot 2H_2O$ (Ref. 6):

$$C_{\mathrm{LAT}} = 7\{3D_2(\Theta_2) + 3(\Theta_3/\Theta_2)^2[D_3(\Theta_3) - D_2(\Theta_3)]\} \ , \tag{15}$$

where 7 corresponds to the number of heavy atoms in the unit cell and where the n-dimensional Debye function (per vibration mode) with the characteristic Debye temperature Θ is given by[34]

$$D_n(\Theta) = n\left(\frac{T}{\Theta}\right)^n \int_0^{\Theta/T} \frac{e^x x^{n+1}}{(e^x - 1)^2}\, dx \ . \tag{16}$$

The first term in Eq. (15) is that expected for a two-dimensional lattice. The second term results from the added assumption that for low enough vibration frequencies (less than $\nu = k\Theta_3/h$) the frequency distribution spectrum is one appropriate for a three-dimensional continuum, rather than the two-dimensional continuum used for frequencies between $\nu = k\Theta_3/h$ and $\nu = k\Theta_2/h$. The fraction of low-frequency three-dimensional modes is taken to be $(\Theta_3/\Theta_2)^2$. Thus, for $\Theta_3 = 0$, Eq. (15) predicts the behavior of a pure two-dimensional lattice, while for $\Theta_3 = \Theta_2$, the prediction is for a pure three-dimensional lattice. The ratio Θ_3/Θ_2 is thus, in some manner, a measure of the dimensionality of the lattice.

When Eqs. (14) and (15) are used with the parameter values $J = 0$, $|D/k| = 59.2$ K (the result found from the χ_a fit for pure Dzyaloshinsky-Moriya coupling), $\Theta_2 = 259$ K, and $\Theta_3 = 69.1$ K, a good fit to the data above 12 K is obtained, with the calculated heat capacity matching the measured data within less than about 2% over the entire region, the average deviation being about 0.8%. The resulting lattice predicted by Eq. (15) is shown as the solid curve in Fig. 4 and when it is subtracted from the measured heat capacity of $RbCoCl_3 \cdot 2H_2O$, the magnetic heat-capacity behavior shown in Fig. 9 is obtained. The solid curve in Fig. 9 is the behavior predicted by Eq. (14). The agreement at the higher temperatures is heartening, especially considering the use of a simple lattice model. It is not unlikely that the deviations of the data from the curve below 12 K are a result of an imperfect lattice estimate combined with two- and three-dimensional magnetic effects which surely must be present and which would be expected to become important at lower temperatures. Indeed, the value of Θ_3/Θ_2 determined indicates the lattice is not perfectly two-dimensional and that it exhibits somewhat greater three-dimensional-like behavior than did the lattice found for $CsMnCl_3 \cdot 2H_2O$.

VI. DISCUSSION

It is gratifying that essentially a single model has been able to describe three relatively different sets of data. However, it is important to emphasize that the fits are not unique, as should be evident from the discussion of the behavior of the equations used. Although the pure Dzyaloshinsky-Moriya predictions ($J = 0$) have been used in fitting χ_a and the heat capacity, it would seem unlikely that symmetric exchange is completely absent, so that the behavior of $RbCoCl_3 \cdot 2H_2O$ is actually only Dzyaloshinsky-Moriya-like in character. The ratio of the antisymmetric to symmetric exchange apparently is large, but otherwise somewhat indeterminate. The $\chi_{c'}$ data give some evidence that J is negative. At this point it is fitting to comment on the uncertainties of the fitted parameters. In fact, because of the nonuniqueness of the fits, beyond the fact that $|D/k|$ appears to be about 59 K, little can be said. The g_a value reported is probably no more uncertain that ±0.1, while the uncertainty in $g_{c'}$ is probably several times greater. Further experiments will be required to learn more about the magnitude of J.

In spite of the nonuniqueness of the fits and the resulting ambiguity in the parameters, it is still possible to propose a spin arrangement consistent with the results, as well as consistent with the structure. Basically, it appears that all spins lie completely in the bc' plane, there being just two sublattices of spins. The sublattices are not parallel to each other, but rather have an angle Θ between them. The c' axis components of the spins of both sublattices are equal and parallel, while the b axis components are equal and antiparallel. An estimate of the size of Θ can be determined in the same manner as done in the $CsCoCl_3 \cdot 2H_2O$ study.[7] By a straightforward consideration of the equilibrium energy involved in the spin configuration, it was shown in that work that

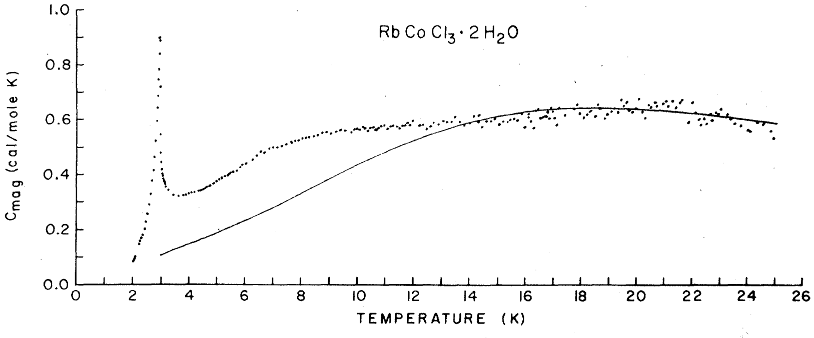

FIG. 9. Magnetic heat capacity of $RbCoCl_3 \cdot 2H_2O$ determined from the experimental data using the fitted lattice. The solid curve is the theoretical prediction for a Dzyaloshinsky-Moriya linear chain.

$\tan(\Theta) = -D/J$ [for the Hamiltonian parameters of Eq. (7)]. Thus, for example, if one uses $D/2J = 10$, then Θ is approximately equal to 87°. If $D/2J$ is infinite, then Θ is 90°. For $D/2J$ as small as 3, one finds Θ to be about 80°. Thus it is clear that whatever actual $D/2J$ applies to $RbCoCl_3 \cdot 2H_2O$, the spin-canting angle is large, with the two sublattices being oriented approximately perpendicular to each other. Such extreme spin canting certainly explains why no easy axis was observed at low temperatures—there is none!

It should be noted that the behavior of the one data set which has not been fit, χ_b, is consistent with the proposed spin configuration. If the spins are oriented such that there are components of the spins perpendicular to the b axis, as well as components which are arranged in an antiparallel fashion to the b axis, then one might well expect, as observed in the data, behavior exhibiting some of the characteristics normally seen in the behavior of the parallel susceptibility of an antiferromagnet, as well as characteristics typical of a perpendicular susceptibility. In fact, such an expectation is supported by the behavior of the susceptibility of $CsCoCl_3 \cdot 2H_2O$ at low temperatures.[11] In that material, susceptibility measurements along the c axis exhibited both characteristics, with the parallel-like behavior becoming evident only at low temperatures near the transition.

The only remaining question about the consistency of the several sets of data is why the heat capacity fit is not better below 12 K. Since the susceptibility data is well described with a one-dimensional model, one might expect the heat capacity to be equally well described by such a model. In fact, as shown by the $[(CH_3)_3NH]CoCl_3 \cdot 2H_2O$ study, such an expectation is not valid. In that study the susceptibility results were well described by the one-dimensional Ising model, but the two-dimensional Ising model was required to give a good description of the heat-capacity results. It thus appears that relatively small deviations from ideal one-dimensional behavior in a magnet affect the magnet's heat capacity far more than its susceptibility is affected.

The consistency of the proposed spin configuration with the crystal structure is easily seen. For example, as is evident from Fig. 1, if the spins were ferromagnetically aligned along the Co-bridging Cl bond, then one would expect that χ_c behavior to be similar to a canted magnet in the paramagnetic state with a net moment in the ordered state. Both χ_b and χ_{a^*} would behave similarly to the perpendicular susceptibility of linear chains, except that χ_b could also be expected to display some characteristics typical of a parallel susceptibility. Alternatively, the same behavior would occur if the spins were aligned essentially antiferromagnetically along the projection in the bc plane of the Co-O bonds. Of course, as the data have indicated, the spins do not lie in the bc plane, but rather in the bc' plane. However, with the exception of considering the a and c' axes instead of the a^* and c axes, the above qualitative description of the behavior of the material is still valid. Furthermore, it is interesting to note that when it is projected into the bc' plane, the angle between Co-O bonds of nearest-neighbor octahedra is about 73°, with the bisector of that angle being parallel to the b axis. It is thus evident that this structure could easily lead to large spin-canting angles if the spins have any strong tendency to align along the Co-O bond.

Indeed, such may well be expected to be the case. The basic reason for this is that for octahedral Co^{2+} the single-ion crystal field, together with spin-orbit effects, splits the lowest orbital triplet of Co^{2+} into six Kramers doublets with such a large separation between the two lowest doublets that only the lowest doublet is of importance in the temperature region considered here. Since there is nearly tetragonal symmetry in the present case, one would expect the moments to lie either almost parallel or almost perpendicular to that symmetry axis. The available evidence on the orientation of the spins in $CoCl_2 \cdot 2H_2O$ (Ref. 35) and $[(CH_3)_3NH]CoCl_3 \cdot 2H_2O$,[12] the two other known compounds which also contain $[CoCl_4(OH_2)_2]^{2-}$ ions, is that there is a strong tendency for the spins to align along the Co-O bond in this geometry. From this point of view, it becomes necessary to question what the antisymmetric exchange formalism used here to describe the spin canting in $RbCoCl_3 \cdot 2H_2O$ truly implies. Both single-ion anisotropy[26] and g-value anisotropy,[36] as well as antisymmetric superexchange,[26] have been shown to produce spin canting. It seems likely from the above discussion that the spin canting could well result from the single-ion anisotropy of Co^{2+} and that thus little can be said about the actual nature of the superexchange coupling in $RbCoCl_3 \cdot 2H_2O$, other than it can *formally* be described as being antisymmetric.

VII. CONCLUSION

The low-temperature magnetic behavior of $RbCoCl_3 \cdot 2H_2O$ gives strong evidence that magnetically the material can be formally considered to consist of weakly interacting linear chains with predominant Dzyaloshinsky-Moriya interactions which result in severe spin canting. This is the first reported example of such a material and should be quite useful in testing aspects of the theory. Indeed, the comprehensive field-dependent solution for the equilibrium thermodynamic properties, as well as the dynamic properties of anisotropic *XY* chains with Dzyaloshinsky-Moriya interactions given by Siskens, Capel, and Gaemers should make further studies of $RbCoCl_3 \cdot 2H_2O$ highly enticing. With the complex spin arrangement proposed here, the apparent existence[20] of several magnetic transitions in the ordered state for the case of a magnetic field parallel to the c axis should be less puzzling. However, NMR and magnetization measurements in the ordered state may be necessary to interpret the exact nature of the transitions.

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