Magnetic behavior of the ferromagnetic quantum chain systems (C$_6$H$_{11}$NH$_3$)CuCl$_3$ (CHAC) and (C$_6$H$_{11}$NH$_3$)CuBr$_3$ (CHAB)

K. Kopinga, A. M. C. Tinus, and W. J. M. de Jonge

Department of Physics, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands

Heat-capacity measurements on (C$_6$H$_{11}$NH$_3$)CuBr$_3$ (CHAB) in the region $0.45 < T < 55$ K are presented. Three-dimensional ordering is observed at $T_c = 1.50$ K. The data are analyzed together with previously reported measurements on (C$_6$H$_{11}$NH$_3$)CuCl$_3$ (CHAC). Both compounds appear to be very good approximations of a ferromagnetic $S = \frac{1}{2}$ Heisenberg linear-chain system with $J/k \approx 50$ K. From the data it is inferred that the intrachain interaction of CHAC contains about 2% uniaxial anisotropy, whereas CHAB contains about 5% easy-plane anisotropy. The results are corroborated by magnetization measurements on CHAB below T_c, which also reveal a metamagnetic transition for $\vec{H} \parallel b$ ($H_c = 210$ Oe). From the value of H_c and the location of the tricritical point the interchain interactions in CHAB were found as $z_{AF}J_{AF}/k = -0.03$ K, $z_F J_F / k \approx 0.08$ K.

I. INTRODUCTION

A large amount of theoretical and experimental studies have been devoted to the thermodynamic properties of chainlike systems. The majority of the experimental studies, however, are confined to systems built up from antiferromagnetic chains, of which especially the "quantum" limit ($S = \frac{1}{2}$) and the "classical" limit ($S = \frac{5}{2}$) have been studied rather intensively.

In the last few years, there has been a renewed interest in the excitation spectrum and the thermodynamic properties of ferromagnetic $S = \frac{1}{2}$ linear chain systems.[1] Despite this theoretical activity, the experimental evidence on these systems is rather scarce. However, the recent synthesis[2] of some quasi one-dimensional compounds, which are built up from ferromagnetic Cu^{2+} ($S = \frac{1}{2}$) chains, has restimulated the experiments on this class of model systems.

The best realization of such a system reported up till now is (C$_6$H$_{11}$NH$_3$)CuCl$_3$ (CHAC). Both specific heat[3] and susceptibility[4] measurements on this compound reveal a rather large intrachain interaction J/k (50–70 K), whereas measurements of the magnetic phase diagram[4] indicate that the interchain coupling J'/k is smaller by three orders of magnitude. Futhermore, a small amount of anisotropy ($\sim$1%) is present in the intrachain interaction.

Since in (quasi) one-dimensional systems even a small amount of anistropy may drastically affect the thermodynamic properties at low temperatures,[1,5,6] and because the specific-heat data on CHAC that we reported previously[3] show a large magnetic contribution just above T_N (2.214 K), which could not be ac-

counted for by the purely isotropic linear chain Heisenberg model, we thought it worthwhile to reanalyze the heat-capacity data on CHAC, using a more refined model. Apart from this, we synthesized the bromine analog of this compound, (C$_6$H$_{11}$NH$_3$)CuBr$_3$ (CHAB), in order to investigate whether the observed characteristics are typical for this type of systems. The behavior of CHAB was investigated by measurements of the heat capacity and the magnetization.

The organization of the paper will be as follows. In Sec. II we will consider the structure and preparation of the chlorine and the bromine compound. Section III will be devoted to the heat-capacity measurements, whereas Sec. IV will report on the measurements of the magnetization. Section V will conclude the paper with a discussion on the behavior of CHAC and CHAB.

II. STRUCTURE AND PREPARATION

Single crystals of CHAC were grown by evaporation at room temperature of a solution of equimolar quantities of cyclohexylammonium chloride and copper (II) chloride in n-propanol. The solution was kept in an N$_2$ atmosphere. The bromine compound was synthesized in an analogous way. Large single crystals (up to a few grams) could be obtained rather easily.

The crystallographic structure[4] of CHAC is schematically drawn in Fig. 1. It consists of bibridged linear chains of CuCl$_3^-$ ions running parallel to the c axis. In the b direction adjacent chains, which are about 8.5 Å apart, are hydrogen bonded by the NH$_3^+$
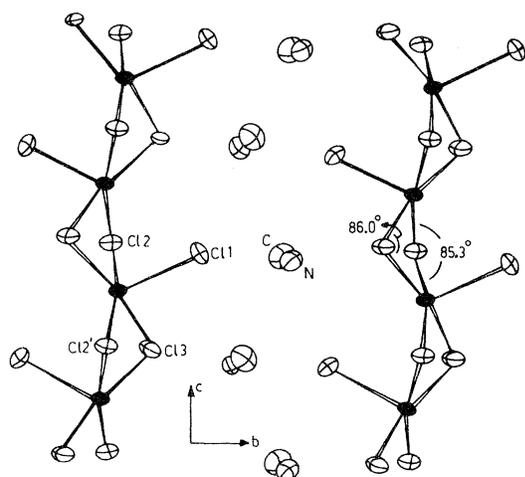
FIG. 1. Schematic representation of the crystal structure of CHAC. The chains running along the c axis are hydrogen bonded in the b direction.

moiety of the cyclohexylammonium groups. The distance between neighboring chains in the a direction is nearly 10 Å.

The crystallographic structure of the bromine compound has not been investigated in great detail. Since, however, the morphology of the single crystals of CHAC and CHAB is identical, we tend to believe that the two compounds are isomorphic.[7] This is confirmed by x-ray measurements on powdered samples of CHAC and CHAB, which yielded largely similar diffraction patterns, apart from a small shift of the various reflections to smaller 2θ values for the bromine compound. The latter observation is consistent with the somewhat larger size of the bromine ion.

III. SPECIFIC HEAT

Heat-capacity measurements at temperatures above 2 K were performed with a vacuum calorimeter of conventional design, which was equipped with a temperature controlled heat screen to enable accurate measurements up to about 60 K. Samples consisting of 20–25 g of small crystals were encapsulated in a copper sample holder, together with some ^{3}He gas (10 Torr at 77 K) which was used to improve the heat exchange within the sample. Since crystals of both CHAC and CHAB are very stable, no detectable sample decomposition occurred during the encapsulation procedure. The raw data were corrected for the contribution of the empty sample holder (20–40%), which was measured in a separate run.

The data were supplemented with heat-capacity measurements in the region $0.4 < T < 4$ K, which were performed in a ^{3}He calorimeter. In these mea-

surements single crystals with typical dimensions $3 \times 4 \times 7$ mm^3 were used. Temperature readings were obtained from commercially calibrated germanium thermometers, which were measured with a four wire ac resistance bridge operating at 33 Hz. For 2 $< T < 4$ K the sets of data obtained from the two calorimeters did coincide within experimental accuracy (1–2%).

A. $(C_6H_{11}NH_3)CuCl_3$

The experimental data on CHAC are shown in Fig. 2. In a previous paper[3] we have shown that above 6 K the specific heat of this compound can be described by the sum of a magnetic contribution C_M arising from an isotropic $S = \frac{1}{2}$ ferromagnetic Heisenberg linear chain system with $J/k = 45 \pm 5$ K and a lattice contribution C_L appropriate to chainlike structures.[8] Before we comment on the results of the analysis, we will discuss the—somewhat unconventional—procedure by which C_M and C_L were separated.

As a first attempt, simultaneous fits of C_M and C_L were performed to the data in the paramagnetic region above a certain temperature T_B. Since the rms error of these fits did not display a sufficiently sharp minimum as a function of the parameter J/k, we modified the fitting procedure as follows. First, fits to the data above T_B were performed for several fixed values of J/k. The lattice contribution C_L resulting from each fit was extrapolated to $T = 0$ and subtracted from the experimental data. Next, for each value of J/k the magnetic entropy gain S_{exp} was evaluated. The entropy gain for 0.4 K $< T < T_B$ was obtained by numerical integration of $(C_P - C_L)/T$, whereas the entropy gain above T_B was calculated from the theoretical prediction for C_M. The fraction of entropy below 0.4 K was estimated by extrapolating $(C_P - C_L)$ down to $T = 0$ according to the rela-
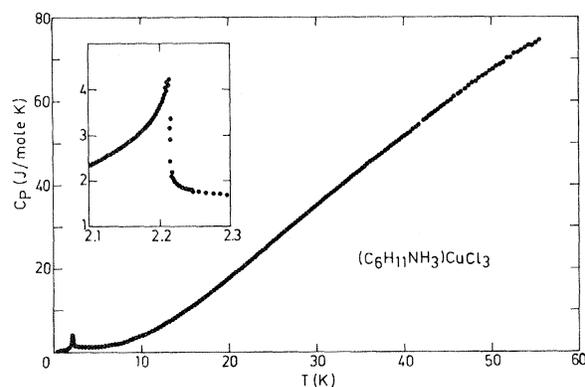

FIG. 2. Total heat capacity of CHAC. The λ anomaly associated with T_c is shown in the insert in more detail.

tion $C = \alpha T^{\beta}$, where α and β were obtained from a fit to the data for $0.4 < T < 0.8$ K. The latter fraction did amount to about 3% of the total entropy. An acceptable range of values of J/k was selected by imposing the condition that the total magnetic entropy gain should equal the theoretical value $R \ln2$. A plot of S_{exp} vs J/k did intercept this value at $J/k = 45$ K. Given the uncertainties in the description of the lattice contribution below T_B and the extrapolation of $(C_p - C_L)$ down to $T = 0$, the error in J/k was estimated to be of the order of 5 K. Actually, the procedure sketched above was applied for $T_B = 6, 8, 10$ and 12 K. The resulting values of the intrachain interaction parameter J/k were found to be equal within a few Kelvin. The rms error of the fits to the data above T_B, however, was comparable to the scatter in the data only for $T_B \geq 8$ K, which might indicate that below this temperature the approximation of the magnetic system by a fully isotropic model starts to detoriate.

As already mentioned in the Introduction, a small amount of uniaxial anisotropy is present in this compound, which has been ignored in the analysis of the heat capacity up till now. Fortunately, numerical calculations[5] on Heisenberg-Ising ferromagnetic $S = \frac{1}{2}$ chains reveal that an uniaxial anisotropy smaller than 2% has a neglegible effect on the magnetic heat capacity above $kT/J = 0.15$, corresponding to temperatures of about 8 K in the case of CHAC. Therefore, the presence of such an anisotropy will not substantially modify the inferred J/k value. One should note that this value (45 K) is about 30% lower than the result $J/k = 70$ K obtained from susceptibility measurements.[4] Partly, this discrepancy may be caused by the fact that our estimate of the error in J/k (5 K) is somewhat too small, but also the interpretation of the susceptibility data is subject to some uncertainties, due to the rather large corrections for temperature independent paramagnetism. Moreover, it is not quite clear to which extent the suggested canting of adjacent moments within the individual chains[4] will affect the theoretical description of the heat capacity and the susceptibility. Nevertheless, both experimental techniques unambiguously demonstrate the very high degree of one dimensionality of CHAC.

The experimental data on CHAC, corrected for the calculated lattice contribution, are shown in Fig. 3 for $T < 15$ K. The dashed curve denotes the heat capacity of a fully isotropic $S = \frac{1}{2}$ Heisenberg linear chain system with $J/k = +45$ K. The drawn curve reflects the effect of 2% uniaxial anisotropy. It is obvious that the observed increase of the experimental data below 6 K can be explained satisfactorily by this refined model, although the behavior near the maximum of the anisotropy-induced "bump" is obscured by the three-dimensional ordering. Inspection of the figure demonstrates again that the analysis of the data above 8 K remains unaffected.
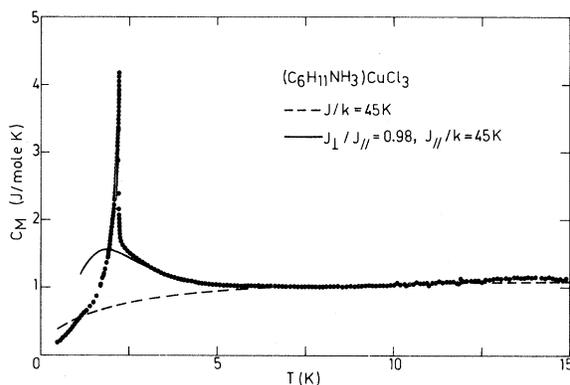

FIG. 3. Magnetic heat capacity of CHAC. The experimental data corrected for the lattice contribution are denoted by black circles. The dashed curve represents the theoretical estimate for a $S = \frac{1}{2}$ ferromagnetic Heisenberg linear chain system with $J/k = +45$ K. The drawn curve reflects the effect of 2% uniaxial anisotropy. ($J_{\perp}/J_{\parallel} = 0.98$, $J_{\parallel}/k = 45$ K.)

B. $(C_6H_{11}NH_3)CuBr_3$

Motivated by the results presented above, we next measured the heat capacity of CHAB in the temperature region $0.4 < T < 55$ K. The experimental data are plotted in Fig. 4. The small λ anomaly at 1.50 K, which is associated with the three-dimensional ordering, is shown in the insert in more detail. The overall behavior of the data is largely similar to the heat capacity of CHAC. Three-dimensional ordering of the bromine compound, however, occurs at lower temperatures, whereas the corresponding λ anomaly has a much smaller magnitude (~ 1 J/mole K compared to ~ 4 J/mole K in the chlorine compound). The major difference between the overall behavior of the data occurs at high temperatures, where the lat-
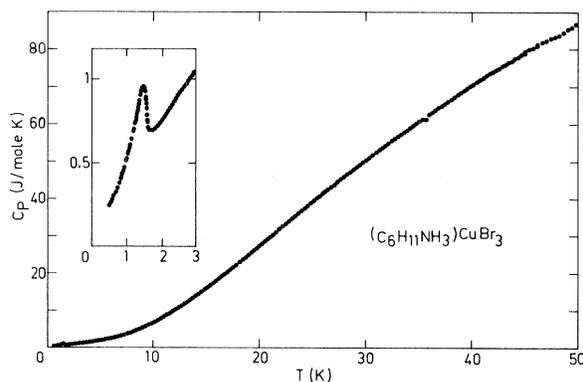

FIG. 4. Total heat capacity of CHAB. The λ anomaly associated with T_c is shown in the insert in more detail.

tice heat capacity dominates. In this region the heat capacity of CHAB is systematically higher than that of CHAC, which is consistent with the larger mass of the bromine ions.

As a first attempt to separate C_M and C_L we subtracted a scaled lattice contribution of CHAC from the experimental data, using a temperature-independent scaling factor

$$C_{L,\,CHAB}(T) = C_{L,\,CHAC}(T/\alpha) \ . \tag{1}$$

A lower bound of α was determined by the condition that the resulting magnetic contribution C_M should be positive in the entire temperature region below 55 K, whereas an upper bound was determined by the condition that the experimental magnetic entropy gain below 55 K should not exceed R ln2. This procedure yielded $0.77 < \alpha < 0.80$. The resulting C_M appeared to have an almost constant magnitude of ~ 1 J/mole K for $10 < T < 20$ K, which is characteristic for a system of ferromagnetic $S = \frac{1}{2}$ Heisenberg chains. This fact is consistent with the isomorphy of CHAC and CHAB anticipated above. For $T > 20$ K, the resulting data show a rather irregular behavior. This can be explained by the fact that at higher temperatures the use of a temperature-independent scaling factor may produce significant deviations, since in that region $C_L \gg C_M$.

Next, we examine the behavior of C_M below 20 K in more detail. The data show a bump at 5.5 K with a magnitude of ~ 1.3 J/mole K. Since in this region $C_M > C_L$, such an effect is most likely caused by a small amount of anisotropy rather than being an artifact induced by the scaling procedure. This anisotropy seems to have an easy-plane like character, since an uniaxial anisotropy would give rise to a maximum of at least 1.5 J/mole K. In view of this result we tried to describe our data with the predictions obtained from numerical calculations[5] on $S = \frac{1}{2}$ Heisenberg-XY linear chains. It appeared that the data below 20 K could be represented rather well by this model system. Using again the condition that the total magnetic entropy gain should equal R ln2 we obtained $J/k = 55 \pm 5$ K, an anisotropy of 5%, and a scaling factor α equal to 0.788. The resulting magnetic heat capacity is shown in Fig. 5 for $T < 15$ K. The theoretical prediction for C_M is shown by a drawn curve. For comparison, we also plotted the behavior of a fully isotropic system having the same value of J/k. The agreement of the data with the anisotropic model is very satisfactory; only minor deviations occur, which presumably reflect the uncertainty in the estimate of the lattice contribution (1.5 J/mole K at 7 K). It is obvious that—in contrast to CHAC—the anisotropy induced "bump" is rather well resolved from the three-dimensional ordering. We will return to this point in the discussion.
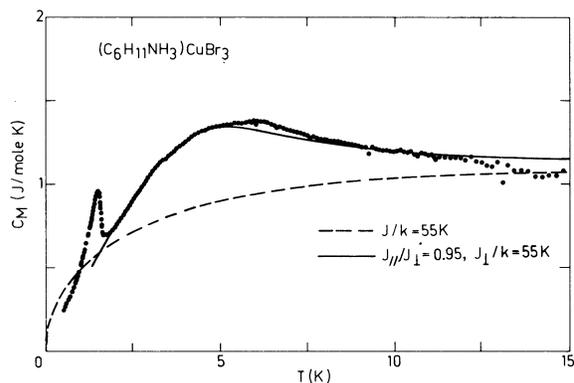
Before considering the magnetization measure-

FIG. 5. Magnetic heat capacity of CHAB. The experimental data corrected for the lattice contribution are denoted by black circles. The dashed curve represents the theoretical estimate for a $S = \frac{1}{2}$ ferromagnetic Heisenberg linear chain system with $J/k = 55$ K. The drawn curve reflects the effect of 5% easy-plane anisotropy ($J_{\parallel}/J_{\perp} = 0.95$, $J_{\perp}/k = 55$ K).

ments, we like to note that it is also possible to describe the lattice heat capacity of CHAB with the detailed expressions given in Ref. 8, instead of using the scaling procedure presented above. Such an approach was found to improve the agreement between theory and experiment above 20 K, but did not substantially alter the results at lower temperatures.

IV. MAGNETIZATION

Magnetization measurements of CHAB were performed with a PAR vibrating sample magnetometer in the temperature region $1.2 < T < 4.2$ K and external fields up to a few kiloGauss. In these experiments single crystals were used with a mass of 15 to 40 mg. The external field was applied along each of the three crystallographic directions. The data recorded at 1.2 K are plotted in Fig. 6. Inspection of this figure shows that for $\vec{H} \parallel b$ a metamagnetic transition occurs at $H_c = 210$ Oe. The data for $\vec{H} \parallel a$ indicate the presence of a weak ferromagnetic moment along this axis; the increase of the magnetization below 100 Oe may arise from the alignment of weakly ferromagnetic domains parallel to H. The data for $\vec{H} \parallel c$ show the regular behavior characteristic for a field direction perpendicular to the easy axis.

For fields parallel to b larger than 210 Oe a ferromagnetic alignment of the chains is obviously energetically more favorable than an antiferromagnetic array. At H_c the antiferromagnetic interchain interaction energy is equal to the Zeeman energy, or

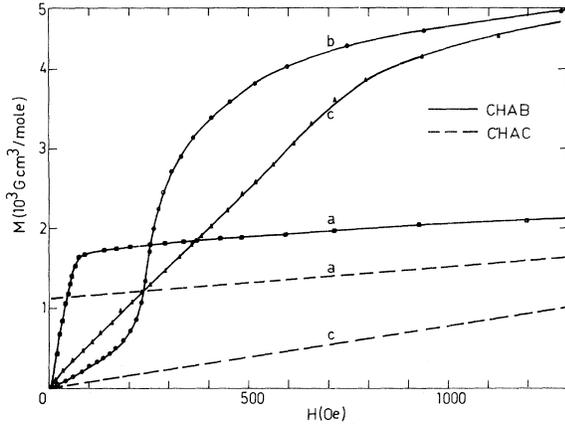$$-2z_{AF}J_{AF}S^2 = g\mu_B H_c S \ . \tag{2}$$

FIG. 6. Magnetization of CHAB as a function of the external magnetic field for the three crystallographic axes a, b, and c. The data are recorded at $T = 1.2$ K. Drawn curves are only meant as a guide to the eye. For comparison, we also plotted similar measurements on CHAC (Ref. 4) for $\vec{H} \parallel a$ and $\vec{H} \parallel c$ (dashed lines).

Insertion of the experimental value for H_c in this equation yields an interchain coupling $z_{AF}J_{AF}/k = 0.03$ K. In the region just above H_c, M varies linearly with H, the slope $(\partial M/\partial H)_{max}$ being equal to about 17 emu/mole. This value is comparable to the value estimated from the demagnetizing factor of the sample, indicating that the transition is of first order. Measurements of the magnetization for $\vec{H} \parallel b$ at higher temperatures reveal that $(\partial M/\partial H)_{max}$ is constant within the experimental inaccuracies to $T = 1.3$ K. Above this temperature no linear region in M vs H can be detected, whereas $(\partial M/\partial H)_{max}$ decreases below 17 emu/mole. From these results we conclude that the metamagnetic transition is no longer of first order, which implies the presence of a tricritical point in the magnetic phase diagram. From the temperature T_t at which this tricritical point occurs the ratio of the antiferromagnetic and ferromagnetic interchain interactions can be estimated[9]:

$$T_t/T_c - 1 = z_{AF}J_{AF}/3z_FJ_F \quad . \tag{3}$$

If we insert $T_t = 1.3$ K, $T_c = 1.50$ K and the value of $z_{AF}J_{AF}$ determined above, a ferromagnetic interchain coupling $z_FJ_F/k \approx 0.08$ K is obtained.

In fact, several characteristics of the magnetization sketched above are identical to those of CHAC, suggesting a largely similar spin structure below T_c. However, one major difference should be emphasized. In CHAB the magnetization along both the b and c direction reaches about 80% of the saturation value $Ng\mu_B S$ (5.8×10^3 G cm^3/mole) already at fields of about 1 kOe, whereas the magnetization along the a direction seems to saturate at much higher fields (>20 kOe). Since the interchain interactions are

very small, this behavior must originate from anisotropy of the intrachain interaction. This will be demonstrated by a straightforward mean-field calculation for a two-sublattice system. The interaction between a pair of neighboring spins belonging to the same sublattice is described by the interaction tensor J_1. For spins belonging to different sublattices the interaction is denoted by J_2. If the spins originally point in the α direction (easy axis), the susceptibility at $T = 0$ in the β direction is given by

$$\chi_\alpha^\beta = \frac{Ng_{\beta\beta}^2 \mu_B^2}{2z_1(J_1^{\alpha\alpha} - J_1^{\beta\beta}) - 2z_2(J_2^{\alpha\alpha} + J_2^{\beta\beta})}, \quad \alpha \neq \beta \tag{4}$$

where z_1 and z_2 denote the number of nearest neighbors on the same or a different sublattice, respectively. In the present compounds J_1 contains the ferromagnetic interaction within a chain, whereas J_2 represents the antiferromagnetic interchain coupling. Since an anisotropy of a few percent in the intrachain interaction gives rise to a value of $(J_1^{\alpha\alpha} - J_1^{\beta\beta})$ in the order of 1 K, and $z_2J_2 = 0.03$ K, Eq. (4) may be simplified to

$$\chi_\alpha^\beta = \frac{Ng_{\beta\beta}^2 \mu_B^2}{4(J_1^{\alpha\alpha} - J_1^{\beta\beta})}, \quad \alpha \neq \beta \quad . \tag{5}$$

If we confront this equation with the observed behavior of M, plotted in Fig. 6, it is obvious that the anisotropy in CHAB has a rather pronounced easy-plane like (XY) character. This behavior is complementary to that of CHAC, where the reported magnetization measurements indicate that the magnetic moments are more or less fixed to one particular direction close to the b axis (Ising like). This is illustrated by the data on CHAC for $\vec{H} \parallel a$ and $\vec{H} \parallel c$,[4] which are represented in Fig. 6 by dashed curves. The behavior for $\vec{H} \parallel b$ is not plotted, since it is largely similar to that of CHAB.

Inspection of Fig. 6 also shows that for fields larger than 100 Oe along the a axis $\partial M/\partial H$ has a value of about 0.3 emu/mole in the bromine compound. This slope is smaller than the results on CHAC for fields parallel to a or c (0.5–1 emu/mole), suggesting that the anisotropy in CHAB is at least a factor 2 larger than that in CHAC. We will return to this point in the discussion.

V. DISCUSSION

In the preceding sections it has been shown that both CHAC and CHAB are very good physical approximations of a ferromagnetic $S = \frac{1}{2}$ Heisenberg linear chain system. The experimental results on both compounds are summarized in Table I. The intrachain interaction in CHAC and CHAB has about the same value ($J/k \approx 50$ K), whereas the interchain

TABLE I. Magnetic properties of CHAC and CHAB determined from measurements of the heat capacity and magnetization.

	T_c (K)	S_{crit}	J/k (K)	$z_{\text{AF}}J_{\text{AF}}/k$	$z_F J_F/k$	$J_\perp/J_\parallel$
CHAC	2.214	19%	45 ± 5	-0.014	0.15	0.98
CHAB	1.50	14%	55 ± 5	-0.030	0.08	1.05

coupling is smaller by almost three orders of magnitude. In both compounds some anisotropy is present in J/k. From the heat-capacity measurements reported above we inferred that CHAC contains about 2% uniaxial anisotropy, whereas CHAB contains 5% easy-plane anisotropy. The fact that the anisotropy in CHAB is easy plane like and is significantly larger than that in CHAC is corroborated by measurements of the magnetization below T_c.

If the anisotropy in CHAC and CHAB would be of dipolar origin, the observed difference between the magnetic properties of these compounds is hardly conceivable. Moreover, in a system composed of ferromagnetic chains dipolar anisotropy would favor an orientation of the magnetic moments parallel to the chain direction (c axis), instead of an orientation close to the b axis found from the magnetization measurements. This suggests that the anisotropy is induced by the local environment of the Cu^{2+} ions, which also may explain the small canting of the magnetic moments, that has been attributed to a tilting of the local g tensors of adjacent magnetic ions.[4] Preliminary EPR measurements on CHAC at 4.2 K support this view, since in external magnetic fields two distinct sets of resonances are detected. One should note that the suggested origin of anisotropy in fact justifies the introduction of anisotropic exchange in the interpretation of the data.

From the location of the three-dimensional ordering temperature ($T_c = 2.214$ K for CHAC, 1.50 K for CHAB) as well as the value of the critical entropy ($S_{\text{crit}} = 19\%$ for CHAC, 14% for CHAB) one might be tempted to conclude that CHAB has a larger degree of one dimensionality. Such a conclusion, however, should only be drawn with great care, since—

even within the same class of model systems— T_c and S_{crit} are not straightforwardly related to the ratio of the interchain and intrachain coupling J'/J. In fact, calculations based on the classical spin model[6] have shown that the introduction of anisotropy shifts T_c to higher temperatures, the effect being more dramatic as J'/J decreases. These calculations also reveal that a uniaxial (Ising) anisotropy has a much more pronounced effect than an easy-plane (XY) anisotropy. This may explain the fact that the three-dimensional ordering of CHAB occurs at lower temperatures than that in CHAC, although the anisotropy and at least one interchain interaction (J_{AF}, cf. Table I) in the bromine compound are substantially larger. Also the experimental observation that—in contrast to CHAC—the anisotropy-induced bump in the magnetic specific heat of CHAB is resolved from the λ anomaly associated with T_c is consistent with these arguments.

Finally, we like to note that the "complementary" anisotropy of CHAC and CHAB makes it worthwhile to synthesize mixed crystals of these two compounds, since this might offer the intriguing possibility to study the crossover from Heisenberg-XY to Heisenberg-Ising behavior in ferromagnetic quantum chains.

ACKNOWLEDGMENTS

[1]See, for instance, J. D. Johnson and J. C. Bonner, Phys. Rev. B 22, 251 (1980), and references therein.

[2]C. P. Landee and R. D. Willett, Phys. Rev. Lett. 43, 463 (1979).

[3]J. C. Schouten, G. J. van der Geest, W. J. M. de Jonge, and K. Kopinga, Phys. Lett. 78A, 398 (1980).

[4]H. A. Groenendijk, H. W. J. Blöte, A. J. van Duyneveldt, F. M. Gaura, C. P. Landee, and R. D. Willett, Physica

106B, 47 (1981).

[5]H. W. J. Blöte, Physica (Utrecht) 79B, 427 (1975).

[6]F. Boersma, W. J. M. de Jonge, and K. Kopinga, Phys. Rev. B 23, 186 (1981).

[7]R. D. Willett (private communication).

[8]K. Kopinga, P. van der Leeden, and W. J. M. de Jonge, Phys. Rev. B 14, 1519 (1976).

[9]J. M. Kincaid and E. G. D. Cohen, Phys. Rep. 22, 57 (1975).