

# Single-crystal ac susceptibility measurements on $[\text{Co}(\text{NH}_3)_6][\text{CuCl}_5]$ , a 3D, $S = 1/2$ Heisenberg antiferromagnet

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Single-crystal ac magnetic susceptibilities of  $[\text{Co}(\text{NH}_3)_6][\text{CuCl}_5]$  along the three crystallographic axes in the temperature range from 1.1 to 90 K are presented. The magnetic behavior is characteristic of a three-dimensional antiferromagnet, its ordering temperature being at  $T_c = 3.8$  K. Susceptibility data can be fit to a Heisenberg  $S = 1/2$  simple cubic model using high-temperature series expansions extrapolated with Padé approximants. Good agreement is found for an exchange constant  $J/k_B = -3.13$  K and values of  $g$  factor  $g_a = 2.09$ ,  $g_b = g_c = 2.04$ ,  $a, b$ , and  $c$  being the crystallographic axes. This result makes  $[\text{Co}(\text{NH}_3)_6][\text{CuCl}_5]$  one of the few examples of a 3D antiferromagnetic Heisenberg  $S = 1/2$  model. The magnetic behavior below  $T_c$  indicates the existence of crystallographic domains due to the structural transition from cubic to tetragonal symmetry that the system has at about 280 K.

## I. INTRODUCTION

Bimetallic compounds have been shown to exhibit very interesting magnetic properties.<sup>1,2</sup> Moreover, coordination compounds of copper(II) have been of continuing interest for several reasons. Copper(II) possesses one unpaired electron irrespective of the local geometry and therefore always has spin  $S = 1/2$ . Since the ground state in an octahedral complex is  ${}^2E_g$ , the orbital degeneracy is usually resolved by the Jahn–Teller effect and, as a consequence, the coordination sphere around the copper ion is generally distorted.

Although many copper(II) compounds exhibit such structural anisotropy, they nevertheless display relatively little magnetic anisotropy. The orbital contribution is largely quenched, the  $g$ -value anisotropy is typically not large, about 5% or 10% ( $g$  always of the order of 2.0–2.3), and being a  $S = 1/2$  system there is no zero-field splitting to complicate the situation. This leads copper(II) to be one of the best ions, after manganese(II) and iron(III), in providing magnetically ordered compounds with only weak anisotropy.<sup>3</sup>

Another feature of copper magnetochemistry is the high tendency the ion exhibits for ferromagnetic interactions. Moreover, there are few copper compounds which order three-dimensionally and copper is better known as a source of dimers, linear chain, and planar magnets.<sup>4</sup>

It is therefore of some interest to report here on the measurements of  $[\text{Co}(\text{NH}_3)_6][\text{CuCl}_5]$ , which show that this compound behaves as a three-dimensional Heisenberg antiferromagnet. [the  $\text{Co}(\text{III})$  cation is diamagnetic.]

Both single-crystal x-ray and neutron diffraction data<sup>5</sup> show that the substance crystallizes at room temperature in

the cubic space group  $Fd\bar{3}c$  with  $a = 21.992$  Å. The environment of the cobalt ion is octahedral and the copper ion is situated in the center of an axially compressed trigonal bipyramid with  $\text{Cu-Cl(ax)} = 2.301$  Å and  $\text{Cu-Cl(eq)} = 2.409$  Å.

At about  $T_s = 280$  K the system undergoes a structural phase transition as deduced from differential scanning calorimetry measurements.<sup>6</sup> Powder diffraction patterns in the temperature range from 300 to 12 K have been recorded.<sup>7</sup> They indicate the existence of a tetragonal splitting of the cubic reflexions below the transition temperature. In the low-temperature phase a tetragonal unit cell, presumably belonging to space group  $I4_1/acd$  and with lattice parameters at 14 K of  $a = 15.507(1)$  Å,  $c = 22.018(2)$  Å, and  $c/(2^{1/2}a) = 1.004$ , is found.

Analysis of EPR spectra measured<sup>7</sup> in the temperature range between 300 and 4 K shows that the  $g$  tensor changes from cubic to tetragonal at about 280 K. The  $g$  anisotropy still increases with decreasing temperature below  $T_s$  and reaches its final value only at 120 K. This experimental result and the fact of the strongly anomalous temperature ellipsoids of the equatorial chlorine ligands has suggested that the stable static geometry of the  $\text{CuCl}_5^{2-}$  polyhedra is a square pyramid. In the high-temperature phase the axially compressed trigonal bipyramid exists as the dynamic average of three square-pyramidal conformations. In the low-temperature phase the stable geometry of the  $\text{CuCl}_5^{2-}$  polyhedra, a static one, is a square pyramid, in which the apical bond is appreciably longer than the equatorial distances. The cooling procedure from 298 K to temperatures below  $T_s$  leads to extensive twinning and hence to a three-domain pattern in the EPR spectra.

## II. EXPERIMENT

$[\text{Co}(\text{NH}_3)_6][\text{CuCl}_5]$  was prepared according to literature methods.<sup>8</sup> Single crystals were obtained by slow evaporation of aqueous solutions of the complex. The sample was chemically identified by elemental analysis. Calculated: Co, 14.6; Cu, 15.8; N, 20.9; H, 4.5; Cl, 44.1. Found: Co, 14.4; Cu, 15.6; N, 20.6; H, 4.4; Cl, 44.0. A crystallographic verification was made by means of a Debye-Scherrer diagram.

In order to verify the structural transition, differential scanning calorimetric measurements were made with a Perkin-Elmer DSC-2 instrument in the range 105–310 K. They show a phase transition at  $T_s = 278.0$  K when heating and a  $T_s = 277.8$  K when cooling, in reasonable agreement with  $T_s = 280$  K previously reported.<sup>6</sup>

Magnetic ac susceptibility measurements in the range 4.2–90 K were conducted in a computer-controlled susceptibility meter already described,<sup>9</sup> on a single crystal of 56.70 mg. Data between 1.1 and 4.2 K were taken in another ac susceptibility meter.<sup>10</sup>

## III. RESULTS AND DISCUSSION

Susceptibility data made with the alternating magnetic field parallel to the three four-fold axes are shown in Fig. 1. Measurements performed along two of the three axes (named *b* and *c*) overlap each other within experimental error. The data show a smooth increase in the susceptibility as temperature decreases, present a maximum at about 7.5 K, and then drop more rapidly. The out-of-phase component of the susceptibility is negligible over the whole range of temperature. The behavior is characteristic of that of a three-dimensional antiferromagnet, its ordering temperature being  $T_c = 3.8$  K as calculated from the maximum value of  $(\partial\chi/\partial T)$ . Susceptibility data can be fit by a Heisenberg  $S = 1/2$  simple cubic model using high-temperature series expansions extrapolated with a [5/5] Padé approximant,<sup>11</sup> as shown in Fig. 2. Good agreement is found for an exchange constant  $J/k_B = -3.13$  K and values of *g* factor  $g_a = 2.09$ ,  $g_b = g_c = 2.04$ , *a*, *b*, and *c* being four-fold crystallographic axes. These results are compared with related systems in Table I.

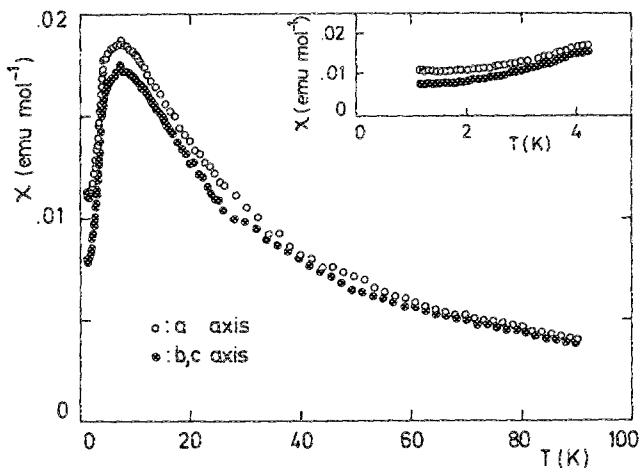


FIG. 1. Measured single-crystal ac susceptibility of  $[\text{Co}(\text{NH}_3)_6][\text{CuCl}_5]$  along the three crystallographic axes.

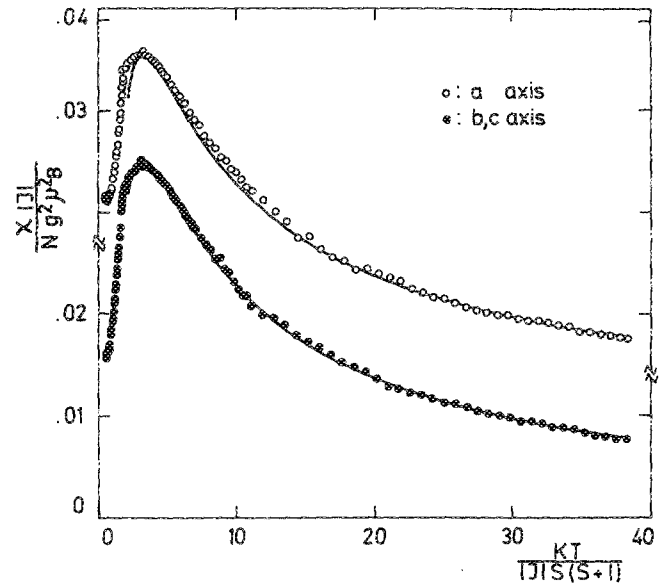


FIG. 2. Experimental and calculated susceptibilities of  $[\text{Co}(\text{NH}_3)_6][\text{CuCl}_5]$  in reduced units. The solid curves are the theoretical prediction for a 3D antiferromagnetic Heisenberg  $S = 1/2$  model as explained in the text. In order to make the figure clearer the sets of data have been separated by breaking the vertical scale.

A striking feature in the data represented in Fig. 1 is that no easy axis for antiferromagnetic alignment is observed. However, the experimental decrease in  $\chi$  is so large that it is not consistent with the behavior expected for  $\chi_1$ . For instance, we may estimate the value for  $\chi_1$  at  $T = 0$  expected on the basis of spin-wave theory from the relation<sup>15</sup>

$$\chi_1(T=0) = [Ng^2\mu_B^2/4z|J|] [1 - (\Delta S/S) - (e/2zS)].$$

In this expression  $z = 6$  for a simple cubic lattice;  $\Delta S$  and  $e$  denote the zero-point spin reduction and the ground-state energy shift, respectively. Values for these quantities have been given by Semura and Huber<sup>16</sup> for the simple cubic Heisenberg model, namely,  $\Delta S = 0.078$  and  $e = 0.58$ . Taking  $J/k_B = -3.13$  one calculates  $\chi_1(T=0) = 0.0155$  for  $g_a = 2.09$  and  $0.0163$  for  $g_b = g_c = 2.04$ , well above experimental values of 0.011 for the *a* axis and 0.008 for the *b,c* axes. However, susceptibility values are not far from those expected for a powdered sample, for  $\chi(T=0) \cong 2/3\chi(T=T_{\text{max}})$  in both sets of data. A logical explanation is that tetragonal distortions could lead to a three-domain structure which prevents the establishment of a macroscopic easy axis and thus a weighted average of  $\chi_{\parallel}$  and  $\chi_{\perp}$  is ob-

TABLE I. Some examples of 3D antiferromagnet  $S = 1/2$  Heisenberg model.

Compound	$T_c$ (K)	$J/k$ (K)	$T_c/\theta$	<i>g</i>	Ref.
$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	4.36	?	?	2.04, 2.19, 2.25	12
$[\text{Cu}(\text{en})_3]\text{SO}_4$	0.109	-0.03	0.60	2.10, 2.26	13
$[\text{Co}(\text{NH}_3)_6][\text{CuCl}_5]$	3.8	-3.13	0.50	2.07, 2.28	14
Nd-Ga-garnet	0.516	-0.34	0.76	?	12
Sm-Ga-garnet	0.967	-0.60	0.81	?	12

tained. The conclusion corroborates above mentioned results obtained from EPR measurements.<sup>7</sup>

A simple analysis of the calorimetric data of the compound also supports a model in which degrees of freedom in the position of the  $\text{CuCl}_5^{3-}$  unit change from 3 to 1. The entropy content of the structural transition can be roughly estimated as  $\Delta S_s/R \cong 0.96$ , as calculated from the ratio  $\Delta H_s/T_s$ , a value reasonably close to  $\ln 3$ .

Therefore, the  $g$  values calculated from the fitting of the susceptibility measurements along directions parallel to the (room-temperature) crystallographic axis have to be understood as an average over a distribution of crystallographic domains. That would explain the apparent discrepancy between the  $g$  values calculated here and those measured by EPR at 120 K,  $g_{\parallel} = 2.28$  and  $g_{\perp} = 2.07$ . The effects of crystallographic domains on the susceptibility data have also been observed in  $[\text{Cu}(\text{C}_5\text{H}_5\text{NO})_6](\text{BF}_4)_2$ .<sup>17</sup> The fact that the susceptibility along the direction parallel to the  $a$  axis of  $[\text{Co}(\text{NH}_3)_6][\text{CuCl}_5]$  slightly differs from the data along the two other directions,  $b$  and  $c$ , could indicate that the proportions of the three domains were not the same, as found in the cubic perovskite  $\text{NH}_4\text{MnCl}_3$ .<sup>18</sup> At this point, more structural data at low temperature would be necessary in order to have a better understanding of the tetragonal phase. Heat capacity measurements of the magnetic phase and susceptibility-field dependence studies in the antiferromagnetic phase are in progress.<sup>19</sup>

#### ACKNOWLEDGMENTS

The authors very much appreciate comments from Dr. R. Navarro. The research in Zaragoza and Barcelona has been supported respectively by grants 3380/83 and 409/84, from the Comision Asesora de Investigacion Cientifica y Technica of the Ministerio de Educacion y Ciencia. The re-

search in Chicago has been supported by Grant No. DMR-8515224 from the Solid State Chemistry Program, Division of Materials Research of the National Science Foundation. Cooperative work has been supported by grant CCB-8504/001 from the American-Spain Joint Committee for Technical and Scientific Cooperation. One of us (M. C. M.) wants also to acknowledge a student fellowship from the Ministerio de Educacion y Ciencia.

- <sup>1</sup>A. N. Scoville, K. Lazar, W. M. Reiff, and C. Landee, *Inorg. Chem.* **22**, 3514 (1983).  
<sup>2</sup>R. Burriel, J. Casabo, J. Pons, D. W. Carnegie, Jr., and R. L. Carlin, *Physica* **132B**, 185 (1985).  
<sup>3</sup>R. L. Carlin, *Magnetochemistry* (Springer, Berlin, 1986).  
<sup>4</sup>R. L. Carlin and R. Block, *Proc. Indian Acad. Sci.* **98**, 79 (1987).  
<sup>5</sup>I. Bernal, J. D. Korp, E. O. Schlemper, and M. S. Hussain, *Polyhedron* **1**, 365 (1982).  
<sup>6</sup>E. F. Epstein, I. Bernal, W. P. Brennan, *Inorg. Chim. Acta* **20**, L47 (1976).  
<sup>7</sup>D. Reinen and C. Friebel, *Inorg. Chem.* **23**, 791 (1984).  
<sup>8</sup>M. Mori, *Bull. Chem. Soc. Jpn.* **33**, 985 (1960).  
<sup>9</sup>J. A. Rojo, Ph. D. thesis, University of Zaragoza, Spain (1982) and C. Rillo, Ph. D. thesis, University of Zaragoza, Spain (1986).  
<sup>10</sup>S. N. Bhatia, R. L. Carlin, and A. Paduan Filho, *Physica B* **92**, 330 (1977).  
<sup>11</sup>R. Navarro, Ph. D. thesis, University of Zaragoza, Spain (1976).  
<sup>12</sup>L. J. de Jongh and A. R. Miedema, *Experiments on Simple Magnetic Model Systems* (Taylor and Francis, London, 1974).  
<sup>13</sup>R. L. Carlin and R. D. Chirico, *Chem. Phys. Lett.* **81**, 53 (1981).  
<sup>14</sup>This work.  $g$  values are given in Ref. 7.  
<sup>15</sup>F. Keffer, in *Encyclopedia of Physics*, edited by H. P. J. Wijn (Springer, Berlin, 1966), Vol. 18.2, p. 109.  
<sup>16</sup>J. S. Semura and D. L. Huber, *Phys. Rev. B* **7**, 2154 (1973).  
<sup>17</sup>A. Lambrecht, R. Burriel, and R. L. Carlin (unpublished).  
<sup>18</sup>J. D. Tornero, F. H. Cano, J. Fayos, and M. Martinez-Ripoll, *Ferroelectrics* **19**, 123 (1978).  
<sup>19</sup>A measurement of the susceptibility along a direction parallel to a binary axis, after this paper was prepared, provided what appears to be  $\chi_1$ . This is not consistent with the domain picture and remains unexplained.