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EXCHANGE COUPLING IN THE ALTERNATING CHAIN COMPOUNDS CATENA-DI---ETC(U)  
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EXCHANGE COUPLING IN THE ALTERNATING CHAIN COMPOUNDS CATENA-DI-~~4~~  
CHLOROBIS(4-METHYLPYRIDINE) COPPER(II), CATENA-DI-~~4~~-BROMOBIS-  
(N-METHYLIMIDAZOLE) COPPER(II), CATENA-HEXANEDIONE BIS (THIOSEMICARBAZATO)-  
COPPER(II), AND CATENA-OCTANEDIONE BIS (THIOSEMICARBAZATO) COPPER(II).

By

J.W. Hall, W.E. Marsh, R.R. Weller, and W.E. Hatfield

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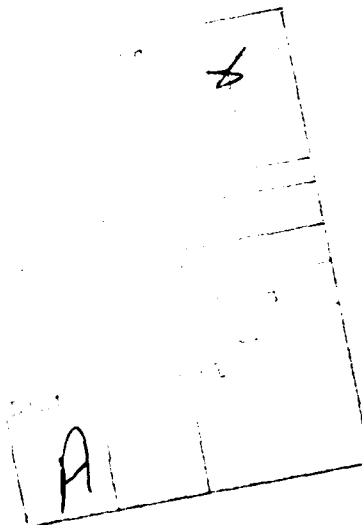
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Exchange Coupling in the Alternating Chain Compounds Catena-di- $\mu$ -chlorobis-(4-methylpyridine)copper(II), Catena-di- $\mu$ -bromobis(N-methylimidazole)-copper(II), Catena-hexanedionebis(thiosemicarbazato)copper(II), and Catena-octanedionebis(thiosemicarbazato)copper(II).

James W. Hall, Wayne E. Marsh, Robert R. Weller, and William E. Hatfield\*

#### Abstract

Magnetic susceptibility data have been collected for catena-octanedionebis(thiosemicarbazonato)copper(II), Cu-OTS, and catena-hexanedionebis(thiosemicarbazonato)copper(II), Cu-HTS, in the temperature range 1.8-120 K, and the data analyzed in terms of an alternating chain Heisenberg exchange model to yield  $J = -10.1 \pm 0.2 \text{ cm}^{-1}$ ,  $\alpha = 0.91 \pm 0.02$ , and  $g = 2.06 \pm 0.02$  for Cu-HTS and  $J = -12.9 \pm 0.2$ ,  $\alpha = 0.90 \pm 0.02$ , and  $g = 2.11 \pm 0.02$  for Cu-OTS. Anomalies in the temperature dependent capacitance data for catena-di- $\mu$ -chlorobis(4-methylpyridine)copper(II) and catena-di- $\mu$ -bromo(N-methylimidazole)copper(II) provide evidence for structural phase transitions presumably from uniform chain structures at room temperature to alternating chain structures at low temperatures. Magnetic parameters for  $\text{Cu}(4\text{-methylpyridine})_2\text{Cl}_2$  are  $J = -9.6 \pm 0.2 \text{ cm}^{-1}$ ,  $g = 2.17 \pm 0.02$ , and  $\alpha = 0.67 \pm 0.02$ . An expression for the magnetic susceptibility of a Heisenberg alternating chain of  $S=1/2$  ions has been developed in terms of the alternation parameter, the exchange coupling constant, and the  $g$  factor.

## Introduction

Paramagnetic organic compounds with alternately spaced linear chain structures have been known and studied extensively for a number of years,<sup>1</sup> since such compounds frequently have unusual magnetic properties and are often alternating Heisenberg antiferromagnets. Exchange coupled transition metal compounds with alternating structures have received much less attention. The most thoroughly studied transition metal example of an alternating Heisenberg antiferromagnet is  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ ,<sup>2</sup> a compound which has a ladder-like structure at room temperature.<sup>3</sup> Other examples of compounds which have (or which have been suggested to have) alternating chain structures and attendant magnetic properties include the pyrazine-bridged binuclear copper acetate chain,  $[\text{Cu}_2(\text{OAc})_4\text{pyr}]_\infty$ ,<sup>4</sup> the low temperature form of tetrathiofulvalenium bis-cis-(1,2-perfluoromethylethylene-1,2-dithiolato)-copper(II) which results from a spin Peierls transition at 12 K,<sup>5</sup> catena-di- $\mu$ -bromobis(N-methylimidazole)copper(II),<sup>6</sup> catena-di- $\mu$ -chlorobis(4-methylpyridine)copper(II),<sup>7</sup> and a series<sup>8</sup> of  $\alpha$ -diketobis(thiosemicarbazonato)copper(II) complexes related to the carcinostatic and carcinolytic agent 3-ethoxy-2-oxobutyraldehyde-bis(thiosemicarbazonato)copper(II), Cu-KTS.<sup>9,10</sup>

In view of the general interest in alternating Heisenberg antiferromagnets and the absence of convenient procedures for the analysis of their magnetic properties, we have repeated the calculations reported by Duffy and Barr for such a model system<sup>11</sup> to obtain numerical data for the generation of an expression for magnetic susceptibility in terms of the exchange coupling constant  $J$  and the alternation parameter  $\alpha$ . In this article we describe the generation of the magnetic susceptibility expression and the application of it for the analysis of new magnetic data for 2,3-hexanedione- and 2,3-octanedione-bis(thiosemicarbazonato)copper(II). In addition, we

have reanalyzed the data for catena-di- $\mu$ -chloro-bis(4-methylpyridine)-copper(II) and present new evidence for structural phase transitions in this compound and in catena-di- $\mu$ -bromobis(N-methylimidazole)copper(II).

### Experimental Section

#### 2,3-Hexanedione-bis(thiosemicarbazone), H<sub>2</sub>HTS

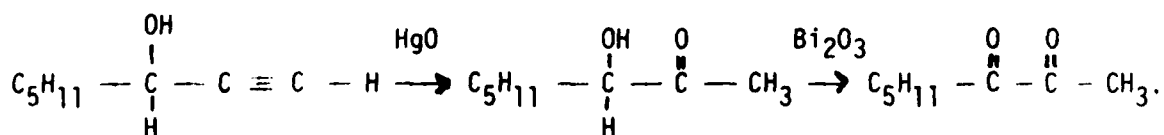
A warm solution of 0.04 mole thiosemicarbazide in 120 ml water containing 6 ml glacial acetic acid was added dropwise to a warm stirred solution of 0.02 mole 2,3-hexanedione in 200 ml of 95% ethanol. The solution was heated and stirred for two hours, after which the yellow precipitate was collected and washed with hot ethanol and acetone.

#### 2,3 Hexanedione-bis(thiosemicarbazonato)copper(II), Cu-HTS

A warm solution of 0.005 moles copper acetate monohydrate in 25 ml water was added dropwise to a hot stirred solution of 0.005 moles H<sub>2</sub>HTS in 120 ml DMF. The dark red solution was evaporated to 50 ml whereupon a black precipitate appeared. The precipitate was collected and recrystallized from 95% ethanol.<sup>12</sup> The complex precipitated as a brown powder. Anal. for Cu(C<sub>8</sub>H<sub>14</sub>N<sub>6</sub>S<sub>2</sub>). Calcd.: C, 29.85; H, 4.38; N, 26.11. Found C, 30.17; H, 4.46; N, 26.08.

#### 2,3 Octanedione-bis(thiosemicarbazone), H<sub>2</sub>OTS

The 2,3-octanedione was prepared by the oxidation of 2-octanone-3-ol which was prepared from 1-octyn-3-ol:



With constant stirring and the solution kept at 65°, 1-octyn-3-ol (0.08 moles) was added dropwise over a period of 1.5 hours to a 5% H<sub>2</sub>SO<sub>4</sub> solution containing 2.5 g HgO. The stirring was continued for about three hours at 65°C, and

then it was allowed to cool and was filtered. The 2-octanone-3-ol was extracted from the filtrate with ether, the extract was dried and the ether removed.<sup>13</sup> The NMR spectrum of the yellow oil was consistent with that expected for 2-octanone-3-ol.

To a solution of 0.04 mole 2-octanone-3-ol in 75 ml glacial acetic acid was added 0.04 mole  $\text{Bi}_2\text{O}_3$  with constant stirring at  $100^\circ\text{C}$ . The mixture was heated for 20 minutes, then 75 ml water was added. The mixture was filtered, and the dione extracted with benzene. The extract was dried, and the benzene was removed<sup>14</sup> under vacuum. The resulting 2,3-octanedione was vacuum distilled to give a yellow liquid. The NMR spectrum showed one large unresolved multiplet.

The preparation of 2,3-octanedionebisthiosemicarbazone utilized the same procedure described for 2,3-hexanedionebisthiosemicarbazone. A warm solution of 0.03 mole thiosemicarbazide in 100 ml water containing 5 ml glacial acetic acid was added dropwise with constant stirring to a warm solution of 0.05 mole 2,3-octanedione in 100 ml ethanol. The solution was heated for two hours, and upon cooling the yellow precipitate which formed was collected and washed with hot ethanol and acetone.

#### 2,3-Octanedionebis(thiosemicarbazonato)copper(II), Cu-OTS

A solution of 0.005 moles copper acetate monohydrate in 40 ml water was added dropwise to a hot stirred solution of 0.005 moles  $\text{H}_2\text{OTS}$  in 50 ml DMF. The solution was heated for two hours. The brown precipitate which formed was collected and recrystallized from 95% ethanol.<sup>24</sup> The reddish-brown powder was dried in a vacuum for 30 minutes. Anal. for  $\text{Cu}(\text{C}_{10}\text{H}_{18}\text{N}_6\text{S}_2)$ . Calcd: C, 34.32; H, 5.18; N, 24.01. Found: C, 34.59; H, 5.15; N, 23.81.

#### Magnetic Measurements

Magnetic susceptibility data were collected using a Princeton Applied Research Model 155 vibrating sample magnetometer (VSM). The vibrating



sample magnetometer was operated from zero-field to 10kOe. The VSM magnet (Magnion H-96), power supply (Magnion HSR-1365) and associated field control unit (Magnion FFC-4 with a Rawson-Lush model 920 MCM rotating-coil gauss meter) were calibrated against NMR resonances ( $H^1$  and  $Li^3$ ) over the field range 0.35 - 10kOe and found to be linear to within better than 1% over the entire range. The field set accuracy is within  $\pm 0.3\%$  at 300 gauss and better than 0.15% at 10,000 gauss.

The magnetometer was initially calibrated against  $HgCo(NCS)_4$ ,<sup>15</sup> and the calibrations were checked against a sample of  $(NH_4)_2Mn(SO_4)_2 \cdot 6H_2O$ .<sup>16</sup> The results using these two standards agreed to within 2% and it is felt that this represents the upper limit to the uncertainty in the measurements of the magnetic susceptibility with the VSM since the field is known to a much higher degree of accuracy. Powdered samples of the calibrants and compounds used in this study were contained in precision milled Lucite sample holders. Approximately 150 mg. of each were used. Diamagnetic corrections for the constituent atoms were made using Pascal's constants, and a correction for temperature independent paramagnetism was estimated from tabulated data.<sup>17-19</sup>

#### Dielectric Measurements

Capacitances were determined as a function of temperature on pressed pellet samples of  $Cu(4\text{-methylpyridine})_2Cl_2$  and  $Cu(N\text{-methylimidazole})_2Br_2$  onto which gold electrodes had been deposited by evaporation. Continuity of the deposited electrodes was determined by surface resistance measurements. Capacitances were measured with a GenRad 1688 Precision LC Digibridge, and the pressed pellet samples were contained in a sample holder consisting of a boron nitride block and spring loaded copper electrodes. The boron nitride block was attached to the cooling head of a CTI Cryogenics SC21 Helix closed

cycle refrigerator with Crycon cryogenics paste. The temperature of the cold head was controlled with a Lake Shore Cryotronics Model DTC-500 Cryogenic Temperature Controller using a calibrated silicon diode. The temperature of the sample was determined using a Fluke 8502A Digital Multimeter, a 10  $\mu$ A constant current source, and a calibrated gallium arsenide diode. The GaAs diode was embedded in the boron nitride block immediately adjacent to the stationary copper electrode. This latter electrode was held in a recess in the boron nitride block with Crycon cryogenics paste. The capacitance was determined as a function of frequency in order to select the proper frequency for the collection of the data sets. At 10 kHz,  $dC/dv$  was essentially zero and had decreased from the larger values observed at lower frequencies. These larger values are due to contact impedances plus the intrinsic value of the capacitance of the sample, while the higher frequency values give an upper limit for the intrinsic capacitance.

#### The Alternating Chain Model

The Hamiltonian for the Heisenberg alternating linear chain may be written as

$$H = -2J \sum_{i=1}^{n/2} [\hat{S}_{2i} \cdot \hat{S}_{2i-1} + \alpha \hat{S}_{2i} \cdot \hat{S}_{2i+1}] \quad (1)$$

where  $J$  is the exchange integral between a spin and its right neighbor and  $\alpha J$  is the exchange integral between a spin and its left neighbor. The model of most interest is for antiferromagnetic exchange ( $J < 0$ ) and for  $0 \leq \alpha \leq 1$ . At the extremes, when  $\alpha = 0$  the model reduces to the dimer model with pairwise interactions and when  $\alpha = 1$  the model reduces to the regular linear chain model. This model has been studied in detail by Duffy and Barr,<sup>11</sup> as well as Bonner and Friedberg<sup>20</sup> and Diederix, et al.<sup>2</sup>

We have repeated the calculations for the reduced magnetic susceptibilities of short alternating rings of up to ten  $S = 1/2$  ions for  $\alpha = 0, 0.1, 0.2, 0.3, 0.4, 0.6, 0.8,$  and  $1.0$  using the cluster approach and programs which have been described earlier.<sup>21</sup> The results of our calculations were in excellent agreement with the previously reported results of Duffy and Barr,<sup>11</sup> and the reduced magnetic susceptibilities are displayed as a function of reduced temperature in Figure 1.

Reduced magnetic susceptibility curves for 10 member alternating chains with  $\alpha = 0, 0.1, 0.2, 0.3, 0.4, 0.6, 0.8,$  and  $1.0$  were fitted to the quadratic/cubic function (2), where the reduced susceptibility  $\chi_r = \chi|J|/Ng^2\mu_B^2$  and the reduced

$$\chi_r = \frac{AT_r^2 + BT_r + C}{T_r^3 + DT_r^2 + ET_r + F} \quad (2)$$

temperature  $T_r$  is given by  $kT/|J|$ . The fits were truncated below  $kT/|J|$  of  $0.5$ , and the constant  $A$  was set equal to  $0.25$  for convergence to the Curie law at high temperatures.

With the expressions for reduced susceptibility for each of the eight alternating chain cases as a starting point, a unified expression for  $\chi_r$  as a function of the alternation parameter was developed. The values for the parameters  $A, B, C, D, E,$  and  $F$  for  $0 \leq \alpha \leq 0.4$  are

$$\begin{aligned} A &= 0.25 \\ B &= -0.12587 + 0.22752\alpha \\ C &= 0.019111 - 0.13307\alpha + 0.50967\alpha^2 - 1.3167\alpha^3 + 1.0081\alpha^4 \\ D &= 0.10772 + 1.4192\alpha \\ E &= -0.0028521 - 0.42346\alpha + 2.1953\alpha^2 - 0.82412\alpha^3 \\ F &= 0.37754 - 0.067022\alpha + 6.9805\alpha^2 - 21.678\alpha^3 + 15.838\alpha^4 \end{aligned}$$

The values for the parameters  $A-F$  for  $0.4 < \alpha \leq 1.0$

$$\begin{aligned} A &= 0.25 \\ B &= -0.13695 + 0.26387\alpha \\ C &= 0.017025 - 0.12668\alpha + 0.49113\alpha^2 - 1.1977\alpha^3 + 0.87257\alpha^4 \\ D &= 0.070509 + 1.3042\alpha \\ E &= -0.0035767 - 0.40837\alpha + 3.4862\alpha^2 - 0.73888\alpha^3 \\ F &= 0.36184 - 0.065528\alpha + 6.65875\alpha^2 - 20.945\alpha^3 + 15.425\alpha^4 \end{aligned}$$

The expression for reduced susceptibility may now be converted to magnetic susceptibility in familiar coordinates to give

$$\chi_m = \frac{Ng^2 \mu_B^2}{kT} \cdot \frac{A + Bx + Cx^2}{1 + Dx + Ex^2 + Fx^3} \quad (3)$$

where  $x = |J|/kT$ . The expression with the two sets of parameters A-F is valid for  $kT/|J| \geq 0.5$  and  $J \leq 0$ , and as shown in Figure 1, reproduces the calculated magnetic susceptibilities of the 10 member rings, which should be good approximations for infinite systems, for various values of  $\alpha$  with an agreement factor  $(|\chi_m^{\text{theo}} - \chi_m^{\text{calc}}|/\chi_m^{\text{theo}})^2$  much better than 1%. The error in the alternation parameter resulting from the fit is largely that inherent in the assumption that the magnetic properties of relatively small rings may be extrapolated to the infinite limit. All of our studies with this model have been carried in the low field region (10 KOe, 1 KOe, 100 Oe); additional studies at higher fields are underway.

## Results

Magnetic susceptibility. Magnetic susceptibility data for Cu-HTS and Cu-OTS are given in Figures 2 and 3. The maxima in the susceptibility curves provide evidence for antiferromagnetic interactions, and the small increase in  $\chi_m$  below 7 K for Cu-OTS is very likely due to the presence of a small amount of paramagnetic impurities.

Attempts to fit the magnetic data by the uniform Heisenberg chain model or the dimer model failed, but excellent fits were obtained for the alternating chain model described above. The solid lines in Figures 2 and 3 were calculated using the Heisenberg alternating chain expression and the magnetic parameters given in Table I. The inability of the uniform chain and dimer models to describe the magnetic behavior is shown by the "best fit" lines in Figures 2 and 3.

The magnetic data for  $\text{Cu}(4\text{-methylpyridine})_2\text{Cl}_2$  had been analyzed in terms of the alternating chain model using the graphical results of Duffy and Barr<sup>11</sup> with the parameters  $J = -8.5 \text{ cm}^{-1}$ ,  $g = 2.13$ , and  $\alpha = 0.6$  being

Table I. Magnetic Parameters for the Alternating Chain Compounds Cu-HTS and Cu-OTS

Compound	$J, \text{ cm}^{-1}$	$\alpha$	$g$
Cu-HTS	$-10.1 \pm 0.2$	$0.91 \pm 0.02$	$2.06 \pm 0.02$
Cu-OTS	$-12.9 \pm 0.3$	$0.90 \pm 0.02$	$2.11 \pm 0.02$

derived from a comparison of the experimental data with the published  $\chi$  vs.  $T$  curves. The alternating chain model presented above yield  $J = -9.6 \pm 0.2 \text{ cm}^{-1}$ ,  $g = 2.17 \pm 0.02$ , and  $\alpha = 0.67 \pm 0.02$ .

Dielectric Measurements. The capacitance of catena-di- $\mu$ -chlorobis-(4-methylpyridine)copper(II) as a function of temperature is plotted in Figure 4, where a first order phase transition is clearly indicated by the peak in the capacitance curve near 50 K. The anomaly in the capacitance curve for  $\text{Cu}(4\text{-methylpyridine})_2\text{Cl}_2$  is similar to the anomaly in the dielectric constant exhibited by  $\text{CsFeF}_4$  as a result of a first order transition at 508 K.<sup>22</sup>

The temperature dependent capacitance data for catena-di- $\mu$ -bromobis-(N-methylimidazole)copper(II) are given in Figure 5. The data are consistent with at least two first order phase transitions, one near 105 K and a second one near 50 K. The data do not permit a conclusion concerning the apparent increase of the capacitance below about 35 K.

## Discussion

The magnetic susceptibility data for Cu-HTS and Cu-OTS may be explained only in terms of the alternating chain model given by the hamiltonian of Eq. (1). This observation is consistent with the structure of the alternating chain in Cu-KTS.

The observation of a first order phase transition in  $\text{Cu(4-methylpyridine)}_2\text{Cl}_2$  in the dielectric measurements in conjunction with the analysis of the low temperature magnetic data suggests that the structure of the complex has changed to an alternating chain. However, an examination of the structures<sup>23-25</sup> of 4-substituted pyridine complexes of copper(II) chloride does not provide a simple model for a high temperature structure which transforms to an alternating chain below 50 K. This remains a fascinating puzzle which merits a low temperature structural study, however, this will be a difficult problem since crystals adequate for an X-ray structure of  $\text{Cu(4-methylpyridine)}_2\text{Cl}_2$  at room temperature have yet to be prepared. Preliminary results from X-ray structural studies at room temperature of twinned crystals are consistent with a uniform chain structure.<sup>26,27</sup>

X-ray structural studies at room temperature on a single crystal of  $\text{Cu(11-methylimidazole)}_2\text{Br}_2$  reveal a uniform chain.<sup>28</sup> However, low temperature magnetic susceptibility and magnetization data have suggested that the material is an alternating Heisenberg antiferromagnet.<sup>6</sup> However, neutron diffraction measurements do not provide evidence for a different structure at 4.2 K.<sup>29</sup> Our present dielectric measurements provide evidence for structural transformations. It is tempting to suggest that the first order transition near 105 K seen in Figure 5 is a result of a "freezing-in" of the expected free rotation of the N-methyl group, and that the transition near 50 K is comparable to the transition to the alternating chain transformation seen in  $\text{Cu(4-methylpyridine)}_2\text{Cl}_2$ . The solution of this problem will require extensive structural studies at several temperatures.

We have digitized a plot of the experimental magnetic susceptibilities of  $\text{Cu}(\text{N-methylimidazole})_2\text{Br}_2$  which was kindly sent to us by Professor J. Reedijk and obtained the parameters  $J = -7.2 \pm 0.2 \text{ cm}^{-1}$ ,  $g = 2.14 \pm 0.02$ , and  $\alpha = 0.4 \pm 0.02$ , which are in good agreement with the published values.

### Conclusion

The alternating Heisenberg chain model permits a description of the magnetic susceptibility of the compounds catena-octanedione- and catena-hexanedionebis(thiosemicarbazonato)copper(II) and catena-di- $\mu$ -chlorobis-(4-methylpyridine)copper(II). It is reasonable to suggest that the sulfur bridged compounds have alternating chain structures since the analogous compound Cu-KTS has been shown by X-ray diffraction studies<sup>10</sup> to have an alternating chain structure. X-ray data for twinned crystals of  $\text{Cu}(4\text{-methylpyridine})_2\text{Cl}_2$ <sup>26,27</sup> are consistent with a uniform chain structure at room temperature, but an anomaly in the dielectric behavior signals a structural phase transition presumably to an alternating chain as suggested by the low temperature magnetic susceptibility data. The phase transition is not reflected in the temperature dependent magnetic susceptibility data owing to the small magnitude of the magnetic susceptibility at the temperature of the phase transition. Also, as shown in Figure 6, there is a close correspondence between the best fits of the alternating chain model and of the Heisenberg uniform linear chain model to the data in the region of the phase transition. The subtle change in structure from the uniformly spaced chain to the alternately spaced chain would not be expected to have a marked influence on the magnitude of the average  $g$  value. In view of the coincidences of the magnitudes of the magnetic susceptibilities calculated by the two models in the region of the phase transition, and of an unlikely change in the magnitude of the average  $g$  value accompanying the phase transition, the absence of an abrupt change in magnetic susceptibility at the phase transition can be understood.

Multiple anomalies were seen in the dielectric behavior of  $\text{Cu}(\text{N-methylimidazole})_2\text{Br}_2$  and we suggest that a structural phase transition from the uniform chain at room temperature<sup>28</sup> has occurred, thus permitting an explanation of the low temperature magnetic and magnetization data. The neutron diffraction results for  $\text{Cu}(\text{N-methylimidazole})_2\text{Br}_2$  at 4 K cannot be understood.<sup>29</sup>

The magnetic susceptibility data have been analyzed in terms of a convenient expression for  $\chi_m$ , which has been developed in terms of the alternation parameter  $\alpha$ , the exchange coupling constant  $J$ , and the  $g$  factor. The expression provides a good approximation for  $\alpha$ ,  $J$ , and  $g$  for magnetic data in moderate magnetic fields.



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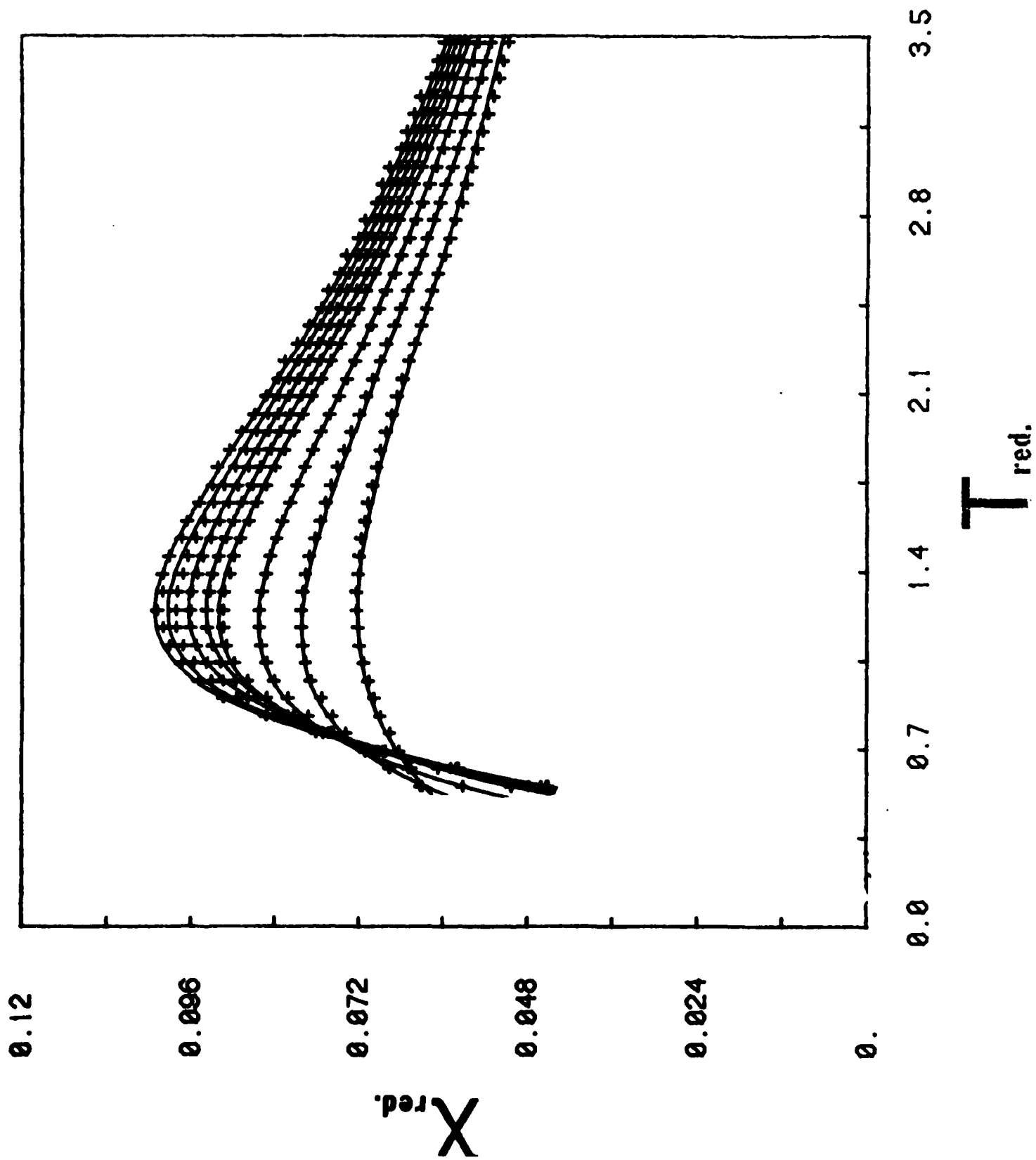
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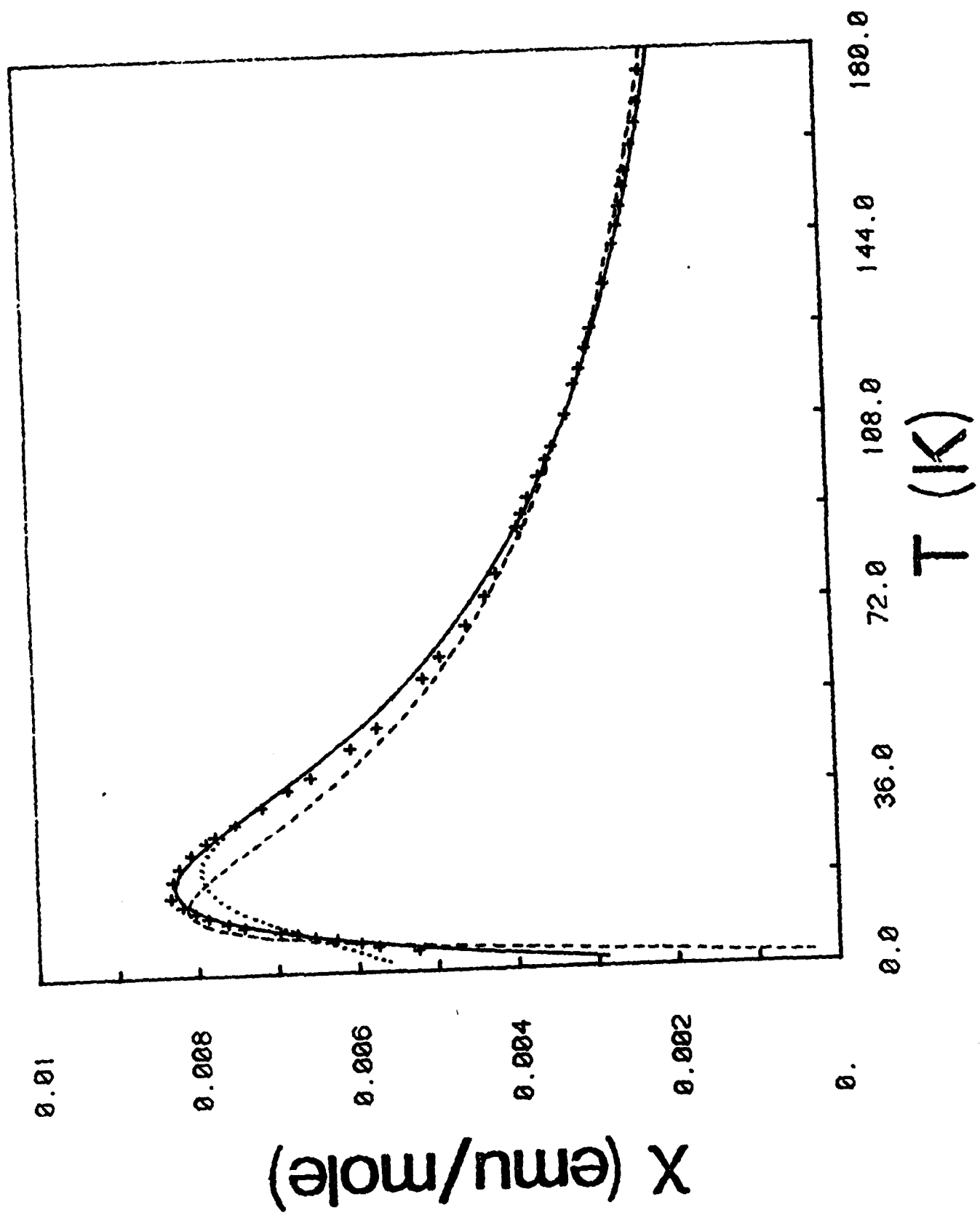
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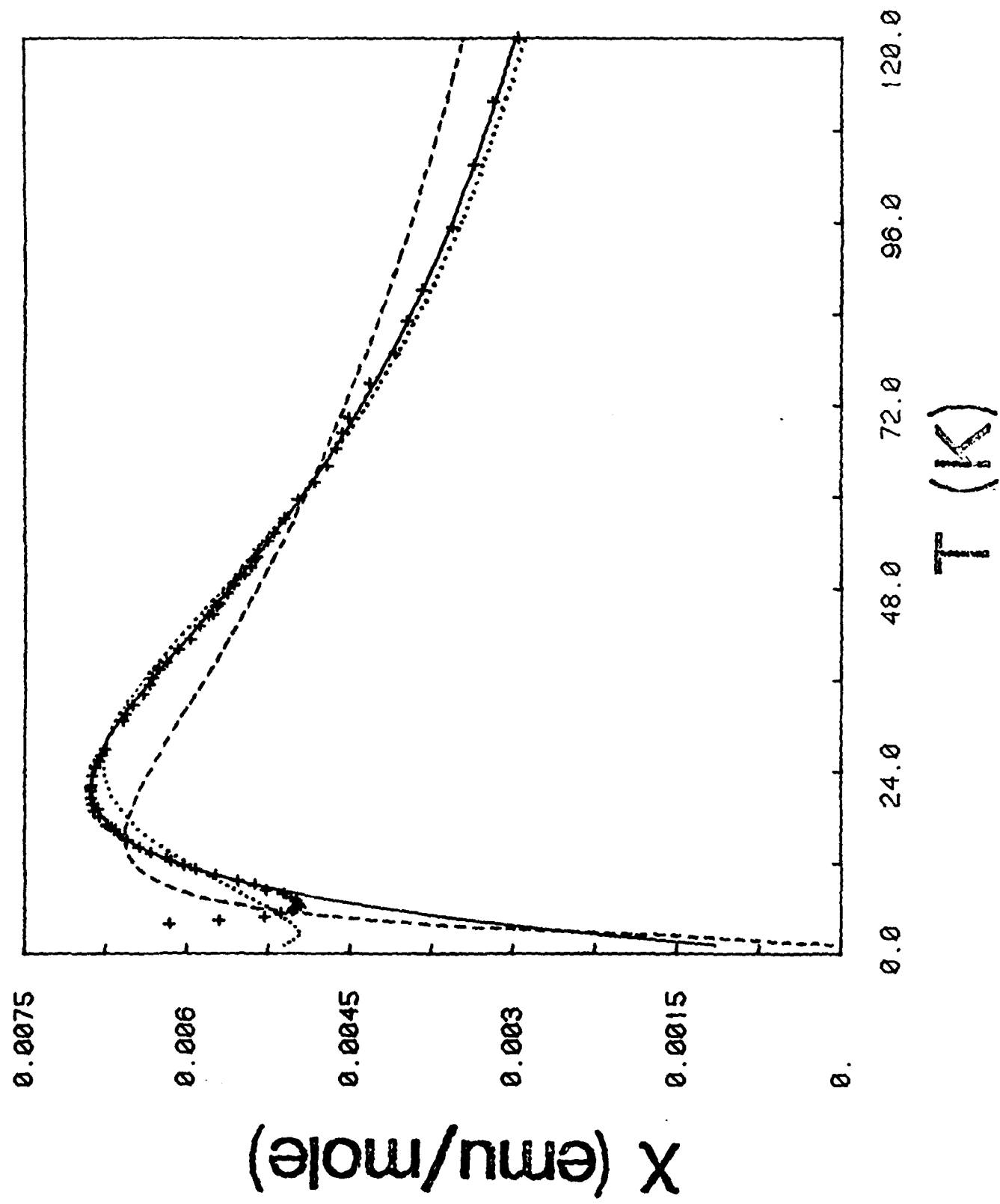
### Captions for the Figures

- Figure 1. Plot of equation 2 (solid line) in reduced coordinates using coefficients listed in text. Points for 10 membered rings (+) are calculated with  $H = 1000$  G,  $g = 2.1$ , and  $\alpha = 0.0, 0.1, 0.2, 0.3, 0.4, 0.6, 0.8$ , and  $1.0$ .
- Figure 2. Magnetic susceptibility versus temperature data for catenahexane-dionebis(thiosemicarbazonato)copper(II). The solid line is the best fit of the Heisenberg alternating linear chain model with  $J = -10.1 \pm 0.2 \text{ cm}^{-1}$ ,  $\alpha = 0.91 \pm 0.02$ , and  $g = 2.06 \pm 0.02$ . For the purposes of comparison the "best fits" to the uniform Heisenberg chain ( $\cdots$ ,  $J = -10.7 \text{ cm}^{-1}$ ,  $J' = 1.76 \text{ cm}^{-1}$ ,  $g = 2.11$ ) and dimer ( $---$ ,  $2J = -6.4 \text{ cm}^{-1}$ ,  $g = 2.23$ ,  $\theta = -32.5$  K) models are also shown.
- Figure 3. Magnetic susceptibility versus temperature data for catenaoctanedionebis(thiosemicarbazonato)copper(II). The solid is the best fit of the Heisenberg alternating linear chain model with  $J = 12.9 \pm 0.2 \text{ cm}^{-1}$ ,  $\alpha = 0.90 \pm 0.02$ , and  $g = 2.11 \pm 0.02$ . For the purposes of comparison the "best fits" to the uniform Heisenberg chain ( $\cdots$ ,  $J = -13.4 \pm 0.2 \text{ cm}^{-1}$ ,  $J' = 8.4 \text{ cm}^{-1}$ ,  $g = 2.10$ ) and dimer ( $---$ ,  $2J = -5.0 \text{ cm}^{-1}$ ,  $g = 2.71$ , and  $\theta = -76.1$  K) models are also shown.
- Figure 4. Temperature dependent capacitance data for a pressed pellet sample of catena-di- $\mu$ -chlorobis(4-methylpyridine)copper(II) ( $\blacksquare$ , temperature increasing, + temperature decreasing).
- Figure 5. Temperature dependent capacitance data for a pressed pellet sample of catena-di- $\mu$ -bromobis(N-methylimidazole)copper(II). ( $\blacksquare$ , temperature increasing, + temperature decreasing).

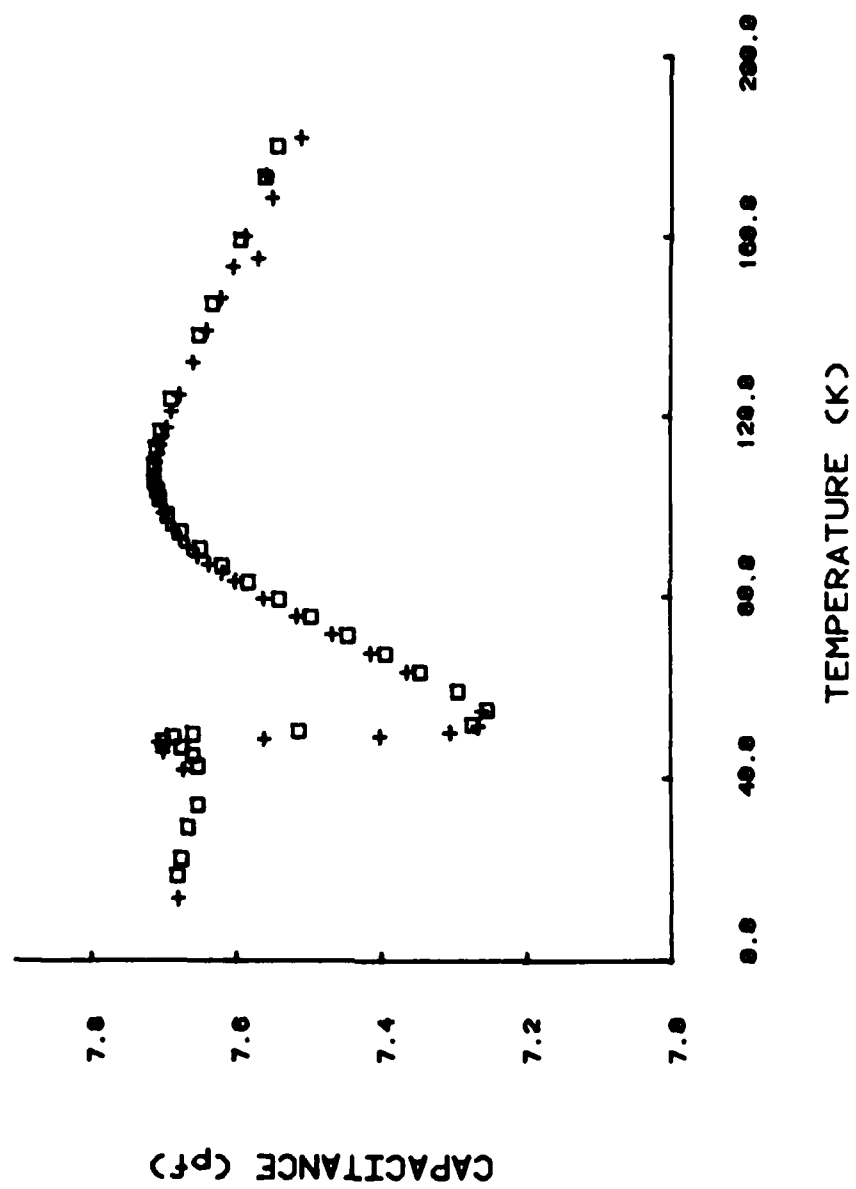
Figure 6. Magnetic susceptibility versus temperature data for  $[\text{Cu}(\text{4-methylpyridine})_2\text{Cl}_2]_\infty$  [from Ref. 7.] Experimental data are denoted by +. The best fit of the alternating chain model to the data is indicated by the solid line, and the best fit of the uniform chain is indicated by the dashed line.

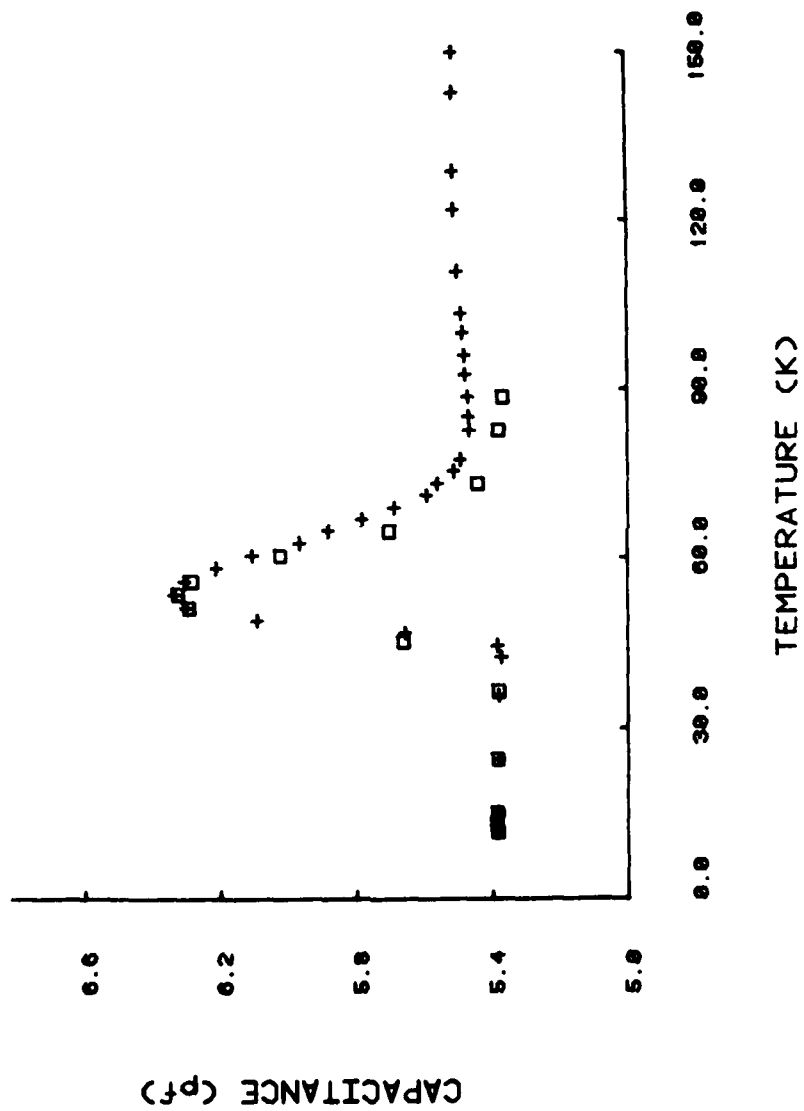


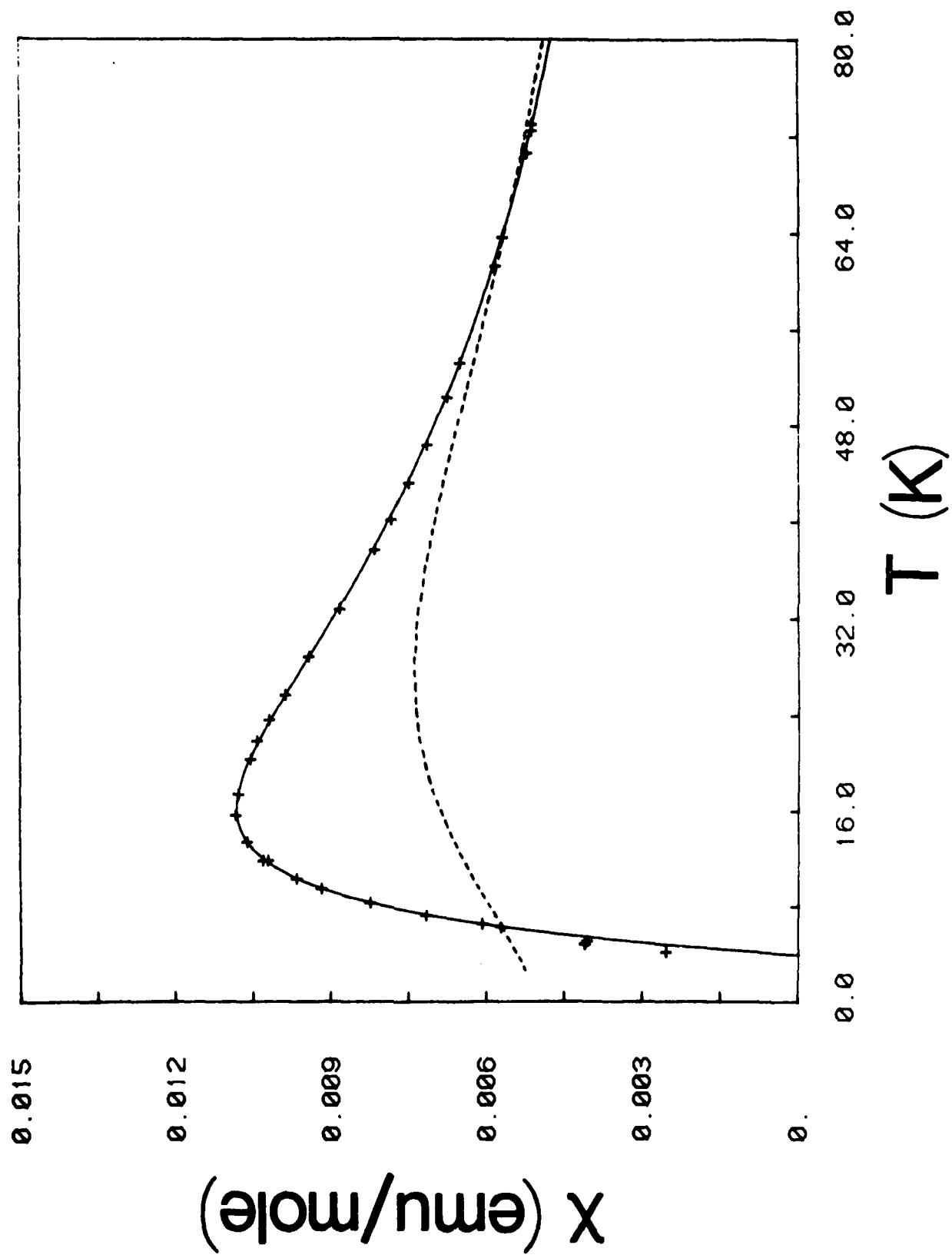












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