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Magnetic Susceptibility of $Cu(NO_3)_2\ 2.5H_2O$ at Low Temperature

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Abstract: The magnetic susceptibility of cupric nitrate "trihydrate" $Cu(NO_3)_2$ $2.5H_2O$ has been measured on the powder and on single crystals in the 14-20 and 0.4-4.2°K ranges of temperature. The susceptibility of the powder has a rounded maximum at 3.2°K, where it is equal to 0.065 CGS/mole, and drops very rapidly towards zero below this temperature. This behavior differs from that of a typical antiferromagnet. The experimental data have been compared with existing theoretical calculations for antiferromagnetic linear chains or binary clusters. In the single crystal, the susceptibility measured in a direction parallel to the monoclinic axis is always larger by 20% than the susceptibility in the perpendicular directions. This is probably due to a uniaxial anisotropy of the g factor.

INTRODUCTION

The study of the cupric salts provides one of the most convenient experimental tests for the theories of interacting paramagnetic ions. The Cu^{++} ion has a spin $S = \frac{1}{2}$, value for which the largest amount of theoretical work has been done. Moreover, the relatively small value of the magnetocrystalline anisotropy simplifies comparisons between experiments and theory.

Very little is known about the magnetic properties of cupric nitrate trihydrate, which is one of the most common cupric salts. The magnetic susceptibility has been measured[1] only above 78°K. The paramagnetic resonance has been observed at room temperature on the powder[2].

We have measured the susceptibility of this salt in both powder and single crystal forms, in the liquid helium and in the liquid hydrogen ranges of temperature. The measurements on the powder have been extended down to 0.4°K, using a He_3 cryostat.

DESCRIPTION OF THE SAMPLES

The salt obtained above 26°C by cooling a saturated solution of cupric nitrate in water is usually referred to as the trihydrate[3] $Cu(NO_3)_2\ 3H_2O$. According to Schreinemakers, Berkhoff, and Posthumus[4], and also to Wilcox and Bailey[5], this salt is rather $Cu(NO_3)_2\ 2.5H_2O$. In a short note[6] on the X-ray determination of the structure, Dornberger-Schiff and Leciejewicz give a projection of the electron density on a plane perpendicular to the monoclinic axis, from which one may infer that the formula is $Cu(NO_2)_2\ 2.5H_2O$.

The material used in the present investigations was obtained from the J. T. Baker Chemical Company, in the "Baker Analyzed Reagent" grade. All samples were recrystallized, by cooling a saturated solution down to 40 or 30°C, in order to insure the proper degree of hydration. Solutions of cupric nitrate should not be heated to more than 70°C, as a white powder precipitates slowly above this temperature. Care should also be exercised to prevent organic materials from coming into contact with this strongly oxidizing salt. Sheets of filter paper catch fire spontaneously when soaked with solution and left to dry in the heat of an electric bulb.

It is easy to obtain large single crystals of the salt. They have an elongated, often needle-like, shape. A plane of easy cleavage runs parallel to the needle axis. The crystal belongs to the $C2/_c$ monoclinic group, with $a = 22.2$ Å, $b = 4.90$ Å, $c = 15.4$ Å, $\beta = 48°$, according to the few X-ray data available[6]. The angles of the faces suggest that the monoclinic axis b is the needle axis. We have performed optical measurements in parallel and in convergent polarized light which fully confirms this. The two optical axes lie in the ac plane. One of them is nearly perpendicular to the cleavage plane.

EXPERIMENTAL PROCEDURE

Magnetic susceptibilities have been measured by means of a mutual inductance bridge, working usually at 275 cps. This bridge is similar to that described by Pillinger, Jastram, and Daunt[7]. The small change of mutual inductance produced by insertion of the sample into the coil is proportional to the susceptibility of the sample. The bridge is calibrated during each run against a sample of powdered manganous ammonium sulphate, the susceptibility of which is given[8] by $\chi = 0.01119/T$ CGS/gm .

In the case of powder measurements, the sample is packed in a thin pyrex or soft glass sphere supported by a thin nylon thread. In the case of single crystal measurements, the sample is tied with nylon thread to a plastic platform which has been glued with epoxy resin to the end of a thin lucite rod. The masses of the sample range from 0.5 gm to 1 gm.

In the 14-20°K range and in the 1.3-4.2°K range, the sample and the mutual inductance coil are in direct contact with a liquid hydrogen bath, or with a liquid helium bath. In the 0.4-1.3°K range, we use a He_3 cryostat. Details of this apparatus will be given in another publication. The sample is in direct contact with the He_3 bath, and a cerium magnesium nitrate sample is used as a standard to calibrate the mutual inductance bridge, and also as a magnetic thermometer. The susceptibility of this salt is given[9] by $\chi = (2.73 \times 10^{-4}/T) + 2.13 \times 10^{-5}$ CGS/gm .

DISCUSSION OF THE RESULTS

The experimental results are shown in Fig. 1. The susceptibility has been measured on the powder. It has been measured on a single crystal, along the monoclinic axis b ; it has also been measured along three directions in the ac plane perpendicular to the monoclinic axis. One of these three directions is parallel to the cleavage plane mentioned before. Another is perpendicular to this cleavage plane. The third one is approximately at 45° to the cleavage plane.

For all samples, the susceptibility is found to have a rounded maximum at 3.2°K. It drops very rapidly below this temperature. The susceptibility of the powder seems to rise again below 0.6°K; tests performed with empty pyrex spheres show however that this rise is mostly due to the parasitic Curie paramagnetism of the sample holder. If this contribution is subtracted from the data, one finds that the susceptibility of $Cu(NO_3)_2$ 2.5 H_2O is vanishingly small in the 0.4-0.6°K range. The paramagnetism of the sample holder becomes negligible at 1.3°K and above.

In the single crystal, the measured susceptibility is the same in the three directions perpendicular to the monoclinic axis. From this it can be deduced that the susceptibility is isotropic in the plane perpendicular to the monoclinic axis. The value $\chi_\perp$ in this plane is 20% lower than the value χ_b along the monoclinic axis, at all temperatures.

This behavior differs from that of a typical antiferromagnet. The powder susceptibility of an antiferromagnet[10] usually drops for vanishing temperature to no less than one half of the maximum value reached close to the Neel point. Moreover, the single crystal susceptibility of an antiferromagnet is very anisotropic; it vanishes at absolute zero (or becomes very small) along the direction of the sublattice magnetization, but remains quite high in other directions.

Our data would rather suggest that the magnetic ions in $Cu(NO_3)_2$ 2.5 H_2O are associated in independent pairs (binary clusters), or that they form one-dimensional chains. The available X-ray structure information[6] is not complete enough to directly decide between these two possibilities. A detailed discussion of these possibilities is given in the next section.

We have investigated the frequency dependence of the powder susceptibility at 1.3°K and at 14.1°K. In both cases, the susceptibility is the same at 130 cps and at 275 cps.

There is a small difference between our powder data and the average $\frac{1}{3}\chi_{\parallel} + \frac{2}{3}\chi_{\perp}$ of our single crystal data in the liquid hydrogen range (Fig. 3). This may be ascribed to some experimental error, or to variations in the physical state of the samples. Cupric nitrate trihydrate is very hygroscopic.

THEORETICAL RESULTS FOR BINARY CLUSTERS AND FOR ANTIFERROMAGNETIC CHAINS

The susceptibility of a system of binary clusters has been calculated by Bleaney and Bowers[11,12]. In writing the exchange hamiltonian H of a cluster, we define the exchange constant J of a cluster in a way which differs from theirs, for reasons which will become clear later:

$$H = -4\,J\;\vec{S}_1 \cdot \vec{S}_2 \tag{1}$$

where $\vec{S}_1$ and $\vec{S}_2$ are the spins of the two $S = \frac{1}{2}$ ions. Assuming that the singlet is the ground state (that is, $J < 0$), the susceptibility of one mole of cupric ions is:

$$\chi = \frac{N_0 g^2 \beta^2 S(S+1)}{3kT}\;\frac{4/3}{1 + \frac{1}{3}\exp\left(\frac{4|J|}{kT}\right)} \tag{2}$$

The relation between the exchange constants used by various authors is given in Table I.

No exact calculation of the susceptibility of an infinite one-dimensional chain of ions with isotropic exchange coupling is available at the present time. Katsura[13] has computed the susceptibility of a ring of $N = 6$ spins. Griffiths[14] has computed the susceptibility of rings of $N = 2, 4, 6, 8, 10$ spins. They use the exchange hamiltonian:

$$H = -2J \sum_{i=1}^{N} \vec{S}_i \vec{S}_{i+1} \qquad (3)$$

with:

$$\vec{S}_{N+1} = \vec{S}_1$$

In Eq. 3, $\vec{S}_i$ is the spin ($S = \frac{1}{2}$) of the i^{th} ion, and the constant J is the same as that used by these authors (see Table I).

In the case of a ring of $N = 2$ spins, it is easy to see that Eq. 3 is identical with Eq. 1. In fact, we have defined the exchange constant of the binary cluster of Eq. 1 in just such a way that this cluster may be considered as a ring of two spins.

The results of these theoretical works are represented on Fig. 2. We plot $u = \log\,(3kT\chi/N_o\,g^2\,\beta^2\,S(S+1))$ versus $|J|/kT$, where χ is the theoretical susceptibility of one mole of ions. On such a diagram, Curie's law would give a horizontal straight line $u = 1$, and the parallel susceptibility of an infinite Ising chain would give an oblique straight line. At high temperature, we see that u (or χ itself) is independent of N ; this is to be expected, as short-range order extends at these temperatures only to distances smaller than the circumference of the ring. The high temperature slope of all theoretical curves is the same.

We have fitted our experimental data in the region above 1.3°K to these theoretical curves (Fig. 2). This requires the choice of the value of the two parameters g and J. The condition that experimental and theoretical values of u be equal at infinite temperature determines g. The condition that the slope of the experimental and of the theoretical u curves be equal at infinite temperature determines J. However, the general curvature of the experimental u curves is independent of the choice of g and J. Using the powder data, the curvature of the experimental u curve is such that it coincides neither with the curve for the binary clusters ($N=2$) nor with that for a very long chain ($N \geqslant 10$); if we choose $g = 2.32$, $J/k = -2.15\,^{\circ}K$, we obtain a close fit to the $N=4$ curve, though this is not likely to have any real physical significance. On the other hand, using an average of the single crystal data, the experimental u curve has a somewhat larger curvature, and can be fitted best to the curve for the binary clusters, using $g = 2.13$, $J/k = -1.28\,^{\circ}K$.

We have also represented our data on a simple diagram of χ versus T (Fig. 3). The fit is made here in such a way that the maxima of the curves coincide. We get $g = 2.11$, $J/k = -1.23\,^{\circ}K$ for the fit to the binary clusters and $g = 2.47$, $J/k = -2.56\,^{\circ}K$ for the fit to a ring of 10 spins. Again, the theory for the ring of 2 spins (binary cluster) is in fair agreement with the average of our single crystal data.

The various g values obtained in the present work may be compared with the value $g = 2.22$ deduced from the high-temperature powder measurements by Escoffier and Gauthier[1]. We have had to correct the molar Curie constant given by these authors, because of the incorrect formula $Cu(NO_3)_2\,3(H_2O)$ used by them. iduno *et alii*[2] found $g = 2.1-2.2$ by paramagnetic resonance on the powder at room temperature, closer perhaps to our fitted value for the binary clusters.

Should cupric nitrate trihydrate prove to be a system of binary clusters, it would provide the first example of such clusters with an exchange constant J/k of only a few °K. In the case of cupric acetate[12] and of the other cupric alkanoates, J/k is two orders of magnitude larger.

REMARKS ON THE LOW-TEMPERATURE SUSCEPTIBILITY OF THE FINITE AND OF THE INFINITE CHAIN

Bulaeskii[15], and also Katsura[16], have recently calculated the susceptibility of an infinite one-dimensional chain with isotropic exchange coupling. Both authors resort to approximations. Bulaeskii finds that the susceptibility remains finite and positive at the absolute zero. However, as Katsura uses an expansion in powers of 1/T, it is not obvious that his theory can be used in the neighborhood of the absolute zero . Moreover, the approximations used by both authors destroy the isotropy of the exchange hamiltonian. Therefore, it is likely that the low-lying spectrum of spin-wave excitations is strongly modified, and the value of the susceptibility cannot be trusted at the lowest temperatures. It is for these reasons that we have not compared our data with these calculations.

There is, unfortunately, even some evidence that the comparison (Fig. 2 and Fig. 3) of our data with the calculations for a finite ring is of doubtful significance. These calculations are interesting mainly because the results might be used as an approximation to the susceptibility of an infinite chain. Ginzburg and Fain[17] have pointed out that the small value of χ for a finite chain at $T \ll |J|/Nk$ probably increases exponentially with the length of the chain. This exponential dependence, in fact, seems to exist already in the low-temperature region of our Fig. 2. The extrapolation to an infinite chain is therefore not possible. They also pointed out that the susceptibility of a very long chain might be field-dependent.

These uncertainties in the theory of a linear antiferromagnetic chain would, of course, become irrelevant, should cupric nitrate prove to be a system of binary clusters rather than a system of infinite chains.

Oguchi[18] has recently discussed the properties of the ground state of antiferromagnets and linear chains. He showed the existence of a relation between a non-vanishing low-temperature susceptibility and a long sublattice switching time. According to this, cupric nitrate would have a short sublattice switching time.

CONCLUSIONS

Our susceptibility data suggest that the cupric ions in $Cu(NO_3)_2$ 2.5 H_2O are associated in binary clusters, or along one-dimensional chains, with antiferromagnetic coupling. The data are in somewhat better agreement with the first assumption than with the second one.

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TABLE I. Relation between our exchange constant J and that of other authors.

Binary cluster (ring of two spins)	$4J = J_{\text{Bleaney and Bowers}} = J_{\text{Figgis and Martin}}$
Ring of N spins ($N = 2, 4, 6, 8, 10$)	$J = J_{\text{Katsura}} = J_{\text{Griffiths}}$

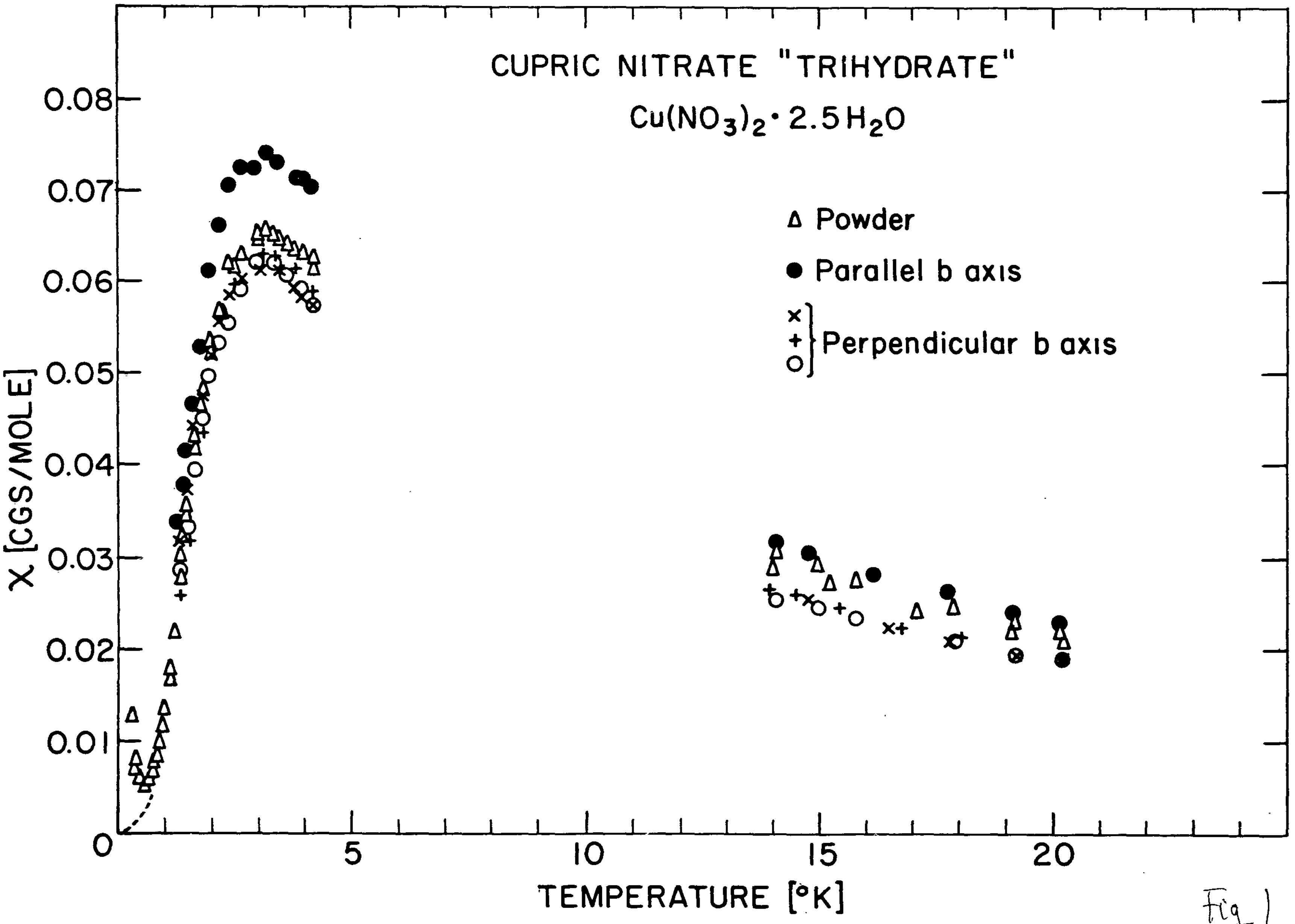
CUPRIC NITRATE "TRIHYDRATE"
$Cu(NO_3)_2 \cdot 2.5H_2O$
Δ Powder
● Parallel b axis
× + ○ Perpendicular b axis
χ [CGS/MOLE]
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
5
10
15
20
TEMPERATURE [°K]

Fig 1

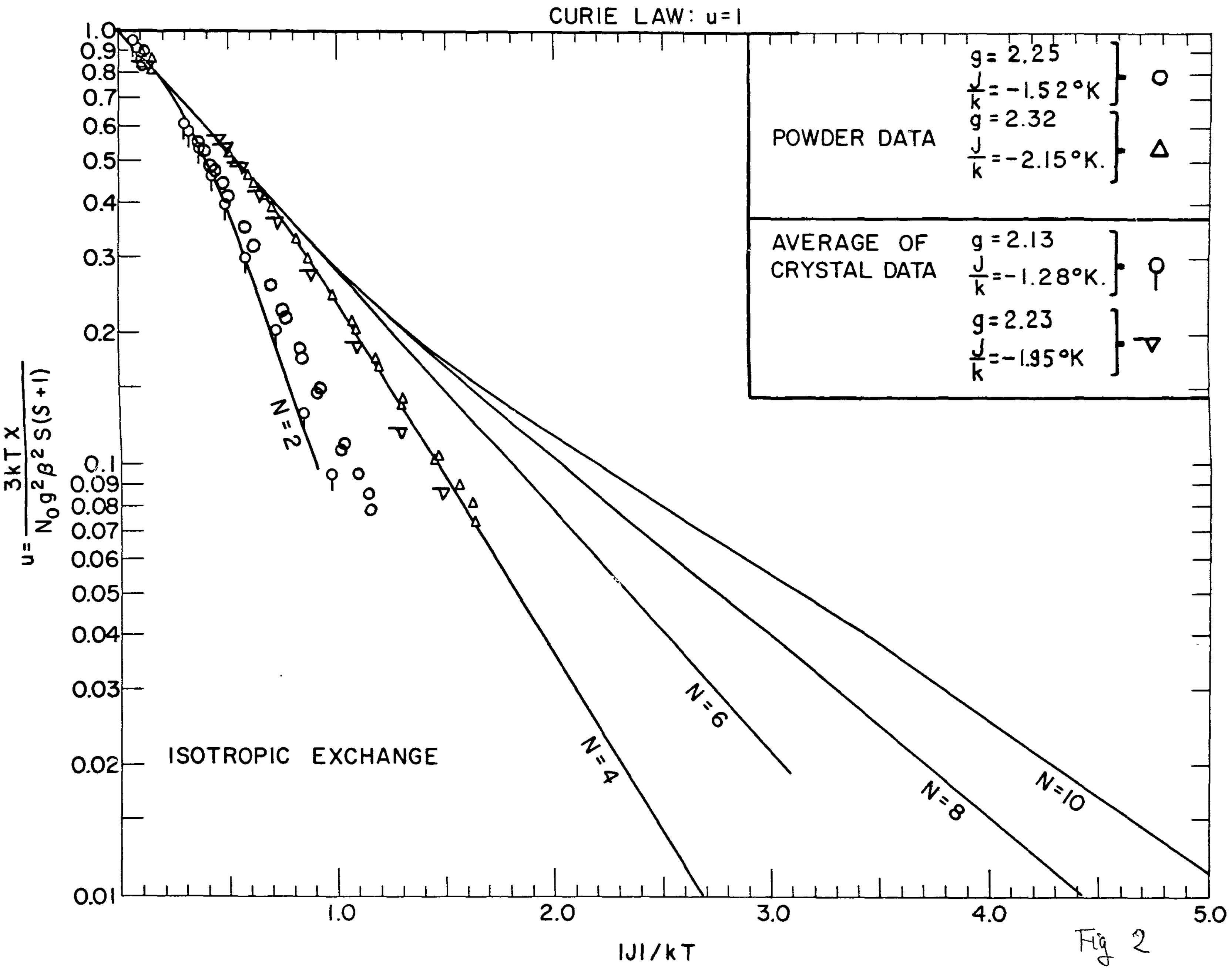
CURIE LAW: u=1
POWDER DATA
g= 2.25
J/k = -1.52°K
g = 2.32
J/k = -2.15°K.
AVERAGE OF CRYSTAL DATA
g = 2.13
J/k = -1.28°K.
g = 2.23
J/k = -1.95°K
N=2
N=4
N=6
N=8
N=10
ISOTROPIC EXCHANGE
u = 3kTχ / N₀g²β²S(S+1)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
1.0
2.0
3.0
4.0
5.0
|J|/kT

Fig 2

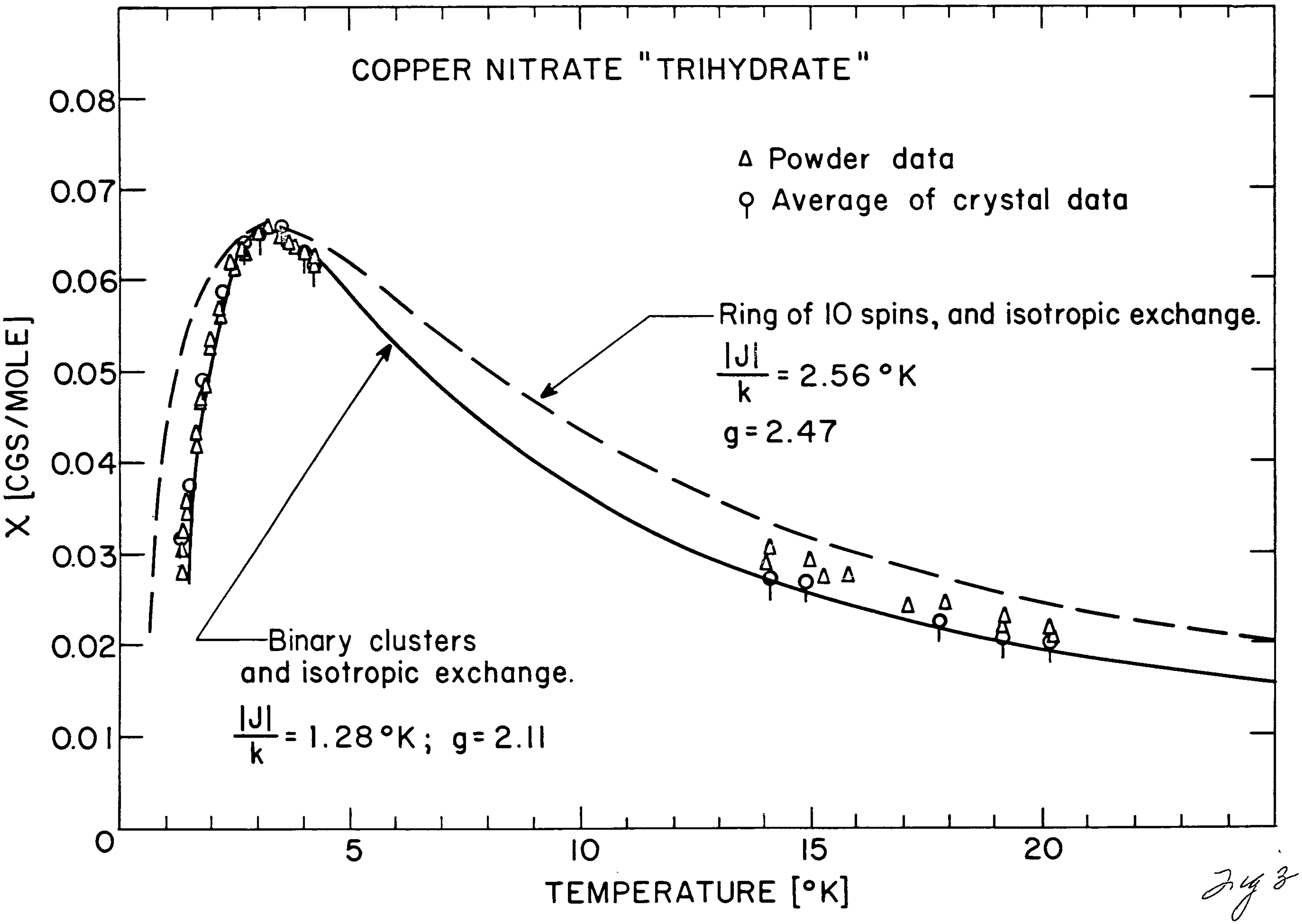
COPPER NITRATE "TRIHYDRATE"
Δ Powder data
ϙ Average of crystal data
Ring of 10 spins, and isotropic exchange.
$\frac{|J|}{k} = 2.56\,°K$
g = 2.47
Binary clusters
and isotropic exchange.
$\frac{|J|}{k} = 1.28\,°K$; g = 2.11
X [CGS/MOLE]
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
5
10
15
20
TEMPERATURE [°K]

Fig 3