Theoretical fitting for the magnetic susceptibility for two-dimensional antiferromagnet

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Abstract : The magnetic susceptibility for the complexes $(C_nH_{2n+1}NH_3)_2FeCl_4$ was measured over a wide temperature range which indicated magnetic and structural phase transitions. The large negative θ values, obtained from the experimental data, indicates the antiferromagnetic character of the complexes. The values of the magnetic constants agree well with the reported values. Theoretical fitting to the experimental data were carried out using high temperature series expansion with modification due to a small applied magnetic field. The exchange interaction constant J/k, obtained from the theoretical model, increases with the increase of the number of carbon atoms in the system indicating the increase of the antiferromagnetic interaction in the layer and a decrease in the ferromagnetic component by increasing the layer spacing.

Keywords : Magnetic susceptibility, antiferromagnet, theoretical model

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1. Introduction

Several interesting structural changes in the high temperature region are known to occur in the complexes of the general formula $(C_nH_{2n+1}NH_3)_2FeCl_4$, $n = 1, 2, 3$ and 4 as also observed in the isomorphous series in which the Fe is replaced by Mn^{++}, Co^{++} and Cd^{++}. Different techniques such as, differential thermal analysis (DTA) [1], birefringence measurements [2], X-ray diffraction neutron diffraction [3] and group theoretical analysis [4] revealed a strange sequence of phase transition starting from the high temperature tetragonal phase I_4 mmm leading to orthorhombic phase *Cmca*. At lower temperatures, the structure changes again to tetragonal symmetry. The complex $(CH_3NH_3)_2FeCl_4$ shows the following structural transition

$$\text{Tetragonal} \xleftrightarrow{\quad T=238 \text{ K} \quad} \text{Orthorhombic} \xleftrightarrow{\quad T=328 \text{ K} \quad} \text{Tetragonal}.$$

The orthorhombic crystal structure [5] has a unit cell with $a = 7.27$ Å, $b = 7.235$ Å and $c = 19.4$ Å. Regardless of the temperature range, the different phases can be described by
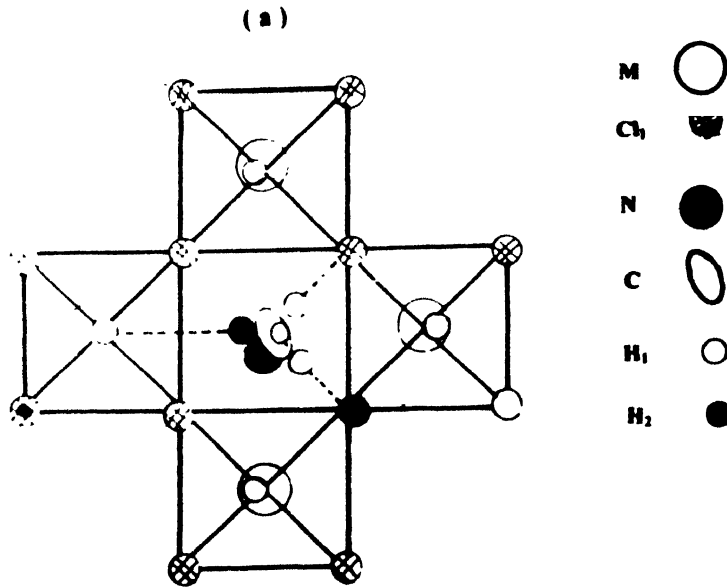
(a)

Figure 1. (a) Schematic projection on the layer plane of the orthorhombic phase *Cmca* of the layered structure.
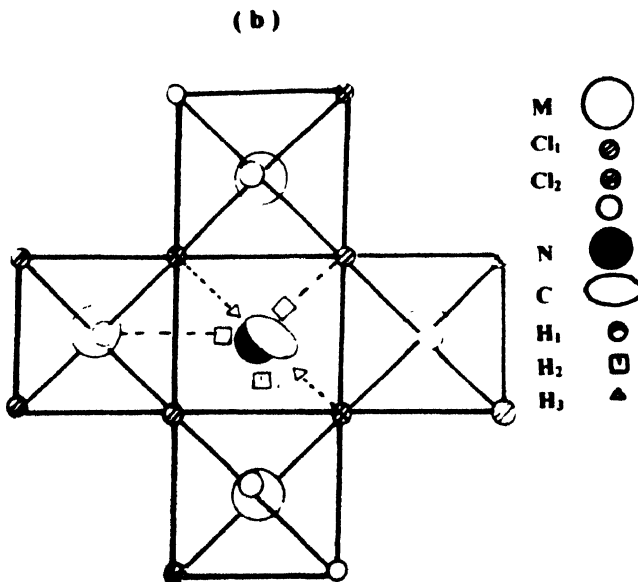
(b)

Figure 1. (b) Schematic projection on the layer plane of the tetragonal phase.

two dimensional layers stacked normal to the longest crystallographic axis with the interlayer distance of 9.6 Å. Each layer is represented by a series of octahedron with Fe in the center and Cl in the corners. The octahedron bonded to four others form an infinite two

dimensional layers. The NH_3 groups are located between the layers forming hydrogen bonding with Cl. The CH_3 groups are directed towards the adjacent layers linking them by van der Walls' forces. The C–N bonds are located on mirror planes and tilted relatively to the long axis with an angle of $20.13°$ at room temperature and $22.09°$ at lower temperature. In the orthorhombic phase, the shorter hydrogen bond length $N–H_2–Cl_2$ is 3.234 Å and lies approximately parallel to the layer on the mirror plane. The other two hydrogen bonds $N–H_1–Cl$ (3.345 Å) are symmetric and are connected to the corner sharing atoms. There are two additional equivalent hydrogen bonds $N–H_3–Cl_2$ with lengths of 3.427 Å making the chlorine atoms to lie in the Fe plane as in Figure 1. These five hydrogen bonds may be interpreted as a superposition of three different orientations of the methyl-ammonium group, one of them is the most probable one, while the other two are equivalent and correspond to the bonding scheme in the orthorhombic phase with the three hydrogen bonds $N–H_1–Cl_2$, $N–H_3–Cl_1$ and $N–H_2–Cl_3$, the latter lying approximately parallel to the layer plane. Thus the methyl-ammonium group (CH_3NH_3) associated with the three bonding planes are related to the flipping of the C–N bond around a point located in the mirror plane. The flipping centers lie between carbon and nitrogen but closer to nitrogen.

2. Experimental

All chemicals used in the present work were in analar grade (BDH). The samples were prepared by dissolving RNH_3Cl and $FeCl_2.4H_2O$ in the molar ratio of 2 : 1 respectively, where $R = CH_3, C_2H_5, C_3H_7$ and C_4H_9. A stream of nitrogen (oxygen free) gas was bubbled through the alcoholic solution to obtain oxygen free atmosphere and to prevent the oxidation of Fe^{++} ions in the solution. Few drops of analar HCl should be added to the solution. The solution was heated at $60°C$ for about 2 hours until it was reduced to $1/3$ of its original volume. Plate like crystals were obtained upon cooling. The crystals were washed with a mixture of ether and ethanol in the ratio of 3 : 1 after which the samples were dried in a vacuum dessicator. Before measuring the magnetic susceptibility, chemical analysis was carried out to ascertain the chemical composition of the samples. The samples were ground in a glove box filled with pure nitrogen gas and packed in the susceptibility tube. The filled susceptibility tubes were completely sealed by an epoxy resin.

The magnetic susceptibility was measured using the conventional Gouy's method. The measurements were carried out using liquid nitrogen cryostat specially designed for Gouy method.

The temperature of the sample was measured using T-type thermocouple with the reference junction in liquid nitrogen. The accuracy of measured temperatures was better than $\pm 1°C$.

3. Results and discussion

Experimental result :

As it was observed from the experimental data shown in Figure 2a, the complexes of the general formula $(C_nH_{2n+1}NH_3)_2FeCl_4, n = 1, 2, 3$ and 4, have the same general features

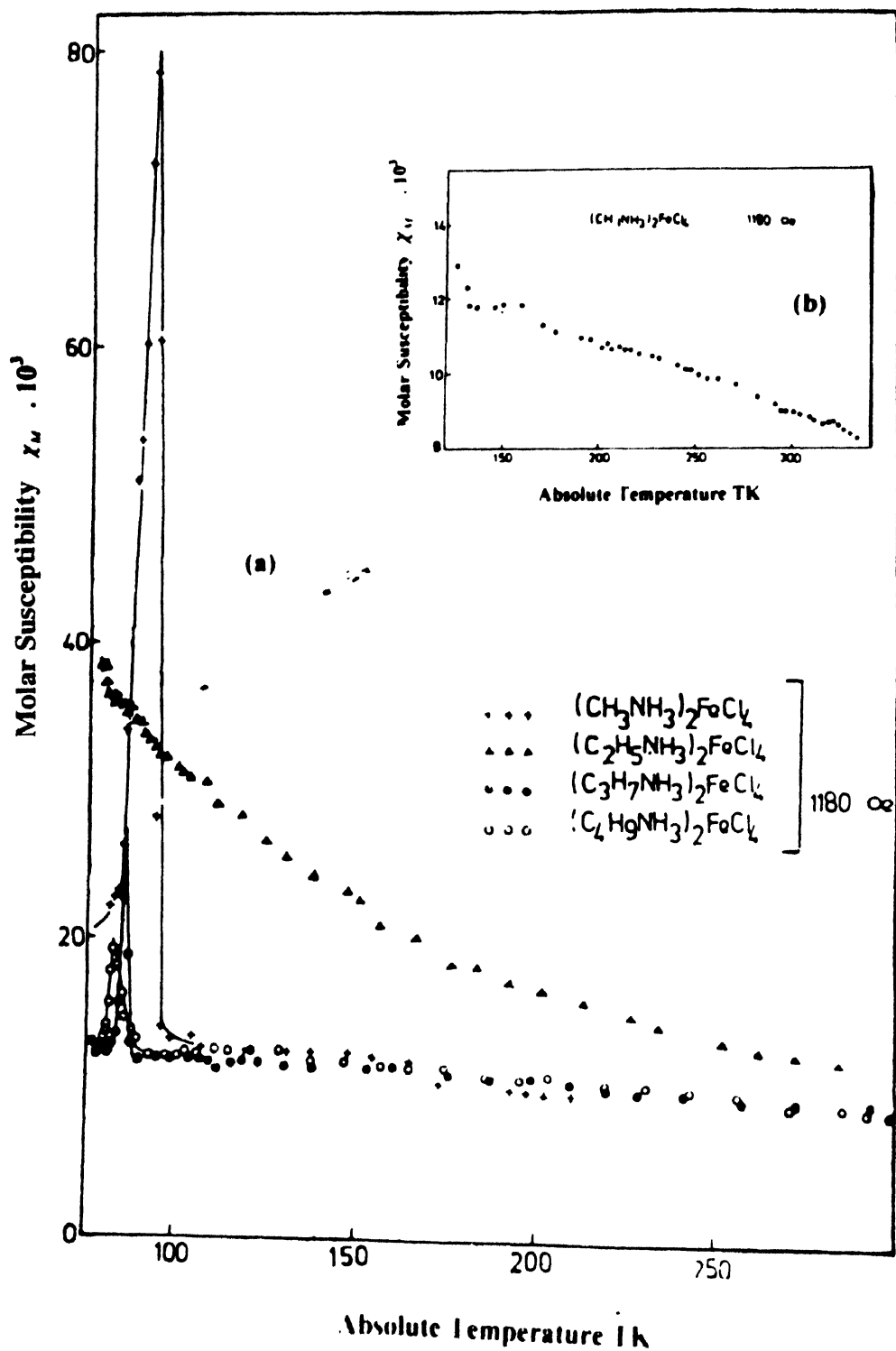**Figure 2.** (a) Relation between absolute temperature and magnetic susceptibility χ_M of $(C_nH_{2n+1}NH_3)_2FeCl_4$, $n = 1, 2, 3$ and 4. (b) $(CH_3NH_3)_2FeCl_4$, (high temperature part).

of susceptibility versus absolute temperature except the compound with $n = 2$. The compounds with $n = 1$, 3 and 4 give a very sharp spike in the low temperature region superimposed on an almost constant background in the high temperature region except for the structural phase transition.

Table 1. A list of the Curie-Weiss constant (θ), Curie-constant (C) and effective magnetic moment (μ_{eff}). In the temperature range from 130 K to 330 K.

Complex		θ	C	μ_{eff}
$(CH_3NH_3)_2FeCl_4$	$T > 240$ K	-200 ± 1.0	4.13	5.75
	$T < 220$ K	-150 ± 15	3.23	5.09
$(C_3H_7NH_3)_2FeCl_4$		-130 ± 7.0	3.60	5.40
$(C_4H_9NH_3)_2FeCl_4$		-130 ± 5.0	3.30	5.20

*T is the absolute temperature.

The large negative θ values are indicative of strong antiferromagnetic interaction. It is well known that these complexes exhibit several structural phase transitions in the paramagnetic region. Some authors [1,2] reported the appearance of structural changes from
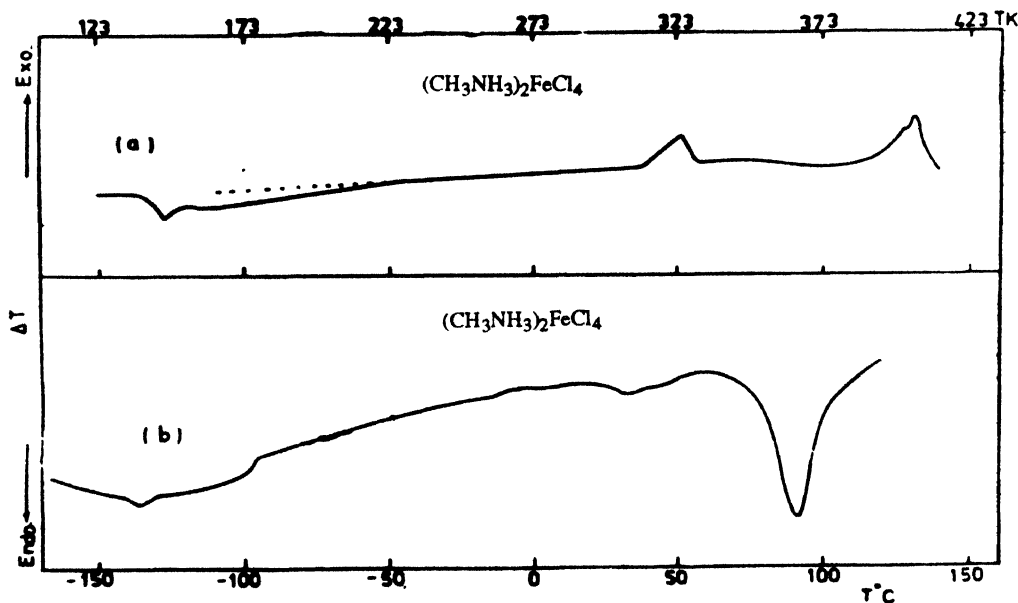
The DTA Results

Figure 3. The DTA results.

magnetic susceptibility data, with the transition temperature lying midway between the maximum and the minimum. Figure 2b is a typical curve for the high temperature phase transition in $(CH_3NH_3)_2FeCl_4$. The peaks resulting from the structural phase transition are

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not very strong, they vary between 6 and 10% above the average value of the susceptibility. A small peak appeared at ~328 K and a broad hump occurred at ~231 K. The third peak, found at ~150 K, is thought to be of magnetic origin.

The DTA spectrum (Figure 3) shows the structural phase transition supporting the susceptibility data. For the isotropic models, the theoretical argument predict the absence of ordering in the 2-d. Heisenberg and X-Y models [6,7]. In the presence of long-range order, the ideal 2-d Heisenberg and X-Y models behave as the linear chain model. There is, however, one fundamental difference between them indicated by the analysis of the high-temperature series expansion for the initial susceptibility in the limit $H \to 0$.

Rushbrooke and Wood [8] pointed out that the series expansion for 2-d non-isotropic lattices suggested the existence of finite temperature at which the magnetic susceptibility diverges just as the case of 3-d non-isotropic lattices where these temperatures are commonly identified with the transition to long-range order. Such identification can not be possibly made for the isotropic 2-d lattice [9].

In case of antiferromagnetic organic complexes, as studied here, a broad maximum in magnetic susceptibility due to the short-range order effects should be found at the high temperature whereas at $T = 0$, the susceptibility should attain a finite value.

Theoretical results :

The series expansion of paramagnetic susceptibility in powers of reciprocal temperature has been calculated [8] for arbitrary spins, and over a wide range of lattice structures, to sixth order terms for the nearest neighbor Heisenberg spin system. The series are valid for either sign of exchange parameter J, the sign changes in going from the ferromagnetic to antiferromagnetic system, causing the antiferromagnetic series terms to alternate in sign and the resulting susceptibility do not exhibit singularity at the phase transition temperature [10].

For the quadratic layer Heisenberg antiferromagnet with exchange Hamiltonian

$$H = \sum_{nn} JS_i \cdot S_j ,$$

(1)

where $\sum_{nn}$ runs over all pairs of nearest neighbor spins i and j, the simplest series (numerically) is that for reciprocal susceptibility χ^{-1} for which we find [1]

$$\frac{N^2 g \mu_B^2}{J\chi} = 3\theta + \sum_{n=1}^{\infty} \frac{C_n}{\theta^{n-1}} ,$$

(2)

where $\theta = kT / JS(S+1)$, g is the Landè g factor, μ_B the Bohr magneton, N the number of spins in the lattice and the values of the coefficients C_n calculated from the general formalism of Ref. [8], are displayed in Table 2.

For a certain value of the parameter J/k, the series expansion (2) determines the susceptibility χ as a function of the temperature T. A fitting program, based on the least square method and on an iteration numerical technique, was developed to determine the

Table 2. Coefficients C_n of series (2) for several different values of spin.

	$S = 1/2$	$S = 1$	$S = 3/2$	$S = 2$	$S = 5/2$
C1	4.0	4.0	4.0	4.000	4.000
C2	2.667	1.834	1.600	1.500	1.448
C3	1.185	0.445	0.304	0.252	0.228
C4	0.149	0.224	0.249	0.258	0.262
C5	–0.191	0.132	0.132	0.124	0.119
C6	0.001	0.019	0.013	0.015	0.017

Table 3. The calculated values of J/k for each complex using eq. (2).

Complex	Magnetic field Oe	J/k
$(CH_3NH_3)_2FeCl_4$	370.0	–54.6075
$(C_2H_5NH_3)_2FeCl_4$	1820	14.0795
$(C_3H_7NH_3)_2FeCl_4$	1820	92.6851
$(C_4H_9NH_3)_2FeCl_4$	1820	107.4030
$(C_3H_7NH_3)_2FeCl_4$	2400	99.8620
$(C_4H_9NH_3)_2FeCl_4$	370.0	113.1190
$(CH_3NH_3)_2FeCl_4$	1820	2.16455

values of J/k from best fitting to the experimental results of χ at different small magnetic fields over the temperature range ($T = 80–240$ K) for the compounds was shown in Table 3. The Mathematica package (version 2.2) was used for this purpose.

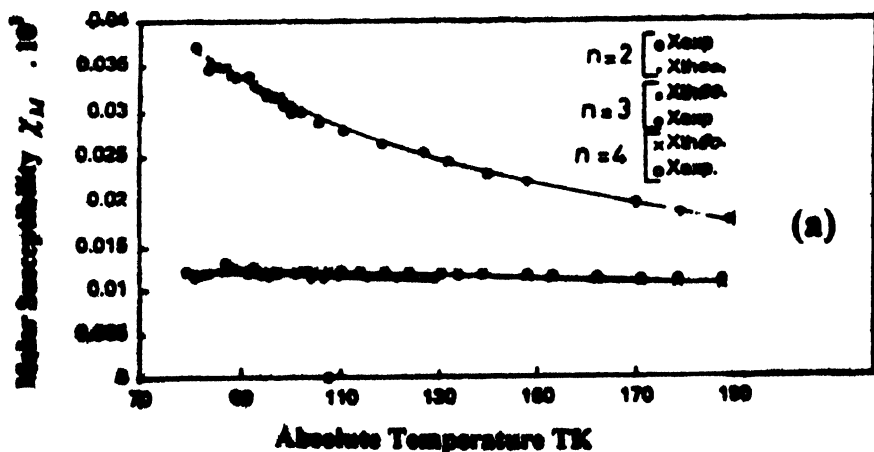**Figure 4.** (a) The experimental and theoretical results of the molar magnetic susceptibility χ_M for the complexes $(C_nH_{2n+1}NH_3)_2FeCl_4$, $n = 2$, 3 and 4

Figures 4(a–c) show the experimental and theoretical results for the susceptibility χ against the absolute temperature T. The figures exhibit that the best fit is obtained for the
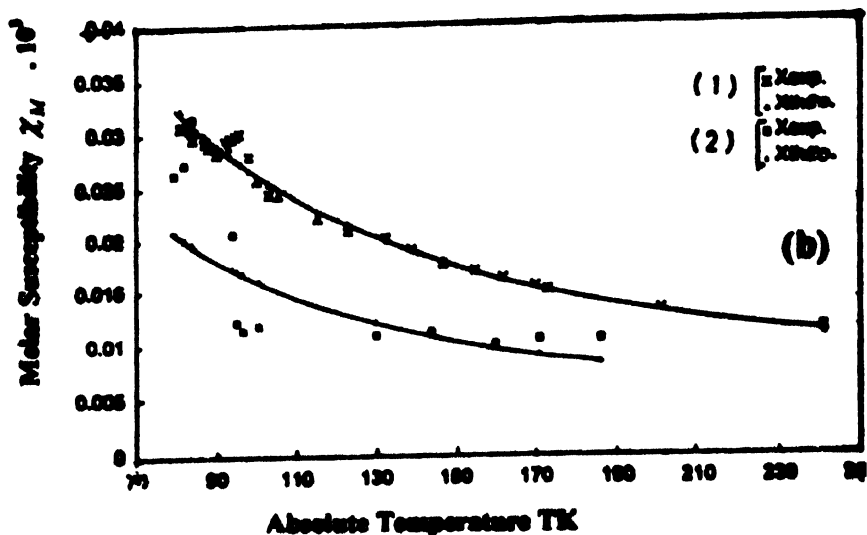

Figure 4. (b) Experimental and theoretical results of χ_M for (1) $(CH_3NH_3)_2FeCl_2Br_2$ at $H = 1820$ Oe and (2) $(CH_3NH_3)_2FeCl_4$ at $H = 370$ Oe.

complex of the smallest number of carbon atoms at magnetic field He = 1820 Oe, in the high temperature region.

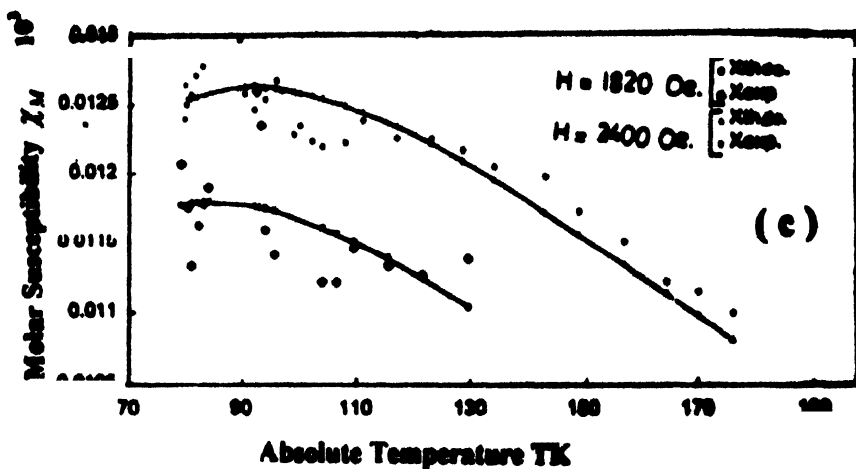**Figure 4.** (c) Experimental and theoretical results for the complex $(C_3H_7NH_3)_2FeCl_4$ at $H = 2400$ Oe and 1820 Oe.

4. Conclusions

(1) The value of J/k increases when the number of carbon atoms in the complex increases.

(2) The value of J/k decreases when the value of the applied magnetic field decreases.

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