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Magnetic susceptibility of antiferromagnetic nickel diglycine dihydrate*

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The magnetic susceptibility χ of nickel diglycine dihydrate has been measured between 0.6 and 120 K. The high-temperature data were taken in powder and follow a Curie law behavior with $\mu_{\text{eff}} = 3.189 \mu_B$ and an antiferromagnetic Curie temperature $T_c = 2.47$ K. At low temperatures the χ vs temperature curves for powder and oriented single crystals deviate from the Curie law; they show a maximum χ at about 2.21 K and an abrupt decrease at lower temperatures. The observed behavior of χ for nickel diglycine dihydrate indicates dominating antiferromagnetic interactions between Ni ions. A phase transition to an antiferromagnetic phase occurs below 2.2 K.

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INTRODUCTION

The chemical environment of the metal ions in metal derivatives of aminoacids is similar to that found in some proteins(1) and their study could be useful in learning more about the electronic structure and magnetic coupling between metal ions in these macromolecules.

In this paper we report measurements of the magnetic susceptibility χ in nickel diglycine dihydrate $[\text{Ni}(\text{NH}_2\text{CO}_2\text{CH}_2)_2 \cdot 2\text{H}_2\text{O}]$ in a wide temperature range.

The data were taken primarily in crystalline powders, but preliminary data in oriented single crystals are also presented. The susceptibility data show a transition of nickel diglycine dihydrate (NiDD) to an antiferromagnetic phase below 2.2 K; at higher temperatures single ion interactions are the most important. A detailed description of the magnetic properties of NiDD is not yet available and we use an effective molecular field model to discuss the experimental data.

EXPERIMENTAL DETAILS

Nickel diglycine dihydrate was synthesized as outlined by Stosick(2) and detailed by Sen et al (3). The material was purified by successive recrystallizations. Single crystals weighting about 10 mg were obtained by slow evaporation (typically two months) at room temperature from a water solution. Powder samples were obtained from the single crystals.

A Faraday magnetometer was used to measure χ between 0.6 K and 120 K. In this temperature range the diamagnetic corrections are relatively small. The magnetic susceptibility of the sample holder was subtracted from the data.

In single crystals, which cleave along the bc plane, we were able to identify the \bar{b} axis and measure χ in the \bar{b} , \bar{c} and $\bar{b}\bar{c}$ directions.

RESULTS AND CONCLUSIONS

The inverse molar susceptibility χ^{-1} vs. temperature T data for powdered NiDD are shown in Fig.1.

For $T > 20$ K the data follow a Curie law

$$\chi^{-1} = (T + T_c) / C \quad (1)$$

A least squares fit of Eq. (1) to the data in Fig. 1 gives $C = 1.269$ emu K/mole and a positive $T_c = 2.47$ K indicating that the antiferromagnetic interactions dominate. Using $\mu_{\text{eff}} = g(S(S+1))^{1/2} = (3kC/N)^{1/2}$, where N is Avodagro's number and $S=1$ for Ni^{2+} ions, we obtain the values $g=2.253$ and $\mu_{\text{eff}} = 3.186 \mu_B$ for the gyromagnetic factor and the effective magnetic moment. These values are expected for high spin octahedral compounds of Ni^{2+} reflecting the effect of the spin-orbit interaction on the crystal field levels of the ion(4).

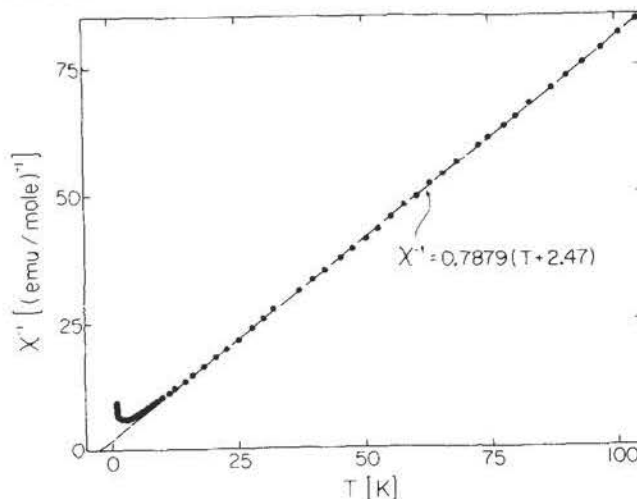


Figure 1: Inverse magnetic susceptibility χ^{-1} vs. temperature T for powdered NiDD. The solid circles are the experimental data and the solid line gives the best fit with a Curie law behavior.

The magnetic susceptibility χ vs. T data for powdered NiDD below 20 K is shown in Fig. 2. The data in this range were taken with a field of 1400 Gauss and were found to deviate from the Curie law behavior. The susceptibility shows a rounded maximum ($\chi=0.172$ emu/mole) around $T=2.2$ K, and an abrupt decrease of χ with decreasing T below 1.5 K, as expected for dominating antiferromagnetic interactions.

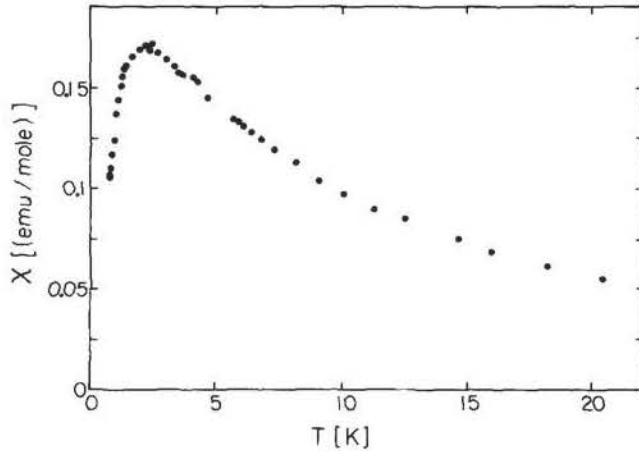


Figure 2: Experimental values for the magnetic susceptibility χ vs. temperature T for powdered NiDD.

We show in Fig. 3 the single crystal data taken below 20K for $H=1400$ Gauss along the \bar{b} , \bar{c} and $\bar{b}\bar{c}$

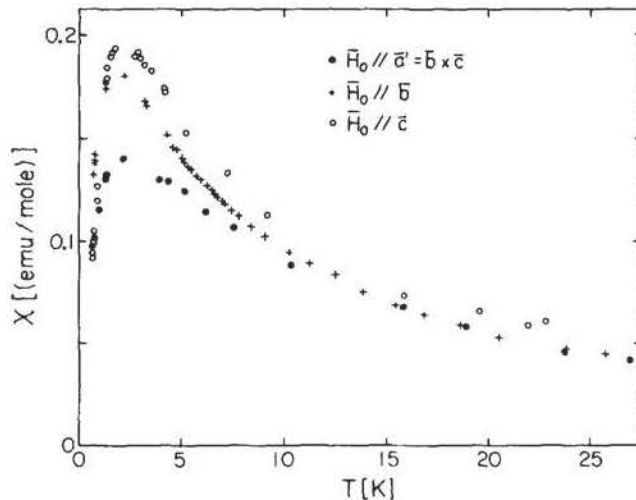


Figure 3: Experimental values for the magnetic susceptibility χ vs. temperature T for magnetic fields along the three crystal axes.

crystal directions. The susceptibility χ along these three directions shows a T dependence similar to that observed in the powdered samples; χ is similar along the \bar{b} and the \bar{c} directions, and it is smaller along the $\bar{b}\bar{c}$ direction. A measurement of the angular variation of χ has not yet been performed and therefore the principal directions of the susceptibility tensor for NiDD are not known.

The crystal structure of NiDD was first studied by Stosick(2) and recently refined by Castellano et al.(5). The space group is $P2_1/c$ with $a=7.616\text{\AA}$, $b=6.601\text{\AA}$, $c=9.651\text{\AA}$ and $\beta=63.48^\circ$, with two NiDD molecules in the unit cell. Each of the two equivalent (but rotated) Ni atoms in the unit cell is surrounded by two carboxyl oxygens, two ammine nitrogens and two water molecules, in a distorted octahedral coordination. The Ni atoms are in layers parallel to

the bc plane, each connected to the four nearest Ni atoms by strong hydrogen bonds. The magnetic interaction between nearest Ni atoms in the same plane is the strongest because the smaller interatomic distance and the existence of the strong hydrogen bond.

The Hamiltonian describing the magnetic properties of NiDD in the presence of an external magnetic field is

$$\mathcal{H} = \sum_{\substack{i=1,N \\ \lambda}} \bar{S}(i,\lambda) \cdot \bar{D}(\lambda) \cdot \bar{S}(i,\lambda) + \sum_{\substack{i=1,N \\ \lambda}} g\beta\bar{H} \cdot \bar{S}(i,\lambda) \\ + \sum_{\substack{i,i'=1,N \\ \lambda,\lambda'}} \bar{S}(i,\lambda) \cdot \bar{J}(i,\lambda,i',\lambda') \cdot \bar{S}(i',\lambda') \quad (2)$$

In Eq. (2), $\bar{S}(i,\lambda)$ is the spin of the Ni ion in the λ site of the i th unit cell, $\bar{D}(\lambda)$ is the fine structure tensor for Ni ions in the λ site and $\bar{J}(i,\lambda;i',\lambda')$ is the magnetic interaction between $\bar{S}(i,\lambda)$ and $\bar{S}(i',\lambda')$. We call $\lambda=A$ and $\lambda=B$ the two sites for Ni ions in the unit cell of NiDD. Specific heat measurements(6) on NiDD indicate a phase transition at $T_0=0.88\text{K}$ and a complex Schottky contribution which allows to obtain $D/k=-14.5\text{K}$ and $|E/k|=1.13\text{K}$ for the principal values of the tensors $\bar{D}(\lambda)$. The principal directions of $\bar{D}(\lambda)$ are not known and the crystal data give no reason to assume that they are the same for both Ni atoms in the unit cell.

A simple molecular field model has been used to analyze the effect of the last term of Eq. (2). The crystal data on NiDD discussed above suggest a two sublattice model, where each sublattice is identified with one of the Ni atoms in the unit cell. Even if the identification of the magnetic sublattices is different from that given by Berger and Friedberg(7) to explain their data in nickel nitrate dihydrate, the algebra involved in our calculations is very similar to theirs. Then the magnetic field acting on the Ni ions in the A and B sublattices is replaced in Eq. (2) by

$$\bar{H}_A = \bar{H} - n_1 \bar{M}_B - n_2 \bar{M}_A \quad \text{and}$$

$$\bar{H}_B = \bar{H} - n_1 \bar{M}_A - n_2 \bar{M}_B$$

where \bar{H} is the external field, \bar{M}_A and \bar{M}_B are the A and B sublattice magnetizations and n_1 and n_2 the molecular field parameters(7). The calculation given by Berger and Friedberg has been extended in order to introduce the effect of the non axial spin Hamiltonian parameter E which is non-zero for NiDD (6). In our calculation we have assumed $\bar{D}(\lambda)$ diagonal and equal for both Ni ions in the unit cell of NiDD.

Using the value of T_0 given above, and the values of T_0 , D/k and $|E/k|$ obtained from the specific heat data(6), we obtained $n_1=1.34$ and $n_2=0.62$ for the intersublattice and intrasublattice molecular field constants, respectively. These values of n_1 and n_2 would indicate antiferromagnetic coupling between nearest and next neighbors in NiDD. This result is qualitatively different from that obtained for nickel nitrate dihydrate(7) where there is a ferromagnetic interaction within each layer of Ni ions and a weaker antiferromagnetic coupling between layers. The values of χ calculated for powder and oriented single crystals of NiDD using this model are in poor agreement with the experimental data particularly below 5K. The reasons for this disagreement are, probably, the fact that the effective field model neglects any effect originating in short range order and also because we are not considering that the tensors $\bar{D}(\lambda)$ are not di-

agonal and are rotated for the two Ni ions in the unit cell of NiDD. It seems that a theory that consider the different orientations of D(A) and D(B), and a less simplistic magnetic structure of NiDD is needed to explain the data. Paramagnetic resonance measurements of the Ni²⁺ ions and neutron diffraction studies of the ordered phase would be useful for this purpose.

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