Despite the fact that Pro restricts the conformation space of its predecessor to extended conformations, its incorporation in an L-Ala-type chain raises K_x significantly due to the accessibility of more compact conformations for Pro. The successful synthesis of the decapeptide antamanid,[22] which contains four Pro residues, is therefore not an unexpected result.

The general agreement between theoretical predictions of the propensity for cyclization and the experimental evidence indicates that the density distribution $W(0)$ of the end-to-end distance r and the angular correlation factor $2\Gamma_0(1)$ are major factors in determining K_x. It should be emphasized that our results were obtained by assuming a random-coil conformation of the peptide chain, precipitated by short-range interactions only. Departures from our predictions for the cyclization tendency of polypeptides are expected when the experimental conditions chosen for the cyclization step are such that long-range interactions, e.g. conditions which enhance the onset of a secondary structure, are no longer negligible.

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Communications to the Editor

Single-Crystal Susceptibilities of an $S = \frac{3}{2}$ Iron(III), Insulating Ferromagnet

Sir:

Several studies[1,2] have been reported recently on the molecules $Fe(X)(S_2CNR_2)_2$ where X is a halogen and R is an alkyl group. These molecules are of interest because, as a result of their tetragonal pyramidal geometry, with C_{2v} symmetry at the iron site, they are among the few examples of a spin $\frac{3}{2}$ ground state for trivalent iron. The most extensively studied example, $Fe(Cl)[S_2CN(C_2H_5)_2]_2$, hereafter $Fe(dtc)_2Cl$, crystallizes in space group $P2_1/c$ and has a geometry in which the chlorine atom is at the apex of the pyramid and the iron atom is at the centroid, 0.62 Å above the plane of the four sulfur atoms of the dithiocarbamate ligands.[3] This particular example of this series of molecules is especially interesting because it has been reported as ordering ferromagnetically at 2.43 K.[2] Further significance attaches to $Fe(dtc)_2Cl$ in that, on the basis of the present measurements, and measurements in the critical region, this substance appears to be one of the very few examples of a three-dimensional Ising ferromagnet.

We have measured the magnetic susceptibility along the three principal axes in single crystals of $Fe(dtc)_2Cl$ using the near-zero-field mutual inductance method. The crystal structure is monoclinic and therefore the b axis, [010], must be the direction of one of the principal axes. Careful measurements along various directions in the ac plane revealed that the other two principal axes, of maximum and minimum susceptibility in this plane, were, within an experimental uncertainty estimated to be 2°, respectively, along the [101] direction and along the direction normal to [010] and [101], that
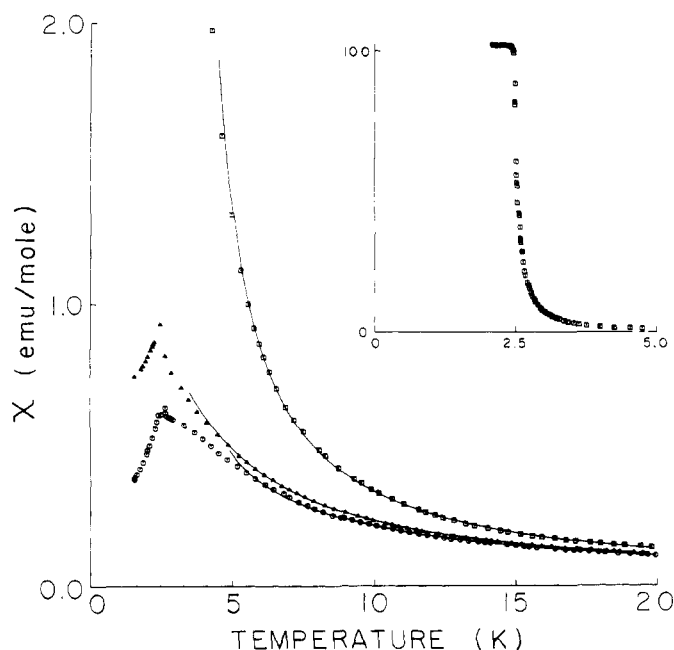

Figure 1. The three principal crystal magnetic susceptibilities of Fe-(dtc)$_2$Cl. Circles, triangles, and squares are experimental data along the [010], (10$\bar{1}$), and [101] axes, respectively. The curves are the best fits to the data with the parameters given in the text. The inset shows the susceptibility in the [101] direction at low temperatures; these data were obtained using a 1-mg crystal and have not been corrected for demagnetization.

is the direction normal to the (10$\bar{1}$) plane. These results, corrected for demagnetization, appear in Figure 1. The susceptibility along the [101] direction increases very rapidly with decreasing temperature until, just below 2.47 K, it attains an

approximately constant value of 102 emu/mol. This leveling behavior is typical of ferromagnetic systems where the susceptibility is limited by a demagnetizing field and has been observed previously.[4,5]

In fitting parameters in a theoretical model to the data the procedure was as follows. The eigenvalues of a spin Hamiltonian appropriate to an ion of spin $3/2$ in C_{2v} symmetry were employed[6] in order to write the partition function for the $^4A_2$ (ground) state. From this, expressions for the principal magnetic susceptibilities of a single molecule were derived. From the molecular symmetry it might be assumed that the directions of the principal molecular susceptibilities χ_x and χ_y would be parallel and perpendicular to the major axis (long side) of the rectangle of four sulfur atoms from the ligands, and parallel to the plane of these sulfur atoms. The χ_z direction would then be normal to this plane, within 1° of the Fe-Cl axis. The orientations of the molecules in the crystal lattice are known, and the crystal magnetic susceptibility in different directions can be calculated. By fitting single ion spin Hamiltonian parameters D, E, g_x, g_y, and g_z, and a molecular field correction for exchange[6-8] due to z neighbors, zJ, to the data from all three crystal directions simultaneously, excellent agreement between observed and calculated susceptibilities was obtained. However, the parameters D/k and E/k assumed the values 2.63 and -1.35 K, respectively. Since $|E/D| > 1/3$ it is known that a better choice of molecular principal axes can be found.[9,10] By taking the molecular z axis to be parallel to the major axis of the rectangle of sulfur atoms, with the x axis also parallel to the plane of the sulfur atoms and with the y axis normal to this plane, the following parameters resulted from a least-squares fit to the data in the 5–20 K range: $D/k = -3.32 \pm 0.05$ K, $E/k = -0.65 \pm 0.05$ K, $g_x = 2.09 \pm 0.05$, $g_y = 2.10 \pm 0.05$, $g_z = 2.12 \pm 0.05$, and $zJ/k = 0.81 \pm 0.05$ K. The indicated uncertainties are conservative estimates and take into account possible systematic errors in our measurements. The root-mean-square deviation in the susceptibilities is 1.0%, the same as it was with the previous choice of molecular axes. With $|E/D|$ now smaller, the mixing of the $|\pm 3/2\rangle$ and $|\mp 1/2\rangle$ Kramers doublets is minimized, and therefore this choice of quantization axes is preferred. We observe that our choice of molecular principal axes is consistent with the measured principal crystal susceptibilities from another point of view. The only off-diagonal element of the crystal susceptibility tensor which does not vanish by symmetry is calculated to be no more than 2%, and usually less depending on the temperature, of any of the diagonal elements. Possible misorientations of the molecular principal axes do not exceed 2°. The solid lines in Figure 1 are the calculated susceptibilities along the principal axes of the crystal susceptibility.

The present results are in general agreement with the findings of Wickman et al.[2] Mössbauer spectra were interpreted to mean that D was negative and that the z axis of the crystal field interaction was essentially parallel to the internal exchange field. The latter was found to be approximately parallel to the major axis of the rectangle of the four sulfur atoms, although fairly large uncertainties in relative orientations among various axis systems referred to in the analysis of the Mössbauer data were present. A consideration of the crystal structure reveals that there are two symmetry related pairs of molecules in the unit cell, the members of each pair being related by inversion and therefore equivalent with respect to magnetic measurements. However, the two pairs are not equivalent; their axes are cocked with respect to one another. In particular, the z axes of the two kinds of molecules are separated by 41.4°, which is twice the angle between either z axis and the crystal direction [101], determined by us to be that of maximum susceptibility. If Wickman's finding that the spin polarization of a single molecule is along z is correct, this implies that intrasublattice exchange (where all equivalent

pairs of one type or the other form a sublattice) is stronger than intersublattice exchange. This can be further tested by measurements of the magnetization in the ordered state. Wickman et al.[2] estimated a value of zJ/k equal to 0.60 K. Our value, 0.81 K, is similar and the sign is ferromagnetic.

On the other hand, Ganguli et al.[11] deduced the parameters $D/hc = 1.12$ cm^{-1} and $E/hc = -0.78$ cm^{-1} from measurements of the anisotropy in the susceptibility at and above 77 K. The choice of molecular axes was that first mentioned in this communication, with z normal to the plane of sulfur atoms. The zero-field splitting between the $|\pm 1/2\rangle$ and $|\pm 3/2\rangle$ states is $\delta = 2(D^2 + 3E^2)^{1/2}$. Using the parameters of these authors one obtains $\delta/hc = 3.51$ cm^{-1} or $\delta/k = 5.05$ K. Our value for the zero-field splitting is 7.01 K. Far-infrared measurements[12] revealed an absorption at 3.85 cm^{-1} or 5.54 K for a powder sample at 1.3 K. The identification of this absorption with the zero-field splitting is not completely clear, because of the effect of the exchange field in the ordered state. At a sample temperature of 4.2 K a broad absorption in the 2.5–5-cm^{-1} region was observed, which includes the zero-field splitting deduced by us (4.87 cm^{-1}). Ganguli and coworkers have not specified clearly their conclusions as to the direction of the principal axes of the crystal susceptibility.

The extremely large anisotropy in the susceptibility observed by us seems consistent only with Ising-like interactions.[13] It has been suggested[2,13] that such interactions might be expected where, with $D < 0$, the $|\pm 3/2\rangle$ Kramers doublet is lower in energy. Preliminary but very promising fits to the susceptibility data along [101] between 2.50 and 3.00 K support the idea that the exchange interactions are Ising like. In the expression for the magnetic susceptibility in the critical region, $\chi T/C = A(1 - T_c/T)^{-\gamma}$, the exponent γ is predicted by theory to be 1.25 for an Ising ferromagnet.[14] We obtain a value for γ below this in fitting our data to this form. The details of this procedure will appear elsewhere. At present we are also studying the heat capacity of this system to further probe the nature of the magnetic ordering.

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