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Susceptibility of $[\mathrm{Fe(C_5H_5NO)_6}](\mathrm{ClO_4})_2$, an $S=\frac{1}{2}$, simple-cubic Ising antiferromagnet

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The susceptibility of polycrystalline $[\mathrm{Fe(C_5H_5NO)_6}](\mathrm{ClO_4})_2$ is reported over the temperature interval 40 mK–4.2 K. The observed transition temperature is 700 ± 10 mK, and the data have been analyzed above 720 mK according to the high-temperature series expansion for the $S=\frac{1}{2}$, simple-cubic Ising antiferromagnet. The fit is excellent, and the parameters resulting are $\langle g\rangle = 5.38 \pm 0.05$ and $J/k = -0.34 \pm 0.02$ K. The experimental procedures are also described in detail.

A continuing interest in studying good examples of magnetic model systems has prompted us to measure the susceptibility of $[\mathrm{Fe(C_5H_5NO)_6}](\mathrm{ClO_4})_2$. This system has been shown[1] to be one of the few good examples of the superexchange-coupled $S=\frac{1}{2}$, simple-cubic Ising model of an antiferromagnet. The ligand $\mathrm{C_5H_5NO}$ is pyridine N-oxide, and the system is a member of the large class of isostructural molecules $[M(\mathrm{C_5H_5NO})_6]X_2$, where $M=$ Mn,[2] Fe,[1] Co,[3–6] Ni,[7–9] or Cu,[10] and X can be fluoborate, perchlorate, or nitrate. All of these systems order in interesting fashion at low temperatures.[11] The crystal structure of $[\mathrm{Fe(C_5H_5NO)_6}]$ $(\mathrm{ClO_4})_2$ has recently been reported in detail.[12] The coordination sphere is a regular octahedron.

The magnetic-energy-level scheme of $[\mathrm{Fe(C_5H_5NO)_6}](\mathrm{ClO_4})_2$ was first deduced by Sams and Tsin[13] from Mössbauer data on polycrystalline samples, which suggested that the magnetic properties should be describable in terms of an effective-spin $S=\frac{1}{2}$ ground-state doublet, with the highly anisotropic splitting factors $g_{\parallel}=9.0$ and $g_{\perp}\simeq 0.6$. These are best-fit parameters to a model based on slow spin-lattice relaxation. The next-higher-lying energy levels were estimated to be at least 170 K above the ground-state doublet, so that they will not be appreciably populated at temperatures below 4.2 K. Thus, an effective-spin $S=\frac{1}{2}$ Ising Hamiltonian $\mathcal{H} = -2J\sum_{i,j} S_{iz}S_{jz}$ should be appropriate for this compound. Indeed, the measured specific heat[1] shows that magnetic ordering occurs at $T_c = 0.719 \pm 0.003$ K, and the data are well fitted by the predictions for the simple-cubic, $S=\frac{1}{2}$ Ising model with $|J/k_B| = 0.32 \pm 0.01$ K. We report here measurements of the zero-field susceptibility of this polycrystalline material and a data analysis according to the same Ising model. The experimental procedures are also described in detail.

EXPERIMENTAL

The compound was prepared in the standard fashion.[14] The measurements below 1 K were made on a powdered sample weighing 103 mg, corresponding to 1.25×10^{-4} mole.

Temperatures down to 40 mK could be obtained by using a S.H.E. Corp. model DRI-40/4000 ^{3}He- ^{4}He dilution refrigerator.

The complex differential susceptibility has been measured from the change in the mutual inductance between a primary and secondary coil brought on by a change in the magnetization of the sample. The detection of changes in the mutual inductance is achieved by using a low-impedance ac bridge in which a superconducting quantum interference device (SQUID) is employed as a null detector. The system consists of a SQUID probe (model MFP/MFPC), a SQUID control unit (model 30), a bridge unit (model RBU), and a two-phase null indicator (model BPD), which are all obtained from the S.H.E. Corporation. The sample is located on the axis of the coil system, within one-half of the secondary coil (Fig. 1). The two halves of the secondary coil are equal, but wound in opposite direction on a glass tube with an outer diameter of 10 mm. They consist each of 16 turns of niobium-titanium wire of diameter 0.13 mm. The primary coil is wound around the secondary ones and is made of 389 turns of the same niobium-titanium wire. A layer of coil foil has been put between the secondary and primary coils in order to provide a good internal thermal equilibrium of the coil system, without introducing disturbing eddy currents. The

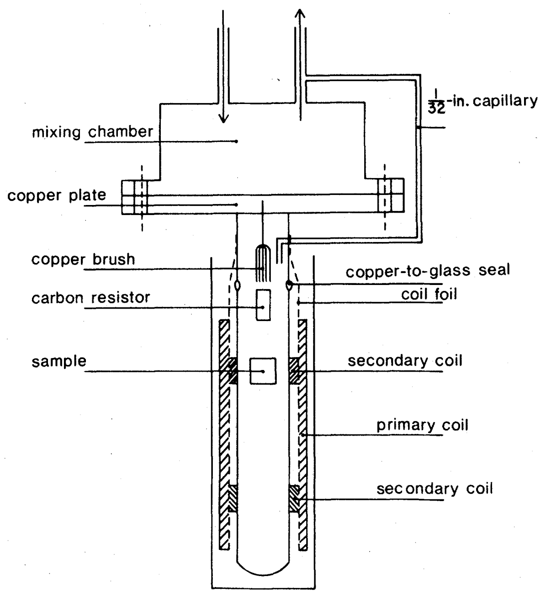

FIG. 1. Experimental arrangement (schematic).

excitation voltage obtained from an internal oscillator in the RBU bridge can be operated at four different frequencies: 16, 32, 80, and 160 Hz. The measurements presented below were all obtained using a frequency of 16 Hz. The maximum excitation current through the primary coil amounts to 0.2 mA, leading to a maximum oscillating field of 10 mOe. In order to minimize system noise the entire coil assembly and SQUID system are surrounded with a superconducting niobium shield.

The thermal contact between the mixing chamber and the sample is achieved in the following way. A copper block is bolted to the copper bottom of the mixing chamber, with Apiezon grease in between to ensure good thermal contact, as shown schematically in Fig. 1. The upper part of the sample chamber, made of a $\frac{3}{8}$-in. copper tube, is soldered with Wood's metal to the copper piece. A commercial copper-to-glass seal connects the copper part to the glass tube on which the coil system is wound. The sample chamber tube is filled with ^{3}He-^{4}He solution, so that a good thermal contact between the sample and the copper piece is achieved. The solution is admitted to the sample chamber through a $\frac{1}{32}$-in. o.d. copper-nickel capillary running between the dilute outlet of the mixing chamber and the copper tube of the sample chamber (see Fig. 1). A copper brush, hard soldered to the copper piece, is used to improve the thermal contact between the copper piece and the solution. The sample is placed on a Delrin holder in such a way that it is exactly in the center of the upper secondary coil.

The temperature of the sample is determined from the resistance of a calibrated germanium thermometer. The resistance is measured with a self-balancing, four-terminal, ac conductance bridge with direct digital readout (model PCB, SHE) operating at 27.5 Hz. The thermometer is located at the outside of the mixing chamber. The temperature of the mixing chamber is controlled by comparing the resistance value of the thermometer with a preset value. The temperature controller (model ATC, SHE) supplies a current to a heater that is also mounted on the mixing chamber. The current changes in such a way that the resistance of the thermometer remains equal to the preset value. A second thermometer was installed inside the sample chamber to monitor temperature changes.

Before beginning the susceptibility measurements we checked the thermal contact between the thermometers and the sample. This was done by measuring the zero-field susceptibility of cerium magnesium nitrate (CMN), which follows Curie's law down to the millikelvin region.[15] A straight line was found by plotting the susceptibility versus the inverse temperature. Small deviations from this linear dependence occurred below 100 mK amounting to 4 mK at the lowest temperature of 40 mK. Corrections have been made to account for this temperature gradient between sample and thermometer. Furthermore, measurements were performed without a sample to obtain the baseline. Down to 100 mK the baseline appeared to be flat, while a small increase in the signal was observed at lower temperatures.

In order to check our experimental procedures, we first measured the susceptibility of single crystals of Cs_3CoCl_5. These data have been reported earlier,[16] and we found good quantitative agreement with the reported data over the whole temperature range.

The data are converted from bridge readings to susceptibility values (in emu/mole) by matching the data between 1 and 2 K with data obtained independently in a liquid-^{4}He apparatus.

RESULTS AND DISCUSSION

The measured susceptibility of polycrystalline $[Fe(C_5H_5NO)_6](ClO_4)_2$ is displayed in Fig. 2. It was found not necessary to correct the data for a temperature dependence of the baseline; however, a correction had to be made for a small amount of paramagnetic impurity (probably Fe^{3+}). Samples used for the heat-capacity measurements[1] were also found to contain an impurity. The impurity contribution below 200 mK could be fitted to a Curie-Weiss law with $C = 0.075$ emu K/mole and $\theta = -80$ mK. Since the sample as a whole is found to have a Curie constant of about 2.71 emu K/mole, the contribution of the impurity in the temperature range $T > 0.5$ K is very small. The corrected data are displayed in Fig.

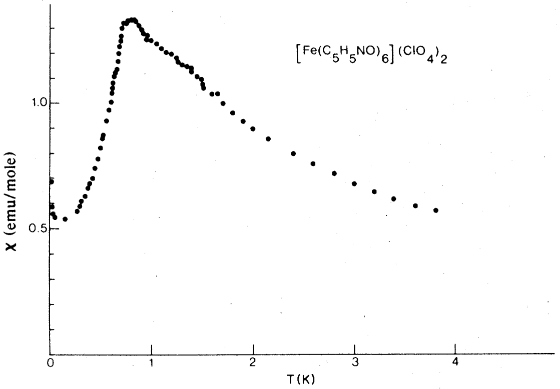

FIG. 2. Measured susceptibility of polycrystalline $[\mathrm{Fe(C_5H_5NO)_6}](\mathrm{ClO_4})_2$.

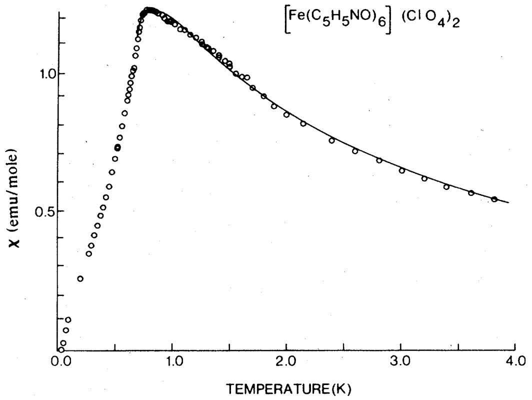

FIG. 3. Corrected susceptibility of polycrystalline $[\mathrm{Fe(C_5H_5NO)_6}](\mathrm{ClO_4})_2$. The points are experimental, while the curve is the fit described in the text.

3. No absorption (χ'') was observed in the susceptibility measurements.

The present experiments were made on powdered samples, since the growth of large enough single crystals proved to be very difficult. Nevertheless, the powder data will be representative for the parallel susceptibility, because of the extreme anisotropy in the expectation values for the ground doublet. For the Ising model one expects[17] that the theoretical $\chi_\perp$ is at most a factor of 2 larger than $\chi_\parallel$ in the region above T_c. The Mössbauer results[13] for the g tensor can be summarized as $g_\parallel = 9.0 \pm 1.0$ and $g_\perp = 0.8 \pm 0.4$ (giving a powder value $\langle g \rangle = 5.2 \pm 0.6$). Since the contributions of $\chi_\perp$ and $\chi_\parallel$ to the powder susceptibility $\chi_p = \frac{1}{3}\chi_\parallel + \frac{2}{3}\chi_\perp$ have to be scaled by their respective g values squared, this implies that $\chi_\perp$ will only contribute at most a few percent to χ_p in the region above T_c. In our case the maximum in $\chi_\parallel$ amounts to about 1.25 emu/mole. Taking into account the factor $g_\parallel^2/g_\perp^2 \simeq 200-400$ the maximum contribution to χ_p from $\chi_\perp$ is estimated as 0.01–0.03 emu/mole. Below T_c, $\chi_\parallel$ will decrease to zero for $T \rightarrow 0$, leaving eventually $\chi_\perp$ as the only contribution. This contribution, together with the Van Vleck TIP-term plus the uncertainty in the baseline are all extremely small compared to $\chi_\parallel$ at the maximum. These corrections are all taken into account by the subtraction for the impurity contribution plus the subtraction of a temperature-independent baseline. In the region $T > T_c$, therefore, we may safely compare the experimental powder susceptibility to the theoretical predictions for the parallel susceptibility.

The ordering temperature obtained from the point of maximum slope in the χ-vs-T curve is 700 ± 10 mK, which agrees well with the result obtained from specific-heat measurements. The data above 720 mK have been fitted using the calculations for the parallel susceptibility of the $S = \frac{1}{2}$, simple-cubic Ising antiferromagnet.[18] The result provided by Sykes *et al.* can be written

$$\begin{aligned}\chi = (C/T)(1 &+ 6v + 30v^2 + 150v^3 + 726v^4 + 3510v^5 + 16\,710v^6 + 79\,494v^7 + 375\,174v^8 + 1\,769\,686v^9 \\ &+ 8\,306\,862v^{10} + 38\,975\,286v^{11} + 182\,265\,822v^{12} + 852\,063\,558v^{13} + 3\,973\,784\,886v^{14} \\ &+ 18\,527\,532\,310v^{15} + 86\,228\,667\,894v^{16} + 401\,225\,391\,222v^{17} + \cdots)\ ,\end{aligned} \tag{1}$$

where $v \equiv \tanh(J/2k_BT)$ and C is the Curie constant for $S = \frac{1}{2}$.

We have recast this equation as its inverse for the data analysis. The sign alteration for the antiferromagnetic case is thereby removed, and the convergence of the series becomes more apparent. The result is written

$$\begin{aligned}(1/\chi) = (T/C)(1 &- 6v + 6v^2 - 6v^3 + 30v^4 - 54v^5 + 318v^6 - 726v^7 + 3726v^8 - 9718v^9 \\ &+ 49\,974v^{10} - 139\,974v^{11} + 728\,022v^{12} - 2\,145\,990v^{13} + 11\,216\,718v^{14} - 34\,399\,650v^{15} \\ &+ 180\,217\,158v^{16} - 569\,546\,400v^{17} + \cdots)\end{aligned} \tag{2}$$

and the data have been fitted by this equation as illustrated in Fig. 3 with the resulting parameters $\langle g \rangle = 5.38 \pm 0.05$

and $J/k_B = -0.34 \pm 0.02$ K. The agreement with the earlier results is excellent. We note that the sign of the exchange constant could not be determined from the specific-heat measurements, but that the present results leave no doubt about the antiferromagnetic sign of the interaction between the nearest magnetic neighbors. We conclude that $[Fe(C_5H_5NO)_6](ClO_4)_2$ does indeed provide an excellent example of the three-dimensional, $S = \frac{1}{2}$ Ising antiferromagnet.

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