MOSSBAUER STUDY OF AN INTRAMOLECULAR ANTIFERROMAGNET

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ABSTRACT

Mossbauer measurements at $4.2 \leq T \leq 22$ K and $0 \leq H_0 \leq 80$ kOe are reported in (Fe Salen Cl)$_2$, a molecular complex containing two coupled Fe^{3+} ions bridged by oxygen atoms. At 4.2 K only the ground state with effective spin $S = 0$ is appreciably populated. Analysis of the magnetic field and temperature dependence of the magnetic hyperfine field yields an exchange constant $J = -6.7$ cm^{-1} and a hyperfine field of -192 kOe per unit spin at each Fe^{3+} nucleus.

In certain transition metal complexes, the paramagnetic ions are situated so that two or more of them cluster close to each other, but the clusters are relatively well isolated from each other. Such systems are found in nature, for example, in certain biologically important enzymes.[1,2] The paramagnetic ions within such clusters can interact strongly with each other and the interactions between clusters will be relatively very weak. We may speak then, of intramolecular magnetism.[3] Such situations are also of interest because they provide the possibility of studying exchange interactions in finite systems. The simplest model for such a system is to consider the paramagnetic ions to interact via the classical exchange Hamiltonian

$$\mathcal{H}_{ex} = -2 \sum J_{ij} \vec{S}_i \vec{S}_j , \qquad (1)$$

where the sum is taken over all pairs of interacting ions within a cluster. In the simplest case of two interacting ions, the energy levels are simply

$$E(S) = -JS(S + 1) \qquad (2)$$

with $\vec{S} = \vec{S}_1 + \vec{S}_2$, where $\vec{S}_1$ and $\vec{S}_2$ are the angular momenta of the two coupled paramagnetic ions. If the ions are identical and the interaction is antiferromagnetic $(J < 0)$ the ground state will have $S = 0$, i.e., will be a singlet state. In contrast to antiferromagnets such as MnO, this a true
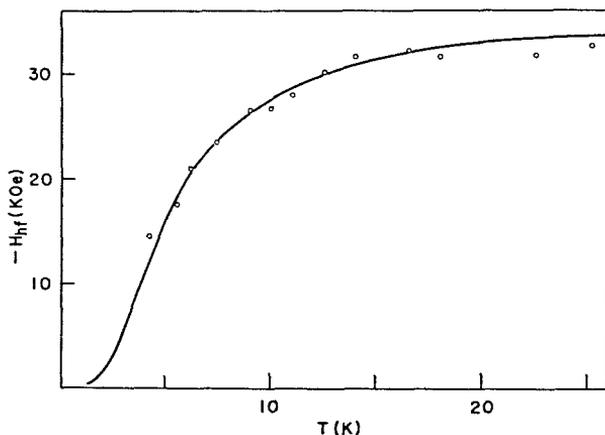
Fig. 2. Hyperfine field H_{hf} plotted as a
function of T for H_O = 80 kOe. The solid
curve is theoretical (Eq. (3)) with J = - 6.7 cm^{-1}
and h(1) = - 96 kOe.

A representative spectrum is shown in Fig. 1. In Fig. 2 we plot the hyperfine field is a function of temperature for H_O = 80 kOe. Note that the observed temperature behavior, increasing $|H_{hf}|$ with increasing T is opposite to that observed in simple paramagnetic systems. $|H_{hf}| \to 0$ as $T \to 0$ in our case because at low temperature only the S = 0 state is appreciably populated and $H_{hf} = A \langle S_z \rangle$ where $\langle S_z \rangle$ is the expectation value for the z component of the total spin for the pair of atoms. As the temperature is increased population of the S = 1 and higher S states with non equal populations of the various S_z substates leads to a non zero value of H_{hf}. Assuming that relaxation between the electronic states is fast with respect to the Larmor precession time, we can write

$$H_{hf} = \frac{\sum\limits_{S=0}^{5} \sum\limits_{S_z=0}^{S} h(S, S_z) \exp\{-[JS(S+1) - S_z g\mu_B H_o]/kT\}}{\sum\limits_{S=0}^{5} \sum\limits_{S_z=-S}^{S} \exp\{-[JS(S+1) - S_z \mu_B H_o]/kT\}} \qquad (3)$$

where $h(S, S_z)$ is the hyperfine field corresponding to the state $|S, S_z\rangle$ and we have taken g = 2. We note that $h(S, S_z)$ is proportional to S_z with same proportionately constant for all the S states and so we can choose one parameter h(1) to characterize the system, where $h(S, S_z) = h(1)S_z$.

The solid lines in Fig. 2 represent a least squares fit of Eq. (3) to the experimental data yielding J = -6.7 cm^{-1} and h(1) = - 96 kOe. The hyperfine field h(1) obtained from the experimental data may be compared with

singlet ground state with $\vec{S}(\text{Total}) = 0$.

We report a study using the Mossbauer effect of $(\text{Fe Salen Cl})_2$, where salen = N, N′ ethylenebis-(salicylaldiminato). The structure of the material has been determined by x-ray analysis[4] and has two Fe^{3+} ions bridged by a pair of oxygen atoms. The temperature dependence of the magnetic susceptibility can be interpreted in terms of the model outlined above, with $S_1 = S_2 = \frac{3}{2}$ and $g = 2$, and with $J = -7.5$ cm^{-1}.[5,6] Our measurements were made with a powder sample over the following ranges of temperature and external magnetic field: $4.2 \leq T \leq 22$ K and $0 \leq H_0 \leq 80$ kOe. The presence of a fairly large quadrupole splitting ($\Delta E_Q = 1.34$ mm/s at 4.2 K) made the spectra obtained in a magnetic field rather complicated, but we were able to extract the significant parameters by analyzing the data with a computer program due to Singh and Hoy,[7] modified by us to reproduce powder spectra. In the analyses we obtained satisfactory fits by holding ΔE_Q to be independent of H_0 and thus obtaining the field at the nucleus, H_n. This is related to the hyperfine field H_{hf} by $H_n = H_0 \pm H_{hf}$. From our data we determined that H_{hf} was negative at all fields and temperatures.

Mossbauer effect studies in this system have been reported previously.[8,9] Buckley et al.[8] made powder measurements in external fields up to 90 kOe at 4.2 K. Our spectra at 4.2 K are similar to theirs, but the interpretations are different. They claim that at 90 kOe the field at the nucleus is 85 ± 6 kOe, but they do not give details of their analysis. At 4.2 K and $H_0 = 80$ kOe our analysis yields $H_n = 65 \pm 2$ kOe.
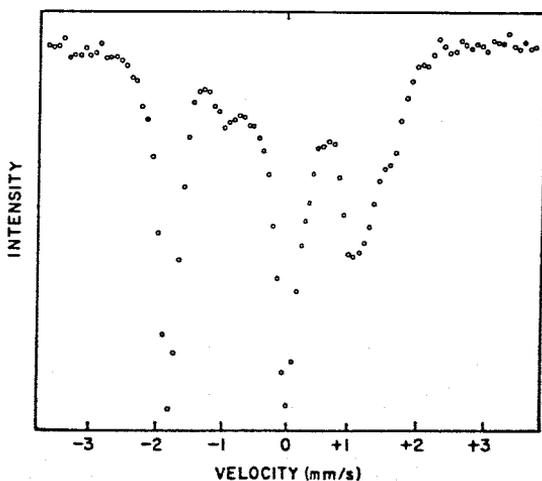

Fig. 1. Mossbauer spectrum of $(\text{Fe Salen Cl})_2$ at 4.2 K and 80 kOe, with H_0 longitudinal.

values of the Fe^{3+} hyperfine field in other systems by simply projecting the $|S, S_z\rangle$ representation onto the $|S_1, S_2; S_{1z}, S_{2z}\rangle$ representation where S_1 and S_2 are the spins on ions 1 and 2 respectively. In the case at hand $S_1 = S_2 = \frac{5}{2}$ and for the $S = 1$, $S_z = +1$ substate we obtain $\langle S_{1z}\rangle = \langle S_{2z}\rangle = \frac{1}{2}$, and hence we obtain -192 kOe per unit spin. This compares with the usual value of $-550 \div \frac{5}{2} = -220$ kOe per unit spin observed in many ionic Fe^{3+} compounds. The difference may be reasonably ascribed to covalency.

We conclude that Mossbauer spectroscopy is a useful and convenient tool for studying intramolecular antiferromagnets such as (Fe Salen Cl)$_2$. We have seen that the data can be anlyzed in terms of a simple molecular exchange model (Eq. (1)) yielding a value for the exchange constant J which is in fair agreement with the value obtained from susceptibility data taken above 22 K.

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