PROTON SPIN-LATTICE RELAXATION IN IRON FLUOSILICATE

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Received 10 January 1974

Proton T_1 of $FeSiF_6 \cdot 6H_2O$ is proportional to $\exp(\Delta/kT)$ at liquid helium temperatures, with $\Delta \approx D - 3E$. We find the crystal field splitting of the Fe^{2+} ion in this salt to be $D = (12.2 \pm 1.0)\ \mathrm{cm}^{-1}$ using $E = 0.54\ \mathrm{cm}^{-1}$.

The paramagnetic properties of ferrous salts follow from the spin Hamiltonian

$$H = \beta H_0 \mathbf{g} S + D(S_z^2 - S(S+1)/3) + E(S_x^2 - S_y^2) \qquad (1)$$

with $S = 2$ for Fe^{2+} ions. If the crystal field splitting D is positive, the susceptibility χ_z goes to zero at low temperature $T \ll D/k$ since the only populated state is then the nonmagnetic singlet $|0\rangle$. The electron moments must fluctuate to act as relaxation centers for the nuclear spins. Hence we expect the nuclear relaxation rate in such a salt to go to zero as

$$1/T_1 \approx \sum_n C_n \exp(-\Delta_n/kT) = \sum_n C_n b_n \,. \qquad (2)$$

Here we have assumed so low temperature (all Boltzmann factors $b_n \ll 1$) that transitions between the excited electron states $|n\rangle$ can be neglected. The lowest excited states from (1) and the only ones to contribute to (2) have energies $\Delta_\pm \approx D \pm 3E$. Hence measurements of T_1 is a way to determine the crystal field splitting.

Our data in fig. 1 for proton relaxation in $FeSiF_6 \cdot 6H_2O$ show an exponential temperature dependence in the liquid helium range. These measurements were done with standard pulse methods at 16 MHz on single crystals aligned with H_0 along the hexagonal z-axis. In this orientation the proton line is not split by magnetic moments on the Fe^{2+} ions [1]. Our data can be fitted for $E = 0$ with $D = 11.0\ \mathrm{cm}^{-1}$ which agrees with $D = 10.9\ \mathrm{cm}^{-1}$ [2] and $D = 10.4\ \mathrm{cm}^{-1}$ [3] derived from susceptibility measurements. However, mm-wave ESR show that $E = 0.54\ \mathrm{cm}^{-1}$ [4] which is not negligible compared to kT, and taking this into account we derive $D = (12.2 \pm 1.0)\mathrm{cm}^{-1}$, close to the ESR-found value $D = 11.8\ \mathrm{cm}^{-1}$ [4]. The susceptibility above helium temperature is little influenced by the magnitude of E, hence we conclude that D probably decreases slightly with increasing temperature in $FeSiF_6 \cdot 6H_2O$. A variation of D with temperature is well known in $NiSiF_6 \cdot 6H_2O$ [5].

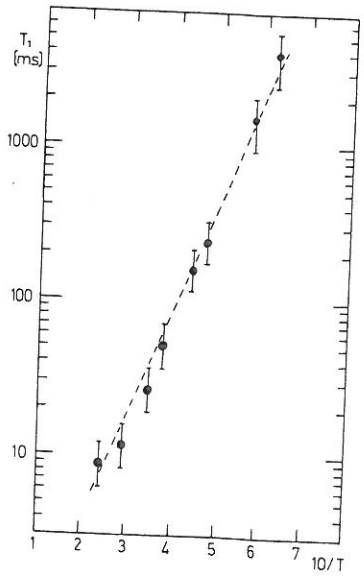

Fig. 1. Proton T_1 in $FeSiF_6 \cdot 6H_2O$ measured at 16 MHz and liquid helium temperatures.

This way of measuring level splittings of paramagnetic ions is similar to that we used on copper acetate [6] where the splitting is caused by antiferromagnetic coupling in Cu^{2+} ion pairs. Jeffries and coworkers [7, 8] have also demonstrated $\exp(-g\beta H_0/kT)$-dependent proton relaxation in Nd/La double nitrates when very low temperatures and very high fields were used to align the Nd^{3+} spins.

The magnitude of the proton relaxation give information about the fluctuation rate in the electron system. Dipolar interaction nucleus i – electron j gives a relaxation rate [9]

$$(1/T_1)_{ij} = \tfrac{9}{2} \frac{g_z^2\beta^2\gamma_I^2 \sin^2\theta_{ij} \cos^2\theta_{ij}}{r_{ij}^6} \times \int_{-\infty}^{\infty} \overline{\langle S_z(0)S_z(t)\rangle} \exp(-i\omega_0 t)\,dt\,. \qquad (3)$$

The autocorrelation function $\overline{\langle S_z(0)S_z(t)\rangle}$ of the ion is determined by the transition probabilities between the ground state $|0\rangle$ and the two mixed states $|\pm\rangle = (\sin\alpha|\mp 1\rangle \pm \cos\alpha|\pm 1\rangle)$ due to interaction with other ions or the lattice. The effective moments of the states $|\pm\rangle$ with energies $\Delta_\pm = D \pm [(3E)^2+(g_z\beta H_0)^2]^{1/2}$ depend upon the degree of mixing given by $\tan 2\alpha = 6E/2g_z\beta H_0$ [10]. The matrix elements for both transitions are equal, we assume that the excited levels have equal widths, and since spin flips up occur with probabilities b_n times the probability W for down transitions, the autocorrelation function in the low temperature limit is

$$\overline{\langle S(0)S(t)\rangle} = (\cos^2\alpha - \sin^2\alpha)^2 (b_+ + b_-) \exp(-Wt)\,. \qquad (4)$$

Hence

$$(1/T_1)_{ij} = \tfrac{9}{2} \frac{g_z^2\beta^2\gamma_I^2 \sin^2\theta_{ij} \cos^2\theta_{ij} (\cos^2\alpha - \sin^2\alpha)^2}{r_{ij}^6} \, \frac{\tau(b_+ + b_-)}{(1+\omega_0^2\tau^2)} \qquad (5)$$

which for constant correlation time $\tau = 1/W$ in the excited states gives $(1/T_1) \sim (b_+ + b_-)$ as expected. Note that the relaxation rate depends strongly upon the magnitude of $(g_z\beta H_0/E)$ through the α term, and $1/T_1$ is proportional to H_0^2 for small fields.

In $FeSiF_6 \cdot 6H_2O$ the protons are $r_{ij} = 2.7$ Å away from the nearest Fe^{2+} ion, and θ_{ij} is 38° or 69° when $H_0 \parallel z$ [11]. Using the average $\sin^2\theta_{ij}\cos^2\theta_{ij}$, $g_z = 2.00$, $E = 0.54\ \mathrm{cm}^{-1}$ [4], $H_0 = 3760$ gauss and neglecting relaxation transitions caused by more distant ions. our relaxation data give $\tau \approx 2.2 \times 10^{-10}$ s assuming $\omega_0\tau \ll 1$.

The correlation time τ can give information on the couplings in the electron spin system. Dipolar and exchange coupling would give flips between unperturbed spins S_j and S_k with frequency [12]

$$\omega_1 = (g^2\beta^2/2r_{jk}^3\hbar)(1 - 3\cos^2\theta_{jk}) + A_{jk}/\hbar\,. \qquad (6)$$

The interaction with other spins will broaden the levels of the pair to give a spin flip probability

$$1/\tau \approx \tfrac{1}{2}\pi\omega_1^2(2\pi\overline{\Delta\omega^2})^{-1/2} \xrightarrow[T\to 0]{} \approx \omega_1^2 h/\delta\Delta\,. \qquad (7)$$

Here $\overline{\Delta\omega^2}$ is the electron spin resonance second moment which in principle can be calculated with the formulas of McMillan and Opechowski [13], and which ideally goes to zero at low temperature. However, the line width will in practice stay finite because of the unavoidable spread $\delta\Delta$ in crystalline field splitting between neighbours due to strains and imperfections in the lattice. Knowledge of $\delta\Delta$ would allow an estimate from τ of the exchange coupling A in $FeSiF_6 \cdot 6H_2O$.

In diamagnetically diluted crystals τ becomes longer and will eventually be determined by the electron spin-lattice relaxation. In this case also we expect exponential temperature dependence of the proton relaxation, and its magnitude will depend upon proton spin diffusion. It is interesting to note that there will be no barrier around the Fe^{2+} ions against the spin diffusion as long as $\omega_0\tau \ll 1$.

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