^{1}H Nuclear Magnetic Relaxation in Impure $CuF_2 \cdot 2H_2O$

C. H. Lee and C. E. Lee*

Department of Physics, Korea University, Seoul 136-701

S. J. Noh

Department of Applied Physics, Dankook University, Seoul 140-210

We have studied the temperature dependence of the ^{1}H NMR spin-lattice relaxation for the impure $CuF_2 \cdot 2H_2O$ over a temperature range from 77 K to room temperature. We find that the remperature dependence of the ^{1}H spin-lattice relaxation is dominated by the eletron spin-flip and the Raman process of eletron spin-lattice relaxation. The electron spin-flip exchange energy was calculated to be 1.8($\pm$ 0.04) K.
*To whom all correspondence should be addressed.

I. INTRODUCTION

Nuclear magnetic resonance (NMR) studies on magnetic substances such as paramagnetic insulators have been carried out extensively since around 1950[1]. NMR studies on paramagnetic insulators can be classified into two categories[1] : the resonant nucleus and unpaired electrons are on the same atom in one case and on different atoms in the other. It seems appropriate, however, to further classify the latter into two groups. When an atom including the resonant nucleus is bonded directly to a paramagnetic ion, the transferred hyperfine interaction[2] between the resonant nucleus and the electron that is partly transferred to the resonant atom generally prevails over the direct dipole-dipole interaction between the resonant nucleus and electron on a paramagnetic ion. Examples of this case is ^{19}F NMR of MnF_2[3]. On the other hand, when the resonant atoms are not bonded directly to a paramagnetic ion, the magntic dipole-dipole interaction is dominant. An example of this case is ^{1}H NMR of $CuSO_4 \cdot 5H_2O$[4], $CuCl_2 \cdot 2H_2O$[5], and $CuF_2 \cdot 2H_2O$[6]. Measurements of nuclear spin-lattice relaxation times in paramagnetic insulators can give us dynamical information of unpaired electrons. It is relatively easy in the case of dominant dipole-dipole interactions to estimate the magnetic hyperfine interaction and hence to obtain the electron correlation time. This is because the interaction to be considered in this case is limited only to the magnetic dipole-dipole interaction, and delocalization of unpaired electrons, even if it exists, usually has a minor effect on the interaction. In the present investigation we have measured the temperature dependence of the ^{1}H NMR spin-lattice relaxation in the paramagnetic $CuF_2 \cdot 2H_2O$ powder to identify the electron spin-lattice relaxation mechanism and to obtain the spin-flip exchange energy in this system of dense paramagnetic ions.

II. Nuclear magnetic relaxation in paramagnetic insulators

Bloembergen, Purcell, and Pound have derived the NMR relaxation times due to the magnetic dipole-dipole interaction[7]. When the resonant nucleus with I = 1/2 are placed in the fluctuating local field caused by flip-flops of unlike spins S, the spin-lattice relaxation time T_{1M} of the nucleus I in a powder sample is expressed as[8]

$$T_{1M}^{-1} = \frac{2\gamma_I^2 \gamma_S^2 \hbar^2 S(S+1)}{15} \times \sum_i \gamma_i^{-6} \left[\frac{\tau_{2s}}{1 + (\omega_I + \omega_S)^2 \tau_{2S}^2} \right.$$

$$\left. + \frac{3\tau_{1s}}{1 + \omega_I^2 \tau_{1S}^2} + \frac{6\tau_{2s}}{1 + (\omega_I - \omega_S)^2 \tau_{2S}^2} \right], \quad (1)$$

where γ, ω, and r_i stand for the gyromagnetic ratio, the Larmor frequency, and the distance between the resonant nucleus and the ith unlike spin, respectively, τ_{1s} and τ_{2s} denote the correlation times, characterizing the time depedence of autocorrelation functions $\langle S_z(t)S_z(0)\rangle$ and $\langle S_+(t)S_-(0)\rangle$, respectively. When the unlike spins are electrons, we can assume $\tau_{1s} = \tau_{2s} = \tau_e$ (the electron-spin correlation time) and also $\omega_I \ll \omega_S$. Thus,

$$T_{1M}^{-1} = 2\frac{\alpha}{15} \times \sum_i \gamma_i^{-6} \left[\frac{3\tau_e}{1+\omega_I^2\tau_e^2} + \frac{7\tau_e}{1+\omega_s^2\tau_e^2} \right], \quad (2)$$

where $\alpha = \gamma_I^2 g^2 \mu_B^2 S(S+1)$. Here g and μ_B indicate the g-factor and the Bohr magneton, respectively. Since our T_{1M} measurements were carried out at 45 MHz and the magnitude of τ_e can be assumed to be on the order of 10^{-11} s as will be verified afterwards, the conditions $\omega_s^2\tau_e^2 \gg 1$ and $\omega_I^2\tau_e^2 \ll 1$ are satisfied. We then finally obtain the following :

$$T_{1M}^{-1} = \frac{2}{5} \alpha \sum_i \gamma_i^{-6} \tau_e. \quad (3)$$

III. Experimental

A home-built quadrature-detection pulsed NMR spectrometer with a 12″ Varian electromagnet was empolyed at a ¹H NMR frequency of 45 MHz. For the spin-lattice relaxation time (T₁) measurements, the inversion recovery method was used. The temperature was varied in the range of 77 K to room temperature using an open-cycle refrigerator (Air Product Heli-tran) by flowing liquid nitrogen and a heater attached to the cold finger. The commercially available powder sample of $CuF_2 \cdot 2H_2O$ with unspecified purity was sealed in a sample cell with a copper-to-glass joint (Kontes) and then threaded into the cold finger for a good thermal contact. According to the elemental analysis it includes the nonmagnetic calcium (Ca^{++}) (0.45 %) and magnesium (Mg^{++}) (0.18 %) ions.

IV. Results and discussion

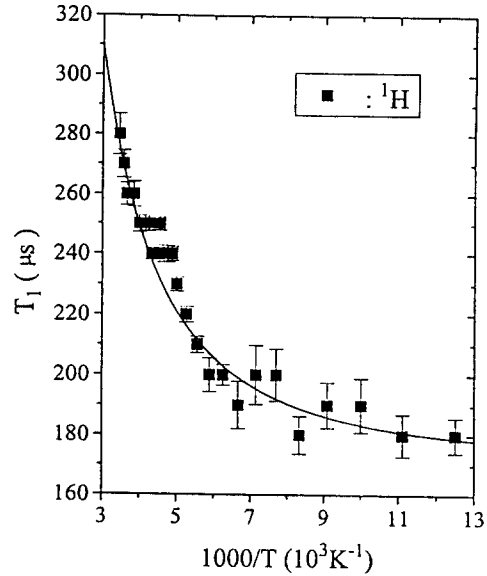The temperature dependence of the ¹H spin-lattice relaxation rate is shown in Fig. 1, in which the

Fig. 1. The temprature dependence of the ¹H spin-lattice relaxation time for impure $CuF_2 \cdot 2H_2O$.

¹H spin-lattice relaxation rate decreases with increasing temperature. The electron spin correlation time τ_e, which is expected to cause the temperature dependence of T_{1M}, can be given by the electron spin-lattice relaxation time T_{1e} and the correlation time τ_f for the electron spin-flip as follows :

$$\tau_e^{-1} = T_{1e}^{-1} + \tau_f^{-1} \quad (4)$$

Since the electron-spin flips are caused by the exchange interaction among neighboring electron spins, τ_f is nearly independent of temperature. On the other hand, T_{1e} is ascribed to the modulation of the crystal electric field or ligand field through motions of the electrically charged ions under the action of lattice vibrations. In fact, it was shown to depend on temperature T as follows[9] :

$$T_{1e}^{-1} = \beta \coth\left[\frac{h\nu_e}{2kT}\right] + \gamma T^n + \frac{\zeta}{\exp(\frac{\Delta}{kT})-1} \quad (5)$$

The first term represents the direct process and v_e is a Larmor frequency of the magnetic ion. The second term corresdponds to the Raman process and the exponent n can take various numerical values depending on the electronic states of the magnetic ion. The last term describes the Orbach process, in which transitions between the two low-lying states of the magnetic ion occur via an excited state whose energy is less than the maximum phonon energy but greater than energies of the ground states, by Δ. In the Raman process, the exponent n in Eq. (6) has been shown to be 7 in the case $T \ll \theta_D$ (Debye temperature) and 2 in the case $T \gg \theta_D$[9]. Therefore, if T_{1e} is determined by the Raman process, T_{1M} is supposed to vary as T^2 or T^7. However, the Debye temperature (θ_D) for $CuF_2 \cdot 2H_2O$ is about 135 K[10] and least-square fit of the equation

$$T_{1M} = \frac{5}{2\alpha \sum \gamma_i^{-6}} \left[\gamma T^n + \tau_f^{-1} \right] \qquad (6)$$

to the experimental data gives the values for fitting parameters, $\gamma = 4.00 \times 10^5$, $\tau_f = 1.84 \times 10^{-11}$ s and n = 2.0 (± 0.1). Thus the observed T_{1M} is best fitted to a T^2 dependence, which is depicted in Fig. 1 by a solid curve, and T_{1e} appears to be given by the Raman process.

Electron-spin flips result from the exchange interaction of the form

$$H_{ex} = \sum_{i<j} J_{ij} S_i \cdot S_j, \qquad (7)$$

where the interaction is assumed to be isotropic for simplicity and J_{ij} is the exchange parameter or coupling constant, which is twice the exchange integral. Using the general expression given by Kubo and Tomita[11] for the exchange frequency ω_{ex} and characterizing the time dependence of spin autocorrelation functions $\langle S_{iq}(t) S_{iq}(0) \rangle$ ($q = x$, y, z) in the same way as τ_e[12], Moriya has derived the following equation on the assumption of the nearest-neighbor interaction :

$$\omega_{ex}^2 = \frac{2}{3} \frac{J^2}{\hbar^2} z S(S+1), \qquad (8)$$

where z is the number of the nearest neighbors of the paramagnetic ion[13]. Thus, the exchange parameter J can be evaluated from the relation $\omega_{ex}^2 = \pi / \tau_f^2$ [11]. Moreover, the paramagnetic Curie temperature Θ, which appears in the Curie-Weiss law for the magnetic susceptibility, is given by

$$\Theta = \frac{z}{3} \frac{J}{k} S(S+1), \qquad (9)$$

in the mean-field approximation[14]. Therefore, the paramagnetic Curie temperature is related to τ_f through the exchange parameter. From Eqs. (6) and (8), we obtained the exchange energy $J/k_B = 1.8(\pm 0.04)$ K for our sample of impure $CuF_2 \cdot 2H_2O$, which is much smaller than $J/k_B = 14 \pm 1$ K reported for pure $CuF_2 \cdot 2H_2O$.

Our recent magnetic susceptibility work in the same sample used in the present study also suggests that the value of the exchange energy J is much smaller in this impure sample than in the pure system[15]. This can be explained by the nonmagnetic impurity effect. Nonmagnetic impurities randomly distributed in the antiferromagnetic sheets strongly distort the electrical interactions within the sample, altering the character of the anisotropic interactions[16]. Since the minimum of exchange energy is acheived for the entire system as a whole, rather than for each pair of spins individually, great changes in the exchange energy can result when the crystal lattice is distorted due to the presence of the impurities.

In conclusion, from the temperature dependence of the ^{1}H spin-lattice relaxation time in a sample of impure $CuF_2 \cdot 2H_2O$, we have found that the ^{1}H spin-lattice relaxation is dominated by modulation of the electron spin-lattice relaxation (Raman process) and electron spin-flip, and obtained the exchange energy $J/k_B = 1.8(\pm 0.04)$ K.

Acknowledgments

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비자성 불순물을 갖는 $CuF_2 \cdot 2H_2O$의 수소 핵자기완화 연구

이창훈 · 이철의

고려대학교 물리학과, 서울 136-701

노승정

단국대학교 응용물리학과, 서울 140-210

비자성 분순물을 갖는 $CuF_2 \cdot 2H_2O$의 수소 핵자기공명을 77-295 K의 온도범위에서 수행하였다. 그 결과 수소의 스핀-격자 완화율을 지배하는 메카니즘이 구리 전자 스핀의 재주넘기(flip)와 전자-포논 상호작용(Raman process)의 변조에 의한 것임을 알 수 있었다. 또한 전자 스핀 재주넘기에 대한 교환에너지 1.8 (±0.04) K를 구할 수 있었다.