

Dynamic Polarization of Protons in Copper Tutton Salts (Dilute $\text{CuK}_4\text{SO}_4 \cdot 6\text{H}_2\text{O}$) and Their Spin-Lattice Relaxation Times

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The protons from waters of hydration of copper and zinc salts are polarized by saturating the electron-spin transitions (forbidden) of copper ions at liquid-helium temperatures. The enhancement of the proton resonance was observed to be due to dipole-dipole interaction with the electron spins (so-called solid-state effect). The rates of decay and growth of these enhanced proton resonance signals were measured as functions of the temperature and the intensity of the microwave field applied to saturate the electron-spin transition. From the measured proton relaxation time (in the range of milliseconds) and its temperature dependence, the electron-spin relaxation times (in the range of microseconds) and their temperature dependence were deduced. It was found that the Cu^{++} ions in the 1:50 dilute Cu:Zn sample relax through spin-orbit interaction (Raman process), and in the 1:5 Cu:Zn sample through both spin-orbit (Raman) and exchange interactions. The observed small values of the relaxation times for electrons indicate that the protons relax preferentially through those electron spins which have no phonon bottleneck.

INTRODUCTION

COPPER tutton salts ($\text{CuK}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$) have been investigated by several authors,¹⁻⁶ to study the electron spin-lattice relaxation mechanisms present at low temperatures and the order of the process (direct or Raman) dominant at liquid-helium temperatures. Gill⁵ reported that in $\text{CuK}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ diluted with $\text{ZnK}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ in the ratio of 1:10⁻⁴ the mechanism was found to be of the Van Vleck (spin-orbit) type, and the process was predominantly Raman from 150 to 4.0°K and direct from 4.0 to 1.3°K. However, when the dilution was slightly less (i.e., 1.2×10^{-3}), his results could not be explained. The relaxation rate decreased faster than the first power of the temperature as the temperature decreased below 4.0°K. It is possible that the true spin-lattice relaxation time (spin-phonon interaction time) is masked by the lattice-bath interaction (phonon-bath interaction time) which is concentration- and size-dependent. This is known in the literature as a phonon bottleneck.^{1,2} Such a phonon bottleneck was observed by Giordemine *et al.*³ in $\text{Cu}(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, and by Nash.⁷ A hot Zeeman phonon with a short mean free path has a very large probability of being reabsorbed and re-emitted by the electron spins as it traverses through the crystal before it collides with the walls. On collision it may give up its energy to the walls or to the phonons of other

modes. In such a process it has been suggested that the electron spin-lattice relaxation time measured will actually be the lattice-bath interaction time, which is generally longer than the spin-phonon interaction time one would measure if the phonons were in equilibrium with the bath. In other words, the measured relaxation time will correspond to the phonon diffusion time from the spin to the boundaries of the crystal. But the electrons belonging to ions close to the surface or on the surface (lying within a phonon mean free path from the boundaries) will have a shorter relaxation time, since the Zeeman phonons in close proximity to the surface have a very large probability of colliding with the walls and giving up their energy. Hence these phonons are in equilibrium with the lattice at all times. Therefore, a measurement of the relaxation times of these electrons close to the surface should yield the true spin-lattice relaxation time (i.e., spin-phonon interaction time), and their temperature dependence should show what relaxation mechanism and process are involved at low temperatures. Experimentally, it is hard to separate the surface electrons from those farther inside the crystal which have a very long relaxation time due to the phonon bottleneck. But the protons in these samples, which relax by dipole-dipole interaction with the electron spins, would selectively prefer a relaxation path of very short time. Therefore, the protons relax to the lattice preferentially through the electrons which have shorter relaxation times. Hence, a study of the spin-lattice relaxation times of protons at low temperature and their temperature dependence should give a measure of the spin-phonon interaction time. In this way one can circumvent the presence of the phonon-bath interaction time and a correlation between proton relaxation time and the electron relaxation time can be achieved. In addition,

* Part of this work is toward his doctoral thesis.

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¹ D. M. S. Bagguley *et al.*, Proc. Roy. Soc. (London) **A204**, 188 (1950); **A201**, 266 (1950); Proc. Phys. Soc. (London) **65**, 594 (1952).

² B. Bleany *et al.*, Proc. Roy. Soc. (London) **A228**, 147 (1955).

³ J. A. Giordemaine *et al.*, Phys. Rev. **109**, 302 (1958).

⁴ N. Bloembergen *et al.*, Phys. Rev. **114**, 445 (1959).

⁵ J. C. Gill, Proc. Phys. Soc. (London) **85**, 119 (1965).

⁶ T. J. B. Swanberg *et al.*, Physics **30**, 1872 (1964).

⁷ F. R. Nash, Phys. Rev. Letters **7**, 59 (1961).

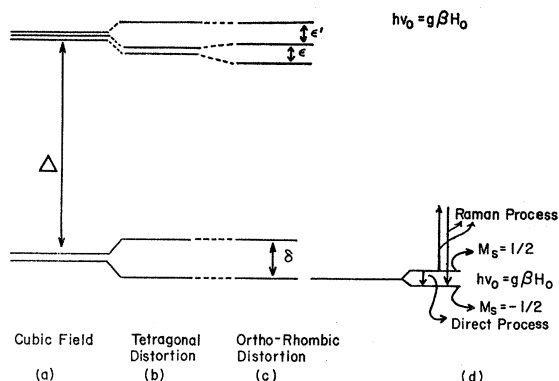


FIG. 1. Energy-level diagram of a $3d^9$ electron.

it is possible to deduce (though not with complete certainty) the mechanism involved in the electron spin-lattice relaxation.

We have not attempted an experimental check of Gill's⁵ observations that the relaxation rate in these copper salts increased with the concentration, and his suggestion that the increase was probably due to the phonon bottleneck. Furthermore, no experiment was performed on the size dependence of the relaxation rates to pin down the existence of such a phonon bottleneck. If there were no phonon bottleneck, the nuclei would relax to the lattice through the surrounding electrons irrespective of whether the electrons are inside of or on the surface of the crystal. The measurements presented here then would pertain to the electrons of the copper ions in general.

THEORY

Electron Spin-Lattice Relaxation

A Cu^{++} ion in a tutton salt is in a $3d^9$ state. In a cubic field Δ its orbital degeneracy is lifted, giving rise to a doublet in the ground state ($x^2-y^2, 3z^2-r^2$) and a triplet (xy, yz, zx) in a higher energy state [Fig. 1(a)]. Neither spin-orbit interaction nor trigonal field distortion can lift the orbital degeneracy of the ground state.⁸ Tetragonal symmetry splits the doublet into two singlets [Fig. 1(b)] and the triplet into a singlet (xy) and a doublet (yz, zx). However, tutton salts show departures from tetragonal symmetry. A small orthorhombic field distortion will finally lift the remaining degeneracy [Fig. 1(c)]. In tutton salts there are two Cu^{++} ions in a unit cell and each divalent ion is surrounded by a distorted octahedron. The magnetic field applied (H_0) in the a - c plane will make the spectra of the two ions coincide. The Kramers degeneracy of the ground state (x^2-y^2 or $3z^2-r^2$) is lifted in the external magnetic field (H_0) as shown in Fig. 1(d). The following are two possible relaxation processes.

Direct Process. A direct process is a transition between the two Zeeman levels, Fig. 1(d) ($M_s = +\frac{1}{2} \rightarrow M_s = -\frac{1}{2}$), by either absorption or emission of a phonon of energy $h\nu_0$ which equals the energy difference between the two Zeeman levels.

Raman or Indirect Process. A Raman process is a transition between the Zeeman levels due to the scattering of a phonon such that the difference in energy of the incident and scattered phonon ($h\nu_1 - h\nu_2 = h\nu_0$) equals the difference in energy between the Zeeman levels. The spin-lattice relaxation mechanism in these salts is due to the spin phonon interaction of the type envisaged by Kronig⁹ and Van Vleck.¹⁰ The vibrations of the lattice modulate the electrostatic interaction of the paramagnetic ion with the neighboring diamagnetic ligands, as a result of which there is a periodic variation of the orbital motion of the electrons which for the most part is quenched. Therefore, from time-dependent perturbation theory we define the relaxation rate in terms of the transition probability between the two states $|a\rangle$ and $|b\rangle$:

$$(2T_1)^{-1} = W_{ab} = (2\pi/\hbar) |\langle a | H_{s-p} | b \rangle|^2 \rho(\nu_0), \quad (1)$$

where $\rho(\nu_0)$ = phonon distribution at frequency ν_0 and H_{s-p} is the spin phonon interaction Hamiltonian. Therefore, to calculate the relaxation rate we need to know (1) $\rho(\nu_0)$ and (2) the matrix element of H_{s-p} . The latter involves the decomposition of lattice vibrations into normal modes of the lattice and these lattice modes into those of the individual ligand complex. This is a very difficult task. Here we attempt an order-of-magnitude calculation by (a) expressing the amplitudes of the local variations of the crystal field in terms of the amplitudes of the lattice vibrations; and (b) finding the matrix element of these local variations of the crystal-field perturbation (V_0) which bring about the spin flip.

The phonon distribution as a function of energy is

$$\rho_D(h\nu_0) = (4\pi/h^3) [(h\nu_0)^2/v^3] V [\exp(h\nu_0/kT) - 1]^{-1}, \quad (2)$$

where V is the volume of the crystal, v is the velocity of sound in the crystal, and T is the temperature of the crystal lattice.

Direct Process. $h\nu_0 = 2\beta H_0$, and for $kT \gg h\nu_0$ we have

$$\rho_D(h\nu_0) = (4\pi/h^3) (2\beta H_0/v^3) V kT. \quad (3)$$

Raman Process. The density of phonons is

$$\rho_R(h\nu) = \int_0^{(h\nu)_{\max}} \rho(h\nu_1) \rho(h\nu_2) d(h\nu_1),$$

with the constraint $h\nu_1 - h\nu_2 = h\nu_0 = 2\beta H_0$. Assuming that at $h\nu = kT$ the phonon density abruptly drops to zero,

$$\rho_R(h\nu) = (16\pi/3h) (v^2/v^6) (kT/h)^5. \quad (4)$$

Now we turn to the calculation of the amplitude of

⁸ W. Low, *Paramagnetic Resonance in Solids* (Academic Press Inc., New York, 1960), Suppl. 2, p. 93.

⁹ R. deL. Kronig, *Physica* 6, 33 (1939).

¹⁰ J. H. Van Vleck, *Phys. Rev.* 57, 426 (1940).

the variations of local crystal field. If we let q be the amplitude of a lattice mode with a frequency ν then $2\pi^2 M q^2 \nu^2 = h\nu$, where M is the mass of the crystal. The crystal field at the site of the Cu^{++} ion is dependent only on mutual displacements of the central ion and the surrounding ligands; therefore, the longer the wavelengths of the lattice mode are, the smaller these mutual displacements are. For wavelengths λ_0 of the lattice modes that are long compared with the interatomic distances R one can write the displacement δR ¹¹ as

$$\delta R = 2\pi R q / \lambda_0 = (R/\nu) (2h\nu/M)^{1/2},$$

where $\nu = \lambda_0 \nu$. Let Δ be the crystal-field energy of the central Cu^{++} ion in an undistorted cubic field. Then the magnitude of the variation of this crystal-field energy due to the mutual displacement (δR) of one or several of the surrounding ligands is

$$[\partial(\Delta)/\partial R] \delta R \simeq (\Delta/R) \delta R \simeq (\Delta/\nu) (2h\nu/M)^{1/2}. \quad (5)$$

Direct Process. Replacing $h\nu_0$ by $2\beta H_0$ and taking the square of the amplitude, which is what we need in Eq. (1), we have

$$W_{ab(\text{direct})} \propto (\Delta^2/\nu^2) (4\beta H/M). \quad (6)$$

Direct Process.

$$\Psi_\alpha^{(1)} = |x^2 - y^2, \alpha\rangle + (i/\Delta) [\lambda + 2\beta H_0 - (\beta H_0/\Delta) (\lambda + 2\beta H_0)] |xy, \alpha\rangle - (i\lambda/2\Delta) (1 + 2\beta H_0/\Delta + 3\lambda/2\Delta) |yz, \beta\rangle - (\lambda/\Delta^2) (\frac{1}{4}\lambda + \beta H_0) |zx, \beta\rangle, \quad (8)$$

$$\Psi_\beta^{(1)} = |x^2 - y^2, \beta\rangle - (i/\Delta) [(\lambda - 2\beta H_0) (1 + \beta H_0/\Delta)] |xy, \beta\rangle - (i\lambda/2\Delta) (1 - 2\beta H_0/\Delta + 3\lambda/2\Delta) |yz, \alpha\rangle + (\lambda/\Delta^2) (\frac{1}{4}\lambda - 2\beta H_0) |zy, \alpha\rangle, \quad (9)$$

$$\Psi_\alpha^{(2)} = |3z^2 - r^2, \alpha\rangle + (\sqrt{3}i\lambda^2/2\Delta^2) |xy, \alpha\rangle - (\sqrt{3}i\lambda/2\Delta) (1 + 2\beta H_0 - \lambda/2\Delta) |yz, \beta\rangle - (\sqrt{3}\lambda/2\Delta) (1 + 2\beta H_0/\Delta - \lambda/2\Delta) |zx, \beta\rangle, \quad (10)$$

$$\Psi_\beta^{(2)} = |3z^2 - r^2, \beta\rangle - (\sqrt{3}i\lambda^2/2\Delta^2) |xy, \beta\rangle - (\sqrt{3}i\lambda/2\Delta) (1 - 2\beta H_0 - \lambda/2\Delta) |yz, \alpha\rangle + (\sqrt{3}\lambda/2\Delta) (1 - 2\beta H_0/\Delta - \lambda/\Delta) |zx, \alpha\rangle, \quad (11)$$

$$|\langle \Psi_\alpha^{(1)} | V_0 | \Psi_\beta^{(1)} \rangle|^2 = (4\lambda\beta H_0/\Delta^2)^2 |\langle i | V_0 | j \rangle|^2, \quad (12a)$$

where i and j refer to the unperturbed eigenstates of the electron in a noncubic field (i.e., $H^1 = 0$).

$$|\langle \Psi_\alpha^{(2)} | V_0 | \Psi_\beta^{(2)} \rangle|^2 = 2(2\sqrt{3}\lambda\beta H_0/\Delta)^2 |\langle i | V_0 | j \rangle|^2. \quad (12b)$$

Therefore, the relaxation rate of Cu^{++} ion in a direct process can now be given to an order of magnitude by combining Eqs. (3), (6), (12a), and (12b):

$$(2T_1)^{-1} = W_{ab} = \frac{2\pi}{\hbar} \left(\frac{4\pi}{\hbar^3} \frac{2\beta H_0}{\nu^3} V kT \right) \left[\frac{\Delta^2}{\nu^2} \left(\frac{4\beta H_0}{M} \right) \right] \left(\frac{4\lambda\beta H_0}{\Delta^2} \right)^2. \quad (12c)$$

¹¹ G. E. Pake, *Paramagnetic Resonance* (W. A. Benjamin, Inc., New York, 1962), p. 122.

Raman Process. Replacing $h\nu$ by kT (as the Raman process is most effective at $h\nu = kT$), and raising it to the fourth power, we have

$$W_{ab(\text{Raman})} \propto (4\Delta^4/\nu^4) [(kT)^2/M^2], \quad (7)$$

since the process involves an incident and a scattered mode. Finally, we turn to the evaluation of the matrix element of the periodically varying local field perturbation V_0 , which is a function of x, y, z coordinates of the electron and of proper symmetry with respect to surrounding ligands. The ground-state wave functions $|a\rangle$ and $|b\rangle$ may either be $|x^2 - y^2, \alpha\rangle$ or $|x^2 - y^2, \beta\rangle$ admixed with other wave functions through the perturbing Hamiltonian $H^1 = \lambda \mathbf{L} \cdot \mathbf{S} + g\beta H_0(L + S)$ or $|3z^2 - r^2, \alpha\rangle$ or $|3z^2 - r^2, \beta\rangle$, which are also admixed through the same perturbation. α denotes a spin-up state of the electron (parallel to \mathbf{H}_0) and β denotes a spin-down state of the electron (antiparallel to \mathbf{H}_0). It is well known that the so-called Van Vleck cancellations occur in some cases if one carries out the admixture only to the first order. This is true with a ground-state wave function like $|3z^2 - r^2\rangle$. Therefore, the wave functions are mixed to the second order to evaluate the matrix elements of the crystal-field perturbation. We assume g is a scalar and equal to 2.

if $\rho = M/V =$ density of the crystal $\simeq 2$ g/cc at 4.2°K for Cu^{++} ion using the following values: $\lambda = -695 \text{ cm}^{-1}$, $\Delta = 8700 \text{ cm}^{-1}$, $\delta = 7700 \text{ cm}^{-1}$ [Fig. 1(c)], $H_0 = 2800 \text{ Oe}$, we calculate $T_1 \simeq 1$ sec.

The relaxation rate is temperature-dependent and is proportional to the first power of T and inversely proportional to fourth power of H_0 .

Raman Process. In a Raman process we need to calculate the matrix elements of the type

$$\frac{\langle \Psi_\alpha^{(1)} | V_1 | i \rangle \langle i | V_2 | \Psi_\beta^{(1)} \rangle}{E_{\Psi_\beta^{(1)}} - E_i + h\nu_1} + \frac{\langle \Psi_\alpha^{(1)} | V_2 | i \rangle \langle i | V_1 | \Psi_\beta^{(1)} \rangle}{E_{\Psi_\beta^{(1)}} - E_i - h\nu_2}, \quad (13)$$

where V_1 and V_2 are the local crystal-field perturbations

and $|i\rangle$ is an intermediate state. For instance, $|i\rangle$ is $|yz, \alpha\rangle$ plus other eigenstates mixed into it through the spin-orbit and Zeeman perturbations. Denoting such a perturbed state by $\Psi_\alpha^{(3)}$ we have in the first order

$$\Psi_\alpha^{(3)} = |yz, \alpha\rangle - (\lambda/2\epsilon) |xy, \beta\rangle - (i\lambda/2\Delta) |x^2 - y^2, \beta\rangle - (3i\lambda/2\Delta') |3z^2 - r^2, \beta\rangle - i[(\lambda + 2\beta H)/2\epsilon^2] |zx, \alpha\rangle, \quad (14)$$

$$\Psi_\beta^{(3)} = |yz, \beta\rangle + (\lambda/2\epsilon) |xy, \alpha\rangle - (i\lambda/2\Delta') |x^2 - y^2, \beta\rangle + (-\sqrt{3}i\lambda/2\Delta') |3z^2 - r^2, \beta\rangle + [i(\lambda - 2\beta H)/\epsilon] |zx, \beta\rangle, \quad (15)$$

where $\Delta' = \Delta - \delta$ and $\Delta \gg \delta \gg \epsilon$. With the assumption $h\nu_2 \simeq h\nu_1 \simeq h\nu \simeq kT$, Eq. (13) will result in

$$[\lambda kT/\Delta^2 \epsilon]^2 |\langle i | V_2 | j \rangle|^2 |\langle k | V_1 | l \rangle|^2. \quad (16)$$

Combining Eqs. (4), (7), and (16), and noting that our estimates are only to an order of magnitude, we have for

$$(2T_1)^{-1} = W_{ab(\text{Raman})} = \frac{2\pi}{\hbar} \left[\frac{16\pi}{3h} \frac{V^2}{v^6} \left(\frac{kT}{h} \right)^6 \right] \left[\frac{4\Delta^4}{v^4} \frac{(kT)^2}{M^2} \right] \left[\frac{\lambda kT}{\Delta^2 \epsilon} \right]^2. \quad (17)$$

If one uses $\epsilon = 250 \text{ cm}^{-1}$ as deduced from hyperfine interaction constants by Bleaney², T_1 will be the order of 1000 sec. But in the absence of orthorhombic distortion, the degeneracy in yz , zx remains and results in $\epsilon \simeq 0$, thereby shortening the relaxation time T_1 enormously, as can be seen from (17), where ϵ is in the denominator. T_1 has no dependence in magnetic field but it is inversely proportional to T^9 .

Nuclear Spin-Lattice Relaxation

In the dipolar Hamiltonian for a system of nuclear (I) and electronic (S) spins, the term

$$C_{op} = (-\frac{3}{2} S_z I_+ \sin\theta \cos\theta e^{-i\varphi}) A \quad (18)$$

appears, where $A = \gamma_I \gamma_S \hbar^2 / r^3$ and r is the distance between the nuclear and electron spin and θ and φ refer to the direction of the vector \mathbf{r} with respect to the external magnetic field \mathbf{H}_0 , taken to lie in the z direction. γ_I and γ_S are the gyromagnetic ratios of the nucleus and electron, respectively. This operator C_{op} may induce the flip of a nuclear spin without the accompanying flip of an electron spin—a process involving much less energy than any other process allowed by the bilinear coupling of two spins.¹² Abragam, Bloembergen, and others have shown that this term

¹² A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon Press, Oxford, England, 1961), p. 380; N. Bloembergen, *Nuclear Magnetic Relaxation* (W. A. Benjamin, Inc., New York, 1961), p. 386.

(18) leads to a nuclear relaxation time T_1' given by

$$(T_1')^{-1} = \frac{3}{2} \frac{\gamma_s^2 \gamma_I^2 \hbar^2}{r^6} \sin^2\theta \cos^2\theta S(S+1) \frac{\tau}{1 + \omega_I^2 \tau^2}, \quad (19)$$

where τ is the longitudinal electron relaxation time and ω_I is the Larmor frequency of the nucleus. If $\omega_s \tau \gg 1$, which is the case in most samples, this process is seen to dominate the relaxation of nuclei. Equation (19) is conveniently written

$$1/T_1' = Cr^{-6}. \quad (20)$$

In samples where the ratio of paramagnetic impurities to nuclei is low, r becomes very large, and extremely long values of T_1' are calculated, in dramatic contradiction to observed nuclear relaxation times. The discrepancy between theory and experiment is resolved by assuming a spin-diffusion process of spin flip-flops between nearest-neighbor nuclei in the lattice. The diffusion process conserves energy as $r > r_0$, r_0 being the so-called critical radius, and enables nuclei far removed from paramagnetic centers to communicate with the electronic spins. Spin diffusion is usually described by an equation of the form

$$\partial p / \partial t = D \Delta p, \quad (21)$$

where p is the nuclear polarization in a small region in space and D is the diffusion constant, of the order $W a^2$, where W is the probability of nearest-neighbor flip-flop and a is the distance between nearest-neighbor nuclei. de Gennes,¹³ Bloembergen,¹² etc., have solved Eq. (21) and find the relationship between the observed nuclear relaxation time and C of Eq. (20) to be¹³

$$1/T_R = 4\pi N b D, \quad (22)$$

where N is the concentration of paramagnetic impurities per unit volume and $b = (0.68)(C/D)^{1/4}$. In paramagnetically dilute samples where the θ dependence of C has been shown to average out, and at sufficiently low temperatures and high magnetic fields where $\omega_I^2 \tau^2 \gg 1$ Eq. (22) can be written

$$T_R^{-1} = (8.54) N D^{3/4} \left[\frac{(3/20\pi) \gamma_s^2 \gamma_I^2 \hbar^2}{\omega_I^2 \tau} \right]^{1/4}. \quad (23)$$

Thus $T_R \propto (\tau)^{1/4}$.

Experimentally, the power to which τ is raised in Eq. (23) is found to vary with concentration, going to $\frac{1}{2}$ at low N . In order to investigate this exponent, it is useful in double-resonance experiments to have the relationship of the spin-diffusion theory to polarization experiments. Defining the polarization time T_p as the time necessary for the nuclear polarization to obtain an enhanced value eI_0 , where I_0 is the initial

¹³ P. G. de Gennes, *Phys. Chem. Solids* **3**, 345 (1958).

TABLE I. Some physical properties of the Cu^{++} salts investigated.

Sample No.	Sample concentration (Cu:Zn) $\text{Cu-ZnK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	N (ions/cc)	g value	Size (mm)	Electron: proton ratio
1S	1:50	5.4×10^{19}	2.44	$9.1 \times 12.5 \times 3.2$	1:600
2S	1:10	2.7×10^{20}	2.44	$9.7 \times 13.0 \times 3.3$	1:120
3S	1:5	5.4×10^{20}	2.44	$9.0 \times 11.5 \times 3.6$	1:60

value of the polarization, we find

$$1/T_p = 4\pi N \Gamma^{1/4} D^{3/4}, \quad (24)$$

where N and D have the same definitions as in Eq. (22) and $\Gamma = W_0$ (constant). Here, W_0 is the direct transition probability for an electronic spin flip induced by the time-varying field H_1 . Through the term W_0 in Eq. (24) we see that the spin-diffusion theory predicts that the polarization time will vary inversely as the one-half power of the applied microwave field. Thus, the variation of T_p with microwave power (P) provides an approach to the determination of the exponent of Γ in Eq. (24) and hence an approach to experimental verification of the spin-diffusion assumption in paramagnetically dilute crystals.

EXPERIMENTAL

The double-resonance technique was used, in which one observes the dynamic polarization of the protons by saturating the electron spin resonance (ESR) with intense microwave fields. The microwave frequency was 9.2 kMc/sec at 2850 G for the $\text{CuK}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ ($g=2.44$) for all three dilutions, Table I. The proton resonance frequency which was scanned for resonance was 12.6 Mc/sec at 2850 G. The rf field used was 2 mG and the microwave field the sample sees is about 7 mG (15 db) at which the ESR has been saturated. An amplitude modulation of the external field H_0 at 80 cps

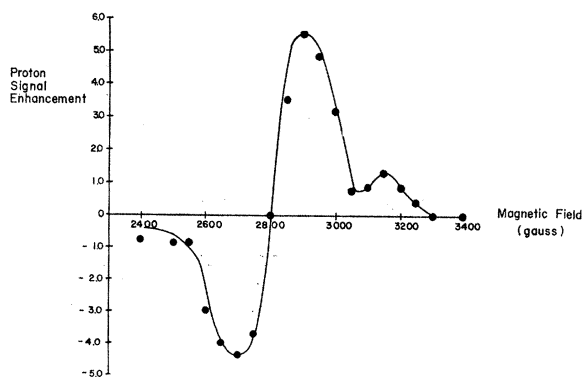


FIG. 2. Polarization curve of the protons in 1/50 Cu-doped $\text{ZnK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ at 1.65°K .

was used to detect nuclear magnetic resonance, which was presented on a fast-rising oscilloscope (Tektronix-540 B). Polarization curves, plotting magnetic field (abscissas) versus the proton signal enhancement were obtained for some samples (Fig. 2). The enhancement is due to the solid-state effect. The separation of the enhancement peaks in all samples corresponds to the width of the ESR line. All the samples were in direct contact with liquid helium.

The relaxation and polarization times were measured at the positive maximum enhancement field by switching the microwave power (P) off and on (by switching the reflector voltage of the klystron). All relaxation times measured were at various rf levels of the Pound oscillator. Polarization times were measured at various microwave levels to study the spin-diffusion processes. The temperature at which these samples were studied was varied from 4.2 to 1.6°K . All samples were run twice to anneal the crystals at very low temperatures.

DISCUSSION

The polarization rate of protons in 1:50 dilute sample was found to be proportional to the fourth root of the microwave power incident on the sample. This indicates that the nuclei relax entirely through spin diffusion and the relaxation times of the electrons as calculated using the Eq. (23) at 4.2°K and 2.0°K are given in the last column of Table II. The electron spin-relaxation time varied inversely as the eighth power of temperature. Therefore, the electrons must be relaxing through the spin-orbit interaction by the Raman process in the temperature range of 4.2 to 2°K . The relaxation times of the electrons are in the microsecond range even at liquid-helium temperature. It seems that the degeneracy of the state is not completely removed by orthorhombic distortion. This degeneracy can explain the shortness of relaxation times since the smaller the value of ϵ due to the orthorhombic field distortion the faster the relaxation rate [Eq. (17)].

In the sample of 1:10 dilution the polarization rate is proportional to the square root of the microwave power. The nuclear relaxation is neither entirely due to spin diffusion nor due to the direct interaction with the electron spin. Hence it is not possible to use either formula (23) or (19) and we cannot draw any conclu-

TABLE II. Polarization and relaxation rates of nuclei as functions of microwave power and temperature.

Sample (Cu:Zn) dilution	Dependence of polarization rate on microwave power P at 2.0°K.	Slope of $\log T_R$ versus $\log T$ (least-squares fit). See Fig. 3.	Temperature dependence of electron-spin- relaxation rate	Nuclear relaxation times at		Electron-spin- relaxation times at	
				4.2°K (msec)	2.0°K	4.2°K	2.0°K (μ sec)
1:50	Proportional to $P^{0.26}$	2(4.2 to 2°K)	T^8	145	1600	0.3	11
1:10	Proportional to $P^{0.5}$	2.5	...	20	150
1:5	Proportional to $P^{0.7}$	1.2	$T^{0.8}$	8	22	0.3	0.8

^a In evaluating the electron relaxation times Eq. (23) was used for the 1:50 sample and (19) for the 1:5 sample. The flip-flop transition probability

W was estimated using the linewidth of the proton resonance at liquid-helium temperatures. All the experimental results are within 20% error.

sions about either the relaxation process of the electron or the electron spin-relaxation time.

In the sample of 1:5 dilution the power dependence of the polarization rate indicates that most nuclei relax by direct interaction with the electron spins. The electron spin-relaxation times are evaluated using Eq. (19) and they are extremely short, in the range of a few microseconds. The relaxation time varies inversely as the first power of temperature. Apparently this process is direct, as seen from Eq. (12c). But (12c) yields a relaxation time which is very long and cannot explain the measured small value of T_1 . A Raman process can explain the small value of T_1 but fails to account for the temperature dependence. This discrepancy can be explained if one takes into account the exchange interaction that usually predominates in samples containing high concentrations of paramagnetic ions.

In such samples the existence of two different relaxation mechanisms at very low temperatures leading to different temperature dependences of T_1 has been established.^{14,15}

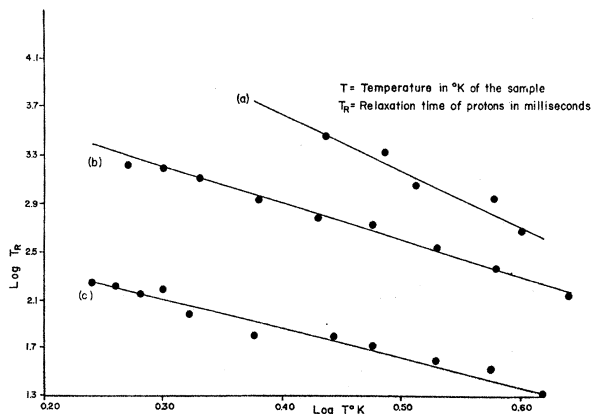


FIG. 3. Relaxation time of protons versus temperature in dilute crystals. Cu/Zn = (a) 1/5, (b) 1/50, (c) 1/10. The base of the logarithms is 10.

¹⁴ J. C. Gill, Proc. Phys. Soc. (London) **A79**, 58 (1962).

¹⁵ J. H. Pace *et al.*, Proc. Phys. Soc. (London) **A75**, 697 (1960).

It has been proposed by Al'tshuler^{16,17} that two electron spins S_1 and S_2 will interact via a Hamiltonian $JS_1 \cdot S_2$, where J is the exchange integral. J is concentration-dependent and large if interelectronic distances are small. This interaction is found to be a powerful relaxation mechanism in medium- and high-concentration samples. It is temperature-independent and gives rise to very short relaxation times. Therefore it seems probable that the electrons in the 1:5 sample relax to the lattice through both relaxation mechanisms, one due to the spin-orbit interaction (indirect $\sim T^{-9}$) and the other due to the exchange interaction (temperature-independent). This would explain the shortness of relaxation times observed and their slow dependence on temperature.

CONCLUSIONS

The double-resonance technique is apparently useful in the study of relaxation phenomena. It should also be an aid in the study of the phonon bottleneck, by allowing one to differentiate the electrons with phonon bottleneck from those without it in high-concentration samples. Finally, it should be emphasized that the temperature dependence of the relaxation rates alone does not exclude the likely existence of relaxation mechanisms for the electrons other than the spin-orbit and the exchange interactions. In very dilute samples (although the salts investigated were of moderate concentration) the relaxation mechanism may involve some electron spin-spin cooperative process and a more detailed study of the concentration dependence of the relaxation rates at very low concentrations should resolve this question.

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¹⁶ S. A. Al'tshuler, Zh. Eksperim. i Teor. Fiz. **43**, 2318 (1962). [English transl.: Soviet Phys.—JETP **16**, 1637 (1963)].

¹⁷ *Spin Lattice Relaxation in Ionic Solids*, edited by A. A. Manekov and R. Orbach (Harper and Row, New York, 1966).