PHYSICAL REVIEW VOLUME 138, NUMBER 5A 31 MAY 1965

Electron Spin Relaxation in Copper Tutton Salts at Low Temperatures*†

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(Received 14 January 1965)

By means of a pulse saturation technique applied at *X*-band frequencies, electron-spin relaxation times have been observed as a function of crystal size in the liquid-helium temperature range for the $CuNH_4$ Tutton salt throughout the concentration range 0.02–100%. The concentration range 12–100% exhibits what is thought to be a phonon bottleneck. This is manifest in a marked size dependence of the observed decay constants. Alternative explanations are considered. For the concentration range 0.05 to 5%, size-dependent decay times have also been recorded. There appears to be a correlation between this kind of size effect and contamination by the paramagnetic impurity of iron. Rapid crystal growth is found to alleviate the size effects throughout the range of concentrations studied. The effects of deuteration have been examined in crystals of 1% concentration and it was found that there was an order-of-magnitude difference in the relaxation times of the hydrated and deuterated salts, size for size, below the helium λ point. The hydrated and deuterated CuK Tutton salts at the same concentration showed no such difference. The supposed spin-lattice coupling is concentration-dependent, and its nature has not yet been established theoretically.

I. INTRODUCTION

SOME preliminary studies of electron-spin relaxation in the dilute copper ammonium Tutton salts by Giordmaine *et al.*,[1] indicated that the time constants, which characterized the recovery of the spins from a saturating pulse, were relatively large and the spin, $S=\frac{1}{2}$, made these crystals attractive in the light of possible size-dependent studies. Later, in an attempt to examine the "cross-relaxation maser" effects,[2] it was discovered[3] that deuteration of the same dilute crystals (concentrations ~1%) resulted in an order-of-magnitude decrease in the electron spin relaxation times. More recently the marked size-dependent relaxation times[4] in the fully concentrated hydrated copper ammonium Tutton salt suggested a lattice-bath bottleneck.

Crystals of the copper ammonium Tutton salt, $CuSO_4\cdot(NH_4)_2SO_4\cdot 6H_2O$, are easily grown and by the substitution of diamagnetic atoms of zinc or magnesium for the paramagnetic atoms of copper, it is possible to achieve any desired degree of spin concentration. The ammonium ions can be replaced by those of potassium, rubidium, or cesium; selenates (SeO_4) can be used instead of the sulfates; and crystallization will take place in either heavy or normal water.

The investigation which was actually carried out was much less ambitious than the above variations suggest, but nevertheless the majority of the phenomena uncovered have successfully eluded quantitative interpretation.

Electron spin recovery times have been observed for $Cu[Zn]SO_4\cdot(NH_4)_2SO_4\cdot 6H_2O$ as a function of concentration and crystal size at 1.34, 2.10, and 4.21°K. The substitution of K for NH_4 was made at 1% concentration and D for H at 1% and 100%. At several different concentrations relaxation times were recorded for crystals which were grown ~1000 times more rapidly than normally. In Sec. II we shall present a summary of the experimental findings. After a brief discussion of the crystals and experimental techniques (Sec. III) the remaining sections will be concerned with examination and interpretation of the data.

II. SUMMARY OF THE EXPERIMENTAL RESULTS

The electron spin relaxation time constants, denoted by $\tau_{1/e}$, were measured at frequencies $\approx 9\times 10^9$ cps, magnetic fields $\approx$3000 Oe, and at temperatures in the liquid-helium range, 1.34–4.21°K.

(a) Slowly grown,[4] fully concentrated crystals of the hydrated $CuNH_4$ Tutton salt $[CuSO_4\cdot(NH_4)_2SO_4\cdot 6H_2O]$ and the deuterated version showed relaxation times (Fig. 1) which were linearly[4] dependent upon the size of the crystal and identical within the experimental error (±10%). Rapid growth[4] removed the linearity but a marked size dependence remained (Fig. 2). When the coolant, which was in direct contact with the slowly grown crystallites, was changed from helium liquid to helium gas, no change in the recovery curves was noticed for the crystallite sizes; 2000, 500, 200, and 90 μ. An upper limit of 7 msec was placed on the spin-lattice relaxation times at 1.34°K. This was obtained from several runs on different collections of crystals whose average size was ≤ 37 μ. Relaxation times for the smallest crystals (≤ 37 μ) were arbitrarily plotted at ~5 μ.

(b) Reference to Fig. 2 shows that for equal parts of copper and zinc (50% concentration) the type of growth did not significantly affect the size dependence

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† This work was supported wholly by the Joint Services Electronics Program (U. S. Army, U. S. Navy, and U. S. Air Force) under Contract No. DA 36-039 SC 90789.

* This is based on part of a dissertation submitted to Columbia University in partial fulfillment of the degree of Doctor of Philosophy, 1962.

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[1] J. A. Giordmaine, L. E. Alsop, F. R. Nash, and C. H. Townes, Phys. Rev. **109**, 302 (1958).

[2] *Quantum Electronics*, edited by C. H. Townes (Columbia University Press, New York, 1960), see the article by F. Nash and E. Rosenwasser, p. 302.

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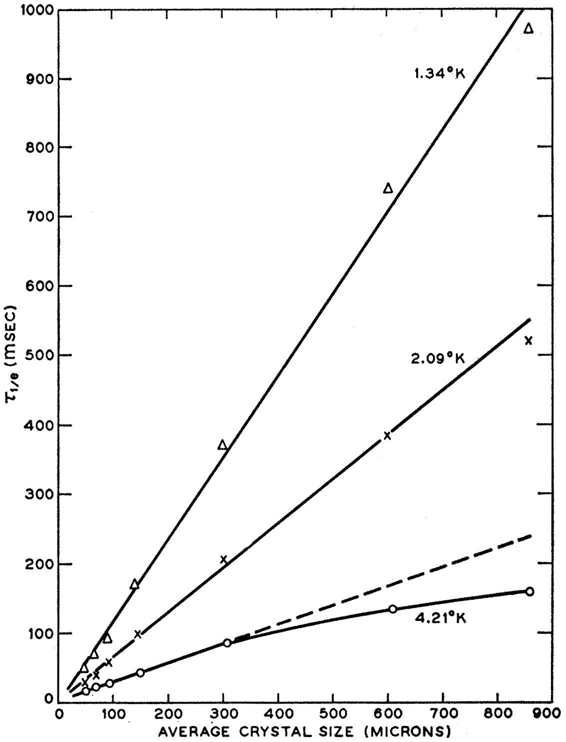


FIG. 1. Relaxation times in *slowly* grown crystals of $Cu(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (100% concentration) versus characteristic size of crystals.

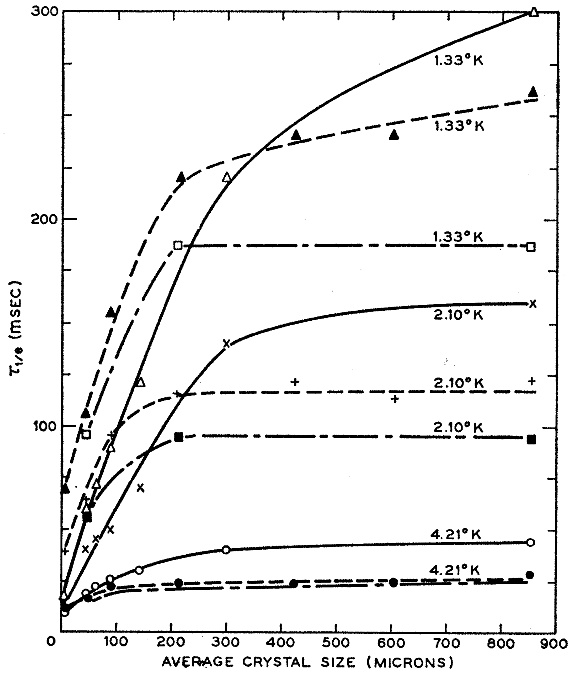


FIG. 2. Relaxation times versus characteristic size of crystals for *quickly* grown crystals of $Cu(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (100% concentration) represented by ———, *slowly* grown crystals of $Cu^{0.5}Zn^{0.5}(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (50% concentration) represented by – – –, and *quickly* grown crystals of $Cu^{0.5}Zn^{0.5}(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (50% concentration) represented by — - — - .

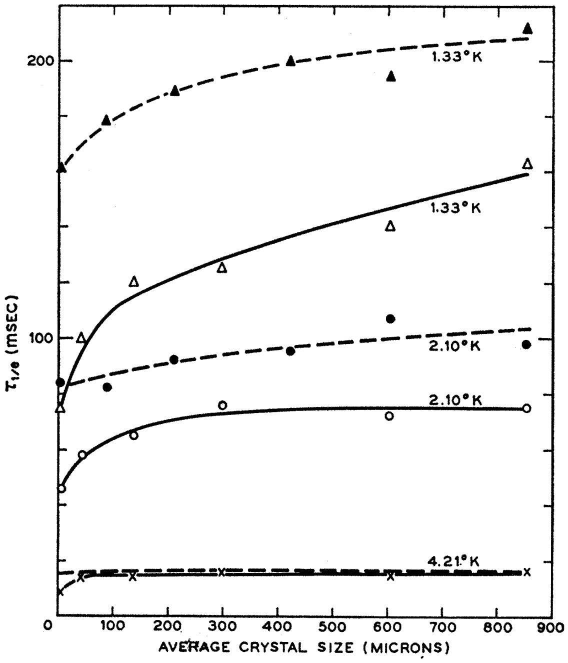


FIG. 3. Relaxation times versus characteristic size of crystals for *slowly* grown crystals of $Cu^{0.25}Zn^{0.75}(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (25% concentration) represented by ———, and *slowly* grown crystals of $Cu^{0.12}Zn^{0.88}(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (12% concentration) represented by – – – .

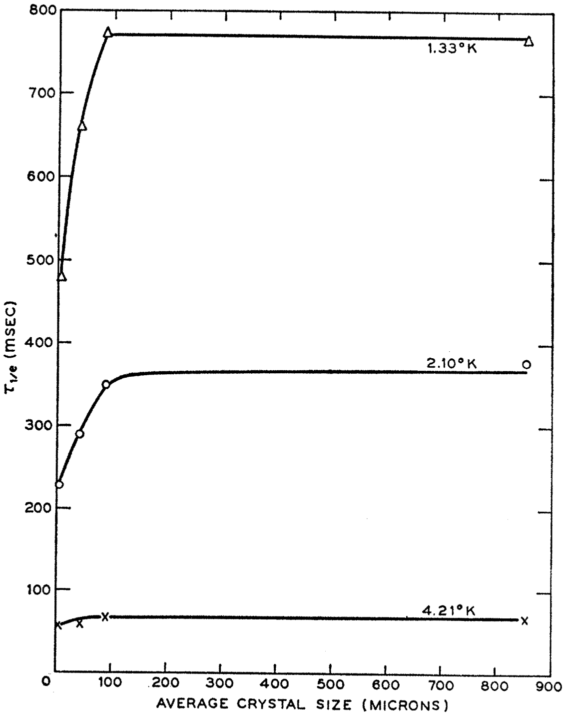


FIG. 4. Relaxation times in *slowly* grown crystals of $Cu^{0.05}Zn^{0.95}(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (5% concentration) versus characteristic size of crystals.

TABLE I. The content in ppm of the paramagnetic impurity of iron for some of the crystalline sample sizes. The accuracy of the determinations is ±30%. All other paramagnetic ions of the first-transition group were present to no greater degree than 10 ppm (the detection limit).

Size (microns)	100% hydrated $CuNH_4$ slowly grown	50% hydrated $CuNH_4$ slowly grown	5% hydrated $CuNH_4$ slowly grown	1% hydrated $CuNH_4$ slowly grown	1% hydrated $CuNH_4$ quickly grown	1% deuterated $CuND_4$ slowly grown	1% deuterated CuK slowly grown	1% hydrated CuK slowly grown	0.3% hydrated $CuNH_4$ slowly grown	0.1% hydrated $CuNH_4$ slowly grown
855	5	10	<10	<10	20	<10	<10	5		
605										
425		10								
300	10									10
213		10				<10			15	
141							<10	20		
89	15		<10	10	20	10			20	10
63										
45			100	70	60	100	50	30	200	20
<37			200	150	50	300	200	200	700	100

and the results are not too different from the rapidly grown fully concentrated crystals.

(c) Figure 3 shows that the size effect is reduced as the concentration is lowered, being almost negligible at 12%. Figure 9 shows that for the concentration range ~12–100%, $\tau_{1/e}$ decreases as the concentration decreases.

(d) Figure 4 gives evidence that a different kind of size dependence is present at 5% concentration. At 1% (Fig. 5) the same sort of size dependence in crystals of normal growth is completely removed by rapid crystallization. Figure 9 reveals that for the concentration range 12–0.3%, $\tau_{1/e}$ increases as the concentration decreases.

(e) For 0.1% and 0.05% concentration (Figs. 6 and 7) size dependence remains although $\tau_{1/e}$ once again decreases with concentration. At 0.02% (Fig. 8) $\tau_{1/e}$ is very insensitive to the bath temperature.

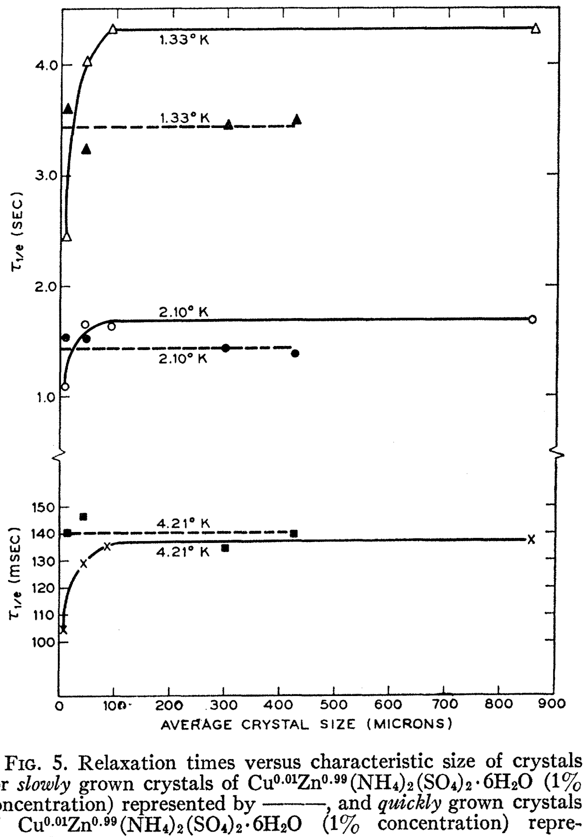


FIG. 5. Relaxation times versus characteristic size of crystals for *slowly* grown crystals of $Cu^{0.01}Zn^{0.99}(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (1% concentration) represented by ———, and *quickly* grown crystals of $Cu^{0.01}Zn^{0.99}(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (1% concentration) represented by - - - - .

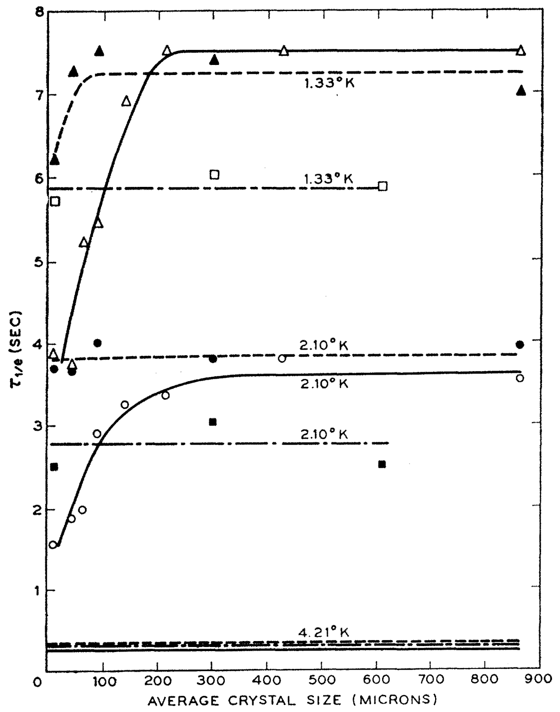


FIG. 6. Relaxation times versus characteristic size of crystals for *slowly* grown crystals of $Cu^{0.003}Zn^{0.997}(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (0.3% concentration) represented by ———, *slowly* grown crystals of $Cu^{0.001}Zn^{0.999}(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (0.1% concentration) represented by - - -, and *quickly* grown crystals of $Cu^{0.001}Zn^{0.999}(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (0.1% concentration) represented by —·—·—.

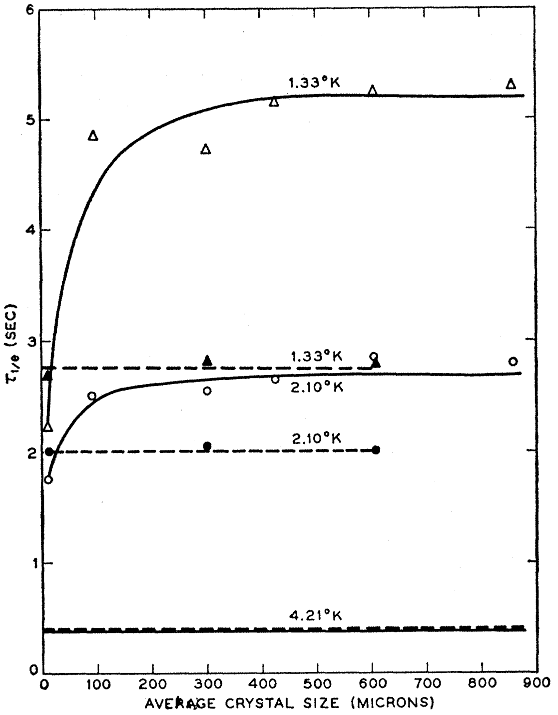


FIG. 7. Relaxation times versus characteristic size of crystals for *slowly* grown crystals of $Cu^{0.0005}Zn^{0.9995}(NH_4)_2(SO_4)_2\cdot 6H_2O$ (0.05% concentration) represented by ———, and *quickly* grown $Cu^{0.0005}Zn^{0.9995}(NH_4)_2(SO_4)_2\cdot 6H_2O$ (0.05% concentration) represented by - - - .

(f) Comparison of Figs. 5 and 10 indicates that the substitution of deuterium for hydrogen in the copper ammonium salt resulted in a change in $\tau_{1/e}$ of a factor of ≈ 8.5, below the λ point. Deuteration of the corresponding copper potassium salt showed no such change (Fig. 11). The extent of deuteration was ~90%.

(g) Table I suggests a correlation between the paramagnetic impurity of iron and the size effect for concentrations $\leq 5\%$, size for size.

(h) The presence of two inequivalent copper sites in a unit cell gives rise to two resonance lines in the fully concentrated salt. The resonances could barely be resolved in the hydrated salt and were fully resolved in the same salt, deuterated.

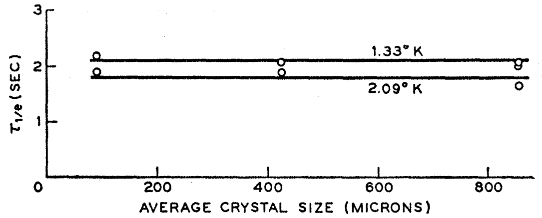


FIG. 8. Relaxation times in *slowly* grown crystals of $Cu^{0.0002}Zn^{0.9998}(NH_4)_2(SO_4)_2\cdot 6H_2O$ (0.02% concentration) versus characteristic size of crystals.

(i) For single crystal measurements at 5%, the hyperfine components [Ref. 1, Fig. 1] all had approximately the same relaxation times which changed by no more than a factor of 2 as the orientation was varied. Single crystal measurements at 1% showed a maximum orientational change in $\tau_{1/e}$ of a factor of 3; the relative spacing of the hyperfine components and their relaxation times necessary for "cross-maser" effects[2] are in agreement with the predictions of Sorokin *et al.*[5]

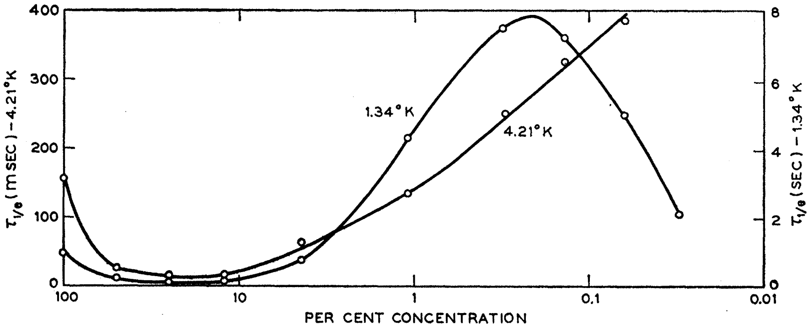
(j) Large fully concentrated single crystals ($L > 1$ mm) for which recovery times ~1 sec were recorded were transparent and at a grazing angle reflected light specularly. Dehydration of the surfaces of crystals never appeared to affect the dynamic decay curves.

III. EXPERIMENTAL TECHNIQUES AND CRYSTALS

The crystals, their spin concentrations, and growth rates accompany the graphs of the experimental results. The percentages indicate the concentrations present in the parent solutions, and in the range 100–0.3% these agree to within $\approx 10\%$ of the concentrations as determined by quantitative chemical analyses. From 0.3–0.02%, the quantitative analyses were ~30% higher than the nominal concentrations. This tendency to "read high" in the low-concentration range is inherent in the chemical analysis so that the over-all agreement is quite satisfactory.

The spin concentration is defined as 100% times the ratio of the number of Cu^{2+} ions to the number of potential Cu^{2+} sites. In all cases the crystals were the product of reagent grade chemicals (iron group im-

FIG. 9. Relaxation times of slowly grown crystals of $Cu^xZn^{1-x}(NH_4)_2(SO_4)_2\cdot 6H_2O$ versus percent concentration for crystals whose characteristic size is 855 μ.



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[5] P. Sorokin, G. J. Lasher, and I. L. Gelles, Phys. Rev. **118**, 939 (1960).

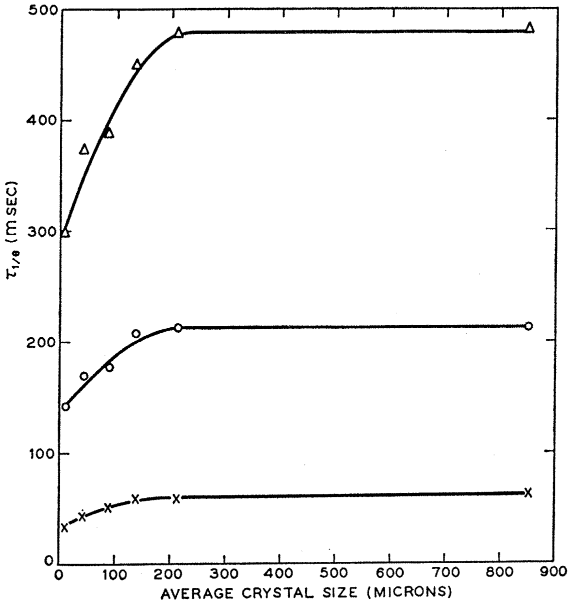

FIG. 10. Relaxation times in *slowly* grown crystals of $Cu^{0.01}Zn^{0.99}(ND_4)_2(SO_4)_2\cdot 6D_2O$ (1% concentration) versus characteristic size of crystals.

purities <0.001%) and distilled water. The growth and preparation of the various sizes of naturally grown single crystals are described elsewhere.[4] For purposes of deuteration the chemicals were dissolved in heavy water, and the growth took place in a dessicator. Microscopic examination of the contents of the ten sieves (ranging in size from 37–1000 μ) used to sort the crystals revealed that most of the single crystals in any given sieve were of about the same size and free of small parasitic particles.

Quantitative analyses were also performed on slowly grown 1% $Cu[Zn](ND_4)_2(SO_4)_2\cdot 6D_2O$ [$L<37, L=89, 212\ \mu$], 1% $Cu[Zn](NH_4)_2(SO_4)_2\cdot 6H_2O$ [$L<37, L=89\ \mu$] and quickly grown 1% $Cu[Zn](NH_4)_2(SO_4)_2\cdot 6H_2O$ [$L<37, L=45$, 89, 300 μ]. For each size three different types of analyses (amine and neocuprione methods and a colorimetric technique) showed that to within ±15%, the copper content was the same.

Each experimental "sample" consisted of a collection of naturally grown, randomly oriented single crystals of the same size (to within ±10%). No attempt was made to correlate the size effects observed with the "shape" of a single crystal. The relationship between the microwave frequency ν and the dc magnetic field H, is given by $h\nu=g\beta H$, $g=2.16$ and β is the Bohr magneton. Due to the increase in "sample" volume, necessary for measurement as the concentration decreased, the cavity frequency varied in steps from 9600 to 8700 Mc/sec. The frequency change from one concentration to the next was a good deal less than this and it was assumed to have no significant bearing on the results.

Paramagnetic resonance data for the Tutton salts can be found in Bleaney *et al.*[6] The apparatus and techniques employed to establish the spin recovery curves are similar to those of Bowers and Mims.[7] It was found that apart from initial nonexponentiality, the decay curves could always be described by a single time constant (the time for $1/e$ recovery) for the region $\Delta N\approx\Delta N_0$. The experimental error was $\sim\pm 10\%$ (this being slightly higher above the λ point due to the bubbling of the helium, despite the use of a Styrofoam cavity insert.)

A measure of the reliability of the results can be gauged from the following: (1) Samples of 100% and 0.3% concentration gave the same results as samples from the same "batches" did six months later. (2) Many repeated "runs" on powders and single crystals over periods of several days gave no indication of a variation in the observed recovery curves, despite a dehydration of the crystal surfaces. (3) During every run the monitoring and saturating powers were varied by at least 6 dB. The length of the saturating pulse was also varied from 4 msec to 10 sec. No variations in relaxation were noted.

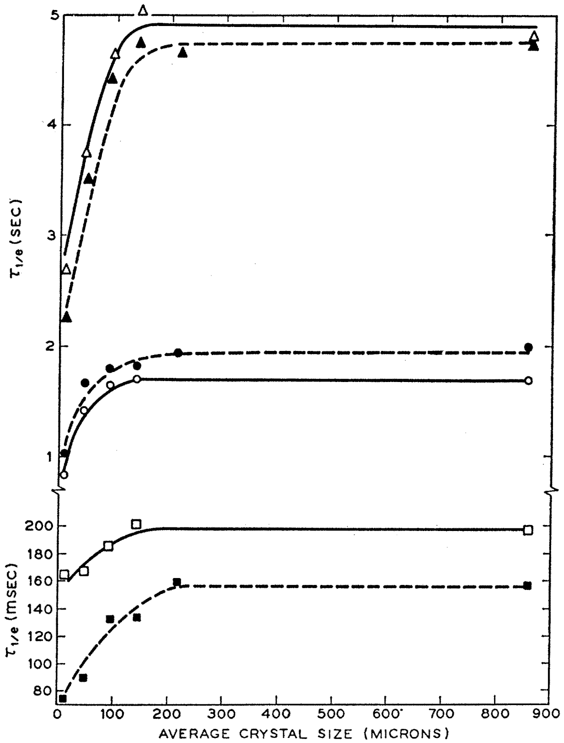

FIG. 11. Relaxation times versus characteristic size of crystals for *slowly* grown crystals of $Cu^{0.01}Zn^{0.99}K_2(SO_4)_2\cdot 6H_2O$ (1% concentration) represented by – – –, and *slowly* grown crystals of $Cu^{0.01}Zn^{0.99}K_2(SO_4)_2\cdot 6D_2O$ (1% concentration) represented by ——.

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[6] B. Bleaney, R. P. Penrose, and B. L. Plumpton, Proc. Roy. Soc. (London) **A198**, 406 (1949); B. Bleaney, K. D. Bowers, and D. J. E. Ingram, Proc. Phys. Soc. (London) **A64**, 758 (1951).

[7] K. D. Bowers and W. B. Mims, Phys. Rev. **115**, 285 (1959).

IV. LINEAR SIZE DEPENDENCE

In this section we will be concerned with the linear size dependence which is displayed in Fig. 1. These data are best explained by a phonon-bottleneck theory, although we shall consider alternative explanations.

A. Phonon Bottleneck

The phonon bottleneck has been quantitatively considered[8–10] in some detail. Under certain circumstances the observed decay time of a spin resonance can be a good deal larger than the actual spin-lattice relaxation time. The "persistence" or "trapping" time is a consequence of the relative slowness of heat transfer from the lattice to the cryogenic environment, and its existence depends upon the dominance of first-order spin-lattice coupling.

In more detail we can picture the phonons of the lattice modes, which are in contact with the "core" of the spin resonance, as being absorbed and re-emitted many times in the course of their spatial "flight." The paucity of these carriers, relative to the number of spins, dictates the shortness of their mean free path in the center of the resonance, and also that the temperature of these modes be more akin to that of the spins. Under the circumstances, a diffusion process would be expected to govern the kinetics of phonon energy transport. However, because of spin-spin interactions, phonons are subject to spectral as well as spatial diffusion, and as a result, the spins come into equilibrium with a range of lattice modes that exceeds the width of the spin resonance. The lattice energy is conveyed to the bath not by those phonons which are effectively trapped but instead by those whose central frequencies lie somewhere in the wings of the spin resonance and whose mean free path is of the same order as the size of the crystal (this being true in the absence of anharmonic lattice interactions).

One finds[10] that the trapping time associated with a Gaussian-shaped resonance for a spin temperature which is approximately equal to that of the helium bath is

$$T_1' \approx 0.8\left(\frac{h\nu}{kT}\right)^2 \frac{NL\eta}{\rho(\nu)\Delta\nu v}\left\{\ln\left[\frac{1}{2}\left(\frac{h\nu}{kT}\right)^2 \frac{NL\eta}{\rho(\nu)\Delta\nu v T_1}\right]\right\}^{1/2}. \quad (1)$$

The parameters which are appropriate for $L \approx 10^{-1}$ cm and $T = 1.34$°K (Fig. 1) are: N = total number of spins per unit volume $= 3\times10^{21}$ spins/cm^3, $\nu = 9.6\times10^9$ cps, $\rho(\nu)$ = mode density $= g4\pi\nu^2/v^3$, v = average acoustic velocity $\approx 2.5\times10^5$ cm/sec, $\Delta\nu$ = full width of spin resonance $\approx 9\times10^8$ cps, and T_1 = spin-lattice relaxation time which is ≤ 7 msec (this upper limit comes from measurements on crystals whose average size $< 37\ \mu$). The acoustic transmission or mismatch factor lies in the range $1 \leq \eta \leq (\rho v)_{\text{solid}}[4(\rho v)_{\text{helium}}]^{-1}$, where ρ is a mass density, and $(\rho v)_{\text{solid}} \gg (\rho v)_{\text{helium}}$. The lower limit corresponds to perfect transmission and the upper limit is the result of a simple acoustic theory.[11]

Although it is quite reasonable to suppose that heat is transmitted from a solid to the surrounding helium liquid by means of phonons,[12,13] detailed experiments[14,15] indicate that transmission at $\nu \sim kT/h$ is at least an order of magnitude more rapid than one would suspect and independent of properties peculiar to helium below the λ point. The work of Jeffries *et al.*,[9,16] and Standley and Wright[17] support this at lower frequencies and indeed they find $\eta \sim 1$. Our experimental findings for gaseous and liquid environments show $\eta = 1$, rather less than the theoretical factor of ≈ 30. The theoretical calculations by Mills[18] shows this to be quite reasonable.

In order to estimate T_1' we shall choose $T_1 = 7$ msec and $g = 3$. Then T_1' (theoretical) ≈ 1.1 sec. From Fig. 1, T_1' (experimental) ≈ 0.98 sec. This agreement is actually better than it should be because of the following uncertainties:

1. Equation (1) applies to an infinite slab of thickness L. For the actual crystals which are roughly cubic one would expect T_1' to be smaller.
2. Equation (1) also neglects the effects of diffusion out to the cutoff frequency[10] which would have the effect of making T_1' smaller.
3. The value of $T_1 = 7$ msec is an upper limit, and a smaller value would make T_1' larger.
4. Since liquid helium will not support transverse modes the degeneracy factor g will lie in the range $1 \leq g \leq 3$ and hence T_1' might actually be larger.

Although the predicted linear dependence of T_1' on crystal size is in evidence, the data of Fig. 1 will not permit a meaningful comparison with the theoretical temperature dependence. The temperature dependence predicted by (1) for the above values of the parameters

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[8] B. W. Faughnan and M. W. P. Strandberg, J. Phys. Chem. Solids **19**, 155 (1961).

[9] P. L. Scott and C. D. Jeffries, Phys. Rev. **127**, 32 (1962).

[10] J. A. Giordmaine and F. R. Nash, following paper, Phys. Rev. **138**, A1510 (1965); this work may be consulted for a more complete listing of references.

[11] If the reflection coefficient for acoustic waves normally incident upon the interface is

$$R = [(\rho v)_{\text{solid}} - (\rho v)_{\text{helium}}]^2 / [(\rho v)_{\text{solid}} + (\rho v)_{\text{helium}}]^2,$$

then $\eta = (1-R)^{-1}$, and for R not very different from unity, η may be interpreted as the number of times that a phonon must present itself at the interface before escape to the helium. If P is the power in a wave packet, then the power remaining after m interface reflections is $R^m P$ and when the power equals P/e,

$$m = [\ln(R^{-1})]^{-1} \approx (1-R)^{-1} = \eta.$$

[12] I. M. Khalatnikov, Zh. Eksperim. i Teor. Fiz. **22**, 687 (1952).

[13] W. A. Little, Can. J. Phys. **37**, 334 (1959).

[14] L. J. Challis, K. Dransfeld, and J. Wilks, Proc. Roy. Soc. (London) **A260**, 31 (1961).

[15] R. C. Johnson and W. A. Little, Phys. Rev. **130**, 596 (1963).

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[17] K. J. Standley and J. K. Wright, Phys. Letters, **3**, 101 (1962).

[18] D. L. Mills, Phys. Rev. **A133**, 876 (1964); **A134**, 306 (1964).

is effectively $T_1' \propto T^{-2.3}$. Allowing for a ±10% uncertainty in the experimental results, one finds a dependence of $T_1' \propto T^{-2.1}$ Such a dependence is then approximately consistent with the theory.

Very little can be said about the nature of the spin-lattice coupling except that the single-phonon process appears to be dominant. The lattice-bath step is quite evidently a puzzle. Our discussion concerning η reveals that there is no satisfactory explanation for the transfer of energy from one substance to another at low temperatures.[12–16] A striking contrast to the conclusions[9,16–18] that $\eta \approx 1$ is the appreciable mismatch $\eta \gg 1$ detected in the ultrasonic echo experiments[19] conducted on quartz rods (end faces optically polished) at $\nu \sim 10^{10}$ cps and $T \approx 4°\text{K}$. Little[20] has shown that if the phonon wavelength is comparable to the surface roughness the heat flow across the crystal-helium interface is smaller than for a smooth surface. If the roughness is in excess of the phonon wavelength then the integrated microscopic interface area will exceed the macroscopic geometrical area. However, large single crystals of the fully concentrated salt which showed relaxation times of ~ 1 sec were transparent, generally quite clear, and they reflected specularly light which was incident at a grazing angle. Dehydration of the crystal surface in repeated experiments had no significant bearing on the results. Since $\lambda_{\text{optical}} \approx \lambda_{\text{phonon}}$ it is probable that no interface irregularities, which could "bottle-up" the phonon energy (and hence yield $\eta_{\text{apparent}} \sim 1$), existed in our case.

However the work of Mills[18] shows that an irregular surface which is characterized by a porosity radius $\ll \lambda_{\text{phonon}}$ can make the interface nonreflecting for sound waves. The examinations which were made of the crystal surface were not sensitive to such a surface layer.

B. Fang's Approach

Recently, Fang[21] has attempted to explain the results[4] of Fig. 1 on the basis of size-dependent considerations originally put forth by Eisenstein.[22] The Eisenstein model appears to involve two assumptions: (1) The spin energy is somehow transferred to the thermal modes (that portion of the Debye spectrum in equilibrium with the bath), and (2) a diffusion equation governs the kinetics of energy transport. A bottleneck can then arise if the thermal conductivity of the lattice is sufficiently small. This bottleneck exists over a bandwidth equal to the Debye cutoff frequency and is in contrast to the bottleneck, in a narrow range at $\nu \sim (kT/3h)$, which was considered in Subsec. A.

By examination of the specific heats of the entire lattice and the spins, it would appear that the mode spectrum is incapable of acting as a reservoir for the spin energy. However, the intuition provided by this approach is misleading since a phonon might typically decay to the bath in one-ten-thousandth the time required for the reorientation of a spin.

Before examining Eisenstein's assumptions we can set an upper limit on the rise of temperature of the entire lattice over that of the bath by equating the power delivered by the spins to the low-frequency oscillators *to* the power delivered by the complete lattice spectrum to the bath, assuming instantaneous equilibration of the low-frequency modes with the main body of oscillators and the existence of a steady-state condition.

Following Little[13] we find that the expression for the heat flow rate across an interface between two media is

$$\dot{Q} = \frac{3\pi k^4 A}{\eta h^3 v^2} \{ f(T_X) T_X{}^4 - f(T_B) T_B{}^4 \} , \tag{2}$$

where T_X and T_B are the crystal and bath temperatures, respectively, A equals the interface area, and v equals the average acoustic velocity of the solid. $f(T) = \int x^3 [\exp(x) - 1]^{-1} dx$, $x = h\nu/kT$, and the integration is over the range of modes responsible for heat transfer. In the derivation of (2) we have taken the mode density to be $12\pi\nu^2 v^{-3}$ since the acoustic model predicts that $\eta \gg 1$. Boundary conditions[13] require that if energy is in a mode of one polarization, this energy will be distributed over modes of other polarizations when refraction and reflection occur at the interface.

At low temperatures, the upper limit of integration can be taken to be infinity, and if T_X is not very different from T_B, $T_X{}^4 - T_B{}^4 \approx 4T_B{}^3 \Delta T$. Equating (2) with $h\nu V(\Delta N_0 - \Delta N)$ $(2T_1)^{-1}$ we find that for a slab of thickness L

$$\Delta T = \frac{5}{32\pi^5} \left(\frac{h}{k}\right)^5 \frac{N \nu^2 v^2 \eta}{T_1 T_B{}^4} \left(\frac{V}{A}\right) , \tag{3}$$

assuming T (spin temperature)$\gg T_X$. For the values used previously in connection with Eq. (1), $V = AL$, and $\eta = (\rho v)_{\text{solid}} / [4(\rho v)_{\text{helium}}] \approx 30$ (since $\rho_{\text{solid}} = 1.9$ g/cm^3, and at 1.4°K, $\rho_{\text{helium}} = 0.145$ g/cm^3 and $v_{\text{helium}} = 2.45 \times 10^4$ cm/sec) we find $\Delta T \approx 0.3°\text{K}$. Experiments[14,15] show that the rate of heat transfer to the bath is at least an order of magnitude larger than our estimate, so that ΔT is negligible. In the present calculation the phonon mean free path $\sim L$, an assumption which we shall justify shortly.

In consideration of Eisenstein's first assumption we we shall examine the potency of anharmonic three-phonon (normal) processes in which there is an interchange of energy among lattice oscillators at different frequencies. Such processes have been examined by Van Vleck,[23] Klemens,[24] and Orbach.[25] The most

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effective process is the interaction of a low frequency ($\nu \ll kT/h$) transverse wave with two longitudinal waves, both of frequency $\sim kT/h$. The relaxation time for energy in a low-frequency mode is given[24] by $\tau_{3\text{ph}}{}^{-1} \approx 10^{19}\gamma^2 \nu T^4 \rho^{-1} v^{-5}$. For $\gamma =$ Grüneisen's constant ≈ 2, $\nu = 9.6 \times 10^9$ cps, $\rho = 1.9$ g/cm^3 and $v \approx 2.5 \times 10^5$ cm/sec we find that $\tau_{3\text{ph}} \approx 1.5 \times 10^{-3}$ sec for $T = 1.34$°K. Direct coupling to the bath (including mismatch) gives $\tau_{LB} = \eta L v^{-1} \approx 1.2 \times 10^{-5}$ sec ($\eta \approx 30$ and $L \sim 10^{-1}$ cm) and is 2 orders of magnitude smaller. Four phonon processes[25] are *a fortiori* negligible.

The assumption of phonon diffusion is correct only if the phonons are significantly scattered by impurity atoms. Klemens[24,26] has examined this process and found that the relaxation time associated with the elastic scattering of phonons from a random arrangement of a single species of defect lattice sites is

$$1/\tau_D = fa^3(\Delta M/M)^2(\omega^4/4\pi v^3). \tag{4}$$

ΔM is the deviation of a unit cell mass from the normal mass M, f is the fractional concentration of defect sites, and a is a unit cell dimension. For more complicated crystals in which a unit cell contains atoms of several elements, Eq. (4) can still be applied, provided that the masses and their deviations are interpreted[27] as properly weighted averages. The general validity conditions[25,28] for (4) are satisfied for our case.

The role of defect scattering in thermal conduction can be gauged if the frequency of the modes which are dominant in energy transfer at low temperatures is known. If we maximize the expression for the thermal conductivity given by Callaway and von Baeyer[29] (in such a way as to exaggerate the importance of defect scattering), we find that the dominant modes have a frequency $\approx 4kT/h$. By defining $l_D \equiv \tau_D v$, we find that for $T = 1.4$°K, $a = 2$ Å, $f = 1/130$ and $\langle(\Delta M)^2\rangle / \langle \bar{M} \rangle^2 \approx 1/750$ (taking into account the isotopic abundances of the elements and the impurities present in the fully concentrated salt, i.e., Fe-10 ppm, Si-50 ppm, Al-10 ppm, etc.), that $l_D \sim 200$ cm. The largest crystal used in our experiments had a side ≈ 0.4 cm.

Thus our reasonable estimates confirm our previous assumption that phonons in the wings of the spin resonance have a mean free path $\sim L$, and suggest that Fang's calculation is not applicable in our particular case.

C. Spin Diffusion

Size effects can in principle arise from conduction within the spin system itself. We may estimate an overall diffusion time from a simple random-walk equation; the net distance traveled in a particular direction is equal to the mean free path times the square root of the number of steps. Mathematically this is $2L/3 = 0.8\, a(T_{\text{SD}}/T_2)^{1/2}$; L is the crystal slab thickness, $(2L/3)$ is an average distance over which energy must be transported in order to be susceptible to direct absorption by the helium bath, $T_2 = (2\pi\Delta\nu)^{-1}$ is the time for one step, $2\Delta\nu =$ full width of the spin resonance and $a =$ mean free path. If $L \sim 10^{-1}$ cm, $a \sim 6 \times 10^{-8}$ cm, $2\Delta\nu \sim 10^9$ cps, then $T_{\text{SD}} \sim 600$ sec and is several orders of magnitude larger than the observed time of ~ 1 sec. More elaborate calculations by Fröhlich and Heitler[30] and Bloembergen[31] give substantially the same results. We note that spin diffusion predicts a strong size dependence ($\propto L^2$) and a weak temperature dependence, neither of which is observed.

Nevertheless there is a manner in which cross relaxation and spatial spin diffusion might be responsible for the size effects observed in Fig. 1. From Table I we see that the iron concentration, for the fully concentrated sample, is $N_{\text{Fe}} \sim 10^{17}$ iron spins/cc and increases with decreasing sample size. The approach that will be used was independently suggested by Van Vleck,[32] Bloembergen and Pershan,[32] and Elliott and Gill.[32] We shall imagine that the "excess" spin excitation spatially diffuses to strongly coupled pairs of Fe spins. Cross relaxation then couples the microwave transition of a Cu^{2+} spin to an energetically similar transition between excited-pair states which lie Δ above the ground state in energy. ($\Delta \gg kT \gg \delta = h\nu$). The probability that two adjacent nearest-neighbor sites of a copper atom be occupied by atoms of iron is $\sim(Zc)^2$ where Z is the number of nearest neighbors for any site and $c = N_{\text{Fe}}/N_{\text{Cu}}$. The number of random steps required in the diffusion of energy among copper spins before a high probability of encounter of a pair-system is $(T_{\text{SD}}/T_2) \sim (Zc)^{-2}$. For $T_2 \sim 3 \times 10^{-10}$ sec, $Z \sim 10$, $c \sim 3 \times 10^{-5}$, we find that $T_{\text{SD}} \sim 3 \times 10^{-3}$ sec. The cross-coupling time for the transfer of excitation from a copper atom to the pair system is $T_{12} \sim T_2 \exp(\Delta/kT)$. Even if $\Delta \sim 20$ cm^{-1}, $T_{12} \sim 0.15$ sec for $T = 1.4$°K. Thus it is not unreasonable to suppose that spin-spin processes are sufficiently potent so that the relaxation which we might be observing would be the "iron-spin-lattice" interaction. If indeed $T_{\text{SD}} + T_{12} \ll 1$ sec then we may define an effective relaxation time for a copper spin (following Elliott and Gill[32]) as $(\tau_{\text{Cu}})_{\text{eff}} \sim (N_{\text{Cu}}/N_{\text{Fe pairs}})\tau_{\text{Fe}}$. The spin-lattice relaxation time τ_{Fe} for the excited state $\propto [\Delta^3(n_\Delta + 1)]^{-1}$ where n_Δ is the average number of phonons at an energy Δ and since $N_{\text{Fe pairs}} \propto c^2 \exp(-\Delta/kT)$ we find that

$$(\tau_{\text{Cu}})_{\text{eff}}{}^{-1} \propto c^2 \textstyle\sum_r \exp[-\Delta(r)/kT] \\ \times \Delta^3(r)(n_\Delta + 1) = c^2 \textstyle\sum_r \Delta^3(r) n_\Delta .$$

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If we assume that the iron spins are dipolar coupled $(\Delta=\Delta_0 a^3/r^3)$ and let $\sum_r \rightarrow \int 4\pi r^2 dr$ we find for $\Delta \gg kT$ that $(\tau_{\mathrm{Cu}})_{\mathrm{eff}}^{-1} \propto (ckT)^2\Delta_0$. Exchange coupling $[\Delta=\Delta_0 \times \exp(-r/a)]$ leads to $c^2(kT)^3 \ln^2(\Delta_0/kT)$. If the data of Fig. 1 are to be explained by the presence of iron then the first expression[32] for $(\tau_{\mathrm{Cu}})_{\mathrm{eff}}^{-1}$ is more appropriate. The variation of c with L falls within the experimental error in the determination of N_{Fe}.

Thus, if the impurity of iron is uniformly spread throughout the crystals in which it is present, then the preceding analysis would indicate that the observation of a relaxation time $\propto LT^{-2}$ is not certain proof of the existence of a phonon bottleneck, although the latter appears to be the more reasonable explanation.

Strains or dislocations which depend upon the crystal size and at which anharmonic processes could occur seem an unlikely explanation for Fig. 1 since the relatively slow growth ($\sim$2 weeks) of the fully concentrated deuterated crystals resulted in a duplication of the data for the hydrated samples. The departure from nonlinearity at 4.2°K is not explained by the competition of three-phonon processes since $\tau_{3\mathrm{ph}}(4.2°\mathrm{K}) \sim 10^{-5}$ sec while direct absorption by the helium occurs in 4×10^{-7} sec.

V. CONCENTRATION AND SIZE DEPENDENCE

In this section we will briefly examine the data presented in Figs. 2–11.

Because of the hyperfine structure and potent cross-relaxation processes the frequency range of modes responsible for energy transport should remain approximately constant down to concentrations $\sim 1\%$. Equation (1) would predict that T_1' should decrease as the concentration is decreased; this is roughly what is observed (Fig. 9). The phonon-bottleneck effect apparently becomes marginal in a region of concentration $\sim 10\%$ (Figs. 3 and 9).

The actual dependence of the observed relaxation times upon the spin concentration cannot be determined from the data (Figs. 1—3). The tiny single crystals of the fully concentrated salt tended to be approximately cubic in shape, whereas the 50% samples had one dimension somewhat smaller than the other two. With dilution (Figs. 2 and 3) the linearity vanishes and some internal conversion process associated with the dilutent appears to limit the extent of the bottleneck. The observed relaxation time (Figs. 1–3) for crystals whose size $\leq 37\ \mu$ increases as the concentration decreases; this may be related to concentration-dependent spin-lattice coupling. In any case, the over-all size effect falls off much more rapidly with increased dilution than one would expect.

From 5% down to 0.05%, the nature of the size effect changes. The relaxation times of the larger crystallites increase with increasing dilution (Fig. 9), a situation which has been observed rather often for paramagnetic atoms of the first-transition group and which might be explained by an elaboration of the suggestions of Van Vleck,[32] Pershan and Bloembergen,[32] and Gill and Elliott.[32] Such approaches can lead to a variety of concentration and temperature dependences.

The reversal in the concentration dependence in the region 0.3–0.02% (Fig. 9) would make the following tentative explanation reasonable. In all crystals there might be a constant density of imperfections or paramagnetic impurities which act as an energy sink for a small number of adjacent spins. When the ratio of copper to zinc falls below a certain level these sinks start to be effective and become increasingly important as the amount of energy that has to be handled decreases. This kind of effect would prevent one from observing spin-lattice relaxation times which either increased or remained constant as the dilution was further increased in a low concentration region. Spin-spin coupling might be responsible for the approximate temperature independence at 0.02%.

The most plausible explanation of the size effect in the concentration range $\leq 5\%$ is related to the sharp increase in iron contamination which commenced at the "knee" of the $\tau_{1/e}$ versus L curves ($\sim 90\ \mu$) and was at least an order of magnitude higher for the smallest sizes (Table I). Table I suggests why the size effect was not marked at 0.1% and also shows that for quickly grown 1% crystals there was some discrimination against the incorporation of iron during growth. Figure 5 appears to confirm this contamination hypothesis.

Since no extensive $\tau_{1/e}$ versus temperature data was recorded, it is pointless to speculate at any length about the nature of mechanisms responsible for the size dependence. Any model will have to agree with the following observations in the concentration range 0.3–5%:

1. The frequency dependence[2] (for large single crystals at 1%) of the observed relaxation time is ν^{-n}, $2\leq n\leq 3$.
2. The temperature dependence is T^{-m}, $1.5\leq m\leq 4$.
3. The copper concentration dependence is N_{Cu}^{-p}, $0.5\leq p\leq 1$.
4. The iron concentration dependence (if it is significant) is N_{Fe}^{-g}, $g\sim 0.2$.
5. Size for size the temperature dependence is approximately constant for a particular copper concentration.
6. Reference to Figs. 5, 10, and 11 indicates apparently that deuteration of the ammonium ion is responsible for an order of magnitude change in $\tau_{1/e}$.
7. Regardless of the copper concentration, the "knee" of the $\tau_{1/e}$ versus L curves always occurs at the same sample size and it is just at this point that the iron concentration begins to increase.

The mechanisms suggested by Van Vleck *et al.*,[32] which have been examined are strongly dependent upon the iron concentration and independent of the Zeeman frequency ν. It is tempting then to associate the plateaus with spin-lattice relaxation. However, as the temperature is increased the "knee" of the curves should be displaced toward smaller sizes and hence larger iron concentrations. This would reflect the competition between direct coupling to the lattice and cross coupling to the atoms of iron. The role played by the iron is not clear but it should have some effect since for the smallest crystallites at 0.3% concentration there are as many atoms of iron as there are of copper.

Rapid growth might reveal enhanced anharmonic effects; however, apart from the fully concentrated samples, the rate of crystallization did not have much effect on the magnitude of the observations (Figs. 2, 5, 6, and 7). For 50% concentration, rapid growth and dilution have qualitatively the same effect. For the fully concentrated samples which were grown quickly the observed temperature dependence of $\tau_{1/e}$ will depend upon whether the frequency conversion processes compete in parallel or in series with direct absorption of energy by the bath. Unfortunately, the data do not allow a meaningful distinction to be made.

Deuteration of the fully concentrated salt (D/H $\sim$90%) showed that the two main lines (due to two inequivalent sites per unit cell) were resolved for a particular crystal orientation. Under the same conditions in the hydrated salt, the lines were not resolved at all. This narrowing is not to be expected unless intervening atoms participate in the interaction between two Cu^{2+} spins.

VI. NATURE OF SPIN-LATTICE COUPLING

The purpose of this section is to demonstrate the inadequacies of the relaxation mechanisms originally proposed by Waller,[33] Van Vleck and Kronig,[34] if the time constants observed for dilute samples are related to spin-lattice coupling.

Because of the concentration dependence of the relaxation times, coupling[33] via the thermal modulation of the dipolar interaction becomes appealing. Al'tshuler[35] has extended Waller's calculation for the case of the simultaneous reorientation of two spins and has also considered the coupling due to modulation of an anisotropic exchange interaction between spins. Even if we allow for abnormally strong interactions such as those of "superexchange" which were proposed[36] to account for the anomalously large specific heat of the $CuHN_4$ Tutton salt, we find that the calculated relaxation times are orders of magnitude larger than those observed.

Nagaoka,[37] employing the approach taken by Van Vleck[34] (spin-lattice coupling via the thermal modulation of the crystalline electric field), has made explicit computations for magnetically dilute copper Tutton salts. For the direct process it was found that $T_1 \propto T^{-1}H^{-4}$ and has a very marked asymmetry with respect to the angle between the magnetic field and the crystalline axes. For $H \sim 3000$ Oe and $T \sim 1°$K, T_1 varies from 10^{-1} sec [(110) direction] to 10^4 sec [(100) direction]. No asymmetry in excess of a factor of 2 was ever observed, and the dependences upon temperature and frequency are noticeably different. The calculation of the Raman process indicated that $T_1 \propto T^{-9}$ and is independent of magnetic field.

The situation is thus only aggravated by the observation that deuteration can have an effect which is quite unexpected,[38] and which suggests that other atoms, apart from impurities, in the molecule are significantly important in the relaxation process. (From Table I it is seen that all the slowly grown crystals of 1% concentration exhibit approximately the same iron contamination size for size.)

ACKNOWLEDGMENTS

It is a great pleasure to acknowledge the author's association with Professor C. H. Townes and Dr. J. A. Giordmaine. The results of the experimental study and their interpretations, such as these are, are the outcome of many discussions with my mentor (C.H.T.) and my colleague (J.A.G.). The staff of the Columbia Radiation Laboratory and especially the shop under the direction of C. Dechert are to be commended for their assistance in the acquisition and construction of the apparatus. For either correspondence or discussion the author would like to thank W. A. Little, P. H. Fang, S. Zemon, B. Biavati, and E. Tucker.

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