ing and x raying over a wide temperature and concentration range in a variety of alkali halides. Furthermore, this model is in accord with the requirement of inversion symmetry,[13] the absence of dielectric loss[14] and magnetic susceptibility,[15] and the inconclusiveness of electron spin resonance[16] of the *M* center.

In light of the above discussion the suggestion of Pick[3] that the *R* and *N* centers are higher aggregates of *F* centers has been examined. Treating unpublished data[17] for NaCl that had been uniformly irradiated with gamma rays at room temperature, it was found that the R_2-center absorption varied approximately as the 1.5 power of the *M*-center absorption. This supports the contention that the *R* center is an aggregate of an *M* and *F* center, or simply three *F* centers as suggested by Pick. A more extensive study is indicated.

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SIZE-DEPENDENT RELAXATION TIMES AT LIQUID HELIUM TEMPERATURES*

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Recovery times have been observed in one of the copper Tutton salts which depend upon the size of the crystal(s) employed.[1] The salt in question is fully concentrated $Cu(NH_4)_2(SO_4)_2 \cdot 6H_2O$. The paramagnetic ion is Cu^{+2} ($S=\frac{1}{2}$) and the two ions per unit cell give rise to two lines.[2] However, at high concentrations the two lines coalesce to form one broad line whose full width at half maximum varies from 170 to 450 oersteds depending upon the angle between the crystal axis and the magnetic field.

The relaxation times were measured with an *X*-band pulse-decay superheterodyne spectrometer, the output of which was the dynamic recovery curve of the spin system.[3] The relaxation times were determined from the exponential tails of the decays, in the region where the spin temperature ≈ lattice temperature.

The crystals reported on were prepared in two different ways. In the first instance a fine powder of crystallites was allowed to grow slowly over a period of 24 hours. The second method involved the preparation of a supersaturated solution by heating. The solution was stirred continually as it cooled to room temperature with the result that a fine powder of tiny crystals was deposited in the bottom of the beaker. In both cases the crystals were then dried by exposure to air and carefully sorted according to size using a series of sieves. The hole sizes in the ten sieves ranged from 37 to 1000 microns. Only naturally grown single crystals were used in these experiments although some single crystals were crushed and tested to see that the size effect was qualitatively unaltered.

The cavity was entirely filled with Styrofoam except for a pocket $\approx 10\ \mathrm{mm}^3$ which was located in the region of the cavity where $H_{\mathrm{rf}} \approx 0$. This placement was to allow the use of an appreciable volume of sample and still keep the cavity loading $\leq 10\%$.[3]

The results are presented in Figs. 1 and 2. It seems reasonable to suggest that crystals which are grown quickly (≈ 1 minute) are sufficiently strained so that some internal energy conversion mechanism alleviates the apparent bottleneck. One might suggest phonon-phonon interactions but the observed temperature dependence is not as strong as this mechanism would imply.

Within the experimental error of $\approx \pm 10\%$ one can see that $\tau_{1/e} \propto L$, where L is some characteristic length of any one of the many crystallites in a given portion of sample.

From measurements made on single crystals whose smallest dimensions were ≈ 1 - 2 mm, it was noted that the transition from the region where $\tau_{1/e} \propto L$ to the region where $\tau_{1/e}$ is independent of L occurs for $L \approx 1$ mm. Furthermore, the relaxation times of the single crystals were $\approx 20\%$ shorter than those times in the sample where $L \approx 855$ microns. Presumably this is related to the fact that large single crystals are somewhat more strained than smaller ones. The same kind of bottleneck has been seen in the deuterated crystals of the same species and concentration and also in 30% concentration hydrated crystals.

In order to test that the liquid helium in contact with the sample was really cooling the individual particles, a very light smear of the $L < 37$ microns sample was made on the surface of the Styrofoam cavity insert in the region of $(H_{\mathrm{rf}})_{\max}$. This was to assure the helium liquid clear access to all the grains in the sample. Exactly the same results were obtained as when the sample consisted of $10\ \mathrm{mm}^3$ of tightly packed powder, in the weak-field region of the cavity.

Spatial spin diffusion as the explanation for this size effect can be ruled out on the basis of an order-of-magnitude calculation of the overall diffusion time as well as dependence upon length and lattice temperature.[4] The theories of phonon imprisonment in paramagnetic crystals[5] would indicate that lattice-bath relaxation times are being observed.[6] Indeed, there is fairly good agreement between the theory[5] and the observed results. To see that phonon trapping is reasonable one can make an order-of-magnitude estimate of the phonon mean free path (m.f.p.) in the central region of the spin

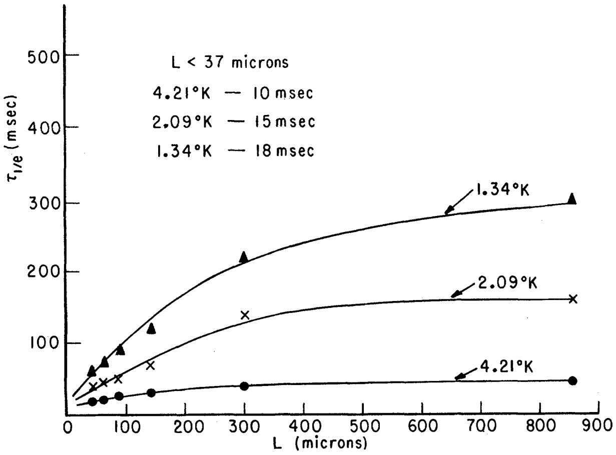

FIG. 1. Relaxation times in quickly grown crystals of 100% $\mathrm{Cu(NH_4)_2(SO_4)_2 \cdot 6H_2O}$ vs characteristic length of crystal.

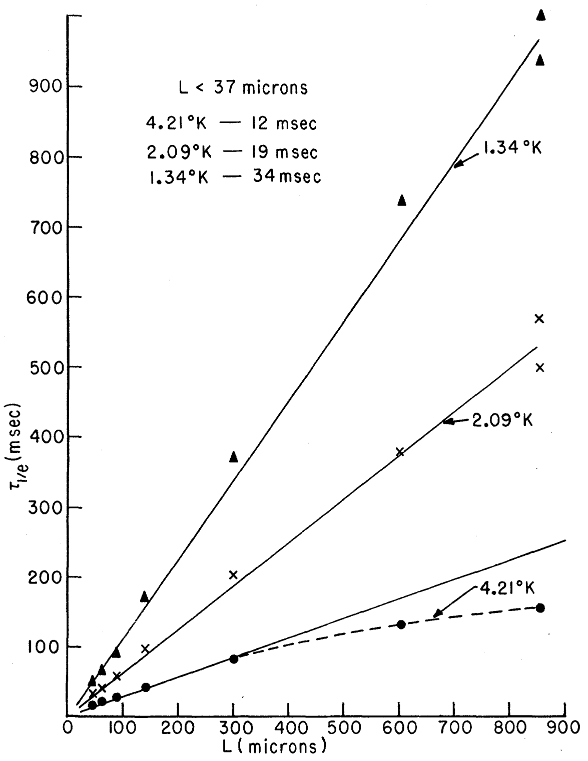

FIG. 2. Relaxation times in slowly grown crystals of 100% $\mathrm{Cu(NH_4)_2(SO_4)_2 \cdot 6H_2O}$ vs characteristic length of crystal.

resonance:

$$\text{m.f.p.} \approx \langle n \rangle_{\text{av}} v\rho(\nu)\Delta\nu T_1/\Delta N$$
$$\approx (kT/h\nu)^2 24\pi\nu^2 \Delta\nu T_1/v^2 N,$$

where $\langle n \rangle_{\text{av}}$ = number of phonons per mode $\approx kT/h\nu$, v is the mean acoustic velocity, $\rho(\nu)$ is the density of lattice modes $= 12\pi\nu^2/v^3$, $\Delta\nu$ is the full width of the spin resonance, T_1 is the spin-lattice relaxation time, and $\Delta N = NkT/2h\nu$. If $T = 1.34$°K, $\nu = 9.6 \times 10^9$ cps, $T_1 = 10^{-2}$ sec, $v = 2.5 \times 10^5$ cm/sec, and $N = 3 \times 10^{21}$ spins/cm^3, then m.f.p.≈ 30 microns or 3×10^{-3} cm.

There are, however, two aspects of this effect which are not clear.

(1) Tests were made on a fully concentrated single crystal in which the sample was cooled by helium gas (pressure ≈ 1 mm of Hg) at 4.21°K, 2.09°K, and 1.34°K. The run was repeated but this time the crystal was cooled directly by liquid helium. Within experimental error the relaxation times in both cases were the same. The test was performed on another single crystal of a different shape and again it did not matter whether the crystal was cooled by helium liquid or gas.

(2) Phonon trapping theoretically[5] depends upon a direct spin-lattice interaction. In addition, experiments which have been performed by the author at lower concentrations indicate that the spin-lattice relaxation time is concentration dependent. However, the theoretical calculations[7] which have been carried out for the concentration-dependent, first order spin-lattice interactions are inadequate to explain the shortness of the spin-lattice relaxation times obtained by extrapolating the present data to $L \approx 0$.

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