PHYSICAL REVIEW VOLUME 126, NUMBER 1 APRIL 1, 1962

Nuclear Magnetic Relaxation in Ionic Crystals at High Temperatures*

P. P. MAHENDROO† AND A. W. NOLLE
Department of Physics, The University of Texas, Austin, Texas

(Received September 25, 1961)

The spin-lattice relaxation time is measured by the recovery method for Na^{23} nuclei and for F^{19} nuclei in NaCl, NaF, BaF_2, and LiF, at temperatures up to approximately 900°K. The Na^{23} relaxation time is well predicted by phonon-phonon interaction theory at the lower temperatures, and by vacancy diffusion theory in higher ranges. The F^{19} relaxation time at the lower temperatures (below 500°K–700°K, depending on the compound) is attributed to spin-spin diffusion in conjunction with paramagnetic impurities; at higher temperatures a decrease consistent with the effects of vacancy diffusion is observed, with an activation energy of 0.65 ev in NaF and of 0.82 ev in BaF_2. The samples are commercially produced single crystals of optical grade.

INTRODUCTION

THE temperature dependence of the nuclear-magnetic relaxation time (T_1) for a solid serves, in suitable cases, to show which relaxation mechanisms are operative, out of the many possible in solids. Therefore we have obtained T_1 for Na^{23} and F^{19} nuclei in several inorganic crystals, primarily in the range between room temperature and 900°K. In this range there is the possibility of observing relaxation controlled by various diffusion processes, and of observing annealing effects. For quadrupolar nuclei (e.g., Na^{23}) we may also find further evidence concerning the well-known multiple phonon processes. The compounds considered are NaCl, NaF, LiF, and BaF_2.

RELAXATION PROCESSES

A number of relaxation processes possible in ionic crystals are listed below, to facilitate later discussion. These processes have been considered in the literature, or are combinations of processes which have been. The first six require quadrupolar nuclei. The symbols are defined in the next section.

1. Van Kranendonk[1] considered the relaxation of quadrupolar nuclei by phonon-phonon interactions, stimulated by electric-field fluctuations in an ideal ionic crystal, and obtained

$$T_1^{-1}=T^2(a-bT^{-2}),\quad \text{for}\quad (T/\theta)\gtrsim 0.5, \tag{1}$$

where a and b are constants.

2. Khutsishvili[2] suggested that for $T>\theta$, the four-phonon interactions predominate, giving a relaxation rate proportional to T^4.

3. Wikner, Blumberg, and Hahn[3] showed that with inclusion of optical modes in Van Kranendonk's analysis, (1) still applies but the predicted relaxation rate is greatly increased, in closer agreement with experiment (e.g., for Na^{23} in NaCl, T_1 is calculated as 30 sec, and observed to be 12 sec).

4. Kondo and Yamashita[4] modified the Van Kranendonk analysis to include charge overlap. The contribution to the relaxation rate, for NaCl, is approximately the same as that from *3*, subject to large uncertainty in the wave functions.

5. Yoshida and Moriya[5] included partial covalency. Since this is important as a correction only for large quadrupole moments, it will not concern us.

6. Diffusion of lattice vacancies produces relaxation through single-phonon processes due to fluctuating electric field gradients. Reif[6,7] adapted Torrey's theory of relaxation due to diffusion in a lattice to obtain

$$\begin{aligned}T_1^{-1}\simeq&(16\pi/45)(1+k')Bp(\omega_0\tau)^{-1}\\&\times[(\omega_0\tau)^{-2}+(5/2)(1+k')^2]^{-1},\end{aligned} \tag{2}$$

where

$$B\equiv(9/64)(2I+3)(2I-1)^{-1}I^{-2}\omega_0^{-1}(\beta e^2Q/\hbar a^3)^2.$$

The geometrical factor k' is 0.116 for vacancies restricted to sites of ions unlike the one undergoing relaxation, in an alkali halide lattice, or 0.3125 for the case of like sites.

7. Torrey[8] treated dipolar interaction in the diffusion of spins of one kind to all points of a simple lattice. The result is easily converted for unlike spins. Evaluating an integral in his work by Reif's approximation,[6] introducing the proper multiplier[9] for the relaxation of nuclei of spin-$\frac{1}{2}$ by nuclei of spin-$\frac{3}{2}$, and making approximations for the case $\omega_{0i}\gg\omega_{0j}$ (which means letting ω_0 become ω_{0i}), we get

$$T_1^{-1}\simeq(\pi/2)\gamma_i^2\gamma_j^2\hbar^2a^{-6}\tau_j[(1+y^2)^{-1}+4(1+4y^2)^{-1}], \tag{3}$$

where the multiplier of the sum-frequency term has

---

* Assisted by the Office of Naval Research.

† Now at Texas Christian University, Fort Worth 9, Texas.

[1] J. Van Kranendonk, Physica **20**, 781 (1954).

[2] G. R. Khutsishvili, J. Exptl. Theoret. Phys. U. S. S. R. **31**, 424 (1956). English translation, Soviet Phys.—JETP 4, 382 (1957).

[3] E. G. Wikner, W. E. Blumberg, and E. L. Hahn, Phys. Rev. **118**, 631 (1960).

[4] J. Kondo and J. Yamashita, J. Phys. Chem. Solids **10**, 245 (1959).

[5] K. Yoshida and T. Moriya, J. Phys. Soc. Japan **11**, 33 (1956).

[6] F. Reif, Phys. Rev. **100**, 1597 (1955).

[7] M. H. Cohen and F. Reif, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 5.

[8] H. C. Torrey, Phys. Rev. **92**, 962 (1953).

[9] N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. **73**, 679 (1948).

been doubled on the basis of later work,[10,11] and where terms in k' have been dropped.

8. Spin-spin diffusion feeds magnetization toward paramagnetic impurities, the interaction with these producing relaxation outside of a characteristic radius, within which the magnetic field of the impurity is too large for spin-spin diffusion to occur.[12,13] The relaxation rate for the system is[13]

$$T_1^{-1} \simeq 8.5 N_p C^{\frac{1}{4}} D_s^{\frac{3}{4}}, \tag{4}$$

where

$$C \equiv (5\pi)^{-1}(\gamma_i \gamma_S \hbar)^2 S(S+1)\tau_c(1+\omega_0^2\tau_c^2)^{-1}.$$

C is a measure of the relaxation rate of a nucleus i at distance r from an impurity. D_s is approximately equal[14] to $a^2/50T_2$. In recovery following saturation, (4) applies after an initial interval where magnetization varies as $(\text{time})^{\frac{1}{2}}$. Alternative cases of spin-spin diffusion,[15] where D_s is so small that all relaxation is by the direct Cr^{-6} process, or where D_s is so great that spatial variation of magnetization is negligible, apparently are not required here. The temperature sensitivity of T_1, corresponding to Eq. (4), is determined by τ_c and T_2, and may be very small.

9. Relative motion of the nuclei and the impurities, when sufficiently rapid, enables all nuclei to interact with the impurities in the fashion first described for translation in liquids,[9] provided the nuclei have everywhere the same diffusion rate. Abragam[16] has shown that a compact solution is obtained when the impurity is an S-type ion. His Eq. (118), adapted for fixed impurities and for diffusion by lattice jumps, gives

$$T_1^{-1} = (16\pi/15) N_p \gamma_S^2 \hbar^2 \gamma_i^2 S(S+1)\tau_i/2a^3. \tag{5}$$

This result assumes that diffusion determines the interaction time in the Cr^{-6} mechanism. For present purposes, we expect that the interaction time cannot exceed about 10^{-10} sec, because of the widths of the electronic levels of the impurities, which are assumed to be iron-group ions. [The form of (5) assumes $\omega_0\tau_i \ll 1$.] Therefore, except at very high temperatures, the mechanism in the following paragraph, which permits slow ionic motions to affect T_1, applies instead of this one.

10. Generally speaking, relative motion of the nuclei and the impurities, corresponding to $\tau_i < T_2$, can bypass the spin-spin diffusion process and allow relaxation to occur primarily at sites adjacent to the impurity. Specifically, for the case $\tau_h < T_1$, we may have the analog of slow chemical exchange in complexes in solution, for which[17] (if $N_p n N_i^{-1}$ is much less than unity)

$$T_1^{-1} = (T_1^{-1})_{\text{other processes}} + N_p n N_i^{-1}(T_{1c}+\tau_h)^{-1}. \tag{6}$$

Even when spin-spin diffusion furnishes the stirring mechanism for the larger distances, weak ionic diffusion can become important in this way, by carrying ions within the sphere inaccessible to spin-spin diffusion; then τ_h in (6) is an effective time spent by a nucleus at some radius within this sphere.

Symbols

a	Nearest-neighbor distance
D_s	Spin-spin diffusion coefficient
e	Electronic charge
I	Nuclear spin
i	Subscript for nucleus being relaxed
j	Subscript for nucleus affecting i
n	Number of sites for ions i at closest approach to an impurity
N_p	Volume concentration of paramagnetic impurities
N_i	Volume concentration of ions i
p	Fraction of available sites occupied by a specified kind of vacancy
Q	Quadrupole moment
r	Distance from impurity to nucleus i
S	Effective spin of impurity (electronic)
T	Kelvin temperature
T_1	Spin-lattice relaxation time for nuclei i
T_2	Transverse relaxation time for nuclei i
T_{1c}	Value of T_1 for a nucleus fixed in a site nearest to an impurity
$y \equiv$	$\omega_0\tau_i/2$
β	Product of antishielding factor and polarization of defects
γ_i, γ_j	Magnetogyric ratios of nuclei
γ_S	Magnetogyric ratio (effective) for impurity
θ	Debye temperature
τ_c	Correlation time for interaction with paramagnetic impurity
τ_h	Time spent in site nearest to impurity
τ_e	Correlation time as limited by paramagnetic relaxation
τ_i, τ_v	Time between jumps for ion or vacancy
ω_0	Larmor frequency

EXPERIMENTAL WORK

T_1 was measured in a field of 6800 oe by the following magnetic recovery method: The sample is first completely demagnetized by a succession of pulses which, for convenience, are made identical with the 90° pulse used to sample the magnetization, and which are usually applied at 60 per second. After the pulsing has been interrupted for a known time, the induction signal

---

[10] I. Solomon, Phys. Rev. **99**, 559 (1955).

[11] R. Kubo and K. Tomita, J. Phys. Soc. Japan **9**, 888 (1954).

[12] P. G. DeGennes, J. Phys. Chem. Solids **7**, 345 (1958).

[13] G. R. Khutsishvili, Proc. Inst. Phys. Acad. Sci. Georgia (U. S. S. R.) 4, 3 (1956).

[14] N. Bloembergen, Physica **25**, 386 (1949).

[15] W. E. Blumberg, Phys. Rev. **119**, 79 (1960).

[16] A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, New York, 1961), pp. 378–386.

[17] N. Bloembergen and L. O. Morgan, J. Chem. Phys. **34**, 842 (1961).

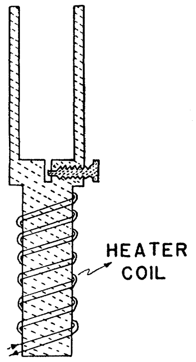

FIG. 1. Temperature control jacket. An outer wrapping of asbestos is not shown.

following the first pulse of a new sequence indicates the recovered magnetization.

For elevated temperature measurements, a copper jacket, shown in Fig. 1, was used. Around the lower portion of the jacket, a solid extension of the shell, was wound a noninductive heater of No. 22 nichrome wire. The cold resistance was 3 ohms, and the maximum applied emf was 30 v. For temperatures above 500°C, a similar jacket with heaters on both ends, which was made with a split shell, was used. For two measurements at liquid nitrogen temperature, a stainless steel Dewar flask was used.

SAMPLES

The samples were single crystals from the recent production of the Harshaw Chemical Company, except for the NaCl sample, which was obtained from a commercial source several years earlier, and which is apparently of comparable purity. No deliberate removal or addition of impurities was attempted, with the exception that the NaF crystal was baked in vacuum at 320°C for 2 hr, and later was baked for 4 hr in O_2 under 0.2 atm pressure, at 240°C. These operations, which did not affect T_1, were done to eliminate variation in O_2 content as the explanation of annealing effects which were found between 250° and 450°C in the first cycling of the sample. The sample was ultimately annealed as described later.

DISCUSSION OF RESULTS

Na^{23} in NaCl

As indicated in the preliminary report of this work,[18] T_1^{-1} for this case behaved according to (1), with minor deviations, up to 700°K, in agreement with the two-phonon theory. T_1 was independent of rotation of the crystal about a major axis which lay along the coil axis, and was 12.3 sec at room temperature. At 775°K, a reduction of T_1 in excess of that given by (1) indicates the beginning of vacancy diffusion. More detailed results for NaCl have been given by Eisenstadt.[19]

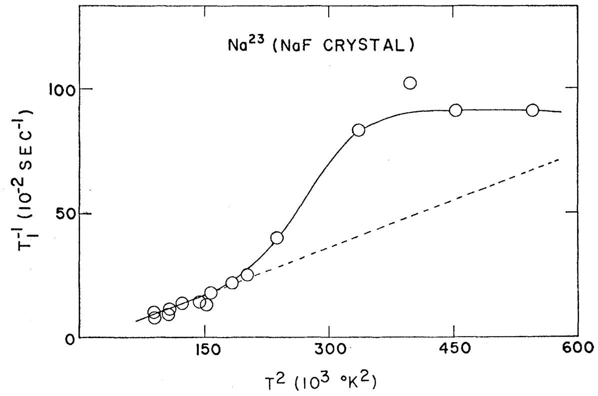

FIG. 2. Relaxation time for Na^{23} in NaF.

Na^{23} in NaF

As shown in Fig. 2, T_1^{-1} here behaves according to the two-phonon process (linear in T^2) only to about 450°K. In the two-phonon range, the magnitude is nearly the same as for NaCl (e.g., 11 sec at room temperature). The two-phonon theory gives nearly quantitative predictions for both compounds; for example, by using the analysis which includes optical modes,[3] we calculate $T_1 = 30$ sec.

The failure of the results above 450°K to fit the two-phonon analysis is attributed to relaxation by vacancy diffusion (mechanism *6*). For NaCl, by contrast, no deviation as great as 10% from the T^2 behavior could be attributed to this, in our data below 700°K; Eisenstadt[19] identified a small T_1 minimum at 540°K with this mechanism in NaCl. In other words, in terms of the maximum relaxation rate due to vacancy diffusion, we find as much as 1 sec^{-1} in NaF, whereas the NaCl results correspond to about 0.2 sec^{-1}, which requires that $\beta^2 p a^{-6}$ in the NaCl samples be about one-fifth of the value for our NaF sample. The a^{-6} factor contributes a ratio of 3, in the proper direction.

Equation (2), Reif's formula, predicts reasonable magnitudes for T_1 due to vacancy diffusion; for $p = 10^{-6}$, with $\omega_0 = 1.7 \times 10^8$ sec^{-1}, and $\beta = 20$, the minimum value of T_1 is approximately 1 sec. The exact shape of the broad maximum of T_1^{-1} in Fig. 2 is not significant, as large annealing effects were found in the subsequent measurements of T_1 for F^{19} in this crystal.

F^{19} in NaF

As shown in Fig. 3, a large annealing effect was found in the T_1 results for F^{19} in NaF. The discussion will refer to the curve taken after the annealing treatment, which consisted of 85 min at 800°C, followed by cooling from 800° to 200°C in 195 min. The annealed sample showed no thermal hysteresis in the values of T_1. The data for this case appear in a semilogarithmic plot in Fig. 4.

The relaxation times of approximately 100 sec, obtained in the relatively flat low-temperature portion of the curve, are consistent with mechanism *8*, spin-spin

---

[18] P. P. Mahendroo and A. W. Nolle, Bull. Am. Phys. Soc. **5**, 111 (1960); P. P. Mahendroo, doctoral dissertation submitted to the University of Texas, 1960 (unpublished).

[19] M. Eisenstadt, Bull. Am. Phys. Soc. **6**, 103 (1961).

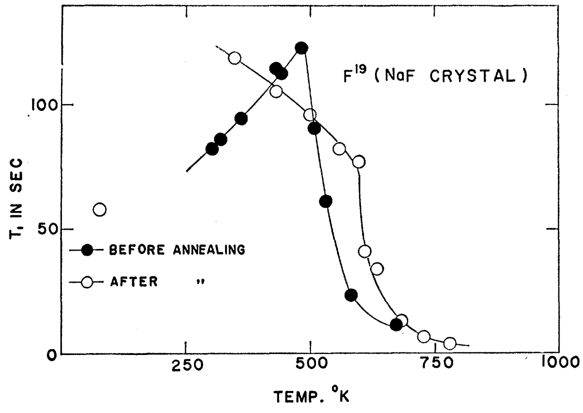

FIG. 3. Relaxation time for F^{19} in NaF.

diffusion. Using a derivative width of 6 oe, which we measured with a powdered sample at room temperature, to compute D_s, we find from (4) that $T_1=100$ sec corresponds to a mole fraction of 0.25×10^{-6} of paramagnetic impurities.[20] This is not unreasonable by comparison with the analysis[21] of other Harshaw alkali halide crystals.

The slope of the high-temperature curve segment in Fig. 4 gives an activation energy of 0.65 ev, which is in the range of known energies of activation for the motion of positive-ion vacancies in alkali halides,[22] but is less than the energy of vacancy formation. Corresponding to this result, we expect τ_v^{-1} to be given approximately[22] by $\exp(-0.65\text{ ev}/k\times650°\text{K})$ times a frequency factor of 10^{14} to 10^{16} sec^{-1}. In the temperature range under consideration, we expect essentially a constant number of vacancies, due to the presence of positive-ion impurities of excess valence, for which p should be[23] several times 10^{-6}, giving finally $\tau_i\simeq\tau_v/p=10^{-4}$ to 10^{-6} sec for positive-ion jumps. This large value of τ_i rules out mechanism *9*, but allows the correct temperature dependence to be obtained with *7* (Torrey diffusion), which requires τ_i to be 10^{-5} sec to give $T_1=100$ sec, as required. On the present evidence, this is the mechanism giving relaxation for temperatures above the knee in Fig. 4.

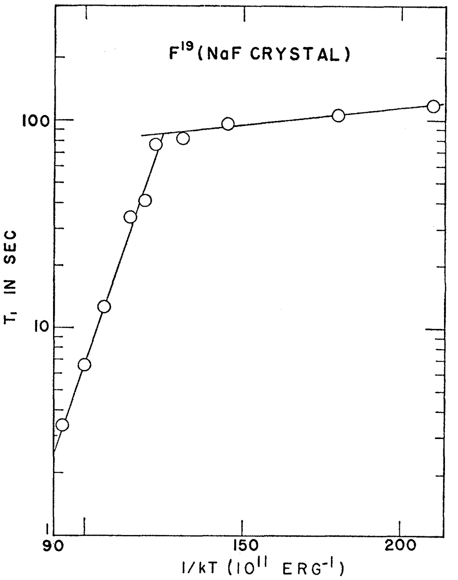

FIG. 4. Semilogarithmic plot of "afteran-nealing" data of Fig. 3.

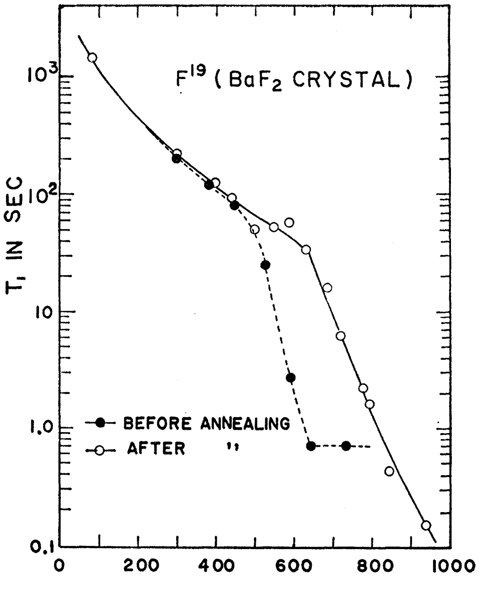

FIG. 5. Relaxation time for F^{19} in BaF_2.

The explanation just given depends, for NaF, on positive-ion jumps, as the anions are less mobile.[22] We cannot completely rule out mechanism *10*, however, which depends on feeble negative-ion diffusion. Lidiard[24] has cited evidence for negative-ion diffusion in NaCl by a vacancy-pair mechanism, corresponding to τ_i of the order 10^{-3} sec at 650°K. This is the right magnitude for mechanism *10*, if $\tau_i\approx\tau_h$, and if T_{1c} is approximately given by $Ca^{-6}=10^{-5}$ sec. We have no specific evidence, however, as to whether our activation energy of 0.65 ev could pertain to the displacements of negative ions adjacent to impurities, as required in this mechanism.

---

[20] Here and elsewhere, for purposes of numerical estimates, we take the major impurity to be Fe^{3+}, with $S=\frac{5}{2}$, and $\tau_c=\tau_e=10^{-10}$ sec. Since room-temperature analysis of the NaF sample by electronic magnetic resonance at 9.4 kMc/sec showed only poorly resolved resonances with widths greater than 100 oe, the details being sensitive to annealing, it is assumed that there is no impurity present with τ_e exceeding 10^{-10} sec.

[21] S. Anderson, J. S. Wiley, and L. J. Hendricks, J. Chem. Phys. **32**, 949 (1960).

[22] F. Seitz, Revs. Modern Phys. **26**, 7 (1954).

[23] This value corresponds to the total excess valence of positive impurities, and therefore exceeds the concentration of paramagnetic impurities.

[24] A. B. Lidiard, J. Phys. Chem. Solids **6**, 298 (1958).

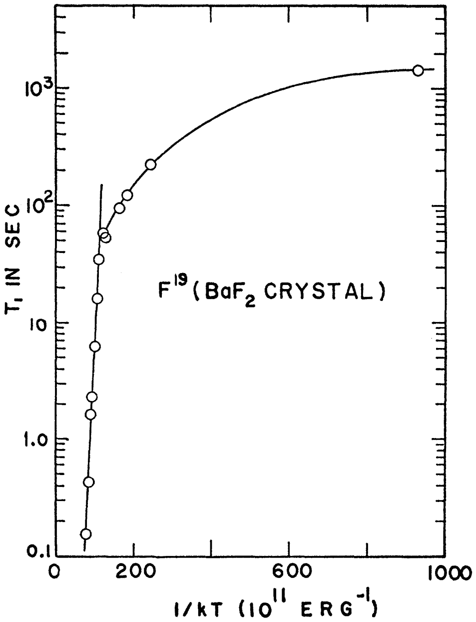

Fig. 6. Semilogarithmic plot of "after-annealing" data of Fig. 5.

F^{19} in BaF_2

A well-defined knee at the beginning of the diffusion-controlled region is also found in the data for BaF_2 in Fig. 5, where a point taken at liquid nitrogen temperature is included. Comparison of the two curves shows a 40-fold increase of T_1 through annealing, presumably because of vacancy precipitation, but negligible effect of annealing in the lower temperature region where ionic motion is not important. The annealing treatment consisted of 2 hr at 800°C, followed by cooling over a 6-hr period to 50°C and then by removal to a desiccator. The activation energy found in the diffusion region (Fig. 6) is 0.82 ev, again of the right magnitude for the propagation of vacancies but not for their formation. Transport measurements[25] have shown that the negative ions are the more mobile in BaF_2; thus the F-to-F dipolar interaction is suggested in this case as the one affected by diffusion. Otherwise, the general conclusions reached for F^{19} in NaF are presumed to hold.

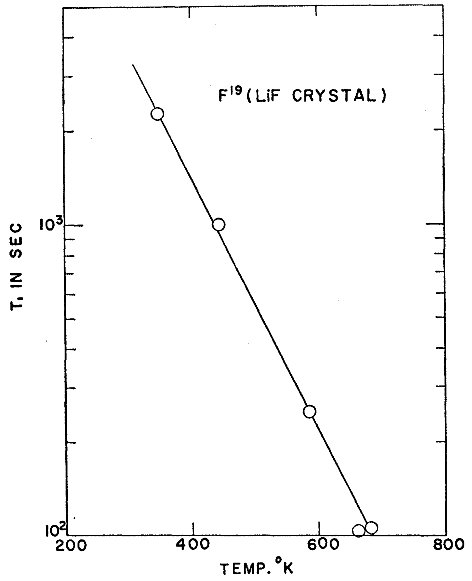

Fig. 7. Relaxation time for F^{19} in LiF.

F^{19} in LiF

Several points were obtained for LiF, as shown in Fig. 7. The data do not justify full analysis, but when plotted for activation energy analysis, appear to approach a slope of about 0.4 ev at high temperature. The remarkable feature is the existence of relaxation times exceeding 2000 sec, which could indicate a paramagnetic impurity concentration two orders of magnitude smaller than in the preceding cases, and which accounts for the sparseness of the experimental data for this sample. No signal was discovered at liquid nitrogen temperature; under the experimental conditions, this requires $T_1 > 2 \times 10^4$ sec.

CONCLUSION

It appears that temperature ranges in which relaxation is controlled by phonon-phonon processes, by spin diffusion to paramagnetic impurities, and by motional interruption of dipolar interactions, have been identified, and that the relaxation rates due to the various mechanisms are at least approximately predicted by appropriate theories. The reduction in the concentration of mobile vacancies by annealing is well demonstrated. The work has been limited by design to commercially available crystals of high purity. Further work with samples having known impurity additions is indicated, both by nuclear resonance and by electron spin resonance.

---

[25] C. Tubandt, H. Reinhold, and G. Liebold, Z. anorg. u. allgem. Chem. **197**, 225 (1931).