Nuclear Magnetic Relaxation in NaCl at High Temperatures

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(Received 20 August 1963)

Measurements of T_1 and T_2, the spin-lattice and spin-spin relaxation times, are reported for Na^{23} and Cl^{35} nuclei in NaCl from room temperature to the melting point. For single-crystal samples below 700°K, T_1 is due to quadrupolar interactions of the nuclei with lattice vibrations and diffusing vacancies, and T_2 arises from the dipolar interaction between nuclei. A jump frequency for positive ion vacancy motion of 4×10^7 sec^{-1} at 510°K is obtained, in good agreement with conductivity measurements. At higher temperatures a number of anomalous features appear and possible explanations are discussed.

I. INTRODUCTION

IN a previous paper[1] we obtained Li and F ion jump frequencies in a LiF crystal with good accuracy by measurement of the nuclear magnetic relaxation times T_1 and T_2. This was possible because the quadrupolar interaction of the nuclei with their environment could be neglected over most of the temperature range studied. For most other ionic crystals it cannot be neglected, and is usually the dominant interaction responsible for relaxation. A number of papers[2-9] have been published on relaxation in such systems at high temperatures. Some of the features are qualitatively understood, such as quadrupolar relaxation due to lattice vibrations and vacancy diffusion. It was hoped that an intensive study of many samples of a single salt would elucidate the various relaxation mechanisms, but a great deal of data on samples of varying purity and structure seems only to have compounded the confusion. In particular, at temperatures within 200° of the melting point highly unexpected results were obtained, for which we have no definite explanation.

We shall present here T_1 and T_2 data from room temperature to the melting point (1073°K) for Na^{23} and Cl^{35} nuclei in seven different samples of NaCl. The interpretable features of the data were quadrupolar relaxation due to lattice vibrations and vacancy motion, which could be observed with most of the samples. Relaxation times due to the magnetic dipolar interaction were calculated using a theory previously developed,[10] but in most cases these were much longer than the observed values. Some possible quadrupolar relaxation mechanisms which might explain the high

temperature results will be discussed, but most of them can be dismissed.

II. PROCEDURE

The experimental method is the same as that described in a previous paper.[1] The Larmor frequency of the Na^{23} nuclei was 10.75 or 4.17 Mc/sec, and for Cl^{35} it was always 4.17 Mc/sec. The samples used are described as follows. Four single crystals[11] will be denoted by I through IV. Samples I and II were run in air, with a Pt, Pt-Rh thermocouple imbedded in a small hole drilled through the crystals. The crystals also made point contact with the gold leads of the rf coil. Extensive T_1(Na) and T_2(Na) data were taken with sample I and extensive T_1(Cl) data with sample II. At the conclusion of the experiments sample I had a faint violet color in the region near the surface, and sample II had a pronounced violet color. We suspect the coloration was caused by gold vapors penetrating the crystal at very high temperatures; much more time was spent near the melting point of NaCl for sample II than sample I. It is doubtful, however, that this had any effect on the data. All subsequent samples were sealed off in quartz vials under about one half an atmosphere of spectroscopically pure argon,[12] with the exception of one sample sealed in vacuum. This procedure eliminated the coloration, and also prevented the absorption of water vapor by the crystals; NaCl is known to absorb considerable quantities of water at elevated temperatures.[13] Little data were taken with sample III, which leaked up to air at some point during the experiments. Considerable T_1 data and some T_2 data were taken for both Na and Cl with sample IV. Because of our concern with absorbed water, which is present in a concentration of about 20 ppm in Harshaw crystals,[13] several samples were used which were zone refined and then distilled in a chlorine and argon atmosphere.[14] Spectroscopic analysis and conductivity measurements[15] indicate that this material had about

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[12] Linde Company, Union Carbide Corporation, New York, N. Y.
[13] D. A. Otterson, J. Chem. Phys. **33**, 227 (1960); **34**, 1849 (1961).
[14] These samples were kindly supplied by R. W. Dreyfus.
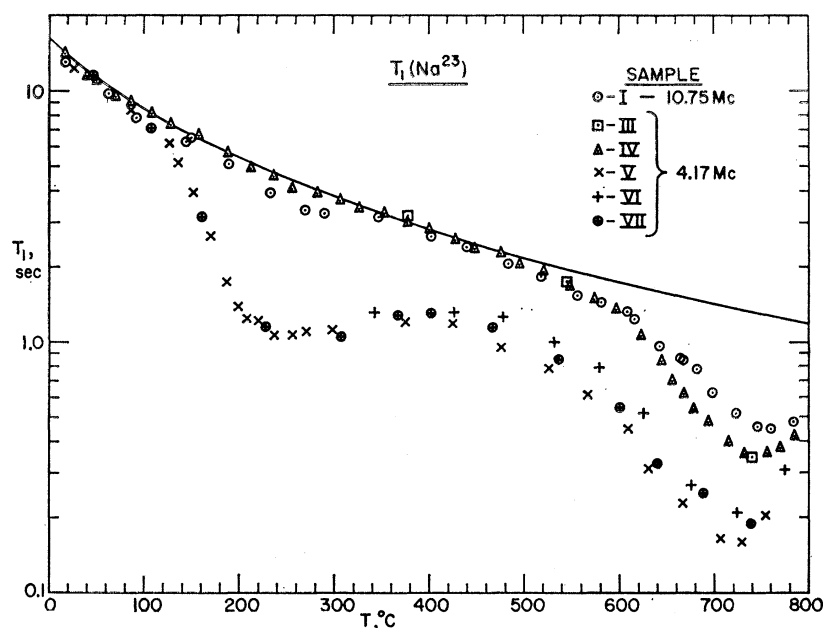[15] R. W. Dreyfus (private communication).

FIG. 1. $T_1(Na^{23})$ in NaCl versus temperature for various samples. The Larmor frequency was 10.75 or 4.17 Mc/sec.

20 ppm of diverse divalent metal ion impurities. The sample was used in the form of small pieces, roughly 1 mm on edge. It was run under three conditions, which will be denoted by V, VI, and VII, respectively. Sample V was heated 20° below the melting point in vacuum for about 10h, to eliminate possible occluded chlorine gas and for annealing. Its quartz container was then filled with argon and sealed. Sample VI was treated in the same way, but sealed off in vacuum. Sample VII was sealed off in argon as received.

The orientation of the single crystals was generally not known. Rotations of the magnetic field H_0 in a (100) plane at room temperature and at 740°C did not reveal any angular dependence of T_1 and T_2 for Na^{23} and Cl^{35}.

No special heating procedures such as slow heating and cooling were used. Generally a succession of measurements were made increasing the temperature after each run, or in decreasing sequence. For a given sample the sodium results were reproducible, but the $T_1(Cl)$ results for samples II and IV seemed to show some dependence on their recent thermal history. This will be mentioned in more detail in the next section.

The pulsed rf magnetic field H_1 was about 20 G. Relative intensity measurements at various temperatures for Na and Cl free-induction decays in the single crystal samples indicate that H_1 was flipping all the spins, i.e., the static quadrupole broadening for the majority of nuclei was less than 20 G. For samples V–VII, the ratio of Cl to Na signals was somewhat low, implying that these samples had more static quadrupole broadening than the single crystals.

III. DATA

Figures 1 and 2 show T_1 for Na^{23} and Cl^{35} as a function of temperature. At temperatures above 700°C

the thermal recovery of the magnetization following a 180° pulse (which we will call a T_1 decay) begins to show nonexponential behavior. The most pronounced nonexponentiality is at the highest temperatures, an example of which is shown in Fig. 3. It can be resolved into the sum of two exponentials, a slow and fast T_1; however, it could be considered equally well as a distribution of fast exponentials plus a slow exponential, where the slow component would be a homogeneous property of the bulk crystal, and the fast components arising from some spatial inhomogeneity. We will discuss these two possibilities below; at any rate, it is the slow T_1 which is shown in Figs. 1 and 2.

For nuclei with quadrupole moments, a fluctuating electric field gradient can provide a powerful relaxation mechanism. In a perfect crystal of cubic symmetry, the field gradient at a nucleus vanishes. This symmetry can be destroyed by lattice vibrations or by vacancies in the lattice; these two imperfections are responsible for the relaxation below 700°K. For relaxation due to lattice vibrations T_{1l}, two features are well established both experimentally[3,5,7,9] and theoretically.[5,16] T_{1l} is isotropic, and varies as T^{-2} at temperatures above the Debye temperature. The quadrupolar interaction strength is known very imprecisely, principally due to its dependence on the electronic charge configuration, a difficult quantity to evaluate. For quadrupolar relaxation due to vacancy motion T_{1v}, again the interaction strength is poorly known, but the time, and hence temperature dependence, should be similar[2] to that of dipolar relaxation via ionic diffusion. The appropriate correlation time is determined by ν_v, the jump frequency of vacancies, instead of the jump frequency of ions as in the dipolar case. The two are
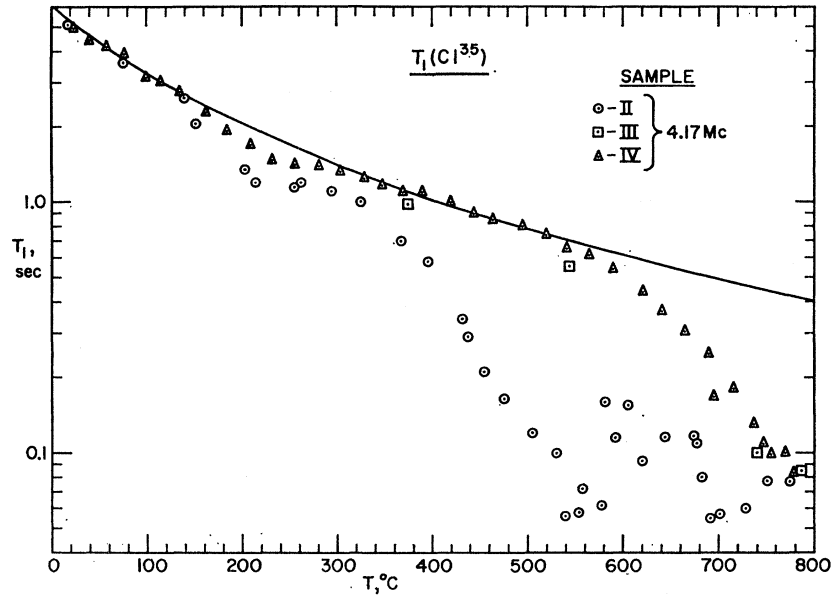
[16] J. Van Kranendonk, Physica 20, 781 (1954).

FIG. 2. $T_1(Cl^{35})$ in NaCl versus temperature for various samples. The Larmor frequency was 4.17 Mc/sec.

related by $\nu_{ion} \approx c_v \nu_v$, where c_v is the concentration of vacancies, hence the minimum in T_{1v} (where $\nu_v \approx \omega_0$, the Larmor angular frequency) will be at a considerably lower temperature than the dipolar minimum (where $\nu_{ion} \approx \omega_0$).

These two quadrupolar relaxation mechanisms are illustrated by the lower temperature data of Figs. 1 and 2. Most of the points fall on the solid lines, which are the best fit of curves of the form AT^{-x} to the data. The exponent x was about 1.9 for both Na and Cl relaxation. Such small deviations from a T^{-2} dependence, also observed by Clark,[3] could be accounted for by the small change of lattice constant with temperature. The data could be fitted equally well with an expression of the form $T_{1l}^{-1}=A+BT^2$. At room temperature the constant term would account for about 10% of the relaxation. Such a term might arise from relaxation due to paramagnetic impurities. In any case, the expected T^{-2} dependence is fairly well confirmed. We have used the form AT^{-x} to obtain extrapolated values in regions of temperature where other relaxation mechanisms are present.

T_{1v} appears as a dip superimposed on the T^{-2} line, with a minimum at about 240°C. Since T_{1l} and T_{1v} should be independent, we can write $T_1^{-1}=T_{1l}^{-1}+T_{1v}^{-1}$, and thus obtain the vacancy contribution to relaxation. Reif[2] has considered relaxation via vacancy motion in some detail. For our purposes it will suffice to consider the simplest approximation for this process, namely, $T_{1v}^{-1} \approx \langle \omega_i^2 \rangle \nu_v (\nu_v^2+\omega_0^2)^{-1}$, where $\langle \omega_i^2 \rangle$ is the mean-squared value of the quadrupolar interaction, in angular frequency units. The time-averaged interaction can be approximated as the square of the interaction strength when a vacancy is in a near neighbor site to a nucleus, ω_{im}^2, times the probability that a vacancy will occupy this site, $12c_v$. The above expres-

sion for T_{1v}^{-1} has a maximum at $\nu_v=\omega_0$; this expression corresponds to $\Delta m=1$ transitions, but there should be another term similar to the above, but using $2\omega_0$, corresponding to $\Delta m=2$. Including both terms, the maximum is at $\nu_v=1.6\omega_0$; hence $T_{1v}^{-1}(\text{max}) \approx 5\omega_{im}^2 c_v \omega_0^{-1}$.

The temperature dependence of T_{1v} for Na and Cl nuclei in the various samples is shown in Fig. 4. For all of the data taken at 4.17 Mc/sec, the minimum in T_{1v} falls at $T=510\pm20°K$. The expression $\nu_v \approx 1.6\omega_0$ is
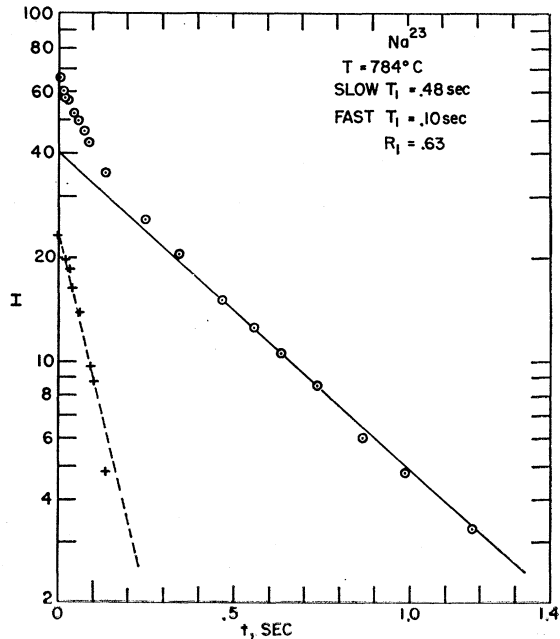

FIG. 3. A T_1 decay for Na^{23} nuclei in NaCl, sample I, at a temperature near the melting point. I is the deviation of the magnetization from its equilibrium value, in arbitrary units. The data are resolved into the sum of two exponentials.
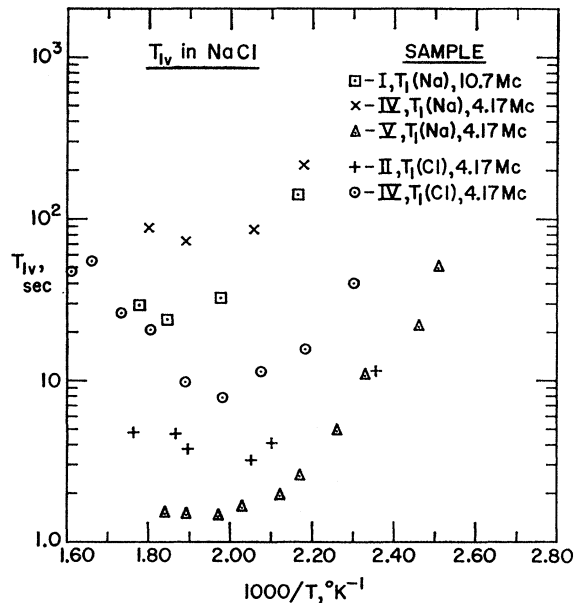
FIG. 4. The vacancy contribution to T_1 for Na^{23} and Cl^{35} nuclei in NaCl versus reciprocal temperature. The Larmor frequencies are shown.

certainly correct to 50%, and the uncertainty in temperature corresponds to an uncertainty of about a factor of 2 in ν_v. Dreyfus and Nowick[17] give $\nu_v = 1.6 \times 10^{15} \exp(-0.80 \text{ eV}/kT)$ based on their conductivity data, and consider their value good to about a factor of 2. Their expression yields $\nu_v = 2 \times 10^7$ at 510°K, and we obtain 4×10^7 at the minimum, a reasonable agreement. The temperature range over which T_{1v} could be extracted was too small to determine an activation energy for vacancy motion, but the slope of the low temperature asymptotes of Fig. 4 were consistent with the value of 0.80 eV quoted above. The minimum of $T_{1v}(Na)$ taken at 10.7 Mc/sec is shifted to a slightly higher temperature, as it should be according to the above equation. Satoh[6] has made extensive measurements of $T_1(Na)$ in NaCl doped with various impurities, and obtains an activation energy for vacancy motion of 0.74 eV, in good agreement with the conductivity value. It is not worthwhile considering the absolute magnitude of T_{1v} in detail, but interesting comparisons can be made of $T_{1v}(\min)$ of the same nucleus in different samples, and different species in the same sample. The only sample for which the impurity content is known[15] is sample V; it has a divalent metal ion content of 2×10^{-5}, a number accurate to about a factor of two. Thus, from Eq. (1), ω_{im} is 0.4 Mc/sec, a reasonable value for the Na nucleus. Assuming this interaction strength to be the same for Na in the other samples, the vacancy concentration of the single crystal samples is estimated as: sample I, 2 $\times 10^{-6}$; sample IV, 2×10^{-7}. These are typical values

for Harshaw NaCl crystals, as determined by electrical conductivity measurements.[15]

For a given vacancy concentration and Larmor frequency, $T_{1v}(Cl)$ would be expected to be much shorter than $T_{1v}(Na)$, because of its greater anti-shielding factor.[18] Furthermore, the positive ion vacancy is closer to the Cl nucleus than the Na nucleus by a factor of $\sqrt{2}$, and since the quadrupolar interaction with a point defect[19] goes as r^{-3}, the interaction is eight times more effective for Cl due to this cause alone. Sample IV is the only one for which both $T_1(Na)$ and $T_1(Cl)$ were measured. Unfortunately, (for these considerations) it was exceptionally pure, and $T_{1v}(Na)$ could not be extracted with any great accuracy. At the minimum, $T_{1v}(Na) \approx 75$ sec, and $T_{1v}(Cl)$ is 3.5 sec, a factor of 20 difference. After accounting for the dependence on distance, one determines that the other terms in the interaction for Cl^{35} are only about 1.6 times those for Na^{23}, a rather low ratio.

The ratio of $T_{1l}(Na)$ to $T_{1l}(Cl)$ of sample IV is 2.8, also much lower than expected. This discrepancy has also been observed by Wikner.[7] The fact that the ratios are small for both the crystal properties of lattice vibration and vacancy motion indicates that the flaws in the relaxation theory lie in the treatment of the closed shell electrons of one or both species.

The T_1 data at the higher temperatures were highly anomalous. We will only consider here the slow component of the T_1 recovery, deferring discussion of its nonexponential character until later. At temperatures approaching the melting point, one would expect that dipolar relaxation due to the translational diffusion of Na and Cl would become important. The jump frequencies of sodium[20] and chlorine[21] ions in NaCl are well known in this temperature range, hence, one can predict from the condition $\omega_0 \approx \nu_{Na}$, ν_{Cl} that for Na a dipolar T_1 minimum should occur at roughly $T = 1090°K$ for data at 10.75 Mc/sec, and $T = 1050°K$ for data taken at 4.17 Mc/sec. The sodium data in Fig. 1 for single crystal samples do exhibit minima at approximately these temperatures, and the minima for the different Larmor frequencies are shifted with respect to one another by the expected amount. However, a detailed calculation using jump frequencies measured by other methods reveals that the additional mechanism at high temperatures (obtained after subtracting extrapolated values of T_{1l} from the measured relaxation times) is far too short to be accounted for by dipolar relaxation alone. Figure 5 shows these calculated values. The sodium relaxation in sample I is too short by a factor of 20, and in sample IV by a factor of 5. The chlorine relaxation in sample IV is too short

[17] R. W. Dreyfus and A. S. Nowick, Phys. Rev. 126, 1367 (1962).

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[19] 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, p. 321.
[20] J. F. Aschner, Ph.D. thesis, University of Illinois, 1954 (unpublished).
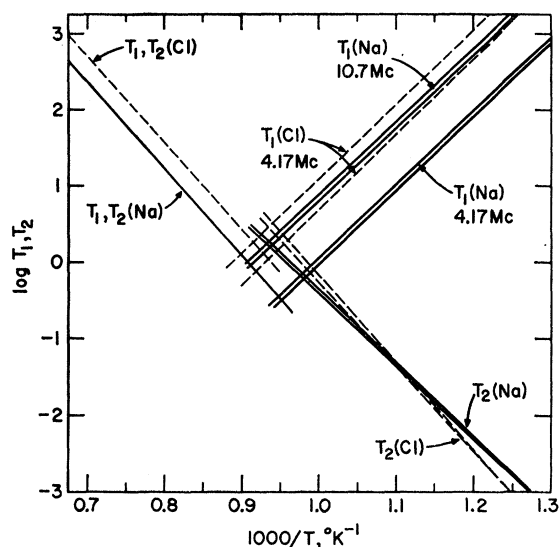[21] N. Laurance, Phys. Rev. 120, 57 (1960).

FIG. 5. Predicted values of T_1 and T_2 for purely dipolar relaxation due to diffusion of Na and Cl ions, based on diffusion data in the literature. For a given nucleus and Larmor frequency, a pair of lines are shown in the region below the T_1 minimum, corresponding to orientations of the magnetic field parallel to the [100] and [110] crystal axes.

by a factor of 25. The discrepancy is smallest in sample IV, the purest crystal used, and for this sample the discrepancy is much greater for Cl than for Na. Thus, the high-temperature relaxation mechanism is most probably quadrupolar. From the temperatures at which the minima occur, the appropriate correlation time seems to be the jump time of the Na or Cl ions. One possible relaxation mechanism with the required correlation time is quadrupolar relaxation via the interaction of moving Na and Cl ions with fixed, or slowly moving divalent impurity ions. This does not seem too likely, however, in view of the high purity of the single crystal samples used. The magnitude of this interaction should be about the same as, or smaller than, the interaction with a vacancy, since the impurity charge relative to the lattice is of the same magnitude as that of a vacancy, and the strain contribution should be smaller. Hence, T_1 due to this mechanism should be about the same or smaller than T_{1v}. Relaxation by rapidly moving impurities suffers these and other objections. It is possible that a large concentration of monovalent impurities of differing ionic radius than the lattice ions may be present. These would not introduce vacancies in the lattice, hence would not affect T_{1v}, but might cause relaxation at the higher temperatures, due to the lattice distortion they introduce. Absorbed water can introduce OH⁻ ions into the lattice.[13] It may be significant that sample IV, which was isolated from the atmosphere, was the closest to pure dipolar relaxation for Na.

The correlation times for both Na and Cl vacancy diffusion are much too short to cause relaxation at the high temperatures. Although the vacancy concentra-

tion increases rapidly with temperature, the vacancy jump frequencies increase even faster; hence, the spectral density for this interaction decreases monotonically at high temperatures. More complex imperfections, such as impurity vacancy pairs, or positive-negative ion vacancy pairs can also be rejected, either because of the wrong correlation time, or inadequate interaction strength or concentration.

There remains the possibility of a quadrupolar interaction with dislocations. This interaction has a longer range than that of a point defect, falling off as r^{-2}. It is almost impossible to estimate the dislocation density for the various samples. A density of 5×10^4 dislocations/cm^2 has been quoted for Harshaw NaCl crystals.[22] However, rough handling or other strains can increase their concentration by several orders of magnitude. For samples V, VI, and VII, the concentration is undoubtedly much larger than the above figure. The single crystals were turned on a lathe, or shaped with a razor blade and drilled, and furthermore were heated and cooled fairly rapidly many times; hence, their dislocation density may have been drastically changed from the original condition. The values of $T_1(Cl)$ showed some dependence on thermal history at high temperatures. For sample IV, the values were obtained while going up in temperature, except for the point at 695°C, which was taken coming down. Similarly, for sample II, the minimum at 560°C (for which we have no explanation) fell on a smooth curve until more measurements were made with a random heating sequence. For a given sample, $T_1(Na)$ did not show such effects, presumably due to its smaller quadrupolar interaction. Clark[3] has also observed such behavior in other alkali halide crystals at high temperatures. Thus, we will only mention the possible relaxation mechanism of a time-dependent interaction with dislocations due to diffusion of Na and Cl ions.

Samples V–VII had much shorter relaxation times than the single crystal samples, and had a high-temperature minimum at a lower temperature. For these crystals it is possible that quadrupolar relaxation due to impurities may be important. The high-temperature results showed a dependence on the heat treatment of the samples. We will not discuss these samples further.

Extensive T_2 measurements were made only for Na²³ nuclei and most of these were made on sample I. Nonexponential decays of the spin-echo signal was very pronounced, much more so than for T_1 measurements. They begin to occur at $T = 850°K$ and become greater as the melting point is approached, as illustrated by Fig. 6. The decay could be separated into two exponentials, and again we will consider the slow component as being representative of the homogeneous crystal, deferring discussion of the nonexponentiality until later. The temperature dependence of the slow component is shown in Fig. 7. The agreement with
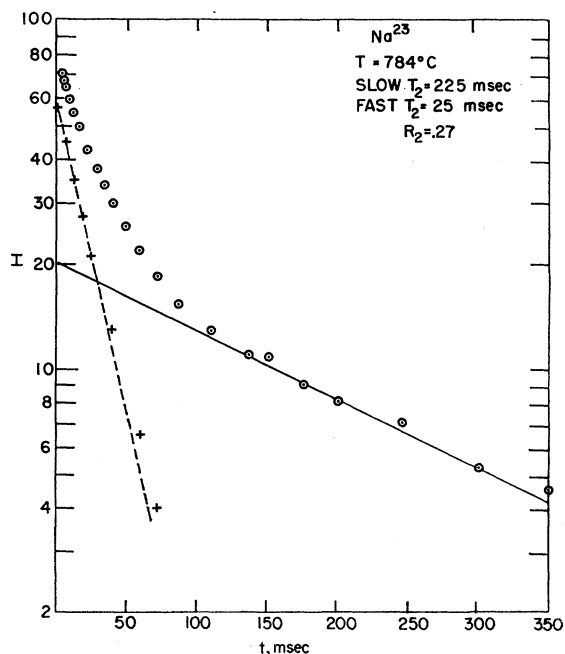
[22] S. Mendelson, J. Appl. Phys. 33, 2175 (1962).

Fig. 6. A T_2 decay for Na[23] nuclei in NaCl sample I at a temperature near the melting point. I is the component of the magnetization in the x-y plane, in arbitrary units. The data are resolved into the sum of two exponentials.

theoretical values for dipolar relaxation is excellent, both in magnitude and temperature dependence, for $T_2(\text{Na})$ in sample I. The slope of the low-temperature asymptote yields an activation energy for sodium ion diffusion of 1.9 eV, in good agreement with the value 1.86 eV obtained by other methods.[23] Data for Na and Cl in other samples were sparse, but consistent with purely dipolar relaxation. The deviation from a straight line at lower temperatures probably indicates the onset of extrinsic diffusion. T_2 data are not shown in the region of 740°K to room temperature, since here the line shape is changing from Lorentzian to Gaussian. The room temperature "rigid lattice" values of $T_2(\text{Na})$ and $T_2(\text{Cl})$ are also shown in Fig. 6. Here the free-induction decay was Gaussian, except for a slight "beat" at long times.[24]

IV. NONEXPONENTIAL EFFECTS

Nonexponential T_1 decays were observed from about 950°K to the melting point for both Na and Cl nuclei, and were more pronounced for Cl. For T_2, the effect began at 850°K, and was much more prominent than for T_1. They were observed in all samples.

The T_1 and T_2 decays could always be fitted with the sum of two exponentials, but this does not eliminate the possibility of a distribution of exponentials due to some spatial inhomogeneity effect in the crystal.

[23] R. W. Dreyfus and A. S. Nowick, J. Appl. Phys. Suppl. 33, 473 (1962).
[24] I. J. Lowe and R. E. Norberg, Phys. Rev. 107, 46 (1957).

There are some theoretical grounds for expecting a sum of two exponentials when the nuclei have combined dipolar and quadrupolar, or mainly quadrupolar interactions. Redfield[25] has calculated the relaxation behavior for this case. We will only briefly discuss this work and its predictions, since it does not seem to apply to our data.

In Figs. 3 and 6 we have decomposed the data into a sum of two exponentials, which we call fast and slow. An important parameter is the intensity of the slow component extrapolated back to zero time. We denote the ratio of this intensity to the total intensity at zero time by R_1 or R_2, for T_1 and T_2 measurements. More than one spin lattice relaxation time is possible only when the spin temperature approximation[5] breaks down, that is, when the I_+I_- interaction between like spins is strongly narrowed. This will usually occur when T_2 begins to approach T_1, which for our case is near the melting point. More than two exponentials cannot occur for a spin of $\frac{3}{2}$. Another condition for a "double decay" is that $P_1 \neq P_2$, where P_1 and P_2 are the quadrupolar transition probabilities corresponding to $\Delta m = 1$ and $\Delta m = 2$ transitions. We have made no attempt to estimate these probabilities, but one would expect them to have a strong angular dependence in
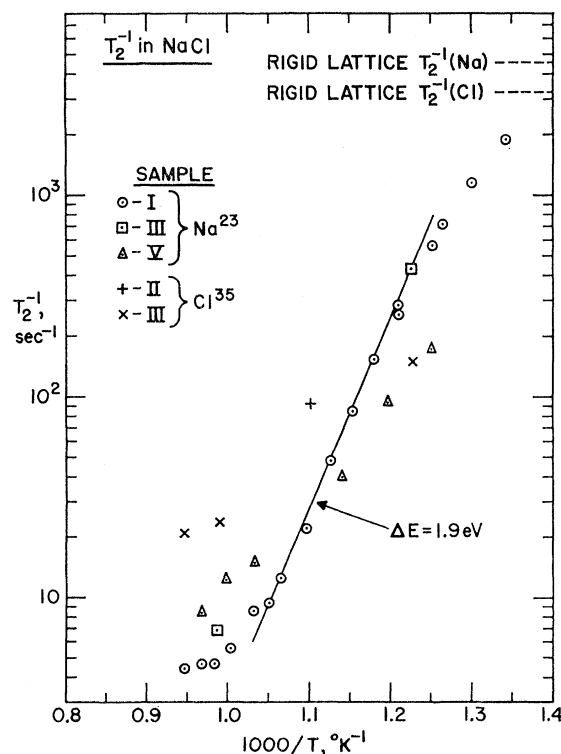

Fig. 7. T_2^{-1} for Na[23] and Cl[35] nuclei versus reciprocal temperature in NaCl for various samples. The slope of the straight line yields the activation energy for Na ion diffusion. Values of T_2^{-1} obtained from measurements at room temperature are shown as dashed lines.

[25] A. G. Redfield (to be published).

the long correlation time limit. No angular dependence was ever observed. The theory predicts very definite limits for R_1, independent of the actual magnitudes of P_1 and P_2. For $P_2 > P_1$, $R_1 \leq 0.2$ and for $P_1 > P_2$, $R_1 \geq 0.8$. It is easy to see how these limits occur for the case $P_2 \gg P_1$ or $P_1 \gg P_2$. For the former, after a $180°$ pulse the inverted populations of the $\frac{3}{2}$ and $-\frac{1}{2}$ levels, and also the $\frac{1}{2}$ and $-\frac{3}{2}$ levels, will rapidly come to thermal equilibrium because of $\Delta m = 2$ transitions. This brings the net magnetization to 0.8 times its equilibrium value, giving $R_1 = 0.2$. A similar argument gives $R_1 = 0.8$ for $P_1 \gg P_2$. However, we observe R_1 gradually decrease from unity to about 0.7 as the melting point is approached. The predictions for T_2 also disagree with observation. The theory yields the result that $R_2 \geq 0.4$ under all circumstances, whereas we observe R_2 going monotonically from unity to 0.25, from $850°$K to the melting point.

Thus, the above effects, if present at all, are certainly masked by other phenomena. We will give here the most plausible explanation of the high-temperature effects consistent with the data. We will assume that we have a spatial distribution of T_1 and T_2; the slow decay is a characteristic of the bulk of the sample, and what we have called the fast decay is really a distribution of decay times for spins near an imperfection. The quantities R_1 and R_2 are a measure of the fraction of spins exhibiting the behavior of the bulk material. Slow T_2 is in good agreement with the theory of dipolar relaxation via diffusion. It seems unlikely that the faster T_2 could be due to a point imperfection. Below $850°$K, the T_2 decay is a single exponential and in agreement with pure dipolar relaxation, therefore, any quadrupolar interaction must be weaker than the dipolar interaction. Since both the quadrupolar inter-

action due to point defects and the dipolar interaction between spins have an r^{-3} dependence, they would both be narrowed at the same rate as the jump frequency of ions increases, hence, a single exponential would always be observed. However, a long-range quadrupolar interaction such as that due to a dislocation (with an r^{-2} dependence) would not narrow until a higher temperature, hence, at some temperature it could become dominant for those nuclei within some effective cylinder around the dislocation. The number of nuclei within this cylinder will increase as diffusion increases, hence, R_2 will decrease with temperature, as observed.

A similar argument can be applied to the T_1 data, but here the slow T_1 is much shorter than the values predicted by dipolar relaxation theory. Possibly the slow T_1 arises from interactions with monovalent impurities, such as OH$^-$ ions.

V. CONCLUSIONS

From room temperature to about $850°$K, T_1 and T_2 data for Na[23] and T_1 data for Cl[35] in single crystals of NaCl are reasonably understood. T_1 arises from the quadrupolar interaction of the nuclei with lattice vibrations and diffusing vacancies, and T_2 from the dipolar interaction between spins. At higher temperatures the data are highly anomalous, and no definite conclusions can be arrived at. We suspect that dislocations play an important role, however, a more thorough knowledge of the structure and purity of the samples would have to be known to verify this.

ACKNOWLEDGMENT