Motion of Mn++-Cation Vacancy Pairs in NaCl: Study by Electron Spin Resonance and Dielectric Loss

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Thermal motion of the bound positive ion vacancy around a Mn^{++} ion in NaCl has been detected as a broadening of some of the multiplets in the Mn^{++} spin resonance spectrum. In addition, dielectric loss measurements at radio frequencies reveal a Debye loss peak which can be directly correlated with this motion. Analysis of these experiments gives the lifetime of the vacancy in the cation site nearest the Mn^{++} to be $1/\tau = 1.2 \times 10^{14} \exp(-E/kT)$, with $E = 0.63 \mp 0.05$ ev. Near 300°C, the lifetime of the vacancy in the next nearest site is approximately one-third less. The Mn^{++}-vacancy interchange is not detected in the resonance and therefore does not set in first. The magnitude and form of the loss peak is in good agreement with the recent theory of Lidiard if the effect of both nearest and next nearest pairs is considered.

I. INTRODUCTION

WHEN divalent metal impurity ions such as Mn^{++} are incorporated in an alkali halide lattice, they go in substitutionally for the alkali metal ions.[1] In a crystal free of other chemical impurities, an equal number of positive ion vacancies are created to maintain charge neutrality. A positive ion vacancy is a missing positive charge, and will experience a Coulomb attraction to the extra positive charge of a Mn^{++} ion. As a result there should be a tendency for the vacancies and Mn^{++} ions to form pairs.

In the preceding paper,[2] it was shown that spin resonance studies of Mn^{++} in the alkali chlorides can give detailed information about this pairing. It was possible to identify the spectra arising from two different types of simple Mn^{++}-vacancy pairs. Some of the lines in these spectra broaden abruptly at elevated temperatures. It will be shown that this broadening arises from the motion of the bound vacancy from one site to another in the vicinity of the Mn^{++} ion. A study of this broadening will be presented for one of the resonance lines of each type of Mn^{++}-vacancy pair in NaCl. From this study it is possible to estimate the lifetime of the vacancy both in the cation site nearest the Mn^{++} ion and in the site next nearest the ion.

Divalent ion-vacancy pairing and the vacancy motion can also be studied by the measurement of dielectric loss. Because a divalent ion-vacancy pair is an electric dipole, it will give rise to a Debye loss peak,[3] which has a characteristic maximum when the frequency of the applied electric field is approximately equal to the rate at which the dipole can reorient. Dielectric loss peaks have been observed in divalent

ion-doped alkali halides by several workers.[4-11] However, a detailed interpretation of these experiments has not been possible because the type and number of complexes contributing to the loss has not been known.

The spin resonance study reported in A gives the information necessary to interpret dielectric loss measurements. The dominant types of vacancy-Mn^{++} complexes were identified and the fraction of the Mn^{++} ions in each of these complexes was determined *vs* temperature. Dielectric loss measurements were performed on the NaCl:Mn samples, and these will be reported in this paper. With the information available from the resonance measurements, it is possible to give a complete analysis of the loss peaks. In addition, the information about the motion of the vacancy obtained from the loss measurements can be correlated directly with that determined from the broadening of the resonance multiplets.

II. SPIN RESONANCE MEASUREMENTS

1. Experimental

The spin resonance spectrometer and the oven for elevated temperature studies have been described in A. The source of the crystals is also described in that reference.

Figure 1 shows the spectrum of Mn^{++} in NaCl at room temperature in a crystal quenched from about 450°C. It is comprised primarily of three spectra, designated II, III_1, and III_2, which were analyzed in A. Spectrum II is identified as arising from isolated Mn^{++}

[1] For a review of the properties of divalent ions in alkali halides, see F. Seitz, Revs. Modern Phys. **26**, 11 (1954). See also A. B. Lidiard, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 20, p. 246.

[2] G. D. Watkins, preceding paper [Phys. Rev. **113**, 79 (1959)]. Henceforth this paper will be referred to as A.

[3] P. Debye, *Polar Molecules* (The Chemical Catalog Company, New York, 1929), Chap. V.
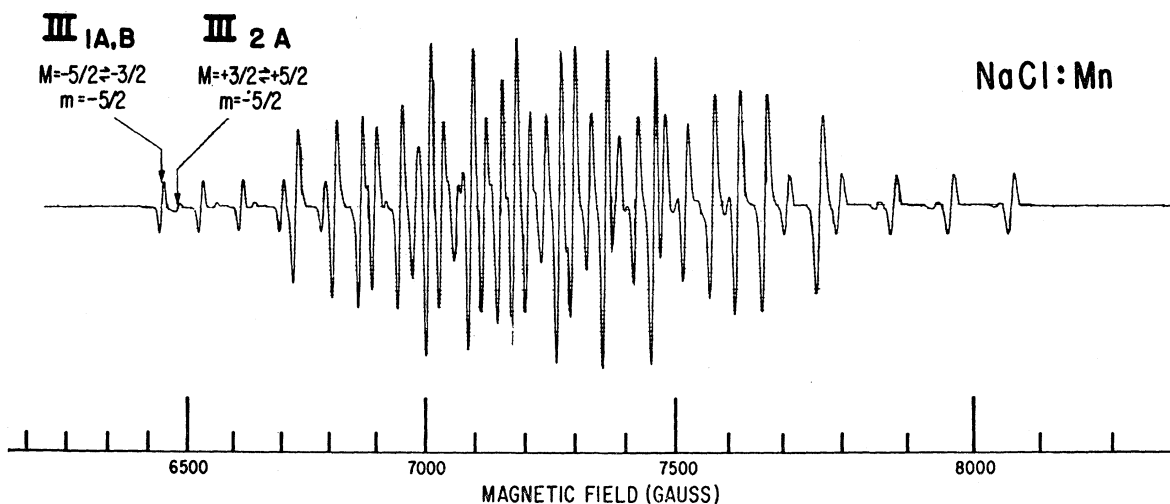
[4] R. G. Breckenridge, J. Chem. Phys. **18**, 913 (1950); *Imperfections in Nearly Perfect Crystals* (John Wiley and Sons, Inc., New York, 1952), p. 219.

[5] Burstein, Davisson, and Sclar, Phys. Rev. **96**, 819 (1954).

[6] Y. Haven, J. Chem. Phys. **21**, 171 (1953); *Report of the Bristol Conference on Defects in Crystalline Solids, 1954* (The Physical Society, London, 1955), p. 261.

[7] G. Jacobs, Naturwissenschaften **42**, 575 (1955).

[8] G. Jacobs, J. Chem. Phys. **27**, 217 (1957).

[9] J. S. Dryden and R. J. Meakins, Discussions Faraday Soc. No. 23, 39 (1957).

[10] J. O. Thomson (unpublished). This work was communicated to the author by Professor R. J. Maurer, University of Illinois.

[11] J. Pasternak, Bull. Am. Phys. Soc. Ser. II, **2**, 343 (1957).

$\text{III}_{\text{IA,B}}$ $\text{III}_{\text{2 A}}$

$M=-5/2 \rightleftharpoons -3/2$ $M=+3/2 \rightleftharpoons +5/2$
$m=-5/2$ $m=-5/2$

NaCl : Mn

MAGNETIC FIELD (GAUSS)

FIG. 1. Room-temperature spectrum in a quenched crystal of NaCl:Mn. The multiplets studied of the nearest ($\text{III}_{1A,B}$) and next nearest (III_{2A}) vacancy-Mn^{++} pair spectra are indicated. The magnetic field is parallel to a cubic axis.

ions, III_1, from Mn^{++}-vacancy pairs with the vacancy in the nearest cation site, and III_2, from pairs with the vacancy in the next-nearest site. The line width of one multiplet from each Mn^{++}-vacancy pair spectrum was studied and these mutliplets are indicated in Fig. 1.

2. Theory of the Line Width

The positive ion vacancy can jump from one bound position to another around the Mn^{++} ion. This motion either changes the orientation of the Mn^{++}-vacancy pairs in the magnetic field or changes the Mn^{++}-vacancy separation, or both. As a result, each time the vacancy moves the spectrum may be completely changed resulting in a lifetime broadening of those transitions which are split by the presence of the vacancy.[12] When the jump rate of the vacancy becomes comparable with the low-temperature width of the resonance line being observed, the line will begin to broaden, and, as the temperature is raised, the width of the line will become dominated by this motion.

It is shown in the Appendix that for the multiplets studied, this motion causes a Lorentzian line shape, as is usually encountered for lifetime broadened spectral lines,

$$g(\nu) = 2\tau/[1 + 4\pi^2\tau^2(\nu - \nu_0)^2]. \qquad (1)$$

It is concluded there that this should be valid over the full range of temperature studied. Here τ is the lifetime of the vacancy in the position giving rise to the resonance multiplet being observed, where only jumps

[12] Motional narrowing is perhaps the more familiar concept. In a broad sense this is motional narrowing also, since the total spectrum is narrowed. In the initial stages of this narrowing, however, the individual components of the spectrum broaden. This has been treated rigorously by Gutowsky, McCall, and Slichter [J. Chem. Phys. 21, 290 (1953)] for what is equivalent to the case of jumping between two possible resonance multiplets, and most of the features of the arguments given here are borne out in their special case.

which change the spectrum are considered as contributing to τ.

The twelve vacancy positions nearest to a Mn^{++} ion and the six next nearest are shown in Fig. 2. Measurements were made with the magnetic field parallel to a cubic axis of the crystal $(\theta = 0°)$. For this orientation, there are only two sets of nearest neighbor sites which give nonequivalent spectra. One set is made up of the four sites designated $1A$ and $1B$, the other, of the eight sites designated $1C$ and $1D$. Similarly, there are two nonequivalent next nearest sites designated $2A$ and $2B$. The nearest neighbor multiplet studied arises from Mn^{++} ions with a vacancy in one of the $1A$ or $1B$ sites. The other multiplet studied arises from ions with a vacancy in one of the $2A$ sites.

A vacancy jumps by interchange with an adjacent cation. As a result, all jumps from the $2A$ site are to nonequivalent sites and therefore τ for the next nearest multiplet gives the lifetime of the vacancy in that site. All jumps from the $1A$ or $1B$ sites are to nonequivalent sites except the possible interchange with the Mn^{++} ion. Therefore, τ for the nearest neighbor multiplet gives the lifetime of the vacancy in the nearest site, excluding interchange jumps with the Mn^{++}.

The interchange with the Mn^{++} must be considered separately. This motion does not change the spectrum, and therefore does not contribute to the broadening. However, this motion tends to average out the hyperfine interaction with neighboring chlorine ions which contributes to the normal line width. If this motion occurs first, a narrowing will be observed prior to the broadening caused by the other motion. If the interchange and other motion occur at about the same rates, a slight modification of the curve of width vs temperature may occur but only in the transition region where the broadening and narrowing motions can compete.
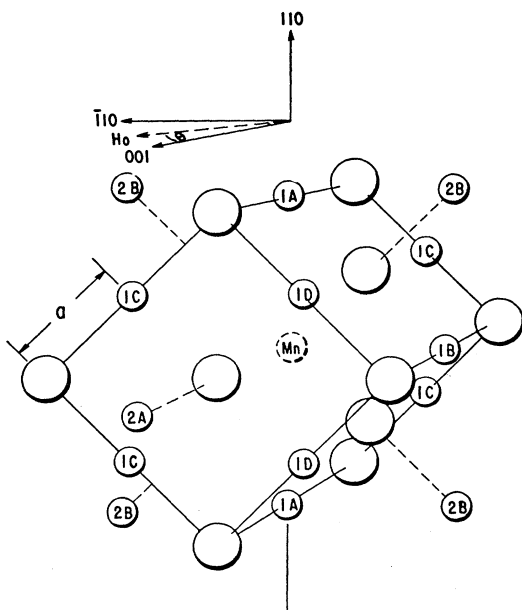
FIG. 2. Model showing the twelve nearest (1) and six next nearest (2) possible cation vacancy sites surrounding the Mn^{++} ion. The larger circles are the anion sites.

Above the transition region, the interchange will have no effect.

3. Results and Discussion of Line-Width Measurements

Figure 3 shows a plot of the logarithm of the line width vs $1/T$ for each of the satellites indicated in Fig. 1. The lines are approximately Gaussian at low temperature and appear Lorentzian within the accuracy of measurement at high temperature.

In order to analyze the data in the transition region, it was assumed that the observed line shape $G(\nu)$ was given by the convolution of the unbroadened line shape $h(\nu)$ and the lifetime broadened function $g(\nu)$ given by Eq. (1). Assuming a Gaussian $h(\nu)$, the peak-peak derivative of $G(\nu)$ was calculated as a function of τ. Using this, τ was determined from the observed derivative line width. The values determined in this way for the nearest neighbor satellite can be approximated by the straight line in Fig. 3, giving, for the lifetime of the vacancy in the nearest site (excluding Mn^{++} interchange), $1/\tau = 1.3 \times 10^{13} \exp(-E/kT)$, with $E = 0.52$ ev.

The estimate of τ is considered accurate to within 20% near 300°C. The higher temperature estimates are somewhat less reliable because the satellite lines overlap. In the transition region the estimate of τ is quite sensitive to the assumed low-temperature line shape (which is only approximately Gaussian). Also, the possible role of Mn^{++}-vacancy interchange in this region is not known. Because of these uncertainties, the activation energy of 0.52 ev may be in error by 30%.
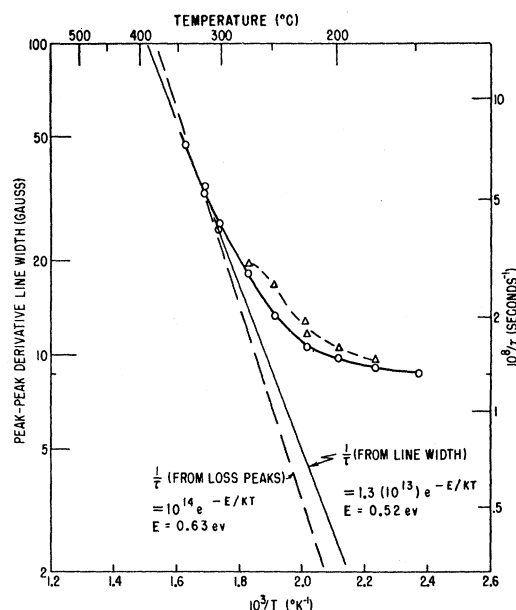
FIG. 3. Dependence of the peak-peak derivative line width on temperature. The circled points are for the multiplet studied of the nearest neighbor Mn^{++}-vacancy pair. The triangled points are for the multiplet of the next-nearest neighbor pair. Estimates of the lifetime τ of the vacancy in the nearest site from line-width analysis and from dielectric loss measurement are also shown.

Since there is no evidence of an initial narrowing we conclude that the Mn^{++}-vacancy interchange does not set in first.

The data on the next nearest vacancy satellite are insufficient to estimate the curve for it. However, from the line breadth we conclude that the lifetime in the next nearest site is approximately two thirds of that in the nearest site at about 250°C.

4. Relaxation Time

The motion of the vacancy around the Mn^{++} ion can also cause relaxation of the spin system. Following the method of Bloembergen, Purcell, and Pound,[13] in which the fluctuating crystal field splittings are analyzed into their Fourier spectra, etc., this contribution to the relaxation time for the $M = -\frac{5}{2} \rightleftharpoons -\frac{3}{2}$ nearest neighbor multiplet is estimated to be ≈ 700 τ.

T_1 was measured for this multiplet by the saturation method[14] and found to be approximately constant from 100°C–250°C at $T_1 = 6 \times 10^{-7}$ second. At 250°C this is still a factor of ten shorter than that calculated above, and we conclude that the vacancy motion is not the dominant relaxation mechanism at least up to this temperature.

[13] Bloembergen, Purcell, and Pound, Phys. Rev. 73, 679 (1948).

[14] It was assumed that the spin packet line shape was determined by the vacancy motion and given by Eq. (1). Above about 200°C, the saturation behavior was that of a homogeneously broadened line.[13] Below this temperature it was that of an inhomogeneously broadened line [A. M. Portis, Phys. Rev. 91, 1071 (1953)]. At room temperature, assuming $T_1 = T_2$ (because $\tau > T_1$), one obtains $T_1 = 2 \times 10^{-7}$ second.

III. DIELECTRIC MEASUREMENTS

1. Experimental

Most previous dielectric loss measurements on NaCl have been made in the temperature range 50–125°C so that the loss peaks would fall in the audio-frequency range. From the spin resonance study in A, it is apparent that this temperature range is a particularly bad one for NaCl:Mn. In this temperature range the solubility of the Mn^{++} ions is low and only a small fraction of the ions are in solution as simple Mn^{++}-vacancy pairs. On the other hand, the temperature is probably too high to quench in an excess of pairs long enough for reliable measurements.

As a result, the measurements reported here were performed in the temperature range 170°C–265°C, where essentially all of the Mn^{++} ions were in solution. An additional advantage of this temperature region is that it overlaps the region in which the vacancy motion is detected in the resonance line width. A direct correlation is then possible between the two experimental approaches.

The dielectric loss measurements were performed by a substitution method using a Boonton type 160A Q-meter. The crystal to be studied was placed between two flat silver electrodes which terminated a 6-inch-long silver-plated stainless steel coaxial line. The assembly was leak tight and a slight excess pressure of helium was maintained in the holder. The sample was heated by placing an oven over the electrodes, the stainless steel lines providing the necessary thermal isolation. Careful shielding of the rf coils and the Q-meter terminals was found to be necessary.

The crystals were cleaved to the approximate dimensions 0.5 in.×0.5 in.×0.030 in. and presented a capacity of about 10 $\mu\mu$f. Ignoring the series inductance of the holder, the loss factor of the sample is given by

$$\tan\delta = (C_0/C_s)\Delta(1/Q). \tag{2}$$

Here C_0 is the total resonating capacity, C_s the capacity of the sample, and $\Delta(1/Q)$ the difference between the reciprocal Q's with the sample holder and with the reference condenser in its place. Above 30 Mc/sec a small correction to Eq. (2) is required because of the series inductance of the holder.

The dielectric measurements were made on single crystals which were pulled from the melt. Harshaw single crystals were remelted as a high purity source of NaCl and $MnCl_2$ was added in the melt. Spectographic analysis indicated negligible Ca^{++} or other divalent impurity present other than Mn^{++}.

2. Theory of Dielectric Loss

The theory of the dielectric loss produced by a vacancy-divalent ion complex has been presented by Lidiard.[15] For a simple pair in which the vacancy spends

significant time only in the twelve equivalent sites nearest the divalent ion, a Debye loss peak occurs with the loss tangent given by

$$(\tan\delta)_c = \frac{8\pi a^2 e^2 N_c}{3\epsilon kT}\left(\frac{\omega\tau_D}{1+\omega^2\tau_D{}^2}\right). \tag{3}$$

Here, a is the nearest anion-cation distance, ϵ the static dielectric constant, N_c the number of pairs per cubic centimeter, and ω the angular frequency. The relaxation time τ_D is given by

$$1/\tau_D = 2(\nu_1 + \nu_2), \tag{4}$$

where ν_1 and ν_2 are the field free probabilities per unit time that the vacancy will jump to another particular nearest site position or that it will interchange with the divalent ion, respectively. In deriving Eq. (3) no local field correction was applied, and the correct numerical constants might be slightly different from those given.

One also has loss due to unbound vacancies, which, for a low concentration of vacancies, is given by

$$(\tan\delta)_u = \frac{16\pi a^2 e^2 \nu_0 N_u}{\epsilon kT}\left(\frac{1}{\omega}\right). \tag{5}$$

Here ν_0 is the field free probability that a vacancy will jump to a particular adjacent position and N_u is the concentration of unbound vacancies. The losses of Eqs. (3) and (5) are separable because of the different frequency dependencies, and the frequency of the maximum in the loss peak gives τ_D which can be related to ν_1 and ν_2 by Eq. (4).

Lidiard has extended the calculation to include next nearest vacancy positions.[15] The main effect is to shift the position of the maximum and change its magnitude slightly. Lidiard includes a table from which the shifts can be estimated.

3. Results

Loss measurements in a crystal containing 63 ∓ 10 ppm Mn^{++} (by spectrographic analysis) are given in Fig. 4. After subtracting the $1/\omega$ term due to free carriers, the dotted loss peaks are obtained. Inspection of these loss peaks reveals: (1) The curves are simple Debye loss peaks within the accuracy of measurement. There is no evidence of a long tail on the high-frequency side as has been observed by several workers in the audio range.[6,7,10] (2) The amplitudes of the peaks show a slight decrease as the temperature is increased. This decrease is expected once all the Mn^{++} ions are in solution because of the thermal dissociation of the complex, and because of the $1/T$ dependence of Eq. (3).[16] This has not generally been observed in the past, most observers reporting the opposite effect.[6,7,10,11]

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[15] A. B. Lidiard, *Report of the Bristol Conference on Defects in Crystalline Solids, 1954* (The Physical Society, London, 1955), p. 283.

[16] The decrease of the loss peak amplitudes is still not quite as large as expected over this temperature range. This suggests that some of the Mn^{++} ions are not in solution at the low-temperature end.
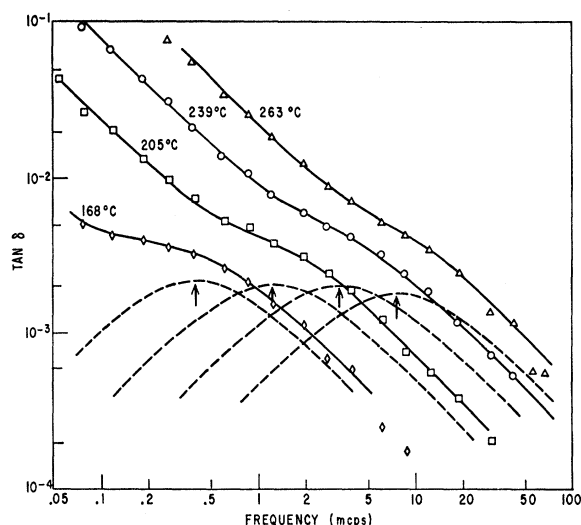
FIG. 4. Dielectric loss in NaCl containing 63 ∓ 10 ppm Mn++. The dashed curves are the extracted loss peaks, the arrows indicating the maxima.

Figure 5 is a plot of the frequency of the loss peak vs temperature. Included are values published by Haven[6] and Breckenridge[4] for loss peak measurements in NaCl:Mn in the audio-frequency range. The curve drawn through these points is given by

$$f_p = 5.5 \times 10^{12} \exp(-E/kT),$$

where $E = 0.63$ ev. The curve has been drawn through the audio-frequency point of Breckenridge. Although the accuracy of the measurements might accommodate a curve through Haven's point, there is reason to feel that it may be less accurate. His experiment was performed at 110°C and definite evidence of a high-frequency tail existed. Breckenridge's result was obtained at a lower temperature in quenched crystals, and simple vacancy complexes may have remained long enough for the measurement.

4. Discussion of Results

These loss peaks may be analyzed using the information about the state of the Mn++ ions obtained from the spin resonance. Since the relative numbers of nearest and next nearest pairs are known from resonance measurements, Lidiard's treatment[15] which includes the effect of both pairs can be used. His results are expressed in terms of the quantities $\xi = \tau_D \nu_3$ and $f = \exp(-\Delta E/kT)$, where τ_D is the Debye time considering only nearest neighbor positions [Eq. (4)], ν_3 is the field free probability per unit time that a vacancy at a next nearest position will jump to a particular nearest position, and ΔE is the difference in binding energy between the two sites. If we assume $\nu_3 = \nu_1 \exp(\Delta E/2kT)$, and ignore the Mn++-vacancy interchange ν_2, we obtain $f \approx 0.4$–0.5 and $\xi \approx 0.78$–0.72 over the temperature range studied. (We have used
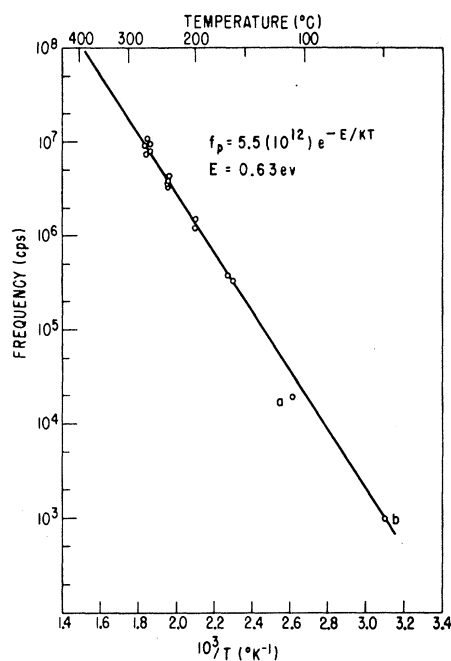

FIG. 5. Frequency of the loss peak maximum vs temperature. Included are audio-frequency measurements by (a) Haven[6] and (b) Breckenridge.[4]

$\Delta E = 0.034$ ev as given in Table II of A.) From Table II of Lidiard's paper we can estimate that the curve will be displaced 20% to high frequencies, i.e., $f_p = (1.2)/(2\pi\tau_D)$, and the amplitude of the peak will be increased 35% over that of Eq. (3) for the nearest pairs alone. The low values of f and ξ insure negligible departure from a simple Debye peak.

From the amplitude of the 239°C peak of Fig. 4, and using the 35% correction to Eq. (3), we estimate a concentration of 37 ∓ 4 ppm nearest neighbor pairs at this temperature. The total concentration of Mn++ in this sample was determined by spectrographic analysis to be 63 ∓ 10 ppm. Assuming that the number of pairs is given by a simple mass action law (see A), this gives an effective binding energy for the nearest neighbor pair of $E_1 = 0.41$ (+0.07, −0.04) ev. In another sample containing 38 ∓ 5 ppm, loss peak analysis gave 20 ∓ 2 ppm nearest neighbor pairs, and $E_1 = 0.41$ (+0.04, −0.03) ev. This is in good agreement with the value estimated from the spin resonance study in A (≈ 0.4 ev) and theoretical estimates[17,18] which also give $E_1 \approx 0.4$ ev. This suggests that no local field correction is necessary to Eq. (3) or in the refined formulas of Lidiard.

Comparison with the estimate of vacancy lifetime determined from the resonance can be made as follows: The lifetime of the nearest vacancy is given by

$$1/\tau = 4\nu_1 + \nu_2 + 2\nu_4 + 4\nu_5 + \nu_6.$$

[17] F. Bassani and F. G. Fumi, Nuovo cimento **11**, 274 (1954).
[18] M. P. Tosi and G. Airoldi, Nuovo cimento **8**, 584 (1958).

Here ν_1 and ν_2 are, as before, the probabilities per unit time of a jump to a particular other nearest site or of interchange with the Mn^{++}, respectively. ν_4, ν_5, and ν_6 are the corresponding jump frequencies to a particular adjacent site $2a$, $6^{\frac{1}{2}}a$, and $8^{\frac{1}{2}}a$ away from the Mn^{++} ion, respectively. The multiplicative factors represent the number of such adjacent sites, the total being twelve. We assume, as before, that the jump rate to any particular site is given by $\nu_1 \exp(-\Delta E/2kT)$ where ΔE is the difference between the binding energy in the site nearest the Mn^{++} and the one in question. We estimate the relative binding energies of these more distant sites using a simple homogeneous dielectric shielding model. This approximation should be fairly good, since the binding energy for the next nearest site is already very close to the Coulombic value. The result is, at 275°C,

$$1/\tau \approx 7\nu_1 = 18 f_p. \tag{6}$$

The 20% shift of the loss peak to higher frequency has been included, but interchange of the Mn^{++} with the vacancy has not.

Using Eq. (6), the data of Fig. 5 gives $1/\tau = 10^{14} \times \exp(-E/kT)$, where $E = 0.63$ ev.

This has been plotted in Fig. 3 along with the results of the line-width measurements. The difference in activation energy of the two estimates of $1/\tau$ is considered within the accuracy of the value determined by the line-width measurements. Otherwise the agreement is excellent. This leaves little doubt that the loss peaks and the line broadening arise from the same mechanism.

IV. SUMMARY AND CONCLUSIONS

Diffusion of the bound vacancy around a Mn^{++} ion has been detected as a broadening of some of the multiplets in the spin-resonance spectrum. Dielectric loss measurements at radio-frequencies have revealed a Debye loss peak that can be correlated with this motion. The good quantitative agreement between the two experiments is considered strong evidence that the dielectric loss originates from simple Mn^{++}-positive ion vacancy pairs, which have been identified by spin-resonance measurements.

Combining the results from both experiments, the best estimate of the lifetime of the vacancy in the cation site nearest the Mn^{++} ion is given by

$$1/\tau = 1.2 \times 10^{14} \exp(-E/kT), \tag{7}$$

with $E = 0.63 \mp 0.05$ ev. These values are considered accurate to within $\mp 20\%$ near 300°C. At this temperature, the lifetime of the vacancy in the next nearest site is approximately one-third less.

The Mn^{++}-vacancy interchange motion is not detected in the resonance and as a result does not set in first. This is reasonable because the extra charge of the Mn^{++} ion will pull the neighboring chlorine ions inward, which should make it harder for the Mn^{++} ion to squeeze out. This pulling in of the chlorine ions should also "open up" the lattice around the ion making the vacancy motion in the vicinity of the ion easier than elsewhere in the lattice. The activation energy for vacancy motion not near a defect is generally estimated to be in the range 0.7–0.9 ev.[1] The lower value determined here of 0.63 ev may indicate the importance of this effect.

This is the first demonstration of dielectric loss peaks which can definitely be identified as arising from simple divalent ion-positive ion vacancy pairs. The measurements in the radio-frequency range reported here connect fairly well to the audio-frequency measurements made by others on this system. This would tend to confirm that these audio-frequency loss peaks also originate from the simple complexes, as had been generally assumed. However, any partially bound vacancy will give rise to a loss peak of sorts. Spin resonance has shown that a good fraction of the Mn^{++} ion-vacancy pairs are not in solution at the lower temperatures usually employed, and some loss may therefore arise from the Mn^{++} ions and vacancies in the precipitated state. Such effects could account for the long tails to the high-frequency side of the peak often observed in the audio measurements.

The intensity of the loss peaks reported in this paper is in good agreement with that predicted by Lidiard.[15] This suggests that the poor agreement generally found in the past for the audio measurements arises from the low solubility of the complexes. This poor agreement appears to exist in most divalent ion-alkali halide systems reported. The low solubility in this temperature range may be a rather general property of these systems.

APPENDIX

In the resonance experiment, the magnetic field and klystron frequency are adjusted to resonance for a particular transition and a particular position of the vacancy. As the vacancy jumps the precessing Mn^{++} spin is sometimes brought into resonance, and, on a subsequent jump, is removed from resonance. If phase coherence in the precession is lost by the time the vacancy has returned to the resonant position, we may treat these periods on resonance as independent. With a vacancy jump probability independent of time, this gives a simple exponential correlation function for the precessing spin resulting in a Lorentzian line shape for

the line[19,20]

$$g(\nu) = 2\tau / [1 + 4\pi^2 \tau^2 (\nu - \nu_0)^2]. \qquad (1)$$

Here τ is the average lifetime of the vacancy in the position giving rise to the resonance line being observed, where only jumps which change the spectrum are considered as contributing to τ.[21]

If we observe a resonance line at frequency ν_i which is produced by a vacancy in the ith site, the requirement for losing phase coherence during the time the vacancy is away can be estimated as follows: The average time spent at site j before the vacancy returns can be determined by simple detailed balance arguments and is given by $\tau_i p_j / p_i$. Here τ_i is the average lifetime in the ith site and p_j and p_i are the probabilities

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[19] M. C. Wang and G. E. Uhlenbeck, Revs. Modern Phys. **17**, 326 (1945).
[20] I. Yokota, Progr. Theoret. Phys. (Japan) **8**, 380 (1952).
[21] We assume that the time required for the jump is very short compared to the time between jumps. As a result possible phase accumulation during the jump is not considered.

of finding the vacancy in the jth and ith site, respectively. The average phase error accumulated at site j is therefore $2\pi\tau_i(\nu_j - \nu_i)p_j/p_i$. In order that phase coherence be lost, the total average phase error accumulated before the vacancy returns to site i must be $\gtrsim 2\pi$. Summing over all sites j, this gives the requirement

$$(\tau_i/p_i) \sum_j p_j(\nu_j - \nu_i) \gtrsim 1. \qquad (8)$$

Only nearest and next nearest vacancy-Mn^{++} pairs are observed. Thus the p_j are small for other vacancy sites and only the motion between the nearest and next nearest sites need be considered. With the values of ν_j and p_j determined from the resonance (see A), Eq. (8) gives $\tau \gtrsim 1.5 \times 10^{-10}$ sec for the nearest neighbor multiplet and $\tau \gtrsim 6 \times 10^{-10}$ sec for the next nearest. At the highest temperature studied the deduced lifetimes are still a factor of ten larger than these limits. We therefore conclude that Eq. (1) is valid over the range of temperatures studied and τ gives the lifetime of the vacancy site giving rise to the multiplet studied.

Configuration Coordinate Model for KCl:Tl Including Spin-Orbit Interaction

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The effect of the crystalline field on the spin-orbit interaction of the $^3P^\circ$ and $^1P^\circ$ states of Tl$^+$ in KCl has now been included in the configuration coordinate model. The potential energy curves for the pure spin states are required to satisfy the condition that after the application of spin-orbit interaction the resulting crystal states account for the absorption and emission spectra, explained by the earlier model, and for the oscillator strengths of the absorption bands. In accordance with the adiabatic approximation, the potential energy curves for the states involved in absorption and emission do not cross and the electronic matrix elements for radiative transitions depend on the configuration coordinate. The curve for the lower excited state has two minima which account for the 3050 A and the 4750 A emission bands. From the single minimum of the upper excited state an additional emission band near the 2470 A absorption band is predicted. With intense excitation at 77°K in a narrow spectral range near 1960 A, which corresponds to excitation only to the upper excited state, the predicted emission has been found. The existence and characteristics of the new emission provide confirmation of the model, particularly of the quantitative effect of spin-orbit interaction.

I. INTRODUCTION

THE configuration coordinate model has been used extensively to explain the properties of localized impurity systems in luminescent crystals. This model is based on the adiabatic approximation according to which the wave function $\psi(r,q)$ for a state of the impurity system can be written

$$\psi(r,q) = \phi(q)\varphi(r,q). \qquad (1)$$

The electronic wave function $\varphi(r,q)$ is a function of the electronic coordinates r and is smoothly modified by changes in the positions, q, of the nuclei whose state of motion is described by $\phi(q)$. In other words, transitions between electronic states do not occur during the changes in nuclear coordinates but rather an electronic

state itself is progressively deformed during an adiabatic change in nuclear coordinates. In this approximation an effective potential, therefore, exists for nuclear displacements and it can be shown that this potential may contain terms up to the fourth power of the displacements.[1]

The configuration coordinate model involves a diagrammatic representation of the energy of the system as a function of adiabatic displacements in the nuclear coordinates. The energy is plotted as a function of the nuclear coordinates of the crystal for each electronic state of the system. Optical transitions occur vertically in accordance with the Frank-Condon principle. In the

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[1] M. Born and K. Huang, *Dynamic Theory of Crystal Lattices* (Oxford University Press, Oxford, 1954), p. 171.