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Determination of Vacancy Jump Frequencies from Dielectric Loss Measurements on Ni^{++}-Doped NaCl Crystals

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Small divalent cation impurities such as Co, Mg, Mn, Ni, etc., in alkali halide crystals give two dielectric relaxation peaks, as they are associated with the nearest-neighbor (nn) and the next-nearest-neighbor (nnn) vacancies. NaCl : Ni^{++} crystals give peaks at frequencies (in Hz) of $(3.69 \pm 0.37) \times 10^{11} e^{-0.62 \pm 0.06\ \mathrm{eV}/kT}$ and $(2.84 \pm 0.28) \times 10^{11} e^{-(0.55 \pm 0.05\ \mathrm{eV})/kT}$. The jump frequencies ω_0 ($\omega_0 = \omega_1 + \omega_2$), ω_3, and ω_4 are expressed in terms of the positions of the two peaks and the ratio of the heights of the two peaks. ω_1, ω_2, ω_3, and ω_4 are the field-free jump frequencies of the cation vacancy defined by (i) ω_1, nn → nn; (ii) ω_2, nn → impurity; (iii) ω_3, nnn → nn; and (iv) ω_2, nn → nnn. At 80 °C, the values of jump frequencies ω_0, ω_3, and ω_4 were found to be $(1.54 \pm 0.17) \times 10^4$, $(1.19 \pm 0.18) \times 10^3$, and $(1.20 \pm 0.20) \times 10^3$ Hz, respectively. It is seen that $\omega_0 > \omega_3, \omega_4$ and that ω_3 and ω_4 are almost equal in magnitude. From the latter fact it is concluded that the concentration of nn and nnn vacancies is almost equal. The relative values of ω_0, ω_3, and ω_4 are consistent with the earlier results of anelastic relaxation measurements.

I. INTRODUCTION

Divalent metallic impurities in alkali halide crystals form dipoles with oppositely charged vacancies.[1,2] These dipoles tend to orient along the externally applied electric field, giving rise to relaxational losses.[3] Several authors have observed dielectric-loss peaks due to such dipoles.[4-9]

For small impurity cations such as Co,[8,9] Mn,[10] and Mg,[7] two dielectric-loss peaks have been observed. Dreyfus[7] suggested that in such cases the cation vacancy can occupy both the nearest-neighbor (nn) and next-nearest-neighbor (nnn) positions relative to the impurity, and that tanδ can be expressed as a sum of contributions from two Debye peaks. The exact expression for tanδ is[7]

$$\tan\delta = \frac{16\pi a^2 e^2 N_i p}{3(2+\omega_4/\omega_3)\epsilon kT(\lambda_1-\lambda_2)} \left[\frac{2(\omega_1+\omega_2+\omega_4)-\lambda_2(1+\omega_4/\omega_3)}{\lambda_1/\omega+\omega/\lambda_1} + \frac{\lambda_1(1+\omega_4/\omega_3)-2(\omega_1+\omega_2+\omega_4)}{\lambda_2/\omega+\omega/\lambda_2} \right] . \qquad (1)$$

Here N_i is the impurity concentration per unit volume, p is the degree of association, a is the lattice constant, and ω is the frequency of the applied field. ω_1, ω_2, ω_3, and ω_4 are the field-free jump frequencies of the cation vacancy, defined as follows: (i) ω_1, nn → nn; (ii) ω_2, nn → impurity; (iii) ω_3, nnn → nn; and (iv) ω_4, nn → nnn. The two relaxation times τ_1 and τ_2 are given by

$$\begin{aligned} (\tau_1)^{-1} = \lambda_1 &= \omega_1+\omega_2+2\omega_3+\omega_4 \\ &\quad + [(\omega_1+\omega_2-2\omega_3+\omega_4)^2+4\omega_3\omega_4]^{1/2} , \\ (\tau_2)^{-1} = \lambda_2 &= \omega_1+\omega_2+2\omega_3+\omega_4 \\ &\quad - [(\omega_1+\omega_2-2\omega_3+\omega_4)^2+4\omega_3\omega_4]^{1/2} . \end{aligned} \qquad (2)$$

Equations (2) have been written in terms of the reciprocals of relaxation times, because in our experiments the frequency of the dielectric-loss peak and not the relaxation time is measured.

The experimental dielectric-loss data give the values of λ_1 and λ_2 and the heights (P_1 and P_2) of the two peaks. Therefore, in principle, it should be possible to derive the values of the four jump frequencies (ω_1, ω_2, ω_3, ω_4) from the experimental dielectric-loss data. However, in the derivation of Eq. (1) it has been assumed that the electric field experienced by the impurity-vacancy dipole inside the crystal is the same as the externally applied electric field. This may not be true in actual practice, as has already been reported.[8] Therefore, if the heights of the two loss peaks are used as experimental parameters in solving Eqs. (1) and (2), erroneous results will be obtained. This error in the final result can be avoided by using the ratio of the heights of the two loss peaks. This means one is assuming that the internal electric field is the same for nn vs nnn vacancies. But this will reduce the number of experimentally observed parameters to three (the two peak frequencies λ_1 and λ_2 and the ratio of the heights of two peaks). However, only three independent variables exist in Eqs. (1) and (2), since ω_1 and ω_2 only appear as the sum ω_0. In the present paper Eqs. (1) and (2) have been solved rigorously to yield expressions for ω_0, ω_3, and ω_4 in terms of the measurable dielectric-loss parameters, namely, λ_1, λ_2, and P_1/P_2. Therefore, the values of these frequencies (ω_0, ω_3, and ω_4) can be determined, provided that the positions of the two peaks and the values of tanδ at the peak positions are accurately known.

Experimentally, in the case of Co-doped NaCl and KCl crystals[8,9] it was not possible to resolve the two peaks from the background loss and get the accurate values of various parameters. Preliminary measurements of dielectric loss in Ni^{++}-doped NaCl crystals showed the presence of two dielectric-loss peaks. At low temperatures the background loss was very small and the two peaks could be well resolved. Therefore, this system was selected to calculate the lattice frequencies using dielectric-loss data. The experimental results on Ni^{++}-doped NaCl crystals are also reported here.

II. EXPERIMENTAL

Single crystals of NaCl were grown from the melt by the Kyropoulos method. Ni-doped crystals were grown from a thoroughly mixed charge containing known weights of $NiCl_2$ and NaCl powders. British Drug House analar-grade powders of NaCl and $NiCl_2$ were used. Samples with dimensions $10 \times 10 \times 0.4$ mm were used for the dielectric-loss measurements. The crystals were coated with aquadag (colloidal graphite) on both of the larger faces. For quenching, these samples were heated in a specially designed furnace to the desired temperature for the desired length of time and then cooled rapidly by placing them on a large cool metal plate.

The dielectric-loss measurements were made in a specially designed sample holder[11] under a vacuum of $\sim 10^{-3}$ mm Hg. The measurements were made with a General Radio-716C capacitance bridge combined with a General Radio-1302A oscillator and a General Radio 1212A unit null detector. A substitution method was used to eliminate the background signals and the effect of the capacitance of the connecting leads. The measurements of tanδ were made in the frequency range 10^2–10^5 Hz and in the temperature range 70–200 °C. The colorimetric method was used for the estimation of Ni in NaCl crystals. For further details reference may be made to earlier work.[8,9,11,12]

III. THEORY

In this section we shall derive expressions for the lattice frequencies ω_0, ω_3, and ω_4 in terms of observed experimental values of the peak positions (λ_1, λ_2) and the ratio of the heights of the two dielectric-loss peaks (P_1/P_2). From Eq. (1) the peak height P_1 is obtained by putting $\omega = \lambda_1$, so that

$$P_1 = (\tan\delta)_1^m = A\left[\frac{2(\omega_0+\omega_4)-\lambda_2(1+\omega_4/\omega_3)}{2}+\frac{\lambda_1(1+\omega_4/\omega_3)-2(\omega_0+\omega_4)}{\lambda_1/\lambda_2+\lambda_2/\lambda_1}\right] . \tag{3}$$

Similarly, by putting $\omega = \lambda_2$ we obtain the following expression for P_2:

$$P_2 = (\tan\delta)_2^m = A\left[\frac{2(\omega_0+\omega_4)-\lambda_2(1+\omega_4/\omega_3)}{\lambda_1/\lambda_2+\lambda_2/\lambda_1}+\frac{\lambda_1(1+\omega_4/\omega_3)-2(\omega_0+\omega_4)}{2}\right] , \tag{4}$$

where

$$A = \frac{16\pi a^2 e^2 N_i p}{3(2+\omega_4/\omega_3)\epsilon k T(\lambda_1-\lambda_2)} . \tag{5}$$

Let

$$\lambda_3 = \tfrac{1}{2}(\lambda_1+\lambda_2) = (2\omega_3+\omega_0+\omega_4) , \tag{6}$$

$$\lambda_4 = \tfrac{1}{2}(\lambda_1-\lambda_2) = [(\omega_0+\omega_4-2\omega_3)^2+4\omega_3\omega_4]^{1/2} , \tag{7}$$

and

$$\lambda_5 = (\lambda_1/\lambda_2 + \lambda_2/\lambda_1)^{-1} , \tag{8}$$

so that

$$M_1 = \frac{P_1}{P_2} = \frac{(\omega_0 + \omega_4)(1 - 2\lambda_5) + (1 + \omega_4/\omega_3)(\lambda_1\lambda_5 - \frac{1}{2}\lambda_2)}{-(\omega_0 + \omega_4)(1 - 2\lambda_5) + (1 + \omega_4/\omega_3)(\frac{1}{2}\lambda_1 - \lambda_2\lambda_5)} . \tag{9}$$

Let

$$M_2 = (1 - 2\lambda_5)(1 + M_1) , \tag{10}$$

$$M_3 = (\lambda_1\lambda_5 - \tfrac{1}{2}\lambda_2) - M_1(\tfrac{1}{2}\lambda_1 - \lambda_2\lambda_5) , \tag{11}$$

and

$$M_4 = M_3/M_2 , \tag{12}$$

so that from Eq. (9) we have

$$\omega_0 + \omega_4 = -M_4(1 + \omega_4/\omega_3) . \tag{13}$$

From Eqs. (6) and (7), we have, say,

$$M_5 = \tfrac{1}{4}(\lambda_3^2 - \lambda_4^2) = 2\omega_3\omega_0 + \omega_3\omega_4 . \tag{14}$$

From Eqs. (13) and (14), we have

$$\omega_3 = -(2M_4\omega_4 + M_5)/(2M_4 + \omega_4) . \tag{15}$$

Using Eqs. (6) and (15) the following expression is obtained for ω_0:

$$\omega_0 = (M_6 + M_7\omega_4 - \omega_4^2)/(2M_4 + \omega_4) . \tag{16}$$

Here, we have

$$M_6 = 2(\lambda_3 M_4 + M_5) \tag{17}$$

and

$$M_7 = \lambda_3 + 2M_4 . \tag{18}$$

Putting the values of ω_0 and ω_3 from Eqs. (16) and (15) in Eq. (14), we obtain the following cubic equation in ω_4:

$$\omega_4^3 + a\omega_4^2 + b\,\omega_4 + c = 0 , \tag{19}$$

where

$$a = -2(M_4 + M_7),$$
$$b = -[2M_6M_4 + M_5(M_7 + 3M_4)]/M_4 , \tag{20}$$
$$c = -(M_6M_5 + 2M_4^2M_5)/M_4 .$$

The values of ω_4 are obtained from the solution of Eq. (19). Only real positive roots of Eq. (19) are to be used.

IV. RESULTS AND DISCUSSION

The results of measurements of the dissipation factor tanδ as a function of frequency on a Ni-doped NaCl crystal are shown in Fig. 1. Curves 1–5 were obtained by making measurements at the following constant temperatures: 80, 100, 120, 140, and 160 °C. Before each set of measurements the crystal was heated at about 350 °C for about 2 h and then quenched to the temperature of measurement. Following earlier convention[8–10] the low- and high-frequency peaks have been named as *A* and *B* peaks, respectively. Both the peaks shift to higher frequencies as the temperature is increased. The logarithm of frequencies of both the peaks yields straight lines when plotted as a function of $1/T$ (Fig. 2). Here T is the temperature of measurement in °K. This shows that the peak frequencies obey the Arrhenius relation and can be expressed as

$$f_{A,B} = f^0_{A,B}\, e^{-E_{A,B}/kT} .$$

Here f_A and f_B are the peak frequencies for *A* and *B* peaks, respectively; f^0_A and f^0_B are the corresponding preexponential factors; E_A and E_B are the activation energies for the *A* and *B* peaks, respectively, and k is the Boltzmann constant. From the slope of the straight lines in Fig. 2 the values of f^0_A, f^0_B, E_A, and E_B were found to be $(3.69 \pm 0.37) \times 10^{11}$ Hz, $(2.84 \pm 0.28) \times 10^{11}$ Hz, 0.62 ± 0.06 eV, and 0.55 ± 0.5 eV, respectively.

Experiments were performed to establish whether both the *A* and *B* peaks were due to Ni-cation vacancy dipoles.

Measurements of tanδ were made on pure crystals of NaCl (without deliberately added Ni^{++} impurity). The tanδ-vs-frequency isothermals were found to be straight lines with unit slope. Neither of the

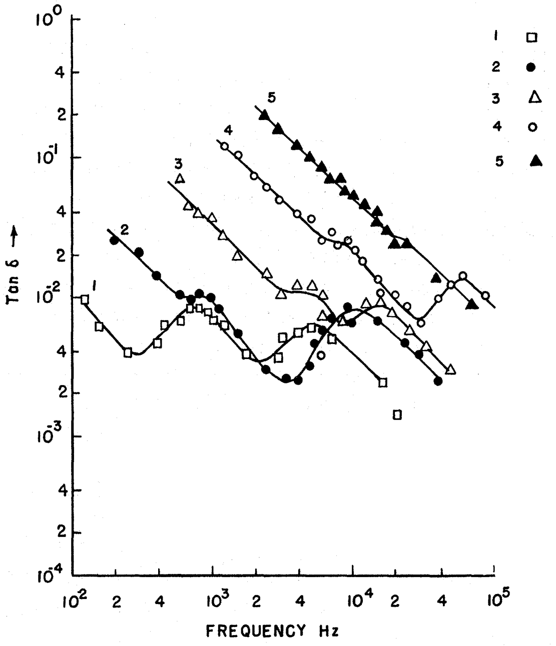

FIG. 1. Loss-tangent–vs–frequency isotherms for NaCl crystals containing 8 ppm of Ni^{++}. Curves 1, 2, 3, 4, and 5 were obtained at 80, 100, 120, 140, and 160 °C, respectively.

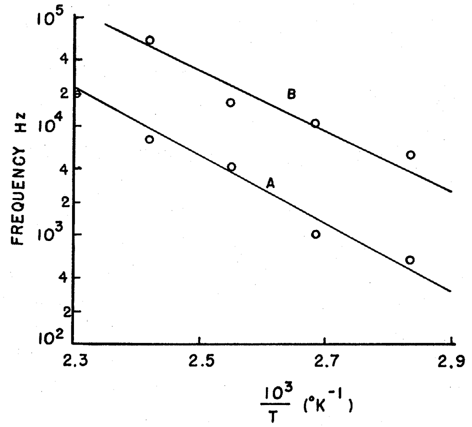

FIG. 2. Plots of $\log_{10} f_A$ and $\log_{10} f_B$ as a function of $1/T$.

A and *B* peaks nor any other peak was observed. The same experiment was repeated on crystals containing different concentrations of Ni. The heights of both the peaks were observed to increase with the increase in the concentration of Ni in these crystals.

Since our crystals were grown in air and the heat treatment was also given in air, it is possible that some of the impurity exists as aggregates[13] and may give rise to one loss peak.[14] To check on this possibility dielectric-loss measurements were made after quenching the crystals from different temperatures. For the temperatures of quenching less than about 300 °C, the heights of both peaks increased with the increase in temperature. The heights of the peaks became constant when the temperature of quenching was $\geq$ 300 °C. This shows that the aggregates of impurity-vacancy dipoles are completely dissociated on heating the crystals to $\geq$300 °C. The results shown in Fig. 1 were obtained after quenching the crystals from ~ 350 °C. Moreover, if the aggregates of impurity-vacancy dipoles are present in these crystals, the value of activation energy obtained from the slope of $\ln \sigma T$ vs $1/T$ straight lines (in the experimental temperature range) should be ~ 1.2 eV.[15] (Here σ is the electrical conductivity of the crystal.) This is about 0.2 eV more than the activation energy for crystals in which no aggregation is present. Since the background loss is proportional to the dc conductivity of the crystal, the logarithm of the product of T with the background $\tan\delta$ at a fixed frequency (10^2 Hz) was plotted as a function of $1/T$. The slope of the straight line obtained in this manner gave the value of the activation energy as 0.99 eV. This value corresponds to crystals free of aggregates.[15] On the basis of these considerations it is concluded that neither the *A* nor *B* peak is due to aggregation of impurity-vacancy dipoles.

Interfacial polarization can be another source of a dielectric-loss peak.[16] To check on this, the variation of capacitance of many crystals was studied as a function of frequency near 100 Hz. No appreciable variation in the value of the capacitance was observed. Further, the heights of the *A* and *B* peaks did not change with the thickness of the crystal.[17] These observations suggest that interfacial polarization is also not giving rise to any dielectric-loss peak. These results and the results of dielectric-loss measurements on pure crystals, crystals doped with different concentrations of Ni, and crystals quenched from different temperatures show that the *A* and *B* peaks are both due to nickel and cation vacancy dipoles.

The behavior of nickel in these crystals is similar to that of cobalt in sodium chloride[8] and potassium chloride[9] crystals and also to that of Mn in KCl crystals,[10] where two loss peaks were observed.

Since in curve 1 (Fig. 1) both the *A* and *B* peaks are well resolved and the background loss is very small, this curve has been chosen for the calculation of the lattice frequencies. In terms of the notation used in Sec. III, we have

$$\lambda_1 = \tau_1^{-1} = 2\pi f_B$$

and

$$\lambda_2 = \tau_2^{-1} = 2\pi f_A .$$

The observed heights of peaks *A* and *B* are P_2 and P_1, respectively. The observed values of λ_1, λ_2, P_1, and P_2 are given in Table I. The values of the lattice frequencies ω_0, ω_3, and ω_4 were calculated using Eqs. (15), (16), and (19). Only one real positive root was obtained on solving Eq. (19). The calculated values of ω_0, ω_3, and ω_4 are also given in Table I.

We see from Table I that the value of ω_0 is larger by an order of magnitude than the values of ω_3 and ω_4. Therefore, from Eq. (2) we have

$$\lambda_1 \cong 2\omega_0$$

and

$$\lambda_2 \cong 2\omega_3 + \omega_4 ,$$

TABLE I. Observed values of the two peak frequencies λ_1 and λ_2; the heights of the two peaks (P_1 and P_2) at 80 °C; and the values of the jump frequencies ω_0, ω_3, and ω_4 calculated from these data.

	Observed values		Calculated values (Hz)
λ_1	$(3.39 \pm 0.34) \times 10^4$ Hz	ω_0	$(1.54 \pm 0.17) \times 10^4$
λ_2	$(4.40 \pm 0.44) \times 10^3$ Hz	ω_3	$(1.19 \pm 0.18) \times 10^3$
P_1	$(6.50 \pm 0.65) \times 10^{-3}$	ω_4	$(1.20 \pm 0.20) \times 10^3$
P_2	$(8.20 \pm 0.82) \times 10^{-3}$		

which is consistent with the values reported in Table I.

Since $\omega_0 = \omega_1 + \omega_2$, these results suggest that the B peak ($f_B = \lambda_1/2\pi \cong \omega_0/\pi$) is due to Ni^{++}-nn vacancy dipoles. Similarly, the A peak $[f_A = \lambda_2/2\pi \cong (2\omega_3 + \omega_4)/2\pi]$ is due to Ni^{++}-nnn vacancy dipoles. Since $\omega_0 = \omega_1 + \omega_2$, in principle it is possible that either ω_1 or ω_2 is giving rise to such a large value of ω_0. It is generally believed that the value of ω_2 is very small. However, Bucci[18] has reported a large value of ω_2 for Be^{++} in NaCl and KCl crystals. In the case of Ni^{++} in NaCl, the value of the activation energy obtained from the diffusion data[19] is 1.3 eV, which is very large compared to the activation energy obtained for migration of free-cation vacancies (0.79 eV).[20] These considerations suggest that in our case ω_2 is very small compared to ω_1 and, therefore, $\omega_0 \cong \omega_1$.

Further, we note from the present results that ω_0 ($\cong \omega_1$) is larger than ω_3 (Table I). Dreyfus and Laibowitz[21] have reported that ω_3 is larger than ω_1 in the case of Ca and Mn impurities. But even there it is found that as the radius of the impurity decreases [in going from Ca^{++} (radius 1.00 Å) to Mn^{++} (radius 0.80 Å)], the value of ω_1 increases and that of ω_3 decreases. If the same trend is maintained, it is expected that in the case of Ni^{++} (radius 0.70 Å), which is smaller than Mn^{++}, the value of ω_1 will increase further and that of ω_3 will decrease further. It is, therefore, not surprising that the value of ω_1 has been found to be larger than that of ω_3 in the present case.

The value of ω_4 is approximately the same as that of ω_3 (Table I.) This suggests that the concentration of nn vacancies is approximately equal to nnn vacancies. In the case of big impurities, ω_4 is negligibly small. The present results are consistent with the results of anelastic relaxation measurements[21] which show that ω_4 increases as the radius of impurity cation decreases.

We conclude from the results reported in this paper that the dielectric-loss data can be used under suitable circumstances (as for the case of Ni^{++} in the NaCl crystal) to calculate the values of different jump frequencies of the cation vacancy in the alkali halide crystals.

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