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Low Frequency Dispersion in Ionic Crystals Containing Foreign Ions*

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The anomalous electrical response at low frequencies previously observed in pure ionic crystals has been studied in ionic crystals containing foreign ions. Measurements of the dielectric loss at one kc as a function of temperature have been made on four salts with a variety of foreign ions at several concentrations. A number of loss maxima were observed which depended in height on the concentration of the foreign ion and the heat treatment of the crystal; and, in their position on the temperature scale on the nature of the salt and foreign ion. An interpretation of the results in terms of defect pairs of various types is presented.

INTRODUCTION

THE anomalous electrical response previously reported¹ in pure ionic crystals has now been studied in ionic crystals containing foreign ions. The frequency and temperature dependence of the dielectric constant and loss¹ indicated the existence of a relaxation process resembling a typical Debye dipole rotation phenomenon in crystals that had been recently grown from the melt or heated to a temperature close to the melting point and cooled rapidly. The source of the polarization in this process has been a matter of considerable interest. It was suggested¹ that in the crystals containing Schottky defects the dipoles probably consisted of an associated pair of anion and cation vacancies on adjacent sites; and, since transfer studies had indicated that only cations were mobile at low temperatures, it was assumed that the reorientation of the pair involved the motion of the positive ions. There were, however, a number of other possibilities that could not be excluded with the information at hand. Dienes² has recently calculated the activation energy required for the migration of a pair of vacancies through the motion of the negative ion and found it to be of the order of a few tenths of an electron volt. This energy is in the range measured and thus must be considered. As is well known, pairs are expected to be formed between divalent impurity cations and vacant cation sites. Grimley³ has attributed the observed effect to pairs of this type. In addition, there was a possibility that the effect might be due in some unexplained way to single vacancies.

In addition to such effects in the alkali halides the nature of the lattice defects in AgCl has been a matter of interest. The presence of two loss maxima in this crystal was taken to indicate Frenkel defects since both the interstitial ion and the vacant site should be mobile. Instead of this interpretation, Grimley³ suggests the presence of two foreign ions.

Measurements on crystals containing known concen-

trations of foreign ions may be expected to shed considerable light on these questions; consequently, studies have been made on crystals from a number of sources, containing a variety of foreign ions and at several concentrations. The results, besides supplying information about points that have been raised previously, provide new information about the mobilities of foreign ions in ionic crystals.

PROCEDURE

One group of samples for this investigation was prepared by coating pure crystals of *ca.* $0.020 \times \frac{1}{2} \times \frac{1}{2}$ in. with a thin layer of the desired impurity and heating until the foreign salt had been distributed evenly through the volume by diffusion. This treatment, which left a clear crystal, normally required several hours at a temperature slightly (*ca.* 25°C) below the melting point. The crystal was then cooled rapidly in air. The source materials for samples prepared in this way were NaCl, AgCl, and KBr from the Harshaw Chemical Company, Cleveland, Ohio, and KCl, grown by A. von Hippel in this Laboratory. The salts added were c.p. grades of Cd, Ni, Cu, and Pb chlorides. The concentration of impurity ion was determined after the electrical measurements were completed by dissolving the crystal in a suitable electrolyte and analyzing the solution polarographically⁴ using the method of standard additions. In the case of AgCl, the crystal was dissolved in KCN solution and the silver plated out. Then the Cd⁺⁺ was determined in the residue. All concentrations are given in mole percent.

Several other crystals, including NaCl+PbCl₂ and a series of NaCl+MnCl₂, were grown at the Naval Research Laboratory, Washington, D. C., and obtained through the courtesy of the Crystal Section of that Laboratory. The composition of these crystals had also been determined polarographically at the N.R.L. The crystals containing the larger amounts of PbCl₂ were somewhat clouded, indicating that the lead chloride was not completely in solid solution.

The remaining crystals, including NaCl+TiCl and AgCl, had been grown previously by Professor A. von Hippel. The compositions of these were also determined using the polarograph.

⁴ Schulman, Battey, and Jelatis, *Rev. Sci. Inst.* **18**, 226 (1947).

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** Present address: National Bureau of Standards, Washington 25, D. C.

¹ R. G. Breckenridge, *J. Chem. Phys.* **16**, 959 (1948).

² G. J. Dienes, *J. Chem. Phys.* **16**, 620 (1948).

³ T. B. Grimley, *J. Chem. Phys.* **17**, 496 (1949).

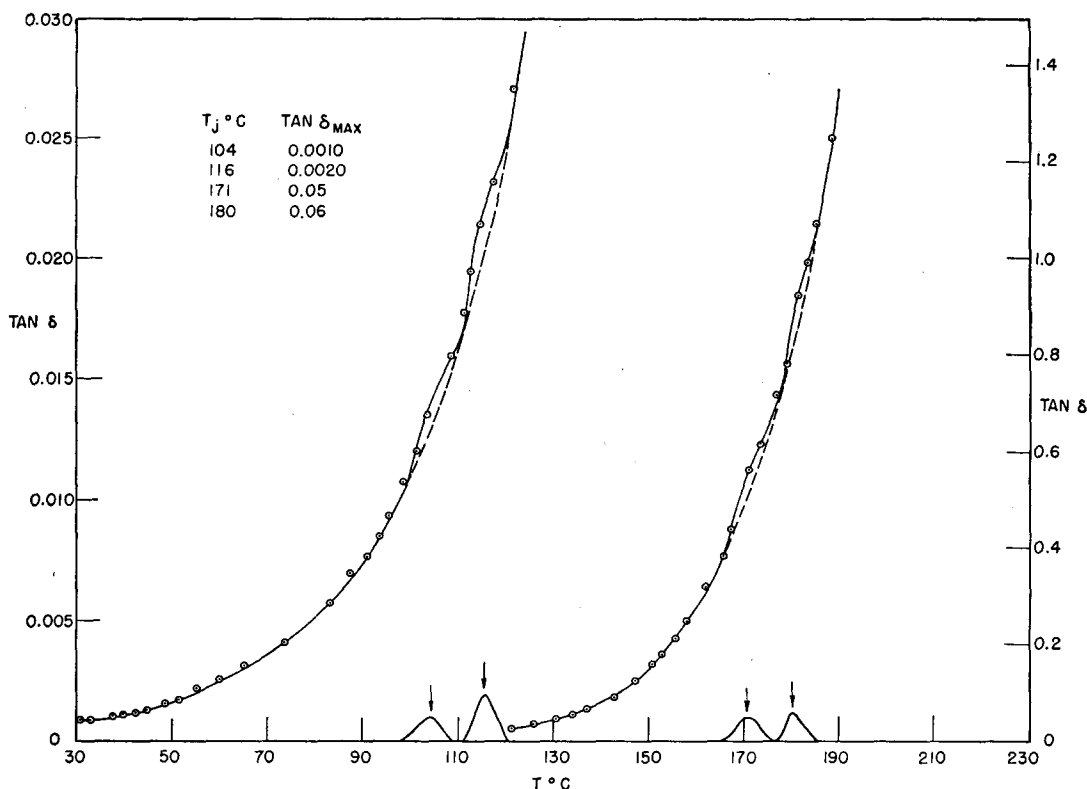


FIG. 1. Loss tangent of NaCl crystal+0.18 percent CdCl₂.

As mentioned previously,¹ heating to within 25°C of the melting point and quenching the crystal rapidly was needed to make the effect visible in the untreated crystals. This procedure was followed for the crystals grown some time ago, while the samples in which the impurity was introduced by heating were measured immediately afterwards. Several samples of NaCl + PbCl₂ from the Naval Research Laboratory were, however, measured without heat treatment, for comparison.

The electrodes and measuring equipment were those described previously.¹ All measurements were made at a fixed frequency (10³ c.p.s.) as a function of temperature.

RESULTS

Typical results of measurements on an alkali halide containing a divalent impurity ion are given in Fig. 1 for NaCl+0.18 percent CdCl₂. It will be observed that four peaks are found, one at 116°C corresponding to that in the pure NaCl, another of comparable height but somewhat broader and displaced in temperature, and two considerably larger peaks (cf. change in scale) at higher temperatures. The same data are given in Fig. 2 plotted as the logarithm of the loss tangent as a function of the reciprocal of the absolute temperature. The increases in loss due to the relaxation processes are visible as deviations from straight lines; however, a single straight line cannot be used indicating a change

in the type of conductivity over the range of measurement.

Similar results on NaCl with various other addition agents are shown in Fig. 3 (X percent MnCl₂); Fig. 4 (0.042 percent NiCl₂); Fig. 5 (0.01 percent PbCl₂, preheated); and Fig. 6 (0.035 percent PbCl₂, unheated). The height of the peak is obtained by subtracting the dashed portion of the smooth curve in the linear plots or, alternatively, the straight line on the semilog plots from the observed curve. The data are summarized in Table I.

The characteristics of KBr and KCl containing divalent foreign ions parallel those found for NaCl. This is illustrated in Fig. 7 (KCl+0.057 percent CdCl₂); Fig. 8 (KBr+0.059 percent CdCl₂); and Fig. 9 (KBr+0.027 percent PbCl₂). In these cases, the KCl seems to act like NaCl; while for KBr, the first additional peak appears above that of the pure crystal rather than below it (cf. Table I).

Somewhat similar results are obtained with univalent foreign ions as shown in Fig. 10 (NaCl+0.029 percent CuCl), Fig. 11 (NaCl+0.056 percent TlCl), and Fig. 12 (NaCl+0.5 percent AgCl). In these cases the Cu⁺ behaves as did the other crystals but for Tl⁺ and Ag⁺ five peaks are found, one of which is that of the pure crystal, two at high temperatures resemble those found for the divalent impurity ions, and two additional peaks, one above and the other below that for the pure crystal appear, the lower peak being the broader one.

A still more complex situation is revealed for AgCl +0.14 percent CdCl₂ (Figs. 13 and 14). Here two of the maxima, those at -126°C and -155°C, are the ones previously reported for the pure material while four new loss peaks have now appeared. All these data are also summarized in Table I.

ACTIVATION ENERGIES AND POLARIZATION PROCESSES

The loss maxima may be used to determine the activation energies for the various mechanisms of polarization. A simple analysis given previously¹ showed that

$$2\pi\nu_m\tau_0 = \exp(-U/kT_j) \quad (1)$$

where ν_m is the measuring frequency, τ_0 is the time constant for the natural frequency of lattice vibrations,¹ T_j is the observed temperature for maximum loss, k is Boltzmann's constant, and U is the activation energy for the jumping process.

The values of U calculated from Eq. (1) are given in Table I in electron volts. A plot of the activation energies for various salts in NaCl as a function of the cation size, using Goldschmidt's values for the ionic radii, is shown in Fig. 15. U_1 , the energy found for the polarization process in the pure crystal, is constant (average *ca.* 0.69 ev); U_4 , the energy corresponding to the large peak at high temperatures increases practically

linearly with the foreign ion size. In the Cu case, the added salt was CuCl₂, but the energy found suggests that the ion is present as Cu⁺. The energy U_3 for the moderate peak, increases as the foreign ion size increases up to the value for Na⁺, then it remains roughly constant at a value of 0.80 ev. The small peak U_2 at low temperatures seems to approach the value of U_1 for ion sizes close to Na⁺ and to become lower as the size changes from Na⁺, reaching roughly 0.60 ev for ions both much larger or smaller than Na⁺.

Our primary objective is an identification of the various loss maxima observed with the appropriate process in the crystal. Let us consider briefly the situation believed to exist in the crystal. The addition of a divalent foreign ion is observed to increase the electrical conductivity in the alkali halides and AgCl markedly.⁵ The interpretation given is that for each divalent cation introduced into the lattice a vacant cation site is produced to preserve electrical neutrality. This is somewhat oversimplified, since it would require a completely random distribution of the foreign ions on the cation sites. Actually there may be considerable aggregation of the foreign ions (note the cloudy NaCl + PbCl₂), and the heat treatments may affect the distribution appreciably. In any case, however, we may assume that, irrespective of heat treatment, a great many cation vacancies are present of which a

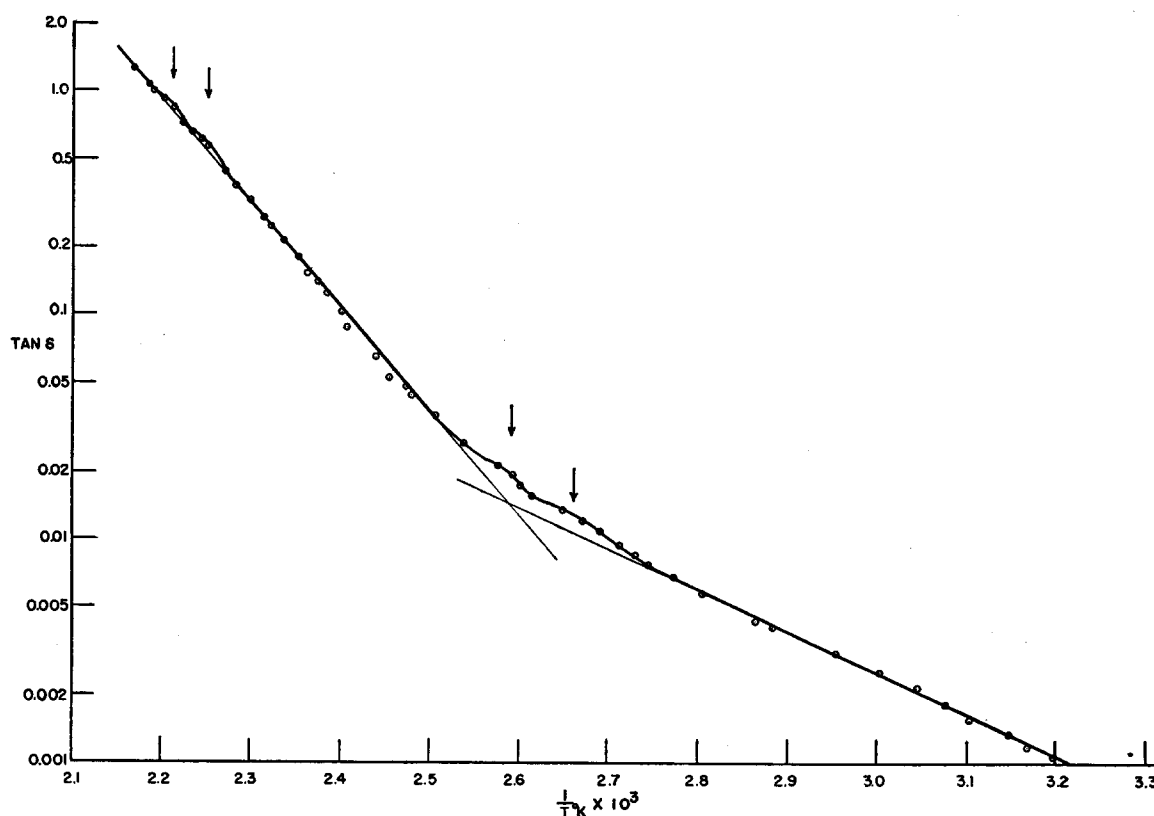


FIG. 2. Loss tangent of NaCl crystal+0.18 percent CdCl₂.

⁵ E. Koch and C. Wagner, *Zeits. phys. Chem. (B)* 38, 295 (1937).

fraction is paired with the foreign ions because of the Coulomb forces between them. On heating the crystal to a temperature close to the melting point and quenching it rapidly, a considerable number of anion vacancies are introduced as well. A fraction of these will also be paired with cation vacancies because of Coulomb attraction.⁶ The number of anion vacancies will, in general, be much smaller than the number of foreign ions or cation vacancies at low temperatures. It should be noted that, in addition to the formation of pairs by electrostatic forces, elastic stresses in the lattice near a foreign ion may be partially relieved if the foreign ion is adjacent to a vacant site; thus there might be a tendency to form foreign ion-vacancy pairs even in the absence of Coulomb forces.

Of the peaks in the alkali halides containing foreign ions, a reasonable interpretation is given most readily for the peak of highest energy, U_4 . We have observed that this peak is present in both the heated and unheated crystals containing divalent ions (Figs. 5 and 6); hence it is present irrespective of the anion vacancies in the crystal. The height of the peak depends on the concentration of the foreign ion (Fig. 3), and the energy depends on the nature of the foreign ion (Fig. 15), indicating a value of 0.80 eV for a cation size corresponding to Na^+ . It should be noted that this is in good agreement with the value (0.77 eV) found by Mapother and Maurer⁷ for the self-diffusion of radio-

active sodium in NaCl in the same temperature range. Finally the peak is a large one (Figs. 1-12) indicating a large dipole moment, large numbers of pairs, or both. These facts are all readily explained if it is assumed that this peak corresponds to a place interchange of the foreign ion and an adjacent cation vacancy.

A somewhat more tentative assignment may be made for the peak next highest in energy. We may summarize the pertinent observations. The peak is large, indicating large numbers, large moment, or both (Figs. 1-12); its height depends on the foreign ion concentration (Fig. 3); and, as shown in Fig. 15, for foreign ions larger than Na^+ the energy has an almost constant value at *ca.* 0.80 eV while for ions smaller than Na^+ it decreases. This peak is also observed in the unheated $\text{NaCl}+\text{PbCl}_2$ (Fig. 6).

A reasonable explanation of all these facts may be obtained from a consideration of the configuration of ions surrounding a foreign ion-vacancy pair (Fig. 16). It will be observed that the vacancy associated with the M^{++} ion may occupy any of the 12 sites in the nearest neighbor positions without dissociation of the pair. Under the influence of the applied field a reorientation of the pair may be achieved either by a place interchange of the foreign ion and the vacant site, or by a place interchange of the vacancy and one of the normal ions on the adjoining sites. The first process we have identified with the peak of highest energy, the

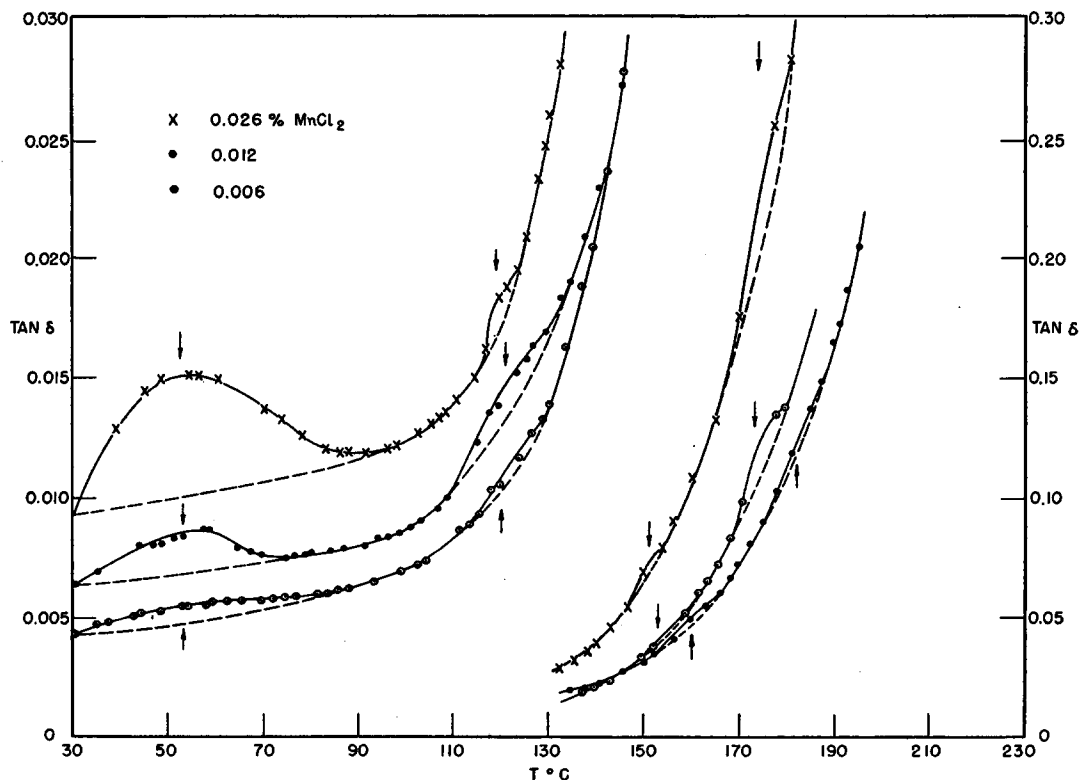


FIG. 3. Loss tangent of NaCl crystal + MnCl_2 .

⁶ F. Seitz, *Rev. Mod. Phys.* **18**, 384 (1946).

⁷ D. Mapother and R. Maurer, *Phys. Rev.* **73**, 1260 (1948).

second process is suggested as the mechanism giving rise to the second peak. It will be noted that the behavior expected for such a mechanism would explain the experimental observations. The process will closely resemble self-diffusion, and, as pointed out, the value found for foreign ions whose radius is equal to or larger than Na^+ is almost constant and equal to the value observed for self-diffusion in NaCl. The number of such configurations would depend on the foreign ion concentration, and it would be expected to be large. The process should take place in unheated crystals containing divalent ions, but for univalent ions heating should be necessary to give sufficient cation vacancies to make the effect observable. Unfortunately no measurements were made on unheated samples of NaCl with monovalent impurity ions.

If this interpretation is accepted, the results would indicate a value of 0.7 ev as a reasonable estimate for the activation energy of self-diffusion in KBr since Pb^{++} has an ionic radius close to K^+ . Similarly, 0.8 ev is indicated for KCl, although this may be low since Cd^{++} is appreciably smaller than K^+ .

The nature of the peak found in the pure crystal may be considered next. Since there has been controversy on this point, we shall discuss the pertinent features in some detail. The results reported in this paper have apparently eliminated the possibility of the effect being due to single cation vacancies. In Fig. 3 especially, it is clear that the height of this peak is only slightly influenced by the presence of the foreign ion; yet increasing the concentration of divalent ions should increase the number of cation vacancies considerably.

Grimley's³ assignment of this peak to pairs formed with a divalent impurity ion and a vacant cation site is also untenable for a number of reasons. The most direct evidence is the behavior with heat treatment. As stated in reference 1, the effect was observable in the Harshaw crystals which are grown from the melt in large blocks without further heat treatment, but crystals from other sources required heating to within 25°C of the melting point and rapid cooling before measurement. On the other hand, heating the small crystals to *ca.* 500°C for some time, followed by slow cooling, makes the effect unmeasurable. This behavior is anticipated from vacancies produced by the heat treatment, but is inconsistent with that observed for crystals with known impurities. In Fig. 6 we see that the unheated NaCl + PbCl_2 from the Naval Research Laboratories shows only a faint indication of a peak at *ca.* 120°C but on heating (Fig. 5) the peak appears.

Quantitative observation of $\tan\delta_{\text{max}}$ for known impurity content also indicates that a residual impurity is unlikely. In Fig. 6 we see that $\tan\delta_{\text{max}} = 0.012$ is found for NaCl + 0.035 percent PbCl_2 in an unheated crystal. In reference 1 a Harshaw crystal of NaCl measured without heating gave $\tan\delta_{\text{max}} = 0.024$ which would correspond to at least 0.05 percent impurity. This is considerably larger than the maximum impurity present in the A.C.S. reagent grade NaCl which is the reported starting material for the crystal growth.

There is further evidence bearing on this point. If the loss maximum at 120°C is due to the reorientation of pairs of the type suggested by Grimley,³ the value

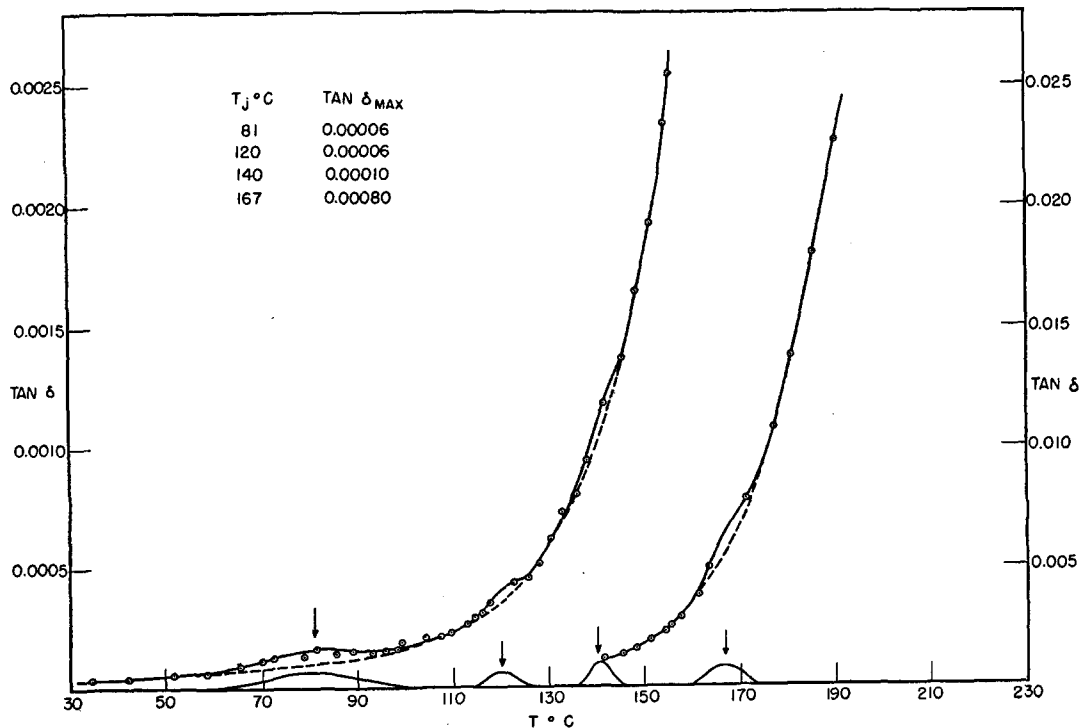


FIG. 4. Loss tangent of NaCl crystal + 0.042 percent NiCl_2 .

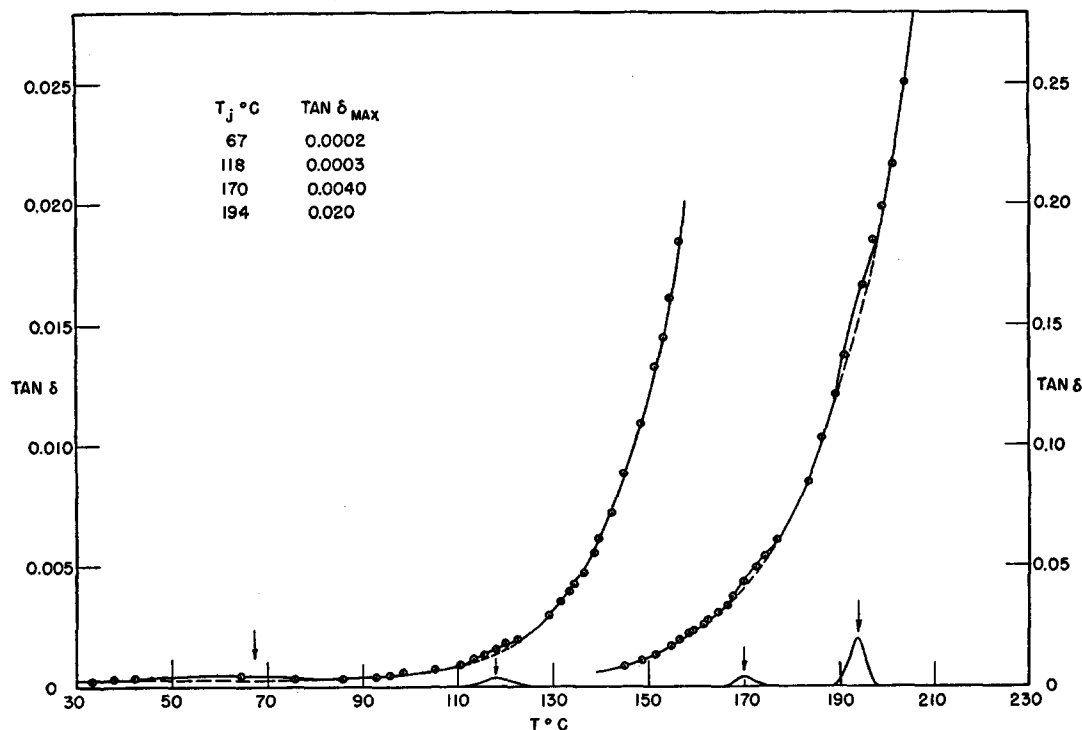


Fig. 5. Loss tangent of NaCl crystal + 0.01 percent PbCl_2 (heated).

of $U=0.68$ eV would indicate an impossibly small ionic radius (ca. 0.1 Å) for the impurity ion (Fig. 15).

The remaining alternative is that the reorientation takes place through the motion of the negative ions. While this possibility cannot be excluded, the evidence available suggests that it is unlikely. The various energies reported previously¹ follow sequences that are consistent with the motion of the cations, e.g., KCl, 0.78 eV; KBr, 0.53 eV; KI, 0.1 eV; RbCl, 0.75 eV; RbBr, 0.58 eV; and RbI, 0.21 eV. In addition, if it is assumed that the peak is actually due to anion migration, it should be possible to observe a peak from the cation migration as well. Measurements made on NaCl, KBr, and LiF over a wide frequency range^{1,8} covered values of energy from ca. 0.1 to 0.8 eV with evidence for only one peak. This would require that the energy for cation migrations has unreasonably small values, ca. 0.05 eV. On the other hand, a value ≥ 0.8 eV for the anion migration would seem not unlikely. Our conclusion, then, is that the peak in the pure crystal is probably due to the reorientation of pairs of cation and anion vacancies through the migration of the cations.

The remaining rather broad peak found near the pure crystal peak may also be given a tentative assignment. Our observations may be summarized as follows: The peak is small (Figs. 1–12); its height depends on the foreign ion concentration (Fig. 3); it is much broader than the other peaks (Fig. 3), indicating a distribution

of activation energies; and it appears only on heat-treating the crystal (Fig. 6).

If, again, it is assumed that because of the elastic forces a foreign ion may be more readily accommodated in the lattice at a site adjacent to a vacancy, we would expect to find foreign ions near pairs of vacancies as well, giving the configuration shown schematically in Fig. 17. It will be noted that the reorientation of the pair without dissociation may be achieved in several ways. The jumps indicated by U_2 and U_2^1 in the absence of the foreign ion would be the U_1 of the pure crystal. The presence of the foreign ion, however, may be expected to modify the energy U_1 somewhat; and U_2^1 would differ from U_2 since it would produce a slightly different configuration. Similarly, U_2^{11} involving the motion of the foreign ion should also be different since it would depend on the nature of the foreign ion.

This model accounts for the experimental observations reasonably well. Since the configuration requires pairs of vacancies formed by heat treatment, it does not occur in the unheated crystals. The number of such complexes would obviously depend on the foreign ion concentration, but the peak is small since the number of pairs is usually very small. The presence of three processes with slightly different energies accounts for the breadth of the peak. U_2 , U_2^1 , and U_2^{11} should all approach U_1 and tend to give a sharper peak, as is observed for Cd^{++} in NaCl (Figs. 1 and 2), if the foreign ion has a radius close to that of Na^+ . A very large foreign ion such as Tl^+ in NaCl may be expected to stretch the lattice locally, allowing the Na^+ ions to

⁸ *Tables of Dielectric Materials*, Vol. III, ONR Contract N5ori-78, T. O. 1, NR-074-041, Lab. Ins. Res., M. I. T., June, 1948.

TABLE I. Low frequency dispersion in ionic crystals containing foreign ions.

Salt impurity mole %	CdCl ₂ 0.18	MnCl ₂ 0.006	MnCl ₂ 0.012	NaCl MnCl ₂ 0.026	NiCl ₂ 0.042	PbCl ₂ 0.01	PbCl ₂ (un) 0.035	KCl CdCl ₂ 0.057	KBr CdCl ₂ 0.059	PbCl ₂ 0.027	CuCl 0.029	NaCl TlCl 0.056	AgCl 0.5	AgCl CdCl ₂ 0.14
$T_j, ^\circ\text{C}$	116 ^a 104 171 180	121 ^a 53 160 182	121 ^a 53 153 173	119 ^a 53 151 174	120 ^a 81 140 160	118 ^a 67 170 194		165 ^a 108 174 181	37 ^a 79 134 180	38 ^a 63 133 157	108 ^a 66 136 153	111 ^a 63 173 197 141	117 ^a 60 165 189 125	-155 ^a -126 ^a -92 -69 -136 -110
$\tan\delta_{\max} \times 10^4$	20 10 500 600	6 8 16 50	14 16 20 110	16 50 30 190	0.6 0.6 1. 8.	3 2 40 200		20 2 24 45	1 2 3 24	3 8 36 40	6 6 50 180	8 17 400 1200 40	8 5 150 600 16	2 1 550 500 2 70
U ev	U_1 U_2 U_3 U_4 U_5 U_6	0.69 ^a 0.67 0.79 0.80	0.70 ^a 0.58 0.77 0.81	0.70 ^a 0.58 0.76 0.79	0.70 ^a 0.63 0.73 0.77	0.70 ^a 0.60 0.79 0.83		0.77 ^a 0.67 0.79 0.80	0.54 ^a 0.62 0.71 0.79	0.54 ^a 0.59 0.71 0.75	0.68 ^a 0.60 0.73 0.76	0.68 ^a 0.60 0.79 0.83 0.73	0.69 ^a 0.59 0.78 0.82 0.71	0.21 ^a 0.26 ^a 0.32 0.36 0.24 0.28
n (No./ m^3) $\times 10^{22}$	n_1 n_2 n_3 n_4 n_5 n_6	1.0 0.49 30. 8.	0.3 0.3 0.9 0.7	0.71 0.75 1.1 1.6 2.7	0.81 2.1 0.03 0.05 0.1	0.15 0.09 2.3 3.0		1.0 0.09 1.2 0.58	0.03 0.07 0.1 0.27	0.1 0.3 1.5 0.44	0.3 0.2 2.6 9.9	0.4 0.74 23. 72. 2.	0.4 0.2 8.5 36. 0.82	0.2 0.1 94. 24. 0.2 1.
$X \times 10^4$	X_1 X_2 X_3 X_4 X_5 X_6	0.44 0.21 15. 4.	0.1 0.1 0.4 0.3	0.31 0.33 0.49 0.70	0.35 0.93 0.71 1.2	0.01 0.01 1.0 1.3		0.62 0.06 0.76 0.35	0.02 0.05 0.07 0.19	0.07 0.2 1.1 0.31	0.1 0.1 1.2 4.4	0.2 0.33 10. 33. 1.	0.2 0.1 3.8 16. 0.36	0.1 0.05 40. 10. 0.5

^a Peak found previously (see reference 1) in the pure crystal.

move readily; while a very small ion such as Mn^{++} in NaCl would be very mobile in preference to the Na^+ , thus giving a decrease in U_2 in both cases. It does not explain the fact, however, that the broad peak in KBr occurs at a slightly higher energy than that found in the pure crystal, and it is actually higher for Cd^{++}

than for Pb^{++} . The explanation of this must await further investigation.

This model gives a suggestion for the existence of extra peaks in NaCl+TlCl and AgCl, since for these large ions U_2^{II} may be appreciably larger than U_2 or U_2^I and appear as a separate peak. In both cases, the

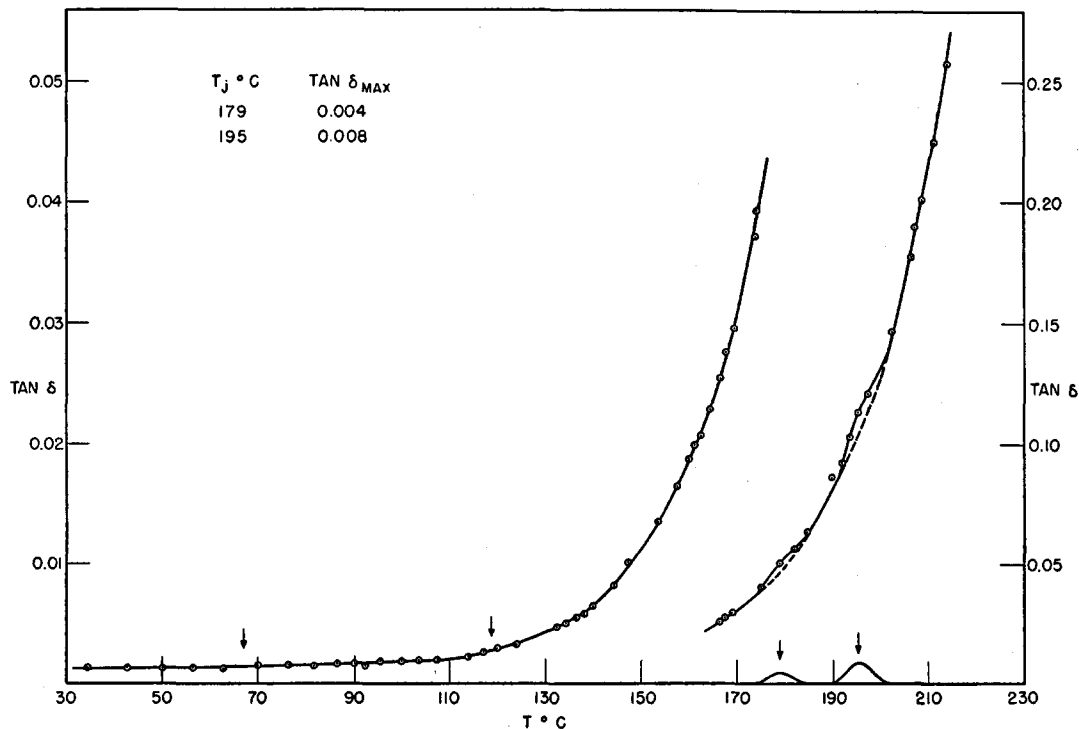


FIG. 6. Loss tangent of NaCl crystal+0.035 percent PbCl_2 (unheated).

fifth peak is slightly above the value of U_1 as would be expected. The rather extreme breadth of the low energy peak also suggests that in these cases U_2 and U_2^1 are appreciably different.

NUMBER OF LATTICE DEFECTS

The assignment of the various loss maxima to definite processes in the crystal allows a more detailed study to be made of the numbers of the different types of defects

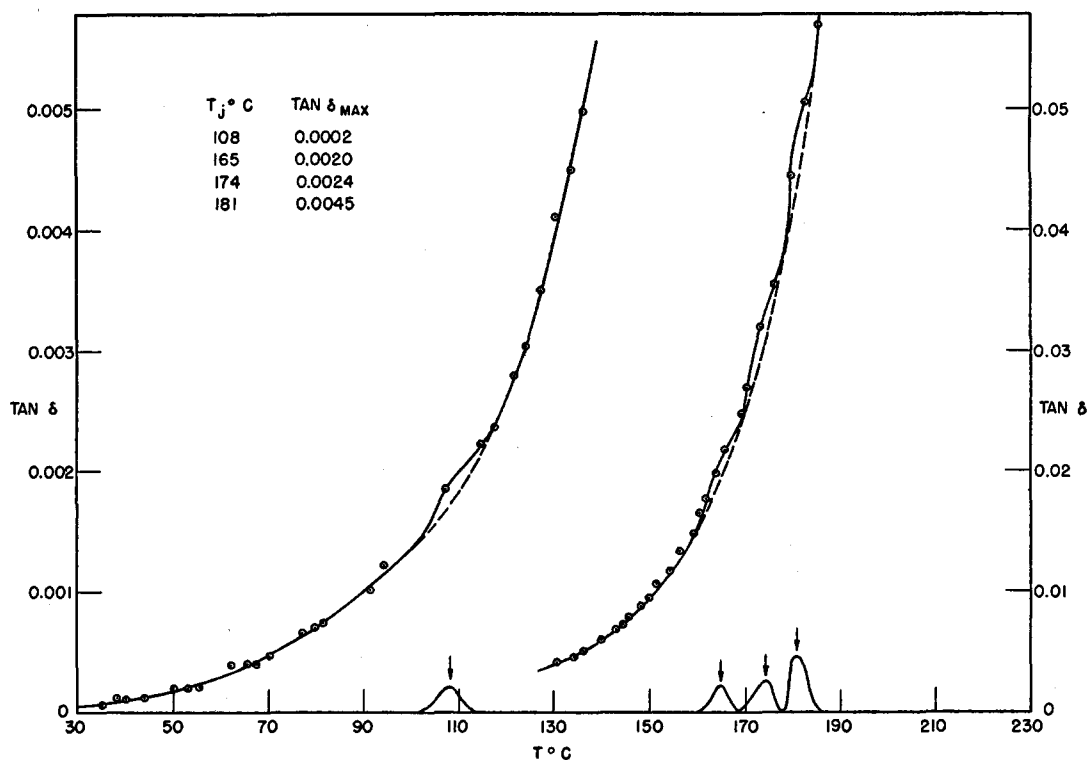


FIG. 7. Loss tangent of KCl crystal-0.057 percent CdCl_2 .

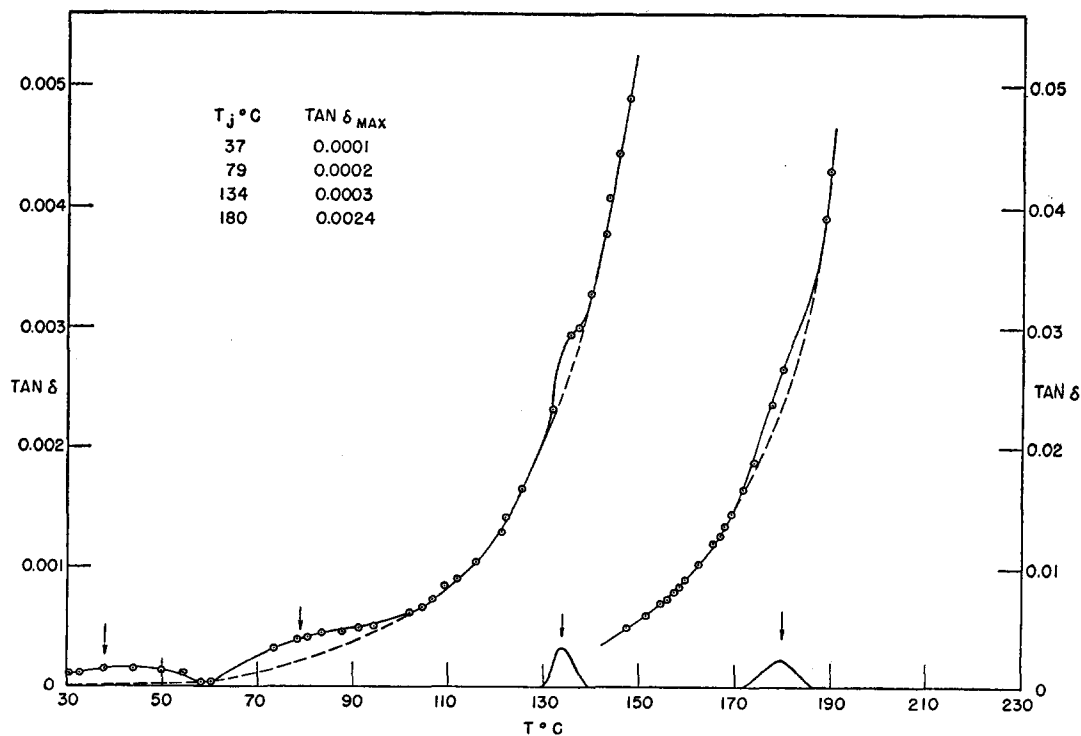


FIG. 8. Loss tangent of KBr crystal+0.059 percent CdCl_2 .

present since the models give information about the charges involved and the distances they move. In reference 1 it was shown that if the reorientation of the pairs was described as a redistribution of the ionic charges between two potential wells under the influence of the applied field, the height of the loss peak could be

related to the effective moment of the moving charges and the number present as follows:

$$\tan \delta_{\max} \approx \frac{n(Zed)^2(K'_{\infty} + 2)^2}{18\epsilon_0 k T_j K'_{\infty}}, \quad (2)$$

where n is the number of polarizing units per unit

FIG. 9. Loss tangent of KBr crystal + 0.027 percent PbCl_2 .

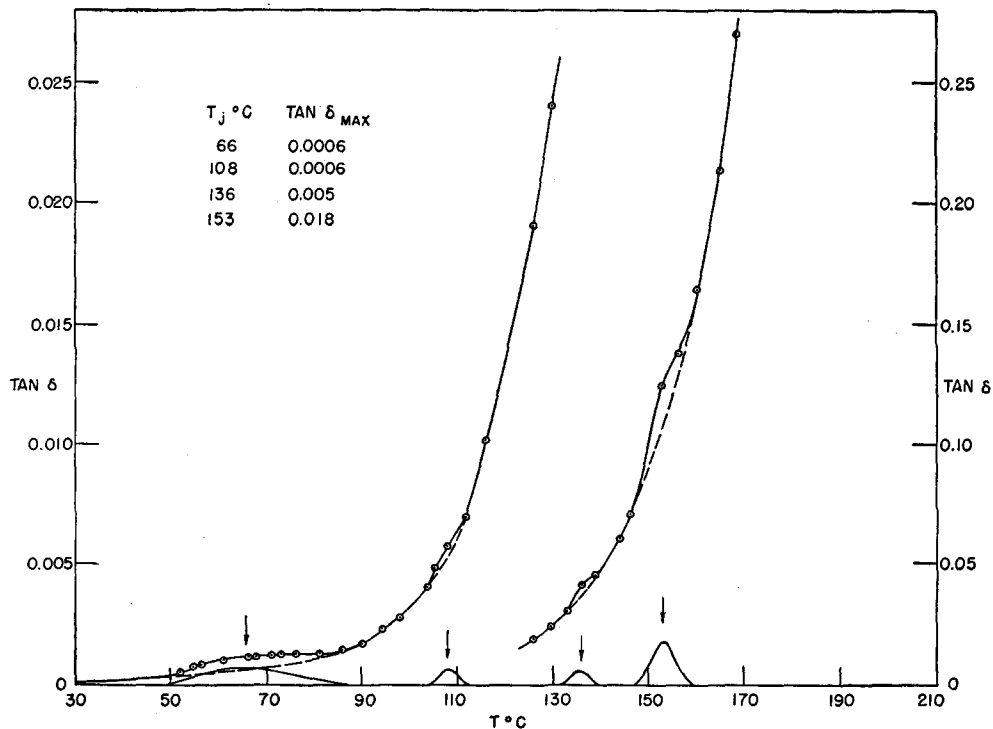
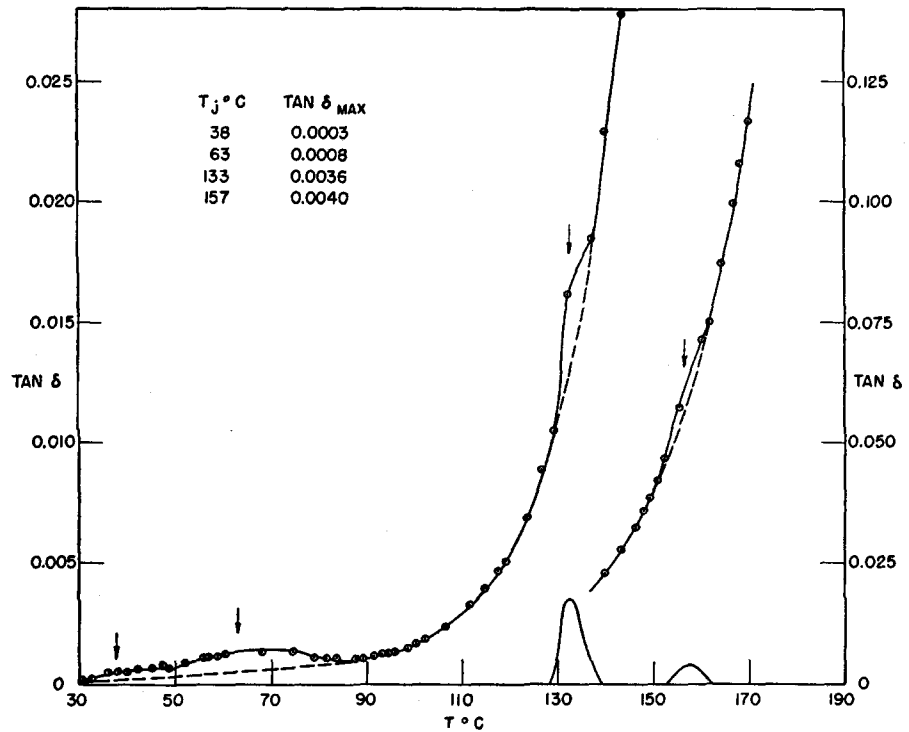


FIG. 10. Loss tangent of NaCl crystal with 0.029 percent CuCl .

volume, Z the ion valence, e the absolute value of the electronic charge, and d twice the separation of the potential wells (in reference 1, d was taken as the lattice constant a). K'_{∞} is the dielectric constant at

frequencies above the dispersion region, ϵ_0 is the dielectric constant of free space, and kT_j are as in Eq. (1). Rationalized m.k.s. units are used so that $\epsilon_0 = 8.865 \times 10^{-12}$ farad/m; $e = 1.59 \times 10^{-19}$ coulomb;

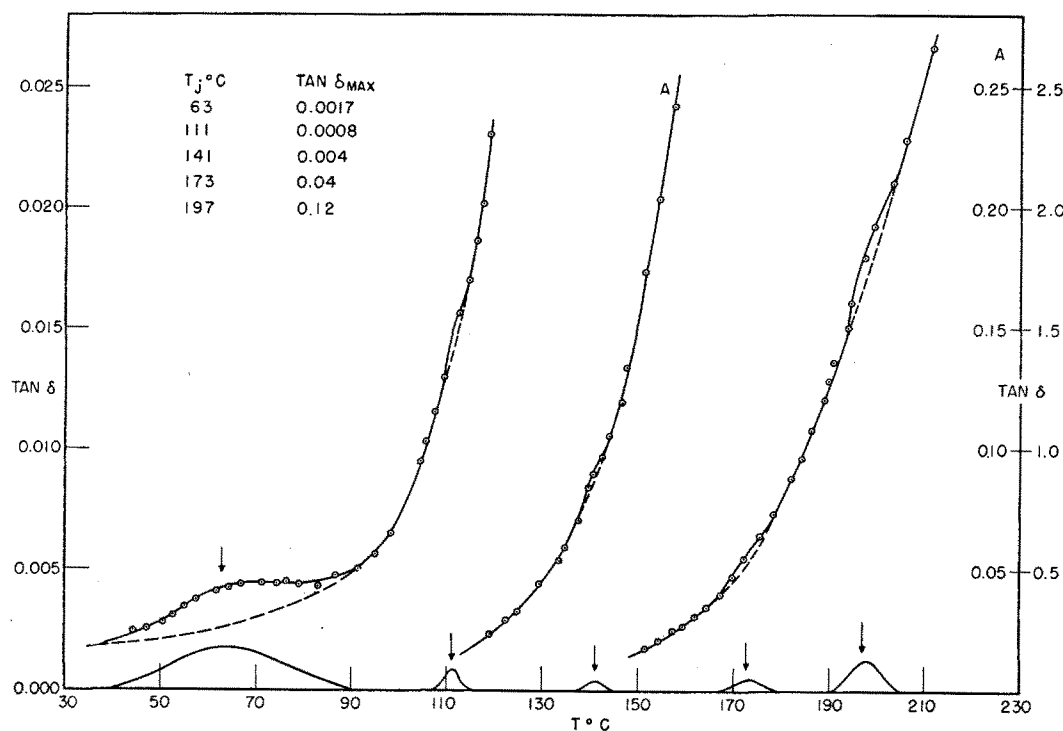


FIG. 11. Loss tangent of NaCl crystal+0.056 percent TiCl.

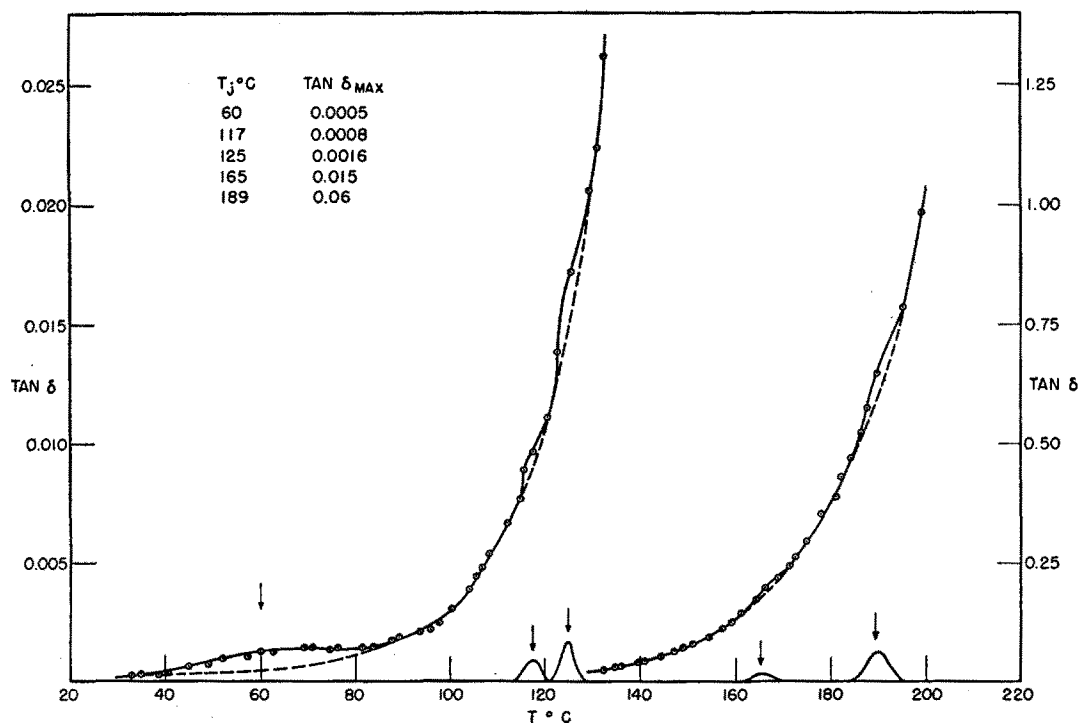
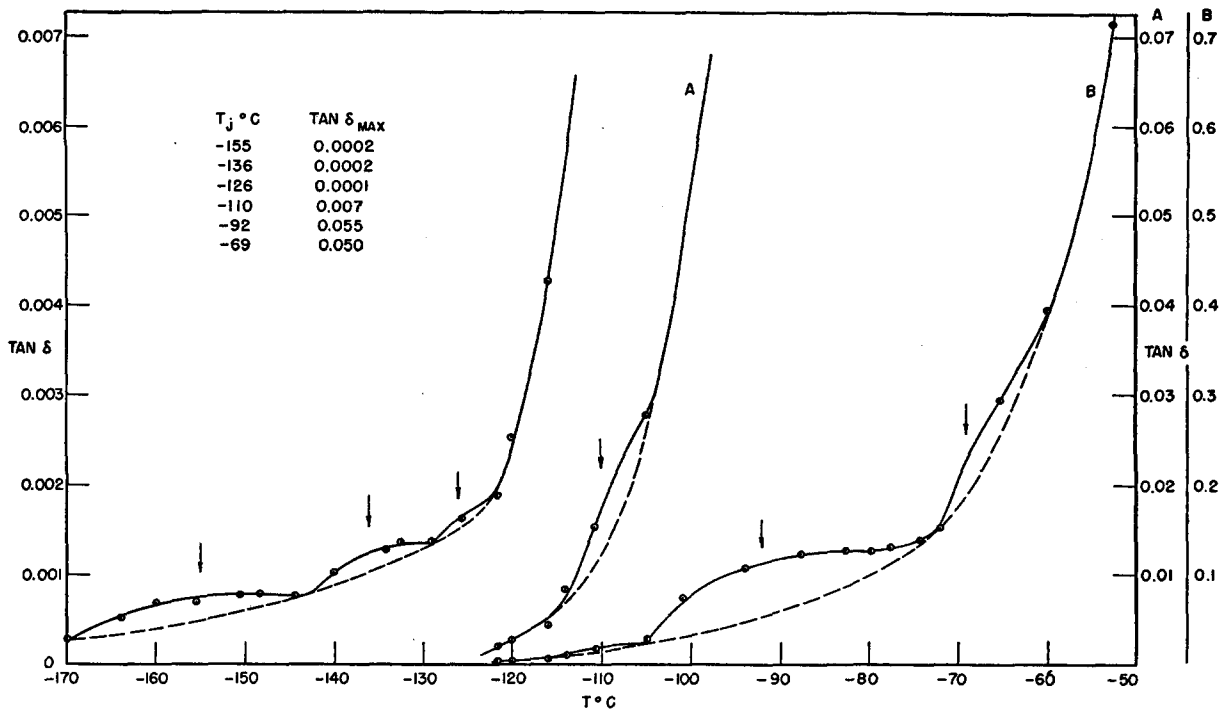


FIG. 12. Loss tangent of NaCl crystal+0.5 percent AgCl.

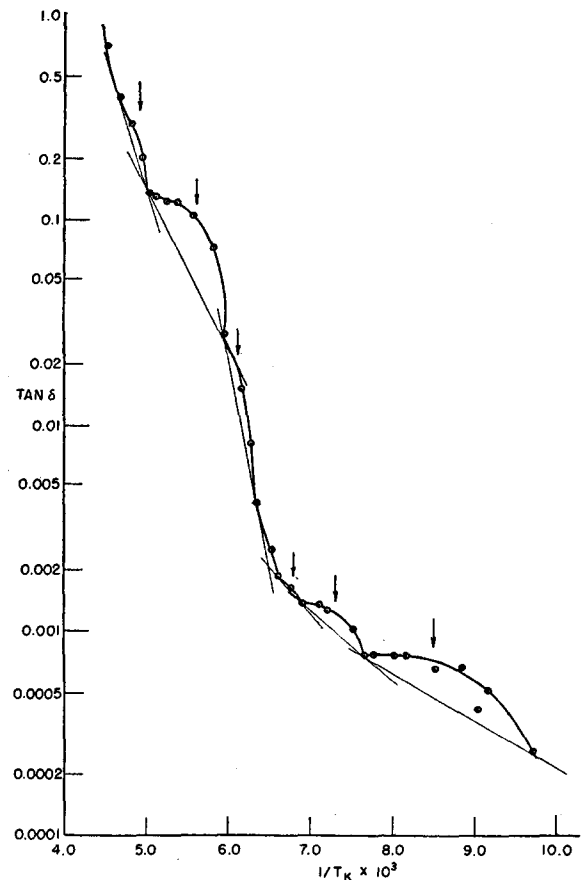
FIG. 13. Loss tangent of AgCl crystal+0.14 percent CdCl₂.

$k = 1.38 \times 10^{-23}$ joule/deg.; d is in meters, and n is in number/m³. Because an approximate expression for the internal field in a dielectric is used in deriving Eq. (2), the results are probably good only to an order of magnitude although the relative values may be more reliable.

The process we have assigned to U_4 for divalent foreign ions moves a charge $2e$ a distance $a/2$ in the field direction (Fig. 16), while U_3 moves a unit charge the same distance. For univalent foreign ion-cation vacancy pairs, both processes move unit charges a distance $a/2$ in the field direction. The number of pairs, n , computed from Eq. (2) and the mole fraction of each, x , are given in Table I.

The models suggested also give some information about the relative numbers of pairs of each type. It will be observed in Fig. 16 that there are four normal ions that may jump without dissociating the pair for each foreign ion. It is anticipated then that $n_3 = 4n_4$. This ratio is not observed experimentally, in general. Usually $n_4 > n_3$, the larger values being observed for ions whose size differs considerably from the size of the ions in the normal lattice (e.g., Mn^{++} in NaCl, Cd^{++} in KBr). It will be noted also that the ratio n_4/n_3 increases with increasing concentration (e.g., Mn^{++} in NaCl). This suggests that there may be a considerable aggregation of foreign ion-cation vacancy pairs in larger complexes to accommodate the foreign ions in the lattice.

We have computed the number of pairs of vacancies, n_1 , and the number of clusters of type n_2 on the assumption that a unit charge moves a distance $a/2$. This is

FIG. 14. Loss tangent of AgCl crystal+0.14 percent CdCl₂.

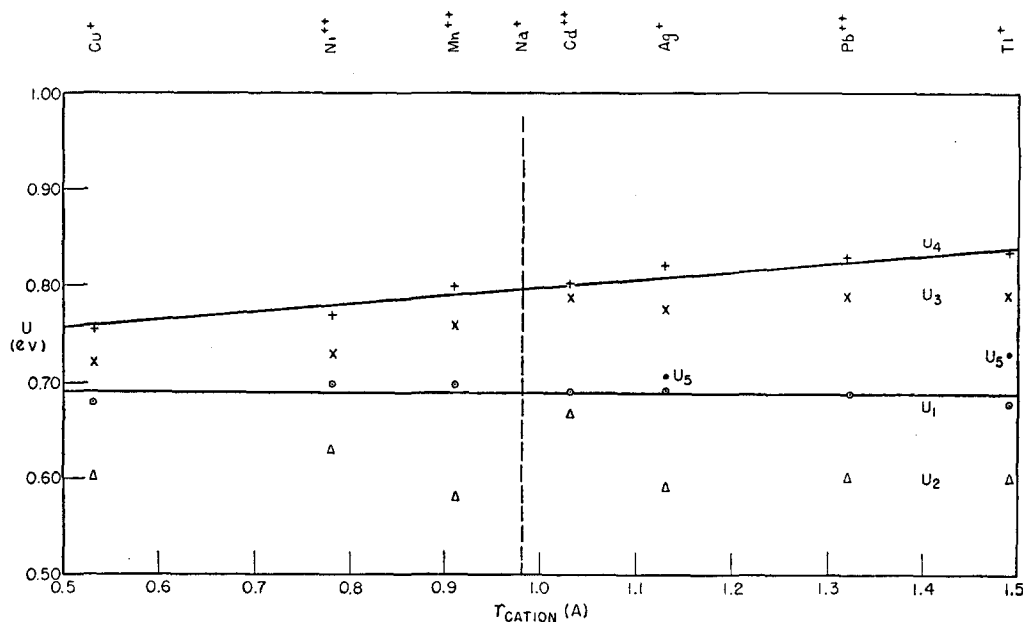


FIG. 15. Activation energies for foreign ions in NaCl.

satisfactory for n_1 , but can be only an approximation for n_2 since, on the basis of our model, a portion of this peak arises from the motion of the divalent ion. In general, it will be observed that n_1 and n_2 are of comparable magnitudes, but that the ratio n_2/n_1 increases with increasing concentration. This also suggests further aggregation of pairs.

The dependence of the number of pairs of various types on the foreign ion concentration may be used to obtain further information about the situation in the crystal. A simple thermodynamic calculation of the degree of association is possible if some restrictions are considered. Schottky defects must migrate to a free surface of the crystal to disappear, hence at low temperatures ($\leq ca. 500^\circ\text{C}$) where the mobility is low a nonequilibrium but constant number of defects is normally present. The various types of pairs may be formed internally so thermal equilibrium in this respect may persist to much lower temperatures.

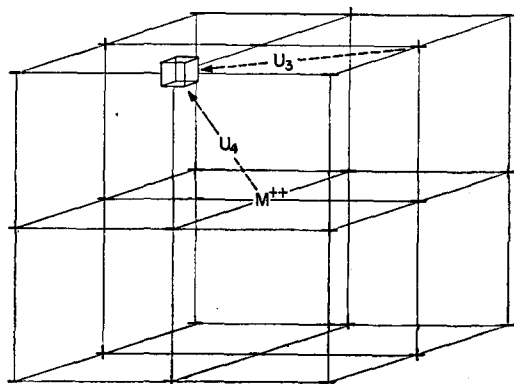
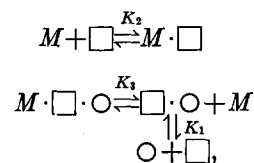


FIG. 16. Mechanisms for pair reorientation.

The three equilibria that are being simultaneously satisfied may be represented schematically as



where M represents a foreign ion, \square a cation, and \bigcirc an anion vacancy, the total number of both being constant. If Y = mole fraction of foreign ion, X_1 = mole fraction of vacancy pairs, X_2 = mole fraction of groups $M \cdot \square \cdot \bigcirc$, X_4 = mole fraction of $M \cdot \square$ pairs, X_n = mole fraction of anion vacancies = mole fraction of cation vacancies produced thermally, we may write the mass action expressions as

$$K_1 = \frac{X_1}{(X_n - X_1)(Y + X_n - X_4 - X_1 - X_2)}, \quad (3)$$

$$K_2 = \frac{X_4}{(Y - X_4 - X_2)(Y + X_n - X_4 - X_1 - X_2)}, \quad (4)$$

$$K_3 = \frac{X_2}{(Y - X_4 - X_2)X_1}. \quad (5)$$

Experimentally we have found $X_4 \ll Y$. Because of the contribution of elastic forces to pair formation with foreign ions, we anticipate $K_2 > K_1$ so that $X_1 \leq X_4$, and, as we have seen, $X_2 \approx X_1$. With these simplifications the equations become

$$X_1 = K_1(X_n - X_1)(Y + X_n) \quad (3a)$$

$$X_4 = K_2 Y(Y + X_n) \quad (4a)$$

$$X_2 = K_3 Y X_1. \quad (5a)$$

Since the heat treatment of our samples has been the same, we may assume X_n is approximately constant for the series of Mn^{++} in NaCl. The curve for X_4 as a function of Y shown in Fig. 18 is obtained for values of $X_n = 5 \times 10^{-4}$ and $K_2 = 7$. We see for this value of X_n , $X_1 \ll X_n$, and Eqs. (3a) and (5a) simplify further to

$$X_1 = K_1 X_n (V + X_n) \quad (3b)$$

$$X_2 = K_1 K_3 Y X_n (V + X_n). \quad (5b)$$

The curves for X_1 and X_2 as functions of Y are obtained for $K_1 = 0.8$ and $K_3 = 1.2 \times 10^4$. While the values for the constants are only very rough, they are nevertheless instructive. We have found X_4/Y experimentally to be *ca.* 5×10^{-3} and from the value found for X_n we see that in the pure crystal $X_1/X_n \approx 4 \times 10^{-4}$. These values are in agreement with the observations of Maurer⁹ on the conductivity of NaCl + CdCl₂ crystals which indicated negligible association of the foreign ions, and with the investigations of Alger¹⁰ on the number of color centers in alkali halide crystals bombarded with high energy x-rays. This work indicated a fraction ≤ 0.025 of the vacancies present as pairs.

Since K_1 presumably does not depend on the impurity ion, we can calculate values of K_2 , X_n , and K_3 for the other foreign ions in NaCl assuming $X_1 \ll X_n$ in all cases. The results are given in Table II.

The values found are consistent with the idea of large association of ions whose size differs markedly from Na⁺, the numerical values suggesting that the elastic forces are of equal importance to electrostatic forces in producing association. The strong tendency to accommodate the foreign ions near existing vacancies is well illustrated by the large values of K_3 .

FOREIGN ION MOBILITIES

If the assignment of the high energy loss peak to the suggested mechanism is correct, a method has been provided for the study of foreign ion mobilities in a crystal lattice since the process is that usually assumed for the migration of an ion in an ionic crystal. There are very few data available for comparison, but the

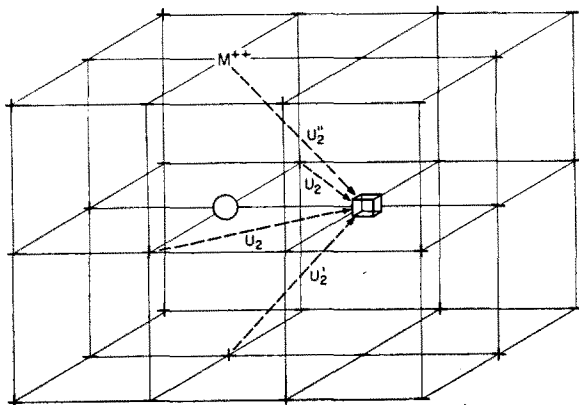


FIG. 17. Reorientation of foreign ion-vacancy pair complexes.

⁹ R. J. Maurer, Tech. Rept. 6, ONR Contract N6ori-47, Carnegie Inst. Tech., September, 1948.

¹⁰ R. S. Alger, Tech. Rept. XV, ONR Contract N5ori-07801, Lab. Ins. Res., M.I.T., January, 1949.

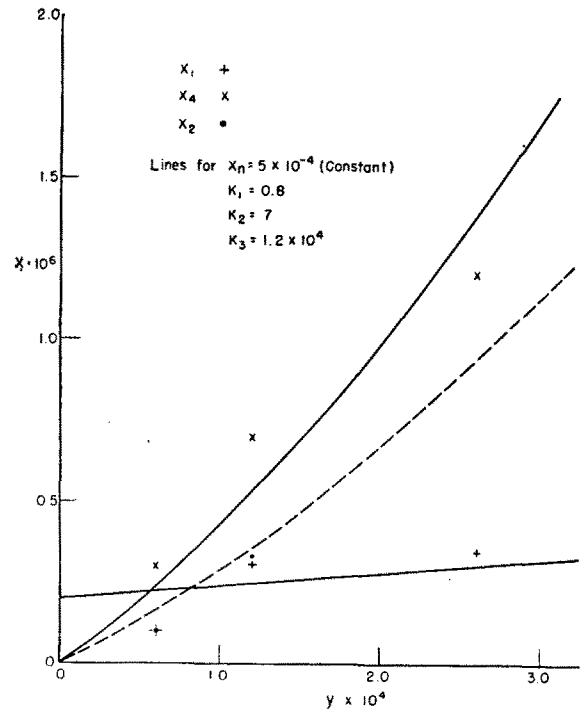


FIG. 18. Ion-vacancy pairs as function of foreign ion concentration.

results quoted by Arzybyschew¹¹ on NaCl + Cu⁺ and NaCl + Ni⁺⁺ may be mentioned. This author gives $E = 1.09$ and 1.10 ev respectively from measurements at temperatures above 675°C , i.e., in the characteristic conductivity region, as compared with 0.75 and 0.78 ev in the low temperature structure-sensitive range investigated in this paper. The results are not directly comparable because of the difference in temperature. Our indicated value for the activation energy for diffusion of an ion the size of Na⁺ in NaCl should, however, be expected to agree with the self-diffusion measurements of Mapother and Maurer⁷ for the same temperature range. The linear increase in U_4 with ion size irrespective of charge indicates that the mobilities are predominantly determined by the mechanical rather than the electrical properties of the ion.

A determination of the constant term in the mobility equation is of interest, but accurate values cannot be obtained with the information available. It was shown previously¹² that the constant term could be given as

$$U_{0k} = 0.490 \times 10^{-12} \frac{Zed^2(K'_\infty + 2)^2}{\epsilon_0 \tau_0 k T_j} \left[\frac{m^2}{\text{volt sec.}} \right], \quad (6)$$

where the terms are as previously defined. For NaCl this becomes

$$U_{0k} = \frac{616Z}{T_j} \left[\frac{\text{cm}^2}{\text{volt sec.}} \right]. \quad (7)$$

Using the values of T_j given in Table I and the appropriate valence, we find U_0 ranging from $1.3 \text{ cm}^2/\text{volt sec.}$

¹¹ S. A. Arzybyschew, Physik. Zeits. Sowjetunion 11, 636 (1937).

¹² R. G. Breckenridge, Tech. Rept. XI, ONR Contract N5ori-78, T. O. 1, Lab. Ins. Res., M.I.T., April, 1948.

TABLE II. Foreign ion association in NaCl.

Impurity	$Y \times 10^4$	$X_n \times 10^4$	K_1	K_2
Mn ⁺⁺	0.6	5.	7.	1.2×10^4
Cd ⁺⁺	18.	3.	1.	2.7×10^2
Ni ⁺⁺	4.2	0.3	0.3	2.1×10^3
Pb ⁺⁺	1.	2.	40.	5.8×10^3
Cu ⁺	2.9	3.	30.	3.1×10^3
Tl ⁺	5.6	2.	80.	3.2×10^3
Ag ⁺	50.	0.4	0.6	1.1×10^2

for Tl⁺ to 2.8 for Ni⁺⁺. These values are of the proper order of magnitude, but the previously mentioned uncertainty in Eq. (2) is reflected here since Eq. (2) is used in deriving Eq. (6).

SILVER CHLORIDE

The measurements on AgCl, both pure and with the Cd⁺⁺ addition, have shown a behavior differing from the alkali halides. Our basic question is whether the silver halides have Frenkel or Schottky defects. There is insufficient experimental evidence available to make a detailed study possible, but some features shown in Figs. 13 and 14 may be given a preliminary interpretation. We may assign the loss peak of highest energy, U_6 , to the motion of the foreign ion in cation vacancy-foreign ion pairs; and the peak of comparable size at slightly lower temperature, U_5 , to the motion of normal cations on adjacent sites to the pair since this configuration should be present with either Frenkel or Schottky defects. The numbers and mole fractions of such pairs have been calculated using the assumptions as to charge and distance given previously for the alkali halides. The results are included in Table I.

It will be noted that in this case the ratio n_5/n_6 is almost exactly 4 as would be predicted on the proposed model. This indicates that the highly polarizable AgCl lattice can accommodate a considerable number of foreign ions without aggregation of the foreign ions. The value of $U_6=0.36$ ev found for Cd⁺⁺ and $U_5=0.31$ ev suggest that the energy for self-diffusion in AgCl should be about 0.3 ev since Cd⁺⁺ and Ag⁺ are not too dissimilar in size.

There is greater difficulty in explaining the loss maxima at lower temperatures involving the peaks found in the original crystal. The interpretation of the two peaks in reference 1 as indicating Frenkel defects was questioned by Grimley³ on the ground that a pair formed between a vacant cation site and an interstitial cation would be unstable. This is, of course, true; however, if Frenkel defects are present in dynamic equilibrium, the configuration must exist in finite amounts since it is the initial stage in the formation and the final stage in the disappearance of a Frenkel defect. The possibility should not be excluded on this basis alone.

Recently, an investigation of the structure and growth mechanism of photolytic silver in silver bromide¹³ strongly suggested the presence of interstitial cations in the interior of the crystal. Since no differences

¹³ C. R. Berry and R. L. Griffith, *Phys. Rev.* **78**, 317 (1950).

in the type of defect would be anticipated between silver bromide and chloride, Frenkel defects seem possible for silver chloride.

It must be admitted that the information at this time is by no means conclusively in favor of the presence of Frenkel defects, since a number of reasonable alternatives may be suggested.

The thermal treatment of the samples was such that a nonequilibrium state is undoubtedly present. This state might easily include Frenkel defects, even if Schottky defects are the normal type since it would seem that the energies of formation should not differ greatly in AgCl.

A possibility requiring only Schottky defects is that the two peaks arise from the reorientation of pairs of vacancies via the motion of both anion and cation vacancies. While this was not observed in the alkali halides, the high polarizability of the silver halides should make the energies more nearly equal for both types of jumps. The observed energy difference, 0.05 ev, seems rather small however.

Grimley's³ suggestion that the peaks are due to two impurity ions is untenable since, as we have seen, a single foreign ion produces three peaks in addition to the one in the pure crystal. It would seem that there is a possibility that the original crystal contained Schottky defects and a single impurity ion, giving four peaks of which only the larger two corresponding to U_3 and U_4 were observed. If this is so, we must assume that the peaks at 0.24 and 0.28 ev in the Cd⁺⁺ case correspond to U_2 and U_1 . Consequently, the $U_3=0.21$ ev and $U_4=0.26$ ev for the unknown impurity are of lower energy than the energy for moving the pair alone, which seems unreasonable.

While the purity of the crystal with respect to foreign ions is stated to be high, it is possible that on exposure to light appreciable amounts of atomic silver are produced. This suggests an attractive alternative since it is expected that because of the elastic forces near the large silver atom, there would be considerable association with vacancy pairs. This would immediately explain the two peaks in the original crystal and the multiplicity of maxima in the Cd⁺⁺ case.

In the absence of a detailed picture, the numbers of these various pairs have been computed assuming $Z=1$ and $d=a/2$ since these values would be typical in any case. The results are included in Table I. Of the several possibilities, the explanation, either in terms of Frenkel defects or atomic silver impurity, seems the more reasonable, but a complete picture must await further investigations of crystals known to contain no excess silver.

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