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line to the C^{13} isotope shift of the $C\equiv C$ stretching frequency.

In conclusion, it seems worth while to indicate that it is desirable to obtain the Raman spectra of methyldeuteroacetylene, methylfluoroacetylene, and a solution of methylchloroacetylene in a solvent other than ethylbromide. In this way one might see whether the unusual behavior predicted for some of the fundamental frequencies, as a result of the calculations, actually occurs. Also, if the near infra-red absorption spectra of methyldeuteroacetylene and the methylhaloacetylenes could be obtained, they might

furnish more information about the value of the $C-C$ stretching frequency for these molecules, since the calculations indicate that this frequency is somewhat greater for the methylhaloacetylenes than for methylacetylene or methyldeuteroacetylene.

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Low Frequency Dispersion in Ionic Crystals*

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A new region of anomalous electrical response has been observed at low frequencies in ionic crystals that have been treated to introduce relatively large number of lattice defects. The crystals thus far studied include various alkali halides and silver chloride. The effect is attributed to a jumping of the positive ions to vacant lattice sites under the influence of the applied field. This jumping is observed as a relaxation process, producing a change in the dielectric constant which is small and frequently within the limits of error of measurement, and an associated peak in the dielectric loss tangent which is readily measurable. This maximum of $\tan \delta$ has been studied both as a function of frequency at a fixed temperature and as a function of temperature at fixed frequency. From the magnitude of the peak and position on the frequency or temperature scales it is possible to calculate the number of lattice defects present in the sample and the activation energy for diffusion U of the positive ion in the crystal. A knowledge of U allows a separation of the activation energy for conduction, $(W/2)+U$, into its components, thus determining W , the activation energy for hole formation.

I. INTRODUCTION

FOR many years there has been considerable interest in the problem of calculating the physical properties of simple ionic crystals of the alkali halide types from the properties of the ideal crystal structure revealed by x-ray investigations. The classical work of this type, primarily due to Born,¹ was reasonably successful in predicting the dielectric constants of the alkali halides in terms of two contributions to the

polarizability: one electronic α_e arising from the distortion of the electron clouds of the individual ions relative to their nuclei, and the other atomic α_a arising from the displacement of positive and negative ions relative to each other. Since the resonance frequencies of the electronic motions lie in the visible or ultraviolet region, and those for the ionic motions lie in the infra-red, both far removed from the range of ordinary electrical measurements, it is anticipated that a dielectric constant independent of frequency and accompanied by very small losses should be observed.

There are, however, a number of other properties of such crystals that cannot be satis-

* This work was sponsored jointly by the Office of Naval Research and the Army Signal Corps, under Contract N5ori-78, T.O. 1.

¹ M. Born and M. Goeppert-Mayer, *Handbuch der Physik* (1933), second edition, Vol. 24/2, p. 639.

factorily accounted for by the simple picture of a perfectly regular structure of polarizable ions: e.g., the electrical conductivity, self-diffusion, and the various color centers. It has been established by the work of Frenkel² and Wagner and Schottky³ that a real crystal contains a large number of lattice defects either in the form of interstitial ions with accompanying vacant sites (Frenkel defects) as in AgCl, or as equal numbers of vacant positive and negative ion sites (Schottky defects) as in the alkali halides. It has been demonstrated that such defects give a satisfactory explanation of the properties mentioned.

In its simplest form the theory indicates that the conductivity is expressed as⁴

$$\sigma = C[N(ea)^2/kT]\nu_0 \exp\{ -[(W/2) + U]/kT \}, \quad (1)$$

where W is the activation energy of formation of a lattice defect and U the activation energy for its diffusion through the crystal, a is the lattice constant, ν_0 is the natural frequency of lattice vibrations, and C is a constant arising from the temperature variation of the exponential terms.

The separation of the exponential term into its component parts is of great theoretical interest since many of the crystal properties depend on one or the other term, but it has been done only in a few special cases. If the number of lattice defects is made practically independent of the temperature by chemical means, e.g., by the addition of CdCl_2 to AgCl , thus introducing one vacant site for each Cd^{++} ion, as was done by Koch and Wagner,⁵ U may be found from

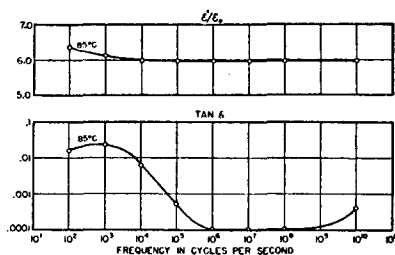


FIG. 1. Dielectric properties of NaCl crystal.

² J. Frenkel, *Zeits. f. Physik* **35**, 652 (1926).

³ C. Wagner and W. Schottky, *Zeits. f. physik. Chemie* **B11**, 163 (1930).

⁴ W. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, New York, 1940).

⁵ E. Koch and C. Wagner, *Zeits. f. physik. Chemie* **B38**, 295 (1937).

the conductivity. Similarly, U may be found from self-diffusion studies using isotopic or radioactive tracers as has been done for PbI_2 by von Hevesy and Seith⁶ and Mapother and Maurer for NaCl ⁷ since the diffusion constant

$$D = D_0 \exp(-U/kT) \quad (2)$$

contains only U . Finally, theoretical calculations of W have been made for three alkali halide crystals (NaCl , KCl , and KBr) by Mott and Littleton.⁸

While the d.c. conductivity of simple ionic crystals has been studied extensively, it has not been realized that the existence of lattice defects gives a possibility for a new mechanism of dielectric polarization that may be observed in a.c. measurements. Such an effect has now been observed in AgCl and several of the alkali halides. An interpretation of the results is presented which allows a determination of the energy U and the number of defects present.

II. PROCEDURE

The measurements were made on crystals from a number of sources. The LiF , NaCl ,

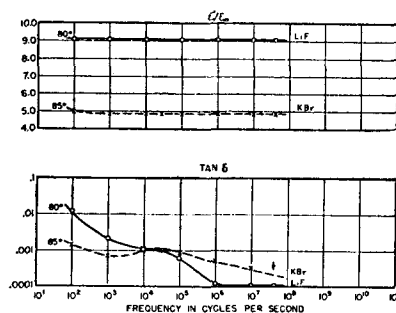


FIG. 2. Dielectric properties of LiF and KBr crystals.

KBr , and AgCl were commercial crystals from the Harshaw Chemical Company, Cleveland, Ohio. KI , which is not commercially available, was obtained from the same company through the courtesy of Dr. H. C. Kremers. The NaF , RbCl , RbBr , RbI , and KCl were grown by Professor A. von Hippel.

⁶ G. von Hevesy and W. Seith, *Zeits. f. Physik* **51**, 790 (1929).

⁷ D. Mapother and R. Maurer, *Bull. Am. Phys. Soc.* **23**, 31 (1948).

⁸ N. F. Mott and M. J. Littleton, *Trans. Faraday Soc.* **34**, 485 (1938).

In order to have the a.c. effects readily observable, it was found necessary for the crystal to have a large number of defects present corresponding to an equilibrium temperature near the melting point. With the standard crystals from the Harshaw Chemical Company no further treatment was necessary, but the other crystals were heated to within 25°C of the melting point and cooled rather quickly to room temperature before measuring. The crystals, in general, were about $\frac{1}{2}$ " square and about 0.020" thick, although the rubidium salt crystals were smaller (*ca.*

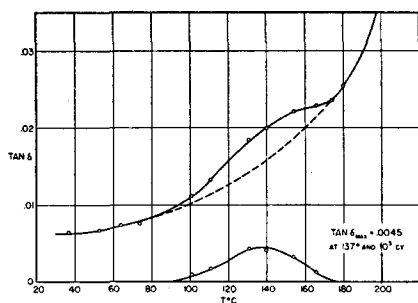


FIG. 3. Loss tangent of NaF crystal.

$\frac{1}{4}$ " square \times 0.010" thick). Electrodes were applied by painting the crystal faces with du Pont Silver Paste No. 4351.

A General Radio No. 716-B capacitance bridge for audiofrequencies, a susceptance variation bridge at high frequencies, and standard sample holders were used. The temperatures were determined by a thermocouple placed adjacent to the sample using a Leeds and Northrup potentiometer. In the earlier work, the dielectric constant and loss were measured over a wide frequency range (10^2 to 4×10^7 cy/sec.) at a fixed temperature (*ca.* 85°C). This was done on LiF, NaCl, and KBr. It soon became apparent that it was much more convenient to measure the crystal properties over a wide range of temperature at a fixed frequency (usually 10^3 cy/sec.), and this was done in subsequent work. To verify the agreement between the methods, NaCl was measured by both procedures.

While the loss tangent was the property of greatest interest, and, in fact, the only one studied in most cases, the dielectric constant was also determined on the three crystals that were measured over the wide frequency range. For the

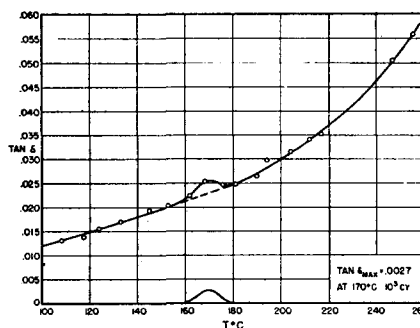


FIG. 4. Loss tangent of KCl crystal.

equipment and samples used, the probable error is about 2 percent in κ' and ± 0.0003 in $\tan \delta$ on the larger samples. For the Rb salts the accuracy is somewhat less, ± 0.0005 in $\tan \delta$. The temperature is accurate to about 1 degree.

III. RESULTS

The results of measurements as a function of frequency are best illustrated by the values found on sodium chloride at 85°C (Fig. 1). The loss tangent shows a peak of 0.024 at 600 cycles/sec. and the dielectric constant an accompanying decrease. For LiF and KBr (Fig. 2) the height of the peak is much smaller and no effect is observed in κ' . A clearly defined maximum is seen in KBr at 2×10^4 cycles/sec. and 85°C with the value 0.0011. In LiF the maximum, also 0.0011, is at 10^4 cycles/sec., but it is superimposed on a true conduction loss which masks the dispersion loss on the low frequency side of the curve.

The measurements as a function of temperature as the independent variable are best illustrated by the results on sodium fluoride (Fig. 3). The contribution to the loss tangent from the dispersion effect of the ions is always superimposed on a loss due to conductivity, but it is possible to subtract this loss from the total, leaving only the dispersion peak. Since we are in the "structure sensitive" conduction region, the conductivity does not increase with temperature according to a simple exponential law, hence this subtraction is done graphically rather than analytically. The resultant loss peak is also shown in Fig. 3. In the case of the NaF it will be observed that the maximum value of the loss tangent, 0.0045, occurs at 137°C at a frequency of 10^3 cycles/sec.

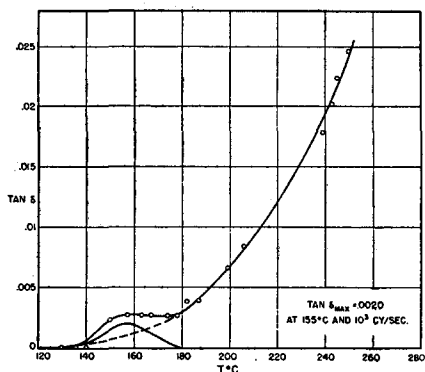


FIG. 5. Loss tangent of RbCl crystal.

Similar measurements at 10^3 cycles/sec. (Fig. 4) on KCl indicate a $\tan\delta_{\max}$ of 0.0027 at 170°C , on RbCl (Fig. 5) 0.0020 at 155°C , and on RbBr (Fig. 6) 0.0017 at 57°C .

The measurements given thus far indicate that, as in the usual dipole rotation investigations, the peak may be shifted to higher frequencies by a rise in temperature or conversely. Since the bridge measurements are most easily carried out at 10^3 cycles/sec., this frequency is usually chosen. In some cases of readily mobile ions, it was found that the loss maxima occurred so far below room temperature that it was necessary to measure at higher frequencies to make the temperature range accessible. This was true for RbI and KI (Fig. 7). The measurements are somewhat less satisfactory on the iodide samples at low temperatures than on other crystals, as indicated by the scattering of the points and the less characteristic shape of the curves, but again the peak is clearly presented. The value for RbI is $\tan\delta_{\max}=0.018$ at -130°C and 10^4 cycles/sec. For KI the peak was estimated to be $\tan\delta_{\max}=0.03$ at -200°C and 10^4 cycles/sec., since the peak could not be completely traversed even at 10^4 cycles/sec. The results on AgCl are of particular interest (Fig. 8), since in contrast to the previous cases, it will be noted that two peaks are found for this crystal. The values are $\tan\delta_{\max}=0.0003$ at -153°C and 0.0008 at -124°C and 10^3 cycles/sec.

Although the data presented here are on single samples, it should be stated that in a number of cases several crystals were studied. The magnitude of the loss peaks was found to vary, but the location of the peaks was constant within a few

degrees. This was true for samples of different dimensions as well, which would eliminate the possibility of interfacial polarization effects.

IV. MECHANISM OF POLARIZATION

As a first step in the interpretation of the experimental results, it will be observed that the behavior of $\tan\delta$ and κ' is that of a typical dielectric relaxation process. Since the effect is small, in most cases the change in the real part of the dielectric constant is within the limits of error of this measurement, but it was found in NaCl. The more sensitive measurements of $\tan\delta$, however, clearly show the behavior expected in such a process.

A discussion of dielectric effects of this type has been given⁹ in terms of rate processes in which it was shown that the real and imaginary parts of the specific dielectric constant are given as in the Debye calculation,

$$\begin{aligned}\kappa' &= \kappa_\infty' + \frac{\kappa_s' - \kappa_\infty'}{1 + (\omega\tau^*)^2}, \\ \kappa'' &= \frac{(\kappa_s' - \kappa_\infty')\omega\tau^*}{1 + (\omega\tau^*)^2},\end{aligned}\quad (3)$$

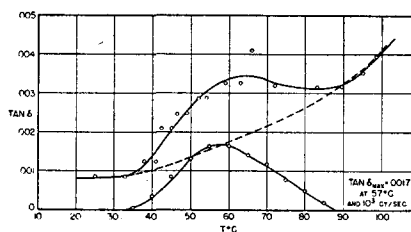


FIG. 6. Loss tangent of RbBr crystal.

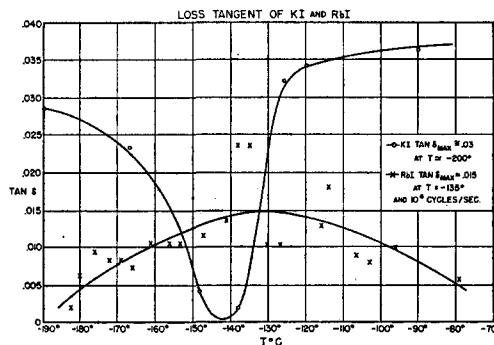


FIG. 7. Loss tangent of KI and RbI crystals.

⁹ (a) S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941); (b) R. Kauzmann, *Rev. Mod. Phys.* **14**, 12 (1942).

where $\tau^* = (\kappa_s' + 2)\tau/(\kappa_\infty' + 2)$ and κ_s' and κ_∞' are defined as the values of κ' for $\omega = 0$ and $\omega \gg \tau$, respectively. τ is defined as the time constant for the orientation process. τ may be expressed as

$$\tau = \tau_0 \exp(+U/kT), \quad (4)$$

where U is the height of the potential barrier and τ_0 is the time constant of free vibration.

These equations may be modified suitably for application to the present case. It is observed that $\kappa' \simeq \kappa_\infty'$ and $\kappa_s' + 2 \simeq \kappa_\infty' + 2$, so that

$$\tan \delta = \frac{\kappa''}{\kappa_\infty'} = \frac{(\kappa_s' - \kappa_\infty')\omega\tau}{\kappa_\infty'[1 + (\omega\tau)^2]}. \quad (5)$$

The maximum value for $\tan \delta$ is found when $\omega\tau = 1$; thus from a measure of the frequency at a given temperature or vice versa for which $\tan \delta_{\max}$ is found, U may be determined if we assume that τ_0 is the time constant for the natural frequency of lattice vibrations, that is,

$$2\pi\nu_m\tau_0 = \exp(-U/kT_j). \quad (6)$$

Then, if this information is combined with values for the activation energy for conduction, $(W/2 + U)$, values for the activation energy for hole formation, W , may be found.

The calculated values of the activation energies are given in Table I. The values of τ_0 are calculated from the natural frequencies given by Barnes¹⁰ for the alkali halides. That for AgCl is computed from the data of Rubens,¹¹ using Försterling's formula¹² to find the natural frequency from the observed reststrahl frequency. The same value of τ_0 is used for both peaks. The activation energies for conduction are those given by Lehfeldt¹³ for the alkali halides, RbI being estimated (Fig. 9); for AgCl, however, the data are those of Koch and Wagner,⁵ so that a direct comparison may be made with their results. The τ_0 used in the calculations of U corresponds to room temperature rather than the measurement temperature. The little information available indicates a shift to lower frequencies of only a few percent between room temperature and 100°C; thus this factor can probably be neglected. A more serious difficulty

is the fact that the natural frequency of an ion adjacent to a vacant site may be quite different from that of an ion in the regular structure, possibly even a factor of two lower. This would make U about 5 percent larger.

The data on the activation energies in the alkali halides are illustrated in Fig. 9 in which U , W , and $(W/2) + U$ from Table I are plotted as a function of the anion radius.

Thus far the interpretation of the results has not involved the properties of the substances being measured beyond the assignment of τ_0 as the natural frequency of lattice vibrations, since the polarization must be due to a motion of the ions of the crystal. Further progress may be made if the mechanism of polarization is detailed in terms of the nature of the lattice defects.

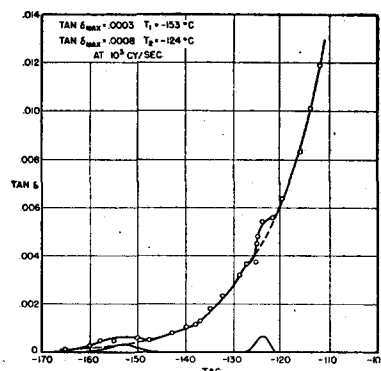


FIG. 8. Loss tangent of AgCl crystal.

In the alkali halides, the defects are of the Schottky type, so that there are equal numbers of vacant positive and negative ion sites. At temperatures below *ca.* 500°C only the positive ions are mobile, however, as has been shown by transference studies;¹⁴ thus in this case the polarization must be attributed solely to a motion of the positive ion vacancies. It is evident that the relaxation effects observed cannot be due to an unrestricted motion of holes or interstitial ions since this process gives rise to the normal conductivity found in all cases. Instead, the polarization probably depends on the redistribution of the positive ion vacancies relative to the negative ion vacancies, or the interstitial

¹⁰ R. B. Barnes, *Zeits. f. Physik* **75**, 723 (1932).

¹¹ H. Rubens, *Sitz. Ber. Preuss. Akad. Wiss.*, 513 (1913).

¹² K. Försterling, *Ann. d. Physik* **61**, 577 (1920).

¹³ W. Lehfeldt, *Zeits. f. Physik* **85**, 717 (1933).

¹⁴ W. Jost, *Diffusion und Chemische Reaktion in Festen Stoffen* (T. Steinkopff, Dresden, 1937).

TABLE I.

Salt	T_i °C	ν_m cy/sec.	τ_0 sec. $\times 10^{12}$	U ev	$\frac{W}{2} + U^{12}$ ev	W ev	U ev
LiF	80	10^4	0.109	0.58	2.20	3.24	
NaF	137	10^3	0.135	0.74	2.25	3.02	
NaCl	85	6×10^2	0.204	0.65	1.90	2.50	0.97 ⁸
	114	10^3	0.204	0.68	1.90	2.44	0.777
KCl	170	10^3	0.236	0.78	2.06	2.56	1.02 ⁸
KBr	85	2×10^4	0.294	0.53	1.97	2.88	1.01 ⁸
KI	(-200)	10^4	0.340	(0.11)	1.77	(3.32)	
RbCl	155	10^3	0.281	0.75	2.12	2.74	
RbBr	57	10^3	0.380	0.58	2.03	2.90	
RbI	-135	10^4	0.430	0.21	(1.84)	(3.26)	
AgCl	-153	10^3	0.31	0.21	0.80	1.20	0.26 ⁸
	-124	10^3	0.31	0.26	0.80	1.08	

ions relative to the vacant sites as found in the case of Frenkel defects. It seems likely that the polarizing units correspond to a pair of associated lattice defects on adjacent sites. This redistribution of charge under the influence of the external field may be described in terms of jumps of the holes over a potential barrier to the adjacent sites in the field direction, thus producing a net moment in this direction. Under a.c. excitation the moment has two possible orientations in opposite directions. The total moment may be calculated from the relative population of sites opposed to or in the field direction relative to the equilibrium distribution. This calculation is analogous to that given by Debye¹⁵ of the moment of an assembly of permanent dipoles with two possible orientations; it was described in terms of a rate process by Kauzmann.^{9b} As a simple picture of this process, we may represent the occupied site and an adjacent vacant site at a distance, a , which is of the order of the normal lattice constant as a double potential well, the heights of the two wells being altered by the applied field as in Fig. 10.

If the moment of a moving charge Ze in one potential well is

$$\mu_0 = Zea, \quad (7)$$

the total moment M will be

$$M = \mu_0(n_1 - n_2), \quad (8)$$

where n_1 is the number of ions in the direction opposed to the field and n_2 is the number in the field direction.

The values of n_1 and n_2 may be found from the equations for change of these quantities with

¹⁵ P. Debye, *Polar Molecules* (Chemical Catalog Company, New York, 1929).

time, assuming a Boltzmann distribution between the wells:

$$\begin{aligned} 2\tau(dn_1/dt) &= -n_1 \exp(-ZeaF/2kT) \\ &\quad + n_2 \exp(+ZeaF/2kT), \\ 2\tau(dn_2/dt) &= n_1 \exp(-ZeaF/2kT) \\ &\quad - n_2 \exp(+ZeaF/2kT). \end{aligned} \quad (9)$$

F is the locally acting field which varies sinusoidally as $F = F_0 \exp(j\omega t)$. τ is the same time constant previously considered. Following the method of solution given by Debye, it is found that the average moment $\bar{\mu}$ per potential well is

$$\bar{\mu} = (1/1 + j\omega\tau)[(Zea)^2 F/kT]; \quad (10)$$

hence its polarizability is

$$\alpha_j = (1/1 + j\omega\tau)[(Zea)^2/kT]. \quad (11)$$

A completely satisfactory relation between dielectric constant and polarizability in a crystal is not available, hence the Clausius-Mossotti equation is generally used, so that

$$\frac{\kappa^* - 1}{\kappa^* + 2} = \frac{N}{3\epsilon_0} \left(\alpha_e + \alpha_a + \frac{n}{N} \alpha_j \right), \quad (12)$$

where n is the number of polarizing units. Since we are dealing with materials of relatively low κ' , the choice of the relation is not critical. The use of the Drude equation as a limiting case would introduce a factor of about 7 in the result while some intermediate value is probably the correct one. From Eq. (12) the values of $\kappa_s' - \kappa_\infty'$ needed in Eq. (3) may be readily found in terms of the jump polarizability.

$$\frac{\kappa_s' - 1}{\kappa_s' + 2} = \frac{\kappa_\infty' - 1}{\kappa_\infty' + 2} + \frac{n(Zea)^2}{3\epsilon_0 kT}, \quad (13)$$

so

$$\kappa_s' - \kappa_\infty' \equiv \frac{n(Zea)^2}{9\epsilon_0 kT} (\kappa_s' + 2)(\kappa_\infty' + 2), \quad (14)$$

which is given as

$$\kappa_s' - \kappa_\infty' \simeq \frac{n(Zea)^2 (\kappa_\infty' + 2)^2}{9\epsilon_0 kT} \quad (15)$$

to the same approximation as used for Eq. (5). The maximum value of $\tan \delta$ is then given by

$$\tan \delta_{\max} = \frac{n(Zea)^2 (\kappa_\infty' + 2)^2}{18\epsilon_0 kT \kappa_\infty'}. \quad (16)$$

In these equations rationalized m.K.S. units have been used so that n is the number of lattice defects per cubic meter; the lattice constant a is in meters; the dielectric constant of free space ϵ_0 is 8.865×10^{-12} farad per meter; the electronic charge e is 1.59×10^{-19} coulomb; and Boltzmann's constant k is 1.38×10^{-23} joules per degree.

The values of n calculated for the various salts using Eq. (16) are given in Table II. The values of κ_∞ used for LiF, NaCl and KBr were those measured in these experiments. The others are those given by Højendahl.¹⁶

In the case of Frenkel defects, either the interstitial ion or the hole or both may be mobile. As pointed out by Mott and Gurney,⁴ there seems no easy way of deciding which would be more mobile, although it would seem likely to be the hole. This would, of course, be identical with the behavior of the Schottky defect. If the interstitial ion is actually the more mobile, the ionic jump would be one lattice distance to the next stable interstitial position in the field direction so that the effect would again be describable by the previous model.

It is formally possible to calculate the mobility of the polarizing units with the information at hand. In view of the differences expected in the energy and constant terms for the mobility in the conduction or reorientation process, however, it seems that the calculation would be fruitful only in terms of a more detailed model. It is planned to investigate this further at a later date.

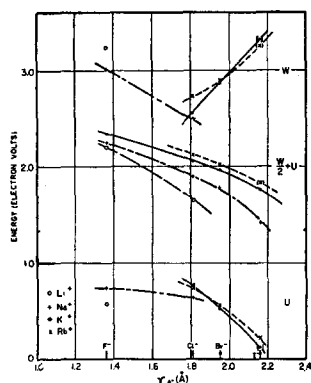


FIG. 9. Activation energies of the alkali halides.

¹⁶ K. Højendahl, Kgl. Danske Vid. Sels. Math.-fys. Medd 16, No. 2 (1938).

V. DISCUSSION

A. The Activation Energies in the Alkali Halides

It will be noted that the values of U are of reasonable magnitude, although not in complete agreement with the calculated values obtained by Mott and Littleton.⁸ These authors estimate an accuracy of 10 percent in the computed W , with somewhat less accuracy in U , while the experimental values found for U are about 30 percent higher. While the previously mentioned corrections are in the direction of improved agreement, it does not seem that this much difference can be accounted for. It is likely that the U values found by this method ought to differ from those of Mott and Littleton. Their calculation assumed that the lattice defects are widely separated while the relaxation effect depends on a coupling between holes of opposite sign which would modify the energy. The agreement with the experimental results of Mapother and Maurer⁷ is reasonably good, which indicates that the results of Mott and Littleton are somewhat too high.

The systematic variation of U from salt to salt is illustrated in Fig. 9. As pointed out by Lehfeldt,¹³ there are two important factors contributed to U . First, there is a purely steric effect so that U diminishes as the ratio of the cation to anion radius decreases, which is clearly in evidence. Secondly, the polarizability of the cation increases with increasing cation radius. The larger ions then may be more readily distorted, thus requiring less energy to pass between the neighbors to the vacant site than if it were a hard sphere. Thus the rubidium salts have values

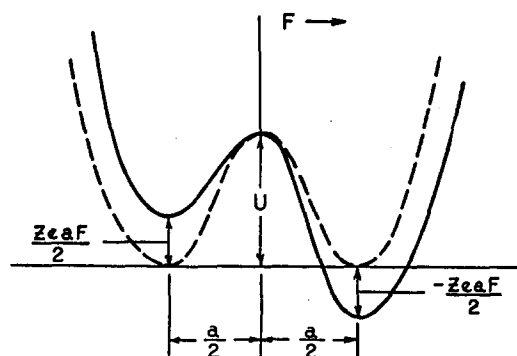


FIG. 10. Schematic potential for ionic motion in an electrical field.

of U which are almost the same as for the potassium salts in all the measured crystals, even though the normal ion radius is larger.

This type of measurement may be easily extended to more complicated cases. Although the interpretation becomes more difficult, it seems from experiments in progress that activation energies for the motion of foreign ions in crystals or for mixed crystals with a diffusing ion in common may be measured equally readily. These experiments will be described in a subsequent paper.

B. Lattice Defects and Activation Energies of Hole Formation in the Alkali Halides

The figures for the number of polarizing units present in the samples, while they are not characteristic but depend on the prehistory of the crystal, are, none the less, of interest. The data show that a crystal may have somewhat more defects than previously had been thought likely. Seitz¹⁷ had estimated that, at the melting point, NaCl might have about 10^{22} holes per cubic meter. This value was based on d.c. conductivity data alone. More recent studies on F centers¹⁸ have suggested that this estimate was too low and that 10^{24} defects per cubic meter could be produced easily in evaporated layers. This being the case, the value of 2.1×10^{23} is not unreasonable. A crystal containing this number of lattice defects is obviously not in thermodynamic equilibrium; the value instead corresponds to a temperature close to the melting point. It may seem

remarkable that such an unstable condition could be frozen in, but when it is realized that the crystals, particularly those from Harshaw, are obtained from the melt in a rather large block and that the only mechanism for the disappearance of Schottky defects is the diffusion of the holes to the crystal surface, which would be a very slow process at room temperature in a large sample, the large number of defects becomes reasonable. Heating the small samples used for dielectric measurements for a short time at 500°C is sufficient to destroy the effect since the equilibrium concentration of defects is quickly reached and is too small to be readily observable. Because the disappearance of the defects also depends on the diffusion mechanism, it seems that a study of the time decay of the loss should also give a measure of the activation energy of diffusion. It is planned to investigate this further.

The importance of measurements of the number of defects to related fields, e.g., the color centers or electron trapping in crystal counters, is evident. Unfortunately, the interpretation of the measured n is made difficult by the fact that the mechanism of polarization is not completely described by the simple model. A more general treatment of the polarizability of a lattice containing defects is in progress and it is hoped that this study will give a clearer insight into the true situation in such crystals.

When a comparison is made of the calculated values of Mott and Littleton for W with the results in Table I, a difference is found that parallels that found for the U values. The experimental figures are about 25 percent higher for the chlorides and 50 percent higher for the bromides. This difference is accentuated by the fact that the observed values seem to pass through a minimum for the chlorides and so larger differences are expected for the other salts.

This minimum is not entirely unexpected, as can be seen from a simple calculation of the activation energies of hole formation given by Jost.¹⁹ This author pointed out that the energy of hole formation could be computed from the difference of the lattice energy W_L , which is known, and the polarization energy of the crystal

TABLE II.

Salt	ϵ'	$\tan\delta_{\max}$	$n \times 10^{-23}$ No./m ³	$N \times 10^{-25}$ No./m ³	$\frac{n}{N} \times 10^6$
LiF	9.11	0.0011	0.15	6.07	0.25
NaF	6.00	0.0045	0.70	4.00	1.7
NaCl	5.90	0.024	2.1	2.26	9.4
	5.90	0.0014	0.15	2.26	0.67
KCl	4.68	0.0027	0.27	1.61	1.7
KBr	4.90	0.0011	0.081	1.40	0.58
KI	4.94	(0.03)	(0.4)	1.14	(4.)
RbCl	5.0	0.0020	0.17	1.36	1.3
RbBr	5.0	0.0017	0.10	1.12	0.93
RbI	5.0	0.018	0.40	1.01	4.0
AgCl	12.3	0.0003	0.006	2.36	0.03
	12.3	0.0008	0.03	2.36	0.1

¹⁷ F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1941).

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

¹⁹ W. Jost, *J. Chem. Phys.* **1**, 466 (1933).

when the defect is formed. If the defect is represented as a hole of radius R in a continuous homogeneous medium of dielectric constant κ_{∞}' ,

$$W = W_L - (e^2/2R)[1 - (1/\kappa_{\infty}')]. \quad (17)$$

The radius of the cavity, R , must be considered as an arbitrary parameter, but, if it is of the order of a lattice distance a , appropriate values of W are obtained. Both the lattice energy and the polarization energy decrease as the anion size increases, but not necessarily at the same rate.

We may, of course, calculate the values of R appropriate for our results. They are found to be of reasonable magnitude ranging from *ca.* 0.36 a for AgCl to *ca.* 2.0 a in RbBr.

The values of W found in this way are of interest in the same type of studies as the values of n previously mentioned. In addition, the depth of the electron traps is dependent on W so that we may expect to obtain further information about the color centers from the measurements.

C. Activation Energies and Lattice Defects in Silver Chloride

The results with silver chloride give the most striking evidence in favor of the general interpretation of the dispersion in terms of moving lattice imperfections. In particular, the discovery of two peaks for silver chloride, whereas only one was found for the alkali halides, is immediately explained by the nature of the Frenkel defects present in this crystal, since one peak may be assigned to the effect of the moving holes and the other to interstitial ions. The identification of the peaks with the proper process is also of interest, but, with the information at hand, seems to be uncertain. It is likely, however, that the lower peak corresponds to the migration of the holes since Mott and Littleton⁸ had found that this process should require a somewhat lower energy. There is a further ex-

periment that should identify the peaks unequivocally. Measurements on mixed crystals such as those of Koch and Wagner,⁵ that contain far more vacant sites than interstitial ions, should show one peak much higher than the other, thus indicating the peak due to the holes. It is planned to carry out this experiment shortly.

In both cases there is a slight ambiguity in the experimental value of U , since there is some uncertainty in the value of τ_0 needed. As was mentioned, the same value of τ_0 was used for both processes. While, in general, the assumption that the natural lattice frequency may be used for the frequency of the defect is justified, it is true that the frequency of an interstitial ion is probably greater than the natural lattice frequency rather than less as is the case for the neighbors to a hole, so that U would tend to be decreased. If the tentative assignment on the basis of Mott and Littleton's calculation is true, these corrections would tend to make the values of U more nearly the same, so that the true values of mobilities may be very similar for holes or interstitial ions. In any case, the agreement between the experimental results of Koch and Wagner ($U=0.26$ ev)⁵ and that found by this method ($U_1=0.21$ ev and $U_2=0.26$ ev) is excellent.

While the particular sample of AgCl used in Table I has relatively few lattice defects, the very low value of W (≈ 1.1 ev) allows a great number of imperfections in the normal crystal. Another sample, for example, measured without preheating, was found to have 1.3×10^{23} polarizing units per cubic meter and in no case was heat treatment needed to make the effect measurable.

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