dary ionization coefficient, ω/α, is apparent in the changed field in the cathode region of the gap, the field in the anode half being unchanged.

A decrease of positive-ion mobility increases both the field and the positive-ion density in the cathode region, but the positive column is largely unaffected. Conversely, a decrease of electron mobility increases the field near the anode and greatly increases the charge density in the plasma, but the cathode region is unchanged.

There are considerable changes in the field and charge distributions as a function of pd. These are shown in Figs. 9 and 10 for pd values of 1 and 10 cm (mm Hg). The variation of the quantities plotted, e.g., E/p, with p is quite small for constant pd, seldom as large as 1%. It is noted that the edge of the negative glow, as evidenced by the extrapolation of the field to zero or by the current and charge distributions, moves closer to the cathode as pd increases. This behavior is noted experimentally. It is also noted that the field in the plasma increases proportionally at higher pd values leading to a greater voltage drop across the positive column. Since no loss mechanism, e.g., wall currents, is now included in the calculations, the actual voltage drop should be greater yet.

V. CONCLUSIONS

When Townsend's ionization mechanisms are modified by the effect of space-charge formation, the voltage-current static characteristic of a parallel-plate, cold-cathode argon discharge may be calculated, for current values well up into the glow discharge region. Comparison of experimental data with the calculated curves is made difficult because of the marked constriction of actual discharges in the breakdown current region. Experimental current densities can be calculated only if the varying area of the discharge is known. Estimated discharge areas yield good agreement between calculated and experimental static characteristics. It is planned to present such comparisons in a later paper. The variation of the electric field, current, and charge densities across the gap, are qualitatively very similar to those reported in the literature.

ACKNOWLEDGMENT

Entropy of Vacancies in Ionic Crystals

O. THEIMER
Department of Physics, University of Oklahoma, Norman, Oklahoma
(Received August 25, 1958)

The entropy of vacancies in sodium chloride is calculated from the ionic displacements produced by the Coulomb field of the vacancies and from the corresponding changes of the lattice frequencies. Using the displacements recently calculated by Tosi and Fumi it is found that, contrary to earlier expectations, the sum of all the frequency changes is positive. Some physical consequences of this result are discussed.

A THEORETICAL investigation of the entropy of vacancies in ionic crystals is of interest for various problems, e.g., the association of vacancy pairs.[1] Furthermore, it may serve to check the consistency of different theories dealing with the properties of vacancies. The entropy has been made accessible to calculation by the work of Tosi and Fumi[2] who determined the ionic displacements ξ_σ $(\sigma = x, y, z)$ produced by the electric field of vacancies. Estimates of entropies based on these displacements and the corresponding changes of the lattice frequencies will be given in the following sections. They confirm the conjecture of the author[1] that the accumulated effect of the displacements of the nearest and also the more distant vacancy neighbors is quite important. In fact, these displacements produce a net increase of the lattice frequencies which is larger than the decrease produced, according to Mott and Gurney,[3] by the vacancy itself. Comparison of the calculated entropies with certain empirical data indicate that the repulsive forces between strongly polarized ions in the neighborhood of a vacancy do not satisfy the force law which is valid for the ions in the ideal lattice. Uncertainties of this kind introduce a large error into the following calculations and render an interpretation of numerical results quite difficult.

ENTROPY OF A SYSTEM OF VACANCIES IN IONIC CRYSTALS

Neglecting the electrostatic interaction between isolated vacancies, the entropy can be written

$$S = n_d S_d + n_a S_a + S_c(n_d, n_a), \tag{1}$$

[1] O. Theimer, Phys. Rev. **109**, 1095 (1958).
[2] M. P. Tosi and F. G. Fumi, Nuovo cimento **7**, 95 (1958).

[3] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Clarendon Press, Oxford, 1940), p. 31.

where n_d and n_a are the numbers of dissociated and associated vacancy pairs, S_d is the entropy change of the whole crystal per dissociated vacancy pair, S_a the corresponding change produced by one associated pair, and $S_c(n_d,n_a)$ the configuration entropy or entropy of mixing. We consider only the entropies S_d and S_a which are related to the lattice frequencies by relations of the form[3]

$$S_d = k \sum_{i=1}^{6N} \ln(\nu_i/\nu_i'), \qquad (2)$$

where the ν_i are the normal frequencies of the N cations and N anions in the crystal and the ν_i' are the frequencies of the same lattice vibrations perturbed by a vacancy pair. If the frequency changes $\Delta\nu_i = \nu_i' - \nu_i$ are small, S_d may be approximated by the equation

$$S_d \cong -k \sum_{i=1}^{6N} \frac{\Delta\nu_i}{\nu_i} \cong -\frac{1}{2}k \sum_{i=1}^{6N} \frac{\Delta(\nu_i^2)}{\nu_i^2}. \qquad (3)$$

Since the sum of the squares of the frequencies is equal to the trace of the dynamical matrix of the crystal,[4]

$$4\pi \sum_{i=1}^{6N} \nu_i^2 = \sum_{i=1}^{6N} \frac{1}{m_i} \frac{\partial^2 U}{\partial x_i^2} = \sum_{i=1}^{6N} \frac{1}{m_i} f_{ii}, \qquad (4)$$

one has, approximately,

$$S_d \cong -\frac{1}{2}k \sum_{i=1}^{6N} \frac{\Delta f_{ii}}{f_{ii}} \cong -\frac{k}{2f} \sum_{i=1}^{6N} \Delta f_{ii}, \qquad (5)$$

where U is the potential energy of the crystal associated with vibrations and f is any one of the $6N$ diagonal matrix elements which are all equal in ideal sodium chloride type crystals. Thus, the calculation of the entropy reduces to a determination of the changes of the force constants Δf_{ii} which are simple functions of the ionic displacements.

A further simplification results from Laplace's equation for the electrostatic potential according to which electrostatic forces do not contribute to the trace of the dynamical matrix. Thus the entropy of vacancies depends only on the short-range repulsive forces.

CALCULATION OF MATRIX ELEMENTS FOR SODIUM CHLORIDE

a. General Principles

We use the Born-Mayer formula[4] for the repulsive forces between two ions,

$$U(kl) = \beta(kl)b \exp\{[r(k)+r(l)-r(kl)]/\rho\}$$
$$= B(kl) \exp[-r(kl)/\rho], \qquad (6)$$

in which[1,5]

$$\beta(++) = 1.25, \quad \beta(+-) = 1.00, \quad \beta(--) = 0.75,$$
$$\rho = 0.345 \text{ A}, \quad b = 0.229 \times 10^{-12} \text{ erg},$$
$$r(\text{Na}^+) = 0.98 \text{ A}, \quad r(\text{Cl}^-) = 1.81 \text{ A}.$$

The force constants $f_{\sigma\sigma}(k)$ ($\sigma = x, y, z$) for the ion k, obtained from (6) by differentiation, are

$$f_{\sigma\sigma}(k) = \frac{\partial^2 U}{\partial x_\sigma^2(k)}$$
$$= \sum_l U(kl) \left[\frac{x_\sigma^2(kl)}{\rho^2 r^2(kl)} + \frac{x_\sigma^2(kl)}{\rho r^3(kl)} - \frac{1}{\rho r(kl)} \right], \quad (7)$$

$$\sum_\sigma f_{\sigma\sigma}(k) = \sum_l U(kl) \left[\frac{1}{\rho^2} - \frac{2}{\rho r(kl)} \right], \qquad (8)$$

where l labels the ions in the neighborhood of ion k; only the six nearest neighbors ($l = 1, 2, \cdots 6$) are found to contribute substantially to the $f_{\sigma\sigma}(k)$. In the ideal crystal

$$\sum_\sigma f_{\sigma\sigma}(k) = 3f, \qquad (9)$$

but if the electric field of a vacancy changes the nearest neighbor distances $r(kl)$ by amounts $\Delta r(kl)$ one has

$$\sum_\sigma f_{\sigma\sigma}(k) = \frac{1}{2}f \sum_{l=1}^{6} \exp\left[-\frac{\Delta r(kl)}{\rho} \right]\left[1 + \frac{2\rho\Delta r(kl)}{r^2} - \cdots \right]$$
$$= \frac{1}{2}f \sum_{l=1}^{6} \left[1 - \frac{\Delta r(kl)}{\rho} + \frac{1}{2}\frac{\Delta^2 r(kl)}{\rho^2} + \cdots \right], \quad (10)$$

where

$$\Delta r(kl) = [\xi(l) - \xi(k)] \cdot 1(kl), \qquad (11)$$

and $1(kl)$ is a unit vector pointing from ion k to ion l. Positive (negative) $\Delta r(kl)$ represents dilation (compression) of the "bond" $r(kl)$.

The outward displacements of the nearest neighbors of a vacancy in sodium chloride are given by Tosi and Fumi[2] as 0.191 A for sodium and 0.286 A for chlorine vacancies.

The displacements of the more distant vacancy neighbors can be obtained from the ionic displacement polarization

$$\mathbf{P}_{\text{ion}} = \frac{(\epsilon - \mu^2)}{4\pi\epsilon}\mathbf{D} = 0.0477\mathbf{D} \quad \text{for NaCl}, \qquad (12)$$

where ϵ and μ are the static dielectric constant and the index of refraction for visible light. In first approximation, i.e., neglecting the anharmonicity of lattice forces,

$$\mathbf{P}_{\text{ion}} = 2Ne\xi/V, \quad (V = \text{crystal volume}) \qquad (13)$$

[4] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, 1954).

[5] F. Bassani and F. G. Fumi, Nuovo cimento 11, 274 (1954).

and

$$\xi = 0.0477 V\mathbf{D}/2Ne = 0.0477 r_0^3 \mathbf{D}/e \text{ cm}$$

$$(r_0 = 2.81 \text{ A}). \quad (14)$$

If D represents the Coulomb field of a vacancy, one has

$$\xi(r) = 0.0477 r_0^3 \mathbf{r}/r^3. \quad (15)$$

For studying the effect of anharmonicity consider a positive ion and its two negative neighbors along the direction of a homogeneous external field $\mathbf{E}$. In first approximation the field changes all the bond lengths by the same amount $|\Delta^{(1)}r(kl)| = 2\xi$ independent of whether the bond is compressed or dilated. In second approximation one has $|\Delta^{(2)}r(kl)| = 2\xi \pm \delta$ for the dilation and compression side, respectively, where δ is an anharmonicity correction. For evaluating δ we note that the ions are coupled together by anharmonic restoring forces F_r, which can be obtained by expanding the repulsive potential (6) about the field-free equilibrium distance r_0 [6]:

$$F_r = U(r_0)[\Delta r/\rho^2 - \tfrac{1}{2}(\Delta r)^2/\rho^3 + \cdots]. \quad (16)$$

Since, in equilibrium, the restoring force F_r and the external force Ee have to be equal, one obtains δ from the equation

$$\Delta r/\rho^2 - \tfrac{1}{2}(\Delta r)^2/\rho^3 = \pm Ee/U(r_0), \quad (17)$$

with the approximate solution [7]

$$|\Delta^{(1)}r| = \rho^2 Ee/U(r_0) \equiv 2\xi,$$
$$|\Delta^{(2)}r| = |\Delta^{(1)}r \pm \tfrac{1}{2}(\Delta^{(1)}r)^2/\rho + \cdots| \equiv 2\xi \pm \delta. \quad (18)$$

By combining Eqs. (10) and (18), the quadratic terms cancel and one gets

$$\sum_\sigma f_{\sigma\sigma}(k) = \tfrac{1}{2}f \sum_{l=1}^{6}\left[1 - \frac{\Delta^{(1)}r(kl)}{\rho} - \cdots\right]. \quad (19)$$

b. Matrix Elements $f_{\sigma\sigma}(k)$

The contribution of the vacancy neighbor k to the sum of diagonal matrix elements can be calculated from the formulas (19), (15), (11), and from the nearest neighbor displacements given by Tosi and Fumi. One single approximate formula can be obtained by suitable expansions for ions which satisfy the condition $r \geqslant r_0$, where r is the distance between ion

---

[6] We neglect the electrostatic lattice forces as they contribute much less to anharmonic effects than the repulsive forces.

[7] If we use for ξ the expression (15), then we obtain for the correction $\delta(r)$ in distance r from a vacancy, $\delta(r) = 6.5 \times 10^{-40}/r^4$. $\delta(r)$ represents a net increase in bond length of a bond at a distance r from a vacancy, and the sum over all bonds gives the net linear expansion of the crystal caused by the electric field of one vacancy:

$$\Sigma\delta(r) \cong \frac{1}{r_0}\int_{r_0}^{\infty}\delta(r)d(r) = \frac{6.5 \times 10^{-40}}{r_0}\int_{r_0}^{\infty}\frac{dr}{r^4} = 0.033 \text{ A} = 0.012 r_0.$$

TABLE I. The changes $\Delta f_{\sigma\sigma}(k)$ of the diagonal elements of the dynamical matrix produced by a dissociated vacancy pair. The vector $\mathbf{r}$ with components $k_\sigma r_0$ is the position vector of ion k measured from the vacancy. $\mathfrak{N}$ is the number of equivalent ions in distance r. The changes $\Delta(i)$ of the nearest neighbor distances are measured in 10^{-11} cm.

$\langle k_1 k_2 k_3 \rangle$	$\mathfrak{N}$	r/r_0	$\Delta(1)$	$\Delta(2)$	$\Delta(3)$	$\Delta(4)$	$\Delta(5)$	$\Delta(6)$	$\mathfrak{N}\Sigma_\sigma f_{\sigma\sigma}(k)$
$\langle 100 \rangle$Na$^+$	6	1	-222	$-$	-44	-44	-44	-44	$0.45f$
$\langle 100 \rangle$Cl$^-$	6	1	-317	$-$	-44	-44	-44	-44	$1.30f$
$\langle 110 \rangle$	24	$\sqrt{2}$	-44	-44	66	66	24	24	$-3.20f$
$\langle 111 \rangle$	16	$\sqrt{3}$	-41	-41	-41	24	24	24	$1.17f$
$\langle 200 \rangle$Na$^+$	6	2	-222	11	11	11	11	46	$0.39f$
$\langle 200 \rangle$Cl$^-$	6	2	-317	11	11	11	11	46	$0.51f$
$\langle 210 \rangle$	48	$\sqrt{5}$	-34	66	-22	11	-8.5	-8.5	$-0.23f$
$\langle 211 \rangle$	48	$\sqrt{6}$	27	-41	18	18	-8.5	-8.5	$-0.31f$
$\langle 221 \rangle$	48	3							$0.22f$
$\langle 300 \rangle$	12	3							$-0.10f$
$\langle 310 \rangle$	48	$\sqrt{10}$							$0.16f$
$\langle 311 \rangle$	48	$\sqrt{11}$							$-0.06f$
$\langle 222 \rangle$	16	$\sqrt{12}$							$-0.05f$
$\langle 321 \rangle$	96	$\sqrt{14}$							$-0.08f$
								$\Sigma_{k\sigma}\Delta f_{\sigma\sigma}(k) =$	$0.17f$

and vacancy,

$$\sum_\sigma \Delta f_{\sigma\sigma}(k) = -\frac{0.0485 f r_0^5}{r^5}\left[84 - 165\frac{r_0^2}{r^2}\right.$$
$$\left. - \left(140 - 315\frac{r_0^2}{r^2}\right)\left(\frac{x^4 + y^4 + z^4}{r^4}\right)\right], \quad (20)$$

with x, y, z being the components of $\mathbf{r}$. Numerical results are given in Table I which contains the matrix elements for groups of $\mathfrak{N}$ equivalent ions having the same distance r from the vacancy and one of the $\mathfrak{N}$ equivalent positions $\langle \pm k_1 \pm k_2 \pm k_3 \rangle$ obtained by permuting the k_i and multiplying by the factor two, i.e., summing over vacancy pairs. Table I exhibits the following characteristic features of the matrix elements:

(1) The group $\langle 100 \rangle$ of the six nearest neighbors of a vacancy has to be treated separately for sodium and chlorine vacancies because of the difference between the nearest-neighbor displacements produced by the different vacancy types.[2] The nearest neighbors of a vacancy differ from all the other ions in the crystal by the absence of one of the six "bonds" $r(kl)$ characteristic for a lattice of sodium chloride type. Each of these missing bonds contributes the term $-\tfrac{1}{2}f$ to the trace of the dynamical matrix.[3] However, Table I shows that the five remaining bonds are strongly compressed so that the net nearest-neighbor effect is an increase of the sum of the force constants of magnitude $1.75f$.

The bonds emanating from the second-nearest neighbors $\langle 110 \rangle$ are mostly dilated and, hence, make a negative contribution to the trace of the dynamical matrix. But the ions of group $\langle 200 \rangle$, of which one would also expect a negative contribution, are so strongly affected by the excessive nearest-neighbor displacements that they make actually a positive contribution which is decisive for the sign of the total change of force constants.

(2) The difference in sign of the contributions of different groups has two causes. One is a trivial conse-

quence of the ionic charges: If the charge of an ion and of its six neighbors is inverted, compressed bonds will change into dilated bonds, and vice versa, and Δf changes sign. Another factor influencing the sign is the direction of the vector $\mathbf{r}$ which determines the sign of the square bracket in Eq. (20). Because of the oscillations in sign, the sum of all the force constants converges very rapidly. This can be immediately seen if one replaces the summation over k approximately by an integration over all space and division by the cell volume $r_0{}^3$. Actually one takes as cell volume $2r_0{}^3$, since one has to carry out the summations over positive (k^+) and negative (k^-) ions separately and has to take the difference of the two sums. One obtains

$$\sum_{k^+\sigma} \Delta f_{\sigma\sigma}(k^+) = -\frac{0.0485 f r_0{}^5}{2r_0{}^3} \int_0^\pi \int_0^{2\pi} \int_{R^+}^\infty \frac{1}{r^5}\left[84-165\frac{r_0{}^2}{r^2}\right.$$

$$\left. -\left(140-315\frac{r_0{}^2}{r^2}\right)\left(\frac{x^4+y^4+z^4}{r^4}\right)\right] r^2\sin\vartheta\,d\vartheta\,d\varphi\,dr$$

$$= -0.26 r_0{}^4(R^+)^4, \quad (21)$$

and an identical result with opposite sign for negative ions. Taking for R^+ and R^- the smallest two distances not contained in Table I, i.e., $R^+=4r_0$, $R^-=(17)^{\frac12}r_0$, one finds that the contribution of all the distant neighbors, not contained in Table I, to the change of the dynamical matrix is 0.00012.

The case of associated vacancy pairs could be handled by the same methods that have been used in the preceding for pairs of dissociated vacancies. However, because of the great sensitivity of force constants to small ionic displacements, the nearest-neighbor shifts calculated by Tosi and Fumi[2] for associated vacancy pairs are probably not accurate enough for our present purpose.[8]

DISCUSSION OF THE CALCULATED ENTROPIES

According to Eq. (5) and Table I the entropy of a dissociated vacancy pair, S_d, is $-0.085k$. This value may be compared with an empirical result of Etzel and Maurer[9] who found that the free energy of vacancy formation is a linear function of the temperature of the form

$$g(T)=2.02-3.3kT \text{ ev.} \quad (22)$$

Thus, the experimental value of S_d is $3.3k$, i.e., different in sign and forty times larger than the calculated

entropy. We note, however, that the experimental value refers to high temperatures of several hundred degrees while the theoretical value corresponds to low temperatures, since thermal averages of ionic distances and force constants have not been used for the calculation. Nothing is known, at present, of the temperature dependence of S_d and it is quite difficult to estimate the magnitude of this effect. Nevertheless, it is improbable that the striking discrepancy between theory and experiment should be caused solely by temperature.

In fact, there is at least one physical assumption underlying the preceding calculation of entropies which is not quite correct and may seriously affect numerical results. It is related to the polarization of the ions in the field of vacancies, which is quite strong for the first- and second-nearest neighbors and affects the ionic polarizabilities and the parameters in the force law (6). The change of the electronic polarizability in an electric field E is well known and can be described by formulas of the type[10]

$$\alpha=\alpha_0(1-3\alpha_0{}^{\frac23}E^2\times10^{22}) \text{ cgs.} \quad (23)$$

The effect is quite strong for the nearest neighbor of a sodium vacancy but is smaller than the difference in the polarizability of the chlorine ion given by Pauling[11] and Tessman, Kahn, and Shockley,[11] respectively. Since the latter difference hardly affects[2] the nearest-neighbor displacements ξ, the field dependence of the polarizability can be neglected.

The situation is probably quite different for the repulsive force law (6) which should be quite sensitive to deformation of the electron clouds of ions. This effect may strongly influence the ionic displacement ξ calculated by Tosi and Fumi, and the force constants calculated in the present paper, which depend on the force law explicitly through Eqs. (7) and (8) and implicitly through the ionic displacements in Eqs. (10) and (11). Since the repulsive force law for deformed ions is not known, the discrepancy between the calculated entropies and the experiments of Etzel and Maurer cannot, at present, be explained in a unique fashion. There is, however, no doubt that this discrepancy could be removed only if the nearest-neighbor displacements of Tosi and Fumi were considerably reduced in magnitude. For instance, *if the repulsive force law is not modified*, the nearest-neighbor displacements must be reduced from 0.191 A and 0.286 A to about 0.04 A and 0.06 A, respectively, in order to give a vacancy entropy of magnitude $3.3k$.

[8] Tosi and Fumi assume *a priori* that the displacements of the ten nearest neighbors of an associated vacancy pair are all equal in magnitude.

[9] H. W. Etzel and R. J. Maurer, J. Chem. Phys. 18, 1003 (1950).

[10] O. Theimer, Proc. Indian Acad. Sci. 28, 506 (1948).

[11] C. Kittel, *Solid State Physics* (John Wiley and Sons, Inc., New York, 1956), p. 165.