optical scattering is simply $\hbar\omega_l$ times the difference between the probability per unit time for absorption and that for emission. To obtain this difference we need only change the plus sign in the angular bracket of (7) to a minus. The resulting rate of change of carrier energy is

$$\frac{d\mathcal{E}}{dt}=\frac{2eE_0\hbar\omega_l}{(2m\mathcal{E})^{1/2}}\left[N_q\sinh^{-1}\left(\frac{\mathcal{E}}{\hbar\omega_l}\right)^{1/2}-(N_q+1)\sinh^{-1}\left(\frac{\mathcal{E}-\hbar\omega_l}{\hbar\omega_l}\right)^{1/2}\right]. \quad (8)$$

For $\mathcal{E}\gg\hbar\omega_l$ the rate of energy loss, according to (8), is given actually by the spontaneous emission since absorption and stimulated emission essentially cancel in this limit. Because the dependence of the angular bracket on energy is essentially logarithmic for $\mathcal{E}\gg\hbar\omega_l$ it is seen that the rate of energy loss decreases approximately as $\mathcal{E}^{-1/2}$ in the limit of large $\mathcal{E}$. This is also true of the collision frequency. Since the rate of energy input from the field is, roughly, inversely proportional to the collision frequency, it is clear that the combination of these two changes could result in an instability if only this scattering mechanism were operative. Of course, the appearance of breakdown in ionic crystals (to which this calculation is not applicable since perturbation theory is not valid there) has been connected with just this mechanism. In the III–V compounds it seems clear, if only on the evidence that breakdown does not occur, that other mechanisms take over when the polar optical scattering gets less effective.

To obtain from (8) the average rate of energy loss of all the electrons in a given sample under a given set of external conditions, it is, of course, necessary to average over the correct electron distribution for the given conditions. What this distribution is depends on the size of the electric field, all of the scattering processes operative, the band structure, etc. The fact that a relaxation time does not exist for the polar optical scattering for $\mathcal{E}\sim\hbar\omega_l$ makes the determination of the distribution function quite difficult, of course. In the absence of knowledge about this function it has frequently been assumed that it is a Maxwell-Boltzmann distribution with temperature T_e greater than the lattice temperature T. When (8) is averaged over such a distribution the result is

$$\left\langle\frac{d\mathcal{E}}{dt}\right\rangle=-\left(\frac{2k_0\Theta_D}{\pi m}\right)^{1/2}eE_0\frac{e^{x_0-x_e}-1}{e^{x_0}-1}x_e^{1/2}e^{x_e/2}K_0(x_e/2)\,, \quad (9)$$

where Θ_D is the Debye temperature, x_0 and x_e represent $\hbar\omega_l/k_0T$ and $\hbar\omega_l/k_0T_e$, respectively, and K_0 is a Bessel function. This result was obtained earlier in somewhat less direct fashion by taking the average of $\mathcal{E}$ times the collision operator for polar optical scattering over the Maxwell-Boltzmann distribution.[6]

---

[6] B. V. Paranjape, Rep. Brit. Elec. Ind. Res. Ass. L/T 285, 1953 (unpublished). See also, R. Stratton, Proc. Roy. Soc. (London) A246, 406 (1958).

PHYSICAL REVIEW VOLUME 143, NUMBER 2 MARCH 1966

Theory of Diffusion in Ionic Crystals

James G. Mullen*
Physics Department, Purdue University, Lafayette, Indiana

(Received 30 August 1965)

A theory of the Schottky defect is given, and an explicit formula is derived for the formation energy in terms of the elastic and dielectric constants. The Einstein model of an ionic solid is the basis for the theory, with ion correlations treated as a perturbation. Also, semiempirical equations are derived for the energy of motion of positive- and negative-ion vacancies, for both self-diffusion and monovalent-impurity diffusion. The theory is applied to several cases, and the agreement with experiment is excellent.

SINCE the pioneering work of Jost[1] a number of papers have appeared which are related to the problem of forming and moving Schottky defects in solids. The most noted of these efforts is that due to Mott and Littleton[2] which has served as a pattern for most of the other calculations.[3–8]

Before discussing the present calculation it is desirable to review earlier theoretical work on the subject. The Jost theory has never been very useful because no

---

* Work supported in part by the Advanced Research Projects Agency.

[1] W. Jost, J. Chem. Phys. 1, 466 (1933).

[2] N. F. Mott and M. J. Littleton, Trans. Faraday Soc. 34, 485 (1938).

[3] P. Brauer, Z. Naturforsch. 7a, 372 (1952).

[4] F. G. Fumi and M. P. Tosi, Discussions Faraday Soc. 23, 92 (1957).

[5] R. Guccione, M. P. Tosi, and M. Asdente, J. Phys. Chem. Solids 10, 162 (1958).

[6] T. Kurosawa, J. Phys. Soc. Japan 13, 153 (1958).

[7] G. Arai and J. G. Mullen, Bull. Am. Phys. Soc. 9, 657 (1964); M. P. Tosi, M. Doyama, and J. G. Mullen, *ibid.* 10, 77 (1965).

[8] For a review see A. B. Lidiard, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 20, p. 246.

satisfactory way of estimating the effective radius of the positive- and negative-ion vacancies was possible within the framework of the model. The Mott-Littleton model has been used with success for NaCl and KCl, but has only recently been applied to a large number of materials[6] and then with disappointing results. Possible sources of difficulty in the Mott-Littleton theory are easily found, when some of the assumptions in the theory are examined. The region far from the defect (usually taken as second neighbors to the defect and beyond) is treated in a quasicontinuum approximation, where it is postulated that the sum of the dipoles in a given region equals the macroscopic polarization, i.e., we write $P=(\mu_1+\mu_2)/2r_0^3$, Yet, it is questionable if this relation is meaningful when applied only a few neighbor distances from the defect. Also the macroscopic polarzation P does not have any obvious place in a theory of the Schottky defect, as it arises from the application of Maxwell's equations to a continuous medium, while the induced charge in the actual problem is not the result of a continuum of dipoles but must be related to a small number of ions which are at only about one atom distance from the defect. It is further assumed that the analysis derived for a uniform field can be used to calculate the displacement polarizability; but this cannot be valid, because of the elastic displacement of the outer ions resulting from the relatively large, displacements of those ions nearest to the defect. Attempts have been made to include this elastic displacement term, but the treatment is not satisfactory, as the discretely treated dipoles are allowed to relax in the wrong quasicontinuum dipole field, which is then changed to accomodate the elastic propagation of the ion displacements in the region which is treated discretely. Parameters such as the polarizabilities, dielectric constant, and lattice constant are assumed to give the correct answers when room-temperature values are used, i.e., the temperature dependence of the various parameters is assumed to average out in such a way as to leave the answer unchanged. Ion distortion, ion overlap, and the pressure dependence of parameters such as the electronic polarizabilities have never been satisfactorily incorporated into the model, although the first has been shown to be important when treated approximately by using deformation dipoles. Thus, while the answers calculated for the Schottky formation energies have been in agreement with experiment for NaCl and KCl, it seems certain that this has been somewhat fortuitous. For example, the inclusion of second-neighbor forces[8] makes the agreement between theory and experiment much worse than indicated by the original Mott-Littleton numbers. Agreement with experiment was restored by introducing an elastic displacement term by the dubious procedure outlined. The way to get around these problems is clearly to approach the problem from first principles, but the difficulties of such an approach are so great that a solution to the problem from this viewpoint has not even been attempted. Despite the difficulties, it might be hoped that idealized models like that due to Mott and Littleton would be useful in predicting trends in formation and motion energies for Schottky defects in ionic crystals of the same type having somewhat different properties, e.g., the alkali halides. The recent calculations by Kurosawa[6] along these lines proved very disappointing, inasmuch as he found the energy needed to form a Schottky defect to be 2.2±0.2 eV for all of the cases considered (LiF, NaCl, NaBr, KCl, KBr, RbBr, AgCl), which is not in accord with experiment.

The purpose of the present paper is to propose a model which is so simple that it can easily be applied to both self- and impurity diffusion, and to show that this model gives good agreement with experiment for alkali halide crystals having a wide range of physical properties. Unfortunately, the model used is no better than the Mott-Littleton model from the point of view of basic theory, and includes assumptions which are equally unwarranted. Thus, the value of the present highly idealized model is that it works and it is simple enough that the results can easily be evaluated for cases not specifically treated in this paper.

Our approach involves using an analysis analogous to that of the quasi-continuum region used in the Mott-Littleton calculation, but with a different criterion for putting dipoles onto the surrounding ions. Instead of introducing a displacement polarizability, which is defined on the basis of a nonexistent uniform field, we calculate the displacement dipoles directly, assuming that the local electric field is D/K, where K is an effective dielectric constant, and assuming an Einstein model of the ionic solid. Pictorially, the solid is regarded as consisting of ions which are attached to their lattice points by harmonic springs, resulting in equal frequencies of vibration for ions which are of the same mass.

Diffusion of Host-Lattice Ions

We regard the energy to form the Schottky defect as being given by

$$E_f=E_L+E_{\mathrm{rel}}$$

where E_L is the lattice energy per pair of ions and E_{rel} is the change in energy upon relaxation. This equation is based upon the assumption that the lattice energy is required to remove each ion if no relaxation occurs, while the lattice energy is regained when a pair of removed ions is returned to a kink on the surface.

The contribution to E_{rel} resulting from the electronic polarizabilities is, for the positive-ion vacancy,

$$-\frac{e^2}{2Kr_0^4}\left[\sum\frac{\alpha_+}{(r_+/r_0)^4}+\sum\frac{\alpha_-}{(r_-/r_0)^4}\right] =-\frac{e^2}{2Kr_0^4}(6.33\alpha_+ +10.20\alpha_-)\,,$$

where α_+ is the electronic polarizability of the positive host ions and α_- is the electronic polarizability of the negative host ions, r_0 is the nearest-neighbor distance, and K is the dielectric constant. We will have a similar term for the negative-ion vacancy.

To calculate the contribution from the displacement dipoles, each ion is considered to be tied to its equilibrium position by an Einstein spring, whose spring constant is $2r_0c_{11}$, where c_{11} is the usual notation for the elastic constant associated with longitudinal vibrations which propagate along a cube axis. This choice is based on the assumption that nearest-neighbor ions are coupled by harmonic springs whose spring constants are r_0c_{11}.[9] The factor of two in the expression for the Einstein spring constant relates the coupled spring system to the Einstein spring system, imagining the motion of one ion to be at least to first approximation independent of the other ions, as is required by the Einstein model. It is easily seen from the one-dimensional case that the Hamiltonian in the coupled system is of order $\sum \frac{1}{2}k_sx^2$ greater than that of the Einstein system when a field is applied resulting from the correlation in the motion of the ions, where x is the displacement from equilibrium. We will later use this relation to make a perturbation correction to the relaxation energy of the Einstein system.

Thus, the first order contribution to $E_{\rm rel}$ resulting from the displacement of the ions is

$$-\frac{e^4}{2k_sKr_0^4}\left[\sum\frac{1}{(r_+/r_0)^4}+\sum\frac{1}{(r_-/r_0)^4}\right]=\frac{8.27e^4}{k_sKr_0^4}$$

for the positive ion vacancy, and twice this for the Schottky defect.

We can improve on the calculation of the relaxation energy by taking into account the correlation between positive- and negative-ion motion with the aid of first order perturbation theory. In the above we have written the contribution to $E_{\rm rel}$ in the independent-ion model taking

$$E_{\rm rel}^{(1)}=-\tfrac{1}{2}e|\Delta V(0)|\,,$$

where $|\Delta V|$ is the change in magnitude of the potential energy at the defect resulting from relaxation. Because the motion of the ions in the coupled-spring system is always correlated, i.e., in an electric field adjacent ions of opposite charge always move in opposite directions, the Hamiltonian of the coupled spring system differs from that of the Einstein system by a term of order $\sum \frac{1}{2}k_sx^2$, where k_s is the Einstein spring constant, taken as twice the spring constant of the coupled system. If we assume that the Einstein model gives the displacements correct to first order, then we can evaluate the second-order correction to the relaxation energy, $E_{\rm rel}^{(2)}$, since the interaction energy must be quadradic in the displacement at the minimum, by regarding the term $\sum \frac{1}{2}k_sx^2$ as a perturbation on the Einstein energy. We have then

$$E_{\rm rel}^{(2)}=\sum \tfrac{1}{2}k_sx_0^2\,,$$

where

$$\sum \tfrac{1}{2}k_sx_0^2=\frac{k_s}{2}\,\frac{e^4}{k_s^2K^2r_0^4}\left[\sum\frac{1}{(r_+/r_0)^4}+\sum\frac{1}{(r_-/r_0)^4}\right],$$

or

$$E_{\rm rel}^{(2)}=8.27e^4/K^2k_sr_0^4.$$

It must be emphasized that this term is not the one which is in the original Einstein Hamiltonian and which is included in $E_{\rm rel}^{(1)}$ when we impose equilibrium conditions. Since the perturbation term is only $\sim 1/K$ times $E_{\rm rel}^{(1)}$, the application of perturbation theory to this problem is at least internally consistent.

Combining the above terms we have for the energy to form a Schottky defect

$$E_f=E_L-(8.27e^2/Kr_0^4)\times[\alpha_++\alpha_-+(2e^2/k_s)(1-1/K)]\,,\qquad(1)$$

where the term $(1-1/K)$ can be looked at as a correction to the first order spring constant k_s. Applying this formula to NaCl gives $E_f/2=1.08$ eV, compared with a measured value[10–14] of 1.0–1.2 eV.

It should be noted that the theory of the formation energy of the Schottky defect given here, like the Mott-Littleton theory, contains assumptions which are not justifiable *a priori*. The two most important of these are: (1) that the effective dielectric constant can be represented by the static dielectric constant, and (2) that the Einstein model gives the relaxed displacements correct to first order. The validity of these assumptions must rest on a comparison of the results with experiment. It might be mentioned in connection with assumption (2), however, that the spring constant chosen for the Einstein model must be at least to first order as we have chosen it. To choose the Einstein spring constant twice as large as the one given here would mean that the effect of the correlated motion would be so great that the Einstein model would be completely invalid. A plausibility argument which can be given in defense of the Einstein model is that at the beginning the relaxation process the electrical forces are much larger than the spring forces, being e^2/r^2 initially and e^2/Kr^2 finally. Thus, the effect of the restoring springs is not important until the field has been adequately screened. This implies that the effect of ion correlation will only alter the equilibrium displacement slightly, since the change in position of the ions on re-

---

[9] See, e.g., C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York), p. 96.

[10] D. Mapother, H. N. Crooks, and R. J. Maurer, J. Chem. Phys. **18**, 1231 (1950).

[11] H. L. Downing, Jr., Ph.D. thesis, Atomic Energy Commission, Technical Report No. COO-1197-9 (unpublished).

[12] W. Lehfeldt, Z. Physik **85**, 717 (1933).

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

[14] C. Bean, Ph.D. thesis, University of Illinois, 1952 (unpublished).

laxation must be sufficient to help in screening the bare charge of the defect before the restoring springs have any effect whatever.

The assumption that the effective dielectric constant is equal to the static dielectric constant implies that the Lorentz antishielding term is small. Mott and Littleton[2] have discussed the problem of calculating the antishielding term and conclude that it is less than the simple $(4\pi/3)P$ because of ion overlap. A certain amount of antishielding may be considered to be contained in the present theory if we consider the dielectric constant to change as we apply the perturbation. To calculate such a change in K would require additional assumptions in the theory and would give a different final displacement from the $(e^2/k_sKr_0^3)(1-1/K)$ prescribed by the simple interpretation, which assumes that the perturbation only modifies the spring constant. We believe that the simple interpretation is best, although the displacements are then only approximately determined. This is not a serious difficulty, since even the nearest ion to the defect is displaced only ~0.1 Å, which cannot be accurately determined experimentally. Thus, to measure the position of a sodium ion directly to 0.02 Å would mean that the momentum would be uncertain by $\hbar/\Delta x$ and the corresponding kinetic energy would be of order 0.3 eV or 3000°K. Even the possibility of a precise measurement of the time and spatial averages appears unlikely because of the magnitude of the thermal vibrations and ion distortion. It is pointless, then, to make additional assumptions to refine the displacement calculation, because such refinements can never be tested experimentally. An objection to the simple interpretation is that it indicates a field at the first-neighbor ions which is smaller than is obtained by summing the contributions from the charged defect and the surrounding dipoles. This objection is valid, however, only if one assumes that the point-dipole approximation describes fields at ions as well as at the defect, which may not be true because of ion overlap and distortion. This criticism, in any event, relates to the prescription for the displacements and fields at the final equilibrium and need not affect the calculation of the formation energy, which is the only predicted quantity in the theory that can be reliably measured.

Another assumption which will be important in cases where ion sizes are very different is the assumption that the coupled spring system can be represented by nearest-neighbor springs only. In a material like LiCl such an assumption is clearly not valid, and the theory cannot be applied in its present form.

We calculate the energy of motion by straightforward, partially empirical, procedure. We picture the motion process to result from the breaking one of the Einstein springs holding an ion which is next to a vacancy. The energy of motion is then postulated to be the work required to move the ions which surround the jumping ion to the saddlepoint configuration. We take the path of the diffusing ion to be the straight-line path connecting the ion with its adjoining vacancy. This may not be rigorously true for a small ion like Na^+ in NaCl, although it will be an adequate approximation for the present analysis. If, in addition to the above, we approximate the ions by hard spheres, then the energy of motion is represented by $E_m=(1-1/\sqrt{2})^2k_sr_0^2$, where k_s is again the spring constant $2c_{11}r_0$. This term gives $E_m=1.17$ eV compared with an experimental value[10–14] of 0.8 eV for Na diffusion in NaCl. To remedy this discrepancy we introduce an empirical constant, $c\cong 0.8^2$, to give the correct motion energy for NaCl and regard this as accounting for the deviation of the ions from hard spheres. We then take the motion energy to be given by

$$E_m=ck_s(1-1/\sqrt{2})^2r_0^2. \tag{2}$$

Many details, such as the change in Coulomb energy between the saddle-point configuration and the equilibrium configuration, have not been explicitly included in our treatment of E_m. Thus, our formula for estimating E_m is the result of an oversimplified picture. The calculated motion energies, however, are in reasonable agreement with experiment and the treatment can be considered as a useful phenomenological description. It would be possible to include contributions to E_m resulting from changes in the Coulomb interaction by a procedure analogous to the treatment of E_f. This has not been done because it would needlessly complicate the problem without improving the result. The ions are so far from their equilibrium positions in the saddle-point configuration that the interaction between ions is not known with any confidence from the standpoint of any of the theoretical models. Also, the local strains that occur in the saddle-point configuration are so great that ion overlap and the dependence of the polarizabilities on pressure are large enough that their omission makes any attempt to include other details of doubtful value. The present analysis does not reveal a difference in E_m for cation diffusion compared with anion diffusion of the host lattice ions. Fortunately, this disagreement with experiment is not large, and it may be within the experimental errors for many cases.

The formation, motion, and activation energies have been calculated for a number of alkali halides with the above relations, using the experimental data shown in Table I. The results are shown in Table II, with a comparison of the activation energies as measured by determining the temperature dependence of the ionic conductivity.

In applying Eq. (1) it will be noted that E_f depends rather sensitively on some of the parameters of the theory such as r_0, c_{11}, and K. The accuracy with which these parameters is known is such that the excellent agreement between theory and experiment shown in Table II must be regarded as partly fortuitous. Never-

TABLE I. Parameters used in calculating energies of formation motion of a Schottky defect. Room-temperature values are used for all of the parameters.

Material	E_L(eV)[a]	$r_0\times10^8$ cm[a]	$\alpha_+\times10^{24}$ cm[b]	$\alpha_-\times10^{24}$ cm	K[c]	11×10^{-11} dyn/cm^2[c]
LiF	10.51	2.014	0.03	0.64	9.27	11.12
NaCl	7.92	2.820	0.41	2.96	5.62	4.87
NaBr	7.53	2.989	0.41	4.16	5.99	3.87
KF	8.23	2.674	1.33	0.64	6.05	6.58
KCl	7.19	3.147	1.33	2.96	4.64	3.98
KBr	6.87	3.298	1.33	4.16	4.78	3.46
KI	6.50	3.533	1.33	6.43	4.94	2.67
RbCl	6.91	3.291	1.98	2.96	4.64[d]	3.64

[a] M. P. Tosi, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1964), p. 54.

[b] J. Tessman, A. Kohn, and W. Shockley, Phys. Rev. **92**, 890 (1953).

[c] *American Institute of Physics Handbook* (McGraw-Hill Book Company, Inc., New York, 1957).

[d] A value taken to be the same as KCl based on a theoretical estimate.

theless, the agreement is good enough that the theory can be used with some confidence in calculating energies associated with Schottky defects. Our result $E_f=2.8$ eV for LiF is in decidedly better agreement with the experimental value of 2.7 eV than the result of Kurosawa[6] is, and for AgCl we estimate $E_f\cong 6$ eV, which is consistent with the experimental evidence that this crystal contains only Frenkel defects.

TABLE II. Calculated self-diffusion parameters.

Material	E_f(eV)	E_m(eV)	E(eV)	E_{exp}[a]	$\Delta r/r_0$[b]
LiF	2.82	0.67	2.08	1.99	0.061
NaCl	2.17	0.80	1.88	1.89	0.055
NaBr	2.26	0.76	1.89	1.68	0.052
KF	3.26	0.92	2.55	2.35	0.047
KCl	2.29	0.91	2.05	2.05	0.050
KBr	2.35	0.91	2.09	1.97	0.047
KI	2.29	0.86	2.00	1.77	0.045
RbCl	2.53	0.95	2.21	2.12	0.046

[a] See R. J. Friauf, *American Institute of Physics Handbook* (McGraw-Hill Book Company, Inc., New York, 1957), pp. 9–63.

[b] Calculated fractional outward relaxation of the six ions which are nearest neighbors to the vacant site, i.e., $\Delta r/r_0=(e^2/k_sKr_0^3)(1-1/K)$.

Impurity Diffusion

The model is readily applied to impurity diffusion. We illustrate this by calculating the change in activation energy for Rb diffusion in NaCl. Taking the Einstein spring constant for a Rb ion in NaCl to be infinite, the binding energy between the Rb ion and a positive ion vacancy can be approximated by

$$E_B=-(e^2/8Kr_0^4)[\alpha_+-\alpha_I+(e^2/k_s)(1-1/K)]\,, \quad (3)$$

where the subscript I refers to the Rb impurity ion. The numerical value for the case of Rb diffusion is -0.03 eV. It should be noted that the binding is negative, i.e. the result indicates that large Rb ions repel positive-ion vacancies, although the interaction is so weak that this term could be taken to be zero for many purposes.

For the energy of motion we have

$$E_m=ck_s\{[r_I-r_++(1-1/\sqrt{2})r_0]^2-3(r_I-r_+)^2\}\,, \quad (4)$$

where k_s is the Einstein spring constant for host ions in the lattice; this formula should apply generally when the impurity ion is larger than the host ion it replaces. The second bracketed term arises from the gain in strain energy resulting from the relaxation of four of the chlorine ions which relax inwards when the moving impurity ion leaves its equilibrium position. This equation gives an energy of motion for Rb diffusion in NaCl of 1.20 eV and an activation energy of 2.31 eV. Thus, the calculation indicates that the activation energy for Rb diffusion should be about 0.43 eV greater than Na diffusion in NaCl. By the same method we estimate that Rb diffusion in KCl would have an activation energy 0.20 eV greater than K diffusion, with the binding energy between a positive ion vacancy and a Rb ion taken to be zero.

Conclusions

We have shown that the activation energies for self-diffusion can be obtained by simple arguments which give excellent agreement with experiment, but which are about 0.1 eV greater than the measured values. Equation (1) gives the energy of formation for a Schottky defect and Eq. (2) gives the energy of motion for either the positive- or the negative-ion vacancy, which are equal within the present approximations. Equation (3) estimates the binding energy between a vacancy and a very large monovalent impurity, and Eq. (4) can be used to estimate changes in motion energy for monovalent impurities which are larger than the host ion replaced. The theory can be extended to the case of small monovalent impurity ions, although explicit formulas have not been derived. Temperature-dependent correlation factors have been assumed unimportant for the cases considered, and no attempt has been made to incorporate them into the theory.