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Vacancies and Monovalent Cation Impurities in the Alkali Halides*

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A consistent treatment of point defects in ionic crystals, using the Mott-Littleton description of the long-range lattice polarization and the short-range interionic potential proposed by Tosi and Fumi, is developed and applied to an investigation of several defect configurations in a few alkali halide crystals. These are: (a) an isolated vacancy at either lattice site, (b) a substitutional alkali impurity, and (c) the saddle-point configuration for motion of both a (positive or negative) host ion and a substitutional alkali impurity into a vacancy. The results of the calculations are discussed and compared with the available experimental evidence on ionic conductivity, host-ion and impurity diffusion, and impurity solubility.

I. INTRODUCTION

LATTICE calculations of parameters of point defects in ionic crystals, such as their energies of formation, motion, and association, require a fairly accurate description of both the interionic potential and the mechanisms of ionic polarization. The description of the polarization around defects has generally been patterned after the early treatment of the vacancy given by Mott and Littleton,[1] which combines an atomistic calculation of the relaxation of the first neighbors in the appropriate effective field with a dielectric theory description of the long-range polarization. Some refinements of the original model have been investigated for a single defect[2–5]; relaxation mechanisms such as the elastic relaxation first introduced by Brauer[2] and the deformation dipole relaxation considered by Kurosawa[3] have led to increases in the calculated Schottky defect energy. On the other hand, the short-range ionic interactions are also generally important for the determination of the ionic displacements around a defect and of the pertinent relaxation energy,[6] and play an essential role in calculations of the energy of motion of defects.[7] In a number of calculations of motion energies for various defects it has been found necessary to adopt a short-range potential of essentially heuristic character, the so-called Born-Mayer-Verwey potential.[8]

The availability of a revised potential based on the cohesive properties of the perfect crystal[9] and of more complete experimental information on basic defect properties make it worthwhile to re-examine the evaluation of the energy parameters of point defects in these crystals. From this point of view, we are interested in considering not only the vacancy, but also alkali impurity ions. In the absence of a consistent treatment of the corrections to the early model the Mott–Littleton scheme naturally provides a consistent, first-order approximation for the treatment of different defect configurations.

The defect configurations considered in this paper are: (a) an isolated vacancy at either lattice site, (b) a substitutional alkali impurity, and (c) the saddle point configuration for motion of both a (positive or negative) host ion and a substitutional alkali impurity into a vacancy. The energy of the latter configuration is evaluated relative to the state in which the impurity and the vacancy are dissociated, so that the result can be directly related to the activation energy for diffusion of the impurity. We also present a preliminary estimate of the energy of interaction between the impurity and the vacancy. The calculations are carried out for NaCl, KCl, and RbCl crystals, the impurities being Na^+, K^+, and Rb^+. The results of the calculations are compared with the available experimental evidence, which is fairly complete for these systems.

Although there is clearly room for further improvements in the model, particularly in the treatment of the lattice polarization, the agreement of the theory with experiment is at least semiquantitative.

II. DESCRIPTION OF THE MODEL AND NUMERICAL DATA

In past treatments of the energy of formation of a vacancy, either in the perfect crystal or in the neighborhood of another defect, it has been customary to determine the equilibrium configuration of the first-neighbor ions by a force-balance condition and then to evaluate the formation energy as the average of the potential energies at the position of the vacancy before and after its creation. We follow an alternative approach, basically analogous to that followed by Kurosawa[3] for the vacancy formation, which unifies the treatments of the isolated defect and of the saddle-point configuration. We express the energy of a given defect configuration, relative to the perfect crystal, as the sum of the energy required to create the defects in the rigid

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

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

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

[4] J. R. Hardy, J. Phys. Chem. Solids 15, 39 (1960); 23, 113 (1962).

[5] A. Scholz, Phys. Status Solidi 7, 973 (1964).

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

[7] R. Guccione, M. P. Tosi, and M. Asdente, J. Phys. Chem. Solids 10, 162 (1959).

[8] E. J. W. Verwey, Rec. Trav. Chim. 65, 521 (1946); E. J. W. Verwey and J. H. de Boer, *ibid.* 59, 633 (1940).

[9] F. G. Fumi and M. P. Tosi, J. Phys. Chem. Solids 25, 31 (1964); M. P. Tosi and F. G. Fumi, J. Phys. Chem. Solids 25, 45 (1964).

lattice and of the relaxation energy. The latter involves the change in the charge-charge Coulomb and the short-range interaction energy of the ions upon relaxation, the interaction energy of the ionic charges and dipoles with the ionic dipoles, and the "quasi-elastic" energy of formation of the dipoles. We approximate the change in the interaction energy of ions further than first neighbors from the defects, among themselves and with the first neighbors, by treating the ionic displacements as equivalent to displacement dipoles and by expanding the short-range energy change to quadratic powers in their displacements. We can also use the force-equilibrium conditions for the perfect crystal, in which the electric field and the short-range force on each ion vanish separately, to reduce sums over the infinite crystal to sums over the inner region. We have then to minimize the relaxation energy with respect to all the relaxation parameters. The equilibrium conditions for the first neighbors yield the correct force balance and the correct dipole in the field of the far ions; while for the far ions, they allow us to reduce the energy *at equilibrium* to a linear function of their relaxation parameters. In the actual determination of the relaxation parameters, instead of minimizing exactly the relaxation energy which involves the correlated displacements of all the ions, we adopt the Mott-Littleton expressions for the relaxation of the ions further than first neighbors, and minimize numerically the relaxation energy with respect to the displacements and the dipoles of the first neighbors.

The advantages of this procedure are that it yields directly the value of the relaxation energy at equilibrium and that it can easily be extended to give an atomistic treatment of further shells of ions around the defects by an appropriate modification of the last step. We give below the pertinent formulas in a compact form for an arbitrary defect configuration.[10]

We adopt the convention to denote a defect site by a suffix d, a defect or a near ion by a suffix k, and a far ion by a suffix l. The rigid-lattice energy change in creating the defects is then written as

$$U_{\mathbf{rl}}=e^2/r_0\Big(\sum_d q_dV_d+\tfrac{1}{2}\sum_{dd'}{}' q_dq_{d'}/t_{dd'}\Big)+\sum_{dk}{}'\left[\varphi_{dk}(t_{dk})-\bar{\varphi}_{dk}(t_{dk})\right]+\sum_{dl}\left[\varphi_{dl}(t_{dl})-\bar{\varphi}_{dl}(t_{dl})\right]. \quad (1)$$

Here, q_d is the effective charge of a defect[11] and V_d is the Madelung potential at the site d; $\mathbf{t}_{ij}$ is the vector distance form the site j to the site i in the rigid lattice, φ_{ij} is the short-range interaction energy of two ions in the defect crystal, and $\bar{\varphi}_{di}$ is the short-range interaction energy of the ith ion and the ion replaced by the defect d. Thus, $\bar{\varphi}_{di}$ is zero for an interstitial, while φ_{di} is zero for a vacancy. The case $i=j$ is excluded from the primed sums.

The relaxation energy is conveniently divided into three parts: the change in the interaction energy of the defects and the near ions among themselves (U_1) and with the far ions (U_{12}), and the energy change of the far ions (U_2). We denote by $\boldsymbol{\xi}_k$ and $\mathbf{v}_k$ the displacements and the electronic dipoles in the inner region and by $\pm M'\sum_d q_d\hat{t}_{ld}/t_{ld}^2$ and $M_\pm'\sum_d q_d\hat{t}_{ld}/t_{ld}^2$ the displacement and the (displacement and electronic) dipole of a positive or negative far ion in the Mott–Littleton scheme. By carrying out the indicated manipulations of $U_{12}+U_2$ we find the following expression of U_2 at equilibrium:

$$U_2=-\tfrac{1}{2}(e^2/r_0)\Big[\sum_{dd'} q_dq_{d'}(M_+'S_{dd'}{}^{+}+M_-'S_{dd'}{}^{-})+\sum_{dk} q_d(z_k\boldsymbol{\xi}_k+\mathbf{v}_k)\cdot(M_+'\mathbf{T}_{kd}{}^{+}+M_-'\mathbf{T}_{kd}{}^{-})\Big]-\sum_{kl}\left[\varphi_{lk}(r_{lk})-\varphi_{lk}(s_{lk})\right]$$
$$+\tfrac{1}{2}M'\sum_{dkl} z_lq_d\hat{t}_{ld}\cdot\left[\hat{s}_{lk}\varphi_{lk}'(s_{lk})-\hat{t}_{lk}\varphi_{lk}'(t_{lk})\right]/t_{ld}^2+\tfrac{1}{2}M'\sum_{dd'l} z_lq_{d'}\hat{t}_{ld}\cdot\hat{t}_{ld'}\left[\varphi_{ld}'(t_{ld})-\bar{\varphi}_{ld}'(t_{ld})\right]/t_{ld'}{}^2. \quad (2)$$

Here, z_i are the ionic charges, $\mathbf{r}_{ij}=\mathbf{t}_{ij}+\boldsymbol{\xi}_i-\boldsymbol{\xi}_j$, $\mathbf{s}_{ij}=\mathbf{t}_{ij}-\boldsymbol{\xi}_j$, and $\varphi'(\bar{\varphi}')$ is the derivative of $\varphi(\bar{\varphi})$ with respect to its argument. The evaluation of the lattice sums $S^\pm$ and $\mathbf{T}^\pm$ is discussed in the Appendix. The expression (2) for U_2 is correct to quadratic terms in the relaxation parameters of the far ions, except for the omission of a term, the interaction energy of the long-range polarization with the undisplaced charges of the defects and their neighbors, which is cancelled by the same term in U_{12}.

The expressions of U_1 and U_{12} read:

$$U_1=(e^2/r_0)\Big\{\tfrac{1}{2}\sum_{kk'}{}' z_kz_{k'}(1/r_{kk'}-1/t_{kk'})+\sum_{kk'}{}' z_k(\mathbf{v}_{k'}\cdot\hat{r}_{kk'}/r_{kk'}{}^2)+\tfrac{1}{2}\sum_{kk'}{}'\left[\mathbf{v}_k\cdot\mathbf{v}_{k'}-3(\mathbf{v}_k\cdot\hat{r}_{kk'})(\mathbf{v}_{k'}\cdot\hat{r}_{kk'})\right]/r_{kk'}{}^3$$
$$+\tfrac{1}{2}r_0{}^3\sum_k \mathbf{v}_k{}^2/\alpha_k\Big\}+\tfrac{1}{2}\sum_{kk'}{}'\left[\varphi_{kk'}(r_{kk'})-\varphi_{kk'}(t_{kk'})\right], \quad (3)$$

where α_k is the electronic polarizability, and

$$U_{12}=(e^2/r_0)\Big[-\sum_{kk'}{}' z_kz_{k'}(1/s_{kk'}-1/t_{kk'})+\sum_{dk}{}' q_dz_k(1/s_{dk}-1/t_{dk})-\sum_{kk'}{}' z_k(\mathbf{v}_{k'}\cdot\hat{s}_{kk'}/s_{kk'}{}^2)+\sum_{dk}{}' q_d(\mathbf{v}_k\cdot\hat{s}_{dk}/s_{dk}{}^2)$$
$$+\sum_{dk} q_d(z_k\boldsymbol{\xi}_k+\mathbf{v}_k)\cdot(M_+'\mathbf{T}_{kd}{}^{+}+M_-'\mathbf{T}_{kd}{}^{-})\Big]+\sum_{kl}\left[\varphi_{kl}(r_{kl})-\varphi_{kl}(t_{kl})\right]. \quad (4)$$

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[10] A detailed derivation of these formulas will be given in an Argonne National Laboratory Report.

[11] We are measuring charges in units of the elementary charge e, distances and displacements in units of the nearest-neighbor distance r_0, and dipoles in units of er_0.

TABLE I. Parameters of the isolated vacancy.[a]

	NaCl				KCl				RbCl			
	Positive ion		Negative ion		Positive ion		Negative ion		Positive ion		Negative ion	
ξ	0.053	0.068	0.077	0.078	0.063	0.073	0.071	0.074	0.057	0.065	0.060	0.065
ν	−0.069	−0.064	0.0057	0.0056	−0.049	−0.047	0.020	0.020	−0.045	−0.043	0.027	0.027
U_{relax}	−3.28	⋯	−2.84	⋯	−2.78	⋯	−2.56	⋯	−2.58	⋯	−2.45	⋯
U_{rl}	7.98	7.98	8.14	8.14	7.28	7.28	7.40	7.40	7.09	7.09	7.18	7.18
U_v	4.70	4.71	5.30	5.27	4.50	4.50	4.84	4.82	4.51	4.49	4.73	4.70

[a] The two values given in each case pertain to the present procedure and to the customary procedure. Here and in the following tables energies are in eV, displacements and dipoles in units of r_0 and of er_0, respectively; a negative value for a relaxation parameter denotes an inward-pointing displacement or dipole.

In the derivation of U_{12} we have neglected the variation of the Madelung potential and field at the site k with ξ_k.

The energy U_1+U_{12} has to be minimized with respect to ξ_k and ν_k. The latter equilibrium condition yields, of course, ν_k as the product of the polarizability times the effective field, while the former condition yields the force-balance condition. The electrostatic force entering it does not consist merely of the usual charge-times-field term, but contains also a term involving the product of the ionic dipole with the field gradient. In the case of the isolated vacancy this second term acts on the first neighbors as an additional restoring force, and should therefore lead to a reduction in their displacements. Furthermore, the energy of formation differs somewhat from the average of the potential energies at its position. The numerical consequences of these discrepancies from the customary procedure will be discussed in Sec. III.

It remains to specify the short-range potential and the numerical data used in the calculations. We write the short-range interaction energy of two ions as

$$\varphi_{ij}(r_{ij})=\beta_{ij}b\exp[(r_i+r_j-r_{ij}r_0)/\rho]-c_{ij}/(r_{ij}r_0)^6-d_{ij}/(r_{ij}r_0)^8. \quad (5)$$

Here, β_{ij}, b, and ρ are the usual Pauling coefficients and the "strength" and "hardness" parameters for the Born repulsive energy, r_i and r_j are the ionic radii, and c_{ij} and d_{ij} are the coefficients of the dipole-dipole and dipole-quadrupole van der Waals energies. In evaluating relaxation energies we have truncated the van der Waals interactions, as well as the Born repulsive interactions, at second-neighbor ions.

We have adopted the values of the repulsive parameters reported by Tosi and Fumi[9] (Table I, first part), using for the alkali impurities the values of ρ appropriate to their chlorides. For the van der Waals coefficients we have adopted the values reported by Mayer,[12] using in the impurity-halogen interactions, the Mayer values appropriate to the pertinent chlorides, and, in the impurity-alkali host interactions, values computed from Mayer's primary data by his procedure. Finally, we have evaluated the Mott-Littleton relaxation parameters M', M_+', and M_-' from the electronic polarizabilities of Tessman *et al.*[13] and from the displacement polarizability determined by the short-range interactions.

III. NUMERICAL RESULTS

A. The Vacancy

We report in Table I the values of the displacement and the electronic dipole of the first neighbors of a vacancy, and of the relaxation energy $U_1+U_{12}+U_2$ at equilibrium, as well as the rigid-lattice energy change U_{rl} and the energy U_v required to extract an ion from the crystal. For comparison, we also give in each case the corresponding values computed by the customary procedure. The improved treatment indeed yields smaller local displacements, as expected, but this decrease in the local distortion is, of course, partly compensated by an increase in the local electronic dipoles. These effects are smaller for the negative-ion vacancy, whose neighbors carry a small electronic dipole. The agreement between the values of U_v yielded by the two procedures is satisfactory; the average potential-energy recipe, by itself, tends to raise somewhat the energy U_v (by 0.1 eV or less).

The foregoing conclusions are somewhat at variance from those reached by Kurosawa,[3] who may have adopted the same local relaxation in his comparison of the two procedures. We may also note that, when the short-range interactions are truncated at first-neighbor ions, the formulas given in Sec. II yield the expression for the energy of formation of a vacancy at equilibrium reported by this author. There are, however, minor discrepancies in the treatment of the short-range force on the near ions.

TABLE II. Parameters of the substitutional alkali impurity.

	Rb^+–KCl	K^+–RbCl	K^+–NaCl	Na^+–KCl	Rb^+–NaCl	Na^+–RbCl
ξ	0.018	−0.015	0.037	−0.031	0.061	−0.042
ν	0.0032	−0.0025	0.0084	−0.0060	0.013	−0.0075
U_{relax}	−0.04	−0.02	−0.18	−0.07	−0.62	−0.11
U_{rl}	0.26	−0.12	1.13	−0.40	2.16	−0.36
U_i	0.22	−0.14	0.95	−0.46	1.54	−0.47

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[12] J. E. Mayer, J. Chem. Phys. 1, 270 (1933).

[13] J. R. Tessman, A. H. Kahn, and W. Shockley, Phys. Rev. 93, 890 (1953).

TABLE III. Parameters of the host-ions migration.

	NaCl		KCl		RbCl	
	Positive ion	Negative ion	Positive ion	Negative ion	Positive ion	Negative ion
ξ_1	0.083	0.095	0.093	0.096	0.101	0.102
ξ_2	0.030	0.045	0.037	0.041	0.031	0.033
ν_1	0.041	−0.0029	0.027	−0.010	0.021	− 0.012
ν_2	−0.055	0.0042	−0.038	0.015	− 0.034	0.021
U_{relax}	−4.04	−3.62	−3.76	−3.55	− 4.56	− 4.43
U_{rl}	9.59	9.82	9.11	9.22	10.09	10.15
U_{sp}	5.55	6.20	5.35	5.67	5.53	5.72

B. The Substitutional Impurity

We report in Table II the values of the parameters for a substitutional alkali impurity. The quantity U_i is the energy required to replace (or, if its value is negative, gained in replacing) an alkali ion in its chloride by the indicated impurity.

The present model involves the neglect of the long-range lattice distortion around the impurity, which is of elastic origin. While this approximation is consistent with our treatment of the other defects, we expect our values for the local relaxation and for the relaxation energy to be affected by sizable uncertainties, in the light of the results of Hardy.[4] We may note, however, that the relaxation energy is only a small part of the energy U_i and is, in fact, generally quite small. Our values of U_i, therefore, can be confidently used as a reliable reference for the energy of the saddle-point configuration for the impurity.

C. The Saddle-Point Configuration

The saddle-point configuration for motion of an ion into a vacancy is chosen, as in Guccione *et al.*,[7] to be at the $(\frac{1}{2},\frac{1}{2},0)$ point in the unit cell. The displacement $\xi_1\sqrt{2}$ and the dipole $\nu_1\sqrt{2}$ of the two neighbors of the ion in the saddle-point position lie along the cube-face diagonal, whereas the other eight neighbors of the three defects are taken to have equal displacements ξ_2 and dipoles ν_2 lying along the cube edge. The parameters of the configuration for host ions and for alkali impurities are given in Tables III and IV, respectively. Here the quantity U_{sp} is the energy increase of the crystal in the saddle-point configuration over the perfect crystal.

We may remark that the values of the displacements and dipoles reported in Tables I, III, and IV show suggestive regularities. As one expects, the value of ξ_1 in a given salt increases with the radius of the migrating ion, and the value of ν_1 correspondingly decreases. On the other hand, the ion at the saddle-point position causes a reduction of the electrostatic force on the neighbors of the vacancy, and both ξ_2 and ν_2 (in absolute magnitude) are smaller than ξ and ν for the isolated vacancy. As the radius of the migrating ion increases, this effect becomes more pronounced, since the displacements of the two neighbors of the migrating ion increase its "effective charge."

TABLE IV. Parameters of the impurity-ions migration.

	NaCl		KCl		RbCl	
	K^+	Rb^+	Na^+	Rb^+	Na^+	K^+
ξ_1	0.134	0.169	0.040	0.125	0.019	0.071
ξ_2	0.027	0.025	0.043	0.032	0.040	0.035
ν_1	0.028	0.022	0.039	0.021	0.039	0.027
ν_2	− 0.051	− 0.048	−0.041	− 0.037	−0.038	−0.035
U_{relax}	− 6.86	−12.69	−2.52	− 6.24	−2.18	−2.93
U_{rl}	13.65	20.28	6.98	12.08	6.44	8.02
U_{sp}^{i}	6.79	7.59	4.46	5.84	4.26	5.09

IV. DISCUSSION

Table V collects the theoretical values for the basic energy parameters of the positive and the negative-ion vacancy. The energy of formation of the Schottky defect E_S has been obtained from the results reported in Table I as $E_S = U_v^+ + U_v^- - \frac{1}{2}(U_{\text{rl}}^+ + U_{\text{rl}}^-)$, where the last term is the energy of the perfect crystal per ion pair. The energies of formation of the two vacancies, E_v^+ and E_v^-, have been obtained as $E_v^\pm = U_v^\pm - \frac{1}{2}U_{\text{rl}}^\pm$, thereby neglecting the change in polarization energy associated with placing an ion back into a vacancy source. Because of this approximation, the theoretical values of $E_v^- - E_v^+$ given in the table are expected to be overestimates of this quantity in the salts under consideration, where the negative ion has a larger polarizability. Finally, the energies of vacancy migration for the host ions E_m^+ and E_m^-, have been obtained from the results reported in Tables I and III as $E_m^\pm = U_{\text{sp}}^\pm - U_v^\pm$.

TABLE V. Energy parameters of the vacancies.

	NaCl		KCl		RbCl	
	Theory	Experiment	Theory	Experiment	Theory	Experiment
E_s	1.94	2.12 ±0.06[a]	2.00	2.22–2.31[a,b,c]	2.10	...
$E_v^- - E_v^+$	0.52[d]	0.26 ±0.12[e]	0.28[d]	...	0.18[d]	...
E_m^+	0.85	0.80 ±0.02[a]	0.85	0.59–0.84[a,b,c]	1.02	...
E_m^-	0.90	1.06[f]	0.83	0.95 ±0.1[c]	0.99	...

[a] Reference 14.

[b] P. W. M. Jacobs and J. N. Maycock, Jr., Ref. 15.

[c] Reference 17.

[d] Estimated upper limit.

[e] Reference 18.

[f] From the activation energy for Cl^- diffusion in pure NaCl reported by N. Laurance, Ref. 16, after subtraction of $\frac{1}{2}E_s = 1.06$ eV.

TABLE. VI. Energy of solution of substitutional alkali impurities.

	Rb^+–KCl	K^+–RbCl	K^+–NaCl	Na^+–KCl	Rb^+–NaCl	Na^+–RbCl
Theory	0.02	0.06	0.23	0.26	0.62	0.45
Experiment	0.04[a]	0.04[a]	0.24[b]	0.20[b]	···	···

[a] From N. Fontell *et. al.*, Ref. 23.
[b] Estimated from the data of W. T. Barrett and W. E. Wallace, Ref. 24.

The table gives also the recent experimental values available for NaCl and KCl.[14–19] For RbCl, only the activation energies for ionic conductivity at high temperatures[20] (2.12 eV) and for the self-diffusion of Rb[21] (1.99 eV) have been determined experimentally. The theoretical value for this energy is 2.07 eV.

The over-all agreement of the theory with experiment displayed in the table can be considered satisfactory, in view of the fact that the theory is based on a self-consistent simple model. We note, however, that our values do not necessarily represent the true migration barriers, since the migration path may be somewhat different from the path that we have chosen.[7] More precise information on the potential at short separations, and improvements in the treatment of the lattice polarization, would be necessary for a meaningful theoretical investigation of this point.

The repulsive interionic potential used in these calculations differs from those used previously in two respects. First, its hardness is intermediate between that of the Born-Mayer potential and that of the Born-Mayer-Verwey potential in KCl, and actually closer to the latter in NaCl. The present potential is fully consistent with the ionic-model analysis of the cohesive properties, in that it fits the experimental values of the first and second derivative of the short-range part of the lattice energy at the equilibrium interionic distance. We note in this connection that, while the assumption of a common r^{-n} repulsion in the solid and in the molecule is essential in the ionic-model analysis of molecular properties given by Verwey and de Boer,[8] the r^{-12} form derived from this analysis is definitely inconsistent with the compressibility data in the solid state; for an r^{-n} repulsion, these data yield values of n of about 9 in the salts that we are considering.[22] Therefore, the Verwey potential is useful to gauge the sensitivity of defect energies to the probable hardening of the repulsion at small separations, but cannot be regarded as providing a quantitative description of these effects. Second, the apportionment of the repulsive contribution to the cohesive energy between the various ion pairs in each crystal is different from that in the old potentials. The analysis of the cohesive properties is not very sensitive to these details, but evidence in favor of the essential correctness of this change is afforded by the comparison of the ionic radii with the apparent sizes of ions in crystals.[9]

These effects, as well as the improved treatment of the nearest-neighbors distortion, lead to an increase in both $U_v^- - U_v^+$ and $U_{sp}^- - U_{sp}^+$ in such a way that the theoretical migration barriers for a positive and a negative ion in the same salt are consistently practically the same. The increase in the value of $U_v^- - U_v^+$ is consistent with the experimental results of Strumane and De Batist[18] for NaCl, but, because of the difficulty mentioned at the beginning of this section, this comparison does not provide a stringent test of this aspect of the theory. The consistent vanishing of $E_m^- - E_m^+$ is a disappointing result; the experiments indicate that this quantity may be as large as 0.3 eV in both NaCl and KCl. At any rate, the theoretical analysis indicates that this difference in migration barriers is associated with second-order effects and should therefore be rather small. Perhaps additional diffusion and ionic-transport number measurements would be desirable to firmly settle this point.

Tables VI and VII present the theoretical values for the energy parameters of the substitutional alkali impurities. The energies of solution per solute molecule at infinite dilution, given in Table VI, have been obtained from the results reported in Tables I and II by the relation[6] (energy of solution) $= U_i -$ (lattice energy

TABLE VII. Activation energies for substitutional impurities.

	NaCl		KCl		RbCl	
	K^+	Rb^+	Na^+	Rb^+	Na^+	K^+
E_i	1.14	1.35	0.42	1.12	0.22	0.72
E_d	2.11	2.32	1.42	2.12	1.27	1.77

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[14] R. W. Dreyfus and A. S. Nowick, J. Appl. Phys. **33**, 473 (1962).

[15] A. R. Allnatt and P. W. M. Jacobs, Trans. Faraday Soc. **58**, 116 (1962); P. W. M. Jacobs and J. N. Maycock, Jr., J. Phys. Chem. Solids **24**, 1693 (1963).

[16] N. Laurance, Phys. Rev. **120**, 57 (1960).

[17] R. G. Fuller, Phys. Rev. **142**, 524 (1966). We are indebted to Dr. Fuller for an unpublished report of his work.

[18] R. Strumane and R. De Batist, Phys. Status Solidi **6**, 817 (1964).

[19] For a complete compilation of the older experimental results on ionic conductivity and diffusion see R. J. Friauf, S. O. Morgan, and W. J. Merz, in *American Institute of Physics Handbook* (McGraw-Hill Book Company, Inc., New York, 1963). An excellent, recent review of the theory of matter transport in solids has been given by R. E. Howard and A. B. Lidiard, Rept. Progr. Phys. **27**, 161 (1964).

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

[21] G. Arai and J. G. Mullen, Phys. Rev. **143**, 663 (1966).

[22] M. P. Tosi, Solid State Phys. **16**, 1 (1964).

Table VIII. Long-range polarization potentials.

$d \backslash d'$	(0,0,0)	$(\frac{1}{2},\frac{1}{2},0)$	(1,1,0)
(0,0,0)	6.08458	5.49363	4.27462
	3.89552	3.62205	3.24314
$(\frac{1}{2},\frac{1}{2},0)$	5.49363	6.13475	5.49363
	3.62205	3.71689	3.62205

Table IX. Long-range polarization fields.

$d \backslash k$	$(-1,0,0)$[a]	(0,0,1)[b]	(1,0,0)[a]
(0,0,0)	−1.88284	1.82897	1.61150
	−0.28342	0.25023	0.31978
$(\frac{1}{2},\frac{1}{2},0)$	−1.76170	1.72724	0.50885
	−0.48797	0.18920	−0.10755
(1,1,0)	−1.21992	1.12429	−0.70711
	−0.52557	0.19349	−0.42757

[a] Component along the [100] direction.
[b] Component along the [001] direction.

of solvent)+(lattice energy of solute). The experimental values given in the table for the systems KCl–RbCl and NaCl–KCl have been estimated from the heat of formation of solid solution versus composition data reported by Fontell *et al.*[23] and by Barrett and Wallace,[24] respectively, by an extrapolation to infinite dilution. The agreement between theory and experiment is quite good.

The values of the energy $E_i = U_{\text{sp}}{}^i - (U_i + U_v{}^+)$ of the saddle-point configuration for the impurity, relative to a crystal containing a positive-ion vacancy and a substitutional impurity at infinite separation, and of the energy $E_d = E_i + \frac{1}{2}E_S$, are reported in Table VII. Barring temperature-dependent correlation effects, E_d represents the activation energy for diffusion of a substitutional impurity in the intrinsic temperature range. The agreement of the theoretical values with the recent experimental values[21] of the activation energy for diffusion of Rb^+ in NaCl (2.11 eV) and in KCl (2.04 eV) is comparable to the agreement displayed in Table V for the host-ion migration, although the theoretical values are somewhat too large, especially in the former system. No experimental studies of comparable accuracy are available for the diffusion of monovalent impurities smaller than the host ions.

The values of E_i, when compared with the values of $E_m{}^+$ given in Table V, display clearly a size effect in impurity migration. In reality, however, one can expect size effects in monovalent impurity diffusion of comparatively simple interpretation only if the impurity radius is quite close to the host-ion radius, even if one assumes a vacancy mechanism. On the one hand, the "saddlepoint" configuration that we have considered may actually become a stable associated configuration for sufficiently small monovalent (or divalent) impurities, because the Coulomb energy of the crystal is lowered in this configuration. In this connection, we should point out that a simple calculation, based on the present model, of the energy of interaction between a positive ion vacancy and an alkali impurity constrained to sit at the (110) position yields a small repulsion, of the order of a few hundredths to a tenth of an eV, for small impurities and an attraction of the same order of magnitude for large impurities. On the other hand, the migration path along the cube-face diagonal is favored by the Coulomb interactions, but opposed by the short-range repulsive interactions, with respect to other paths through the body of the cell,[7] so that different migration paths may become competitive as the impurity radius increases. Among the systems studied in this work, this is very likely to occur for Rb^+ in NaCl, and possibly also for K^+ in NaCl. It is noteworthy that the pre-exponential term in the diffusion coefficient for Rb^+ in NaCl is unaccountably large[21] (about an order of magnitude larger than in KCl).

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APPENDIX: EVALUATION OF LATTICE SUMS

The sums $S_{kd}{}^{\pm}$ and $\mathbf{T}_{kd}{}^{\pm}$ entering Eqs. (2) and (4) represent the potential and the field (in units of $-q_d M_{\pm}'$) at the kth site due to the dipoles induced by the defect d in the positive or negative far ions. Thus:

$$S_{kd}{}^{\pm} = \sum_l{}^{(\pm)} \hat{t}_{ld} \cdot \hat{t}_{lk} / (t_{ld}{}^2 t_{lk}{}^2) , \tag{6}$$

$$\mathbf{T}_{kd}{}^{\pm} = \sum_l{}^{(\pm)} [\hat{t}_{ld} - 3\hat{t}_{lk}(\hat{t}_{ld} \cdot \hat{t}_{lk})] / (t_{ld}{}^2 t_{lk}{}^3) , \tag{7}$$

where the sums are restricted to positive or negative ions.

We evaluate these sums by direct summation over shells of ions up to $t_{ld} \simeq 10$ and approximate their remainders by the remainders of the sums $S_{dd}{}^{\pm}$ and $\mathbf{T}_{dd}{}^{\pm}$, a method which allows high numerical accuracy.[25] In effect, the $\mathbf{T}$ sums converge fairly rapidly, and for the isolated-defect configuration our calculation reproduces the values obtained by Mott and Littleton[1] by direct summation over 23 shells.

The values of the sum of interest for the saddle-point configuration are collected in Tables VIII and IX.

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[23] N. Fontell, V. Hovi, and L. Hyvönen, Ann. Acad. Sci. Fennicae Ser. **AI**, No. 65 (1949).

[24] W. T. Barrett and W. E. Wallace, J. Am. Chem. Soc. **76**, 366 (1954).

[25] H. B. Rosenstock, Phys. Rev. **131**, 1111 (1963).

For each pair of sets of coordinates, we give first the value of the sum over ions having the same sign as the migrating ion at the $(\frac{1}{2},\frac{1}{2},0)$ position, and then the value of the sum over ions of opposite sign. The S sums agree within 1% with those calculated by Guccione *et al.*[7] by the same method, with a direct summation up to $t_{ld} \simeq 4$.

Finally, the evaluation of Eq. (1) for the saddle-point configuration involves the evaluation of the dipole-dipole and dipole-quadrupole van der Waals potentials of the perfect lattice (excluding the two vacancies) at the $(\frac{1}{2},\frac{1}{2},0)$ position. The pertinent sums can be obtained from the sums A_s and C_s over points of a simple cubic and of a face-centered-cubic lattice reported by Jones and Ingham,[26] for $s=6$ and $s=8$, as $\frac{1}{6}(2^{s/2}C_s - A_s)$.

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[26] J. E. Jones and A. E. Ingham, Proc. Roy. Soc. (London) **A107**, 636 (1925).

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Lattice Vibration Spectra of $GaAs_xP_{1-x}$ Single Crystals*

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The energies of the two-phonon summation bands and the reststrahlen bands have been measured in $GaAs_xP_{1-x}$ single crystals. The data were obtained by observing the transmittance and the reflectivity at 300°K in the region of 400 to 800 cm^{-1} and 220 to 500 cm^{-1}, respectively. Crystals were prepared by open-tube epitaxial vapor-growth techniques and were not subject to any free-carrier absorption in the near infrared. The alloys show absorption peaks at frequencies which are only slightly shifted from the transverse optic TO(Γ) phonons, as well as several optical and acoustical zone-boundary phonons, characteristic of both GaP and GaAs. The reststrahlen-like band spectra of these alloys are explained by a virtual-crystal model in which average parabolic potentials are given to the three species of atoms in the lattice. This model does not require the assumption of gross composition inhomogeneities, which are known to be absent in these crystals.

I. INTRODUCTION

THE determination of the vibrational spectra of disordered systems is a problem that has attracted many workers in the past few years. Dean[1] applied mathematical techniques to obtain quantitatively accurate results for the spectra of disordered diatomic chains. A complete theory of three-dimensional disordered systems is yet to be developed. The alternative approach is to study such systems by the experimental method.

Some data have already been reported for a few semiconductor binary alloy systems. Oswald[2] studied a reststrahlen band in various composition alloys of $InAs_xP_{1-x}$, which has a frequency close to that of pure InP. He found that the wavelength increased very slightly and the intensity decreased with increasing x. Since the maximum wavelength of his measurement was 35 μ, he could not study any changes associated with a pure InAs band[3] of 45 μ at large x.

The infrared spectral absorptances of thin films of $GaAs_ySb_{1-y}$ have been studied by Potter and Stierwalt.[4] They found a single peak whose frequency shifted continuously with increasing y from that of pure GaSb to that of pure GaAs. This result is qualitatively different from the type of results presented below.

Finally, the vibrational spectra of Si-Ge alloys have been studied. Braunstein[5] found infrared absorption spectra which indicated the existence of modes associated with both pure Ge and pure Si.

In contrast, Logan *et al.*[6] reported that the composition dependence of a particular phonon mode, obtained from a tunneling experiment, was continuous and single-valued in the alloy. It should be noted that first-order photon-phonon interaction cannot be observed in Si-Ge alloys because of their homopolar nature, whereas it can be observed in diatomic compounds. In addition, the interpretation of the tunneling experiments in disordered crystals is somewhat uncertain. It is clear that more experimental work is needed in this field.

In this work, the interaction of photons with phonons in $GaAs_xP_{1-x}$ single crystals was investigated over a

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[1] P. Dean, Proc. Roy. Soc. (London) **A254**, 507 (1960).

[2] F. von Oswald, Z. Naturforsch. **14a**, 374 (1959).

[3] G. Picus, E. Burnstein, B. W. Henvis, and M. Hass, J. Phys. Chem. Solids **8**, 282 (1959).

[4] R. F. Potter and D. L. Stierwalt, in *Proceedings of the International Conference on The Physics of Semiconductors, Paris, 1964* (Academic Press Inc., New York, 1965), p. 1111.

[5] R. Braunstein, Phys. Rev. **130**, 879 (1963).

[6] R. A. Logan, J. M. Rowell, and F. A. Trumbore, Phys. Rev. **136**, A1751 (1964).