to many factors but probably occurs because of the difference in radiation temperature. When specimens which had previously been irradiated at 60°C were electron irradiated at temperatures higher than 90°C there was a noticeable decrease in the total F-center concentration. This suggests that radiation annealing is important at temperatures in excess of 90°C.

Mention should perhaps be made at this point of a somewhat puzzling result of the investigation. Even though it was possible to produce measurable quantities of F centers by electron and neutron irradiation there was no evidence for the creation of a corresponding number of positive-ion vacancies even though magnesium should have a larger displacement cross section than oxygen. In the past, positive-ion vacancies which have trapped holes, V_1 centers, have been identified in lightly irradiated MgO crystals,[12,28] and it was hoped that the production of positive-ion vacancies could be monitored optically as was the creation of the negative-ion vacancies. However, it was found that for electron irradiation the absorption band due to V_1 centers grew rapidly at very low doses and then saturated long before there was any evidence of F-center absorption.

CONCLUSION

The strong temperature and radiation intensity dependence of the coloration in alkali halide crystals is well documented.[1–3] This as well as the energy dependence of F-center production in these materials[29] indicates that the dominant radiation damage mechanism is not one of elastic collisions. On the other hand, the results presented above for MgO are very consistent with the idea that the primary damage mechanism is that of elastic collisions. Therefore, we are drawn to the tentative conclusion that crystal ionicity or crystal bonding may make a significant difference in the mechanism of radiation damage.

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Ionic-Model Theory of Polar Molecules*

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A simple extension of the current models of lattice dynamics is used to evaluate the binding energy, the internuclear distance, the electric dipole, and the vibrational frequency of the alkali-halide molecules from solid-state properties. An extensive comparison with experimental data suggests that the models may be useful as an empirical scheme of interpolation between the perfect crystal and the molecule. A polarization catastrophe in the standard ionic theory is discussed.

QUALITATIVE considerations suggest that the classical theory of ionic systems should provide a reasonably accurate first-order description of the properties of the alkali-halide molecules. Thus, the observed electric dipoles are quite close to their polarized-point-ion value and, as in the solid, the interpenetration of the ions still affects only the tails of the outer electron shells. These considerations have prompted investigations of these molecules by the classical theory,[1,2] which have, however, found it necessary to postulate a very sizeable stiffening of the short-range potential appropriate to the solid in order to fit such molecular properties as the internuclear distance and the vibrational frequency. In this note we show that the difficulty arises from the treatment of induced dipoles and that the discrepancy between the solid and the molecule is largely removed by the inclusion of short-range polarization.

In a tight-binding approach one may express the Hamiltonian of the ion pair through the multipole expansion, including short-range couplings between the various poles in addition to the classical electrostatic couplings. We write the potential energy of the ion pair, as a function of the internuclear distance r and of the electronic dipoles m_+ and m_-, as follows:

$$U(r,m_+,m_-)=-\frac{e^2}{r}-(m_++m_-)\frac{e}{r^2}-\frac{2m_+m_-}{r^3}+\frac{m_+^2}{2\alpha_+}+\frac{m_-^2}{2\alpha_-}+m_-B(r)+\varphi(r). \quad (1)$$

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By comparison with the multipole expansion it is apparent that, in addition to the standard assumption on the magnitude of the monopoles, we have made the following approximatons: (1) We have neglected quadrupoles and higher multipoles; (2) we have linearized the dipole contribution; (3) we have neglected the distance dependence of the electronic polarizabilities α_+ and α_-; (4) we have neglected the short-range coupling between the two dipoles; (5) we have neglected the antimorph of the term $m_- B(r)$ for the positive ion. No quantitative information is available on the first three points, and we will comment later on the last two. We have allowed for deviations from a polarizable point-ion model through the inclusion of the term $m_- B(r)$, where the function $B(r)$ is assumed to be proportional to the repulsive part of the short-range potential $\varphi(r)$ through the deviation of the Szigeti effective charge from unity. Specifically,

$$B(r) = -\frac{e}{2\alpha_-}\left(1 - \frac{e^*}{e}\right)\varphi_{\text{rep}}(r) \bigg/ \left[\varphi_{\text{rep}}'(r_0) + \frac{2}{r_0}\varphi_{\text{rep}}(r_0)\right], \quad (2)$$

where e^*/e is the Szigeti effective charge and r_0 is the lattice parameter. After linearization, this model is basically equivalent to a simple version of the shell model which already gives a rather accurate account of the photonon dispersion curves in the alkali halides with physically reasonable values of the parameters.[3] Except for our approximation (5), it coincides with the model used by Kurosawa[4] in his theory of the Schottky defect.

The dipoles and the energy as functions of the internuclear distance are given by

$$m_+(r) = \alpha_+\left[\frac{e}{r^2} + \frac{2m_-(r)}{r^3}\right], \quad (3)$$

$$m_-(r) = \alpha_-\left[\frac{e}{r^2} + \frac{2m_+(r)}{r^3} - B(r)\right], \quad (4)$$

$$U(r) = -\frac{e^2}{r} - \tfrac{1}{2}[m_+(r) + m_-(r)]\frac{e}{r^2} + \tfrac{1}{2}m_-(r)B(r) + \varphi(r). \quad (5)$$

As is apparent from these equations, the term $B(r)$ may be interpreted either in the shell model as a short-range bodily shift of the outer electron shell of the negative ion whose self-energy is explicitly included, or as a screening of the point-ion electric field of the positive ion arising from deformations in the overlap region, the self-energy of the deformations and the modifications of the charge-charge term being included in the short-range potential. On the other hand, the deformation dipole model of Hardy[5] interprets the deformations in the overlap region as a dipole which is transferred to the center of the negative ion. This model leads to the same equations for the dipoles, but the term $\frac{1}{2}m_-(r)B(r)$ in Eq. (5) would contain only the electrically induced dipoles.

We have used the models discussed above to carry out the following calculations. First the energy $U(r)$ is minimized to find the equilibrium internuclear distance r_e and the binding energy $-U(r_e)$. Then, the electric dipole of the molecule is evaluated as

$$d = er_e - m_+(r_e) - m_-(r_e). \quad (6)$$

Finally, the vibrational frequency of the molecule is evaluated from the second derivative of the energy at equilibrium as

$$\omega_e = 4.1210\left[\left(\frac{d^2U(r)}{dr^2}\right)_{r=r_e} \bigg/ \mu_A\right]^{1/2} \text{cm}^{-1}, \quad (7)$$

where μ_A is the reduced mass of the molecule in atomic-weight units. All the parameters of the theory in its present simple form can be determined for each molecule from the cohesive and dielectric properties of its solid by standard procedures.

In carrying out these simple calculations, we have tested the effects of the functional form of the potential and of the many-ion contributions to the crystal stiffness by adopting an exponential and an inverse power potential, fitted to the thermally corrected lattice parameter and compressibility,[6] and the Born-Mayer popotential, inclusive of the van der Waals interactions.[7] We report in Table I the average of the three results for each molecular property as well as its full range of variation. Uncertainties in the thermal correction of the compressibility are probably more important in some instances, and we may have underestimated somewhat the stiffness of the potential in view of the well-known deviations from the first Szigeti relation. The electronic polarizabilities were taken from Tessman *et al.*[8]: The analysis of these authors suggests that our approximation (4) is not very important. The Szigeti effective charge was taken from Hardy[5]; reasonable uncertainties of a few percent in e^*/e affect the results by amounts comparable to those given in the table. The results are quite insensitive to the detailed partition of the polarization among the two ions, justifying our approximation (5).

We regard the agreement between the model and experiment displayed in the table as satisfactory, in view of the fact that no molecular property was fitted in these calculations. The agreement is good for the internuclear distance and the vibrational frequency and scattered for the electric dipole, while the binding energy is over-

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TABLE I. Internuclear distance, electric dipole, binding energy, and vibrational frequency of the alkali-halide molecules.[a]

	$1-\frac{e^{*}}{e}$[b]	r_e (Å)		d(Debye)		$-U(r_e)$ (eV)		ω_e (cm^{-1})	
		Theory	Expt.	Theory	Expt.	Theory	Expt.	Theory	Expt.
LiF	0.17	1.508±0.106	···	6.55±0.47	···	8.13±0.29	7.80	903±108	···
LiCl	(0.27)	2.058±0.108	···	7.86±0.51	···	6.51±0.20	6.53	695±57	···
LiBr	(0.32)	2.249±0.109	2.1704	8.40±0.52	6.19±0.15	6.09±0.17	6.25	616±53	(480)
LiI	···	2.096[c]	3.2919	3.11[c]	6.25±0.20	6.94[c]	5.92	821[c]	50
NaF[d]	0.07	1.733±0.066	···	6.98±0.42	···	7.22±0.14	6.52	603±45	···
NaCl	0.26	2.383±0.046	2.3606	9.58±0.26	8.5±0.4	5.71±0.05	5.64	402±28	380
NaBr	0.31	2.527±0.056	2.5020	9.97±0.27	···	5.42±0.06	5.41	325±23	315
NaI	0.29	2.677±0.093	2.7115	9.88±0.48	···	5.17±0.10	5.15	289±26	286
KF[d]	(0.12)	2.104±0.049	···	8.47±0.30	8.62	6.19±0.07	5.88	426±32	405
KCl	0.20	2.635±0.054	2.6666	10.24±0.29	10.48	5.21±0.03	5.01	312±20	305
KBr	0.24	2.823±0.040	2.8207	10.86±0.40	10.41	4.94±0.03	4.79	253±16	230
KI	0.31	3.061±0.044	3.0478	11.67±0.24	11.05	4.61±0.03	4.53	214±14	200
RbF	(0.05)	2.137±0.146	···	7.63±0.78	···	6.16±0.25	5.65	415±41	390
RbCl	0.16	2.813±0.045	2.7868	10.74±0.28	···	4.99±0.04	4.83	274±17	270
RbBr	0.18	2.945±0.050	2.9448	11.03±0.32	···	4.79±0.04	4.60	201±13	181
RbI	0.21	3.194±0.044	3.1769	11.78±0.28	···	4.50±0.03	4.36	172±11	147

[a] The experimental values of r_e, d, and ω_e are from A. Honig *et al.* [Phys. Rev. **96**, 629 (1954)]; the thermal correction in r_e is of the order of $(0.4\%)^2$ and, therefore, negligible for our purposes. The binding energy relative to the free-ion state has been redetermined from thermochemical heats, ionization potentials, and electron affinities; uncertainties are probably of the order of 0.1 eV or larger. As discussed in the text, the uncertainities attached to the theoretical results are not a measure of the uncertainty of the theory.

[b] From J. R. Hardy, Ref. 5; values in parentheses are from J. M. Boswarva and A. B. Lidiard [Atomic Energy Research Establishment, Research Report T. P. 232, 1966 (unpublished)] and are apparently estimates based on Hardy's work. Hardy's value for NaF is in violent disagreement with the value 0.17 calculated by E. E. Havinga [Phys. Rev. **119**, 1193 (1960)] with a more recent value of the static dielectric constant. The use of Havinga's value raises the dipole moment by 1 D and decreases the binding energy by 0.3 eV.

[c] Evaluated without short-range polarization by the inverse power potential. No minimum was found with the other potentials.

[d] No minimum was found with the Tosi-Fumi potential.

estimated by 0.2 eV on the average. The use of the deformation dipole model does not change grossly the quality of the results; the system is slightly stiffened, by amounts lying within or just outside the ranges given in the table.

The algebraic solution of Eqs. (3) and (4) shows that the model undergoes a polarization catastrophe at $r=(4\alpha_{+}\alpha_{-})^{1/6}$. This is a consequence of the linear response assumption, although its location is determined by our approximations (3) and (4). When we neglect the short-range polarization, no minimum can be found in several instances, while, in those instances where the potential is stiffening sufficiently at small separations to provide a metastable minimum, the results are grossly inadequate. An illustration of the quality of the results is provided by lithium iodide, for which the Szigeti effective charge is not known experimentally and is difficult to estimate from Hardy's work. Clearly, the same difficulty may in principle arise in other configurations where neighboring ions carry parallel induced dipoles which reinforce each other. Convergence difficulties have been reported in recent studies of the configuration of the surface[9] and of small impurities[10] in the alkali halides. These studies and a preliminary application of our model to the study of the surface[11] indicate that, owing to second-neighbor repulsions, such difficulties become relevant in the solid state only when small ions are involved.

The success of the present models in the range of internuclear separations of interest in our calculation is therefore due to the fact that the inclusion of short-range polarization maintains the induced dipoles small over a sizable range of separation. In this connection, we may recall that the instabilities[12] and the grave deficiencies[13] of early lattice dynamics calculations were also removed by the same physical effect.[3,5,13] There is little doubt, however, that the classical theory has here been extended close to the limit of its applicability. In particular, the model is clearly not a sensible one when the deformation dipole becomes comparable with the electrically induced dipole; this occurs at separations of the order of 0.6 to 0.7 times the lattice parameter. The internuclear distances in the molecule are of the order of (0.8 to 0.9)r_0.

In conclusion, we feel that, while detailed quantum-mechanical calculations are necessary for a full exploration of this problem and may provide information on the ionic polarization mechanisms of relevance to the solid state, the present calculations suffice to provide insight on its main features.

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