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Solubility of Divalent Impurities in the Alkali Halides

R. C. Bowman, Jr.

Monsanto Research Corporation, Mound Laboratory, Miamisburg, Ohio 45342*

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The Born model of ionic solids was used to determine theoretical solution enthalpies of divalent impurities in the alkali halides, in the limit of infinite dilution. These calculations are based upon a generalized Mott-Littleton theory for reasonable values of the host-impurity parameters. Results are reported for Sr^{++} and Ba^{++} in NaCl, KCl, and RbCl.

Many physical properties of ionic solids are sensitive to the presence of trace amounts of aliovalent impurities. Although this is a general phenomenon, most studies¹⁻³ have been concerned with the cubic alkali halides containing small quantities of divalent impurity cations. This interest is the result of the availability of good-quality single crystals to which small concentrations of specified impurities have been added. Thus, interpretation¹ of the experimental results is greatly simplified. Since the alkali halides can be adequately described by the Born theory of ionic solids, it is possible to obtain theoretical values of defect parameters after a reasonable effort.

The solubility of an impurity ion in a crystal lattice is an important parameter. For a divalent impurity in the alkali halides, the enthalpy of solution, χ , can be readily obtained from ionic conductivity measurements in the "extrinsic" temperature region. Although lattice calculations⁴⁻⁶ based upon the Born-Mayer model have successfully predicted χ values for monovalent impurities in the alkali halides, similar calculations^{7,8} for divalent impurities have failed. According to Fumi and Tosi,⁵ the major difficulty in these later studies has been the use of experimental lattice energies for the halides of divalent cations while using theoretical parameters in the remainder of the calculation. Most divalent metal halides cannot be properly treated by the Born theory because they possess noncubic crystal structures. This problem does not arise for the monovalent impurities. In this report, theoretical χ values are reported for the solubility of Sr^{++} and Ba^{++} in NaCl, KCl, and RbCl crystals,

in the limit of infinite dilution. Also, Sr^{++} and Ba^{++} Born parameters consistent with recent alkali-halide data⁹ have been estimated for the cubic SrCl_2 and BaCl_2 salts.

The lattice-model expression for the enthalpy of solution of divalent impurities in alkali halides is

$$\chi = 2W_+ - W_1 + 2W_{LA} - W_{LB}.$$

Here, W_{LA} and W_{LB} are the lattice energies of the alkali halide and the halide of the divalent cation, respectively; W_+ is the energy required to remove an alkali ion from the pure alkali halide to a state of rest at "infinity"; and W_1 is the energy required to remove a divalent impurity ion at equilibrium on a cation lattice site to a state of rest at infinity. The lattice energies can be obtained by straightforward application of the familiar Born-Mayer model.¹⁰ Because ions around a defect relax when the defect is produced and in directions depending upon the parity of charges of the ions and the defect, calculation of the energy required to remove an ion is taken as the average of the energies at the lattice site for the initial and final configurations. The energies W_+ and W_1 can only be determined when the

Table I. Born parameters and lattice energies for SrCl_2 and BaCl_2

	r_{++} (Å)	r_-^a (Å)	ρ (Å)	b (eV)	W_L (eV)
SrCl_2	1.35	1.65	0.278	0.2004	21.876
BaCl_2	1.50	1.65	0.281	0.2110	21.853

^aRef. 9.

Table II. Enthalpies of solution of divalent cation impurities in the alkali chlorides. Relaxation parameters and experimental χ values are also included.

Crystal	Impurity	λ_+	λ_1	W_+ (eV)	W_1 (eV)	χ_{calc} (eV)	χ_{exp} (eV)
NaCl	Sr ⁺⁺	0.0892	0.0072	4.676	14.548	0.900	0.78, ^a 1.80, ^b 1.80 ^c
	Ba ⁺⁺	0.0892	0.0540	4.676	13.243	1.182	0.99, ^a 2.00 ^b
KCl	Sr ⁺⁺	0.0832	-0.0794	4.475	14.954	1.548	1.43 ^d
	Ba ⁺⁺	0.0832	-0.0336	4.475	13.688	1.791	
RbCl	Sr ⁺⁺	0.0770	-0.1148	4.359	15.164	1.646	
	Ba ⁺⁺	0.0770	-0.0698	4.359	13.906	1.881	

^aRef. 13.^bRef. 14.^cRef. 15.^dRef. 16.

relaxations λ_+r_0 (displacement of six nearest neighbors of the cation vacancy) and λ_1r_0 (displacement of six nearest neighbors of the impurity ion) are known. Here, r_0 is the equilibrium separations between cations and anions in pure alkali halides. In this work, the relaxations λ have been calculated using a generalization of the "force-balance" method developed by Mott and Littleton.¹¹ Terms arising from Coulombic, electric polarization, elastic polarization, and exponential-overlap repulsive interactions are included in the equations. The elastic polarization terms are based upon the recent Boswarva-Lidiard¹² model while the other contributions are given by traditional expressions.¹ Interactions between next nearest neighbors are explicitly included in all calculations although van der Waals and deformation dipole terms have been neglected.

The numerical data and lattice energies for the alkali halides are taken from the work of Boswarva and Lidiard¹² while the data for SrCl₂ and BaCl₂ are listed in Table I. These Sr⁺⁺ and Ba⁺⁺ Born-Mayer parameters are required for the impurity-host interaction potentials and have been determined from the Tosi-Fumi^{9,10} chloride radius and the cohesive energies deduced using a thermochemical cycle.

Theoretical χ values obtained from the calculation scheme outlined above are collected in Table II along with the corresponding relaxation parameters and energies. Experimental values of χ determined in recent ionic conductivity studies are also included in Table II. The calculated values for Sr⁺⁺ and Ba⁺⁺ in NaCl are in fair agreement with the solution enthalpies determined from the slope of the conductivity curve in the precipitation region.¹³ However, they are significantly smaller than more reliable values obtained by studies^{14,15} on crystals with varying concentrations of the impurity. These low χ values may be a manifestation of the known³ "polar-

ization catastrophe" which could arise from the excessive ion overlap in this system. This explanation is supported by the good agreement between calculated and experimental χ values (Table II) for the KCl-Sr⁺⁺ system¹⁶ where there is much less ionic overlap. Experimental solution enthalpies for the other systems are not available to allow further comparison.

In summary, positive enthalpies of solution were calculated for all systems considered in the present study in contrast to earlier work compiled by Lidiard,¹ where negative χ values were determined for all impurities except Cd⁺⁺ (not treated here). The Ba⁺⁺ ion is predicted to be more insoluble (i.e., a larger χ) than Sr⁺⁺ for all salts studied. While being reasonable for NaCl and KCl because of larger ionic radii and mass differences, this result is rather surprising for RbCl. Although Sr⁺⁺ has a mass nearly equal to Rb⁺, its ionic radius is significantly smaller.⁹ Intuitively, the greater relaxation about Sr⁺⁺ is expected to reduce the solubility of this ion relative to Ba⁺⁺. However, the mass difference may be an important parameter. An experimental study of the solubilities in this system should prove most interesting.

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Cascade Theory of Inelastic Scattering of Light

R. M. Martin* and C. M. Varma

Bell Telephone Laboratories, Murray Hill, New Jersey 07974

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Scattering of light from solids with incident frequency above the band gap is shown to occur as a cascade process in which the electron (hole) makes successive transitions between real states with a small probability of radiative recombination at each step. This gives rise to multiple LO-phonon Stokes-shifted lines in agreement with experimental results.

Light-scattering experiments¹⁻⁵ in semiconductors using incident frequency near resonance with fundamental electronic transitions show an increase in the cross section over those measured away from resonance. The increase is especially striking for Stokes lines shifted by multiples of the longitudinal-optical (LO) phonon energies. The most dramatic results²⁻⁵ have been obtained when both incident- and scattered-photon energies (ω_i and ω_s) are above the band gap E_g ; in such cases it has been possible to observe LO-shifted lines to seemingly arbitrary order. Indeed, Leite, Scott, and Damen² have observed ninth order Stokes lines in CdS. Since the electron-phonon coupling constant α is only about 0.7, the origin of such high-order processes is both puzzling and interesting.

We show here that for photons above E_g , inelastic scattering of light occurs via a cascade process in which the electron-hole pair centered by the photon scatters successively to real states separated by the LO-phonon energy ω_0 (neglecting phonon dispersion). From each state there is a small probability of radiative decay at frequencies shifted from the incident frequency by an integral number of LO-phonon energies. The result of such a cascade process is that so long as $\omega_i, \omega_s > E_g$, the relative intensities of the various Stokes-shifted lines are independent of the coupling constant α and depend only on the dispersion curves of the electron and hole bands. This behavior contrasts with Raman scattering

for $\omega_i < E_g$ where the intensity of the n th order line varies as α^n .

To elaborate on these remarks, consider the processes that occur when a photon resonant with a line in the continuum of electronic states is incident on the crystal. Real absorption is the dominant process on the time scale of recombination, and an electron-hole pair of momentum $\vec{k}_i \approx 0$ is created. We classify the processes that can occur with the electron-hole pair thus created as (i) LO-phonon emission; (ii) radiative recombination; (iii) other processes, elastic or inelastic, involving scattering with impurities, acoustic phonons, transverse-optic phonons, etc. For $\alpha \lesssim 1$ it is a good approximation to neglect processes in which more than one LO phonon is emitted simultaneously. The lifetime τ_{LO} for a real transition of the electron (hole) to a state of energy ω_0 below the initial state is $O(10^{-13}$ sec); the lifetime of (ii) and (iii) together is much longer, $O(10^{-9}$ sec) [the lifetime due to (ii) is discussed in more detail below]. We thus conclude that the electron-hole pair successively occupies real states of energy $n\omega_0$ ($n=1, 2, \dots$) below the initial state as shown in Fig. 1. Since a negligible number of electrons are lost from the cascade due to (ii) and (iii), the probability per absorbed photon of radiative recombination from the n th step is simply the branching ratio

$$S_n = \tau_R^{-1}(n) / \tau_{LO}^{-1}(n), \quad (1)$$

where $\tau_R(n)$ is the radiative lifetime at the n th