Cu(1) and 1·06 (7) e for Cu(2)] are greater than the corresponding values for $CrSO_4.5H_2O$ [a mean value of 0·10 (4) e for the ligating water molecules, and 1·1 (2) and 0·7 (2) e for the $Cr(1).4H_2O$ and $Cr(2).4H_2O$ moieties respectively].

The average charges on the sulfate O atoms are comparable for the two structures, being −0·30 (3) e for $CrSO_4.5H_2O$ and −0·32 (1) e for $CuSO_4.5H_2O$. However, the agreement between the individual charges on the sulfate O atoms does not compare so favourably, indicating a need for caution when interpreting individual charges.

Calculations were performed on a Perkin-Elmer 3240 computer using programs from the *XTAL* system (Stewart & Hall, 1985). We thank C. Chantler for use of the program *PARTN*, which is compatible with the *XTAL* system. We also thank B. W. Skelton for providing the X-ray data.

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Ionic Radii and Optical Susceptibilities in the Halite-Type Alkali Halides

BY W. KUCHARCZYK

Institute of Physics, Technical University, ul. Wólczańska 219, 93-005 *Łódź, Poland*

(*Received* 8 *December* 1986; *accepted* 2 *June* 1987)

Abstract

The ionic radii providing the observed optical susceptibilities in alkali halides have been determined. The result is the set of crystal radii $r_a \simeq 0{\cdot}78$, 0·91, 0·92, 0·98, 1·08, 1·20, 1·24, 1·32, 1·31, 1·51, 1·61, 1·66, 1·40, 1·66, 1·73 and 1·82 Å and $r_h \simeq 1{\cdot}23$, 1·66, 1·83, 2·02, 1·23, 1·62, 1·75, 1·92, 1·37, 1·64, 1·69, 1·87, 1·43, 1·64, 1·71 and 1·85 Å for LiF, LiCl, LiBr, LiI, NaF, NaCl, NaBr, NaI, KF, KCl, KBr, KI, RbF, RbCl, RbBr and RbI, respectively. The calculations were performed at an assumed constant compensation coefficient related to the deficiency of the free-electron model.

Theory

*The Phillips–Van Vechten theory of dielectric proper*ties of solids (Phillips, 1968; Phillips & Van Vechten, 1969; Van Vechten, 1969) and the bond-charge model (Levine, 1973*a*,*b*) are the basis of numerous calculations of diverse optical phenomena (see *e.g.* Chemla, 1980; Shih Chun-Ching & Yariv, 1982; Tsirelson, Korolkova, Rez & Ozerov, 1984; Kucharczyk, 1987*a*; Sangwal & Kucharczyk, 1987). The starting point for all the calculations is Penn's nearly-free-electron model of the dielectric constant at long wavelengths (Penn, 1962)

$$\varepsilon(\infty) - 1 = (\hbar\omega_P / E_g)^2, \qquad (1)$$

0108-7681/87/050454-03$01.50

where E_g is the average energy gap and ω_P is the plasma frequency. The plasma frequency in diatomic crystals can be generally written in the form

$$\omega_P^2 = (Ne^2/m\varepsilon_0)[1 - E_g/4E_F + \tfrac{1}{3}(E_g/4E_F)^2]D. \quad (2)$$

Here, ε_0 is the permittivity of free space, e and m are the electron charge and mass, respectively, N is the number of valence electrons per unit volume, D is the correction factor of the order of unity related to the d-state cores and E_F is the Fermi energy given in terms of the Fermi wave vector k_F by

$$E_F = (\hbar k_F)^2/2m, \quad (3)$$

where

$$k_F = (3\pi^2 N)^{1/3}. \quad (4)$$

The effective energy gap E_g can be decomposed into a homopolar and a heteropolar part according to the relation

$$E_g^2 = E_h^2 + C^2. \quad (5)$$

In the Phillips–Van Vechten theory, the ionicity and covalency are usually described in terms of parameters f_i and f_c, defined as

$$f_i = C^2/(E_h^2 + C^2), \quad (6a)$$

$$f_c = E_h^2/(E_h^2 + C^2). \quad (6b)$$

The parameter f_c in halite-type alkali halides ranges from 0·110 to 0·044 (Van Vechten, 1969; Levine, 1973*a*). In (5), the homopolar part E_h depends simply on the bond length d as

$$E_h = Ad^{-s}, \quad (7)$$

where $s = 2{\cdot}48$ and A is a constant. For E_h in eV and d given in Å, $A = 39{\cdot}74$. The heteropolar part of E_g is related to the ionic binding and represents the difference in screened potentials of the two atoms at the bond centre. According to the Phillips–Van Vechten theory, C in alkali halides may be given by the relation

$$C = be^2(Z_a/r_a - Z_h/r_h)\exp(-k_s d/2), \quad (8)$$

where

$$d = r_a + r_h. \quad (9)$$

Z_a and Z_h denote the numbers of valence electrons, so here $Z_a = 1$ and $Z_h = 7$, respectively, r_a and r_h are the distance between the appropriate atom and the centre of gravity of the bond charge, k_s is the Thomas–Fermi screening wave number and b is a coefficient compensating for the deficiency of the free-electron model. The screening wave number k_s depends on the bond length because

$$k_s = (4k_F/\pi a_B)^{1/2}, \quad (10)$$

where a_B is the Bohr radius.

Taking into consideration (1) to (5) and (7), from the experimental lattice constant and refractive data one can derive the heteropolar term C (Van Vechten, 1969; Levine, 1973*a*). On the other hand, C depends through (8) on the radii r_a and r_h. The aim of the present paper is to study what set of radii can be expected to provide the experimental values of the refractive index of alkali halides with the NaCl structure. It was previously shown that the coefficient b should be approximately constant within a given structure type (Van Vechten, 1969; Levine, 1973*a*). Therefore, as a test of the proper choice of r_a and r_h, we consider the constancy of this prescreening factor. It should be mentioned that our approach for calculating the ionic radii of alkali halides is quite different from the existing approaches, *e.g.* Maslen's (1967) approach.

Numerical

The coefficients b were first obtained for the alkali halides by Van Vechten (1969). These values were evaluated by taking into consideration the covalent radii, from a hypothetic crystal having a zincblende structure with the same lattice constant as the actual NaCl lattice constant. Another method was suggested by Levine (1973*a*) to predict $\varepsilon(\infty)$ even for unknown crystals. Levine noticed that for the averaged radii $r = d/2$ the factor b approximately does not change with crystal structure but depends on the average coordination number. Taking $r_a = r_h = d/2$, one can obtain from (8) for sixteen halite-type alkali halides $b = 3{\cdot}53 \pm 16\%$. Recently, it was noted (Kucharczyk, 1987*b*) that a smaller spread in the values of b can be obtained by employing the Fumi & Tosi (1969) set of additive ionic radii. Taking into account sets of additive ionic radii $r_{a,h}^{\rm add}$ modified so as to fulfil (9), we have put

$$r_a = r_a^{\rm add} d/(r_a^{\rm add} + r_h^{\rm add}), \quad (11a)$$

$$r_h = r_h^{\rm add} d/(r_a^{\rm add} + r_h^{\rm add}), \quad (11b)$$

and using (8) one can derive $b = 4{\cdot}16 \pm 11\%$, $4{\cdot}02 \pm 10\%$, $4{\cdot}15 \pm 10\%$ and $4{\cdot}15 \pm 12\%$ for the sets of Gourary & Adrian (1960), Fumi & Tosi (1969), Tosi & Fumi (1964) and Sysiö (1969), respectively. Analogously, employing the ionic radii measured in the X-ray scattering experiments (Inkinen & Järvinen, 1968; Järvinen & Inkinen, 1967; Krug, Witte & Wölfel, 1955; Kurki-Suonio & Fontell, 1964; Linkoaho, 1969; Meisalo & Inkinen, 1967; Merisalo & Inkinen, 1966; Patomäki & Linkoaho, 1969; Schoknecht, 1957; Witte & Wölfel, 1955), one finds $b = 4{\cdot}12 \pm 5{\cdot}5\%$. For some crystals, slightly different experimental radii are reported. Taking into account the X-ray-determined ionic radii for LiF, LiCl, NaCl, KCl, KBr and RbCl for which a smaller experimental error was reported (Merisalo & Inkinen, 1966; Inkinen & Järvinen, 1968; Linkoaho, 1969; Patomäki & Linkoaho, 1969; Meisalo & Inkinen, 1967; Järvinen & Inkinen, 1967, respectively), one obtains $b = 4{\cdot}16 \pm 3{\cdot}3\%$. The small

Table 1. *Ionic radii in halite-type alkali halides*

Δ denotes the experimental accuracy limits. All values are in Å.

Crystal	r_a^{theor}	r_h^{theor}	r_a^{exp}	r_h^{exp}	Δ
LiF	0·78	1·23	0·92[a]	1·09[a]	±0·1[b]
			0·78[c]	1·23[c]	±0·04[c]
LiCl	0·91	1·66	0·91[d]	1·66[d]	±0·08[d]
LiBr	0·92	1·83			
LiI	0·98	2·02			
NaF	1·08	1·23			
NaCl	1·20	1·62	1·17[e]	1·65[e]	±0·1[b]
			1·18[b]	1·64[b]	±0·1[b]
			1·15[f]	1·67[f]	±0·06[f]
			1·21[g]	1·61[g]	±0·05[g]
NaBr	1·24	1·75			
NaI	1·32	1·92			
KF	1·31	1·37			
KCl	1·51	1·64	1·45[h]	1·70[h]	±0·07[h]
KBr	1·61	1·69	1·57[i]	1·73[i]	±0·07[i]
KI	1·66	1·87			
RbF	1·40	1·43			
RbCl	1·66	1·64	1·71[j]	1·58[j]	±0·05[j]
RbBr	1·73	1·71			
RbI	1·82	1·85			

References: (*a*) Krug, Witte & Wölfel (1955); (*b*) Schoknecht (1957); (*c*) Merisalo & Inkinen (1966); (*d*) Inkinen & Järvinen (1968); (*e*) Witte & Wölfel (1955); (*f*) Kurki-Suonio & Fontell (1964); (*g*) Linkoaho (1969); (*h*) Patomäki & Linkoaho (1969); (*i*) Meisalo & Inkinen (1967); (*j*) Järvinen & Inkinen (1967).

spread in the factor b suggests that, to a first approximation, it can be treated as a constant for the given crystal structure and the same $\Delta Z = Z_\alpha - Z_\beta$, where Z_α and Z_β are the numbers of valence electrons, independent of the lattice constant and crystal ionicity. On the basis of this assumption, one can evaluate the ionic radii which lead to the measured refractive index at long wavelength. The ionic radii r_a and r_h can be related to values of C listed by Van Vechten (1969) and Levine (1973*a*) by the expression

$$C = 14{\cdot}4b(7/r_h - 1/r_a)\exp(-k_s a/4). \quad (12)$$

Here a is the lattice constant, r_a and r_h are given in Å and C in eV. From (9) and (12) one can obtain

$$2Xr_a^2 + r_a(16 - aX) - a = 0, \quad (13a)$$

$$2Xr_h^2 - r_h(Xa + 16) + 7a = 0, \quad (13b)$$

where

$$X = [C\exp(k_s a/4)]/14{\cdot}4b. \quad (14)$$

From (13*a*) and (13*b*), it is straightforward to find

$$r_a = [aX - 16 + (256 + a^2X^2 - 24aX)^{1/2}]/4X, \quad (15a)$$

$$r_h = [aX + 16 - (256 + a^2X^2 - 24aX)^{1/2}]/4X. \quad (15b)$$

To derive the ionic radii in alkali halides we used the averaged prescreening factor $b = 4{\cdot}15$. Throughout the treatment we employed C derived from experimental data and listed by Levine (1973*a*) and lattice constants from Landolt-Börnstein (1973). The values of the theoretically obtained ionic radii are given in Table 1 and compared with the experimental values.

Concluding remarks

Our results show the following trends for the ionic radii in alkali halides: (*a*) the predicted fluorine radii are greater and iodine radii are smaller than the additive values; (*b*) the radii of all alkalis increase with increasing radii of halogen; (*c*) the radius of fluorine increases with an increase in the alkali radius; (*d*) the radius of chlorine is weakly dependent on the alkali radius; and (*e*) the radii of bromine and iodine decrease with an increase in the alkali radius. Generally, Table 1 shows that the derived radii are in satisfactory agreement with experiment.

The author is grateful to Dr K. Sangwal for reading through the manuscript.

This work was carried out under Research Project CPBP 01.06, 6.04.

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