

The fractional ionic character of alkali and silver halide crystals

JAI SHANKER and M P VERMA

Department of Physics, Agra College, Agra 282002

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Abstract. The fractional ionic character of alkali and silver halide crystals is defined in terms of the deviations from the additivity rule for polarizabilities of ions. The electronic polarizabilities of ions are calculated using an empirical relationship according to which the electronic polarizability of an ion can be assumed to be directly proportional to the cube of its radius. The calculated ionicities indicate that the alkali halides are nearly or more than 90% ionic and silver halides are much less ionic which is also evident from the Phillips ionicity scale.

Keywords. Fractional ionic character; alkali halide crystals; silver halide crystals; Phillips ionicity.

1. Introduction

Crystals of alkali halides are known to be very close to the ideal picture of an ionic solid. The electrostatic energy coupling of the ions makes a major contribution to the binding energy and the simple Born model successfully explains the cohesion in these solids (Tosi 1964). The electron density maps of LiF and NaCl (Witte and Wolfel 1955) show that the ionic charges in these crystals are nearly equal to $\pm e$. The fact that the alkali halides are strongly ionic is also evident from the ionicity scale of Phillips (1970) on which they hold the top positions. Phillips's criterion for the ionicity is more accurate spectroscopically than that of Pauling (1960) which is based on the data on heats of formation of solids. A knowledge of ionic character is often useful in understanding the nature of the chemical bond and in getting important information about crystalline properties such as lattice structure, and dielectric, elastic and non-linear optical properties. As is evident from the ionicity scale most solids useful from the practical viewpoint and amenable to simple theoretical analysis are neither completely ionic nor completely covalent. Even the alkali halide crystals with ionicities greater than 0.90 (Phillips scale) do not have purely ionic bonds.

The ionic crystals other than alkali halides, for instance the silver halides, show significant deviations from the ionic nature and are known to be partly covalent and have significant van der Waals interactions (Lynch 1967). The x-ray diffraction measurements on AgBr (Vogl and Waidelich 1968) clearly show that a substantial density of electron cloud is located around the sites symmetrically similar to $a(\frac{1}{4}, \frac{1}{4}, 0)$ which are points midway between second neighbours. These charge densities which indicate covalent binding must also contribute to the electronic polarizations in the

solid and such contributions should be distinguished from the polarizabilities linked with the ions which owe their origin to the deformations and displacements of the loosely coupled electron shells relative to their ion cores. It appears that the total polarizability per unit cell of the crystal determined from measurements of dielectric constants should differ from the polarizabilities associated with the two ions in the unit cell and the fractional difference could be thought of as a measure of the covalent character of the solid (Lorenz *et al* 1968). In other words the deviations from the additivity rule assumed for polarizabilities of ions in a crystal may be assumed to be due to the departure from ideal ionic character. On the basis of this idea we have given a new definition of the fractional ionic character of ionic solids.

2. Additivity rule and fractional ionic character

The electronic polarizabilities of ions are derived either on the basis of the theory of quadratic Stark effect or by adopting the principles of additivity followed by Roberts (1949) and Tessman *et al* (1953). The electronic polarizabilities deduced theoretically by Pauling essentially correspond to a certain interaction-free-state sometimes called the free ion polarizability and those derived from an analysis of the molar refractivities using the additivity rule by Tessman *et al* (1953) correspond to the crystalline state.

The additivity rule implies that a single value can be assigned to each ion as its electronic polarizability which remains unchanged in all the crystals containing this ion. The molecular electronic polarizability α_{AB} of a diatomic crystal can be expressed as an additive function of the electronic polarizabilities of the cation (A) and the anion (B):

$$\alpha_{AB} = \alpha_A + \alpha_B \quad (1)$$

Pirenne and Kartheuser (1964) have pointed out that even in case of alkali halides eq (1) is not exactly satisfied and significant deviations can be observed as we go from lighter alkali halides to heavier ones. In the frame of the individual ion model, one can phenomenologically write (Pirenne and Kartheuser 1964, Heinrichs 1970):

$$\alpha_{AB} = \alpha_A + \alpha_B + \lambda \alpha_A \alpha_B \quad (2)$$

where λ is an appropriately chosen positive constant and depends upon the crystal structure.

It appears that this interaction term $\lambda \alpha_A \alpha_B$ can be related to the covalent interactions in these solids since in ideally ionic solids this term must vanish as suggested by Tessman *et al* (1953). It is reasonable therefore to correlate the deviations from the additivity with the fractional ionic character of crystals. We thus obtain a new definition of the fractional ionic character which can be mathematically expressed as

$$f_i = \frac{\alpha_A + \alpha_B}{\alpha_{AB}} \quad (3)$$

Further, it can be easily realised that equation (3) will give an approximately good measure of the ionic characters of only such solids which are predominantly ionic. This definition can be meaningful only if we can determine the polarizabilities of ions independently. Fortunately such an independent determination is now possible through an empirical relationship between polarizability and radius for an ion recently proposed by us (Jai Shanker and Verma 1972, Jai Shanker *et al* 1973). According to this relation the electronic polarizability of an ion is directly proportional to the cube

of its radius in different crystalline or free states. Numerical calculations for a number of ionic solids have revealed that the relation is satisfied by all the ions to a very good approximation. Accordingly we can write

$$\frac{\alpha_c}{r_c^3} = \frac{\alpha_f}{r_f^3}, \quad (C \equiv A, B) \quad (4)$$

where α_c and r_c are the electronic polarizability and radius respectively of an ion in a crystal and α_f and r_f are the corresponding values in the free state.

3. Calculations

In order to calculate the crystal polarizabilities (α_c) we have used the free ion radii (r_f) of Pauling (1960) and free ion polarizabilities (α_f) of Pauling (1927). The crystal radii (r_c) are taken from the work of Tosi and Fumi (1964) from the table of individual ionic radii which exactly restore the inter-ionic separations in each alkali halide crystal. These radii are determined using the general Huggins-Mayer form for overlap repulsive potential which allows the hardness parameter to vary. However, the theoretical studies of Fumi and Tosi (1964) do not include the silver halide crystals; we have used the ionic radii (r_c) deduced from the x-ray diffraction measurements by Vogl and Waidelich (1968) for AgBr. For AgCl we have deduced from simple additivity rule the radius of Cl^- ion assuming the same radius for Ag^+ as in AgBr. This assumption has been proved to hold approximately as is evident from the quantum mechanical work of Van Vechten and Phillips (1970). Thus we can calculate the sum ($\alpha_A + \alpha_B$) from eq (4) in each alkali and silver halide crystal.

The calculated values of ($\alpha_A + \alpha_B$) are listed in table 1 and compared with the experimental molecular electronic polarizabilities α_{AB} computed from the Lorentz-Lorenz expression using the low temperature data of high frequency dielectric constant measured by Lowndes and Martin (1969). The resulting ionicities calculated from equation (3) are given in the last column of the table.

4. Results and discussion

Our calculations of the ionicities depend on the ionic radii and any error in these radii should appear three times enlarged in the polarizabilities of the ions. However, since the ionic radii are chosen to be such as to restore the lattice parameter there will be a partial cancellation of such an error in ($\alpha_A + \alpha_B$). We can, therefore, expect that the fractional ionic character f_i will not be very much in error from the correct values. It is important to note from table 1 that the ionicities calculated by us are always less than one as they should be.

Table 1. Calculated values of ($\alpha_A + \alpha_B$) and α_{AB} (in \AA^3) and f_i from eq (3).

	($\alpha_A + \alpha_B$)	α_{AB}	f_i (from eq (3))		($\alpha_A + \alpha_B$)	α_{AB}	f_i (from eq (3))
LiF	0.7733	0.918	0.84	KCl	3.8876	4.145	0.93
LiCl	2.9724	2.986	0.99	KBr	4.8466	5.321	0.91
LiBr	4.0504	4.137	0.98	KI	6.8404	7.456	0.91
LiI	6.1844	6.323	0.97	RbF	2.5163	2.572	0.97
NaF	0.9627	1.165	0.83	RbCl	4.6621	4.72	0.98
NaCl	2.9846	3.253	0.92	RbBr	5.6645	5.899	0.96
NaBr	3.9462	4.513	0.87	RbI	7.6834	7.976	0.96
NaI	5.9595	6.517	0.91	AgCl	3.88	5.049	0.77
KF	1.8403	2.008	0.92	AgBr	4.37	6.346	0.69

The errors that persist will obviously be strongest in the lighter members of the alkali halide family since their radii and polarizabilities are small. In view of the use of the additivity rule the errors in the heavier members must successively become insignificant. The values reported in table 1 show unmistakably that as we go from sodium to rubidium halides the ionicities systematically go on increasing as found by Phillips (1970) while the ionicities of lithium salts do not occupy their proper position in this sequence. This is understandable in view of the above comment regarding the significance of possible errors and an incorrect estimation of ionic radii in lithium halides as pointed out by Tosi and Fumi (1964).

On our scale the ionicities of silver salts are much smaller as compared to those on Phillips scale and should be considered as more realistic. This is because theories applicable to ionic solids do not in general give even an approximately good description of the properties of silver halides. We should, however, mention that the free state ionic radii of Pauling in silver halides used in the present calculations add up to an interatomic separation somewhat larger than the observed value. The free state ionic polarizabilities reported by Pauling correspond to the gaseous state in which the entire electron cloud should be associated with the silver and halogen ions. As against this in the solid state, part of the electron cloud is located around the points mid-way between the second neighbours. It is therefore understandable that the interionic separation in the gaseous state is somewhat larger than that in the solid state. It is essentially this difference that had led to low values of the ionic polarizabilities in the crystal and hence in the ionicities. Pauling has himself suggested that his difference in the interionic separations and sum of radii may be connected to the fractional ionic character of the silver salts.

Since our calculations of ionicities strongly depend on polarizability radius cube relation the realistic values for ionicities obtained by us should be considered as an additional support to this relation initially suggested by us on empirical grounds.

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