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Crystalline behaviour of the electronic polarizabilities and sizes of ions in silver and thallous halides.

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The crystals of silver and thallous halides have attracted the attention of numerous investigations (Mayer 1933, Lynch 1967, Bottger & Geddes 1967, Jai Shanker 1973) because of their complicated nature of the chemical bonding between the ions. The present of d-electrons in Ag^+ and Tl^+ ions causes the deviations from the purely ionic bonding. The evaluation of polarizabilities in silver and thallous halides is useful for understanding the dielectric behaviour of these crystals. In the present study we evaluate the electronic polarizabilities and sizes of ions in those crystals by taking into account the effect of Madelung potential as suggested by Ruffa (1968) and the polarizability-radius cube relation (Jai Shanker *et al* 1973). The method of calculation will not be discussed in detail here as it has already been presented in an earlier paper (Jai Shanker & Verma 1975).

The crystalline state polarizability (α_c) of an ion is related to its free state value (α_f) by the expression

$$\frac{\alpha_c}{\alpha_f} = \left(\frac{E_f}{E_f - V_M} \right)^2 \qquad \qquad \text{.. (1)}$$

where E_f is the energy parameter corresponding to free state introduced by Ruffa and V_M is the Madelung potential existing at the ion site. It should, of course, be remembered that V_M is not the only contributing potential and for the completeness of the formalism one should also account for other interacting terms like short range repulsive potentials. However, it is apparent from the work of Mayer (1933) that the magnitude of repulsive potential is much smaller than that of V_M. Therefore, assuming V_M to be a dominant contribution to the crystal potential we obtain approximate values of (α_c) for cations from eq. (1) taking α_f from Pauling (1927). The values of α_c thus obtained (table 1), for Ag$^+$ and Tl$^+$ ions in their halides, are utilised to calculate the sizes (r_c) of these ions corresponding to crystalline state using the polarizability-radius cube ($\alpha - r^3$) relation (Jai Shanker *et al* 1973). According to $\alpha - r^3$ relation one can write

$$\frac{\alpha_c}{\alpha_f} = \frac{r_c^3}{r_f^3} \qquad \qquad \text{... (2)}$$

The values of (α_c/α_f) are directly deducible from eq. (1). The ionic radii determined by Pauling (1960) are free state radii for the reasons discussed by Tosi (1964). It is also evident from an analysis of the electronic charge distributions corresponding to free ion wave functions recently performed by Deb & Ghosh (1975) that Pauling's radii are nearly equal to those in free state. Thus using the values of r_f from Pauling and (α_c/α_f) from eq. (1) we have calculated r_c from eq. (2) for Ag$^+$ and Tl$^+$ ions in their halides.

The crystalline state polarizabilities of anions, however, cannot be estimated from eq. (1). This is due to the fact that for anions the situation is somewhat different because the excitation levels contribute substantially to the anion polarizability in the crystal. In order to circumvent the difficulty we follow a different procedure to estimate the anion polarizabilities. First, we determine the crystalline state radii (r_c) of anions from the experimental interionic separations (Mayer 1933) by subtracting the appropriate cation radius evaluated from eqs. (1) and (2). The values of r_c for halogen ions, thus obtained, have been utilised to estimate α_c for these ions from eq. (2) using the values of α_f and r_f from Pauling (1927, 1960).

The results obtained have been listed in (table 2) alongwith the input parameters (E_f and V_M). It is informative to observe from table 1 that the electronic polarizability and radius of Ag$^+$ or Tl$^+$ ion show a smooth trend of variation from

a chloride to the corresponding iodide crystal   This trend of variation is similar
to that predicted by Lowndes & Martin (1969) for the effective ionic charges
in silver and thallous halides   In fact the variations of polarizability, radius
and the effective charge of the ion from crystal to crystal are related with the
character of bonding between the ions (Lucovsky *et al* 1971).

In table 2 we present a comparison of the calculated crystalline state
polarizabilities (Average values) with the corresponding values derived by Tessman
et al (1953) from experimental refraction data on crystals (given within paran-
theses)   For the sake of contrast, we have also cited the polarizabilities of free
ions in table 2.   It is interesting to remark from table 2 that the polarizabilities
calculated in the present study agree with the experimental values within nearly
10% except for I ion and differ from the free state polarizabilities in a manner
suggesting the loosening of cations and tightening of anions in the crystalline
state   The loosening and tightening effects were long ago predicted by Fajans
& Joos (1924) and were subsequently confirmed by Petrachen *et al* (1960)   For
iodide ion, we have obtained substantially lower values of electronic polarizability
and ionic radius, particularly in AgI crystal   This prediction needs further
attention.   It is noteworthy to mention that AgI differs in the following respects
from the other crystals under study . (i) it crystallizes in the zinc—blende struc-
ture and hence the number of nearest neighbours is reduced to 4 in contrast to
NaCl (CsCl) structure where the coordination number is 6 (8).   It can be
understood that the reduction in the number of nearest neighbours is directly
responsible for the lower values of electronic polarizability and ionic radius in
AgI crystal.   (ii) It is apparent from the theory of chemical bonding (Phillips
1970) that AgI is a crystal with significant covalent character.   The effect of this
covalency on the ionic radii has been analysed in detail by Van Vechten & Phillips
(1970) and their analysis also suggests that the ionic radius and electronic polariza-
bility of I^- ion should be much smaller in AgI crystal than in highly ionic crystals.

Table 1.   The values of input parameters (E_f and V_M in eV), cal-
culated crystalline electronic polarizabilities (α_c in Å^3)
and crystalline radii (r_c in Å)

Crystal	E_f	V_M	α_{c_+}	α_{c_-}	r_{c_+}	r_{c_-}
AgCl	53 99	8.98	2.48	2.87	1.10	1 67
AgBr	53.99	8 63	2.44	3.69	1.09	1.79
AgI	53.99	8.30	2.41	3 71	1.08	1.73
TlCl	49.91	7.52	4.86	2.67	1 70	1.63
TlBr	49.91	7.28	4.80	3.45	1.69	1.75
TlI	49.91	6 92	4 73	5.17	1.68	1.94

Table 2.   Average values of crystalline electronic polarizabilities (in Å³) of ions.

	Ag⁺	Tl⁺	Cl⁻	Br⁻	I⁻
Calculated	2 44	4.70	2.77	3.57	4.44
Experimental	2.40	5 20	2 96	4.16	6.43
Free State	1.72	3.50	3.66	4.77	7.10

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