SHORT COMMUNICATIONS

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Electron density in RbBr and CsI crystals in the self-consistent local-density-functional approximation (LDA).[*]

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Abstract

The electron density in RbBr and CsI crystals - composed of 'isoelectronic' alkali and halogen ions - has been computed self-consistently by the method of augmented spherical waves in the LDA approximation. The heat of formation of the salts from the alkali metal and the halogen molecule - calculated from the pertinent total energies - is in very good agreement with experiment. The LDA structure factors for the low-order 'sum' and 'difference' reflections are compared with the structure factors obtained from Hartree-Fock free-ion wave functions. The agreement is excellent for the 'sum' reflections, but for the 'difference' reflections the LDA structure factors are smaller. This result parallels our earlier results for NaF and KCl crystals and again indicates a 'contraction' of the anion and an 'expansion' of the cation in passing from free ion to ion in crystal.

We have used the method of augmented spherical waves (Williams, Kübler & Gelatt, 1979) in the local approximation to the density functional (LDA) (Kohn & Sham, 1965) with the correlation term in the form given by Hedin & Lundqvist (1971) to compute self-consistently the electron density $\rho(\mathbf{r})$ in the 'isoelectronic' salts RbBr (NaCl structure) and CsI (CsCl structure), in complete analogy with our previous work on NaF and KCl (Böbel, Cortona, Sommers & Fumi, 1983).

As a test of the quality of the computed $\rho(\mathbf{r})$, we have again calculated the heat of formation of the salt (AB) from the alkali metal (A) and the halogen molecule $(\frac{1}{2}B_2)$ using the pertinent total energies, as follows (see Böbel *et al.*, 1983, §2):

$$H = E_{AB} - E_A - \tfrac{1}{2}(2E_B^a + E_{\rm diss}).$$

The numerical results for the two salts are given in Table 1 and agree very well with the experimental values.

We have then computed the structure factors for the low-order 'sum' and 'difference' Bragg reflections, the latter being particularly sensitive to ionic deformations. These are reported in Table 2.

Table 2 reports also the corresponding structure factors obtained from Hartree-Fock free-ion wave functions (*International Tables for X-ray Crystallography*, 1974).

Table 2 reports finally the LDA structure factors *for free ions.* In general, the LDA approximation by itself does not give bound free negative ions, and a self-interaction correction is necessary (Böbel & Cortona, 1983), but it turns out that the free $\rm Br^-$ and $\rm I^-$ ions are stable in LDA.

The values reported in Table 2 were computed using the experimental value for the lattice parameter in standard thermodynamic conditions, and taking for the LDA *crystal* values the ratio of the radii of the spheres (see Böbel *et al.*, 1983, §2, 2nd paragraph) giving a net ionic charge of $\pm e$ within 1% (RbBr, $r_+/r_- = 0{\cdot}814$; CsI, $r_+/r_- = 0{\cdot}820$).[*]

Table 1. *Heats of formation of* RbBr *and* CsI *crystals* (*energies in rydbergs*)

Compound	E_{AB}	E_A	E_B^a	$E_{\rm diss}^*$	$H_{\rm th}$	$H_{\rm exp}^\dagger$
RbBr	−11013·968	−5872·537	−5141·046	−0·148	−0·311	−0·312
CsI	−28930·258	−15100·759	−13829·139	−0·116	−0·302	−0·288

* From *Handbook of Chemistry and Physics* (1983-84), F 177 & F 179.
† From *Handbook of Chemistry and Physics* (1983-84): for RbBr, D82 & D55; for CsI, D62 & D70.

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[*] It is perhaps worth noting that the ratios of the Pauling crystal radii (Pauling, 1960) are 0·76 and 0·79, respectively [using a coordination correction 6 to 8 (NaCl to CsCl) of +0·04 Å], while the ratios of the FT II (Tosi & Fumi, 1964, Table 4) average crystal radii range from 0·86 to 0·97 and from 0·85 to 0·94 (considering the estimated individual uncertainties of ±0·05 Å). This suggests that while the Pauling (1960) ratios are a little too small, the corresponding FTII ratios are too large. The fact that Fumi & Tosi (1964) (FTI and FTII) find in several instances (FTI, Tables 8, 9 and 10; FTII, Table 4) a crystal radius for $\rm Na^+$ larger than for $\rm F^-$ - even though within the estimated uncertainties of ±0·05 Å - tends to confirm the last statement.

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Table 2. *Structure factors for 'sum' and 'difference' reflections in static* RbBr *and* CsI *crystals*

RbBr

khl	111	311	331	200	220	222	400	440	444	800	10,0,0
LDA crystal	1·29	1·53	1·24	62·3	56·4	52·5	49·6	42·1	37·4	33·8	27·8
HF free ions	1·37	1·58	1·27	62·4	56·6	52·6	49·7	42·2	37·6	34·0	28·0
LDA free ions	1·39	1·56	1·26	62·3	56·5	52·5	49·6	42·1	37·4	33·8	27·8

CsI

hkl	100	111	210	110	200	220	400	431	530	541	444
LDA crystal	1·26	1·67	1·39	92·2	83·4	73·3	61·9	53·1	48·3	44·6	42·4
HF free ions	1·34	1·66	1·45	92·4	83·7	73·6	62·2	53·5	48·7	45·1	42·9
LDA free ions	1·35	1·63	1·41	92·2	83·5	73·3	61·9	53·1	48·3	44·6	42·4

The comparison of the LDA *crystal* structure factors and HF *free-ion* structure factors for the *static* crystals reveals very good agreement (within about 1%) for the 'sum' reflections, while for the 'difference' reflections the LDA factors are smaller than the HF factors - by about 6% for the lowest reflection. The LDA *free-ion* structure factors for the 'sum' reflections are practically identical to the LDA *crystal* structure factors, while for the 'difference' reflections the LDA *free-ion* factors are fairly close to the HF *free-ion* factors.

These results confirm the results reported by Böbel, Cortona, Sommers & Fumi (1983, 1985) *for* NaF *and* KCl *crystals,* and indicate a 'contraction' of the anion and a 'dilation' of the cation in passing from free ion to ion in crystal.

We are most indebted to Professor Riccardo Ferro of the University of Genova for helpful discussions on thermochemical data.

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Corrections and Additions

Acta Cryst. (1985). A**41**, 619

On periodic and non-periodic space fillings of $\mathbb{E}^m$ obtained by projection. Erratum.

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Errors in the paper by Kramer & Neri [*Acta Cryst.* (1984), A**40**, 580-587] are corrected.

p. 585, § 7, first paragraph, last sentence should read: The enumeration of the dodecahedral faces is taken from Kramer (1982), except for an interchange of faces 1 and 6, and leads to Table 1.

p. 585, Table 4, column 'Class representative', third row should read: g_3, g_3^2.

p. 585, Proposition 7.1, first equation should read:

$$D_{1'} = m^{-1}\begin{bmatrix} D_1 & 0 \\ 0 & D_2 \end{bmatrix} m,\ D_1 = D^{[311]^{\iota}},\ D_2 = D^{[311]^{\omega}}.$$

Reference

Kramer, P. (1982). *Acta Cryst.* A**38**, 257-264.