Electron Density in NaF and KCl Crystals in the Self-Consistent Local-Density-Functional Approximation (LDA)*†

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Abstract

The electron density $\rho(\mathbf{r})$ in NaF and KCl crystals – composed of 'isoelectronic' alkali and halogen ions – has been computed self-consistently by the method of augmented spherical waves in the local-density-functional approximation (LDA). Calculations were also carried out of the heat of formation of the salts from the alkali metal and the halogen molecule from the pertinent total energies as well as the diamagnetic susceptibility of the solid. The structure factors were then calculated for the low-order 'difference' and 'sum' reflections, the former of which are particularly sensitive to ionic deformations. The computed structure factors are compared with the structure factors obtained from experiment. The latter are also compared with the structure factors calculated from the Hartree–Fock free-ion atomic factors. The physical conclusion of the paper is that in the NaF and KCl crystals the anion 'contracts' and the cation 'expands' in passing from the free-ion state to the state of ion in crystal. Independent evidence of this type of effect is provided by the Tessman, Kahn & Shockley [*Phys. Rev.* (1953), **92**, 890–895] 'ionic polarizabilities' and by the Fumi & Tosi [*J. Phys. Chem. Solids* (1964), **25**, 31–43; Tosi & Fumi (1964). *J. Phys. Chem. Solids*, **25**, 45–52] 'crystal ionic radii'.

1. Introduction

The changes undergone by the electronic charge density of an ion in forming an ionic solid have been studied over a number of years.

Among the numerous phenomenological studies, we refer only to the early work by Tessman, Kahn & Shockley (1953) and by Pirenne & Kartheuser (1964) on ionic polarizabilities – and specifically on the 'stiffening' of halogens and 'loosening' of alkalis in passing from the free-ion state to the state of ions in crystals (see *e.g.* Kittel, 1971, ch. 13, Table 1) – and to the work by Fumi & Tosi (1964; Tosi & Fumi, 1964) (see *e.g.* Kittel, 1976, ch. 3, Table 9) and by Sysiö (1969) on 'crystal ionic radii' – and specifically on the 'contraction' of the halogens and the 'expansion' of the alkalis.‡

Numerous studies have also been made from the viewpoint of the quantum theory of solids, broadly divisible into three types: model treatments, variational treatments and band-theoretical treatments. We will only quote some of the early references and some papers of the more recent literature.

Yamashita (1952) has considered the F^- ion in LiF. He introduces three variational parameters in the wavefunction for the outer electrons, written as a sum of two exponentials, and he determines these parameters by an energy minimization technique. He finds a reduction in $\langle r^2 \rangle$ of about 5%. Watson (1958) stabilizes the O^{2-} ion in MgO by placing a sphere with uniform positive charge density on its surface around

‡ The criterion discussed by Ashcroft & Mermin (1976, pp. 382–385) for the deviation of interionic distances from additivity in the alkali-halide crystals – the 'touching of the larger ionic spheres' – coincides with the criterion discussed by Phillips (1973, see Fig. 2) for lattice instability of these crystals, and by Pietronero (1978) for their melting. As Pietronero (1978) points out (see p. 3947, third paragraph), these types of arguments apply just as well to the Fumi & Tosi (1964; Tosi & Fumi, 1964) crystal ionic radii as to the traditional ionic radii of Pauling and others. In fact, the Phillips and Pietronero plots are of quite comparable quality for the Fumi–Tosi and Pauling radii. On the other hand, the Ashcroft–Mermin deviations from additivity never occur using the Fumi–Tosi radii.

the O^{2-} lattice site. Lundqvist (1954) considers the H^- ions in LiH and allows a radial deformation of its charge cloud by introducing an effective nuclear charge in the $1s$ orbital of H^- to improve the computed value of the cohesive energy of the solid. He finds a small contraction. Hurst (1959) too treats the H^- ion in LiH, using simple spin-dependent exponential wavefunctions for the two electrons, and minimizes the energy of the ion in the field of point charges on the lattice sites (Madelung field). The ensuing values of the variational parameters show a contraction of the order of 10% of the radial extent of the charge cloud. Petrashen', Abarenkov & Kristofel' (1960) also carry out calculations with a point-charge approximation to the crystal potential in various alkali halides. Their results show a contraction of the electron cloud of the anions and a (relatively smaller) expansion of the electron cloud of the cations. Finally, Ruffa (1963) calculates polarizabilities of halogen and alkali ions in the alkali halides by second-order perturbation theory, using for the crystal wavefunctions antisymmetrized products of free-ion wavefunctions, and finds significant deviations from the free-ion values, of the same type found in the phenomenological analysis by Tessman, Kahn & Shockley (1953). A similar calculation was later performed by Ledovskaya (1969). A useful sum rule for $\langle r^{-1} \rangle$ has been given by Silverman & Obata (1963): this quantifies the correspondence between 'contraction in r-space' and 'increase' of atomic scattering factors and between 'dilation in r space' and 'decrease' of atomic scattering factors. The rule has been applied by Ruffa (1967) to MgO, with the conclusion that the extension of the charge cloud of Mg^{2+} in the crystal is slightly greater than in the free ion.

In the more recent literature, reference should be made to Paschalis and Weiss (1969), Schmidt & Weiss (1979), Aikala & Mansikka (1970, 1971, 1972), Mansikka & Mikkola (1974), Yamashita & Asano (1970), Kim (1973), Kim & Friauf (1971, 1974), Jennison & Kunz (1976), Grosso, Pastori Parravicini & Resta (1976), Grosso & Pastori Parravicini (1977, 1978), Euwema, Wepfer, Surratt & Wilhite (1974) and Zunger & Freeman (1977).

Paschalis & Weiss (1969) and Schmidt & Weiss (1979) introduce Watson's charged sphere in the self-consistent Hartree–Fock–Roothaan procedure (Roothaan & Bagus, 1963) to calculate one-electron wavefunctions for various cations and anions, and they then calculate, for example, the ionic scattering factors and the diamagnetic susceptibility of the crystals. They again find a contraction of the anions with an $\langle r^2 \rangle$ reduction of up to 15% for F^- and a (smaller) expansion of the cations with an $\langle r^2 \rangle$ increase of up to 6% for Li^+. Aikala & Mansikka (1970, 1971, 1972) minimize the crystal energy of LiF and NaF, computed by Löwdin's (1956) tight-binding procedure [starting

from Clementi's (1965) free-ion wavefunctions], by using a scaling parameter for the outer shells of the anion and of the cation. They then compute ionic scattering factors for Li^+, Na^+ and F^-: they find an increase with respect to the free-ion values as functions of $\sin \theta / \lambda$ for *all* the three ions, of the order of 1 to 2%. However, the scaling parameters they find correspond to a contraction of the $2p$ shell and a dilation of the $2s$ shell of the F^- ion, and again to a dilation for the Li^+ $1s$ shell. No scaling parameter was used for Na^+. Mansikka & Mikkola (1974) compute the diamagnetic susceptibility of several alkali halides using Clementi's (1965) free-ion wavefunctions, but correcting for overlap (to second order). The computed values are systematically slightly higher than the experimental values – suggesting a small contraction of the free-ion wavefunctions in the crystals. Grosso et al. (1976), Grosso & Pastori Parravicini (1977, 1978) treat LiH minimizing the energy in a cluster approach, including for the H^- ion scaling and orthogonalization. They then compute Compton profiles, X-ray structure factors and the diamagnetic susceptibility of LiH and find a radial contraction of H^- of the order of 10% or more. Kim (1973) and Kim & Friauf (1971, 1974) study Cl^- and K^+ in KCl. The effect of the crystal field on the free-ion wavefunctions of the outer shells is attributed to the well caused by pseudopotentials located on neighbouring sites and to Löwdin's symmetrical orthogonalization to the states of neighbouring ions, which is carried out on a cluster of 27 ions. This gives a significant contraction of the Cl^- ion, while the K^+ ion is practically unaffected. Kim & Friauf find an effect of at most 0·1 electron on the structure factors, and they obtain good agreement with the experimental hyperfine constants for the F centre. Jennison & Kunz (1976) treat NaF and NaCl, putting a square-well localizing potential on both the *anion and cation* lattice sites. The ionic scattering factors as functions of $\sin \theta / \lambda$ calculated by us from their final wavefunctions are, however, practically identical to those computed from the non-relativistic Hartree–Fock (HF) free-ion wavefunctions (Clementi & Roetti, 1974; Cromer & Mann, 1968). Yamashita & Asano (1970) calculate the crystal wavefunctions in MgO in the self-consistent Hartree–Fock–Slater approximation (Slater, 1974) for the ionic model $Mg^{2+}O^{2-}$ by the Korringa–Kohn–Rostoker method. Their wavefunctions provide a significantly better description of the outer electron shells of O^{2-} than Watson's (1958) model – corresponding to a better localization – as verified by Compton scattering experiments (Togawa, Inkinen & Manninen, 1971). Finally, Euwema et al. (1974) and Zunger & Freeman (1977) study LiF in the HF self-consistent approximation and in the self-consistent local-density formalism, respectively. The resulting values for the structure factors for various Bragg reflections are fairly comparable, and agree reasonably well with the available X-ray data

Table 1. *Heats of formation for* NaF *and* KCl *crystals* (*energies in rydbergs*)

1 rydberg = 2·17 aJ.

Compound	E_{AB}	E_A	E_B^a	E_{diss}^*	ΔH_{th}	(ΔH_{exp}^*)
NaF	−521·714	−322·985	−198·209	−0·1176	−0·461	(−0·437)
KCl	−2114·155	−1196·448	−917·303	−0·1823	−0·313	(−0·331)

* From *Handbook of the American Institute of Physics* (1972).

within their uncertainty (Merisalo & Inkinen, 1966),* the HF values being generally smaller (by at most 2%) and the LDA values generally larger (by at most 4%). The Zunger–Freeman (1977) values also exceed the values given by the HF *free-ion* scattering factors more than the Euwema *et al.* values, indicating a greater contraction of the electron cloud of F⁻.

2. Calculation of electron density, heat of formation and diamagnetic susceptibility of NaF and KCl crystals

We have used the augmented-spherical-wave method, which is a self-consistent method for band structure and total energy calculations (Williams, Kübler & Gelatt, 1979). In the method the electron wavefunction is written as a linear combination of augmented spherical waves, centered on each lattice site. The crystal is divided into overlapping spheres such that the sum of the volumes of the spheres associated with the atoms contained in the primitive cell is equal to the Wigner–Seitz volume. The effective potential is obtained from the spherically-averaged charge density inside each sphere within the LDA: for the exchange-correlation term one uses the Hedin–Lundqvist (1971) parametrization of the Kohn–Sham (1965) expression. The calculation is divided into an intraatomic and an interatomic part. The interatomic calculation produces the energy bands and the components of the density of states for the various angular momenta and for the various sites. This then provides us with the contributions of the various orbitals to the charge distribution inside each sphere, and with the boundary conditions to be satisfied on the surfaces of the spheres. At this stage the intraatomic calculation can be carried out to self-consistency so as to satisfy the boundary conditions imposed by the crystal. A new potential is determined and used in the interatomic calculation and the entire process is carried to self-consistency.

In binary compounds, such as NaF and KCl, the relative size of the two atomic spheres is arbitrary. We have chosen the radii so that the charge density on the surface of the two spheres is equal. It turns out that this

* These data refer to powder samples. See the comment by Suortti (private communication, January 1982) in the first footnote of § 3.

Table 2. *Diamagnetic susceptibility of* NaF *and* KCl *crystals*

Compound	χ_{th}	χ_{exp}^*
NaF	−16·7 × 10⁻⁶	−16·4 × 10⁻⁶
KCl	−43·5 × 10⁻⁶	−39·0 × 10⁻⁶

* From *Handbook of Chemistry and Physics* (1979–80).

corresponds to a transfer of one electron between the two atoms, in agreement with the traditional ionic picture of the alkali-halide crystals. We refer to the paper by Williams, Kübler & Gelatt for a complete discussion of the method.

As a test of the self-consistent electron density obtained for the NaF and KCl crystals, we have computed the heat of formation of these compounds from the alkali metal and the halogen molecule. The heat of formation is calculated as follows:

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

where E_{AB} is the total energy of the compound AB, E_A is the total energy of metal A and the molecular energy of the halogen B (last term in brackets) has been replaced by the free-atom total energy E_B^a plus the (experimental) dissociation energy of the molecule. All energies except E_{diss} are calculated with the same program, thus ensuring a proper cancellation of any internal numerical errors. The numerical results for the two compounds are given in Table 1 and, as can be seen, agree well with the measured values.

As a further test of the computed self-consistent electron density, we have calculated the diamagnetic susceptibility of NaF and KCl crystals by means of the standard formula (see *e.g.* Kittel, 1967, pp. 430–431 and Appendix F). The resulting values are compared with the experimental values in Table 2: the quality of the agreement is quite comparable to that achieved by Mansikka & Mikkola (1974).*

We have finally computed the Fourier components of the electron density – the structure factors – for the

* The experimental values of χ are in fact somewhat uncertain (see *e.g.* Landolt-Börnstein, 1967, Teil 10. II, pp. 1–65). Furthermore, Kittel (1967, p 431) notes that the Langevin formula accounts only roughly for the diamagnetic susceptibility of dielectric solids, while Dorfman (1965, pp. 47 *ff.* and Table 1) states that the experimental values – not corrected for a (small) van Vleck paramagnetic contribution – are too small in absolute value.

Table 3. *Fourier components of the electron density in static* NaF *and* KCl *crystals*

hkl	111	311	331	200	220	222	400	440	444	800	10 0 0
NaF	1·29	1·75	1·47	14·6	11·6	9·76	8·43	5·57	4·37	3·73	3·08
KCl	1·36	1·59	1·14	28·4	24·2	21·6	19·8	16·1	14·4	13·2	11·2

smaller reciprocal-lattice vectors. These are reported in Table 3.

3. Structure factors of NaF and KCl crystals

The NaF and KCl crystals are formed of isoelectronic alkali and halogen ions and thus the structure factors for the low-order 'difference' reflections, in which the two sublattices scatter in antiphase, are particularly sensitive to the deformations of the outer electron shells due to the crystal field, in passing from the free ions to the ions in the crystal (Elliott & Gibson, 1974, § 1.6.3).

We take as experimental X-ray data at room temperature those reported by Howard & Jones (1977) for NaF, and those reported by Patomäki & Linkoaho (1969) for KCl.* The earlier measurements by Sharma (1974a,b, 1975) on NaF are criticized by Howard & Jones (1977) for being affected by extinction. The γ-ray data of Yoder & Colella (1982) on NaF and of Schmidt & Colella (private communication, December 1981) on KCl will be discussed separately (see part c of this section). For KCl the structure factors are taken directly from Table 1 of Patomäki & Linkoaho (1969) and correspond to a best fit of the data to HF free-ion factors (Bagus, 1965). For NaF the structure factors are obtained from Cooper's (1979) reanalysis of the Howard & Jones (1977) data:† for each reflection we take from Table 3 of Cooper (1979) the ratio I_o/I_c of the experimental intensity to the intensity calculated from the ionic factors of Aikala & Mansikka's (1972) model 2,‡ and we multiply this ratio by the square of the structure factor computed from the same ionic factors.

(a) We fit the structure factors for the 'sum' reflections obtained from our calculations (see Table 3) – referred to as LDA – to the structure factors

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* These latter data refer to powder samples and thus suffer from two basic difficulties (Suortti & Jennings, 1977; Suortti, private communication, January 1982): the separation of the Bragg intensity from the total scattering and the elimination of systematic errors, such as extinction and preferred orientations. Suortti & Jennings (1977) underline the conditions under which the precision of structure factors obtained from powder data may approach the precision obtainable from single-crystal data.

† Cooper shows that the intensities of the lower-order 'difference' reflections are little affected by the extinction theory used and in particular always agree best with Aikala & Mansikka's model 2. We are indebted to Dr Cooper for correspondence on this issue (December 1981).

‡ A printing error is present in Table 2 of Aikala & Mansikka (1972). The atomic scattering factors from models 1 and 2 are exchanged.

Table 4. *LDA fit*

	$\bar{B}$	R
NaF	0·896	0·0242
KCl	2·03	0·0143

Table 5. *LDA structure factors for some 'sum' reflections at* 300 K *and their percentage deviations from 'experiment'*

h k l	NaF	KCl
2 0 0	14·0 (−2%)	27·0 (−)
2 2 0	10·7 (−2%)	21·8 (−)
2 2 2	8·60 (−2%)	18·5 (−)
4 0 0	7·14 (−1%)	16·1 (−2%)
4 4 0	3·98 (+1%)	10·7 (+1%)
4 4 4	2·65 (+1·5%)	7·79 (+4%)
8 0 0	1·91 (+1%)	5·81 (−2%)
10 0 0	—	3·11 (+4%)

Table 6. *LDA and 'experimental' structure factors at* 300 K *for the lower 'difference' reflections and percentage deviations between them*

h k l		111	311	331
NaF	theoretical	1·25	1·56	1·20
	experimental	1·25 (−)	1·57 (+0·6%)	1·23 (+2·5%)
KCl	theoretical	1·31	1·38	0·90
	experimental	1·28 (−2·5%)	1·34 (−3%)	0·87 (−3·5%)

obtained from experimental data as indicated above, with a single Debye–Waller factor $\bar{B}$. For KCl no weighting factors are used, while for NaF we take for each reflection a weighting factor estimated from the $\sigma(I_o)$ values given in Table 3 of Cooper (1979) by a procedure parallel to the one described just above for the structure factors.

Table 4 reports the values of $\bar{B}$ and R – as defined by equation (1) of Hamilton (1965) – resulting from the fit.* The values of $\bar{B}$ for NaF and KCl are within the uncertainty of the values of $\bar{B}$ given by Howard & Jones (1977) and Patomäki & Linkoaho (1969), respectively. The quality of the fit is good in both NaF and KCl.

Table 5 reports the LDA structure factors for various 'sum' reflections fitted to the structure factors derived from experimental data, and their percentage deviations from experiment. The 'theoretical' and 'experimental' values agree within a few per cent.

Table 6 reports for the lower-'difference' reflections the LDA structure factors at 300 K and the corresponding structure factors obtained from experiment.

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* A fit for all reflections does not give significantly different values for $\bar{B}$ and R.

Table 7. *HF fit*

	$\bar{B}$	R
NaF	0·889	0·0218
KCl	2·04	0·0154

Table 8. *HF structure factors for some 'sum' reflections at 300 K and their percentage deviations from 'experiment'*

h k l	NaF	KCl
2 0 0	14·1 (−1·5%)	27·0 (−)
2 2 0	10·8 (−1%)	21·9 (−)
2 2 2	8·67 (−1·5%)	18·5 (−)
4 0 0	7·15 (−0·5%)	16·1 (−2%)
4 4 0	3·97 (+0·5%)	10·7 (+1%)
4 4 4	2·63 (+1%)	7·79 (+4%)
8 0 0	1·91 (+1%)	5·82 (−1·5%)
10 0 0	—	3·11 (+4%)

Table 9. *HF and 'experimental' structure factors at 300 K for the lower 'difference' reflections and percentage deviations between them*

h k l		111	311	331
NaF	theoretical	1·32	1·62	1·26
	experimental	1·25 (−6%)	1·57 (−3%)	1·23 (−2·5%)
KCl	theoretical	1·39	1·42	0·92
	experimental	1·28 (−9%)	1·34 (−6%)	0·87 (−6%)

(*b*) We perform analogous fits to those done in (*a*) starting from HF free-ion factors: for KCl we adopt the relativistic Hartree–Fock factors reported in *International Tables for X-ray Crystallography* (1974) while for NaF we use the values reported by Cromer & Mann (1968).

Tables 7 and 8 report, respectively, the $\bar{B}$ and R values obtained from the fits and the values of the fitted HF structure factors for various 'sum' reflections with their percentage deviations from experiment. The fit is quite comparable to the fit discussed in (*a*).

Table 9 reports for the lower-'difference' reflections the HF structure factors at 300 K and the corresponding structure factors obtained from experiment.

(*c*) Yoder & Colella (1982) have just reported γ-ray scattering intensities for NaF for several Bragg peaks. They obtain good agreement with their data by the mosaic-crystal theory, using the ionic factors reported by Cromer & Waber (1965) (computed from Dirac–Slater wavefunctions) and adopting (somewhat arbitrarily) the Debye–Waller factors for Na$^+$ and F$^-$ reported by Howard & Jones (1977). They attribute the good agreement to the reduced spatial extent of the Dirac–Slater wavefunctions (due to the overestimate of the exchange energy by the Slater approximation), which they feel accounts − in some way − for an 'overall contraction' of the ions upon entering the crystal. Of course, the local nature of the Slater exchange energy implies that the Dirac–Slater wavefunctions are contracted relative to Hartree–Fock

Table 10. *Comparison of the measured and calculated structure factors for NaF at 300 K by Yoder & Colella (YC) with other calculated structure factors*

h k l	YC (measured)	YC (calculated)*	HF fit†	LDA fit†
2 2 0	11·0	11·2	10·9	10·7
2 2 2	8·97	8·99	8·71	8·64
4 4 0	4·13	4·15	4·02	4·03
4 4 4	2·76	2·72	2·67	2·69
8 0 0	2·01	1·95	1·95	1·95
10 0 0	1·08	1·08	1·12	1·12
1 1 1	1·33	1·26	1·32	1·25
3 1 1	1·61	1·55	1·63	1·56
3 3 1	1·31	1·26	1·27	1·21
$\bar{B}$		0·901‡ 0·908	0·860	0·866
R		0·0231§	0·0557	0·0593

* We use the exact ionic factors by Cromer & Waber (1965) (and not interpolated values).

† These fits correspond to those performed in §§ 3(*a*) and 3(*b*), *i.e.* only the 'sum' reflections are fitted and the 'difference' reflections are calculated.

‡ Yoder & Colella (1982) use the two different Debye–Waller factors for Na$^+$ and F$^-$ given by Howard & Jones (1977) (whose measured intensities differ from those of Yoder & Colella − see Table 11).

§ Our R (see § 3*a*) differs from the R used in Yoder & Colella's Table 1. The weight given to each reflection is 1%.

wavefunctions throughout the ion, and not only in its periphery, as is physically more plausible.

The main remaining discrepancies between experiment and calculations refer to the 'difference' reflections, and range from 13% for 111, to 11% for 113 and 10% for 133, down to only 2% for 333, the measured intensities being larger. Yoder & Colella (1982) attribute these discrepancies to a charge transfer of 'slightly' less than one electron from the Na to the F atom. Simple estimates based upon transferring only a fraction of an electron from the Na atom to the F atom, and placing the remaining fraction midway between the ions, show that the 'degree of covalency' required to account for the reported discrepancies is of the order of 15%, a physically implausible percentage.

It is also difficult to rationalize physically the increasing discrepancy for the 'sum' reflections with increasing indices between the measured intensities and the values calculated from the mosaic-crystal theory with HF free-ion form factors: these discrepancies range from 4% for 220, to 7% for 222, 11% for 444 up to 11·5% for 800, the measured intensities being larger, and again contradict the physical expectation of a largely peripheral deformation.

We have performed fits of the Yoder & Colella (1982) data for the 'sum' reflections adopting the same HF free-ion factors used in § 3(*b*), as well as the LDA ionic factors used in § 3(*a*), with a single Debye–Waller factor $\bar{B}$. The results for the 'sum' and 'difference' reflections are reported in Table 10 together with experimental and computed values by Yoder & Colella (1982). To test the effect of the choice of the Howard & Jones Debye–Waller factors in Yoder & Colella's (1982) calculations, we have also performed a fit for

Table 11. *Structure factors for* NaF *at* 300 K

h k l	Yoder & Colella (experimental)	Howard & Jones (experimental)	LDA (calculated)
1 1 1	1·33	1·25	1·25
3 1 1	1·61	1·57	1·56
3 3 1	1·31	1·23	1·20
2 2 0	11·0	10·9	10·7
2 2 2	8·97	8·80	8·60
4 4 0	4·13	3·95	3·98
4 4 4	2·76	2·61	2·65
8 0 0	2·01	1·89	1·91

the 'sum' reflections using the Cromer & Waber (1965) ionic factors: the resulting values for the structure factors are very close to those of Yoder & Colella's calculation, and the pertinent R is 0·0222 while $\bar{B}$ is found to be equal to 0·896 (rather than 0·904).

A point to be noted is that the γ-ray structure factors of Yoder & Colella (1982) for NaF are systematically larger than the corresponding X-ray structure factors of Howard & Jones (1977) – also as reanalyzed by Cooper (1979) – and systematically larger than our LDA computed values. This is shown in Table 11. Somewhat larger discrepancies of the same type exist between the unpublished γ-ray structure factors of Schmidt & Colella for KCl (private communication, December 1981), and available X-ray data and LDA theoretical values.

The systematic character of these deviations – and their apparent increase with the mean atomic number of the component elements* – has induced us to look for possible physical causes. We have considered the Rayleigh scattering of γ-rays by electrons *vs* the Thomson scattering (see *e.g.* Brown, Peierls & Woodward, 1955; Johnson & Cheng, 1976), the thermal diffuse scattering (see *e.g.* Willis & Pryor, 1975, pp. 241–244, 232–223, 209–212, 160–165) – for which Yoder & Colella (1982) correct by means of a linear extrapolation under the Bragg peak – as well as the possible direct creation of excitons in the γ-ray scattering process. A comparison of the work by Brown *et al.* (1955) and Johnson & Cheng (1976) reveals that the γ-ray Rayleigh scattering intensity for K electrons of medium- to high-weight elements exceeds the Thomson scattering intensity at small θ's by 15% or so, but that the inclusion of L, M, *etc.* shells practically cancels the discrepancy. Small-angle γ-ray scattering measurements are, however, almost non-existent. Cromer & Liberman (1970) have, on the other hand, reported theoretical values of the dispersion corrections for X-rays which are positive at small Z and become negative at large Z, and their calculations

appear to be confirmed by Creagh's (1975) measurements. Willis & Pryor (1975), at the end of a detailed discussion of the influence of thermal diffuse scattering on Bragg intensities (pp. 232–233, 241–244) – in which they note that the effect can be as large as 25% and that a linear extrapolation of it to the Bragg peak from its wings underestimates the effect – conclude that 'crystallographers might, after all, prefer to cool their crystals to 4 K'! For the moment, the unfortunate conclusion of our analysis is that none of the physical effects considered appears clearly sufficient by itself to account for the observed discrepancies.

4. Discussion of the results and conclusions

We have seen that the self-consistent electron density $\rho(\mathbf{r})$ in NaF and KCl crystals computed with the augmented-spherical-wave method in the local-density approximation gives good values for the heat of formation of these crystals from the alkali metal and the halogen molecule, and for the diamagnetic susceptibility of the crystals. This indicates that the computed $\rho(\mathbf{r})$ is a good approximation to the true $\rho(\mathbf{r})$ in these crystals.

The fit of the structure factors for the 'sum' X-ray reflections calculated from the computed LDA $\rho(\mathbf{r})$ to the values obtained from experiment with a single Debye–Waller factor $\bar{B}$ is of good quality, and the ensuing values for the structure factors of the lower-order 'difference' X-ray reflections agree fairly well with the corresponding values obtained from experiment.

On the other hand, the fit of the structure factors for the 'sum' reflections calculated from the HF free-ion atomic factors to the values obtained from experiment with a single Debye–Waller factor $\bar{B}$ is also of good quality, but the ensuing values for the structure factors of the lower-order 'difference' reflections are *systematically higher* than the corresponding values obtained from experiment.

In other words, while the structure factors for the 'sum' reflections computed from the HF free-ion factors and from the LDA ionic factors are both comparable – within a few percent – with the values obtained from experiment in both NaF and KCl, the structure factors for the low-order 'difference' reflections computed from the HF free-ion factors are *systematically larger* by several percent than the values obtained from experiment, while the latter agree again within a few percent with the structure factors computed from the LDA ionic factors.

These results suggest that for the 'isoelectronic' alkali halides NaF and KCl, in passing from the free ion to the ion in crystal, the anionic form factors increase while the cationic form factors decrease* by compar-

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* In fact, Schneider, Hausen & Kretschmer (1981) have reported 19 absolute structure factors for copper – obtained by γ-ray scattering – which are systematically *smaller* than the values obtained by an LDA-type band calculation by Bagayoko, Laurent, Singhal & Callaway (1980).

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* Note that the cationic HF free-ion atomic factors are larger than the corresponding anionic atomic factors.

able amounts. In other words, the anion 'contracts' and the cation 'expands'. This agrees with the changes in ionic polarizabilities (Tessman, Kahn & Shockley, 1953) and ionic radii (Fumi & Tosi, 1964; Tosi & Fumi, 1964) in passing from free ions to ions in crystals. Additional evidence for a 'greater similarity' of alkali and halogen ions in crystals and in melts than when free has been recently provided by Foldy & Witten (1981) and Foldy & Segall (1982) through their concepts of 'extended symmetry' and 'mirror symmetry' in alkali-halide-ion dynamics. Further evidence for the melts has come from the measurements [Edwards, Enderby, Howe & Page, 1975 (NaCl); Mitchell, Poncet & Stewart, 1976 (RbCl)] and the calculations by simulation with the Fumi–Tosi (1964) II potential [Lantelme, Turq, Quentrec & Lewis, 1974 (NaCl); Adams, McDonald & Singer, 1977 (NaCl); Dixon & Gillan, 1981 (RbCl)] of the partial structure factors $S_{+-}(k)$, $S_{--}(k)$ and $S_{++}(k)$ and/or the radial distribution functions $g_{+-}(r)$, $g_{--}(r)$ and $g_{++}(r)$.

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A Test of a Robust/Resistant Refinement Procedure on Synthetic Data Sets

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Abstract

The conventional crystallographic least-squares procedure has been compared with a robust/resistant modification in which the weight of each reflection is multiplied by a function of the ratio of its residual to a resistant measure of the width of the residual distribution on the previous cycle. Three synthetic data sets were created by adding random errors, according to various probability distributions, to the calculated structure factors for a known crystal structure. A set with a Gaussian error distribution was refined with two sets of weights: one assigned correctly in proportion to the reciprocals of the variances of the data points, the other using unit weights throughout. The second error distribution was Gaussian contaminated by 10% drawn from another Gaussian distribution with its variance nine times greater. The third distribution was a long-tailed distribution derived by dividing a random variable with a Gaussian distribution by an independent random variable with a uniform distribution. Each of the first three cases was refined to convergence using both conventional and robust/resistant procedures, with the modified procedure leading to a result at least as close to the known structure as the conventional procedure. In the fourth case, the conventional procedure gave a poor fit, but the robust/resistant procedure converged to a reasonable approximation to the correct structure.

Introduction

In a previous paper (Nicholson, Prince, Buchanan & Tucker, 1982) we have described the application of a robust/resistant (hereafter designated R/R) refinement algorithm to refinement of the multiple data sets collected from L-(+)-tartaric acid (formerly known as D(+)-tartaric acid) in the International Union of Crystallography's Single Crystal Intensity Project (Abrahams, Hamilton & Mathieson, 1970). The procedure proved to be a very efficient means of separating from the data sets small numbers of data points which were inconsistent with the body of the data, and convergence was thereby achieved for several of the data sets in which least-squares (LS) refinement was unstable in the previous study carried out by Hamilton & Abrahams (1970). In addition, some, but not all, of the variability in refined parameters from the LS refinement was removed.