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

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Abstract

The γ-ray single-crystal structure factors of Schmidt, Colella & Yoder-Short [*Acta Cryst.* (1985), **A41**, 171-175] for the 'isoelectronic' salt KCl are shown to be in excellent agreement with the values computed by us using the method of augmented spherical waves in the LDA approximation. Small differences exist for the 600 and 400 reflections whose structure factors indicate some 'asphericity' in the valence charge density - an effect not included in the theoretical calculation. The corresponding data by the same authors for the ('non-isoelectronic') salt LiF are also in good agreement with the LDA theoretical values available in the literature. A discrepancy remains, instead, between the γ-ray structure factors for 'isoelectronic' NaF by Yoder & Colella [*Phys. Rev. B* (1982), **25**, 2545-2549] and the LDA theoretical values.

1. Introduction

In a recent paper (see Böbel, Cortona, Sommers & Fumi, 1983 § 3(*c*), fifth paragraph) we noted that preliminary γ-ray structure factors for KCl by Schmidt & Colella (private communication, December 1981) were systematically higher than the available X-ray data and our LDA theoretical values. We will see here that the finalized γ-ray data by Schmidt, Colella & Yoder-Short (1985) do not show these anomalies, and are in fact in excellent agreement with our LDA structure factors and in reasonably good agreement with the previously available X-ray data (Patomäki & Linkoaho, 1969).

Schmidt, Colella & Yoder-Short (1985) also report γ-ray structure factors for LiF. We will comment briefly on these data, emphasizing the important difference from the cases of '*isoelectronic*' alkali

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halides such as NaF and KCl, and the good agreement with the LDA structure factors computed by Zunger & Freeman (1977).

A discrepancy remains unfortunately between the γ-ray structure factors for NaF by Yoder & Colella (1982) and our LDA structure factors as well as the X-ray data by Howard & Jones (1977) (see Böbel *et al.*, 1983, § 3(*c*) and Table 11).

2. Electron density in 'isoelectronic' KCl

We treat the γ-ray single-crystal data for KCl at room temperature by Schmidt *et al.* (1985) in an entirely parallel fashion to that used by Böbel *et al.* (1983) for the X-ray single-crystal data by Howard & Jones (1977) on NaF - as reanalyzed by Cooper (1979) - and for the X-ray powder data by Patomäki & Linkoaho (1969) on KCl.

We fit the structure factors for the 'sum' reflections obtained from our calculations by the method of augmented spherical waves in the LDA approximation (see Böbel *et al.*, 1983, Table 3) to the experimental structure factors at 300 K by Schmidt *et al.* (1985) with a single Debye–Waller factor $\bar{B}$. Table 1 reports the values of the fitted LDA structure factors and the experimental values for various 'sum' reflections as well as the value of $\bar{B}$ and the value of R, as defined by Hamilton (1965).* The 'theoretical' and experimental values agree within 1%, except for the 600 and 400 reflections. Our self-consistent electron density is *spherically averaged around each ion site* (see Böbel *et al.*, 1983, § 2), and thus it is not surprising that we do not reproduce the 'small' (2·5%) difference in the structure factors of the 600 and 442 reflections - which is due to a small 'asphericity' - nor the 'slightly' (2·5%) low structure factor of the 400 reflection - probably due to the same cause.†

The computed LDA structure factors for the lower 'difference' reflections are as follows: 111, 1·31; 311, 1·38; and 331, 0·90. The 111 LDA structure factor is in excellent agreement with the experimental value of 1·33 given by Schmidt *et al.* (1985), the only value reported by these authors for 'difference' reflections [while the three LDA values are in reasonable agreement with the experimental values 1·28, 1·34 and 0·87 by Patomäki & Linkoaho (1969)].

We perform next an analogous fit to that described above starting from Hartree–Fock (HF) free-ion factors. Table 1 reports the values of the fitted HF structure factors for various 'sum' reflections, together with the values of $\bar{B}$ and R. The fit is practically identical to the LDA fit. Instead, the computed HF free-ion structure factors for the lower 'difference' reflections are larger (by 3 to 6%) than the LDA structure factors, and the 111 structure factor is also larger (by about 5%) than the experimental value of Schmidt *et al.* (1985). The values are as follows: 111, 1·39; 311, 1·42; and 331, 0·93.

Table 1 reports finally the experimental structure factors for some 'sum' reflections by Patomäki & Linkoaho (1969) (which agree reasonably well with the other values).

In summary, the fitted LDA structure factors and HF free-ion structure factors for the 'sum' reflections are practically identical, and they agree very well with the experimental values of Schmidt *et al.* (1985), but the computed HF free-ion structure factors for the lower 'difference' reflections are systematically larger than the computed LDA structure factors. The 111 experimental structure factor of Schmidt *et al.* (1985) agrees very well with the LDA value.

These results support the conclusion drawn in § 4 *of Böbel et al.* (1983) (*i.e.* a 'contraction' of the anion and an 'expansion' of the cation in passing from the free ion to the ion in crystal). The same conclusion is reached by Schmidt *et al.* (1985).

3. Electron density in 'non-isoelectronic' LiF

Schmidt, Colella & Yoder-Short (1985) also report γ-ray single crystal structure factors at room temperature for LiF.

LiF is *very different* from the *isoelectronic* salts NaF and KCl as *the anionic factor dominates over the cationic factor* both in the 'sum' and 'difference' reflections as can be seen by computing the HF free-ion structure factors for the *static* LiF crystal from *International Tables for X-ray Crystallography* (1974).* Thus, in the LiF crystal one expects to see in the lower-order reflections essentially the effects of the contraction of the F^- ion, *i.e.* an increase of the structure factors relative to the values calculated from free-ion HF wavefunctions.

Actually, for LiF one already has two accurate self-consistent calculations of the electron density, discussed by Böbel *et al.* (1983). The data by Schmidt *et al.* (1985) after elimination of the temperature

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* Both here and in Böbel *et al.* (1983) we proceed as Cooper (1979) in carrying out the least-squares fit and in computing R. For the weighting factors of the various reflections we take 1% of the experimental intensity.

† Differences in intensities of the 442 and 600 reflections have already been reported in NaCl, but with opposite sign (Schoknecht, 1957, Table 4). A simplified discussion of possible asphericities in the NaCl structure has been given by Weiss (1966, ch. 2, § 7; in particular p. 69): this would lead one to expect an increase in intensity of reflections of the *h*00 type and a decrease in intensity of reflections such as 222 and 442 for an e_g-type deformation like the one in Fig. 2.7 of Weiss (1966). In fact, this would be the effect expected on the anion (cation) charge distribution from the anion–anion (cation–cation) overlap deformation, and from the electrostatic deformation of the anion, which tend to concentrate charge in the [100] directions. However, the anion–cation overlap deformation would tend to concentrate the anion and cation charge distributions in the [111] directions, detracting charge from the [100] directions, and thus would lead to a decrease in intensity of the *h*00 reflections. The electrostatic deformation of the cation would have a similar effect.

Table 1. *'Theoretical' and experimental structure factors for some 'sum' reflections of* KCl *at* 300 K

hkl	220	222	400	224	442	600	444	800	10,0,0
LDA fit ($\bar{B}=2.00$ Å^2, $R=0.0207$)	21.9	18.6	16.2	13.0	9.88	9.88	7.86	5.88	3.17
HF fit ($\bar{B}=2.01$ Å^2, $R=0.0255$)	21.9	18.6	16.2	12.9	9.88	9.88	7.86	5.89	3.17
Schmidt *et al.* (1985)	22.0	18.5	15.8	12.9	9.92	9.66	7.81	5.89	3.22
Patomäki & Linkoaho (1969)	21.9	18.4	16.4	12.9	9.78	9.78	7.48	5.91	2.99

factor with the recipe given by Zunger & Freeman (1977) (see footnote 53) agree well with the LDA structure factors for the *static* crystal computed by the latter authors and reasonably well with the X-ray powder data by Merisalo & Inkinen (1966) reduced to the *static* crystal [see Zunger & Freeman (1977), Table IV, last two columns].*

There is a clear tendency in both the theoretical and experimental structure factors at intermediate *hkl* to be higher than the HF free-ion values.

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* The resulting tables have been deposited with the British Library Lending Division as Supplementary Publication No. SUP39799 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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About the Simultaneous Interpretation of Charge and Spin Density Data

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Abstract

The implications of quantum-chemical concepts for the simultaneous interpretation of charge and spin density data are discussed. It is proposed that the scattering of the electrons involved in the metal-ligand interaction, on which both X-ray and polarized neutron information is available, be expressed in terms of the wavefunction, while the remainder of the electron distribution be described in terms of the multipole formalism. The discussion is based on a three-electron subsystem for metal-ligand bonding. At the restricted molecular orbital level it is shown that the magnitude of the overlap spin density is much larger than that of the overlap charge density, which may be close to zero when the electronegativity difference between metal and ligand is considerable. Spin polarization is introduced at the unrestricted molecular orbital level and implies that different κ parameters should be applied to the α and β electrons. Its effect on the spin and charge distribution is of first and second order respectively. The effect of correlation, described by the mixing of two or more configurations, leads to an apparent increase in covalency. The formalisms discussed may be applied in a stepwise manner, first at the spin-restricted level and subsequently with the inclusion of spin polarization and correlation effects.

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