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Experimental Electronic Valence Charge Density of NaCl and $SrCl_2$ along the Nearest-Neighbour Axis

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Abstract

Valence-electron charge distributions have been calculated by difference Fourier inversion of experimental structure factors. The contribution of core electrons has been subtracted by using a one-term Gaussian representation. The results are in agreement with theoretical charge distributions obtained by the local-orbitals Hartree–Fock method.

1. Introduction

Recently Jennison & Barry Kunz (1976) have published the theoretical charge distributions for NaCl and $SrCl_2$ which they obtained using the local-orbitals Hartree–Fock method. The pseudopotential calculation of Nagel, Maschke & Baldereschi (1976) for the theoretical valence-electron distribution in NaCl is also now available. The authors of these publications have compared their results with the experimental curves obtained for NaCl by Schoknecht (1957). The results of Schoknecht are, however, spherically averaged. Here a direct-space approach to the experimental non-averaged electronic charge distribution for NaCl and $SrCl_2$ is presented. The experimental structure factors for NaCl are taken from Linkoaho (1968) and for $SrCl_2$ from Linkoaho, Rantavuori, Korhonen, Kurki-Suonio & Ruuskanen (1972).

2. Method

A one-term Gaussian representation of the X-ray atomic scattering factor of core electrons has been proposed by De Ranter & Van Dijck (1971). The spherically symmetric atomic scattering factor is expressed in the form

$$f(r^*) = G \exp(-\pi^2 g^2 r^{*2}), \qquad (1)$$

where $r^* = 2 \sin \theta/\lambda$ is the magnitude of the reciprocal vector, G is the number of electrons inside the entire core, and g is the half-width of the assumed Gaussian distribution of the core electrons. This representation seems to be reasonable if the value of g is equal to (in fact, slightly larger than) the orbital radius of the outermost core electrons. The applicability of the model is restricted to a range from $r^* = 0$ to $r^* = r_c^*$ (a critical value); outside this range the calculated Gaussian values can no longer be considered as representative for the core electrons. Fortunately, in this case the contribution of the outer electrons is reduced to about zero (De Ranter & Van Dijck, 1971). The difference Fourier synthesis using $(F_{\rm obs} - F_{\rm core})$ as Fourier coefficients then gives the distribution of the outer electrons. I have already applied this method to the analysis of the asphericity of the charge density of the valence electrons in vanadium (Linkoaho, 1972). Surprisingly then, the results were physically sound. This encouraged me to perform a more detailed investigation of the applicability of the one-term Gaussian method presented in this paper. The charge density of the core electrons is given by the Fourier transform of equation (1)

$$\rho(r) = \frac{G}{\pi^{3/2} g^3} \exp(-r^2/g^2), \qquad (2)$$

which is valid for $r > \pi/2r_c^*$ (Schoknecht, 1957). The final total electronic charge density is then the sum of the density of the outer (valence) electrons obtained by the Fourier inversion and the density of the core electrons obtained using equation (2).

3. Results

The experimental valence charge density of NaCl along the edge of the unit cell is shown in Fig. 1. In the calculations I have used a Gaussian representation (1) of the $1s^2 2s^2 2p^6$ configuration for both Na and Cl. The values of the parameters G, g and r_c^*, together with the experimental values of the Debye–Waller coefficients B (Linkoaho, 1968), are shown in Table 1. Essential to the present method is that outside the range $0 \le r^* \le r_c^*$ one has to use total theoretical atomic factors in calculating the values of $F_{\rm core}$ (De Ranter & Van Dijck, 1971). The number of reflections inside this range is given in Table 1. The total theoretical atomic scattering factors given in *International Tables for X-ray Crystallography* (1974) have been used in these calculations. The error estimates given in Figs. 1 and 2

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Table 1. *Characteristic values of the constants*

G is the number of core electrons, which have a Gaussian distribution with a half-width of g, r_c^* is the critical value of the reciprocal vector, and B is the Debye–Waller coefficient used to calculate the results of the difference Fourier inversions shown in Figs. 1 and 2. Electrons outside the core only contribute to the limited number of reflections given in the last row.

	NaCl (300 K) (Fig. 1)		NaCl (80 K) (Fig. 1)		NaCl (80 K)		$SrCl_2$ (80 K) (Fig. 2)	
	Na	Cl	Na	Cl	Na	Cl	Sr	Cl
G	10	10	10	10	4	10	28	10
g (Å)	0·326	0·176	0·326	0·176	0·149	0·176	0·185	0·176
r_c^* (Å^{-1})	0·40	0·95	0·40	0·95	1·66	0·95	0·92	0·95
B (Å^2)	1·81	1·49	0·58	0·51	0·58	0·51	0·42	0·50
Reflections	2	11	2	11	31	11	13	13

have been calculated simply as a variance of a sum of random variables (Cruickshank, 1965).

For the sake of comparison I have also used the Gaussian representation (1) of the $1s^22s^2$ core configuration for Na at 80 K. The results of the corresponding difference Fourier synthesis almost agree with those given in Fig. 1. Eleven measured reflections were needed for calculating the points presented in Fig. 1, whereas 31 were needed in the calculation based on the $1s^22s^2$ core configuration of Na (*cf.* Table 1). I suggest that the good agreement between these two calculations indicates the usefulness of the present method of analysis.

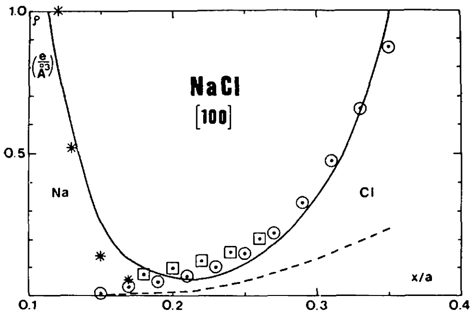

Fig. 1. The experimental valence charge density along the edge of the unit cell for NaCl at 300 K (squares) and 80 K (circles). One-term Gaussian representations for the ten-electron core of Na and Cl have been used in our calculations. The full curve gives the theoretical local-orbitals Hartree–Fock values for the total charge density. The broken curve gives the results of the pseudopotential calculation for valence electrons. The contribution of the core electrons according to equation (2) is negligible, except in the vicinity of the Na ion where the total experimental charge density is given by stars. The vertical size of the squares and circles roughly indicates the experimental errors.

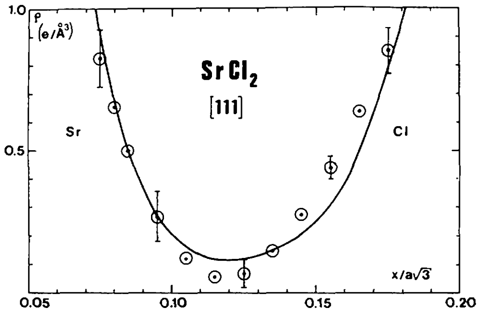

Fig. 2. The experimental valence charge density along the diagonal of the unit cell for $SrCl_2$ at 80 K. One-term Gaussian representations for the 28-electron core of Sr and the ten-electron core of Cl have been used in our calculations. The estimated effect of the experimental errors is shown by vertical bars. The full curve gives the theoretical local-orbitals Hartree–Fock values for the total charge density. The contribution of the core electrons according to equation (2) is negligible.

The experimental electronic valence charge density of $SrCl_2$ at 80 K along the diagonal of the unit cell is shown in Fig. 2. The Gaussian representation of the Cl core was the same as in NaCl. For Sr we have used the $1s^22s^22p^63s^23p^63d^{10}$ configuration (Table 1).

4. Conclusions

It is interesting to compare our results in Figs. 1 and 2 with the theoretical charge distributions (solid curves) for NaCl and $SrCl_2$ (Jennison & Barry Kunz, 1976). The experimental results are in good agreement with the theoretical ones, especially at 80 K, where the effect of thermal vibration is small. The experimental minimum charge densities at 80 K (0·07 ± 0·02 e Å^{-3} for NaCl and 0·05 ± 0·05 e Å^{-3} for $SrCl_2$) compare favorably with the theoretical values (0·070 and 0·109 e Å^{-3} respectively). The pseudopotential calculation (broken curve in Fig. 1) of Nagel *et al.* (1976) gives only about one third of the experimental (NaCl at 80 K) charge density in the vicinity of the mid-point of the unit-cell edge. The calculated charge densities around the Cl ion in the [100] and [110] directions indicate that there is less valence charge density in the latter direction. This is in qualitative agreement with the pseudopotential results.

Remembering the susceptibility of the direct-space Fourier inversion to experimental errors too much stress should not be put on the quantitative results obtained in this work and previously (Linkoaho, 1972). The tenor of this work has been to show some merits of the one-term Gaussian representation, deserving, in my opinion, further serious consideration.

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New Layered Structure of $Bi_2W_2O_9$ Determined by 1 MV High-Resolution Electron Microscopy

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Abstract

The crystal structure of bismuth tungstate, $Bi_2W_2O_9$, has been examined by 1 MV high-resolution electron microscopy. The symmetry is orthorhombic with lattice parameters $a = 5{\cdot}43$, $b = 5{\cdot}41$ and $c = 23{\cdot}7$ Å and space group $Pna2_1$. The point group is determined directly from the images in which each cation site is resolved. The structure is similar to that of conventional layered Bi compounds with respect to the Bi_2O_2 sheets normal to the c axis; however, the layer between the sheets is of a deformed ReO_3 type. The strong chemical bonds between the Bi ions and the apex O atoms cause the rotation of the WO_6 octahedron about the c axis. W ions are displaced antiparallel in the WO_3 layer.

Introduction

Since the discovery of layered Bi compounds by Aurivillius (1949) more than sixty ferroelectrics belonging to this family have been found. The family is represented by the general chemical formula $Bi_2M_{n-1}R_nO_{3n+3}$, where M = Bi, Pb, Na, K, Sr, Ca, Ba and several rare-earth ions, and R = Ti, Nb, Ta, Fe, Ga, W and Cr. The structure consists of $M_{n-1}R_nO_{3n+1}$ perovskite-like layers interleaved with Bi_2O_2 sheets, where n = 1, 2, 3, 4 and 5 (Newnham, Wolfe & Dorrian, 1971).

The phase relations in the Bi_2O_3–WO_3 system have been widely investigated. The compounds Bi_2WO_6 and $Bi_2W_2O_9$ were prepared first by Hey, Bannister & Russell (1938) and later by Gal'perin, Erman, Kolchin, Belova & Chernyshev (1966). They are both orthorhombic with lattice parameters $a = 5{\cdot}45$, $b = 5{\cdot}46$, $c = 16{\cdot}4$ and $a = 5{\cdot}42$, $b = 5{\cdot}41$, $c = 23{\cdot}7$ Å respectively (Hoda & Chang, 1974). X-ray and neutron powder diffraction have revealed that Bi_2WO_6 has the same structure as that of the family mentioned above (Wolfe, Newnham & Kay, 1969). The X-ray powder pattern suggested that $Bi_2W_2O_9$ has a layer structure; however, the structure analysis has never been carried out.

The high-voltage electron microscope (Hitachi – 1250 kV) constructed in our institute has a resolving power near 2·0 Å at an accelerating voltage of 1 MV with axial illumination and a goniometer stage (Horiuchi, Matsui & Bando, 1976). Such a high resolving power enables us to take structure images even from crystals with a relatively small unit cell. This was first demonstrated for a mixed-layer bismuth titanate, $Bi_7Ti_4NbO_{21}$, and the crystal structure was determined on the basis of direct imaging of atoms from more than two directions (Horiuchi, Kikuchi & Goto, 1977).

In the present paper, we try to determine the crystal structure of $Bi_2W_2O_9$ on the basis of super-high-resolution structure images. It is shown that the point group of the crystal is evident directly from the images.

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