$(\Delta\theta_o - \Delta\theta_{\delta,\Delta\lambda/\lambda} - \Delta\theta_{\exp})_{hkl}$, is given in the sixth column of Table 4(*b*). In accordance with the proposed crystal model, the smallest η is found for the very weak 200 reflection, for which the penetration depth of the incident beam is comparatively very large, being about half the diameter of the crystal sphere. The fluctuation of η for the other reflections with $r_{\rm ext}$ between 1.7 and 4.3 μm may once more be due to the experimental error as well as to the variable local values of η for different parts of the sphere surface illuminated by the incident ray.

Concluding remarks

In the preceding section it was shown that, using the proposed resolution function, the beam characteristics - divergence and wavelength spread - as well as the characteristics of the sample - mosaic spread and mosaic block size - can be determined from comparison with experimental FWHMs, measured at different wavelengths. It was also shown that the mosaic spread for samples with high absorption and/or extinction is no longer constant, but may vary appreciably for different reflections. The integrated intensities of the reflections measured with synchrotron radiation are strongly dependent on the varying - and therefore unknown - mosaic structure of the sample. The difficulty of obtaining integrated intensities with sufficient accuracy using synchrotron radiation may partly be due to this fact.

This work was funded by the German Minister of Research and Technology (Förderkennzeichen: 05 405IBB).

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X-ray Scattering Factors of Oxygen and Sulfur Ions: an *Ab Initio* Hartree–Fock Calculation

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(*Received* 20 *March* 1992; *accepted* 12 *June* 1992)

Abstract

The electronic structures of crystalline lithium oxide and lithium sulfide have been theoretically investigated within the Hartree-Fock approximation. X-ray static structure factors are calculated and scattering factors of O^{2-} and S^{2-} ions are deduced following the theoretical model that uses standard scattering curves for the Li^+ ion.

Introduction

The O^{2-}, S^{2-}, N^{3-}, ... ions are known to be unstable when free* (Holbrook, Sabry-Grant, Smith & Tandel, 1990) and they present severe convergence problems in the Hartree-Fock (HF) calculation. To obtain the

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* The second molar electron affinities of atomic oxygen and sulfur at 0 K are 599 (10) and 416 (10) kJ mol^{-1}, respectively.

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Table 1. *Exponents (in a.u.) and coefficients of the Gaussian functions used in the present calculation*

The contraction coefficients multiply normalized individual Gaussian functions.

Atom	Shell no.	Shell type	Exponent	Coefficients	
				s	*p*
Sulfur	1	*s*	106790.0	0.00025141	
			16484.0	0.0019873	
			3477.9	0.011766	
			909.33	0.05163	
			282.73	0.16518	
			100.18	0.35878	
			38.732	0.41355	
			15.511	0.14589	
	2	*sp*	252.43	0.0068366	0.0093636
			62.835	0.068917	0.059224
			21.153	0.11117	0.20122
			8.113	−0.27368	0.39009
			3.3415	−0.64558	0.39798
			1.4438	−0.26117	0.14133
	3	*sp*	4.362	−0.062113	−0.016517
			1.8457	−0.21048	0.032436
			0.69464	0.27644	0.31568
	4	*sp*	0.27468	1.0	1.0
	5	*sp*	0.104	1.0	1.0
Lithium	1	*s*	700.0	0.001421	
			200.0	0.003973	
			70.0	0.01639	
			20.0	0.089954	
			5.0	0.31565	
			1.5	0.4946	
	2	*sp*	0.5	1.0	1.0
	3	*sp*	2.7	1.0	1.0

correct description of these ionic wave functions, several approaches (Huzinaga & Hart-Davis, 1973) and models (Yamashita & Kojima, 1952; Watson, 1958; Pantelides, Mickish & Kunz, 1974; Pandey & Vail, 1989; Luaña, Recio & Pueyo, 1990) have been developed and applied, primarily to the O^{2-} ion.

Most of these methods involve calculating the wave function of the O^{2-} ion stabilized by the crystalline field of its nearest neighbors within an ionic crystal, most often magnesium oxide (MgO). The Watson (1958) model, involving the stabilization of the anion inside a spherical potential simulating the crystalline potential, is the most often used for determining certain physical parameters, in particular the scattering factor - see, for example: for O^{2-}, Suzuki (1960), Tokonami (1965), Sanger (1969), Schwarz & Schulz (1978), Schmidt & Weiss (1979), Schmidt, Sen & Weiss (1980); for S^{2-}, Schmidt & Weiss (1979), Schmidt, Sen & Weiss (1980); for N^{3-}, Schwarz & Schulz (1978), Schmidt & Weiss (1979), Schmidt, Sen & Weiss (1980). This model is often used as a reference in experimental and theoretical studies of this parameter, in spite of its partially empirical nature related to the adjustable value of the radius of the sphere.

In the present study, the scattering factors of the O^{2-} and S^{2-} ions were determined using a theoretical calculation of the structure factors of the ionic compounds Li_2O and Li_2S, which both have the same antifluorite-type structure. The study was carried out using the *CRYSTAL* program (Dovesi, Pisani, Roetti, Causa' & Saunders, 1988) developed for *ab initio* LCAO-HF calculations in periodic systems where the results obtained with this methodology have an excellent precision (Dovesi, Pisani, Ricca, Roetti & Saunders, 1984; Causa', Dovesi, Pisani & Roetti, 1986*a*).

Results and discussion

The details of the calculation are found elsewhere (see, for example, Causa' *et al.*, 1986*a*). They aim at describing the electron distribution of lithium oxide and sulfide, resulting from an *ab initio* all-electron crystalline orbital HF treatment. A moderately extended basis set was used in both cases: the parameters defining the shape and size of the atomic orbitals were variationally optimized. The basis set finalized by Dovesi (1985) for the study of Li_2O is adopted in the present work: it includes two *s* and three *p* Gaussian functions for lithium, four *s* and nine *p* functions for oxygen. For the Li_2S compound, an outer valence shell has been added to the basis set of lithium to permit less ionic configuration (Pisani, Dovesi & Roetti, 1988): the basis set of sulfur includes five *s* and twelve *p* Gaussian functions. The exponents of the diffuse *sp* shells of lithium and sulfur have been reoptimized for the periodic system (see Table 1).

Physical properties and electronic structure

The physical parameters calculated for Li_2S using this basis set are listed in Table 2, which also includes

Table 2. *Calculated energy data and lattice parameter for* Li_2S *and* Li_2O (*Dovesi*, 1985)

Hartree-Fock cohesive energy is obtained by subtracting the HF energy of the isolated atoms (7.433 and 397.492 a.u. for Li and S respectively) from the crystal total energy.

	Li_2O	Li_2S
Total energy (a.u.)	−89.954	−412.645
Kinetic energy (a.u.)	89.905	412.694
Virial coefficient	0.9997	1.0001
HF cohesive energy (a.u.)	0.298	0.287
Lattice parameter (Å)	4.62	5.80

the corresponding Dovesi (1985) values for comparison. The data show that the value of the lattice parameter of Li_2S resulting from optimization of geometry is 1.9% higher than the experimental value ($a_0 = 5.70$ Å at 0 K). The difference between the experimental cohesive energy (0.403 a.u.) deduced from tables of thermodynamic constants and the HF cohesive energy is 0.116 a.u. and represents the correlation contribution. With the assumption that this contribution is mainly due to the transfer of one electron from each cation to sulfur, the difference in correlation energy between the isolated species ($Li \rightarrow Li^+$: −0.002 a.u.; $S \rightarrow S^{2-}$: 0.136 a.u.) was calculated from the Clementi (1963) data. We consider that the value 0.132 a.u. obtained according to this simple model constitutes a good agreement with the value of 0.116 a.u., especially because the correlation energy of the isolated S^{2-} ion, not stable at the HF level, is estimated by extrapolating the data for the isoelectronic series.

To be able to use this work as a reference in experimental studies, structural and electronic properties were calculated with the experimental values of the lattice parameters at 0 K (4.573 Å for Li_2O and 5.700 Å for Li_2S). Using these values, the total HF energy, E_0^{HF}, is barely higher than the energy corresponding to the optimized geometries (1.0×10^{-3} a.u. for Li_2O and 2.0×10^{-4} a.u. for Li_2S).

The Mulliken populations associated with the different occupied bands and atomic orbitals of lithium, oxygen and sulfur are listed in Table 3. These values can be analyzed in confidence, since the overlap populations between nearest neighbors are very low [−0.010 for Li–O, −0.003 for O–O and 0.000 for Li–Li in Li_2O (Dovesi, 1985) and −0.004 for Li–S, −0.027 for S–S and 0.000 for Li–Li in Li_2S] and the basis sets of the atomic orbitals do not contain excessively diffuse functions. When these two criteria are not respected, they render the partition diagram of Mulliken populations highly open to criticism. Under these conditions, examination of Table 3 leads to the following conclusions:

(1) the character of Li_2O and Li_2S is almost fully ionic and is slightly less pronounced for Li_2S than for Li_2O, whereas generally the *M*–S bond is much more covalent than the *M*–O bond (Shannon, 1981);

Table 3. *Contribution to the Mulliken populations of the different species of atomic orbitals corresponding to the different bands and shells*

Li_2O (*B*1 basis set)

	Lithium		Oxygen	
	s	*p*	*s*	*p*
Band				
1	0.000	0.000	2.000	0.000
2	0.996	0.000	0.004	0.004
3	0.999	0.000	0.000	0.001
4	0.000	0.003	1.994	−0.001
5-6-7	−0.017	0.047	0.001	5.939
Shell				
1	1.626	-	1.996	—
2	0.352	0.050	0.467	2.110
3	-	-	0.800	1.496
4	-	-	0.736	2.337
Total	1.978	0.050	3.999	5.943

Li_2S

	Lithium		Sulfur	
	s	*p*	*s*	*p*
Band				
1	0.000	0.000	2.000	0.000
2	0.000	0.000	2.000	0.000
3-4-5	0.000	0.000	0.000	6.000
6	0.999	0.000	0.001	0.002
7	1.000	0.000	0.000	0.001
8	−0.001	0.004	1.993	0.000
9-10-11	−0.011	0.043	−0.002	5.937
Shell				
1	1.627	-	2.000	-
2	0.363	0.046	2.000	5.982
3	−0.003	0.001	0.236	1.121
4	-	-	1.071	2.316
5	-	-	0.685	2.521
Total	1.987	0.047	5.992	11.940

(2) the occupations of the most external Gaussian functions are virtually identical in the two species, in spite of their different exponents ($\alpha_O = 0.186$, $\alpha_S = 0.104$);

(3) all the occupied bands can be unambiguously classified as belonging to lithium, oxygen or sulfur.

The net charge on the valence shell of oxygen is 7.946 e, slightly less than that of oxygen in MgO (7.979 e) (Causa' *et al.*, 1986*a*), confirming the role of this last compound as the ionic model for oxides.

The Mulliken populations corresponding to the different atomic orbitals of the isolated lithium ion were also calculated with the same basis sets described above. When we pass from the isolated Li^+ ion to the Li^+ ion in its crystalline environment, there is a slight increase of the population of the most external Gaussian function (0.383 e → 0.402 e for Li_2O, 0.377 e → 0.407 e for Li_2S), resulting from a very slight expansion of the cation by the crystalline-field effect.

Additional and more precise information concerning the electronic structure of the compounds is furnished by electron charge density maps. These maps projected on the (110) plane of the structure are shown in Figs. 1(*a*) and (*b*). Of particular significance are the Fig. 1(*b*) difference maps obtained by subtracting from the total electron charge density map the superimposition of the HF charge densities of the isolated Li^+, O^{2-} and S^{2-} ions calculated with the same atomic orbital basis sets.

These figures show the resemblance of the projections for both compounds. They are also similar to fully ionic models, thereby confirming the validity of conclusions established on the basis of Mulliken populations. The slight deformation of the isodensity curves is attributed to a contraction of the O^{2-} and S^{2-} ions that results from the crystalline-field effect. A very slight expansion of the Li^+ ion is also observed. This result is somewhat different from previous work, where lithium and oxygen were described using more contracted atomic-orbital basis sets (Lichanot, Gelize, Larrieu & Pisani, 1991). The use of sufficiently flexible atomic-orbital basis sets makes possible this deformation of electron charge density curves, particularly in the direction of the nearest neighbors.

Structure factors of Li_2O *and* Li_2S *and scattering factors of* O^{2-} *and* S^{2-}

The static structure factors (F_0) associated with the diffraction directions of Li_2O and Li_2S were calculated by Fourier transformation of the total electron charge density $\rho(r)$, thereby conserving the anisotropy terms due to ion–ion interactions. More than 90 directions covering the range $0 \leq (\sin\theta)/\lambda \leq 2$ Å^{-1} were examined to arrive at the most precise parametering possible of the curves of scattering factors. The first 52 values of F_0 are listed in Table 4, along with the resulting scattering factors of the O^{2-} and S^{2-} ions.

An additional and more sophisticated atomic-orbital basis set available for Li_2O was also used. It was developed recently by Dovesi, Roetti, Freyria-Fava, Prencipe & Saunders (1991) for the study of the elastic constants of alkaline oxides. This basis set (B_2) includes the same number of atomic orbitals and Gaussian-type functions as the first set B_1 (Dovesi, 1985), but a more severe optimization process in B_2 leads to different exponents and coefficients of the Gaussian functions, which permit a more accurate calculation of the second derivatives of the energy.

With consideration of the fully ionic character of the compounds for which each energy band is attributable to a single species, the scattering factors $f_0(O^{2-})$ and $f_0(S^{2-})$ are deduced from the structure factors of Li_2O and Li_2S using the relationships:

$$F_0(hkl) = f_0(X^{2-}) \qquad \text{odd } hkl, \tag{1a}$$

$$F_0(khl) = f_0(X^{2-}) + 2f_0(\text{Li}^+) \qquad \text{even } hkl \text{ and } h+k+l=4n, \tag{1b}$$

$$F_0(hkl) = f_0(X^{2-}) - 2f_0(\text{Li}^+) \qquad \text{even } hkl \text{ and } h+k+l=4n+2, \tag{1c}$$

where $f_0(Li^+)$ values are taken from *International Tables for Crystallography* (1992).

In Table 4, the values of $F_0(Li_2O)$ and $f_0(O^{2-})$ calculated with the two basis sets B_1 and B_2 are listed for comparison: they are very similar since the agreement factor

$$R = \sum |F_0(B_2) - F_0(B_1)| / \sum F_0(B_2)$$

is only 0.0016. This result proves that these two basis sets are of practically equivalent quality for the calculation of structure factors. Nevertheless, the differences obtained by subtracting from the 'B_2' values those calculated with the B_1 set are alternatively positive and negative when $(\sin\theta)/\lambda$ increases in the region of low-angle reflections, the most affected by the valence electrons.

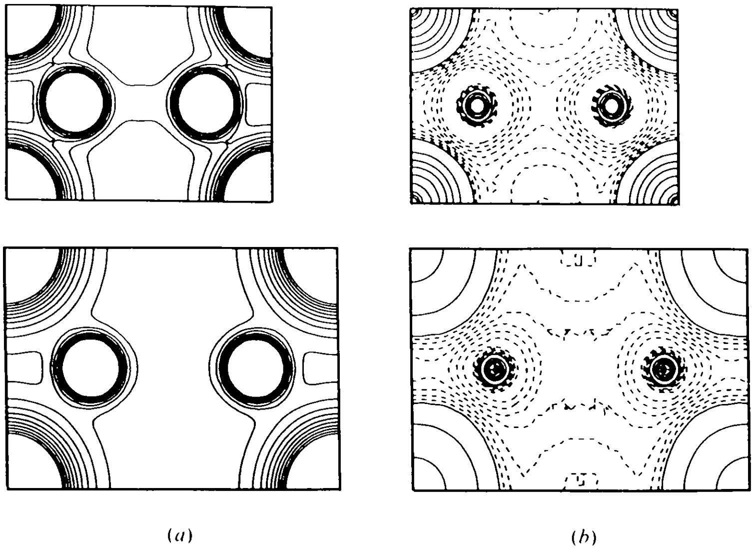

Fig. 1. Electron charge density maps of Li_2O (basis set B_1) and Li_2S in the (110) plane. (*a*) Total electron charge density. The distance between two consecutive curves is 0.01 a.u. (*b*) Electron charge density difference map obtained by subtracting from the total electron charge density the superimposition of the electron charge density of the isolated ions. The distance between two consecutive curves is 0.005 and 0.0005 a.u. for the positive (continuous lines) and negative (dashed lines) curves, respectively.

Table 4. *Static structure factors F_0 and scattering factors $f_0(O^{2-})$, $f_0(S^{2-})$ calculated using* (1)

	Li$_2$O				Li$_2$S	
	*B*1 basis set		*B*2 basis set			
h k l	F_0	$f_0(O^{2-})$	F_0	$f_0(O^{2-})$	F_0	$f_0(S^{2-})$
1 1 1	6.2811	6.2811	6.2817	6.2817	12.8460	12.8460
2 0 0	2.1703	5.6130	2.1718	5.6145	8.3087	11.9336
2 2 0	6.9324	3.9331	6.9326	3.9333	13.1310	9.8284
3 1 1	3.2951	3.2951	3.2862	3.2862	9.0548	9.0548
2 2 2	0.4906	3.1307	0.4832	3.1233	5.8458	8.8694
4 0 0	5.0121	2.6675	5.0014	2.6568	11.0720	8.2918
3 3 1	2.4131	2.4131	2.4107	2.4107	7.9849	7.9849
4 2 0	0.2338	2.3320	0.2342	2.3324	5.3169	7.8834
2 2 4	4.0383	2.1480	4.0390	2.1487	9.9558	7.5781
1 1 5 3 3 3	2.0145	2.0145	2.0191	2.0191	7.3561	7.3561
4 4 0	3.4422	1.8817	3.4471	1.8866	9.1186	7.0584
5 3 1	1.8014	1.8014	1.8083	1.8083	6.8702	6.8702
6 0 0 4 4 2	0.3399	1.7681	0.3485	1.7767	4.8742	6.8000
6 2 0	3.0389	1.7262	3.0439	1.7312	8.4176	6.6130
5 3 3	1.6713	1.6713	1.6776	1.6776	6.4436	6.4436
2 2 6	0.4364	1.6475	0.4442	1.6553	4.6838	6.3789
4 4 4	2.7456	1.6243	2.7496	1.6283	7.8070	6.2114
7 1 1 5 5 1	1.5839	1.5839	1.5890	1.5890	6.0558	6.0558
6 4 0	0.5235	1.5650	0.5297	1.5712	4.4907	5.9957
6 4 2	2.5204	1.5502	2.5235	1.5533	7.2650	5.8429
7 3 1 5 5 3	1.5183	1.5183	1.5221	1.5220	5.6990	5.6990
8 0 0	2.3402	1.4917	2.3424	1.4939	6.7793	5.5028
7 3 3	1.4649	1.4649	1.4675	1.4675	5.3700	5.3700
8 2 0 6 4 4	0.6551	1.4514	0.6583	1.4546	4.1062	5.3184
2 2 8 6 6 0	2.1913	1.4423	2.1926	1.4436	6.3423	5.1894
7 5 1 5 5 5	1.4190	1.4190	1.4206	1.4206	5.0670	5.0670
6 6 2	0.7015	1.4074	0.7036	1.4094	3.9215	5.0194
8 4 0	2.0651	1.3987	2.0657	1.3993	5.9481	4.9011
9 1 1 7 5 3	1.3779	1.3779	1.3786	1.3786	4.7884	4.7884
8 4 2	0.7374	1.3677	0.7385	1.3687	3.7450	4.7446
6 6 4	1.9559	1.3588	1.9559	1.3588	5.5917	4.6362
9 3 1	1.3401	1.3401	1.3402	1.3402	4.5326	4.5326
8 4 4	1.8600	1.3217	1.8596	1.3213	5.2689	4.3930
9 3 3 7 7 1 7 5 5	1.3046	1.3046	1.3042	1.3042	4.2979	4.2979
10 0 0 8 6 0	0.7844	1.2965	0.7842	1.2963	3.4209	4.2608
10 2 0 8 6 2	1.7746	1.2867	1.7738	1.2859	4.9761	4.1700
9 5 1 7 7 3	1.2710	1.2710	1.2702	1.2702	4.0826	4.0826
10 2 2 6 6 6	0.7984	1.2638	0.7978	1.2631	3.2741	4.0485

Such a result may be understood from the difference charge density maps (total electron charge density calculated with the basis set B_2 minus the density obtained with B_1) drawn in Fig. 2. When the valence dimension of the O^{2-} ion is described from the valence to the core regions, the sequence of positive (continuous lines) and negative (dashed lines) isodensity curves confirms the observation made for the structure factors at the small values of $(\sin\theta)/\lambda$. A more important contraction of O^{2-} by the crystalline-field effect of its nearest neighbors is therefore observed when this ion is described by means of the basis set B_1: the higher exponents of the two most diffuse Gaussian-type orbitals of the B_1 set explains its less ionic configuration.

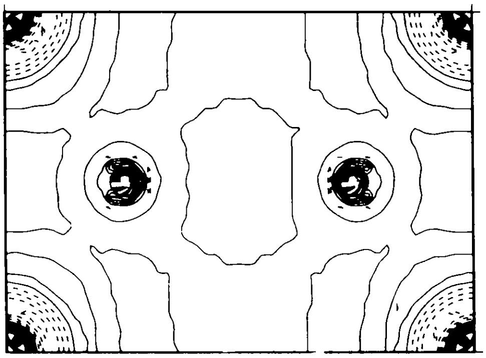

Fig. 2. Electron charge density difference map: total electron charge density calculated with basis set B_2 minus the density calculated with basis set B_1. The distance between two consecutive curves is 0.001 a.u.

The scattering factors of the O^{2-} and S^{2-} ions (Table 4) were fitted with the expression used in *International Tables for Crystallography* (1992):

$$f_0 = \sum_{i=1}^{4} a_i \exp\{-b_i[(\sin\theta)/\lambda]^2\} + c. \qquad (2)$$

To cover the usual range $0 \leq (\sin\theta)/\lambda \leq 2$ Å^{-1}, 40 and 52 additional reflections were examined for Li_2O and Li_2S, respectively. The values of the coefficients a_i, b_i and c are listed in Table 5.

The scattering factors thus interpolated were compared to those calculated from the Watson (1958) model by Schmidt & Weiss (1979) and by Schmidt, Sen & Weiss (1980). This comparison is depicted in

Table 5. *Coefficients a_i, b_i and c in the expression*

$$f_0 = \sum_{i=1}^{4} a_i \exp\{-b_i[(\sin\theta)/\lambda]^2\} + c$$

	$O(Li_2O)$ (*B*1 basis set)	$O(Li_2O)$ (*B*2 basis set)	$S(Li_2S)$
a_1	3.37198	3.04484	4.87674
a_2	0.27366	0.50181	7.04534
a_3	1.55523	1.55609	1.56193
a_4	4.18953	4.20924	3.74579
b_1	7.69746	7.98437	24.26990
b_2	3.17177	3.73146	1.45750
b_3	0.32273	0.32297	0.18409
b_4	24.99640	23.92070	54.05510
c	0.23627	0.23641	0.63332

Fig. 3 where the difference between the scattering factors $\Delta f_0 = f_0(\text{present}) - f_0(\text{Schmidt})$ corresponding to the best agreement factor

$$R = \sum |f_0(\text{present}) - f_0(\text{Schmidt})| / \sum f_0(\text{present})$$

is calculated for the optimized value of the radius (r_w) of the Watson sphere.

Fig. 3 enables the following comments to be formulated. The agreement between our determinations and those deduced from the Watson model is good for Li_2O ($R = 0.0017$: basis set B_1; $R = 0.0015$: set B_2) and for Li_2S ($R = 0.0023$). This confirms the almost fully ionic character of Li_2O and Li_2S, consistent with the conclusions arising from the analysis of Mulliken populations and electron charge density maps. The optimized values of r_w are 1.66 Å for S^{2-} and 1.20 Å for O^{2-} described by basis sets B_1 and B_2. These values are in good agreement with the ionic crystal radii $r(O^{2-}) = 1.24$ Å (O'Keeffe, 1981) and $r(S^{2-}) = 1.70$ Å (Shannon, 1981).

For Li_2O, calculations done with the basis set B_2 lead to a slight improvement in the results. The radius r_w, which is only slightly higher when obtained with set B_2, is not a decisive confirmation of the results shown in Fig. 2, which is accurate since the electron density $\rho(r)$ is a well defined physical quantity and which shows immediately how the calculated distributions differ.

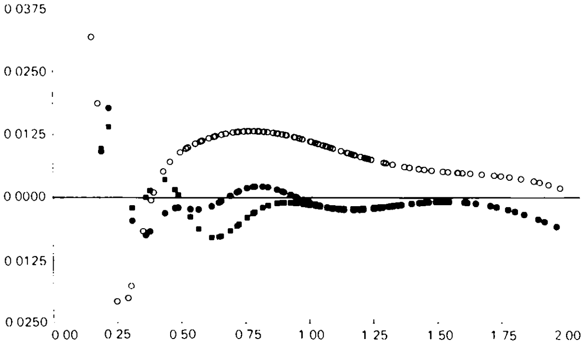

Fig. 3. Variations of the difference $\Delta f_0 = f_0(\text{present}) - f_0(\text{Schmidt})$ *versus* $(\sin\theta)/\lambda$: the scattering factors f_0 (present) are deduced from Table 5. ○: $\Delta f_0(S^{2-})$ in Li_2S for $r_w = 1.66$ Å. ■: $\Delta f_0(O^{2-})$ in Li_2O with basis set B_1 for $r_w = 1.20$ Å. ●: $\Delta f_0(O^{2-})$ in Li_2O with basis set B_2 for $r_w = 1.20$ Å.

It should be noted that the comparison of the $f_0(O^{2-})$ values obtained with the structure factors of MgO and the Watson model by Causa', Dovesi, Pisani & Roetti (1986*b*) showed an equally satisfactory agreement. In the present work, however, the difference between the scattering factors of O^{2-} determined from Li_2O and MgO is not discussed in connection with their structural differences. Even though they are deduced with the same computational methodology, they are calculated with the assumption that Li^+ is a spherical ion, while the calculations of $f_0(Mg^{2+})$ and $f_0(O^{2-})$ in MgO are rigorous, since they are derived from the Fourier transform of the electron density associated with each occupied band.

If the differences $\Delta f_0 = f_0(\text{present}) - f_0(\text{Schmidt})$ were calculated with the values f_0(present) of Table 4 in place of the interpolated values (Table 5), three different curves corresponding to (1*a*), (1*b*) and (1*c*) should be obtained for $(\sin\theta)/\lambda \leq 1.25$ Å^{-1}. They express the anisotropy of the deformation of the O^{2-} and S^{2-} ions by the crystalline-field effect of their nearest neighbors. To give an idea of the strength of this anisotropy, the three families of scattering factors were separately optimized as previously for the O^{2-} ion described by the basis set B_2 for which the most accurate results are obtained. The values r_w thus optimized are 1.20 Å [(1*a*): odd *hkl*], 1.25 Å [(1*b*): $h+k+l=4n$] and 1.17 Å [(1*c*): $h+k+l=4n+2$]. Qualitatively similar results may be obtained for O^{2-} (B_1) and S^{2-}; nevertheless, r_w values were not calculated for S^{2-} owing to a lack of accuracy for a few values of r_w in the region of 1.66 Å investigated by Schmidt, Sen & Weiss (1980).

Finally, in the region of high-angle reflections explored here: $1.25 < (\sin\theta)/\lambda < 2$ Å^{-1}, the basis sets B_1 and B_2 give values of $f_0(O^{2-})$ that are systematically below the reference values. This discrepancy cannot be attributed to a poor description of the oxygen 1*s* cusp in the present calculations since set B_2 is much better than B_1 in this respect, but the two give essentially the same results in that region. Rather, the Watson model adopted by Schmidt & Weiss (1979) might be inadequate to describe the electron distribution in the core region with the same accuracy as obtained with the basis sets B_1 and B_2 which have been optimized in the actual crystalline field.

Concluding remarks

The electronic structure of Li_2O and Li_2S has been studied following the LCAO crystalline orbital Hartree-Fock extended-basis-set computation. The analysis of Mulliken populations, the slight deformation of the electron charge density curves and the values of the scattering factors of the O^{2-} and S^{2-}

ions are parameters that establish the almost fully ionic character of these compounds. The crystalline-field effect causes a contraction of the anions and a slight expansion of the cation. In the absence of recent and precise experimental data on structure factors, the values reported in this study may be used as a reference. They will be refined in the future by the exploration of the importance of polarization functions on the S^{2-} ion in order to improve the agreement factor for Li_2S and to calculate its deformation accurately by the rigorous calculation of scattering factors by Fourier transform of the electron density on a 'per energy band occupied' basis and by taking thermal agitation into account.

The authors wish to express their gratitude to Professor C. Pisani for his helpful suggestions. The calculations were carried out on the IBM-3090/600-VF of the Centre National Universitaire Sud de Calcul (CNUSC), which is gratefully acknowledged.

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***PRISM*: Automated Crystallographic Phase Refinement by Iterative Skeletonization**

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(*Received* 6 *May* 1991; *accepted* 22 *June* 1992)

Abstract

A phase-refinement procedure based on iterative skeletonization of electron density maps is presented. As with traditional solvent-flattening methods, refinement alternates between real-space and reciprocal-space representations of the scattering density. A pseudoatom list derived from the modified skeleton of an initial electron density map provides calculated structure-factor amplitudes and phases. Recombination with the observed $F_{\rm obs}$ values yields a new map that can serve as the starting point for another round of skeletonization. Tests using partial structures to provide starting crystallographic phases have shown this refinement procedure to have a significantly larger radius of convergence than solvent flattening.

Introduction

The procedure to find a solution to the crystallographic phase problem is generally the rate-limiting step in macromolecular structure determination by

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0108-7673/93/010097-08$06.00
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