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***Ab initio* Hartree–Fock Study of Lithium and Sodium Sulfides: Electronic and Scattering Properties**

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Abstract

The electronic structure of lithium sulfide and sodium sulfide in the solid state is established at the Hartree–Fock level, as implemented in the *CRYSTAL* program. Two all-electron basis sets are adopted for each compound. Mulliken analysis, band structure, density of states and electron charge density are studied: these exhibit the highly ionic character of both compounds; this seems rather surprising because of the weak electronegativity and large polarizability of the sulfur. Form factors of the sulfur are deduced from the structure factors and analysed in order to show the deformations of this anion in the crystal environment. Finally, electron momentum density and Compton profiles confirm the almost fully ionic character of the compounds and prove the quality of the calculated wavefunctions.

1. Introduction

Lithium sulfide (Li₂S) and sodium sulfide (Na₂S) are the first two compounds of a series of two and five polysulfides, respectively, in the equilibrium phase diagram of the metal–sulfur system (Oei, 1973); their study presents particular interest in the development of new solid-state batteries, since the metal polysulfides are well known for their outstanding electrical properties, including fast ionic conduction (Janz & Rogers, 1981; Kizilyalli, Bilgin & Kizilyalli, 1990).

These two compounds belong to the family of the alkaline sulfides: they have the same antifluorite-type structure, with the *F_{m3m}* space group. In spite of their simple and symmetric structure, there is a relative lack of physical data, particularly in the elastic and inelastic scattering field. Among the principal and most recent results, those obtained by Bühner, Altorfer, Mesot, Bill, Carron & Smith (1991) and Bühner & Bill (1977, 1980), from inelastic neutron scattering, can be cited: the phonon-dispersion curves established at low temperatures allowed these authors to compute lattice dynamic properties, such as elastic constants and mean-square ionic displacements.

To explain the scarcity of experimental X-ray data, Kizilyalli *et al.* (1990) highlight numerous difficulties in the preparation and handling of Na₂S and in the rapid deterioration of the samples exposed to X-rays, and also the peculiarities of sulfide crystal structures.

In a few theoretical studies (Agnihotri, Singh & Sanyal, 1984; Jain & Shanker, 1982; Thakur & Pandey, 1975; Agarwal, Sharma, Sharma, Sharma & Shanker, 1977; Holbrook, Sabry-Grant, Smith & Tandel, 1990), interionic potentials are discussed and used to calculate binding energy, elastic constants, bulk modulus, Debye temperature and electron affinities of chalcogenide ions. It can be noted, therefore, that, among this data, there is nothing concerning the electronic structure of the two sulfide

compounds. These features justify the present quantum-theoretical study, which is carried out by means of the *CRYSTAL* program (Dovesi, Pisani, Roetti, Causà & Saunders, 1988): it is based on an *ab initio* all-electron crystalline orbital LCAO (linear combination of atomic orbitals) HF (Hartree-Fock) approximation for the study of periodic systems (Pisani, Dovesi & Roetti, 1988). The method is frequently applied to ionic and semi-ionic compounds (Dovesi, Roetti, Freyria-Fava, Aprà, Saunders & Harrison, 1992).

A preliminary study (Azavant & Lichanot, 1993) has shown that Li_2S has a highly ionic character, as in Li_2O and Na_2O . This result seems rather surprising: indeed, it is customary to think that sulfur leads to less ionic bonds than oxygen (Shannon, 1981) because of its weaker electronegativity and larger polarizability. A comparative study with the homologous Na_2S compound becomes interesting to generalize this property, in spite of some results given in the literature (Bührer & Bill, 1980; Agnihotri *et al.*, 1984).

In the present study, two principal parts are developed after the description of the computational conditions and the atomic orbitals basis set. In the first part, the physical properties, which allow the nature of the bonds to be characterized, are presented (Mulliken analysis, density of states, band structure, electron charge density). In the second part, the X-ray elastic scattering is studied in detail, while the Compton profile is more briefly analysed.

2. Basis set problems

The electronic structures of lithium sulfide and sodium sulfide crystals were investigated with the *CRYSTAL* program (Dovesi *et al.*, 1988), in which the accuracy and speed of the calculations have been recently improved (Dovesi, Saunders & Roetti, 1992). This program utilizes the LCAO *ab initio* method in the Hartree-Fock approximation and allows us to calculate the wave function of 1D, 2D and 3D periodic systems. As discussed in several papers, this method has proved to be very accurate in obtaining structural parameters, electron energies and the electronic structure of ionic or semi-ionic compounds: the electronic correlation energy, not taken into account in the HF approach, can be calculated *a posteriori* by different schemes (Colle & Salvetti, 1975; Perdew, 1986) or, for highly ionic compounds, using Clementi's data (Clementi, 1963), corresponding to electron transfer from cations to anions.

The choice of the atomic orbitals basis set is certainly an important point for the quality of the results. Without knowing *a priori* the character of the lithium and sodium sulfides in the solid state, two

basis set types were used: the first basis set is suitable to describe the elements as ions, while the second is more convenient for atoms. In the following, these sets will be called BSI (basis set for ions) and BSA (basis set for atoms), respectively. BSI was already used for the study of the elastic properties of Li_2S and Na_2S (Lichanot, Aprà & Dovesi, 1993): the cation sets are 6-1 G for Li^+ and 8-511 G for Na^+ , while the sulfur set is 6-311 G. In BSA, lithium is described by a 6-11 G set implemented in the study of Li_2O (Dovesi, 1985), the sodium basis set is the same as that used in BSI and the sulfur 6-631 G set arises from that published earlier by Francl, Pietro, Hehre, Binkley, Gordon, De Frees & Pople, (1982). Polarization functions were added to the sodium and sulfur elements to allow a better electron-relaxation mechanism through the whole unit cell. With this choice of BSI, 1s core electrons of Li^+ and S^{2-} ions are described by a contracted set of six and eight Gaussian type functions (GTF's), respectively, the 2sp and 3sp electrons of S^{2-} by six and three contracted GTF's, respectively, while one and two individual sp GTF's are added to Li^+ and S^{2-} to describe outer electrons. A Li_2S unit cell has 32 atomic orbitals (five and 22 corresponding to Li^+ and S^{2-} , respectively). The exponents of the individual outer sp shells and polarization functions optimized in lithium sulfide and sodium sulfide crystals are given in Table 1.

As Table 1 shows, the exponents of the most diffuse sp GTF's and of the polarization functions of the sulfur are practically the same in all cases; only the sulfur d orbital in BSA is less diffuse when this element belongs to Li_2S .

Preliminary comments can be made about the influence of the additional polarization d function in choosing the example of the two sulfide compounds described by BSI. If the polarization function is added to the sulfur, the total energy of the Li_2S and Na_2S unit cell is lowered by 8×10^{-4} and 2×10^{-4} Hartree, respectively, while the stabilization is 1.3×10^{-3} Hartree when it is added to the sodium. With the estimated precision of the calculations, the addition of the polarization function to sulfur does not modify the lattice parameter nor the ionic character of the compounds, as deduced from a Mulliken population analysis.

3. Results and discussion

3.1. Lattice-parameter and energy data

Isotropic deformation of the cell is studied by modifying the lattice parameter near its equilibrium value. 13 values of a_0 were explored in the range $a_0 \pm 3\%$ and the corresponding HF energies calculated. A least-squares fit was performed for the $E(V)$ function

Table 1. Exponents (Bohr⁻²) of the individual outer Gaussian type functions (GTF's) used in the present calculations

Each atomic orbital *s*, *sp* or *d* is a linear combination of *n* GTF's. The coefficients of the 3*sp* shell of the sulfur in BSA are given by Francl *et al.* (1982).

	Li ₂ S				Na ₂ S			
	BSI	BSA	BSI	BSA	BSI	BSA	BSI	BSA
	Li	S ²	Li	S	Na ⁺	S ²	Na	S
α_{sp}	-	0.27468	0.500	2.61584 0.922167 0.341287	0.548	0.27468	0.548	2.61584 0.922167 0.341287
α_p	0.519	0.106	2.120	0.119522	0.215	0.096	0.163	0.105
α_d	-	0.383	-	0.650	0.400	0.433	0.368	0.340

Table 2. Crystal energy, $E_0(\text{HF})$, binding energy, $BE(\text{HF})$, and correlation energy, E_{cor} , per unit cell at the equilibrium geometry; lattice parameter a_0 (Å) and bulk modulus B (GPa)

$BE(\text{HF})$ values are calculated (see text) from the following calculated or adopted atomic energies: in BSI: $E_0(\text{Li}) = -7.4313$, $E_0(\text{Na}) = -161.8513$, $E_0(\text{S}) = -397.4925$; in BSA: $E_0(\text{Li}) = -7.4295$, $E_0(\text{Na}) = 161.8513$, $E_0(\text{S}) = -397.4769$. All the energies are in Hartree.

	Li ₂ S		Expt.	Na ₂ S		Expt.
	BSI	BSA		BSI	BSA	
$E_0(\text{HF})$	-412.6459	-412.6233	-	-721.4308	-721.4099	-
$BE(\text{HF})$	-0.2908	-0.2874	-	-0.2357	-0.2304	-
$BE(\text{HF} + \text{cor})$	-0.408	-0.404	-0.395	-0.341	-0.335	-0.326
a_0	5.811	5.764	5.688	6.634	6.602	6.504
B	41.0	46.9	45.7	28.2	28.2	49.0

to the Murnaghan equation of state (Murnaghan, 1944). The a_0 equilibrium values, the corresponding HF total energies $E_0(\text{HF})$ and the bulk modulus B are given in Table 2. The values of the binding energy at the HF level $BE(\text{HF})$ and corrected by the correlation energy $BE(\text{HF} + \text{cor})$ are also given in Table 2. BE corresponds to the difference between the total crystal energy and the HF atomic energies calculated with the same basis set for inner electrons plus additional functions included to describe the tails of the outer electrons. As was already reported in the study of highly ionic compounds such as Li_2O and Na_2O (Dovesi, Roetti, Freyria-Fava, Prencipe & Saunders, 1991), for example, or in our previous work (Lichanot *et al.*, 1993), the correlation energy E_{cor} is mainly due to electron transfer from cations to anions and can be estimated in a satisfactory way with the ionic correlation deduced from the data of Clementi (1963). In this model, the calculated values are $E_{\text{cor}}(\text{Li}_2\text{S}) = 0.117$ Hartree and $E_{\text{cor}}(\text{Na}_2\text{S}) = 0.105$ Hartree. The binding energies thus corrected are in very satisfactory agreement with the experimental ones determined at 0 K from Janaf thermochemical tables for Li, Na, S and Na_2S (Janaf Thermochemical Tables, 1985) and from Juza & Uphoff (1956) for Li_2S .

Examination of Table 2 shows that, on the whole, the results obtained with BSI or BSA are very close and in satisfactory agreement with the experimental ones. However, some slight differences can be observed and call for the following comments (i) Li_2S and Na_2S are stabilized by about 0.02 Hartree when

the energies are calculated with BSI: this result is attributable to a lower sulfur energy corresponding to a richer basis set used to describe core electrons. The binding energy of a given sulfide does not depend on the basis set, which constitutes a reliable and natural result, since the sulfur energy vanishes in the subtraction; (ii) the comparison between the experimental lattice parameters at 0 K as deduced by Lichanot *et al.* (1993) and our values leads to better agreement when a_0 is calculated with BSA (1.4%) than with BSI (2%): this result is somewhat surprising; (iii) finally, a first analysis of the B values seems to indicate that BSA is more suitable to account for the experimental values, especially in the Li_2S case. However, it must be recalled that the B values obtained with BSI not only by isotropic deformation (Table 2) but by the calculation of the elastic constants of Li_2S and Na_2S are in excellent agreement (Lichanot *et al.*, 1993): such a result must be proved with the use of BSA before concluding that the quality of BSA is better than BSI.

3.2. Electronic structure

The band structure of Li_2S and Na_2S and the associated density of states are calculated and given in Table 3 and Fig. 1. Table 3 summarizes the position, the width and the population of the energy bands. The band structure is analysed by performing a band-by-band Mulliken analysis: the populations given in Table 3 can be taken to be reliable, because overlap populations are very low (the highest overlap

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

The energy E corresponds to the bottom of the band with the band width ΔE . The values in italics are obtained with BSA.

(a) Li ₂ S								
Band	E (a.u.)	ΔE (eV)	Lithium		Sulfur		d	
			s	p	s	p		
1	-91.887	0.0	0.000	0.000	2.000	0.000	0.000	
2	-8.894	0.0	0.000	0.000	2.000	0.000	0.000	
3-5	-6.575	0.0	0.000	0.000	0.000	6.000	0.000	
6-7	-2.422	0.0	1.996	0.000	0.002	0.005	0.000	
8	-0.894	0.8	0.000	0.004	1.991	0.001	0.000	
9-11	-0.466	3.6	-0.010	0.042	0.002	5.931	0.004	
Shell								
1			1.616	-	2.000	-	-	
			<i>1.623</i>	-	<i>2.000</i>	-	-	
2			0.370	0.046	2.000	5.982	-	
			<i>0.366</i>	<i>0.047</i>	<i>1.998</i>	<i>5.978</i>	-	
3			-	-	0.238	1.125	0.004	
			<i>0.000</i>	<i>0.002</i>	<i>1.118</i>	<i>2.992</i>	<i>0.001</i>	
4			-	-	1.059	2.283	-	
			-	-	<i>0.881</i>	<i>2.958</i>	-	
5			-	-	0.699	2.546	-	
Total								
			1.986	0.046	5.996	11.936	0.004	
			<i>1.989</i>	<i>0.048</i>	<i>5.996</i>	<i>11.928</i>	<i>0.001</i>	
				2.032		17.936		
				<i>2.037</i>		<i>17.925</i>		
(b) Na ₂ S								
Band	E (a.u.)	ΔE (eV)	Sodium			Sulfur		d
			s	p	d	s	p	
1	-91.858	0.000	0.000	0.000	0.000	2.000	0.000	0.000
2-3	-40.436	0.000	2.000	0.000	0.000	0.000	0.000	0.000
4	-8.862	0.000	0.000	0.000	0.000	2.000	0.000	0.000
5-7	-6.543	0.000	0.000	0.000	0.000	0.000	6.000	0.000
8-9	-2.755	0.008	2.001	0.000	0.000	0.000	-0.001	0.000
10-15	-1.479	0.035	0.000	5.999	0.000	0.003	-0.001	0.000
16	-0.835	0.440	0.001	0.002	0.001	1.995	-0.001	0.000
17-19	-0.389	2.070	0.001	0.009	0.011	0.006	5.953	0.001
Shell								
1			2.000	-	-	2.000	-	-
			<i>2.000</i>	-	-	<i>2.000</i>	-	-
2			1.392	4.759	-	2.000	5.982	-
			<i>1.390</i>	<i>4.754</i>	-	<i>1.998</i>	<i>5.977</i>	-
3			0.570	1.107	0.012	0.238	1.099	0.001
			<i>0.580</i>	<i>1.144</i>	<i>0.013</i>	<i>1.188</i>	<i>3.039</i>	<i>0.011</i>
4			0.040	0.144	-	1.120	2.351	-
			<i>0.029</i>	<i>0.111</i>	-	<i>0.823</i>	<i>2.923</i>	-
5			-	-	-	0.647	2.518	-
Total								
			4.002	6.009	0.012	6.004	11.949	0.001
			<i>3.999</i>	<i>6.008</i>	<i>0.013</i>	<i>6.009</i>	<i>11.940</i>	<i>0.011</i>
				10.023			17.954	
				<i>10.021</i>			<i>17.959</i>	

population is 0.025 and corresponds to the first neighbour's S—S in Li₂S described with BSI), and also because the external atomic orbitals of lithium, sodium and sulfur are not particularly diffuse. The examination of Table 3 shows that the two sets BSI and BSA lead to practically the same results. For this reason, the Mulliken populations obtained only with BSI are given in Table 3, while the ones calculated with BSA are reported in italics only in shell populations.

The results have common features and thus allow the following conclusions: (i) The two compounds are almost fully ionic and the sodium sulfide is slightly more ionic than Li₂S since the mean net charge on the sulfur is 1.956 e in Na₂S and 1.930 e in Li₂S. This last result is confirmed by examining the p valence band of sulfur (9–11 in Li₂S, 17–19 in Na₂S), where the participation of lithium is two times greater than sodium. It can be noticed that this highly ionic character constitutes a significant dis-

crepancy with other results obtained for Na_2S and deduced either from experiment (0.72 e) (Bührer & Bill, 1980) or from an interatomic potential model (0.96 e) (Agnihotri *et al.*, 1984). (ii) As for highly ionic compounds [see for example, MgO (Causà, Dovesi, Pisani & Roetti, 1986a)], the band structure is very simple, since most of the bands are in fact single levels attributable to pure or nearly pure orbitals. (iii) The comparison of the Li_2S and Na_2S Mulliken populations with those of the corresponding oxides (Dovesi *et al.*, 1991) shows that Li_2O and Li_2S have the same ionic character, while Na_2O is slightly more ionic than Na_2S , which is not surprising.

The shape of the structure of the p valence band of sulfur is practically the same for Li_2S and Na_2S , when they are described by BSI or BSA. We have chosen to show in Fig. 1 the Li_2S (BSI) structure because it is larger than Na_2S and therefore the details of the curves along the path $\Gamma\cdots\text{K}$ of the first Brillouin zone are more precise: the associated density of states is also drawn. It can be noticed that this band structure is in agreement with that reported in a previous study (Ouazzani, Lichanot, Pisani & Roetti, 1993), where the sulfur was described by an effective core pseudo-potential: this work has shown the importance of knowing this structure in order to analyse accurately its alterations in the context of surface formation. At this stage of the discussion, it is interesting to point out that other ionic sulfide compounds, such as MgS with the NaCl structure type, have the same p valence band structure, and a 5.08 eV band width (Stepanyuk, Grigorenko, Katsnelson, Farberovich, Szász & Mikhailin, 1992). The evolution of the width of the sulfur p band with the distance between first neighbouring sulfurs $R(\text{S}-\text{S})$ in the series MgS (5.08 eV; 3.67 Å), Li_2S (3.61 eV; 4.02 Å) and Na_2S (2.07 eV; 4.60 Å) is quite similar to that obtained for the corresponding oxides (Dovesi, Roetti *et al.*, 1992): this result is an additional argument which shows the highly ionic character of these sulfides.

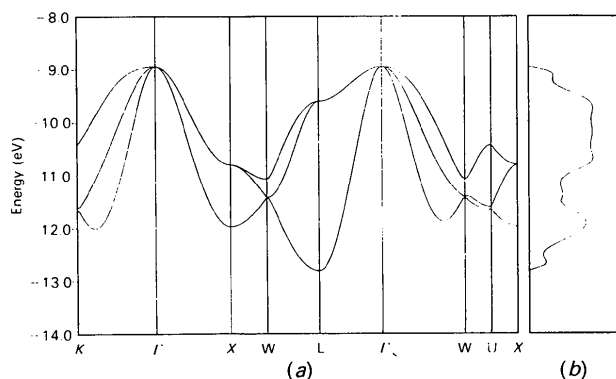


Fig. 1. (a) Structure of the sulfur p valence band in Li_2S (BSI) along high-symmetry directions of the first Brillouin zone. (b) Total density of states DOS's.

The electron charge density projected on the (110) plane of the structure is drawn in Fig. 2 for Na_2S (BSI). The electron charge-density maps of Li_2S are similar and have been given already in our previous work (Azavant & Lichanot, 1993). Figs. 2(a) and 2(b), which represent total and difference electron charge-density maps, symbolize perfectly the ionic character of the compound. Fig. 2(b), obtained by subtracting from the total electron charge density the superposition of the HF charge densities of the isolated ions calculated with the same basis set (Table 1), shows that the contraction of the anion in the direction of its neighbouring cations by the crystalline field effect is small, in spite of its larger size and polarizability: for example, the S^{2-} semi-empirical dipole polarizability is two and a half times greater than O^{2-} in the series of the compounds having the NaCl structure type (Mahan, 1980). Finally, an accurate comparison with the analogous map of Li_2S displays a slightly greater deformation in the latter case, which seems to confirm the less ionic character of Li_2S .

3.3. Elastic scattering: sulfur form factors

The static structure factors $F_0(hkl)$ have been calculated by Fourier transformation of the total electron charge density $\rho(\mathbf{r})$:

$$F_0(hkl) = (1/N) \int \rho(\mathbf{r}) \exp(-i\mathbf{s}\cdot\mathbf{r}) d\mathbf{r},$$

where the integral is extended over the N cells of the crystal.

104 directions were considered and only the first 52 are reported in the second and third columns of Table 4, parts (a) (Li_2S) and (b) (Na_2S). BSI and BSA lead to practically the same results since the

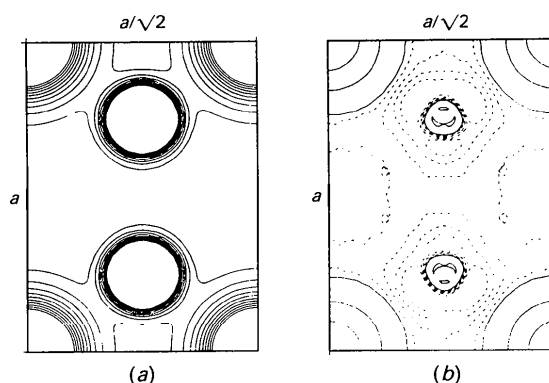


Fig. 2. Electron charge density of Li_2S (BSI) projected on the (110) plane. (a) Total electron charge-density map, the distance between two consecutive curves is 0.01 a.u. (b) Difference electron charge-density map obtained by subtracting from the total electron charge density the superposition of the electron charge density of the isolated ions. The distance between two consecutive curves is 0.005 a.u. and 0.0005 a.u. for the positive (continuous) lines and negative (dashed) lines, respectively.

Table 4. *Static structure factors* $F_0(hkl)$ *of* Li_2S *and* Na_2S *form factors of* Li^+ $f_0(\text{Li}^+)$ *and* Na^+ $f_0(\text{Na}^+)$ *and form factors of* S^{2-} $f_0(\text{S}^{2-})$, *as deduced from relationships (1a), (1b) and (1c)*

$F(hkl)$ is the structure factor calculated at $T = 298$ K with isotropic harmonic Debye–Waller factors $B_{\text{S}^{2-}} = 0.43 \text{ \AA}^2$, $B_{\text{Li}^+} = 0.54 \text{ \AA}^2$ for Li_2S and $B_{\text{S}^{2-}} = 0.63 \text{ \AA}^2$, $B_{\text{Na}^+} = 0.54 \text{ \AA}^2$ for Na_2S .

(a) Li_2S

hkl	$F_0(hkl)$		$f_0(\text{Li}^+)$		$f_0(\text{S}^{2-})$		$F_T(hkl)$
	BSI	BSA	BSI	BSA	BSI	BSA	
111	12.8479	12.8659			12.8479	12.8659	12.7110
200	8.3080	8.3046			11.9304	11.9262	8.2034
220	13.1297	13.1201	3.6224	3.6216	9.8302	9.8218	12.7507
311	9.0542	9.0349			9.0542	9.0349	8.7207
222	5.8467	5.8264	3.0202	3.0190	8.8669	8.8454	5.6431
400	11.0717	11.0583	2.7766	2.7757	8.2951	8.2826	10.4517
331	7.9856	7.9772			7.9856	7.9772	7.4904
420	5.3184	5.3106	2.5631	2.5624	7.8815	7.8729	5.0142
224	9.9553	9.9542	2.3744	2.3739	7.5809	7.5803	9.1374
115 333	7.3563	7.3576			7.3563	7.3576	6.7186
440	9.1179	9.1224	2.0571	2.0571	7.0608	7.0653	8.1378
531	6.8701	6.8746			6.8701	6.8747	6.1091
600 442	4.8749	4.8792	1.9228	1.9230	6.7977	6.8022	4.3740
620	8.4169	8.4213	1.8019	1.8022	6.6150	6.6192	7.3055
533	6.4435	6.4473			6.4435	6.4473	5.5783
226	4.6842	4.6875	1.6925	1.6929	6.3767	6.3804	4.0976
444	7.8065	7.8093	1.5933	1.5936	6.2132	6.2157	6.5898
711 551	6.0557	6.0578			6.0557	6.0578	5.1041
640	4.4910	4.4927	1.5028	1.5032	5.9938	5.9960	3.8294
642	7.2646	7.2660	1.4202	1.4206	5.8443	5.8453	5.9647
731 553	5.6989	5.6998			5.6989	5.6997	4.6765
800	6.7792	6.7796	1.2750	1.2753	5.5042	5.5042	5.4143
733	5.3700	5.3702			5.3700	5.3702	4.2903
820 644	4.1063	4.1065	1.2109	1.2112	5.3173	5.3177	3.3257
228 660	6.3423	6.3421	1.1518	1.1520	5.1905	5.1901	4.9275
751 555	5.0669	5.0668			5.0669	5.0668	3.9412
662	3.9215	3.9215	1.0970	1.0972	5.0186	5.0187	3.0950
840	5.9482	5.9476	1.0462	1.0463	4.9020	4.9013	4.4958
911 753	4.7884	4.7880			4.7884	4.7880	3.6263
842	3.7449	3.7447	0.9990	0.9990	4.7439	4.7438	2.8801
664	5.5919	5.5910	0.9550	0.9550	4.6369	4.6360	4.1119
931	4.5327	4.5320			4.5327	4.5320	3.3422
844	5.2692	5.2680	0.8755	0.8755	4.3937	4.3926	3.7698
933 771 755	4.2979	4.2971			4.2979	4.2971	3.0856
10,0,0 860	3.4207	3.4203	0.8396	0.8395	4.2603	4.2598	2.4979
10,2,0 862	4.9764	4.9750	0.8059	0.8057	4.1705	4.1692	3.4641
951 773	4.0826	4.0816			4.0826	4.0816	2.8538
10,2,2 666	3.2738	3.2733	0.7742	0.7740	4.0480	4.0473	2.3294

(b) Na_2S

hkl	$F_0(hkl)$		$f_0(\text{Na}^+)$		$f_0(\text{S}^{2-})$		$F_T(hkl)$
	BSI	BSA	BSI	BSA	BSI	BSA	
111	13.5714	13.5700			13.5714	13.5700	13.4136
200	5.2232	5.2255	8.9696	8.9704	12.7159	12.7152	5.1848
220	26.7851	26.7859	8.1112	8.1126	10.5628	10.5607	26.0486
311	9.6967	9.6974			9.6967	9.6974	9.2999
222	5.3139	5.3171	7.3848	7.3864	9.4557	9.4557	5.1685
400	22.3904	22.3942	6.7645	6.7660	8.8614	8.8622	21.1843
331	8.4771	8.4750			8.4771	8.4750	7.8907
420	4.1211	4.1259	6.2312	6.2322	8.3412	8.3384	3.9421
224	19.6184	19.6180	5.7684	5.7688	8.0817	8.0804	18.0556
115 333	7.8326	7.8314			7.8326	7.8314	7.0770
440	17.5856	17.5850	5.0099	5.0093	7.5659	7.5664	15.7413
531	7.3701	7.3709			7.3701	7.3709	6.4628
600 442	2.1131	2.1099	4.6969	4.6960	7.2808	7.2821	1.9992
620	15.9936	15.9929	4.4195	4.4183	7.1546	7.1564	13.9226
533	6.9791	6.9817			6.9791	6.9817	5.9387
226	1.4362	1.4312	4.1727	4.1711	6.9091	6.9109	1.3802
444	14.6976	14.6957	3.9520	3.9502	6.7936	6.7953	12.4414
711 551	6.6413	6.6427			6.6413	6.6427	5.4847
640	0.9320	0.9269	3.7541	3.7522	6.5761	6.5774	0.9358
642	13.6173	13.6141	3.5759	3.5739	6.4655	6.4663	11.2087
731 553	6.3282	6.3285			6.3282	6.3284	5.0720
800	12.7003	12.6961	3.2696	3.2675	6.1612	6.1612	10.1651
733	6.0351	6.0344			6.0351	6.0344	4.6942
820 644	0.2950	0.2913	3.1374	3.1354	5.9799	5.9795	0.4051
228 660	11.9099	11.9055	3.0172	3.0152	5.8755	5.8751	9.2692
751 555	5.7568	5.7565			5.7568	5.7565	4.3453

Table 4 (cont.)

<i>hkl</i>	$F_0(hkl)$		$f_0(\text{Na}^+)$		$f_0(\text{S}^{2-})$		$F_T(hkl)$
	BSI	BSA	BSI	BSA	BSI	BSA	BSI
662	0.1056	0.1022	2.9076	2.9056	5.7095	5.7089	0.2580
840	11.2226	11.2181	2.8073	2.8054	5.6080	5.6074	8.4932
911 753	5.4981	5.4978			5.4981	5.4977	4.0274
842	0.0241	0.0272	2.7154	2.7134	5.4067	5.3998	0.1624
664	10.6191	10.6150	2.6311	2.6293	5.3569	5.3564	7.8149
931	5.2563	5.2557			5.2563	5.2557	3.7367
844	10.0856	10.0819	2.4820	2.4804	5.1216	5.1213	7.2180
933 771 755	5.0282	5.0278			5.0282	5.0278	3.4690
10,0,0 860	0.1595	0.1623	2.4160	2.4144	4.6724	4.6664	0.0719
10,2,0 862	9.6110	9.6078	2.3549	2.3534	4.9012	4.9010	6.6894
951 773	4.8147	4.8144			4.8147	4.8144	3.2237
10,2,2 666	0.1843	0.1870	2.2983	2.2969	4.4122	4.4067	0.0589

agreement factor R defined by

$$R = [\sum_{hkl} |F_0(\text{BSI}) - F_0(\text{BSA})|] / [\sum_{hkl} F_0(\text{BSI})]$$

is as good as 0.06% for Li_2S and 0.02% for Na_2S .

By considering the strong ionic character of the two compounds, the S^{2-} form factors $f_0(\text{S}^{2-})$ are extracted from $F_0(hkl)$ with the following relationships

$$F_0(hkl) = f_0(\text{S}^{2-}) \quad \text{odd } hkl \quad (1a)$$

$$F_0(hkl) = f_0(\text{S}^{2-}) + 2f_0(\text{M}^+) \quad \text{even } hkl \text{ and } h+k+l=4n \quad (1b)$$

$$F_0(hkl) = f_0(\text{S}^{2-}) - 2f_0(\text{M}^+) \quad \text{even } hkl \text{ and } h+k+l=4n+2. \quad (1c)$$

The cation form factors $f_0(\text{M}^+)$ are calculated by Fourier transformation of the density matrix projected on the energy bands which characterize them (bands 6–7 for Li^+ ; bands 2–3, 8–9 and 10–15 for Na^+). The fourth and fifth, sixth and seventh columns of Table 4 give $f_0(\text{M}^+)$ and $f_0(\text{S}^{2-})$ for each basis set, respectively. It is interesting to notice that the difference between $f_0(\text{Li}^+)$ in Li_2S and $f_0(\text{Li}^+)$ deduced from *International Tables for Crystallography* (1992, Vol. C, p. 500) is practically constant (+0.015) in the whole region $0 \leq \sin \theta/\lambda \leq 2.0$ while this difference in the Na^+ case is less, negative for $0 \leq \sin \theta/\lambda \leq 1.2$ and practically zero for $\sin \theta/\lambda \geq 1.2$. Such a result can be related to the higher ionic character of Na_2S in which the electron cloud of the Na^+ ion is very close to that of the free ion.

The $f_0(\text{S}^{2-})$ values of Table 4 were fitted using the following expression from *International Tables for Crystallography*

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

and the coefficients a_i , b_i and c are listed in Table 5.

The factors $f_0(\text{S}^{2-})$ are interpolated with the help of (2) and of the coefficients of Table 5, then com-

Table 5. Coefficients a_i , b_i and c used in (2) for analytical approximation to the form factors of sulfur in Li_2S and Na_2S

	S^2 in Li_2S (BSI)	S^{2-} in Li_2S (BSA)	S^{2-} in Na_2S (BSI)	S^2 in Na_2S (BSA)
a_1	4.94600	5.92910	4.22428	4.32781
a_2	7.03169	7.01355	7.20202	7.20579
a_3	1.53449	1.49864	53.54820	53.43290
a_4	3.74110	3.15890	4.25442	4.15284
b_1	24.48010	26.74480	22.68420	22.96560
b_2	1.46610	1.47581	1.44509	1.44638
b_3	0.19507	0.21589	0.00321	0.00322
b_4	55.57970	68.53740	51.76620	52.42690
c	0.67622	0.74900	-51.51540	-51.39980

pared with those of the S^{2-} ion, when stabilized inside a Watson sphere (Watson, 1958) of adjustable radius r_w , whose surface is uniformly charged by $q = +2|e|$.

In these calculations, the sulfur is described by the basis set published by McLean & Chandler (1980): it consists of 13s and 10p primitive GTF's: an additional polarization function was added and optimized ($\alpha_d = 0.542$). After the SCF calculation, an electronic correlation was introduced through the configuration interaction with perturbatively selected interactions CIPSI procedure (Huron, Rancurel & Malrieu, 1973). The wave function was built up from a variational subspace of about 1300 determinants; the electronic correlation effect thus obtained is very small since it represents 0.1% of the 'spherical' form factor.

The agreement between our interpolated form factors $f_0(\text{S}^{2-})$ and those corresponding to the Watson model $f_{0,w}(\text{S}^{2-})$ is calculated by

$$R = [\sum_{hkl} |f_0(\text{S}^{2-}) - f_{0,w}(\text{S}^{2-})|] / [\sum_{hkl} f_0(\text{S}^{2-})],$$

for different r_w values. Fig. 3 shows the variations $R(r_w)$ for Li_2S and Na_2S described by the two basis sets. The values $r_{w,m}$, describing the best possible agreement [$r_{w,m} = 1.65(0.01) \text{ \AA}$ for Li_2S and $r_{w,m} = 1.83(0.01) \text{ \AA}$ for Na_2S], do not depend on the nature of the basis set and show that the Watson radius is greater by 10% in the Na_2S case than in that of Li_2S .

Now, if the variations of the difference $\Delta f_0 = f_0(S^{2-}) - f_{0,w}(S^{2-}) = \varphi(\sin \theta/\lambda)$ given for example for Li_2S are considered, examination of Figs. 4 and 5 allows us to notice the following. The Δf_0 values of Fig. 4 calculated for $r_{w,m} = 1.65 \text{ \AA}$ and corresponding to BSI and BSA lead to a shape of the curves which is classic and similar to the ionic MgO curve, for example (Causà, Dovesi, Pisani & Roetti, 1986*b*), and show, on the other hand, that they are independent of the basis set used, except in the Li_2S case where slight differences exist in the region of low angle reflections $\sin \theta/\lambda \leq 0.75 \text{ \AA}^{-1}$: this result is certainly connected to a less ionic character of Li_2S already responsible for a greater contraction of the electron charge density. The Δf_0 values of Fig. 5 corresponding to BSI are calculated for $r_{w,m} = 1.65 \text{ \AA}$, as in Fig. 4, and also for the extreme r_w values of Fig. 3 ($r_{w,1} = 1.50 \text{ \AA}$ and $r_{w,2} = 1.83 \text{ \AA}$), in the region $0 \leq \sin \theta/\lambda \leq 1.0 \text{ \AA}^{-1}$ where the precision is the best: the three curves are of sinusoid type, with rapidly damping amplitudes and with 'pseudo-periods', which are as high as r_w 's are small [$s_1 = 0.54 \text{ \AA}^{-1}$ ($r_{w,1} = 1.50 \text{ \AA}$); $s_m = 0.46 \text{ \AA}^{-1}$ ($r_{w,m} = 1.65 \text{ \AA}$); $s_2 = 0.39 \text{ \AA}^{-1}$ ($r_{w,2} = 1.83 \text{ \AA}$)]. More precisely, if reference is made to the best agreement (index m), it can be noticed that the ratios $|r_{w,2} - r_{w,m}|/|r_{w,1} - r_{w,m}| = 1.20$ and $|s_1 - s_m|/|s_2 - s_m| = 1.14$ are practically the same. Such a result is not surprising when considering the 'pseudo-periods' as corresponding to the Fourier transform of a step function of width r_w .

Without mistaking $r_{w,m}$ with the ionic radius of the sulfur, which could be accurately determined by a topological analysis of the charge densities (Bader, 1990), it is useful to recall the value (1.70 \AA) of the 'crystal radius' of the sulfur adopted by Shannon (1981) to establish mean interatomic distances in numerous sulfide compounds, and the value (1.84 \AA) of Pauling's sulfur radius.

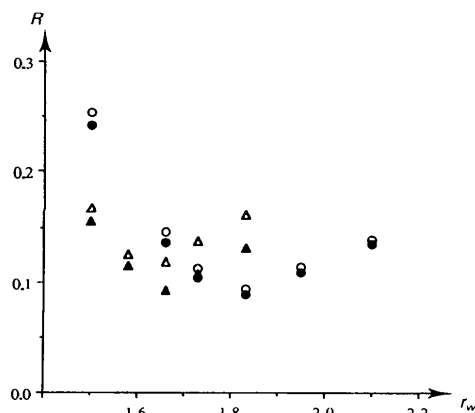


Fig. 3. Variations of the agreement factor $R = [\sum_{hkl} |f_0(S^{2-}) - f_{0,w}(S^{2-})|] / [\sum_{hkl} f_0(S^{2-})]$ versus the Watson radius r_w : Δ : Li_2S in BSA; \blacktriangle : Li_2S in BSI; \circ : Na_2S in BSA; \bullet : Na_2S in BSI.

In this study, the sulfur anisotropic deformation is analysed by comparing the calculated values of $f_0(S^{2-})$ (Table 4) with those deduced from the Watson model. Three curve types corresponding to 1a, 1b and 1c relationships appear for a given compound and a given set. For each, $\Delta f_0 = f_0(S^{2-}) - f_{0,w}(S^{2-}) = \varphi(\sin \theta/\lambda)$ is calculated and optimized as previously by obtaining the best agreement factor in the function of the Watson radius. The values of $r_{w,m}$ thus obtained are given in Table 6 where the notation $r_{w,m}(a)$, for example, corresponds to the best agreement between our calculated $f_0(S^{2-})$ and $f_{0,w}(S^{2-})$ concerning the directions (a) (odd h,k,l). The examination of the values given in this table shows that (i) the results, like the precedent ones, are independent of the basis set used; (ii) the mean Watson radius $r_{w,m}$ corresponds to the value $r_{w,m}(a)$ in the direction (a) where the structure factors $F_0(hkl)$ do not depend on the cation contribution (relation 1a); (iii) the same $r_{w,m}$ value obtained for Li_2S in the three direction types shows an isotropic contraction

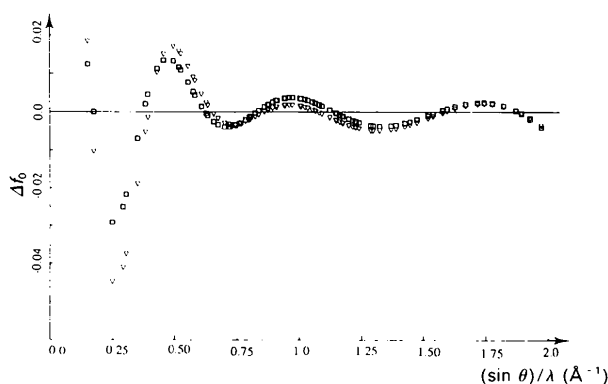


Fig. 4. Variations of the difference $\Delta f_0 = f_0(S^{2-}) - f_{0,w}(S^{2-})$ versus $\sin \theta/\lambda$ for Li_2S corresponding to $r_{w,m} = 1.65 \text{ \AA}$: ∇ : Li_2S in BSA; \square : Li_2S in BSI.

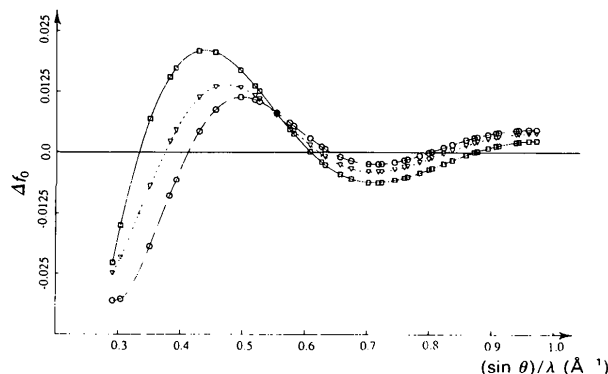


Fig. 5. Variations of the difference $\Delta f_0 = f_0(S^{2-}) - f_{0,w}(S^{2-})$, limited to the region $\sin \theta/\lambda \leq 1.0 \text{ \AA}^{-1}$, for Li_2S (BSI) corresponding to: \square : $r_{w,1} = 1.50 \text{ \AA}$; ∇ : $r_{w,m} = 1.65 \text{ \AA}$; \circ : $r_{w,2} = 1.83 \text{ \AA}$.

Table 6. Values of the Watson radius (\AA) corresponding to the best agreement between our calculated $f_0(\text{S}^{2-})$ (Table 4) and the form factors of the sulfur anion stabilized inside the Watson sphere

$r_{w,m}$ is the mean Watson radius obtained with the use of the 104 reflexions; $r_{w,m}(a)$, $r_{w,m}(b)$ and $r_{w,m}(c)$ are the Watson radii obtained with the use of the reflexions occurring in the relationships (1a), (1b) and (1c), respectively.

	Li ₂ S		Na ₂ S	
	BSI	BSA	BSI	BSA
$r_{w,m}$	1.65	1.64	1.84	1.83
$r_{w,m}(a)$	1.65	1.61	1.84	1.84
$r_{w,m}(b)$	1.66	1.53	1.99	2.01
$r_{w,m}(c)$	1.66	1.65	1.76	1.76

of the sulfur in this compound, while the different values in the Na₂S case indicate a rather significant anisotropy of the sulfur, with a compression and an expansion in the directions corresponding to even h,k,l with $h+k+l=4n+2$ (c) and $h+k+l=4n$ (b), respectively.

Finally, the thermal motion effect on the structure factor $F_0(hkl)$ was studied by using the values of the Debye-Waller factors B already published in the literature for $T=298$ K. Actually, B is a 3×3 tensor that is reduced to only one component in the isotropic case of cfc crystals. The triperiodic HF calculation at the static geometry is used to obtain the density matrix in the direct space $P(\mathbf{g})$ over the atomic orbitals basis set. The scattering integrals $\langle \mu(A) | \exp - (i\mathbf{s}\cdot\mathbf{r}) | \nu(B) \rangle$, where $\mu(A)$ and $\nu(B)$ are atomic orbitals centred on A and B atoms, are then analytically calculated, taking into account the displacements u_A and u_B of the atoms. The displacements are assumed independent and the integrals over them are calculated according to the distribution law $\exp - [1/2 u_{A,B}^2 / \langle u_{A,B}^2 \rangle]$ (Willis & Pryor, 1975). The product between the element of matrix $P_{\mu\nu}(\mathbf{g})$ and the scattering integral corrected by the thermal vibration is carried on, then the sum over the N cells of the crystal is made. When μ and ν belong to the same atom ($A \equiv B$), the thermal correction corresponds exactly to the Debye-Waller factor $\exp - (1/2 \langle u_{A,B}^2 \rangle s^2)$. The $F_T(hkl)$ at $T=298$ K are listed in the last column of Table 4 for Li₂S and Na₂S, only in the case of BSI. For Li₂S, the $B_{\text{Li}^+} = 0.54$ and $B_{\text{S}^{2-}} = 0.43 \text{ \AA}^2$ values deduced from a study of the elastic neutron diffraction (Bührer *et al.*, 1991) were used. In the Na₂S case, the values $B_{\text{Na}^+} = 4.34$ and $B_{\text{S}^{2-}} = 2.68 \text{ \AA}^2$, deduced from the study of the inelastic neutron scattering made by the same authors (Bührer & Bill, 1980), lead to a very large and surprising correction of the static structure factors. Actually, the comparison of the values of the cation and sulfur mean-square displacements shows that $\langle u_{\text{Na}^+}^2 \rangle$ is eight times greater than $\langle u_{\text{Li}^+}^2 \rangle$ and $\langle u_{\text{S}^{2-}}^2 \rangle$ in Na₂S six times greater than $\langle u_{\text{S}^{2-}}^2 \rangle$ in Li₂S.

Table 7. Total average Compton profile $J(q)$ (a.u.) in Li₂S and Na₂S, described with BSI and BSA

q	Li ₂ S		Na ₂ S	
	BSI	BSA	BSI	BSA
0.0	7.624	7.616	11.059	11.087
0.1	7.573	7.565	10.996	11.024
0.2	7.414	7.406	10.797	10.825
0.3	7.142	7.136	10.450	10.475
0.4	6.754	6.750	9.950	9.971
0.5	6.258	6.256	9.316	9.331
0.6	5.668	5.671	8.578	8.587
0.7	5.013	5.021	7.790	7.792
0.8	4.334	4.346	7.019	7.017
0.9	3.691	3.709	6.329	6.324
1.0	3.149	3.163	5.741	5.735
1.2	2.402	2.406	4.823	4.817
1.4	1.973	1.969	4.128	4.125
1.6	1.693	1.687	3.573	3.574
1.8	1.486	1.482	3.119	3.122
2.0	1.323	1.319	2.734	2.738
2.5	1.008	1.008	1.982	1.983
3.0	0.775	0.775	1.457	1.457
3.5	0.596	0.595	1.089	1.089
4.0	0.459	0.458	0.826	0.826
5.0	0.275	0.274	0.493	0.493
6.0	0.169	0.169	0.303	0.303
7.0	0.106	0.106	0.186	0.186
8.0	0.067	0.066	0.109	0.109
9.0	0.041	0.041	0.056	0.056
10.0	0.023	0.022	0.019	0.019

Such a result seems overestimated when considering the data corresponding to the families of the alkaline fluorides (Aikala & Mansikka, 1972; Bobel, Cortona & Fumi, 1989), chlorides (Bobel *et al.*, 1989) and oxides (Vidal-Valat & Vidal, 1978), where the cation mean-square displacement is practically the same and the anion mean-square displacement is greater only by a factor of two in the sodium fluoride compared with the lithium fluoride. In these conditions, it seems better to use for Na⁺ the same value as that for Li⁺, *i.e.* $B_{\text{Na}^+} = B_{\text{Li}^+} = 0.54 \text{ \AA}^2$ and for S²⁻ the experimental value obtained in the zincblende ZnS case (Hewat, 1972), $B_{\text{S}^{2-}} = 0.63 \text{ \AA}^2$. It can be also noticed that a very similar value $B = 0.604 \text{ \AA}^2$ characterizes the sulfur in PbS (Inagaki, Toyoda & Sakai, 1987).

3.4. Inelastic scattering: Compton profiles

In the momentum space, the electron-momentum distribution (EMD) along the three main symmetry directions and the corresponding Compton profiles (CP) are calculated using the impulse approximation. Average CP, namely $J(q)$, EMD and CP, anisotropies are given in Table 7 and in Figs. 6 and 7, respectively.

To our knowledge, no experimental data exists because of the same difficulties already mentioned in the *Introduction*. The present results complement those obtained from the electron charge density and the structure factors, and can be used as a reference for experimental studies.

Examination of Table 7 shows that BSI and BSA lead to similar values: this result, also valid for EMD and CP anisotropies, is the reason why the data obtained only with BSI are given below.

At present, the discussion will be limited to the examination of Figs. 6 and 7 because the structural and geometric information, that can be deduced from them, is more precise and richer and the results will be compared with the very accurate ones obtained for MgO (Causà, Dovesi, Pisani & Roetti, 1986*b,c*; Aikala, Paakkari & Maninnen, 1982) and LiH (Asthalter, Weyrich, Harker, Kunz, Orlando & Pisani, 1992; Pattison & Williams, 1976; Dovesi, Ermondi, Ferrero, Pisani & Roetti, 1984), and other highly ionic compounds.

As Figs. 6 and 7 show, the electron-momentum density anisotropy is high only for the small values of the electron momentum (≤ 2.0 a.u.) and attributable to the valence electrons. This result is confirmed when considering the contribution to the EMD of the different energy bands that allows us to

assign the anisotropy especially to the $3p$ electrons of the sulfur. In addition, it can be noticed that the greatest anisotropy corresponds to the (100) direction since the shape of the (100) EMD curve significantly differs from the two others, which are quite similar: this result is also revealed by the CP anisotropies $\Delta J(q)$ (Fig. 7), which are double when this direction is considered. On the whole, such data are very close to those obtained for LiH and MgO, which also present CP anisotropy curves with a very simple structure: it can be nevertheless noticed that the MgO anisotropy runs to higher q values ($q = 4.0$ a.u.) and the $\Delta J(q)$ differences are about two times smaller than those obtained for LiH, Li_2S and Na_2S .

If reference is made to the direct space representation, the information contained in the directional EMD and CP is now analysed from the auto-correlation function $B(r)$, which is defined as the Fourier transform of the CP function $J(q)$ and also provides a significant check of the quality of the calculated wavefunctions.

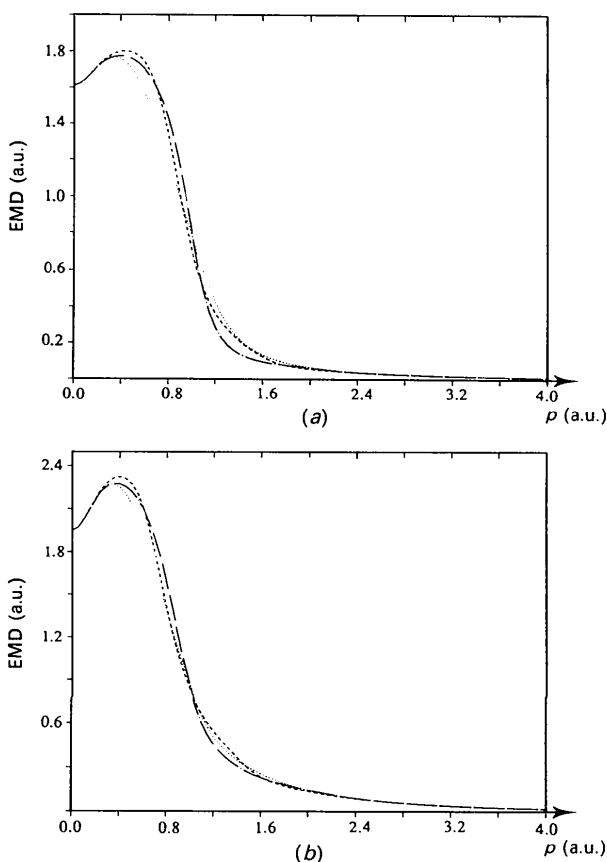


Fig. 6. Variations of the electron momentum density EMD (a.u.) along the three crystallographic directions versus the electron momentum p (a.u.) in (a) Li_2S and (b) Na_2S , both described by BSI. [100] direction; - - - - [110] direction; - · - · [111] direction.

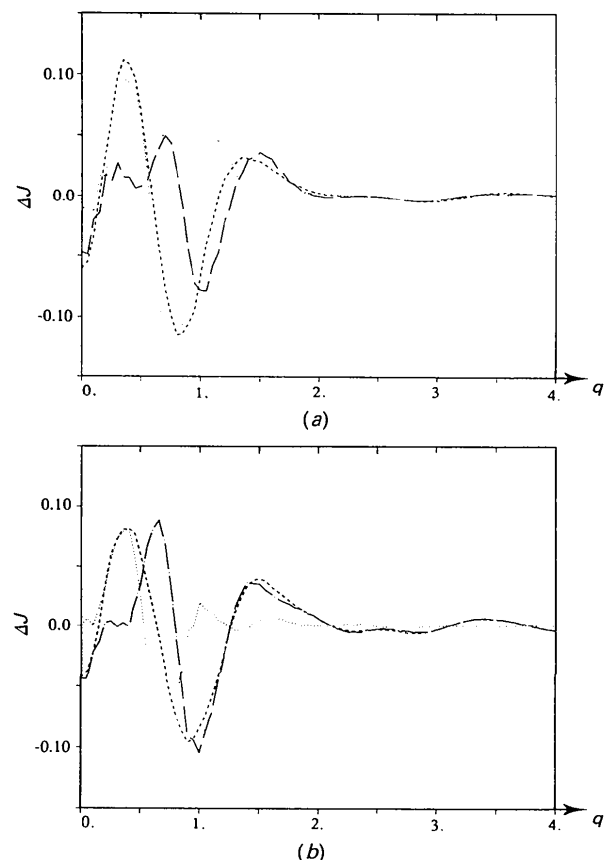


Fig. 7. Compton profile anisotropies ΔJ (a.u.) versus the electron momentum projected on the scattering vector q (a.u.) for (a) Li_2S and (b) Na_2S , both described by BSI. $\Delta J = J_{100} - J_{110}$; - - - $\Delta J = J_{100} - J_{111}$; - · - · $\Delta J = J_{110} - J_{111}$.

Table 8. Zero passages (a.u.) of the autocorrelation function corresponding to the valence contribution along the three main crystallographic directions

The values in parentheses correspond to the reticular zero passages imposed by symmetry and calculated with the lattice parameters of Table 2: a_0 (Li₂S) = 10.77 a.u. and a_0 (Na₂S) = 12.29 a.u.

	[100]	[110]	[111]
	4.67	4.53	4.57
Li ₂ S	10.70 (10.77)	7.62 (7.62)	7.68
	11.35	10.53	11.60
	15.90	15.26 (15.23)	18.75 (18.66)
		18.10	
	5.16	5.02	5.32
Na ₂ S	12.30 (12.29)	8.68 (8.69)	10.70
	13.05	11.43	17.10
		17.30 (17.38)	(21.29)

In the Na₂S case, the core-electron contribution to CP runs to very high q values according to a very slowly decreasing curve. The Fourier transform of such a curve gives rise to numerous oscillations in the interesting part ($4.0 < r < 20.0 \text{ \AA}$) of the $B(r)$ function. For this reason and in order to analyse more precisely the main features of this function, $B(r)$ was only calculated for the valence electrons. The main results that are deduced from the directional $B(r)$ can be summarized as follows: (i) the $B(0)$ values (7.98 in the Li₂S case, 7.97 in the Na₂S case) correspond well to the number of valence electrons; (ii) the zero passages of $B(r)$ along the three main crystallographic directions are given in Table 8: among these values, it can be noticed that the 'reticular zero passages' are satisfactorily reproduced, which means that these two compounds are non-conducting systems and that the calculated wavefunctions are of quality.

The non-reticular zero passages and a detailed description of the behaviour of the $B(r)$ functions around the first minimum give information about the contributions to the electronic structure: a detailed analysis, as in the MgO case (Aikala *et al.*, 1982), will be performed in further work for the same series of compounds.

4. Concluding remarks

The electronic structure of the lithium and sodium sulfides in the solid state has been established from the HF-LCAO approximation and the elastic and inelastic scattering properties are deduced. The two all-electron basis sets BSI and BSA which were used focused on the ions and the atoms, respectively, and the studies led to the same results. The correlation energy deduced from the ionic model, the analysis of the Mulliken populations and of the density of states projected on the energy bands, the electron charge-density maps, the calculation of the structure factors

and of the Compton profiles both show the fully ionic character of these two compounds.

The compared analysis of the sulfur form factors in Li₂S and Na₂S, and of the sulfur ion stabilized inside the Watson sphere allow us to show the isotropic contraction of S²⁻ in Li₂S and a significant anisotropic deformation in Na₂S.

Finally, the values of the structure factors have been calculated at room temperature by considering the influence of the thermal motion of the ions and by a consequent perturbation of the static density matrix. Unfortunately, the absence of experimental data prevents us from confirming or negating the values of the mean-square displacements of the ions reported in the literature: thus, our structure factors must be considered as indicative values for experimental studies.

The analysis of the Compton profile results also confirms the fully ionic character of Li₂S and Na₂S, and proves the quality of the wavefunctions used.

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Structure of SAPO-31 Refined from Single-Crystal Diffraction Data: Substitution of P by Si Established by Diffraction Methods

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Abstract

SAPO-31 is a silicoaluminophosphate with an idealized composition $\text{Al}_9\text{P}_8\text{SiHO}_{36}$ and a crystal structure close to $\text{AlPO}_4\text{-31}$, a microporous substance of zeolite framework topology ATO, $M_r = 1095.72$, rhombohedral, hexagonal setting, space group $R\bar{3}$, $a = 20.839$ (2), $c = 5.041$ (1) Å, $V = 1886$ (1) Å³, $Z = 2$, $D_x = 1.93$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 0.72$ mm⁻¹, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $F(000) = 1081$, 2440 single crystal X-ray intensities measured, 391 averaged unique intensities, refinement on $|F|$, $R = 0.051$, $wR = 0.018$, including all unobserved and weak F_{hkl} . A previous refinement based on synchrotron X-ray

powder diffraction data for $\text{AlPO}_4\text{-31}$ is confirmed with much higher precision. The Si atoms in SAPO-31 replace statistically part of the P atoms in the framework. This type of substitution has thus been established by X-ray diffraction methods for the first time in a microporous silicoaluminophosphate.

Introduction

The synthetic compound $\text{AlPO}_4\text{-31}$ is one of a series of microporous aluminophosphates that are in many ways analogous to zeolites, but have a neutral framework. This type of compound is usually crystallized in the presence of so-called template molecules, in the present case of di-*n*-propylamine [DPA, $(\text{C}_3\text{H}_7)\text{NH}(\text{C}_3\text{H}_7)$]. The crystal structure of calcined $\text{AlPO}_4\text{-31}$ was solved from synchrotron X-ray

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