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Theoretical *Ab Initio* Calculations of the Structure Factors of Fluorite (CaF_2)

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Abstract

Ab initio calculations of static structure factors of fluorite (CaF_2) are performed by a linear combination of atomic orbitals Hartree–Fock method as implemented in the *CRYSTAL* program. The effect of thermal motion is then introduced by taking into account the atomic mean square displacements given in the literature at different temperatures and leads to dynamic structure factors. Finally, a very slight displacement of fluorine ions with respect to their ideal position is considered, to simulate an anharmonic vibration or disordered structure so as to improve the agreement with experimental data.

Introduction

In a recent theoretical study of fluorite (CaF_2), Catti, Dovesi, Pavese & Saunders (1991) perfected and used an atomic orbitals (AO) basis set for calcium and fluorine, which allowed them to calculate and compare successfully with experiment some ground-state properties: lattice parameter, binding energy, electronic and band structures, and elastic constants. The fully ionic nature of fluorite is clearly shown.

In the present work, we have calculated the static structure factors of fluorite from the wave functions and density matrix obtained by *CRYSTAL*, an *ab initio* periodic Hartree–Fock program (Dovesi, Pisani, Roetti, Causà & Saunders, 1989; Dovesi, Roetti & Saunders, 1992) by using the same all-electron basis set and computational parameters as those previously defined by Catti *et al.* (1991).

A perturbation of the Fock matrix by thermal motion, assuming that atomic displacements are independent and that the atomic orbitals follow nuclear movements (Azavant, Lichanot, Rérat & Chaillet, 1994), allows us to calculate dynamic structure factors at any temperature by introducing the thermal mean square amplitudes of the atoms given in the literature. Thus, it becomes possible to compare theoretical and experimental values, provided that the latter have been corrected for secondary factors (scale, Lorentz, polarization, absorption, extinction, anomalous scattering, thermal diffuse scattering). For comparison with our calculations, we have considered all the experimental data sets obtained for fluorite in the last 30 years since Togawa's (1964) work. They include: (i) the measurements obtained on the same crystal (American Crystallographic Association single-crystal intensity project) by Abrahams *et al.* (1967) and their assessment and analysis done respectively by Mackenzie & Maslen (1968) and by Cooper (1970); (ii) the data obtained by Zachariasen (1968) with a small spherical crystal; (iii) the data set collected from a crystal of 90 μm by Bachmann, Kohler, Schulz & Weber (1985). These authors have also obtained intensities with synchrotron radiation for the same crystal and for a smaller one of 6 μm. The study of microcrystals (2 μm^3) performed by Rieck, Euler & Schulz (1988) with synchrotron X-ray diffraction allowed the collection of extinction-free data at short wavelengths for use in high-accuracy crystal structure analysis, as shown by Rieck, Schulz & Siedel (1991) and Cheetham & Wilkinson (1992).

As we see, the data are numerous but not always very accurate. Those collected with a conventional X-ray tube by Abrahams *et al.* (1967) are considered to be outside the range of small sin θ/λ values indicated by Mackenzie & Maslen (1968) and analysed by Cooper (1970) to obtain very valid Debye–Waller factors. Those collected with synchrotron radiation and microcrystals concern on the contrary the small sin θ/λ values and lead to abnormally high Debye–Waller factors (Rieck *et al.*, 1988). It is therefore useful and interesting to present a theoretical study of the structure factors of fluorite over a large range of sin θ/λ values to 1.5 $Å^{-1}$ with the same precision for the small and high angles.

The structure of this paper is as follows: in §I, the static structure factors are calculated and analysed *versus* the deformation of the ions. §II corresponds to the comparison between the room-temperature experimental data and our dynamic structure factors calculated with the same atomic mean square amplitudes. The variations of the structure factors with temperature and position of fluorine in the cell are also studied.

I. Static structure factors

The method of calculation and the description of the atomic orbitals basis set are already published by Catti *et al.* (1991). It is recalled that we only use the all-electron *ab initio* Hartree–Fock computational scheme described by Pisani, Dovesi & Roetti (1988) and implemented in the *CRYSTAL* program (Dovesi *et al.*, 1989) and that the two basis sets are 8-6-511G* for calcium and 7-311G for fluorine, respectively: the star indicates the presence of *d* polarization functions in the calcium basis set represented by a three-Gaussian-functions contraction.

CaF_2 is cubic $Fm3m$ with four formula units in the cell. The lattice parameter adopted in these calculations is the experimental one extrapolated to $T = 0$ K (5.445 Å), as deduced from the thermal expansion given by White (1980) and from the unit-cell edge at 300 K ($a = 5.463$ Å; Wyckoff, 1968). With these data, the wave function and electron density have been calculated.

To illustrate these calculations, we have chosen to present shell Mulliken populations and to compare them with those of the isolated ions described with the same basis sets. As Table 1 shows, the classical situation of a fully ionic compound is found with a net charge of 0.934 e^- on fluorine. A significant contraction of the anion induced by the crystalline field of the neighbouring cations is also observed: the Mulliken population of the most diffuse function of fluorine in CaF_2 is smaller by 0.28 e^- than that of free F^-. This result is also shown by Catti *et al.* (1991) from total and differential electron charge density maps.

Table 1. *Atomic Mulliken populations per valence-electron shell in* CaF_2 *and in the isolated ions* (*f*) *described by the same basis sets*

	2*sp*	3*sp*	4*sp*	5*sp*	3*d*	Total
Ca in CaF_2	8.078	4.562	2.519	0.870	0.103	16.132
F in CaF_2	3.933	2.898	1.103			7.934
Ca^{2+} (*f*)	8.081	4.560	2.533	0.826		16.000
F^- (*f*)	3.919	2.702	1.380			8.000

From the electron density $\rho(\mathbf{r})$, the scattering factor is deduced according to

$$f(\mathbf{s}) = \int \rho(\mathbf{r}) \exp(-i\mathbf{s}\cdot\mathbf{r}) d\mathbf{r}, \qquad (1)$$

where **r** and **s** are the electron position and the scattering vectors, respectively, with

$$\rho(\mathbf{r}) = \sum_{\mu,\nu,\mathbf{g}} P^{\mathbf{g}}_{\mu\nu} \chi^{0}_{\mu}(A, \mathbf{r}) \chi^{\mathbf{g}*}_{\nu}(B, \mathbf{r}); \qquad (2)$$

$\chi^0_\mu(A, \mathbf{r})$ is the μth AO on atom A in the reference zero cell, $\chi^{\mathbf{g}}_\nu(B, \mathbf{r})$ is the νth AO on atom B in the crystal cell

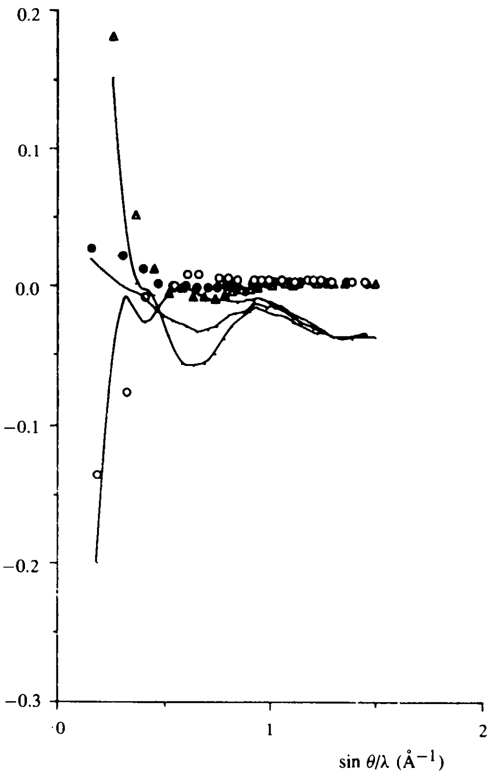

Fig. 1. Differences $F_0 - F_c$ *versus* sin θ/λ. F_0 values are given in Table 2. Symbols • for odd h, k, l, △ for $h+k+l = 4n$ and ○ for $h+k+l = 4n+2$ correspond to the differences where F_c values are calculated from our AO basis set. The full lines correspond to the differences where F_c values are calculated from *International Tables for Crystallography* (1992).

Table 2. *Static F_0 and dynamic structure factors F_{300}, $F_{300}(\delta)$ calculated at $T = 300$ K for an ideal and a disordered structure, respectively*

F_{300}^{DW} is the structure factor calculated from the Debye–Waller model. In these calculations, the atomic mean square displacements given by Bachman *et al.* (1985) are adopted: $B_{\mathrm{Ca}} = 0.61$ and $B_{\mathrm{F}} = 0.81$ Å^2 (B_{IV} experiment). $F_{300}(B_{\mathrm{IV}})$ corresponds to the observed X-ray conventional structure factors corrected by extinction factor and anomalous scattering.

h	k	l	$(\sin\theta/\lambda)_0$(Å^{-1})	F_0	F_{300}^{DW}	F_{300}	$F_{300}(\delta)$	$F_{300}(B_{\mathrm{IV}})$
1	1	1	0.1590	62.228	61.227	61.332	61.163	71.296
2	0	0	0.1836	0.576	1.441	0.932	0.932	2.432
2	2	0	0.2597	97.656	92.699	93.344	93.344	115.292
3	1	1	0.3045	46.412	43.895	43.968	44.140	46.248
2	2	2	0.3181	6.520	7.116	6.840	6.842	7.204
4	0	0	0.3673	73.832	67.231	67.420	67.420	74.800
3	3	1	0.4003	38.456	34.939	34.980	34.812	36.096
4	2	0	0.4107	8.824	8.846	8.820	8.824	8.948
4	2	2	0.4499	61.288	53.418	53.468	53.464	56.312
3	3	3	0.4771	34.000	29.674	29.685	29.564	29.876
4	4	0	0.5194	53.792	44.862	44.840	44.836	46.804
5	3	1	0.5432	31.260	26.194	26.196	26.328	26.456
6	0	0	0.5510	10.864	9.988	10.024	10.024	10.208
6	2	0	0.5808	48.924	39.012	38.976	38.976	40.096
5	3	3	0.6021	29.400	23.641	23.644	23.508	23.920
4	4	4	0.6362	45.532	34.697	34.672	34.672	35.688
5	5	1	0.6558	27.984	21.610	21.604	21.700	21.620
6	4	0	0.6622	11.492	9.843	9.864	9.864	9.884
6	4	2	0.6872	42.992	31.321	31.296	31.296	32.604
5	5	3	0.7053	26.836	19.893	19.892	19.784	20.068
8	0	0	0.7346	40.984	28.545	28.520	28.520	28.492
7	3	3	0.7516	25.836	18.384	18.384	18.492	18.360
6	4	4	0.7572	11.316	9.098	9.112	9.112	8.948
6	6	0	0.7792	39.328	26.180	26.164	26.164	26.412
5	5	5	0.7952	24.932	17.031	17.028	17.128	16.580
6	6	2	0.8005	11.056	8.626	8.640	8.640	8.396
8	4	0	0.8213	37.896	24.111	24.100	24.100	23.668
7	5	3	0.8366	24.080	15.794	15.792	15.716	15.408
8	4	2	0.8416	10.720	8.130	8.140	8.140	8.072
6	6	4	0.8614	36.624	22.265	22.260	22.260	22.128
9	3	1	0.8760	23.276	14.656	14.656	14.740	14.196
8	4	4	0.8997	35.460	20.601	20.600	20.600	20.292
7	5	5	0.9137	22.508	13.604	13.608	13.708	13.392
8	6	0	0.9183	9.916	7.132	7.140	7.140	7.104
8	6	2	0.9365	34.380	19.088	19.084	19.084	18.880
9	5	1	0.9499	21.768	12.634	12.636	12.556	12.640
6	6	6	0.9543	9.488	6.653	6.660	6.660	6.800
9	5	3	0.9847	21.056	11.732	11.736	11.824	11.836
8	6	4	0.9890	9.048	6.195	6.200	6.204	6.284
10	2	4	1.0059	32.424	16.433	16.432	16.432	16.380
7	7	5	1.0184	20.376	10.897	10.904	10.816	10.692
9	5	5	1.0510	19.716	10.126	10.128	10.048	9.968
10	4	4	1.0550	8.176	5.353	5.360	5.360	5.104
8	6	6	1.0709	30.672	14.186	14.188	14.188	–
11	3	3	1.0826	19.084	9.408	9.412	9.480	–
12	0	0	1.1019	29.852	13.188	13.188	13.188	–
11	5	1	1.1133	18.476	8.746	8.742	8.816	–
12	2	0	1.1171	7.340	4.617	4.620	4.620	–
12	2	2	1.1321	29.080	12.268	12.272	12.272	–
9	7	5	1.1432	17.896	8.132	8.136	8.212	–
8	8	6	1.1760	6.564	3.980	3.984	3.988	–
11	5	5	1.2008	16.808	7.041	7.044	7.108	–
10	6	6	1.2043	6.200	3.698	3.704	3.704	–
12	4	4	1.2182	26.948	9.902	9.904	9.904	–
9	7	7	1.2286	16.300	6.555	6.560	6.492	–
10	8	4	1.2320	5.852	3.436	3.440	3.440	–
9	9	5	1.2557	15.812	6.105	6.108	6.048	–
8	8	8	1.2724	25.680	8.601	8.604	8.604	–
11	7	5	1.2823	15.348	5.689	5.692	5.636	–
12	6	4	1.2856	5.204	2.974	2.976	2.980	–
10	8	6	1.2986	25.084	8.021	8.024	8.024	–
12	6	6	1.3496	23.968	6.987	6.988	6.988	–
11	7	7	1.3589	14.084	4.620	4.620	4.672	–
10	8	8	1.3866	4.112	2.248	2.252	2.252	–
12	8	6	1.4344	3.660	1.965	1.968	1.968	–
11	9	7	1.4548	12.652	3.525	3.528	3.484	–
10	10	8	1.4920	21.124	4.662	4.664	4.664	–
12	8	8	1.5144	20.716	4.364	4.364	4.364	–

associated with the translation vector **g** and $P^{\mathbf{g}}_{\mu\nu}$ is the corresponding element of the density matrix (Pisani *et al.*, 1988). The static structure factor F_0 is expressed as a function of $P^{\mathbf{g}}_{\mu\nu}$ and of the static diffusion integrals which are calculated analytically (Ferrero, 1981). The calculated F_0 values are reported in column 3 of Table 2 for 69 independent reflections covering the range $0 \leq \sin\theta/\lambda \leq 1.5$ Å^{-1}.

For an ionic compound such as CaF_2 and for its ideal fluorite-type structure, the independent-atom model (IAM) leads to the following expressions for the structure factors:

$$\begin{aligned} F_c &= 4f_{\mathrm{Ca}^{2+}} && \text{for odd } h, k, l \\ F_c &= 4f_{\mathrm{Ca}^{2+}} + 8f_{\mathrm{F}^-} && \text{for } h+k+l = 4n \\ F_c &= 4f_{\mathrm{Ca}^{2+}} - 8f_{\mathrm{F}^-} && \text{for } h+k+l = 4n+2. \end{aligned} \qquad (3)$$

The differences between the values F_0 of Table 2 and the values F_c calculated by adopting the same atomic orbitals basis sets for $f_{\mathrm{Ca}^{2+}}$ and f_{F^-} are reported in Fig. 1.

Examination of this figure, which represents the deviation of the real structure factors from those corresponding to the IAM, is only significant for small $\sin\theta/\lambda$ values (<0.5 Å^{-1}), where the influence of valence electrons is the largest. This result shows that the positive and negative differences $F_0 - F_c$ are attributable to the deformation of the electron clouds in the crystal with respect to isolated ions. In the direction corresponding to odd h, k, l, the scattering factor $f_{\mathrm{Ca}^{2+}}$ in the fluorite is barely larger than the scattering factor of the isolated ion and corresponds to the small contraction of Ca^{2+} in the crystal (Catti *et al.*, 1991). For even h, k, l, the real values F_0 are largely different from the F_c ones: this deviation is therefore attributable mainly to the great part of the fluorine anion in the expression of the structure factor and to its significant contraction in the crystal.

Basis-set effect

Instead of calculating the scattering factors of the isolated ions with our AO basis sets, the same properties have also been evaluated using data reported in *International Tables for Crystallography* (1992), and the new differences $F_0 - F_c$ are shown as full lines in Fig. 1. The shape of the curves is similar as before, but a 0.025 mean difference between the results obtained with the two types of basis sets is observed. As this difference is approximately the same for all sin θ/λ values, and the f_{F^-} calculated with our basis set are practically equal to those reported in *International Tables for Crystallography*, it is clear that this deviation is only attributable to a richer description of the core electrons of the calcium in our basis set than in the one used in *International Tables for Crystallography*. To confirm this result in part, calculations of the scattering factor of the isolated calcium ion have been done with our atomic orbital basis set without the 3*d* polarization function. Differences of 0.035 and of −0.02 are observed for the first two reflections and for the three following ones, respectively: these are the only significant differences between the scattering factor $f_{Ca^{2+}}$ values calculated with and without polarization functions.

II. Dynamic structure factors

To calculate structure factors at any temperature, the atomic thermal motion described by mean square displacements $\langle u^2 \rangle$ is introduced by affecting the couples of atomic orbitals (μ, ν) with which the elements of the density matrix are associated. This is done in the context of the Debye hypothesis where atoms are in mutually independent vibration. The distribution probability law $p(\mathbf{u})$ of finding an atom with a displacement $\mathbf{u}$ given by Willis & Pryor (1975) is adopted, and the AOs are assumed to follow the movements of the nuclei. This method leads to an expression of the dynamic structure factor F_T formally identical to the static factor F_0, with new exponents α_i' of the Gaussian functions in the AOs defined with respect to the static ones (α) by $\alpha_i' = \alpha/(1 + 2\alpha B_{ii})$; B is the tensor of mean square displacement $\langle u^2 \rangle$ and $i (= 1, 2, 3)$ denotes each of the three Cartesian directions (Azavant *et al.*, 1994).

Comparison with the experiment

The structure factors are calculated at room temperature by using the atomic mean square displacements given in the experimental papers and are compared with the corresponding measured values corrected for the anomalous dispersion (*International Tables for Crystallography*, 1992). The agreement factor R is defined as

$$R = \sum_{h,k,l} |F_T - F_e| \Big/ \sum_{h,k,l} F_e,$$

where F_e represents the experimental value of the structure factor for the *hkl* reflection and F_T is our calculated value. Table 3 reports the R values obtained for eight data sets denoted ACA, Z_{Mo}, Z_{Cu}, B_I, B_{II}, B_{III}, B_{IV} and Ri. In the American Crystallographic Association (ACA) data (Abrahams *et al.*, 1967), we have only considered those of experiment 2 for which the extinction factor is precisely given by Cooper (1970); Z_{Mo} and Z_{Cu} are symbols associated with the results obtained by Zachariasen (1968) for Mo$K\alpha$ and Cu$K\alpha$ radiations, respectively; B_I, B_{II}, B_{III} and B_{IV} are symbols corresponding to the data of Bachmann *et al.* (1985) obtained with a 6 µm crystal and 90% polarization, a 6 µm crystal and 94% polarization, a 90 µm crystal and 50% polarization and a 90 µm crystal and 0% polarization (conventional X-ray tube); Ri is the symbol associated with the data of Rieck *et al.* (1988). As an example, the experimental values B_{IV} of Bachman *et al.* (1985) corrected with an extinction factor and for anomalous dispersion (*International Tables for Crystallography* 1992) are given in column 7 of Table 2 for comparison with our results (column 5 or 6 of the same table).

Table 3. *Agreement factor R between our theoretical structure factors and experimental values obtained at room temperature for n independent reflections*

The atomic mean square displacements B (in Å^2) used in our calculations are those optimized by the authors. Symbols are explained in the text.

	ACA	Z_{Mo}	Z_{Cu}	B_I	B_{II}	B_{III}	B_{IV}	Ri
B_{Ca}	0.53	0.60	0.60	0.38	0.38	0.64	0.61	1.50
B_F	0.78	0.80	0.80	0.83	0.83	0.92	0.81	2.60
R(%)	18	2.5	3	2.7	6.4	8.9	4.6	6.7
	(16)			(1.8)	(2.8)	(2.9)	(2)	(3.6)
n	36	34	11	16	19	41	46	9
	(28)			(15)	(16)	(37)	(42)	(7)

Generally speaking, the comparison between our theoretical and the measured structure factors sometimes shows (just as that of the different experimental data sets) very large differences in the group of the eight lowest-angle reflections which contains the five strongest and also the two smallest F values. If a few (from one in B_I to four in B_{III} or B_{IV}) characterized by these large differences are omitted, the number of independent data given in parentheses in Table 3 is obtained, and the corresponding R value is reported in parentheses. Examination of the R values shows that the agreement between our theoretical structure factors and the experimental ones is satisfactory if we exclude the ACA data for which several reasons have been already given by Mackenzie & Maslen (1968) and Cooper (1970) to explain the disagreement. It is convenient to notice that the R values corresponding to the Z_{Cu}, B_I, B_{II} and Ri experiments actually underestimate the agreement, since the data are not very numerous and occur in the range of the smaller sin θ/λ values, which is affected by the largest errors.

Thermal variations of the structure factors: comparison with the Debye–Waller model

The previous comparison between our theoretical data and the experimental ones at room temperature allows us to calculate accurate and homogeneous values of the structure factors over a large range of sin θ/λ corresponding to 69 investigated reflections.

Column 5 of Table 2 reports our results at 300 K (F_{300}) while, in column 4, the values of the structure factors F_{300}^{DW} obtained within the Debye–Waller model are given. For these calculations, we have adopted the experimental lattice parameter at room temperature $a_{300} = 5.463$ Å (Wyckoff, 1968) and the more recent X-ray values of $B_{\mathrm{Ca}} = 0.61$ and $B_{\mathrm{F}} = 0.81$ Å^2 (Bachman *et al.*, 1985), which are accurate and in good agreement with other X-ray values (see Table 3) in the range of the small values of $\sin\theta/\lambda$. Comparison between the values of these two columns allows us to show the effect of electron density deformation, which is only taken into account in the F_{300} values. Examination of Table 2 shows differences between F_{300} and F_{300}^{DW} values smaller than 0.5%, proving that fluorite is a nearly fully ionic compound. However, for the reflections 200 and 222 belonging to the even-index group $h+k+l = 4n+2$ for which small structure-factor values result from the competition between calcium and fluorine components, much larger differences are found, 55 and 4%, respectively. Although these values are the most sensitive to the precision of the calculations, they show the overlap and/or contraction effect of the valence-electron clouds of fluorine and calcium: this result confirms the shape of the static corresponding curve ($h+k+l = 4n+2$) of Fig. 1 in the range of the smallest $\sin\theta/\lambda$ values. Other compounds with face-centred-cubic structure and a large electronic overlap between neighbouring atoms, such as silicon, present the same behaviour for the 222 reflection (Azavant *et al.*, 1994; Spackman, 1986; Pisani, Dovesi & Orlando, 1992). For a fully ionic compound such as magnesium oxide, the values of F_{300} and F_{300}^{DW} are the same for this reflection (Azavant *et al.*, 1994), indicating no contraction of the electron density.

Structure factors have also been calculated at three temperatures, 50, 300 and 400 K, for which the experimental lattice parameters $a_{50} = 5.446$, $a_{300} = 5.463$ and $a_{400} = 5.475$ Å are deduced from a_{300} (Wyckoff, 1968) with the help of the data of White (1980) and of Schumann & Neumann (1984). In these calculations, we have adopted the atomic mean square displacements given by Elcombe & Pryor (1970): these latter values are not X-ray results but come from model calculations based indirectly on phonon dispersion measurements. From the obtained values, not given in this paper, the structure factor is a decreasing function *versus* temperature for all reflections except 200 and 222. For the reflections corresponding to odd h, k, l and $h+k+l = 4n$, which have large and more accurate structure factors, the curves $\ln(F_T/F_0) = f(\sin\theta/\lambda)^2$ at a given temperature are linear and the slopes allow us to calculate a Debye–Waller factor B. For odd h, k, l, the values obtained at 50, 300 and 400 K are $B_{50} = 0.186$, $B_{300} = 0.516$ and $B_{400} = 0.673$ Å^2, respectively, and represent the B displacements associated with calcium. These values are, of course, equal to those of Elcombe & Pryor (1970) used to calculated F_T. For the reflections corresponding to $h+k+l = 4n$, the slopes lead to $B_{50} = 0.233$, $B_{300} = 0.589$ and $B_{400} = 0.763$ Å^2, values that represent rather well a mean Debye–Waller factor B defined by $B = (m_{\mathrm{F}}B_{\mathrm{F}} + m_{\mathrm{Ca}}B_{\mathrm{Ca}})/(m_{\mathrm{F}} + m_{\mathrm{Ca}})$, where m_{F} and m_{Ca} are the fluorine and calcium atomic weights, respectively. These results show that at the three studied temperatures the F_T values are similar to those corresponding to the Debye–Waller model and thus confirms the fully ionic character of fluorite and therefore the absence of appreciable overlap between electron clouds.

Anharmonic vibration or disordered structure of fluorine

All the calculations presented so far correspond to the ideal structure where the Ca, F and F′ sites are (0,0,0), $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$, $(\frac{3}{4},\frac{3}{4},\frac{3}{4})$, respectively. In the case of fluorite structure, however, it is known that the Bragg intensities measured by neutron (Willis, 1965) or X-ray (Abrahams *et al.*, 1967) diffraction for reflections occurring at the same value of $\sin\theta/\lambda$ are significantly different (*e.g.* reflections 933, 771, 755). Such a result can be explained by an anharmonic vibration or a disordered structure of fluorine (Willis, 1965).

In this structure, the symmetry of the fluorine site is indeed $\bar{4}3m$ and the absence of a centre of symmetry makes anharmonic vibrations possible. Theoretically, the addition of a cubic term in the development of the crystal potential for the anion and the substitution of the new potential expression into the anion temperature factor allow the modification of the harmonic term of this factor and this result to be accounted for (Willis & Pryor, 1975). Within the group of odd-index reflections sharing the same value of $\sin\theta/\lambda$, the stronger reflection (755) has Miller indices of the type $h+k+l = 4n+1$ while the weaker reflections (933, 771) correspond to the $h+k+l = 4n-1$ group.

In the CaF$_2$ case at room temperature, the neutron intensities of the Bragg reflections lead to $F_{755}/F_{933} = 1.12$ (Willis, 1965) while this ratio is equal to 1.013 (16) when calculated from X-ray data (Abrahams *et al.*, 1967; Zachariasen, 1968; Bachman *et al.*, 1985). To explain these results and the absence of detectable splitting of the structure factors in even-index groups with the same $\sin\theta/\lambda$, an anharmonic potential parameter β_{F} is introduced in the fluorine temperature factor. Its value would be very small and negative ($\beta_{\mathrm{F}} \simeq -4 \times 10^9$ J^{-3}) according to Cooper (1970) and does not contribute to modify the B_{Ca} and B_{F} values.

To simulate the anharmonic vibration of fluorine with the *CRYSTAL* program, it is possible to move this atom along the [111] direction by a shift δ_{F} with respect to its ideal position. The modified arrangement of F and F' sites $(\frac{1}{4}+\delta), \ldots$, still related by a centre of inversion, is optimized in order to obtain $F_{\mathrm{II}}/F_{\mathrm{I}} = 1.013$ with $B_{\mathrm{Ca}} = 0.61$ and $B_F = 0.81$ Å^2 (F_{I} and F_{II} are the

Table 4. *Structure factors F calculated at* 300 K *with* $\delta = -0.0008$ *for odd h, k, l reflections having the same value of* $\sin\theta/\lambda$

$F_{\rm I}$ and $F_{\rm II}$ correspond to $h + k + l = 4n - 1$ and $4n + 1$, respectively. The values in parentheses correspond to the $F_{\rm II}/F_{\rm I}$ ratio of the $B_{\rm IV}$ experiment.

$\sin\theta/\lambda$ (Å^{-1})	0.4756	0.6536	0.7030	0.7926	0.9107	0.9467	1.1395
$h+k+l=4n-1$					933		
hkl	511	551	731	555	771	951	11,5,3
$F_{\rm I}$	29.564	21.488	19.784	16.916	13.520	12.556	8.072
$h+k+l=4n+1$							
hkl	333	711	553	751	755	773	975
$F_{\rm II}$	29.848	21.700	20.012	17.128	13.708	12.732	8.212
$F_{\rm II}/F_{\rm I}$	1.010	1.010	1.011	1.012	1.014	1.014	1.017
	(0.994)	(1.006)	(1.002)	(1.020)	(1.001)	(1.000)	(–)

structure factors associated with odd-index groups with $h + k + l = 4n - 1$ and $4n + 1$, respectively). The number of symmetry operators is reduced from 48 to 12 (space group $R\bar{3}m$) and the $\delta_{\rm F}$ value thus obtained is -8×10^{-4} Å. This value is very small and negative, meaning a displacement of the fluorine towards the neighbouring calcium in the [111] direction. With this value, all the structure factors of the odd-index groups with the same $\sin\theta/\lambda$ value corresponding to $h + k + l = 4n + 1$ are stronger than those corresponding to $h + k + l = 4n - 1$ and the structure factors of the even-index groups with the same $\sin\theta/\lambda$ value are not split, confirming all the experimental data. The structure factors $F_{300}(\delta)$ calculated with $\delta_{\rm F} = -8 \times 10^{-4}$ Å and the ratios $F_{\rm II}/F_{\rm I}$ calculated for a few odd-index groups are given in column 6 of Table 2 and in Table 4, respectively. The experimental $F_{\rm II}/F_{\rm I}$ values of Bachman *et al.* (1985) are given in parentheses in this table for comparison. Examination of Tables 2 and 4 shows that lowering the site symmetry of fluorine by a small shift towards Ca along the [111] direction improves the agreement with X-ray data. This would imply, however, a positive rather than negative sign of $\beta_{\rm F}$ according to Willis & Pryor (1975).

Concluding remarks

The *ab initio* LCAO Hartree–Fock approach allowed us to calculate accurate structure factors of fluorite over a large range of $\sin\theta/\lambda$ values. Perturbation of the static structure factor by introducing an atomic mean square displacement tensor leads to the dynamic structure factors, which can be compared with the experimental ones (when properly corrected for secondary effects).

In spite of a non-negligible dispersion of experimental data, comparison of our theoretical results with experiment gives a satisfactory agreement. Moreover, the introduction of a very slight deviation of the F atom with respect to its ideal position still improves this agreement. However, the negative sign of the anharmonic vibration parameter $\beta_{\rm F}$ is not confirmed by the present results.

The precision of our calculations shows that the structure factors associated with the 200 and 222 reflections indicate a small but significant contraction of the electron clouds, particularly for F$^-$, with respect to isolated ions.

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