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Electron Density in the Alkali Halide Crystals*†

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Abstract

Structure factors at room temperature are computed for LiF, NaF, NaCl and KCl by means of theoretical ionic form factors and theoretical Debye-Waller factors. The values obtained are compared with the best available experimental data. For LiF, KCl and NaF - for which good experimental data are available - there is generally very good agreement, with only a few sizeable discrepancies for NaF that can be attributed to deficiencies of the experimental data. It is concluded that there is no apparent need to question the validity of the Debye-Waller theory as recently proposed in the literature.

1. Introduction

In two recent papers (Böbel, Cortona, Sommers & Fumi, 1983, 1985) on the 'isoelectronic' alkali halides NaF and KCl we have shown that the structure factors for the 'sum' reflections calculated with the method of augmented spherical waves (ASW) and the local density approximation (LDA) to the exchange-correlation potential can be fitted very well to the best available experimental data at room temperature [NaF: X-ray data by Howard & Jones (1977); KCl: γ-ray data by Schmidt, Colella & Yoder-Short (1985)] with a single Debye-Waller (DW) factor and that the ensuing structure factors for the low-order 'difference' reflections agree very well with the same data. The values that we obtained for the DW factors are within the uncertainties of the DW factors reported in the experimental papers.

Several years earlier Zunger & Freeman (1977) had shown that the structure factors for LiF, calculated with the self-consistent LCAO method (which includes non-spherical components of the lattice potential ignored in our ASW calculations) in LDA agree well with the (relatively old) powder X-ray data of Merisalo & Inkinen (1966) reduced to the static crystal with an approximate formula‡ using the experimental DW factors. Böbel *et al.* (1985) have pointed out that these theoretical values also agree very well with the recent γ-ray data by Schmidt *et al.* (1985) reduced to the static crystal with the same approximate formula using the pertinent experimental DW factors.

Recently Jansen & Freeman (1986) have computed structure factors for NaCl with the full-potential linearized augmented-plane-wave method (which also includes non-spherical components of the lattice potential) in LDA. They compared these theoretical structure factors with the available (rather old) X-ray data (*e.g.* Schoknecht, 1957; Witte & Wölfel, 1955). They analyze in particular the Schoknecht (1957) data, reducing them to the static crystal using Schoknecht's theoretical DW factors§ and his anionic and cationic form factors (obtained by sum and difference of interpolated structure factors of the 'even' and of the 'odd' reflections). They find strong discrepancies (up to 100%) for the high-order 'difference' reflections¶ that they attribute to strong dynamical deformations of the ions due in particular to optical phonons, thus questioning the validity of the DW theory of the thermal effects on the structure factors.

In fact it is not clear why these deformations should affect only the high-order 'difference' reflections and not the low-order ones, which are more sensitive to the outer electron distribution. It should also be noted that Pryor (1966) [see also Willis & Pryor (1975), p. 134] has estimated with a simple shell model that dynamical deformations of the anion in NaCl give only a difference of at most 1% in the structure factors at room temperature at any value of $(\sin\theta)/\lambda$. Buyers, Pirie & Smith (1968) have also shown that dynamical deformations of the ions (assumed directly proportional to the displacement from equilibrium) give a null effect on the DW factors for the NaCl-type structure, owing to symmetry, and an estimated change of the order of 2% in the form factor of the anion in NaCl for a relative displacement of 0·1 Å.

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† A preliminary report on this work was presented at the XIV International Congress of Crystallography, Perth, Australia, 12-20 August 1987 (Böbel, Cortona & Fumi, 1987).

‡ This formula does not require knowledge of the separate cationic and anionic contributions to the experimental structure factors and it is not equivalent to the procedure used by Jansen & Freeman (1986) for NaCl.

§ These DW factors were calculated with the approximate Debye formula neglecting the zero-point contributions. The latter amount to more than 20% of the totals.

¶ In particular the 771 and 777 reflections. It must be noted that these are the reflections for which Schoknecht reports his highest experimental error (10%) and that this error is considerably magnified when the structure factors are reduced to the static crystal by means of the cationic and anionic form factors obtained by the procedure mentioned above.

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Table 1. *Structure factors at* 295 K *for* LiF

hkl	F_{calc}	$(F_{\mathrm{exp}}-F_{\mathrm{calc}})/F_{\mathrm{calc}}$ (%)	F_{calc}	$(F_{\mathrm{exp}}-F_{\mathrm{calc}})/F_{\mathrm{calc}}$ (%)	F_{exp}
111	4·77	−0·4	4·77	−0·4	4·75
220	5·22	−1·0	5·24	−1·3	5·17
311	2·17	1·8	2·18	1·4	2·21
222	4·03	0·5	4·05	0·0	4·05
331	1·43	1·4	1·45	0·0	1·45
422	2·33	2·1	2·37	0·4	2·38
511	1·12	2·7	1·14	0·9	1·15
333	1·12	0·0	1·14	−1·7	1·12
442	1·62	1·8	1·65	0·0	1·65
600	1·62	0·6	1·65	−1·2	1·63
444	1·23	−0·8	1·27	−3·9	1·22
800	0·90	0·0	0·94	−4·2	0·90
	$B(\mathrm{Li}^+) = 0{\cdot}958$ Å^2 $B(\mathrm{F}^-) = 0{\cdot}655$ Å^2		$B(\mathrm{Li}^+) = 0{\cdot}908$ Å^2 $B(\mathrm{F}^-) = 0{\cdot}615$ Å^2.		

Table 2. *Structure factors at* 295 K *for* KCl

hkl	F_{calc}	$(F_{\mathrm{exp}}-F_{\mathrm{calc}})/F_{\mathrm{calc}}$ (%)	F_{calc}	$(F_{\mathrm{exp}}-F_{\mathrm{calc}})/F_{\mathrm{calc}}$ (%)	F_{exp}
111	1·33	0·0	1·33	0·0	1·33
220	21·89	0·7	22·11	−0·3	22·05
222	18·60	−0·3	18·88	−1·7	18·55
400	16·25	−2·8	16·58	−4·7	15·80
422	13·02	−1·1	13·42	−4·1	12·87
442	9·97	−0·5	10·42	−4·8	9·92
600	9·97	−3·2	10·42	−7·4	9·65
444	7·93	−1·6	8·42	−7·3	7·80
800	5·97	−1·2	6·47	−8·8	5·90
10,0,0	3·25	−0·9	3·68	−12·5	3·22
	$B(\mathrm{K}^+) = 1{\cdot}929$ Å^2 $B(\mathrm{Cl}^-) = 1{\cdot}994$ Å^2		$B(\mathrm{K}^+) = 1{\cdot}742$ Å^2 $B(\mathrm{Cl}^-) = 1{\cdot}784$ Å^2		

2. Comparison of theoretical and experimental structure factors at room temperature

In the present paper we compute in a uniform fashion the structure factors at room temperature for the four salts LiF, NaF, NaCl and KCl and we compare them with the best available data. We use our ASW-LDA ionic factors for NaF and KCl and the Hartree-Fock free-ion factors for LiF and NaCl: indeed for the latter two (non-isoelectronic) salts the resulting structure factors for the static crystal differ by only a few percent (at most 4%) from the values calculated by Zunger & Freeman (1977) for LiF and by Jansen & Freeman (1986) for NaCl for all reflections, which is quite sufficient for our purposes. We also use theoretical DW factors at room temperature [Reid & Smith (1970); Gupta (1975); Dolling, Smith, Nicklow, Vijayaraghavan & Wilkinson (1968) (LiF); see also Willis & Pryor (1975), §§ 4.5 and 4.7.2] calculated from experimental phonon dispersion curves which include the effects of the dynamical deformations of the ions on the lattice frequencies, but not the effects on the ionic form factors. The use of theoretical DW factors avoids the masking of (possible) systematic discrepancies between theory and experiment which is of course allowed by the use of fitted DW factors.

Tables 1 to 4 report our results for LiF, KCl, NaF and NaCl. For each salt we report the calculated values of the structure factors at room temperature F_{hkl} (in order of increasing $h^2+k^2+l^2$); the experimental values [LiF and KCl: Schmidt *et al.* (1985); NaF: Howard & Jones (1977); NaCl: Schoknecht (1957) and Göttlicher (1968)] and the percent deviations $(F_{\mathrm{exp}}-F_{\mathrm{calc}})/F_{\mathrm{calc}}\times 100$: the first part of each table uses the *B* factors of Dolling *et al.* (1968) (for LiF) and Reid & Smith (1970), while the second part uses the corresponding values of Gupta (1975).

For 'non-isoelectronic' LiF the agreement of the calculated values - in particular those using the Dolling *et al.* *B* factors - with the data of Schmidt *et al.* is excellent. The maximum discrepancy is below 3% and there is no systematic trend in the discrepancies. (The *B* factors of Gupta do not appear to account quite as well for the temperature effect for the high-order reflections.)

For 'isoelectronic' KCl the agreement is again excellent (within 3%) with the Reid & Smith *B* factors and there is again no systematic trend in the discrepancies (Gupta's *B*'s give instead discrepancies which increase up to 12% for the high-order reflections). Schmidt *et al.* state that they measured only the 111 'difference' reflection because the high-order ones were too weak: clearly this casts doubt on the values reported by Patomäki & Linkoaho (1969) for the latter reflections and, in fact, for them the discrepancies between theory and experiment reach high values (up to 40%).

For NaF a few remarks are in order. The agreement between theory and experiment is good (within 5%

Table 3. *Structure factors at* 295 K *for* NaF

hkl	F_{calc}	$(F_{\text{exp}}-F_{\text{calc}})/F_{\text{calc}}$ (%)	F_{calc}	$(F_{\text{exp}}-F_{\text{calc}})/F_{\text{calc}}$ (%)	F_{exp}
111	1·25	0·0	1·25	0·0	1·25
220	10·74	1·4	10·78	1·0	10·89
311	1·57	0·0	1·57	0·0	1·57
222	8·64	1·8	8·68	1·4	8·80
331	1·21	1·6	1·22	0·8	1·23
422	5·22	−0·8	5·27	−1·7	5·18
333	0·93	−5·4	0·93	−5·4	0·88
511	0·93	−4·3	0·93	−4·3	0·89
440	4·03	−2·0	4·08	−3·2	3·95
531	0·69	−4·3	0·70	−5·7	0·66
620	3·24	−2·2	3·29	−3·6	3·17
533	0·49	−2·0	0·50	−4·0	0·48
444	2·69	−3·0	2·74	−4·7	2·61
551	0·36	−22·2	0·37	−24·3	0·28
711	0·36	0·0	0·37	−2·7	0·36
642	2·27	−3·1	2·32	−5·2	2·20
553	0·28	−7·1	0·29	−10·3	0·26
731	0·28	−17·8	0·29	−20·7	0·23
800	1·94	−2·6	1·99	−5·0	1·89
733	0·22	−18·2	0·23	−21·7	0·18
660	1·69	−5·3	1·74	−8·0	1·60
822	1·69	−2·9	1·74	−5·7	1·64
842	1·41	−6·4	1·45	−9·0	1·32
	$B(\text{Na}^+) = 0{\cdot}868$ Å^2 $B(\text{F}^-) = 0{\cdot}867$ Å^2		$B(\text{Na}^+) = 0{\cdot}837$ Å^2 $B(\text{F}^-) = 0{\cdot}837$ Å^2		

Table 4. *Structure factors at* 295 K *for* NaCl

G: Göttlicher (1968); S: Schoknecht (1957).

hkl	F_{calc}	$(F_{\text{exp}}-F_{\text{calc}})/F_{\text{calc}}$ (%)		F_{calc}	$(F_{\text{exp}}-F_{\text{calc}})/F_{\text{calc}}$ (%)		F_{exp}	
		(G)	(S)		(G)	(S)	(G)	(S)
111	4·51	3·6	12·0	4·52	3·3	11·7	4·67	5·05
200	20·56	−0·9	−0·3	20·50	−0·5	0·0	20·4	20·50
222	14·11	1·7	−2·3	14·19	1·1	−2·7	14·3	13·80
400	12·30	0·8	1·3	12·40	0·0	0·5	12·4	12·46
331	2·31	−1·5	11·7	2·36	−3·8	9·3	2·27	2·58
333	2·32	−2·7	22·8	2·38	−5·0	19·7	2·26	2·85
600	7·35	−9·5	13·9	7·49	−11·2	11·7	6·65	8·37
442	7·35	−10·1	12·5	7·49	−11·9	10·4	6·60	8·27
533	2·17	−9·9	14·3	2·26	−13·5	9·7	1·95	2·48
444	5·71	−15·4	17·7	5·85	−17·4	14·9	4·83	6·72
551	2·02	−13·7	16·3	2·10	−17·1	11·9	1·74	2·35
800	4·18	−18·4	18·9	4·32	−21·0	15·0	3·41	4·97
555	1·48	−17·2	11·5	1·58	−22·4	4·4	1·22	1·65
771	1·03	−19·9	20·4	1·12	−26·3	10·7	0·825	1·24
10,0,0	2·20	−23·5	30·9	2·32	−27·5	24·1	1·68	2·88
666	1·92	−23·0	50·5	2·04	−27·4	41·7	1·48	2·89
12,0,0	1·08	—	44·4	1·16	—	34·5	—	1·56
777	0·49	—	26·5	0·54	—	14·8	—	0·62
14,0,0	0·49	—	40·8	0·54	—	27·8	—	0·69
	$B(\text{Na}^+) = 1{\cdot}556$ Å^2 $B(\text{Cl}^-) = 1{\cdot}348$ Å^2			$B(\text{Na}^+) = 1{\cdot}516$ Å^2 $B(\text{Cl}^-) = 1{\cdot}271$ Å^2				

or so) for the 'sum' reflections and the low-order 'difference' reflections with the Reid & Smith *B* factors. Owing to the 'isoelectronic' nature of the salt, the high-order 'difference' reflections are very weak and thus the experimental structure factors rather uncertain: in particular, for reflections with the same high value of $h^2+k^2+l^2$ there are differences of 10 to 25% (see 551 *vs* 711 and 553 *vs* 731) which can be due only in part to aspherical effects [see the pertinent discussion for NaCl and KCl of Böbel *et al.* (1985)].

For NaCl there do not appear to exist really good data. The data by Schoknecht (1957), or the equivalent data by Witte & Wölfel (1955), are thirty years old and were not corrected for thermal diffuse scattering (TDS). Estimates of the TDS corrections to the structure factors were reported twenty years ago by Göttlicher (1968) [see also Willis & Pryor (1975), § 9.4]: they increase with *hkl* reaching 20% at 666. It should, however, be noted that the uncorrected Göttlicher structure factors at high *hkl* are appreciably smaller than those of the other sets, the ratio of the Göttlicher to the Schoknecht values reaching 0·6 at 666. Our computed values fall between the values of Schoknecht and the corrected values of Göttlicher. Indeed the percent deviations reported in

Table 4 for Schoknecht and Göttlicher are (mostly) positive and (mostly) negative, respectively: their magnitudes are large in both cases. Jansen & Freeman (1986) report calculated values larger than the experimental values by Schoknecht (1957), in particular for the 555, 771 and 777 reflections for which they find the largest discrepancies (28, 45 and 101%). These differences between our results and those of Jansen & Freeman are clearly due to the DW factors used.

3. Concluding remarks

Our results appear to indicate that whenever good room-temperature data are available [LiF and KCl: Schmidt *et al.* (1985), NaF: Howard & Jones (1977)] the agreement between the structure factors calculated with the DW theory and the experimental values is generally very good and the few large discrepancies for NaF can be attributed to deficiencies of the experimental data. For NaCl, one cannot draw any definite conclusion owing to the lack of good experimental data.

Our results show that there does not seem to be any need to call into question the validity of the DW theory, as Jansen & Freeman (1986) appear to propose.

We should finally note that the low-temperature diffraction experiments suggested by Jansen & Freeman (1986) are not only technically difficult but would not eliminate the problem of taking into account the vibrational effects of the zero-point motions, which still involve contributions from all lattice frequencies.

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The Morphology of Calaverite ($AuTe_2$) from Data of 1931. Solution of an Old Problem of Rational Indices

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Abstract

The anomalous high-index faces (*hkl*) of the mineral calaverite ($Au_{1-x}Ag_xTe_2$) measured goniometrically in the year 1931 by Goldschmidt, Palache & Peacock [*Neues Jahrb. Mineral.* (1931), **63**, 1-58] are re-interpreted and related to the wave vector **q** of the displacive incommensurate modulation which was recently found in the crystal structure. All crystal faces (including the high-index ones) can be given four low indices (*hklm*), using **q** as a fourth basis vector. From this an almost hundred-year-old anomaly in crystal morphology is in principle solved.

1. Introduction

The present investigation started from a suggestion made in 1984 by J. D. H. Donnay to one of the authors at the XIII International Congress of Crystallography in Hamburg in 1984 to reconsider the problem of

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