

a feasible method which keeps the advantages of the above reduction procedure (McWeeny, 1953; for different approaches to the evaluation of some TC Slater integrals *cf.* Bonham, Peacher & Cox, 1964; Guerillot, Ganachaud & Lissillour, 1968).

When the final form cannot be evaluated analytically, the method above of replacing integration by differentiation is useless. This is the case when the radial basis $\{q_p\}$ is numerical. However, for OC integrals, the three-dimensional integrals over \mathbf{r} can be reduced to one-dimensional ones by similar techniques. Here

$$\begin{aligned} f_{pq}(\mathbf{s}) &= \int_0^\infty dr r^2 q_p(r) q_q(r) \int d\omega P_{l_p}(x, y, z) P_{l_q}(x, y, z) \\ &\times \exp(i\mathbf{s} \cdot \mathbf{r}) = \int_0^\infty dr r^2 q_p(r) q_q(r) \\ &\times 4\pi (-i)^{l_p+l_q} D_{l_p+l_q}(s_x, s_y, s_z) j_0(sr), \end{aligned} \quad (17)$$

where j_0 is the zero order spherical Bessel function. Application of D_l to j_0 is easily performed employing the properties of the functions j_n . Computation of the remaining integral over r requires evaluation of $j_n(sr)$ up to $n=l_p+l_q$ at all argument values of the numerically defined q_p . A different treatment of this problem was given by Freeman (1959).

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The Deformations of the Ions in NaCl and AgCl Crystals and the Temperature Parameters of Ions in Some Alkali Halides

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Results of X-ray powder intensity measurements and spherical harmonic expansions have been used for investigating deformations of the ions in NaCl and AgCl crystals. It is found that within the limits of experimental accuracy the ions in crystalline NaCl are spherically symmetric. Compared with free ions, the charge around Ag in AgCl has spread farther and a part of it is located inside the Cl sphere. The electron clouds inside the Ag and Cl spheres are, however, almost spherically symmetric. It has been shown that the results of recent X-ray measurements concerning the Debye-Waller coefficients of the ions in alkali halide crystals have one prominent feature: the square of the relative vibration amplitude of an individual ion, which is proportional to the ratio B/a^2 (B is the Debye-Waller coefficient and a the length of the edge of the unit cell), increases when the number of electrons of its company increases. It is proposed that this dependence is mainly due to the repulsive forces between the next-nearest-neighbours.

1. Introduction

It has been often proposed that there are some unspherical deformations of the ions of alkali halide

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crystals in spite of the high symmetry of these crystals and of their ideal ionic character. For example, Korhonen (1956) has analysed the measurements of Wasastjerna (1944) and found deformations in the electron

cloud of the Cl^- ion in NaCl and KCl. The results of the calculations of Korhonen & Vihinen (1961) and those of Kurki-Suonio & Fontell (1964), both based on the measurements of Vihinen (1960), also indicate some unspherical deformations of Cl^- in NaCl. The deformations found are, however, very small. The measurements and calculations of Korhonen & Linkoaho (1964; 1966) indicate another type of deformation: a very strong electron transfer from the Ag^+ to the Cl^- ion in the AgCl crystal compared with the situation in the free ions. Since the measurements and calculations already mentioned a new analysing technique has been developed (Kurki-Suonio & Meisalo, 1967; Dawson, 1967; Kurki-Suonio, 1968). In fact recent measurements by Patomäki & Linkoaho (1969) and their calculations performed with the help of this technique indicate that the ions in KCl are almost exactly spherically symmetric, contrary to Korhonen's (1956) suggestion. We now have also very recent measurements of NaCl (Linkoaho, 1968) at our disposal. We shall, therefore, apply the new analysing method to the results of these measurements on the NaCl and AgCl crystals.

The values of the measured motion parameters of the ions in some alkali halides at room temperature seem to be somewhat peculiar. For example, in NaCl (Linkoaho, 1968) and LiCl (Inkinen & Järvinen, 1968) the experimental motion parameters of individual ions differ considerably from the theoretical ones based on the deformation dipole (DD) model of Karo & Hardy (1963), while the mean values of the motion parameters in both halides are close to the theoretical values. We shall consider this question in § 4 in the light of some recent accurate X-ray measurements.

2. The ionic radii in NaCl and AgCl

To investigate the deformations of the ions in NaCl and AgCl crystals we need to know the ionic radii for these ions. The theoretical values available differ considerably from each other, depending on whether the principle of minimum density or that of minimum overlap is applied (Maslen, 1967). The experimental information on the ionic radii in crystals is valuable in many other applications than the present one: for example, the calculations of ionic polarizabilities by Ruffa (1963, 1964) and the calculations of enthalpies of hydration of ions by Morris (1968). We have, therefore, calculated the required radii from the measured structure factors by using the method proposed by Kurki-Suonio & Fontell (1964) and at the end of this section we compare

some results obtained by this method with the theoretical values.

We have calculated the ionic charge inside several spheres, both anion and cation centred, by varying the radius of the sphere. From these values we obtained the charge densities inside thin shells and the radii of the ions were chosen so that (a) their sum was equal to the distance between the nearest neighbours in the crystal and (b) the charge densities at these distances from the ionic centres were equal. The resulting radii and some other data are shown in Table 1. We have used residual terms based on the theoretical atomic factors of Cromer & Mann (1968) up to the value of 600 for the sum $h^2 + k^2 + l^2$. For NaCl we used the structure factors and motion parameters of Linkoaho (1968), measured at 300°K. The results of these calculations were confirmed by the values calculated from the results of the low temperature measurements. The only difference was that the charge density function was smooth at 300°K but strongly oscillating at 80 and 4°K. These oscillations persisted although, in calculating the residual term, we used the theoretical structure factors up to the value of 1200 for the sum $h^2 + k^2 + l^2$. For AgCl we used structure factors from the measurements of Korhonen & Linkoaho (1966), but the dispersion corrections of Cromer (1965) were used for obtaining the corrected measured values, and the theoretical values of Cromer & Mann (1968) for the atomic factors were used in calculating the motion parameters. The new values of the motion parameters, $B_{\text{Ag}} = 2.195 \text{ \AA}^2$ and $B_{\text{Cl}} = 2.09 \text{ \AA}^2$ are almost the same as the old ones. Also the differences between the old and the new theoretical structure factors are generally small, except in the very first reflexions.

In Table 2 the ionic radii in some alkali halides, calculated from measured structure factors are shown, together with the theoretical values (Maslen, 1967). The experimental radii are closer to the minimum density radii than to the radii derived on the principle of minimum overlapping. The agreement between the experimental and minimum density radii is very good, although the experimental radii of the cations are generally larger, and those of the anions smaller, than the theoretical values based on the free-ion densities. This result is in agreement with the theory of Petrashen, Abarenkov & Kristofel (1960) according to which 'the field of the point lattice of the crystal results in a compression of the electron clouds of anions and (relatively smaller) spreading of the electron clouds of cations as compared with free ions'.

Table 1. *The ionic radii (R), the charge (Q) inside the sphere of radius R , the charge density (ρ_R) on the surface of the spheres and charge density (ρ_{out}) outside the spheres in NaCl and AgCl*

Crystal	Ion	R (\AA)	Q (e)	ρ_R ($e \cdot \text{\AA}^{-3}$)	ρ_{out} ($e \cdot \text{\AA}^{-3}$)
NaCl	Na^+	1.21 ± 0.05	10.1 ± 0.1	0.074	0.009
	Cl^-	1.61 ± 0.05	17.2 ± 0.15		
AgCl	Ag^+	1.03 ± 0.05	43.2 ± 0.1	0.225	0.020
	Cl^-	1.74 ± 0.05	19.5 ± 0.2		

3. The deformations of the ions

(a) NaCl

A summary of our calculations of spherical harmonic expansions (*cf.* Kurki-Suonio, 1968) is shown in Table 3. In one case (Cl^- at 80°K) the detailed figure is shown (Fig.1). The values of Δf are the differences between the atomic factors of ions in crystals and those of free ions. For comparison, the $K0$ component and the 'ghost' component $K6$ of Cl^- in NaCl at 300°K are also shown (Figs.2 and 3). The calculations were performed by use of a little 'too large' ionic radii 1.4 Å and 1.8 Å for Na^+ and Cl^- , respectively, to avoid the effects of possible overlapping (Kurki-Suonio, 1968). We have used the differences between the measured and theoretical structure factors given in our experimental work (Linkoaho, 1968). According to Table 3 very small unspherical (the component $K0$ is spherically symmetric) deformations seem to exist in Na^+ at 300°K ($K4$ component, which refers to d -symmetry), in Cl^- at 300°K ($K6$, f -symmetry!) and at 4°K ($K4$). We suggest that deformations resulting from unspherical thermal vibrations should exist most prominently at 300°K, and those due to static field, at 4°K. The deformations in Table 3 however, exist quite randomly. We therefore conclude that they are not real deformations and that they are probably caused by small systematic errors in the experimental results. Besides this the spherical components ($K0$) are very small and indicate that the Na^+ and Cl^- ions in NaCl are almost exactly the same as the theoretical free ions (Bagus, 1965; Freeman, 1959).

(b) AgCl

The values of the ionic radii used in the AgCl calculations were 1.2 Å and 1.8 Å for Ag and Cl, respectively. The results of the calculations of spherical harmonic expansions in this case indicate that:

Table 3. The results of the calculations of spherical harmonic expansions in NaCl

The plus sign indicates the presence of deformation larger than the estimated experimental inaccuracy. K_n denotes the order n of the spherical harmonics K calculated.

Ion	Temperature	$K0$	$K4$	$K6$	$K8$	$K10$
Na^+	300°K	+	+	-	-	-
	80°K	+	-	-	-	-
	4°K	-	-	-	-	-
Cl^-	300°K	+	-	+	-	-
	80°K	+	-	-	-	-
	4°K	+	+	-	-	-

(a) there is a very strong electron transfer from Ag to Cl ($K0$ component, Fig.2, *cf.* also Table 1);

(b) the unspherical components in the ions are small (of the order of 0.2–0.3 electron units) compared with the measurement accuracy (Fig.3). As the inaccuracies in the AgCl measurements are the result of experimental difficulties (blackening of the specimens, for ex-

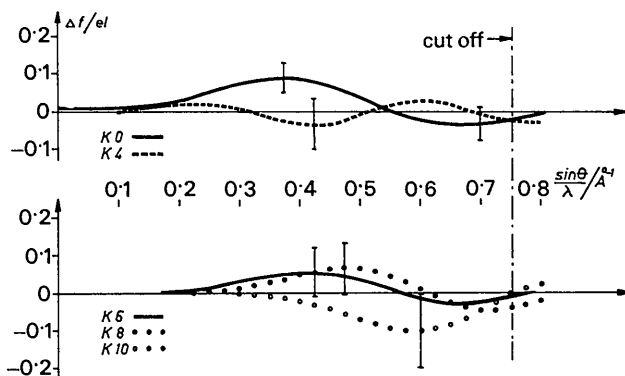


Fig. 1. The radial coefficients of the cubic harmonic expansion of Δf for Cl^- in NaCl at 80°K. All possible components in this symmetry are shown up to the tenth order.

Table 2. Some ionic radii calculated by the method of equal charge densities inside anion and cation centred shells with the use of experimental structure factors

The first number in the second column gives the reference to the experimental, and the second number to the theoretical work.

Crystal	Reference	Ion	R_{meas}	R_{theor}	
				Min. density	Min. overlap
LiF	1, 7	Li^+	0.78 ± 0.04 Å	0.78 Å	0.66 Å
		F^-	1.23 ± 0.04	1.24	1.35
LiCl	2, 7	Li^+	0.91 ± 0.08	0.87	0.71
		Cl^-	1.66 ± 0.08	1.70	1.86
NaCl	3, 7	Na^+	1.21 ± 0.05	1.14	0.99
		Cl^-	1.61 ± 0.05	1.66	1.81
KCl	4, 7	K^+	1.45 ± 0.07	1.47	1.35
		Cl^-	1.70 ± 0.07	1.66	1.77
RbCl	5, 8	Rb^+	1.71 ± 0.05	1.65	-
		Cl^-	1.58 ± 0.05	1.64	-
KBr	6, 7	K^+	1.57 ± 0.07	1.50	1.36
		Br^-	1.73 ± 0.07	1.78	1.92

1. Merisalo & Inkinen (1966)
2. Inkinen & Järvinen (1968)
3. Linkoaho (1968)
4. Patomäki & Linkoaho (1969)

5. Järvinen & Inkinen (1967)
6. Meisalo & Inkinen (1967)
7. Maslen (1967)
8. Tosi & Fumi (1964)

ample), more than double those in the NaCl measurements, and the differences between the measured structural factors and the theoretical values are considerable, even near the cut-off point, the significance of the unspherical components is concluded to be small. A large K_{10} component in Cl at high values of $\sin \theta/\lambda$ confirms this conclusion.

4. The relative vibration amplitudes of the ions

Menz (1968) has very recently measured the vibration amplitudes of some ions by use of electron diffraction. His measurements indicate that the relative vibration amplitudes of the ions are inversely proportional to their atomic masses. The measurements of Menz included, however, only four ions (Li^+ , F^- , Na^+ and Cl^-) and of these, the F^- ion did not fit his 'law'. Several accurate X-ray measurements have recently been made, which include thermal data of ions Li^+ , F^- , Na^+ , Cl^- , K^+ , Br^- and Rb^+ at 300°K and of some of them at 80°K . In Tables 4 and 5 we show the corresponding values of the ratio B/a^2 (B is the Debye-Waller coefficient and a is the length of the edge of the unit cell),

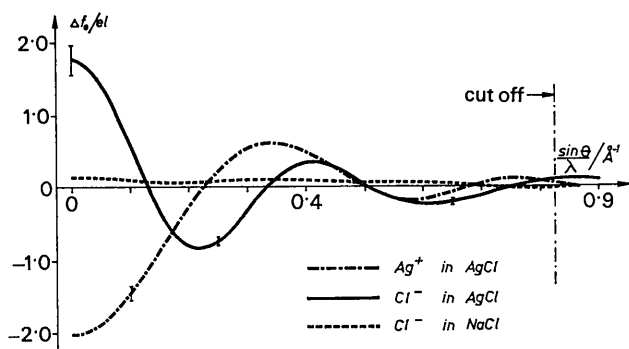


Fig. 2. The spherically symmetric radial coefficients of the cubic harmonic expansion of Δf for Ag and Cl in AgCl and NaCl at 300°K .

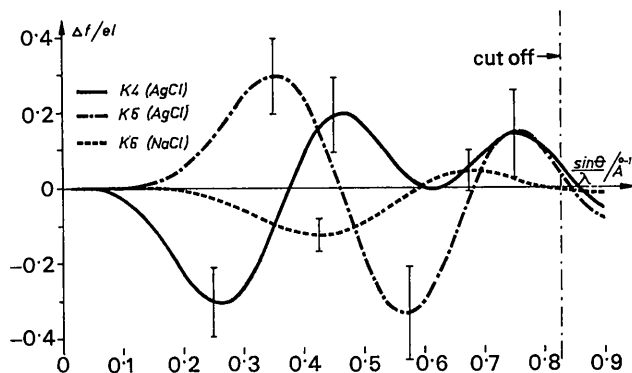


Fig. 3. The radial scattering factors of the K_4 and K_6 type deformations for Cl^- in AgCl and NaCl at 300°K .

which is proportional to the square of the relative vibration amplitude, $\langle u^2 \rangle/a^2$. From the single-crystal neutron diffraction results of Levy, Agron & Busing (1963) for NaCl and from those of Pryor (1966) for KBr, we obtain the values $B/a^2 \times 10^2 = 5.12 \pm 0.13$, 4.46 ± 0.13 , 5.05 ± 0.23 and 5.23 ± 0.23 for Na^+ , Cl^- , K^+ and Br^- , respectively, at 300°K . These values are in excellent agreement with the theoretical values (*cf.* Table 4), except for the case of Cl^- , where the agreement is inferior. The polycrystal value of Pryor (1966), on the other hand, shows, in the case of Br^- , a clear disagreement with the theory (DD model of Karo & Hardy, 1963) and this discrepancy is opposite to the disagreement in the X-ray results of Meisalo & Inkinen (1967). In the former values $B_{\text{K}} < B_{\text{Br}}$ and in the latter ones $B_{\text{K}} > B_{\text{Br}}$. The calculations of Buyers & Smith (1968), those of Cowley & Cowley (1966) and Pryor (1966) are in agreement in the sense that $B_{\text{K}} < B_{\text{Br}}$. It is conceivable that the B values for X-rays and neutrons may not be the same (Raichenko, 1965). Pryor (1966), however, points out that the difference in the core and shell vibration amplitudes does not cause a detectable difference in the B values. This statement is confirmed by the X-ray structure factor measurements of Vihinen (1963) in NaCl, which are extended to the value 1.6 of $\sin \theta/\lambda$. Pryor (1966) also emphasizes the significance of the thermal diffuse scattering correction.

Table 4 obviously shows that the ratio B/a^2 does not depend linearly on the mass number of the ion, contrary to the statement of Menz (1968). Excluding the relatively high values belonging to the Li^+ ion, this ratio seems to be almost constant. In Table 5 the ratio B/a^2 decreases monotonically with increasing mass number, but the dependence seems not to be linear. Unfortunately, the values of the heavy ions are missing. The most prominent feature of Table 4 is that, in every case, the ratio B/a^2 of an individual ion increases when the number of electrons of its company increases. This dependence, which appears also in the measurements of Menz (1968), seems to be quite linear, as indicated in Fig. 4 for the case of the Cl^- ion, where more than two points were available. Unfortunately, there are few data available at 80°K , but according to these there is no such dependence present at 80°K , or this dependence is very slight.

5. Conclusions

The X-ray diffraction measurements on NaCl crystal at 300 , 80 and 4°K indicate that the ions in crystalline NaCl are spherically symmetric and, further very much like the theoretical free ions. To be more specific, we conclude that if the accuracy of measurement is of the same order as in this case (± 0.1 e.u. or better), the unspherical deformations should exceed 0.2 electron units to be significant (*cf.* Kurki-Suonio, 1968, p. 383). Indeed this seems to be the situation in KBr (Meisalo & Inkinen, 1966) and RbCl (Järvinen & Inkinen, 1967) crystals while the ions in KCl (Patomäki & Linkoaho,

1969) are spherically symmetric. The values of the charge inside the Ag and Cl spheres in AgCl, shown in Table 1, and the spherically symmetric coefficients of the cubic harmonic expansion of Δf for Ag and Cl in Fig. 2, clearly demonstrate how the electrons have moved in crystalline AgCl compared with the situation in the free ions. The charge around Ag has spread farther and a part of it is located inside the Cl sphere. The other part is to be found in the classically 'empty' regions of the crystal (*cf.* Korhonen & Linkoaho, 1966). However, these considerable deformations of the electron clouds around Ag and Cl in crystalline AgCl leave the electron clouds inside the spheres with radii 1.03 and 1.74 Å almost spherically symmetric, as is shown in Fig. 3.

The recent AgBr results of Vogl & Waidelich (1968) are consistent with the present conclusions and also with the previous conclusions of Korhonen & Linkoaho (1966).

As has been pointed out, there is a discrepancy between the measured and theoretical (DD model of Karo & Hardy, 1963) values of the Debye-Waller coefficients B of the individual ions in many alkali

halides at 300°K. This discrepancy seems to have disappeared at 80°K. The thermal diffuse scattering correction is included in the experimental results, and

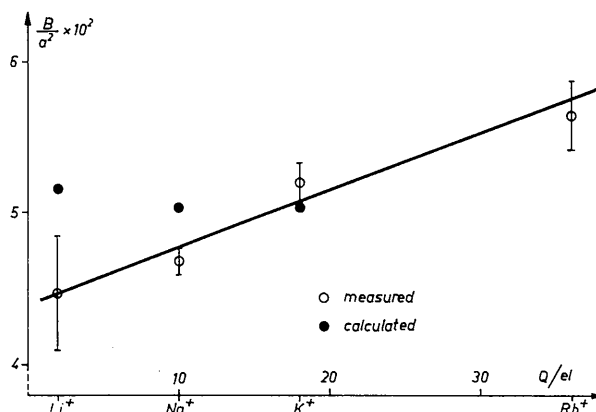


Fig. 4. The squares of the relative vibration amplitudes (in convenient scale) of Cl^- ion in LiCl, NaCl, KCl and RbCl as a function of the electron number of the cation.

Table 4. The values of the ratio B/a^2 , where B is the Debye-Waller coefficient and a is the length of the edge of the unit cell, for the ions in several alkali halides

These values are calculated from X-ray diffraction results at 300°K. The first number in column 2 gives the reference to the experimental, and the second number to the theoretical, work. The upper number in columns 3-9 gives the theoretical value and the lower numbers the measured value with the error estimate.

Crystal	Ion Ref.	$B/a^2 \times 10^2$						
		Li ⁺	F ⁻	Na ⁺	Cl ⁻	K ⁺	Br ⁻	Rb ⁺
LiF	1, 10	6.23	5.12					
LiCl	2, 10	6.84 ± 0.18	4.38 ± 0.18		5.16			
		6.59			4.47 ± 0.38			
NaF	9, 11		4.83	4.91				
			5.03 ± 0.33	5.03 ± 0.33				
NaCl	3, 11			5.16	5.03			
				5.69 ± 0.11	4.68 ± 0.11			
KCl	4, 11				5.02	4.88		
					5.20 ± 0.13	5.25 ± 0.13		
KBr	6, 11					5.07	5.14	
						5.63 ± 0.34	5.12 ± 0.34	
RbCl	5				5.64 ± 0.23			5.27 ± 0.23

Refs. 1-6 as in Table 2. 9. Meisalo & Merisalo (1966). 10. Merisalo & Inkinen (1968). 11. Buyers & Smith (1968).

Table 5. The values of the ratio B/a^2 for the ions in some alkali halides calculated from X-ray diffraction results at 80°K

The meanings of the numbers in columns 2 and 3-6 are the same as in Table 4.

Crystal	Ion Ref.	$B/a^2 \times 10^2$			
		Li ⁺	F ⁻	Na ⁺	Cl ⁻
LiCl	2, 10	3.14			1.72
		3.56 ± 0.38			1.57 ± 0.38
NaF	12, 11		1.98	1.89	
			2.03 ± 0.33	1.90 ± 0.33	
NaCl	3, 11			1.76	1.57
				1.85 ± 0.16	1.63 ± 0.16

Refs. 2 and 3 as in Table 2, refs. 10 and 11 as in Table 4. 12. Merisalo (1967).

therefore we cannot explain the disagreement in this way. We have seen that the ratio B/a^2 at the Cl^- ion seems to be a linear function of the electron number of the cation at 300°K . Buyers & Smith (1968) have very recently calculated the Debye–Waller coefficients of Na^+ and Cl^- in NaCl from the next-nearest-neighbour model (NNN) of Hardy & Karo (1966). These calculations show that the ratio of the sodium to the chlorine Debye–Waller coefficient at 300°K is increased and this improves the agreement between the calculated and measured coefficients. The effect between the nearest neighbours could also explain the dependence indicated in Fig. 4. From these considerations we conclude that the discrepancy between the measured and calculated Debye–Waller coefficients (*cf.* Table 4) at 300°K is a result of the repulsive forces between the next-nearest neighbours not included in the theory (DD model of Karo & Hardy, 1963).

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Non-crystallographic Shubnikov Groups

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It is argued that magnetic structures are likely to be found which will most fruitfully be explained with the aid of non-crystallographic magnetic point groups. The point groups are classified into families of 'halving subgroups' and it is shown diagrammatically, with the aid of representation theory, how non-crystallographic Shubnikov groups can be constructed.

Introduction

Crystallographers who think in terms of just 32 point groups immediately limit the mathematical equipment

available for interpreting the physical properties of crystals. The fact that only 32 point symmetries are admissible as units for repetition in Bravais lattices does not mean that other symmetries must be de-