The Spherical Symmetry of the Ions in Potassium Chloride Crystal

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The measured structure factors for KCl at 300°K, including corrections due to the thermal diffuse scattering and dispersion, are given. The absolute scale of the structure factors has been obtained by a direct intensity measurement of the primary X-ray beam with use of both Cu $K\alpha$ and Mo $K\alpha$ radiation. The Debye–Waller factors and the ionic radii derived from the measured structure factors are 2.08 ± 0.05 Å², 2.06 ± 0.05 Å², 1.45 ± 0.07 Å and 1.70 ± 0.07 Å for K⁺ and Cl⁻, respectively. The calculations of the radial coefficients of the cubic harmonic expansion for K⁺ and Cl⁻ indicate that these ions are almost exactly spherically symmetric.

Introduction

Non-spherical deformations of ions have been reported in some ionic crystals (Meisalo & Inkinen, 1967; Järvinen & Inkinen, 1967). The KCl crystal is expected to have a very ideal ionic character. As a consequence, the deformations should be negligible. The calculations of Korhonen (1956), however, based on the measurements of Wasastjerna (1944), indicate some evidence of non-spherical charge distribution around the Cl⁻ ion. With a more reliable measurement technique and also more effective tools for calculations now at our disposal, we have chosen KCl as an object of our study.

Specimens

The KCl powder was prepared partly by the usual grinding method and partly by precipitating KCl in methanol by the addition of diethyl ether. The fine grained precipitate was dried and pressed, as well as the ground powder, in a polished mould by using as weak pressures as possible, just sufficent to keep the powder together, to avoid possible preferred orientation. Some specimens with high ratio of the intensities of the 200 and 220 reflexions were discarded. Eight different specimens were used in the final measurements.

Measurements

The integrated X-ray diffraction intensities were measured by two different methods (Korhonen & Vihinen, 1958; Meisalo & Inkinen, 1967). In the first method, however, more accurate apparatus was used. By the second method only the intensities from the reflexions 200 to 642 (Cu $K\alpha$ radiation) plus some very weak intensities (Mo $K\alpha$ radiation) were obtained.

The intensities of the different specimens were measured on the same scale partly by using the same settings of the apparatus and partly by using a reference spe-

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cimen in every series of measurements. The final intensities were obtained by averaging from about 60 series.

Scale of the structure factors

The integrated intensities were corrected for temperature diffuse scattering (Suortti, 1967). These corrections varied from 0.25% (200) to 4.1% (642) in Cu $K\alpha$ measurements and from 1.4% (800) to 13.4% (886) in Mo $K\alpha$ measurements. The scale of the structure factors was determined by an absolute measurement (*cf.* Meisalo & Inkinen, 1967), using here both Cu $K\alpha$ and Mo $K\alpha$ radiation. As mass absorption coefficients for Cu $K\alpha$ radiation we used those of *International Tables for X-ray Crystallography* (1962) and for Mo $K\alpha$ radiation the values of Weiss (1966). The structure factors thus obtained are 27.45 for the 200 reflexion (Cu $K\alpha$)

Table 1. *Experimental dispersion- and TDS-corrected structure factors F_0 of KCl at 300°K, semitheoretical structure factors F_c calculated from free-ion form factors with temperature parameters $B_K = 2.08$ Å², $B_{Cl} = 2.06$ Å², and the differences $\Delta F = F_0 - F_c$*

The values are for a molecular unit of KCl. Overlapping reflexions combined by curly brackets have been divided in the theoretical ratio.

h k l	F_o	F_c	ΔF
1 1 1	1.28	1.38	-0.10
2 0 0	26.98	26.98	0
2 2 0	21.87	21.82	0.05
3 1 1	1.34	1.40	-0.06
2 2 2	18.42	18.43	-0.01
4 0 0	16.37	16.02	0.35
3 3 1	0.87	0.90	-0.03
4 2 0	14.42	14.20	0.22
4 2 2	12.92	12.76	0.16
{3 3 3 / 5 1 1}	0.55	0.56	-0.01
4 4 0	10.63	10.58	0.05
5 3 1	0.32	0.38	-0.06
{4 4 2 / 6 0 0}	9.78	9.72	0.06
6 2 0	9.17	8.96	0.21
5 3 3	0.39	0.29	0.10
6 2 2	8.39	8.29	0.10
4 4 4	7.48	7.68	-0.20
{5 5 1 / 7 1 1}	0.30	0.24	0.06
6 4 0	7.10	7.13	-0.03
6 4 2	6.59	6.62	-0.03
{7 3 1 / 5 5 3}	0.21	0.22	-0.01
8 0 0	5.91	5.73	0.18
{6 4 4 / 8 2 0}	5.38	5.33	0.05

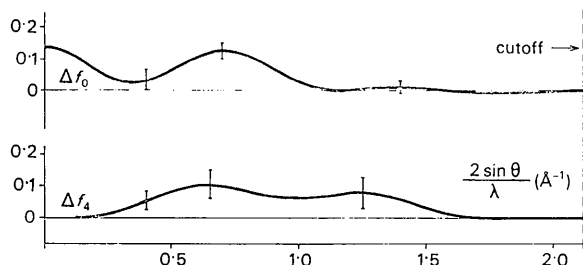| h k l	F_o	F_c	ΔF
{6 6 0 / 8 2 2}	5.11	4.97	0.14
6 6 2	4.57	4.63	-0.06
8 4 0	4.43	4.31	0.12
8 4 2	4.02	4.02	0
6 6 4	3.66	3.75	-0.09
8 4 4	3.04	3.26	-0.22
{8 6 0 / 10 0 0}	2.99	3.04	-0.05
{8 6 2 / 10 2 0}	2.86	2.84	0.02
{6 6 6 / 10 2 2}	2.56	2.65	-0.09
{8 6 4 / 10 4 0}	2.37	2.30	0.07
10 4 2	2.22	2.15	0.07
{8 8 2 / 10 4 4}	1.72	1.75	-0.03
{8 6 6 / 10 6 0}	1.62	1.63	-0.01
10 6 2	1.50	1.53	-0.03
{8 8 4 / 12 0 0}	1.35	1.42	-0.07
12 2 0	1.30	1.33	-0.03
{10 6 4 / 12 2 2}	1.12	1.24	-0.12
{8 8 6 / 10 8 0 / 12 4 2}	1.07	1.02	0.05

Fig. 1. The radial coefficients Δf_0 and Δf_4 of the cubic harmonic expansion of Δf for Cl⁻ in KCl. The limit of the measurements (cutoff) is also shown.

and 21·49 for 220 (Mo $K\alpha$), both of them dispersion corrected (Cromer, 1965). The final scale of the structure factors was determined as a mean value of these measurements. Thus the final value of $F(200)$ (Table 1) is 1·7% lower and that of $F(220)$ 1·7% higher than the absolute values and the accuracy of the final scale better than 2%.

Debye–Waller factors of ions

The theoretical structure factors are based on the atomic factors calculated, at the desired points of the reciprocal lattice, from analytical wave functions of Bagus (1965). The semitheoretical structure factors at 300 °K (Table 1, column 3) were obtained by multiplying the theoretical ones by temperature factors, exp $(-B \sin^2\theta/\lambda^2)$, where the Debye–Waller factors were $B_K = 2·08 \pm 0·05$ and $B_{Cl} = 2·06 \pm 0·05$ Å². These have been calculated from our measurements by the method of Fourier difference series (cf. Meisalo & Inkinen, 1967). The value of the lattice edge used everywhere was $a = 6·292$ Å.

The Debye temperature calculated from these factors for KCl is $\Theta = 213 \pm 8$ °K, which agrees with an experimental value 223 °K (Obsieger, 1963) and a theoretical one 220 °K (Sen, 1964). The theoretical Debye–Waller factors at 300 °K recently calculated (Merisalo & Inkinen, 1968) are $B_K = 1·94$ and $B_{Cl} = 1·98$ Å². These calculations are based on the model of Karo & Hardy (1963). B_{Cl} is in good agreement with our measurements but B_K differs a little from our value $2·08 \pm 0·05$ Å².

The spherical symmetry of ions in KCl

To study the spherical symmetry of the K and Cl ions we have calculated the coefficients of the cubic har-

monic expansions to the atomic factor differences (Kurki-Suonio & Meisalo, 1967; Kurki-Suonio, 1968). For that purpose we have determined the ionic radii of K⁺ and Cl⁻ by the method of equal charge densities inside K- and Cl-centred shells (cf. Meisalo & Inkinen, 1967). As a result we have obtained $R_K = 1·45 \pm 0·07$ Å and $R_{Cl} = 1·70 \pm 0·07$ Å. These spheres contain 97·5% of the whole electron number and the mean electron density outside these spheres is only 0·031 e.Å⁻³. The ionic radii used in further calculations were, however, $R_K = 1·60$ and $R_{Cl} = 1·80$ Å, because the effects of overlapping are thus avoided (Kurki-Suonio, 1968).

The achieved spherical component Δf_0 and, in this crystal symmetry, the first possible non-spherical component Δf_4, which relates to d-electrons, are shown for Cl⁻ in Fig. 1 as a function of 2 sin θ/λ. It is obvious from Fig. 1 that the Cl⁻ is almost exactly spherical and that the charge distribution is much like the one in the theoretical free ion. According our calculations the situation is the same also in relation to K⁺ ion.

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