paper for the 5-3·5 Å range has not been studied but it is obvious that a coarse model should be built of larger blocks rather than from a set of atoms to obtain a reasonable relation between the number of parameters describing the model and those of the structure factors used for the refinement.

In modern protein crystallography the following main stages can be distinguished as necessary.

1. Initial phase determination, for example, by the method of isomorphous replacement.
2. Intermediate phase improvement resulting in a preliminary model for the protein molecule.
3. Final refinement of the molecular model.

Attempts to obtain reliable phases at the first stage of phase determination for most of the proteins with a medium and large molecular mass have failed. Thus, an elaboration of a powerful method for the second stage is very desirable, with the application of additional information for phase improvement by different methods. The method proposed in this paper could be one of them.

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Electron Density Studies of KCl and LiF by γ-ray Diffractometry

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Abstract

Use of hard electromagnetic radiation ($\lambda = 0{\cdot}12$ Å) in diffraction experiments, in conjunction with thin crystals in transmission geometry (Laue case), minimizes multiple scattering, often referred to as the 'extinction problem'. A large crystal slab, completely intercepting the incident beam, was used in this experiment. Several structure factors have been measured in LiF and KCl, with greater accuracy than ever before, using the γ-ray spectrometer of the University of Missouri at Columbia. In the case of LiF the results indicates some compression of the valence electron densities, similar to what has been found earlier for NaF. In the case of KCl all reflections agree well with the values calculated from free-atom Hartree-Fock wave functions except for the 004 and 006, which are appreciably weaker than corresponding reflections with similar or identical $\sin\theta/\lambda$ values. This result indicates asphericity of the valence electron density. The 111 is also much weaker than the calculated value, indicating that the negative ions are slightly compressed and the positive ions slightly expanded with respect to the free-ion charge densities.

1. Introduction

Using high-energy γ-rays ($E \geq 100$ keV) for diffraction experiments, in conjunction with thin crystal slabs set for Laue-case diffraction, greatly minimizes the occurrence of extinction, which makes it possible to extract structure factors from intensity measurements with accuracies by far superior to those hitherto obtained in traditional X-ray experiments ($E =$ 6-20 keV) (Schneider, 1974, 1976). The physical rea-

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son is that extinction is a consequence of multiple scattering, and using high-energy photons the probability of this process is greatly reduced because the cross section for individual scattering events decreases with increasing energy.

The charge densities of alkali halides have been extensively investigated in the past, using powder and single-crystal methods (Brill, 1967). While the theory is able to predict very accurately the charge density of a free atom, deviations due to crystal-field effects, such as exchange interactions, are more subtle and difficult to discern, owing to the combined effects of dubious extinction corrections and truncation errors in Fourier syntheses. Our approach is to perform a limited number of highly accurate measurements on an absolute basis, using a large thin crystal slab set for the Laue case of diffraction, and to draw conclusions from comparing our experimental intensities with those predicted using free-atom scattering factors. In a previous experiment on NaF with γ-ray diffractometry (Yoder & Colella, 1982) we were able to detect an overall compressional effect of the crystal potential on the free-atom wave functions.

2. Experimental

The details of the experimental technique, such as precautions against multiple reflection effects, have been given elsewhere (Yoder & Colella, 1982). Since the beam was completely intercepted by the crystal slabs, all measurements were put on an absolute basis, by measuring the power of the incident beam I_0. This was done in two ways: (i) by using a series of calibrated absorbers, (ii) by comparing with the 220 reflection diffracted by a perfect Si slab, for which the integrated intensity was calculated using a value of F_{220} determined by the *Pendellösung* method.[*] The two methods were in agreement within 0·5%. The thickness used for KCl was scaled from that used previously for NaF, so as to correspond to the same extinction length for 220, which in the case of NaF gave all extinction-free structure factors except for the 200 (Yoder & Colella, 1982). Two KCl crystals were prepared, with thicknesses equal to 0·388 and 0·367 mm, and about 1 cm^2 in area. The crystals were both cut from a boule obtained from Harshaw Chemical Company (Cleveland, Ohio), using a wire saw, lapped with 600-1200-3200 grit SiC, and etched for about a minute at room temperature in a 50-50 mixture of water-ethanol. One slab was parallel to the (110) planes, the other one was parallel to the (100) planes, in both cases within 5-6′. Several reflections with the same *hkl* Miller indices were measured on both crystals, and consistent data were obtained in each case, so that no distinction will be made in presenting the final results. A conservative estimate of the experimental percentage errors in our experimental intensities is ±1.0%. This mosaic spread was about the same for both crystals (~10-12′), but the (100) crystal in some cases exhibited split peaks, about 0·3° apart. It was usually enough to rotate the crystal by 90° around the [100] normal to the surface and repeat the measurement on an equivalent reflection to eliminate or greatly reduce the split peaks. A (110) LiF crystal was prepared in a similar manner. The thickness was 0·415 mm, and it was etched for 4 min at room temperature in a mixture of 1 part 20% sulphuric acid and 1·5 parts saturated boric acid. No split peaks were found, and the mosaic spread was 3-4′.

3. Discussion – KCl

The reflections measured in KCl span a range of $\sin\theta/\lambda$ between 0·14 and 0·80 Å^{-1}. Only one odd reflection, the 111, could be measured, because the next one, the 311, was too weak. The general strategy was to pin down the Debye-Waller factors by means of high-order *hkl* reflections (the 10,0,0, for example), under the assumption that any deviation from free-atom scattering factors occurs in the valence electrons, which contribute essentially nothing to reflections like 10,0,0. In view of the fact that only one odd reflection was available, and that K and Cl are close in the Periodic Table, it was found adequate to fit all our results with one single thermal factor: $B = 1{\cdot}98$ Å^2. For the 10,0,0 the thermal effect is enormous: it results in a reducing factor equal to 0·29. The experimental values found in the literature range from $B_K = B_{Cl} = 1{\cdot}78$ Å^2[*] to 2·38 Å^2 (Jayalakshmi & Viswamitra, 1970) so our value is well within the range of values found by other authors.

Table 1 shows the complete list of all reflections that have been measured, with values calculated using free-atom scattering factors for K^+ and C^-(Cromer & Mann, 1968). Fig. 1 shows a plot of intensity differences (experimental minus calculated values) as a function of $\sin\theta/\lambda$. While most reflections seem to agree well with the values calculated for spherical free atoms, there are three notable exceptions: the 400, the 600 and the 111. It is remarkable to see how different are the 600 and the 442, which correspond to the same $\sin\theta/\lambda$, and the 400 and 222, whose $\sin\theta/\lambda$ values are very close. There seems to be a systematic trend for the *h*00 reflections to be smaller than the free-atom values. This trend disappears for higher orders, as expected, if the effect is due to deformations due to crystal-field effects in the valence

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[*] It was found by Aldred & Hart (1973) that $f_{220} = 8{\cdot}436$ with Ag *Kα* (λ = 0·561 Å). From this value we subtract $f' = 0{\cdot}057$, determined by X-ray interferometry (Cusatis & Hart, 1975).

[*] Deduced from $\theta_M = 230$ K, obtained from Mössbauer diffraction experiments (Albanese, Ghezzi & Merlini, 1973).

Table 1. *List of experimental and calculated integrated intensities and structure factors for* KCl

Percentage difference is $(R_i^e - R_i^c)/R_i^e$, where R_i^e are experimental values and R_i^c are calculated values. The index *i* stands for *hkl*.

hkl	R_{hkl} exp. ($\times 10^7$)	R_{hkl} theor. ($\times 10^7$)	Percentage difference (%)	F_{hkl} exp.	F_{hkl} theor.
220	122·0	121·0	+1·06	88·2	87·7
222	70·7	70·9	−0·28	74·2	74·3
400	44·4	46·6	−4·82	63·2	64·7
224	24·1	24·3	−0·83	51·5	51·7
442	11·7	11·7	−0·17	39·7	39·7
600	11·1	11·7	−5·61	38·6	39·7
444	6·24	6·39	−2·40	31·2	31·6
800	3·07	3·13	−1·92	23·6	23·8
10,0,0	0·733	0·732	0·10	12·9	12·9
111	0·727	0·795	−9·37	5·32	5·56

electron density. Differences in reflections with identical or similar sin θ/λ values are due to aspherical charge densities. Our results are consistent with removal of valence charge from the *h*00 directions and creation, presumably, of 'lobes' along the 110 directions. See discussion given by Böbel, Cortona, Sommers & Fumi (1985), second footnote. Also noteworthy is the low value of the 111, which is a difference reflection. The positive ions (K^+) are predicted by the free-ion Hartree-Fock theory to be smaller in size than the negative ions (Cl^-), owing to electrostatic attraction towards the nucleus. A weak 111 intensity means that the negative and positive ions in the crystal are not so different in size as predicted. Intuitively one expects this to be the case, since negative-ion vacancies, for example, are stable locations for electrons, as shown by the existence of *F* centers, which means that the negative ions, being more easily compressible than the positive ions, will be contracted by the crystalline potential.

Since the 111 intensity results from the difference between two large almost identical numbers, one may wonder whether the observed discrepancy might arise from improper thermal factors. The answer is no. We have used one single Debye-Waller factor for the two ions, which is very close to 1 for the 111 anyway, making use of the fact that the two atoms are very similar. Really, the K^+ ion is more massive. Presumably its mean-square vibrational amplitude will be slightly smaller, if anything. Its *B* factor will be smaller than that of the Cl^- ion, and its temperature-corrected scattering factor will be increased. Therefore, any changes in Debye-Waller factors resulting from differences between K^+ and Cl^- ions will produce effects in the opposite direction with respect to the experimental observation.

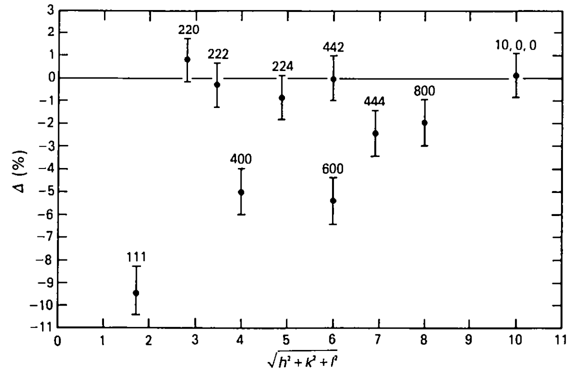

Fig. 1. Plot of percentage differences, as given in Table 1, *vs* $(h^2+k^2+l^2)^{1/2}$, for KCl.

4. X-ray results

Similar results, as far as the 111 is concerned, have already been found with X-rays in a separate set of experiments (Yoder & Colella, 1977). In contrast to the work described in this paper, we used relatively soft X-rays, and the symmetric Bragg case of diffraction, with a thick crystal. This was a different, opposite, approach to solving the extinction problem. When absorption is high, multiple scattering is hindered by the fact that an X-ray photon disappears before having a chance of being scattered a second time. This happens when the absorption length is shorter than the extinction length. Two X-ray wavelengths were used: Cu $K\alpha$ ($\lambda = 1{\cdot}54$ Å) and Cr $K\alpha$ ($\lambda = 2{\cdot}29$ Å). Perfect Si crystals [(111) and (311)] were used as monochromators, so that dynamical theory could be used to evaluate exactly the polarization ratio in the incident beam. While a little bit of extinction was present with Cu $K\alpha$, as confirmed from Berg-Barrett photographs of the (111) surface, which showed a textured pattern, no extinction was found to exist with Cr $K\alpha$ radiation, in which case the integrated intensities of the 111, 222 and other *hhh* reflections were found to be uniform across the surface.* Our calculations also indicate that the difference between dynamical and kinematical theory, in calculating the 111 integrated intensity, amounts to 1% with Cr $K\alpha$. While other strong reflections were found in good agreement with free-atom values - the 444 with Cu $K\alpha$, the 311 with Cr $K\alpha$, and the 333 with both - the 111 was systematically lower, by 15% with Cu $K\alpha$ and by 19% with Cr $K\alpha$. It is not surprising that some discrepancy exists between measurements at different wavelengths, owing to uncertainties in the calculated values. The 111 is in fact a difference reflection, and its value depends critically on the difference between the anomalous dispersion corrections for K and Cl (Cromer & Liberman, 1970), which are not very accurately known

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* See discussion and Fig. 1 in the paper by Hirsch & Ramachandran (1950). In our experiments we had: $|g| = 1{\cdot}07$ and $k = 0{\cdot}22$ for Cu $K\alpha$ ($\lambda = 1{\cdot}54$ Å). The universal curves of Fig. 1 show that extinction is small, but non-zero, in this case. With Cr $K\alpha$ ($\lambda = 2{\cdot}29$ Å) we had: $|g| = 2{\cdot}59$ and $k = 0{\cdot}50$, in which case extinction is completely absent.

Table 2. *List of experimental and calculated integrated intensities and structure factors* LiF

Percentage difference is $(R_i^e - R_i^c)/R_i^e$, where R_i^e are experimental values and R_i^c are calculated values. The index *i* stands for *hkl*.

hkl	R_{hkl} exp. ($\times 10^7$)	R_{hkl} theor. ($\times 10^7$)	Percentage difference (%)	F_{hkl} exp.	F_{hkl} theor.
220	66·5	67·2	−1·05	20·7	20·8
222	33·1	32·6	+1·51	16·2	16·1
224	8·09	7·70	+4·82	9·53	9·30
442	3·15	3·01	+4·44	6·59	6·44
600	3·08	3·01	+2·27	6·52	6·44
444	1·49	1·49	0·00	4·88	4·88
800	0·697	0·700	−0·43	3·59	3·60
111	91·2	91·7	−0·55	19·0	19·0
113	10·3	9·88	+4·08	8·84	8·66
331	3·37	3·24	+3·86	5·81	5·69
115	1·78	1·67	+6·18	4·60	4·46
333	1·69	1·67	+1·18	4·48	4·46

(Aldred & Hart, 1973). This problem can be appreciated when considering that, for Cr *Kα*, the imaginary part of the structure factor is 58% of the real part.

An added bonus of γ-ray diffractometry, at $E \geq$ 100 keV, is the fact that the anomalous dispersion corrections can be neglected, thereby eliminating an important source of uncertainty.

5. Comparison with theory

Our results are discussed in the following paper (Böbel, Cortona, Sommers & Fumi, 1985) and compared with self-consistent calculations based on the method of augmented spherical waves in the local-density-functional approximation (LDA). Crystal-field effects are automatically taken into account in these calculations. While the anomalies observed experimentally on the 400 and 600 reflections are not reproduced in the calculations, the 111 reflection is correctly predicted to be about 9% lower than the free-atom value.

6. LiF results

The results for LiF are shown in Table 2 and Fig. 2. The theoretical values have been calculated in the same manner as the values given in Table 1. The choice of the Debye–Waller factors is always a critical element in analyzing the data. As can be seen from Table 3, the values found in the literature span a wide range. We found that the values $B_{\rm Li} = 0{\cdot}96$ Å^2, $B_{\rm F} = 0{\cdot}66$ Å^2 (Killean, Lawrence & Sharma, 1972) gave the best fit for the 800, for which the temperature effect is important (of the order of 45%). Our confidence in these *B* values for analyzing our data is reinforced by the fact that they are almost identical to those calculated from inelastic neutron scattering data (Dolling, Smith, Nicklow, Vijayaraghavan & Wilkinson, 1968).

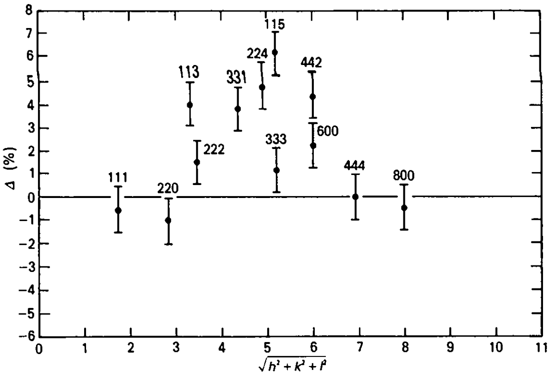

Fig. 2. Plot of percentage differences, as given in Table 2, *vs* $(h^3+k^2+l^2)^{1/2}$, for LiF.

Table 3. *Temperature factors for* LiF

$B_{\rm Li}$(Å^2)	$B_{\rm F}$(Å^2)	References	Method
1·02	0·82	Linkoaho & Merisalo (1970)	Powder-corrected for anomalous dispersion
0·96	0·66	Killean, Lawrence & Sharma (1972)	Single crystal; X-rays
1·01	0·68	Howard & Khadake (1974)	Single crystal; X-rays
1·67	0·52	Martin & O'Connor (1978)	Single crystal; γ-rays
1·04	0·74	Dawson & Howard (1974)	Single crystal; X-rays

It is clear from Fig. 2 that some discrepancies show up at intermediate values of sin θ/λ. Surprisingly, the 111 is now in perfect agreement with the free-atom value, as opposed to the case of KCl. The experimental intensities are systematically greater than those calculated. This fact indicates a compressional effect on the wave functions, due to the crystal potential, an effect that has already been seen in NaF (Yoder & Colella, 1982). The difference between 115 and 333, above experimental error, may indicate a slight degree of asphericity.

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Electron Density in KCl and LiF Crystals in the Self-Consistent Local-Density-Functional Approximation (LDA)*

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Abstract

The γ-ray single-crystal structure factors of Schmidt, Colella & Yoder-Short [*Acta Cryst.* (1985), **A41**, 171-175] for the 'isoelectronic' salt KCl are shown to be in excellent agreement with the values computed by us using the method of augmented spherical waves in the LDA approximation. Small differences exist for the 600 and 400 reflections whose structure factors indicate some 'asphericity' in the valence charge density - an effect not included in the theoretical calculation. The corresponding data by the same authors for the ('non-isoelectronic') salt LiF are also in good agreement with the LDA theoretical values available in the literature. A discrepancy remains, instead, between the γ-ray structure factors for 'isoelectronic' NaF by Yoder & Colella [*Phys. Rev. B* (1982), **25**, 2545-2549] and the LDA theoretical values.

1. Introduction

In a recent paper (see Böbel, Cortona, Sommers & Fumi, 1983 § 3(*c*), fifth paragraph) we noted that preliminary γ-ray structure factors for KCl by Schmidt & Colella (private communication, December 1981) were systematically higher than the available X-ray data and our LDA theoretical values. We will see here that the finalized γ-ray data by Schmidt, Colella & Yoder-Short (1985) do not show these anomalies, and are in fact in excellent agreement with our LDA structure factors and in reasonably good agreement with the previously available X-ray data (Patomäki & Linkoaho, 1969).

Schmidt, Colella & Yoder-Short (1985) also report γ-ray structure factors for LiF. We will comment briefly on these data, emphasizing the important difference from the cases of '*isoelectronic*' alkali

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