Anharmonic Contributions to the Debye–Waller Factors of UO₂

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The integrated intensities of UO₂, with the cubic fluorite-type structure, have been measured at 20 °C by neutron diffraction. If structure factors are calculated assuming harmonic temperature factors for the uranium and oxygen atoms, there are systematic differences between the observed and calculated intensities of odd-index reflexions, whereas good agreement is obtained for even-index reflexions. These results can be explained as the effect of anharmonicity on the temperature factor of the oxygen atoms, which occupy non-centrosymmetric sites. The introduction of one additional parameter to describe this anharmonic effect leads to good agreement $(R \sim \frac{1}{2} \%)$ for all measured reflexions.

1. Introduction

The object of the present paper is to present some highly accurate structure factor data on UO₂, to demonstrate the inadequacy of the conventional treatment of thermal motion in interpreting these data, and to describe the necessary modifications to this theory.

The effect of thermal motion on the intensity of a Bragg reflexion is calculated by multiplying the scattering amplitude of each atom in the unit cell by its temperature factor $T_j(S)$. S is the reciprocal lattice vector where $|S| = 2 \sin \theta / \lambda$, and T_j is the Fourier transform of the smearing function $t_j(\mathbf{r})$ of atom j; $t_j(\mathbf{r})$ is defined as the probability of finding atom j at a distance $\mathbf{r}$ from its equilibrium position.

For any crystal with harmonic interatomic forces, T_j is Gaussian in form and can be written

$$T_j = \exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{23}kl + b_{13}hl)] , \quad (1)$$

where the constants b_{11} *etc.* are the six anisotropic temperature factors, defining the size and orientation of the thermal vibration ellipsoid. If the atoms occupy sites with cubic point symmetry, the ellipsoid degenerates into a sphere and T_j is characterized by a single isotropic factor B_j^*, where

$$T_j = \exp(-B_j \sin^2\theta / \lambda^2) = \exp(-\tfrac{1}{4}B_j S^2) . \quad (2)$$

This spherical symmetry is a consequence of the invariance of quadratic forms under transformations of a cubic point group. When the atomic interactions are anharmonic (*i.e.* the force on an atom is no longer proportional to its displacement) then T_j in equation

(2) includes higher powers of S and so, even in a cubic crystal, departures from spherical symmetry are allowable.

Anisotropy in the temperature factors of a cubic crystal, with atoms at sites of cubic symmetry, was first observed by Willis (1963) in a high-temperature neutron diffraction study of UO₂. He showed that some reflexions with the same |S|, but belonging to different reciprocal lattice vectors S, were not equal in intensity, as they should be on the harmonic theory. Anharmonic effects were also observed in CaF₂ (Willis, 1965) and in UO₂₊ₓ (Willis, 1964).

To account for the effect of anharmonicity, Willis adopted a generalized fluorite arrangement, where each anion is replaced by four quarter-anions set down at the corners of a small tetrahedron at the anion sites (Fig. 1). This artifice simulated the tetrahedral distortion of the smearing function $t(\mathbf{r})$ of the anion, caused by the anharmonic interactions of the anion with its tetrahedral frame of cations. It predicted the presence of anharmonic contributions to the structure factors of odd-index reflexions, such that reflexions with $h+k+l=4n+1$ possess intensities exceeding the harmonically calculated values, whereas those with $h+k+l=4n-1$ have intensities lower than the harmonic values. These predictions accorded qualitatively with the observations.

Willis's procedure was criticized by Hamilton (1965a), who showed that it gave a displacement parameter δ [see § 3(a)] of marginal statistical significance, at least in the case of the CaF₂ data at 20 °C. Hamilton did not extend his analysis to the higher temperature range for CaF₂ and UO₂, where the anharmonic effects were much stronger. Ladell (1965) suggested that the neutron measurements provided no evidence for anharmonic behaviour.

The original interpretation of Willis was also criticized by Pryor (1966) on the grounds that the hypothetical displacements of the anions in the Willis theory

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* In this paper, we shall henceforth refer to T_j as the 'temperature factor' of the atom j, and to B_j as its '*B* factor'. The term 'Debye–Waller factor' refers to a reflexion (in reciprocal space), rather than to an atom (in direct space): it will be used to denote the reduction in intensity of a reflexion caused by thermal vibration.

are much larger than the usual expressions for inter-atomic potentials would lead one to expect.

These objections to the validity of the experimental results and to their interpretation are answered in the present paper. In the next section we present further experimental data on UO_2 at 20 °C. These results are more accurate and extend to longer reciprocal lattice vectors (*i.e.* higher values of $|S|$) than before. In § 3 we outline the Willis theory of accounting for anharmonic effects, and its relation to a more complete and satisfactory theory proposed by Dawson (1967). In § 4 we describe the interpretation of the new UO_2 results by the Dawson theory, deriving a value for the 'anharmonic parameter' β_O of oxygen (replacing the parameter δ in the Willis theory), which agrees with that deduced by Dawson, Hurley & Maslen (1967). We discuss briefly, in the final section, proposals for experimental work which would subject Dawson's theory to a more critical examination than that described here.

2. Structure factors of UO_2 at 20 °C: interpretation by harmonic model

A spherical crystal of radius 1·6 mm was chosen for the investigation: it had been examined earlier and was known to be free of extinction for reflexions of medium

intensity (with $h+k+l=4n\pm1$) and for weak reflexions $(h+k+l=4n+2)$. Three-dimensional measurements were made with the Hilger–Ferranti automatic neutron diffractometer. As far as possible, measurements of each reflexion were taken on 12 'variants', defined as symmetrically equivalent but distinct hkl planes (*i.e.* permutations not including both hkl and $h\bar{k}l$). Because of the lower multiplicity, only three variants of 006 and four variants of 333 and 555 were
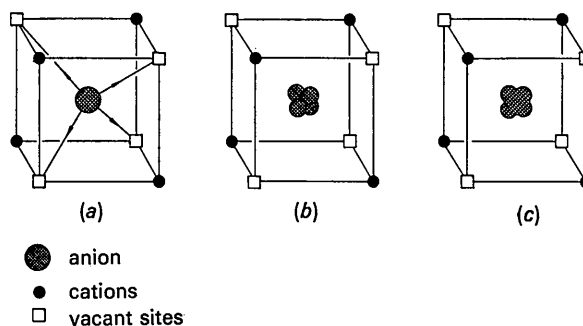

- anion
- cations
- vacant sites

Fig. 1. Anion in the fluorite structure vibrates preferentially along the four tetrahedral directions shown by arrows (*a*). This aspherical motion is represented by four quarter-anions in the Willis treatment (*b*), and by a tetrahedrally distorted smearing function in the Dawson theory (*c*).

Table 1. *Structure factors of* UO_2: *measurements at* $\lambda = 1\cdot038$ Å

hkl	$h^2+k^2+l^2$	$h+k+l=4n+1$ or $4n-1$	F_{obs}	$\sigma(F_{obs})$	F_{calc}^{harm}	$F_{obs}-F_{calc}^{harm}$	F_{calc}^{anh}	$F_{obs}-F_{calc}^{anh}$
133	19	−	3·216	0·006	3·220	−0·004	3·215	+0·001
333 }	27	+	3·181	0·003	3·176	+0·005	3·178	+0·003
115 }		−	3·166	0·007	3·176	−0·010	3·172	−0·006
135	35	+	3·128	0·004	3·132	−0·004	3·132	−0·004
335	43	−	3·082	0·006	3·088	−0·006	3·078	+0·004
117 }	51	+	3·050	0·006	3·046	+0·004	3·046	+0·004
155 }		−	3·033	0·007	3·046	−0·013	3·040	−0·007
355 }	59	+	3·015	0·007	3·003	+0·012	3·016	−0·001
137 }		−	3·002	0·005	3·003	−0·001	2·999	+0·003
024	20		−1·085	0·005	−1·088	+0·003	−1·088	+0·003
006 }	36		−0·921	0·012	−0·937	+0·016	−0·937	+0·016
244 }			−0·946	0·005	−0·937	−0·009	−0·937	−0·009
226	44		−0·860	0·011	−0·865	+0·005	−0·865	+0·005
046	52		−0·793	0·006	−0·797	+0·004	−0·797	+0·004

Table 2. *Structure factors of* UO_2: *measurements at* $\lambda = 0\cdot866$ Å

hkl	$h^2+k^2+l^2$	$h+k+l=4n+1$ or $4n-1$	F_{obs}	$\sigma(F_{obs})$	F_{calc}^{harm}	$F_{obs}-F_{calc}^{harm}$	F_{calc}^{anh}	$F_{obs}-F_{calc}^{anh}$
733	67	+	2·997	0·020	2·981	+0·016	2·982	+0·015
751 }	75	+	2·934	0·020	2·940	−0·006	2·936	−0·002
555 }		−	2·918	0·023	2·940	−0·022	2·904	+0·014
911 }	83	−	2·896	0·012	2·897	−0·001	2·888	+0·008
753 }		−	2·879	0·012	2·897	−0·018	2·869	+0·010
755 }		+	2·845	0·005	2·816	+0·029	2·845	0·000
771 }	99	−	2·788	0·007	2·816	−0·028	2·804	−0·016
933 }		−	2·797	0·007	2·816	−0·019	2·798	−0·001
773 }	107	+	2·793	0·025	2·776	+0·017	2·801	−0·008
951 }		−	2·754	0·025	2·776	−0·022	2·767	−0·013
11,1,1 }	123	+	2·723	0·024	2·698	+0·025	2·703	+0·020
775 }		−	2·684	0·023	2·698	−0·014	2·660	+0·024
971 }		+	2·674	0·010	2·660	+0·014	2·675	−0·001
11,3,1 }	131	−	2·669	0·009	2·660	+0·009	2·659	+0·010
955 }		−	2·631	0·010	2·660	−0·029	2·628	+0·003
11,3,3 }	139	+	2·645	0·012	2·622	+0·023	2·645	0·000
973 }		−	2·591	0·012	2·622	−0·031	2·599	−0·008

measured; apart from these exceptions the F_{obs} values in Tables 1 and 2 are averaged over twelve variants. 10000–20000 neutron counts were recorded for each variant, and the standard deviation of the distribution of measurements over twelve variants was usually slightly larger than the standard deviation calculated from the counting statistics for a single observation. For example, the standard deviation from counting statistics was typically 1·0%, and that from the distribution was 1·0 to 1·7%.

An important source of error in accurate Bragg intensity measurements is double-Bragg scattering. It is well known that this will cause the intensity to vary with the azimuthal setting ψ (angle of rotation about the normal) of the reflecting plane. We checked for this effect by rotating about the reciprocal lattice vector for several reflexions, but could never detect it. As an extra precaution we measured each of the twelve variants of a reflexion at different values of ψ.

The peaks were scanned in an ω–2θ mode using a counter aperture 1·2 cm square at a distance of 25 cm from the crystal. Background was counted on either side of the Bragg peak. No correction was made for thermal diffuse scattering.

The neutron measurements were made in two groups

(i) 9 odd-index ($4n \pm 1$) reflexions and 5 even-index ($4n + 2$), measured at a wavelength of 1·038 Å;

(ii) 17 odd-index reflexions, at higher $\sin\theta/\lambda$ than in (i), measured at a wavelength of 0·866 Å.

These results are listed in Table 1 ($\lambda = 1\cdot038$ Å) and Table 2 ($\lambda = 0\cdot866$ Å). All observations at a given wavelength were made on the same relative scale: no attempt was made to determine intensities absolutely, nor to determine experimentally the scale factor relating the two sets of observations. The two scale factors were obtained from a least-squares analysis, as described below. The results quoted in the tables have been multiplied by the appropriate scale factor to bring them to an absolute scale. F_{obs} is the observed structure factor, derived from the mean of the intensity measurements on the variants. $\sigma(F_{obs})$ is the standard error of the observed 'variants'.

The fourth column in Tables 1 and 2 gives F_{calc}^{harm}, the structure factor calculated from the traditional harmonic formulation in which the effect of thermal vibration is represented by terms of the type given by equation (2). Thus

$$F_{calc}^{harm} = 4b_U T_U^h \qquad \text{for } h+k+l = 4n \pm 1$$
$$= 4b_U T_U^h - 8b_O T_O^h \text{ for } h+k+l = 4n+2 \quad (3)$$

where $T_U^h = \exp(-B_U \sin^2\theta/\lambda^2)$ and b_U is the coherent nuclear scattering amplitude for uranium, and similarly for oxygen. Values of the ratio b_U/b_O, and of B_U and B_O, were derived from a least-squares analysis of the 1·038 Å data based on equations (3), treating these three quantities and an overall scale factor as adjustable parameters. Table 3 gives the values of b_U/b_O, B_U and B_O, with the estimated standard deviations in brackets. For the analysis of the odd-index reflexions

in Table 2, there were only two adjustable parameters, the scale factor and B_U. It is encouraging that the two values of B_U in Table 3, derived from two independent sets of data over different ranges of $\sin\theta/\lambda$, overlap. The computer program used for the least-squares harmonic analysis was that of Busing, Levy & Martin (1962); individual F_{obs}'s were weighted by the reciprocal of the σ values in Tables 1 and 2, but the results were only marginally altered by replacing these individual weights by unit weights.

Table 3. *Results of harmonic analysis*

Wavelength (Å)	Number of F_{obs}'s	$\dfrac{b_U}{b_O}$	B_U (Å^2)	B_O (Å^2)
1·038	14	1·440 (5)	0·209 (11)	0·428 (11)
0·866	17	—	0·214 (14)	—

In spite of the apparently good agreement between F_{obs} and F_{calc}^{harm}, some of the deviations in Table 2 are 3 to 4 times the standard error of F_{obs}. Furthermore, when two or three reflexions appear at the same $h^2 + k^2 + l^2$, the observed F in both Tables 1 and 2 tends to be larger than the calculated F if $h+k+l = 4n+1$ and smaller if $h+k+l = 4n-1$. The $4n+2$ reflexions in Table 1 have deviations which are not more than twice the standard error of F_{obs}, and the harmonic model is adequate.

These systematic discrepancies in the observed intensities are similar to those reported previously in UO_2, ThO_2 and CaF_2 at high temperature (Willis, 1963, 1965), and can be explained in terms of anharmonic contributions to the Bragg intensities. In the next section we shall describe briefly the methods used by Willis and by Dawson for including these contributions in the analysis of the experimental data.

3. Extension of conventional vibration theory to include anharmonic effects

(a) Willis treatment

When Willis first observed systematic deviations between F_{obs} and F_{calc}^{harm}, he suggested that the deviations could be ascribed to anharmonic interactions between the anions and their tetrahedral frame of cations. These interactions produce an aspherical distortion of the smearing function of the anions. Willis simulated this distortion by considering a generalized fluorite structure in which each anion is replaced by four quarter-anions, displaced away from the nearest neighbour cations to positions such as $\frac{1}{4}+\delta,\frac{1}{4}+\delta,\frac{1}{4}+\delta$. The parameter δ characterizes the influence of anharmonic interactions. On the basis of this model one can show, for small δ,

$$F_{calc}^{anh} = F_{calc}^{harm} \pm 8b_O \cdot 8\pi^3\delta^3 \cdot hkl \cdot \exp(-B_O' \sin^2\theta/\lambda^2)$$
$$\text{for } h+k+l = 4n \pm 1$$
$$= F_{calc}^{harm} \text{ for } h+k+l = 4n+2 ,$$

where B_O' is now the B factor for the quarter-anions.

This theory described the experimental results successfully: in particular, it explained why intensities were anisotropic (depending on the direction as well as the magnitude of S) for the odd reflexions. But two objections can be made to the theory. First, the smearing of the anions is described partly by the isotropic temperature factor, B'_O, of the hypothetical quarter-anions, and partly by the four-way splitting; thus B'_O, which is less than B_O, has no obvious physical interpretation. Second, the interpretation of δ is not straightforward either. One might think that $\delta\sqrt{3}$ represents the shift in the mean position of an anion constrained to vibrate in a $\langle 111 \rangle$ direction, but this is not so (Pryor, 1965). δ is an empirical parameter which is related solely to the interpretation of the diffraction data.

The theory of Dawson gives essentially the same results as Willis's theory but avoids both these difficulties. Dawson retains the $\frac{111}{444}$ position for the anion and introduces a tetrahedral modification to its smearing function to account for anharmonicity.

(b) Dawson treatment

We start with the concept of a single-particle potential $V(\mathbf{r})$: $V(\mathbf{r})$ gives the variation, with displacement $\mathbf{r}$ from the mean atomic position, of the potential energy of the atom in the thermally agitated crystal. In a crystal with harmonic forces, and with atoms at sites of cubic symmetry, $V(\mathbf{r})$ could only be

$$V(\mathbf{r}) = V_0 + \tfrac{1}{2}\alpha(r_x^2 + r_y^2 + r_z^2), \qquad (7)$$

where α is a constant depending in a complex way on the interatomic potentials. (The relation betwen α and the Born–von Karman force constants could be obtained from a detailed sum over the normal modes of vibration.) Employing classical statistics, the smearing function is
$$t(\mathbf{r}) = N \exp[-V(r)/k_B T]$$

where k_B is Boltzmann's constant and the normalizing constant N is

$$N = (2\pi k_B T/\alpha)^{-3/2} \exp(-V_0/k_B T).$$

The limitation to classical statistics implies that T exceeds the Debye temperature. The temperature factor $T(\mathbf{S})$ is the Fourier transform of $t(\mathbf{r})$:

$$T(\mathbf{S}) = \exp(-\tfrac{1}{2}S^2 k_B T/\alpha)$$

so that $k_B T/\alpha$ can be identified with the mean-square atomic displacement $\langle r^2 \rangle_{av}$ or with $B/8\pi^2$.

In a cubic crystal with anharmonic forces, the form of $V(\mathbf{r})$ depends on the site symmetry. For the anion in UO₂, occupying a site of tetrahedral $\bar{4}3m$ symmetry, the next term after the quadratic (harmonic) term in (7) is a third-order term containing $r_x r_y r_z$. There is no

third-order term for the cation, as the centre of symmetry associated with $m3m$ symmetry requires that all odd-index terms in the potential expansion are identically zero; the next terms after the harmonic term are two quartic terms, describing the e_g and t_{2g} modifications of the spherical smearing function. We expect, therefore, that the principal anharmonic correction to the structure factor comes from the $\beta_O\, r_x r_y r_z$ term of the anion, where β_O is the coefficient of the third-order term in the expansion of $V(\mathbf{r})$ for oxygen. If this is the only correction, the expressions for F_{calc} are (Dawson, 1967):

$$F_{calc}^{anh} = F_{calc}^{harm} \pm 8b_O T_O^{harm} \left(\frac{B_O}{4\pi a_0}\right)^3 \frac{hkl}{k_B T} \beta_O \qquad (8)$$

$$\text{for } h+k+l = 4n \pm 1$$

and

$$F_{calc}^{anh} = F_{calc}^{harm} \text{ for } h+k+l = 4n+2, \qquad (9)$$

where B_U, B_O are the isotropic harmonic temperature factors for uranium, oxygen, and a_0 is the edge of the unit cell. It is straightforward to extend (8) and (9) to include higher-order anharmonic corrections, but the experimental data for all fluorite systems which have been examined to date do not seem to require this extension.

In the refinement of the UO₂ data based on equations (8) and (9), β_O must be treated as an adjustable quantity, in addition to the quantities B_U and B_O. For a lattice with no thermal expansion, β_O is independent of temperature for all temperatures exceeding the Debye temperature. With the same limitations, the harmonic parameters

$$\alpha_U = 8\pi^2 k_B T/B_U \quad \text{and} \quad \alpha_O = 8\pi^2 k_B T/B_O$$

are also independent of temperature.

If we identify the parameter δ of the Willis theory with the quantity

$$\frac{B_O}{8\pi^2} \cdot \frac{1}{a_0} \left(\frac{\beta_O}{k_B T}\right)^{\frac{1}{3}}$$

of the Dawson theory, equations (5) and (8) for the odd-index reflexions are identical in the two theories.

4. Reinterpretation of Bragg intensities using Dawson (anharmonic) theory

A full-matrix least-squares computer program based on equations (8) and (9) was kindly written for us by Dr B. H. Bracher. The program allows variation of any combination of the five parameters b_U/b_O, B_U, B_O, β_O and overall scale factor. The last two columns of Tables 1 and 2 list the quantities F_{calc}^{anh} and $F_{obs} - F_{calc}^{anh}$, where F_{calc}^{anh} is the structure factor calculated with this

Table 4. *Results of anharmonic analysis*

Wavelength (Å)	Number of F_{obs}'s	$\dfrac{b_U}{b_O}$	B_U (Å²)	B_O (Å²)	β_O (10⁻¹² erg.Å⁻³)
1·038	14	1·440 (3)	0·206 (6)	0·426 (9)	−8·0 (3·0)
0·866	17	−	0·202 (5)	−	−9·6 (1·0)

program. For the 1·038 Å data in Table 1, all five parameters were varied. For the 0·866 Å data, b_U/b_O and B_O were fixed at the values given by the 1·038 Å analysis, and only three parameters (B_U, β_O and scale factor) were varied: this procedure was necessary because no even-index reflexions were measured at 0·866 Å. Table 4 gives the final values, with estimated standard deviations in brackets, of b_U/b_O, B_U, B_O and β_O for the 1·038 Å data, and of B_U and β_O for the 0·866 Å data.

We note first that the introduction of the β_O parameter leads to an appreciable improvement in the agreement between observed and calculated structure factors. This can be expressed in terms of the R index, defined by $R = \sum\limits_{hkl} w_{hkl} ||F_{obs}| - |F_{calc}^{anh}|| / \sum\limits_{hkl} w_{hkl} |F_{obs}|$,

where the weights w_{hkl} are the reciprocals of $\sigma(F_{obs})$ in Tables 1 and 2. The R indices for the anharmonic analysis, and for the harmonic analysis ($\beta_O = 0$) described in § 2, are listed in Table 5. The R index ratio, defined as the harmonic R index divided by the anharmonic R index, is 1·38 for the 1·038 Å measurements and 2·12 for the 0·866 Å measurements.

Table 5. R indices

Wavelength (Å)	Anharmonic analysis	Harmonic analysis	R-index ratio
1·038	0·21 %	0·29 %	1·38
0·866	0·32 %	0·68 %	2·12

The significance of these R index ratios can be evaluated by applying the procedure described by Hamilton (1965). In the following paragraphs we shall test the hypothesis, H_0, that the oxygen atoms have anisotropic (anharmonic) temperature factors.

One extra parameter (β_O) is included in the anharmonic model, and so the dimension of the hypothesis is 1. There are fourteen measurements at 1·038 Å and five variable parameters, giving nine degrees of freedom.

From Hamilton's table

$$R_{1,9,0.010} = 1.47$$

and

$$R_{1,9,0.025} = 1.34 .$$

The observed R index ratio is 1·38 so that we accept the hypothesis at the 2·5% level but can reject it at the 1% level. The 1·038 Å results, therefore, do not show conclusively the need to refine the data with the anharmonic model: this is also suggested by Table 4 where the value of β_O, $-8.0(3.0) \times 10^{-12}$ erg.Å^{-3}, differs from zero by less than three standard deviations.

The 0·866 Å measurements are more conclusive. Here the number of observations is 17 and the number of adjustable parameters (B_U, β_O and scale factor) is 3, giving 14 degrees of freedom. Hamilton's table gives

$$R_{1,14,0.005} = 1.34 ;$$

the observed R index ratio is 2·12, so that we readily accept the hypothesis H_0 at the 0·5% level. This again is reflected in the more precise estimate of β_O, $-9.6(1.0) \times 10^{-12}$ erg.Å^{-3}, obtained from the 0·866 Å data.

Returning to Table 4, we note that the values of b_U/b_O, B_U and B_O are different from those published earlier (Lipson & Cochran, 1966):

$$b_U/b_O = 1.474(10),$$

$$B_U = 0.31(0.04) \text{ Å}^2, \quad B_O = 0.49(0.06) \text{ Å}^2 .$$

These earlier values must be considered as superseded by the figures in Table 4. The β_O value in the Table agrees satisfactorily with the value

$$\beta_O = -9.4(1.5) \times 10^{-12} \text{ erg.Å}^{-3} ,$$

deduced by Dawson, Hurley & Maslen (1967) from the analysis of the high-temperature UO$_2$ data of Willis (1963).

There are at least two possible sources of systematic error, whose presence would not be revealed by the least-squares anharmonic analysis, and which would cause errors in the parameters listed in Table 4. A very small degree of extinction, amounting to a reduction in intensity of the low-angle reflexions by one per cent, cannot be ruled out: this would be compensated in the analysis by an artificial reduction of B_U and B_O. Second, the neglect of thermal diffuse scattering, which rises to a maximum at the Bragg position, leads also to an underestimate of the B factors (Pryor, 1966).

A simple relation between B_U and B_O follows from the assumption that the single-particle potentials of uranium and oxygen include nearest neighbour interactions only. The α parameter in equation (7) is then derived by adding eight interatomic potentials for the uranium atom and four interatomic potentials for oxygen. Thus $\alpha_U = 2\alpha_O$. But $\alpha = k_B T/B$, so that

$$B_U = \tfrac{1}{2}B_O .$$

This relationship is obeyed quite well by the figures in Table 4.

5. Conclusions

In the case of UO$_2$ at 20 °C, anharmonic effects are very small: the changes in intensity are not much more than one per cent, even for the most sensitive reflexions. The anharmonic parameter β_O was derived from the 0·866 Å measurements with an estimated fractional standard deviation of 10 %. For the measurements at 1·038 Å, the anharmonic effects were barely significant: this is not surprising, since few reflexions in these data possessed high index-products, $h \times k \times l$. The purpose of the higher-wavelength measurements was to define B_O and the ratio of the scattering lengths b_U/b_O, so that these values could then be used in the analysis of the lower-wavelength, odd-index data. The values of B_U are the same for both sets of data, within the esti-

mated limits of error, but the B factors may possess other sources of error not apparent in a least-squares analysis (see § 4).

We have shown that it is possible to measure neutron structure factors with an estimated error not larger than $\frac{1}{2}\%$. It is tedious to do this – the F_{obs}'s represent the mean of twelve independent measurements of the hkl variants – but it is not particularly difficult.

The results demonstrate the presence of anharmonic effects and their dependence on the index-product. Further points in the theory can only be verified by taking measurements over a range of temperatures. It is more profitable to do this on other fluorite-type systems, such as BaF_2, SrF_2 and CaF_2, where the scattering length ratio (anion *versus* cation) is more favorable: neutron studies of these crystals will be reported separately.

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Der Beitrag der thermisch diffusen Streustrahlung zur Intensität der Röntgeninterferenzen und die Elektronendichteverteilung im NaCl

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The intensities of the X-ray-reflexions from NaCl single crystals were measured under two different experimental conditions, for which the contribution of the thermal diffuse scattering (TDS) was calculated from the elastic constants according to the Waller–Faxen Theory. The TDS contribution to the intensities of the reflexions was determined by three-dimensional numerical integration over reciprocal space. From the corrected intensities the structure factors, the atomic scattering factors, the temperature factors and the electron density in the $(x,y,0)$ plane of the unit cell were calculated. For the two experimental conditions the same results were obtained after the TDS correction had been applied. The TDS influences only the Debye–Waller factors but not the distribution of the valency electrons.

Einleitung

Am Steinsalz wurden bereits zahlreiche Messungen der Röntgeninterferenzen durchgeführt, mit dem Ziel, die Atomformfaktoren der Na^+ und Cl^--Ionen experimentell zu bestimmen, den Einfluss der Gitterschwingungen zu ermitteln und die genaue Elektronendichteverteilung anzugeben.* In allen früheren Arbeiten wurden die Intensitäten nicht auf die Beitrage der thermisch diffusen Streustrahlung (TDS) hin korrigiert. Nilsson (1957) hat für NaCl die Korrekturen unter Benutzung der von I. Waller (Waller, 1928) angegebenen Nähe-

rungsformeln berechnet und hat gefunden, dass bei Reflexen hoher Ordnung die Anteile der TDS, die bei der Intensitätsmessung erfasst werden, mehr als $\frac{1}{3}$ der Intensität der Bragg-Reflexe betragen können. Die Grösse dieser Anteile hängt sehr stark von den experimentellen Bedingungen bei der Intensitätsmessung ab, besonders von der Grösse des Fensters vor dem Detektor, dessen Abstand vom Kristall, sowie vom Querschnitt und der Divergenz des Primärstrahles. Da nicht mehr genau bekannt ist, welche Werte diese Grössen bei den früheren Messungen hatten und weil man damit rechnen muss, dass die unterschiedlichen Messergebnisse der einzelnen Autoren auf verschieden grosse erfasste Beiträge der TDS zurückzuführen sind, wurden in der vorliegenden Arbeit die Intensitäten der Steinsalzreflexe neu vermessen und dabei die experimentellen Bedingungen so gewählt, dass die Korrekturen für die TDS möglichst einfach und genau berechnet werden

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* Compton (1917), Bragg, James & Bosanquet (1921a, b, 1922), Darwin (1922), Kirkpatrick (1923), James (1925), James & Firth (1927), Waller & James (1927), Bearden (1927), Renninger (1934), Brill, Grimm, Hermann & Peters (1939), Wasastjerna (1946/47), Renninger (1952), Witte & Wölfel (1955), Schoknecht (1957).