Acta Cryst. (1980). A**36**, 582–584

Re-analysis of Single-Crystal Neutron-Diffraction Data on UO_2 Using Third Cumulants

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(*Received* 10 *October* 1979; *accepted* 15 *January* 1980)

Abstract

The single-crystal neutron diffraction data on UO_2, recorded by Willis [*Proc. R. Soc. London Ser. A*, (1963), **274**, 134–144] over the temperature range 293 to 1373 K have been re-analysed. The analysis was carried out with a structure-factor equation which included the third-cumulant coefficient, c_{123}, of the O atom. (The symmetry of the fluorite structure reduces the remaining third-cumulant coefficients of O and all the third cumulants of U to zero.) Apart from the overall scale factor, there were three parameters to be refined at each temperature: the isotropic B factors of U and O and c_{123} of O. The temperature variation of the B factors is in reasonably close agreement with that predicted from lattice dynamics [Dolling, Cowley & Woods (1965), *Can. J. Phys.* **43**, 1397–1413]. If c_{123} is to be ascribed to the influence of anharmonic forces on the motion of the atoms, an Einstein model of the interatomic potential predicts that c_{123} should be approximately proportional to T^2, where T is the absolute temperature. The experimental data are consistent with this prediction, but data of higher accuracy are required for a rigorous test.

Introduction

The structure-factor equation including third cumulants is of the form

$$F_c(\mathbf{H}) = \sum_{\kappa=1}^{n} f_\kappa \exp\,(2\pi i x_i h_i - b_{ij} h_i h_j - i c_{ijk} h_i h_j h_k), \tag{1}$$

where $\mathbf{H}$ is the diffraction vector, h_i ($i = 1, 2, 3$) are the Miller indices, and the summation is over the n atoms in the unit cell. If the third-cumulant coefficients c_{ijk} are set to zero, x_i refers to the fractional coordinates of the mean position of the κth atom in the unit cell and the b_{ij}'s are the usual anisotropic temperature-factor coefficients. f_κ is the scattering factor for X-rays or the coherent neutron-scattering amplitude for neutron diffraction. The repeated-index summation convention is assumed in writing (1).

The refinement of third-cumulant coefficients is rarely carried out, because each atom κ has up to ten third-cumulant coefficients and it is necessary to have exceptionally good diffraction data to derive them. However, a suitable data set is provided by the single-crystal neutron diffraction measurements of Willis (1963) on UO_2. Especial care was taken in this study, where measurements were made at a number of temperatures between 293 and 1373 K, to correct the intensities for extinction and other systematic errors. Moreover, for the fluorite structure of UO_2 (space group *Fm*3*m*), all third-cumulant coefficients are zero by symmetry, with the exception of c_{123} for the O atom. Symmetry also requires that the temperature factors are isotropic, so that the b_{ij}'s in (1) reduce to two quantities, B_U and B_O, where $B_U = 8\pi^2 u_U^2$ and $B_O = 8\pi^2 u_O^2$. Thus if we exclude the overall scale factor, the number of refinable parameters at each temperature is just three: B_U, B_O and c_{123}^O.

In this paper we give the results of analysing the data of Willis in terms of these three parameters. In the original analysis, all third cumulants were set to zero and the O atoms were displaced slightly from $(\frac{1}{4}\frac{1}{4}\frac{1}{4})$ to $(\frac{1}{4}+\delta\,\frac{1}{4}+\delta\,\frac{1}{4}+\delta)$. Although it is physically unreasonable to displace the O atoms from their equilibrium positions, the introduction of the δ parameter is a simple device for simulating the effect of the third-cumulant coefficient c_{123}^O. The new approach based on third cumulants is a more satisfactory way of carrying out the analysis.

Single-particle potential theory

Let us represent the dependence of the single-particle potential of the O atom on its thermal displacement xyz by a function of the form

$$V = V_0 + \tfrac{1}{2}\alpha_0(x^2 + y^2 + z^2) + \beta_0 xyz. \tag{2}$$

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The quadratic term is isotropic, in accordance with our earlier statement regarding the isotropy of the b_{ij}'s, and the cubic term (xyz) is written so as to conform with the point symmetry of the O atom. Equation (2) may be considered to be the Einstein potential of an O atom vibrating in a potential well of symmetry $\bar{4}3m$.

It can be shown (Willis & Pryor, 1975) that the third-cumulant coefficient c^0_{123} and the potential coefficient β_0 are related by

$$c^0_{123} = 8\pi^3 \frac{k_B^2 T^2 \beta_0}{a_0^3 \alpha_0^3}, \tag{3}$$

where k_B is Boltzmann's constant, a_0 is the lattice parameter (= 5·4710 Å at 293 K) and T is the absolute temperature. In the absence of lattice expansion, we should expect that the potential coefficients α_0 and β_0 in (2) are independent of temperature. Thus c^0_{123} should be approximately proportional to T^2.

Analysis of UO_2 measurements

A least-squares program for refining B_U, B_O and c^0_{123} was written by one of us (RGH), and was used to refine the F_0 data listed in Table 1 of Willis (1963). The results are given in Table 1. At all temperatures R is 2% or less, and there is no systematic variation of R with temperature. On the other hand, on carrying out a conventional refinement with all third cumulants set to zero, R showed a systematic increase from 2% at room temperature to 5% at the highest temperature. This suggests that the data are sufficiently accurate to yield significant non-zero values for the third-cumulant coefficients, but that they are not good enough for the refinement of any higher-order cumulants.

Fig. 1 shows a plot of c^0_{123} *versus* T^2. Unfortunately, the error bars on the third-cumulant coefficients are large, and it is only possible to state that (3) is approximately obeyed.

A more satisfactory comparison of observation and theory follows by considering the temperature variation of the second cumulants, B_U and B_O. Fig. 2 is a plot of the B factors *versus* absolute temperature. Some results from a powder analysis of UO_2 (Albinati *et al.* 1980) are also included on the figure. The broken lines refer to the calculated plots of Dolling, Cowley & Woods

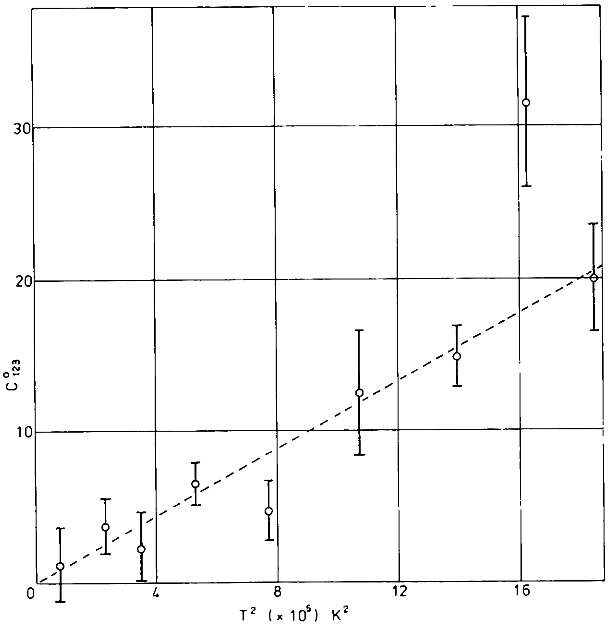

Fig. 1. Temperature variation of third-cumulant coefficient for oxygen. Broken line is best fit to a T^2 law.

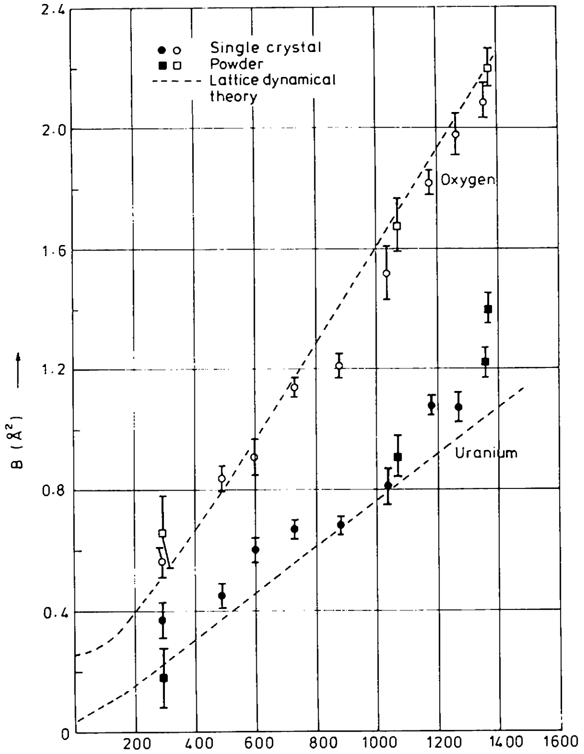

Fig. 2. Temperature variation of the B factors for uranium and oxygen. The broken lines are given by lattice-dynamical theory (Dolling, Cowley & Woods, 1965).

Table 1. *Refinement of second and third cumulants of* UO_2

Temperature (K)	B_U (Å²)	B_O (Å²)	c^0_{123} (×10^4)	R (%)
293	0·37 (6)	0·56 (5)	1·3 (2·5)	2·0
486	0·45 (4)	0·84 (4)	3·7 (1·9)	1·6
598	0·50 (4)	0·91 (6)	2·0 (2·2)	1·1
728	0·67 (3)	1·14 (3)	6·3 (1·6)	1·2
881	0·68 (3)	1·21 (4)	4·9 (2·2)	0·7
1036	0·81 (6)	1·52 (9)	11·2 (4·1)	2·1
1181	1·09 (3)	1·82 (4)	14·5 (2·0)	1·4
1268	1·07 (5)	1·98 (7)	31·8 (4·9)	1·5
1360	1·22 (5)	2·09 (6)	20·1 (3·4)	1·7

(1965), based on a lattice-dynamical analysis of their measured phonon dispersion relations. On the whole, there is reasonably good agreement between observation and theory. The theory neglects anharmonic contributions to the Debye–Waller factors, and this could account for the observed displacements for U exceeding the calculated displacements, especially at high temperatures.

Conclusions

The data of Willis (1963) have been re-analysed with a structure-factor equation including third cumulants. The only non-vanishing third cumulant for UO_2 is c_{123} for the O atom. Introducing c^0_{123} into the analysis accounts for anisotropic anharmonic thermal motion of the O atom. c^0_{123}, B_U and B_O have been derived over the temperature range 293 to 1373 K. The e.s.d.'s of c^0_{123} are too large to allow a rigorous check of the theoretical dependence on temperature, but B_U and B_O are in reasonable agreement with those predicted by the theory of lattice dynamics.

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Acta Cryst. (1980). A**36**, 584–588

X-ray Diffraction from Faulted Close-Packed Structures. Analytic Solution for Integrated Intensities

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(*Received* 3 *September* 1979; *accepted* 18 *January* 1980)

Abstract

Analytic expressions for the integrated intensities of reflexions from faulted close-packed structures have been obtained. These involve a single root of the characteristic equation (the root which corresponds to the reflexion under consideration), its coefficients and the initial conditions. The particular utility of the solution for cases where one or more roots of the characteristic equation have unit modulus is demonstrated.

Introduction

Diffraction from close-packed crystals with stacking faults has been investigated by a large number of workers and has been reviewed by Warren (1959, 1969), Wilson (1962), Cohen & Hilliard (1966) and Anantharaman, Rama Rao & Lele (1972) among others. In their pioneering papers, Wilson (1942) and Hendricks & Teller (1942) developed distinct approaches to a solution of this problem. The present paper describes a simplification in the procedure for the evaluation of integrated intensities following the difference-equation method of Wilson (1942). This method also enables an analytical solution for the diffuse diffracted intensity when the characteristic equation found from the difference equation has roots with unit modulus.

Formulation of the problem

In general, the diffracted intensity from a possibly faulted crystal is given by (Warren, 1959)

$$I(h_3) = \psi^2 \sum_m \langle \exp [i\Phi_m] \rangle \exp (2\pi imh_3/n), \qquad (1)$$

where h_1, h_2, h_3 are continuous variables in reciprocal space, ψ^2 is a function of $h_1 h_2$ which vanishes except when $h_1 = H$, $h_2 = K$, H and K being hexagonal indices with integer values, and Φ_m, the phase difference across a pair of layers m layers apart, is given by

$$\Phi_m = (2\pi/3)(H-K)\, q_m, \qquad (2)$$

q_m being the displacement of the m layer from the origin

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