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Short Communications

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The rapid computation of mean path length for spheres and cylinders.

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Abstract

Extension of the interpolation formulae of Dwiggins [*Acta Cryst.* (1975), A**31**, 146–148] for the rapid calculation of absorption corrections is shown to allow the equally rapid calculation of the mean path length, $\bar{T}$, required for extinction corrections. The coefficients required to set up the calculations are tabulated. They approximate $\bar{T}$ to within 0·5% R at low 2θ and 2% R at $\theta = 90°$ for $\mu R \leq 2{\cdot}5$ and also provide the derivatives required to estimate μR by the least-squares analysis of powder diffraction profiles for $\mu R > 1$.

Accurate analyses of X-ray and neutron diffraction data require correction of individual intensities for extinction in the sample. The correction requires knowledge of the mean path length of the beam

$$\bar{T} = \frac{1}{VA}\int_V te^{-\mu t}\,{\rm d}V, \qquad (1)$$

where t is the path length in a crystal with absorption coefficient μ of a ray scattered in volume element dV. For a general shape, the mean path length $\bar{T}$ is evaluated in conjunction with the computation of the transmission factor A by numerical integration.

For two cases, of the spherical sample in any orientation and the cylindrical sample when data is collected in the plane normal to its axis, tabulation of the calculations is feasible. Bond (1959), Rouse, Cooper, York & Chakera (1970) and subsequently Dwiggins (1975*a*,*b*) provided values of $A^* \equiv 1/A$ for values of the scattering angle θ, and the product, μR, of the absorption coefficient and the sample radius. Pryor & Sanger (1970) obtained values of $\bar{T}$ for spheres by Gaussian integration for $\mu R \leq 10$ while Flack & Vincent (1978) employed numerical differentiation of Dwiggin's (1975*b*) tabulation for $\mu R \leq 2{\cdot}5$. Rouse *et al.* (1970) and Dwiggins (1975*a*) provide analytical approximations for μR less than 1 and 2·5, respectively.

In this note we show that Dwiggins's (1975*a*) approximation formulae may be extended to cover A^* and $\bar{T}$ for both spheres and cylinders, obtaining an accuracy of 0·5% in A^* and achieving the accuracy in $\bar{T}$ necessary for extinction

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Table 1. *Coefficients for interpolation of* A^* *and* $\bar{T}$

θ_j	0°	15°	30°	45°	60°	75°	90°	Units
K_1 (sph)	3/2	3/2	3/2	3/2	3/2	3/2	3/2	
K_2	−7·5234	−9·4320	−15·1019	−24·3812	−35·219	−44·842	−47·745	10^{-2}
K_3	−7·0935	−10·737	−18·027	−11·088	14·265	40·021	61·084	10^{-3}
K_4	−2·3096	−2·1332	−1·4693	7·4205	24·832	44·308	37·394	10^{-3}
K_5	1·8323	1·1711	4·6784	3·0970	−10·284	−27·987	−25·879	10^{-3}
K_6	−5·1259	−1·2652	−14·491	−16·740	21·910	77·007	71·458	10^{-4}
K_7	6·0265	0·7932	16·489	−21·391	−22·391	−85·570	−78·812	10^{-5}
K_1 (cyl)	$16/3\pi$	$16/3\pi$	$16/3\pi$	$16/3\pi$	$16/3\pi$	$16/3\pi$	$16/3\pi$	
K_2	−5·7832	−8·1900	−15·651	−27·048	−40·317	−51·497	−55·837	10^{-2}
K_3	−14·737	−19·551	−22·883	−27·345	−8·807	26·637	41·420	10^{-3}
K_4	5·2399	1·2934	−12·301	6·844	40·689	61·371	68·963	10^{-3}
K_5	−4·0958	−2·8349	9·6249	7·503	−11·295	−29·397	−36·556	10^{-3}
K_6	13·178	12·731	−19·881	−30·211	9·4468	60·356	80·965	10^{-4}
K_7	−14·500	−14·846	14·414	34·222	3·1492	−49·206	−70·573	10^{-5}
$(C^{-1})_{0j}$	3	0	0	0	0	0	0	All values multiplied by 3 to eliminate fractions
$(C^{-1})_{1j}$	−73	$48+24\sqrt{3}$	−24	12	−8	$48-24\sqrt{3}$	−3	
$(C^{-1})_{2j}$	518	$-396-200\sqrt{3}$	488	−268	184	$-496+200\sqrt{3}$	70	
$(C^{-1})_{3j}$	−1600	$1920+560\sqrt{3}$	−2192	1536	−1136	$1920-560\sqrt{3}$	−448	
$(C^{-1})_{4j}$	2432	$-3520-640\sqrt{3}$	4032	−3328	2752	$-3520+640\sqrt{3}$	1152	
$(C^{-1})_{5j}$	−1972	$3072+256\sqrt{3}$	−3328	3072	−2816	$3072-256\sqrt{3}$	−1280	
$(C^{-1})_{6j}$	512	−1024	1024	−1024	1024	−1024	512	

corrections and for least-squares estimation of the product μR in the analysis of powder diffraction data.

Noting the alternative expressions for $\bar{T}$,

$$\bar{T} = \frac{1}{A^*}\frac{\mathrm{d}A^*}{\mathrm{d}\mu} = R\,\frac{\mathrm{d}\ln A^*}{\mathrm{d}\mu R}, \tag{2}$$

we employ term-by-term differentiation on Dwiggins's (1975*a*,*b*) formula:

$$A^*(\mu R, \theta_j) = \exp \sum_{n=1}^{N} K_n(\theta_j)[\mu R]^n \tag{3}$$

to obtain

$$\bar{T}(\mu R, \theta_j) = \frac{1}{\mu}\sum_{n=1}^{N} nK_n(\theta_j)[\mu R]^n. \tag{4}$$

The sum in (4) converges more slowly than that in (3) and $N = 7$ is necessary to approximate $\bar{T}$ for $\mu R \leq 2{\cdot}5$. One coefficient is obtained exactly for zero absorption by integration of (1):

$$K_1(\theta_j) = \bar{T}(0, \theta_j)/R = \frac{3}{2} \quad \text{for spheres}$$

$$= \frac{16}{3\pi} \quad \text{for cylinders.}$$

To obtain the remaining coefficients for each θ_j, (3) and (4) are fitted simultaneously to values, for μR in the range 0 to 2·5, of A^* from Dwiggins (1975*a*,*b*) and $\bar{T}$ calculated from A^* by the numerical differentiation procedure used by Flack & Vincent (1978). Fitting to A^* values alone fails to provide an adequate approximation to $\bar{T}$ because the series in (3) converges to 0·05% for $N = 6$ (Dwiggins, 1975*a*,*b*) and hence cannot determine the longer series required in (4).

In order to interpolate between the values found for the points $\{\theta_j\}$ Dwiggins (1975*a*) suggested the sum

$$A^*(\mu R, \theta) = \sum_{m=0}^{M} L_m(\mu R)\sin^{2m}\theta. \tag{5}$$

The coefficients $L_m(\mu R)$ are established for $M = 6$ by solving (5) for the values $\{A_j^* = A^*(\mu R, \theta_j)\}$ obtained from (3). That is,

$$L_m = \sum_{j=1}^{7} (C^{-1})_{mj}A_j^*,$$

where $C_{mj} = \sin^{2m}\theta_j$. The elements $(C^{-1})_{mj}$ of the inverse matrix are given in Table 1 together with $K_n(\theta_j)$ for spheres and cylinders for θ_j at 15° intervals from 0 to 90°.

Term-by-term differentiation of (5) leads to

$$A^*(\mu R, \theta)\bar{T}(\mu R, \theta) = \sum_{m=0}^{M} P_m \sin^{2m}(\theta), \tag{6}$$

where $P_m = R\partial L_m/\partial\mu R$. The similar forms of (5) and (6) suggest that the computational procedure for A^* may be extended to $\bar{T}$.

Solving (6) in the same manner as (5),

$$P_m = \sum_{j=1}^{7} (C^{-1})_{mj}A_j^*\bar{T}_j$$

with the values $\{\bar{T}_j = \bar{T}(\mu R, \theta_j)\}$ obtained from (4). Parallel computations of (5) and (6) may then be performed for each experimental value of $\sin\theta$.

The relative error introduced by (5) and (6) for interpolating in θ is better than 10^{-3} in all cases.

For the analysis of powder diffraction profiles from cylindrical absorbing samples, the absorption parameter μR can be incorporated in the Debye–Waller and scale factors for $\mu R < 1$ (Hewat, 1979). For $\mu R > 1$, A^* can no longer be approximated by adjusting these factors. The present work then provides a rapid means of calculating the absorption and the derivatives needed to estimate μR in the least-squares procedure. Equation (1) may be rearranged to give

$$\frac{\mathrm{d}A^*}{\mathrm{d}\mu R}=\frac{\bar{T}A^*}{R}$$

which can be computed as a function of $\sin\theta$ with (6).

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An X-ray diffraction study of lithium.

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Abstract

An accurate X-ray diffraction investigation has been carried out on two single crystals of lithium. The data from crystal 1 were obtained at temperatures of 248 and 296 K, and those for crystal 2 in the temperature range 293 to 423 K. The measured integrated intensities have been analysed for the presence of anharmonicity in the atomic vibrations by using a temperature factor based on a one-particle potential of the form $V(u)=\frac{1}{2}\alpha u^2+\gamma u^4+\delta(u_x^4+u_y^4+u_z^4-\frac{3}{5}u^4)$. An average value for the parameter δ of 290 ± 140 eV nm^{-4} was found. No significant value of γ was found in the analysis of data from crystal 1, but a value of −360 ± 40 eV nm^{-4} was obtained from the higher-temperature data of crystal 2.

Introduction

Previous results on the analysis of accurate X-ray diffraction data for anharmonic features in the Debye–Waller factor have been given for sodium by Field & Medlin (1974) and Field & Bednarz (1976), and for potassium by Bednarz & Field (1982). Here we present results of a final experiment on lithium.

Experimental

Two crystals of 99·95% pure material were prepared according to the method of Bednarz (1977). Intensities were recorded from crystal 1 at 248 K, but while doing so a sudden permanent change in the mosaic spread occurred. Thus two independent data sets were collected at each of the temperatures 248 and 296 K, one being characterized by small isotropic mosaic spread, and hereafter referred to as data subset 1*B*, and the other by a large anisotropic mosaic spread, hereafter referred to as data subset 1*A*. An attempt to record data at 200 K destroyed the crystal. The intensities of 17 independent reflections were recorded from crystal 2 at 293 K and the temperature dependence of one 220 reflection was measured in the range 293 to 423 K.

Analysis

The theory and methods of analysis were generally as detailed in Bednarz & Field (1982), hereafter referred to as paper I. In particular, equation (2) in I is the expression used for the temperature factor for the one-particle-potential model for lithium.

Two models were used in the data analysis. In model 1, it was assumed that the potential parameter γ in equation (2) of I was zero, while in model 2, γ was allowed to vary. The value of the Gruneisen constant γ_G was taken from Martin (1965) to be 0·86 and the volume coefficient of expansion χ_v was taken from Kittel (1971) to be 135 MK^{-1}.

Results

The subsets 1*A* and 1*B* of the data from crystal 1 were analysed independently for each of the temperatures 248 and 296 K. With model 1, consistent results were obtained for all the parameters except δ, for which a range of 190 ± 110 to 460 ± 80 eV nm^{-4} was obtained. The agreement between refined and measured scale factors was excellent. Average values for the potential parameters from these refinements are listed in Table 1. In this table, α_{293} represents the value of α at 293 K and $u_{\text{r.m.s.}}$ is the root-mean-square vibration amplitude determined by

$$u_{\text{r.m.s.}}=\left(\frac{3k_BT}{\alpha}\right)^{1/2}.$$

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