A Charge-Density Study of Crystalline Beryllium*

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The X-ray structure factors for crystalline beryllium measured by Brown [*Phil. Mag.* (1972), **26**, 1377] have been analyzed with multipole deformation functions for charge-density information. Single exponential radial functions were used for the valence charge density. A valence monopole plus the three harmonics, $P_3^3(\cos\theta)\sin 3\varphi$, $P_6(\cos\theta)$ and $P_7^3(\cos\theta)\sin 3\varphi$, provide a least-squares fit to the data with $R_w = 0.0081$. The superposition of these density functions describes a bonding charge density between Be atoms along the c axis through the tetrahedral vacancy. The results reported here are in qualitative agreement with a recent pseudo-potential calculation of metallic beryllium. The final residuals in the analysis are largest at high $\sin\theta/\lambda$ values. This suggests that core charge deformation is present and/or anharmonic motion of the nuclei is appreciable.

Introduction

Brown (1972) recently reported the X-ray structure-factor amplitudes for the 27 lowest-angle Bragg reflections of single crystals of beryllium. The reflections were measured on an absolute scale and have a reported relative standard deviation of 0·5 % on average. Brown found that a Hartree–Fock scattering factor for the free Be atom and a free-electron model had R indices, respectively, of 4·56 and 4·14%. Except for the 100 reflections, both models predicted values substantially larger than the observed amplitudes at $\sin\theta/\lambda < 0.45$ Å^{-1}. Brown introduced $2p$ orbital products for bonding scattering factors which resulted in some improvement for the low-angle structure factors. For this model the R index for the five low-order reflections was 0·034 as compared with 0·077 and 0·064 for the free atom and free electron models respectively.

The author decided to apply the rigid pseudoatom model (Stewart, 1976) to an electron population analysis of Brown's data. The space group for Be is $P6_3/mmc$ with atoms at $\frac{1}{3},\frac{2}{3},\frac{1}{4}$ and $-\frac{1}{3},-\frac{2}{3},-\frac{1}{4}$. The site symmetry at these positions is $\bar{6}m2$. Multipole moments consistent with this symmetry were to be selectively introduced into the scattering-factor model. The criterion for selection is the goodness of fit in the least-squares analysis. It was conjectured that the superposition of several multipoles would account for the observed data and provide one with an analytical charge-density model for the bonding scheme in crystalline beryllium.

Scattering-factor model

The charge density about the beryllium atom was separated into core and valence radial distribution

functions. The core density was restricted to a monopole with the radial function taken from the product $(\chi_{1s})^2$, where χ_{1s} is the self-consistent field $1s$ atomic orbital for (^1S) Be as taken from Clementi (1965). For most studies this function was populated with two electrons. The anomalous dispersion terms for Be with Ag $K\bar{\alpha}$ are less than or equal to 0·001 in absolute value (Cromer & Liberman, 1970) and therefore are neglected in the model. All valence radial distribution functions were restricted to single exponential functions of the type

$$R_{n,\alpha}(r) = (4\pi)^{-1}[\alpha^{n+3}/(n+2)!]r^n \exp(-\alpha r) \qquad (1)$$

where n is a discrete variable and α is a continuous variable. For all multipoles α is shared, but n is allowed to differ from one function to another. The several multipoles, up to seventh order, which transform as the totally symmetric representations of point group $\bar{6}m2$ are shown in Table 1. The Fourier transforms of the tesseral harmonics are of the same functional form as those in Table 1 but refer to the direction cosines of the Bragg vector and all contain a factor of $4\pi(-1)^{l/2}$ where l is the order of the multipole. Thus the angular terms for the Bragg vector are spanned by the functions in Table 1 and the radial scattering factor in $|S|$,

Table 1. *Multipoles considered for charge-density analysis of* Be

The site symmetry is $\bar{6}m2$. Coordinates are $x\|$a, $y\|$c . a, $z\|$c. q_x, q_y, q_z are direction cosines.

Tesseral harmonic	Cartesian representation
$P_0(\cos\theta)$	1
$P_2(\cos\theta)$	$(\frac{3}{2})\,(q_z^2-\frac{1}{3})$
$P_3^3(\cos\theta)\sin 3\varphi$	$15(3q_x^2-q_y^2)q_y$
$P_4(\cos\theta)$	$(\frac{5}{8})\,(7q_z^4-6q_z^2+\frac{3}{5})$
$P_5^3(\cos\theta)\sin 3\varphi$	$(\frac{105}{2})\,(3q_x^2-q_y^2)q_y(9q_z^2-1)$
$P_6^6(\cos\theta)\cos 6\varphi$	$(10395)\,(q_x^2-q_y^2)[(q_x^2-q_y^2)^2-12q_x^2q_y^2]$
$P_6(\cos\theta)$	$(\frac{21}{16})\,\{[(11q_z^2-15)q_z^2+5]q_z^2-\frac{5}{21}\}$
$P_7^3(\cos\theta)\sin 3\varphi$	$(\frac{3465}{8})\,(3q_x^2-q_y)q_z^2[(13q_z^2-6)q_z^2+\frac{3}{11}]$

$$f_{n,\alpha,l}(|S|) = [\alpha^{n+3}/(n+2)!] \int_0^\infty r^{n+2} j_l(|S|r) e^{-\alpha r} \, dr \qquad (2)$$

where $|S| = 4\pi a_0 \sin\theta/\lambda$, $a_0 = 0.529177$ Å and α is in units of bohr^{-1}. A population parameter C is assigned to each generalized scattering factor. For most studies the valence monopole scattering factor was populated with a fixed value of two electrons.

It is assumed that the pseudoatom is rigid in that it follows the motion of its nucleus. The nuclear motion is assumed to be in a harmonic potential. With the rigid pseudoatom approximation and the neglect of thermal diffuse scattering, the Be structure-factor model is,

$$F_c(\mathbf{H}) = \sum_{sym} f(\mathbf{S,n},\alpha,\mathbf{C}) \exp\,[-\beta_{11}(h^2 + hk + k^2) - \beta_{33}l^2]$$

$$\times \exp\,\{2\pi i[(h+2k)/3 + l/4]\} \qquad (3)$$

where $f(\mathbf{S,n},\alpha,\mathbf{C})$ is the generalized scattering factor discussed above and $\sum_{sym}$ contains the identity operator and the inversion operator of $\mathbf{S}$ (or $\mathbf{H}$). The pseudoatom thermal parameters, β_{11} and β_{33}, are related to the mean square amplitudes of vibration by

$$\beta_{11} = 2\pi^2 a^{*2} U_{11}$$
$$\beta_{33} = 2\pi^2 c^{*2} U_{33} \qquad (4)$$

where the reciprocal lattice parameters (Mackay & Hill, 1963) are: $a^* = 0.50516 \pm 0.00004$, $c^* = 0.27899 \pm 0.00002$ Å^{-1}.

The least-squares function,

$$\varepsilon = \sum_{\mathbf{H}} w|F_o - F_c|^2 \qquad (5)$$

is minimized with respect to β_{11}, β_{33}, $\mathbf{C}$ and α for selected values of n and for one or more multipoles. $|F_o(\mathbf{H})|$ and $w(\mathbf{H})$ [i.e. $\sigma(\mathbf{H})^{-2}$] are taken from Brown (1972). $F_o(\mathbf{H})$ is always assigned the same phase as

Table 2. *Refinements with Hartree–Fock (^1S) Be scattering factor*

Thermal parameters are the only variable. Estimated standard deviations are shown in parentheses and refer to the last digit. The total number of data is 27.

U(Å^2) or U_{11}(Å^2)	0.0078 (2)	0.0080 (3)
U_{33}(Å^2)		0.0075 (6)
R_w	0.0373	0.0370
R^*	0.0334	0.0323

$* \; R = \Sigma||F_o| - |F_c||/\Sigma|F_o|.$

given by the $F_c(\mathbf{H})$ model. The figure of merit in the present study is

$$R_w = \{\varepsilon/\sum w|F_o|^2\}^{1/2} \qquad (6)$$

so that a minimum in ε is a minimum in R_w.

Preliminary results: monopole scattering factors

The data were first analyzed with a Hartree–Fock atomic scattering factor for (^1S) Be. In this case an isotropic thermal parameter and the two anisotropic thermal parameters, respectively, were determined by minimizing (5). These results are summarized in Table 2. The weighted R is much larger than the average error in the data (0.037 versus 0.005). Moreover, the free-atom model does not reveal any significant anisotropy in the atomic motion.

It was decided to seek an optimal single exponential valence monopole function by refining α and U (isotropic) with a finite grid of n values. The valence electron population was fixed at 2 and the core monopole scattering factor was held invariant to the product of the $1s$ Hartree–Fock orbital. The results of this study are displayed in Table 3. Two features should be noted. The variable isotropic temperature parameter was insensitive to the extension of the valence, monopole density function. The optimum valence density monopole function occurs for $n = 7$ and $\alpha = 4.38 \pm 0.12$ bohr^{-1}. This corresponds to a radial maximum at 0.85 Å which is about four tenths of the nearest neighbor internuclear distance. A more diffuse radial density function results in an increase of R_w from the minimum value of 0.0216. At this level of analysis the valence charge can be accounted for with a moderately diffuse, but single exponential density function. The monopole scattering-factor model alone, however, does not afford a root-mean-square fit to the data that is consistent with Brown's estimated errors in the measured amplitudes. A refinement with anisotropic temperature parameters did not result in significant improvement of the least-squares fit.

Results with multipole scattering factors

The deformation functions in Table 1 were introduced into the structure-factor model (3) one at a time. For each case a grid search on n in the radial function (1) or (2) was carried out. In addition to the determination

Table 3. *Refinement of valence monopole scattering factor*

The total number of data is 27. $\varrho_{val,0} = 2(4\pi)^{-1}[\alpha^{n+3}/(n+2)!]r^n \exp(-\alpha r)$.

n	2	3	4	5	6	7	8	9	10	11
α (bohr^{-1})	1.54	2.14	2.72	3.28	3.84	4.38	4.94	5.50	6.04	6.60
r_{max} (Å)*	0.69	0.74	0.78	0.81	0.83	0.85	0.86	0.87	0.88	0.88
U (Å^2)	0.0072	0.0072	0.0072	0.0072	0.0072	0.0072	0.0073	0.0073	0.0073	0.0073
R_w	0.0402	0.0344	0.0292	0.0253	0.0227	0.0216	0.0127	0.0227	0.0244	0.0264

$* \; r_{max} = 0.529177 \, n/\alpha.$

of the multipole population parameter, the exponential parameter α and an isotropic thermal parameter were used as least-squares variables. Of the seven deformation functions studied, the lowest R_w was found for the harmonic $P_6(\cos\theta)$. This function promotes bonding along the c axis through the tetrahedral vacancy. The radial maximum for this term was 1·51 Å. The results of this refinement are entered in Table 4 under the first column. It is interesting to note that the least optimal function of the seven was $P_6^6(\cos\theta)\cos 6\varphi$. The population was virtually zero for all refinements. This deformation term could promote bonding charge density among the Be atoms in the basal plane. The null result in these studies demonstrates that the valence charge about Be has at least a measurable $\bar{6}$ symmetry; a valence density function with full sixfold symmetry is not consistent with Brown's measured structure factors.

respectively. The function $P_7^3(\cos\theta)\sin 3\varphi$ primarily builds up charge in the plane at $z = 0·25$ over the octahedral vacancy. The results for the best triplet in this work are shown in Table 4 in the third column. In this final study the thermal parameters were refined anisotropically and found to be significantly different. The least-squares correlation matrix for this last refinement is given in Table 5. The column of large correlation is between α and the population parameters, an anticipated result, but no correlation was large enough to render the least-squares matrix numerically unstable towards inversion. The observed and calculated structure factors with this final model are given in Table 6.

Table 4. Refinements of Be with multipole deformation functions

Estimated standard deviations are in parentheses and refer to the last digit(s). The total number of data is 27.

α (bohr^{-1})	4·56 (10)	4·73 (7)	5·17 (8)
n_0	7	7	7
n_6	13	15	15
C_6	1·70 (43)	1·86 (27)	3·08 (32)
n_5		14	14
C_5		0·36 (10)	0·55 (6)
n_7			19
C_7			2·83 (58)
U (Å^2) or U_{11}	0·00723 (11)	0·00724 (11)	0·00724 (8)
U_{33} (Å^2)			0·00662 (15)
R_w	0·0166	0·0129	0·0081
R	0·0169	0·0127	0·0066

As a second stage in the present study, pairs of deformation functions were introduced into the model. Altogether 21 different pairs were investigated in the same way as for the single deformation function. In this case, however, a grid search on n for the valence monopole was not carried out. The best pair of functions was found to be $P_6(\cos\theta)$ and $P_5^3(\cos\theta)\sin 3\varphi$. The results are tabulated in Table 4 under the second column. The fifth-order harmonic has a radial maximum at 1·57 Å, while for $P_6(\cos\theta)$ the radial maximum is at 1·68 Å. The $P_5^3(\cos\theta)\sin 3\varphi$ function contributes charge density to the octahedral vacancy and at $z = 0·25$ to the vacancy over the Be atom at $z = -0·25$.

For the final study of valence deformation functions, triplets were introduced into the structure-factor model. In this case all 35 combinations were considered. The lowest mean-square error was found when the seventh-order harmonic $P_7^3(\cos\theta)\sin 3\varphi$ was used in conjunction with the best pair of harmonics (P_6 and $P_5^3\sin 3\varphi$) from the previous study. The radial maxima for these deformation functions were 1·43, 1·54, and 1·94 Å for the fifth, sixth and seventh-order harmonics

Table 5. Least-squares correlation matrix for refinement on thermal parameters and three best deformation functions

	U_{11}	U_{33}	α	C_5	C_6	C_7
U_{11}	1·000					
U_{33}	−0·196	1·000				
α	−0·261	−0·331	1·000			
C_5	−0·190	−0·165	0·674	1·000		
C_6	−0·195	−0·293	0·794	0·432	1·000	
C_7	−0·261	−0·324	0·899	0·571	0·748	1·000

Table 6. Observed and calculated structure factors for Be

F_c is based on the three best deformation functions.

h	k	l	$|F_o|$	F_c	$|\Delta F|$ ($\times 10^3$)
1	0	0	1·715	−1·715	0
1	1	0	2·502	2·507	5
2	0	0	1·129	−1·125	4
2	1	0	0·818	−0·821	3
2	2	0	0·998	0·972	26
3	0	0	1·306	1·325	19
1	0	1	2·606	−2·607	1
2	0	1	1·889	1·876	13
2	1	1	1·367	−1·377	10
0	0	2	2·978	−2·975	3
1	0	2	1·403	1·403	0
1	1	2	2·191	−2·182	9
2	0	2	0·997	0·999	2
2	1	2	0·710	0·724	14
3	0	2	1·165	−1·171	6
1	0	3	2·019	2·018	1
2	0	3	1·483	−1·473	10
2	1	3	1·080	1·071	9
0	0	4	2·040	2·073	33
1	0	4	0·943	−0·939	4
1	1	4	1·523	1·515	8
2	0	4	0·679	−0·682	3
2	1	4	0·514	−0·499	15
1	0	5	1·232	−1·224	8
2	0	5	0·893	0·895	2
0	0	6	1·079	−1·116	37
1	0	6	0·507	0·504	3

In the analysis of diatomic molecular charge densities with restricted radial pseudoatoms, Bentley & Stewart (1976) found that population of the core charge density with two electrons was unduly restrictive in the charge-density representation. From this experience

it was decided to allow a variable population parameter for the core density monopole, but to constrain the total charge of Be to 4 e. The results of this refinement were 2.00 (± 0.02) e in the core monopole function and no significant change in all other parameters. Thus it appears that the monopole functions with a fixed population of 2 e each is consistent with the Be structure factors under study.

Discussion of results

The best charge-density model found in this investigation nominally consists of six parameters so that it would appear that the factor of overdetermination is 4·5. The introduction of a second thermal parameter and the grid search on n for the radial functions actually makes the number of parameters ten, of which eight are used to represent the valence density model. The four different radial scattering factors have appreciable amplitudes up to sin θ/λ of 0.63 Å^{-1}. In this shell, only 12 measured structure factors occur. Although the valence radial scattering factors were used for all measured reflections (27 in all) it can be argued that the overdetermination here is effectively only $1\frac{1}{2}$–2.

At the suggestion of a referee the author has included a tabulation of Hamilton (1965) significance tests in Table 7. The results show that the more restrictive models compared to the most flexible model (column three of Table 4) can be rejected at the 0·5% significance level. These tests, however, do not provide a final judgement for the correctness of the best charge-density model used in this study.

clearly displays the deficiency of the charge-density model at high values of sin θ/λ (0.7–0.9 Å^{-1}). The valence scattering model is more than adequate to reduce the $w|\Delta F|^2$ to values < 1. But the Be core scattering factor and the two anisotropic thermal parameters are not sufficient to reduce the $w|\Delta F|^2$ at large sin θ/λ to values near unity. The author decided to see if a single core deformation function would appreciably reduce these residuals. The core radial function was $r^n \exp(-\alpha r)$ where $\alpha = 2\zeta_{1s}$ (ζ_{1s} from Clementi & Raimondi, 1963) and n is the order of the harmonic. The corresponding scattering factor is proportional to $(S/\alpha)^n[1 + (S/\alpha)^2]^{-(n+2)}$, which for $\alpha = 7.36$ bohr^{-1}, is a maximum near 0.7 to 0.8 Å^{-1} and is relatively flat. All seven harmonics in Table 1 were tried one at a time with a single population parameter and the valence charge-density model held constant. Best results were afforded with introduction of $P_6^6(\cos\theta)\cos 6\varphi$ that netted an R_w of 0.0074. The goodness of fit dropped from 2.33 to 2.19. A comparable result was found for $P_6(\cos\theta)$, $R_w = 0.0076$ and goodness of fit of 2.26. These rather different angular functions led to a reduction of different residuals in the high sin θ/λ region. It is clear that a single core deformation function does not reduce all the residuals to a satisfactory level. The high-angle residuals imply a rather complicated deformation of the static charge density near the nucleus (0.2–0.6 Å) and/or anharmonic motion of the nucleus.

An electron-density map was constructed by a Fourier summation of the residuals. The values in the density map varied from -0.05 to 0.03 e Å^{-3}. General features in the map were difficult to interpret. This is probably due to series termination since the large re-

Table 7. *Hamilton significance tests for R factor ratios for several refinements of* Be

The total number of observed data is 27. The full model has 6 (10) parameters.

Model	b^*	R_w	$\mathscr{R}$	$\mathscr{R}_{b,21,0.005}$	$\mathscr{R}_{(b),17,0.005}$
Hartree–Fock atoms, U	5 (9)	0·0373	4·605	1·454	1·752
Valence monopole, U	4 (7)	0·0216	2·667	1·403	1·696
Monopole, 1 deformation, U	3 (5)	0·0166	2·049	1·349	1·579
Monopole, 2 deformations, U	2 (3)	0·0129	1·593	1·287	1·444
Monopole, 3 deformations, U_{11}, U_{33}	0 (0)	0·0081	1·000	1·000	1·000

* b is the dimension of the hypothesis. Values in parentheses include powers of r for the bases $r^n \exp(-\alpha r)$ in the dimension of the hypothesis.

A plot of $w|\Delta F|^2$ *versus* sin θ/λ is displayed in Fig. 1. The distribution of these weighted residuals squared
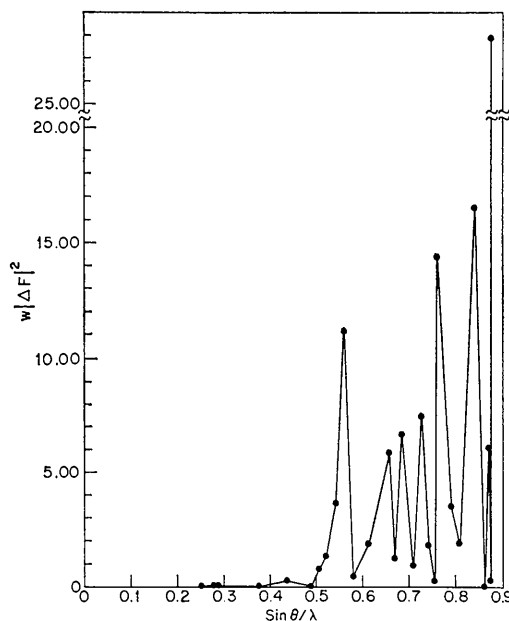

Fig. 1. Plot of the weighted squared residuals *versus* sin θ/λ for final electron-density model.

siduals are at high values in sin θ/λ. Thus the ΔF electron density map does not provide a clear picture as to the nature of the high-order residuals.
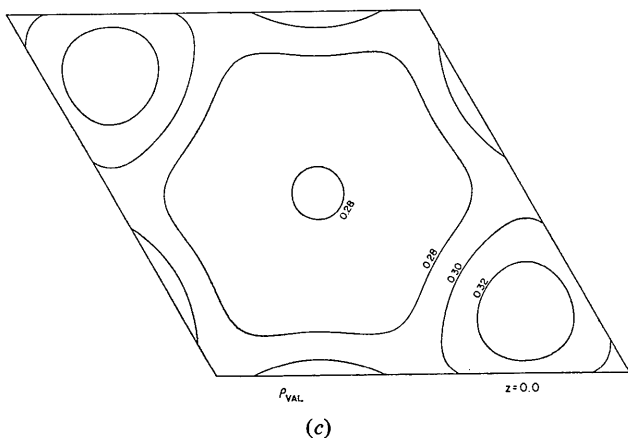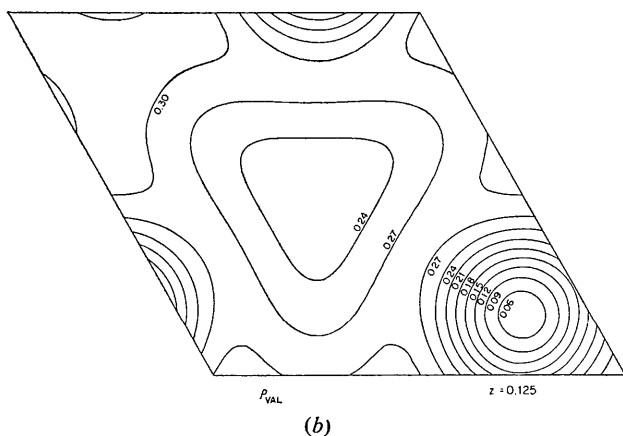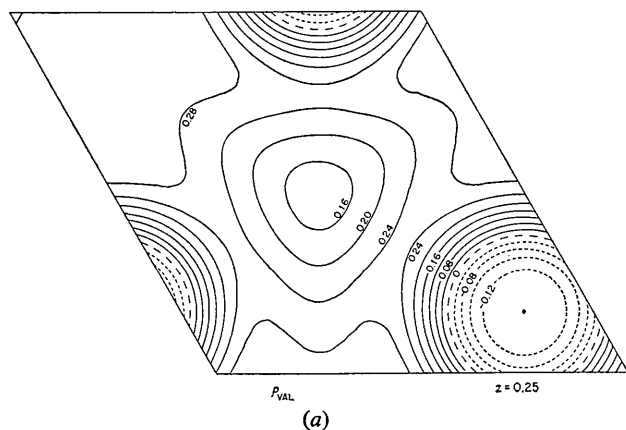

(a)

(b)

(c)

Fig. 2. Valence charge-density contours for Be in planes parallel to (001). Units are e Å^{-3}. Border runs from $-\frac{1}{2}$ to $+\frac{1}{2}$ for x and y lattice coordinates. (a) $z=\frac{1}{4}$, Be nucleus is shown as dot at $\frac{1}{3}, -\frac{1}{3}, \frac{1}{4}$. (b) $z=\frac{1}{8}$, (c) $z=0$.
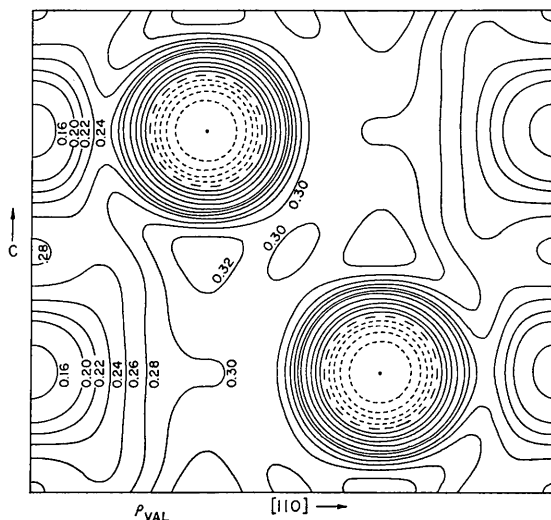
Fig. 3. Valence charge-density map for Be in the (110) plane. Units are e Å^{-3}. Border along c runs from $-\frac{1}{2}$ to $\frac{1}{2}$ and for [110] from 0,1 to 1,0 for x,y lattice coordinates.

It is interesting to note that the valence scattering model is sufficiently flexible to reveal apparent anisotropy in the nuclear motion. The final least-squares result (column three in Table 4) is $\langle u_{11}^2 \rangle^{1/2} = 0.0851 + 0.0009$ Å and $\langle u_{33}^2 \rangle^{1/2} = 0.0814 \pm 0.0018$ Å. The root-mean-square amplitude of vibration along the c axis is significantly smaller than the amplitude in the basal plane. This is consistent with the apparent bonding scheme built up by the superposition of the deformation functions. Be does depart from ideal hexagonal closest packing in that atoms in adjacent hexagonal layers are about 3% closer (2.2256 Å) than atoms in the same layer (2.2858 Å).

The total static valence electron-density map can be constructed from the least-squares results in column three of Table 4. This was done by generating 90 atoms in the Be lattice and computing the charge density in the unit cell from a superposition of the analytical charge-density functions centered on these atoms. Sections parallel to the hexagonal plane are shown in Fig. 2. The small negative region about the Be nucleus at $z=\frac{1}{4}$ is completely offset by inclusion of the core density function. Notice how the valence charge forms a maximum at $\frac{1}{3}, -\frac{2}{3}$ along the c axis for the three sections. In addition there appears a modest concentration of charge in the octahedral vacancy at $z=0$. A more revealing density map is parallel to the c axis and a cut along the [110] as shown in Fig. 3. The results suggest that the Be bonding in the lattice is along c and forms a maximum concentration of charge below the tetrahedral vacancy near $z=0$. The map displayed in Fig. 3 is astonishingly similar to a theoretical electron-density map published by Inoue & Yamashita (1973). When normalized to four valence electrons per unit cell, the pseudopotential calculation by Inoue & Yamashita predicts a maximum of 0.32 e Å^{-3} near the

same position as found in this work (see Fig. 3). The octahedral vacancy in the Inoue & Yamashita map has a charge less than or equal to 0·26 e Å⁻³. The agreement with the map found in this work seems quite acceptable.

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Errors in Atomic Parameters and in Electron Density Distributions Due to Thermal Diffuse Scattering of X-rays

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Errors in X-ray diffraction intensities due to first-order thermal diffuse scattering (TDS) have been calculated from the elastic constants of the crystal. Formulae given in the literature were generalized in such a way that they include quantum effects and zero-point vibrations. It is shown that, within the approximations used, the influence of quantum effects and zero-point vibrations is negligible above 5K if ordinary measuring conditions are applied. For $C_6H_5COCOC_6H_5$ and $NH_4HC_2O_4.\frac{1}{2}H_2O$ an estimate is made of the influence of TDS intensity errors on least-squares parameters and electron density distributions at 15, 110 and 293K. A critical discussion of the long-wave method used is given.

Introduction

In earlier papers (*e.g.* Göttlicher, 1968; Willis, 1969) the errors in X-ray diffraction intensities due to thermal diffuse scattering (TDS) have been discussed and estimates of their influence on the parameters of the atoms have been given. However, estimates of the errors in the parameters and electron density distribution due to neglect of TDS corrections, have not yet been made for crystals containing molecules with low symmetry. In the present paper we discuss the errors for dibenzoyl (DBZ; $C_6H_5COCOC_6H_5$) and ammonium hydrogen oxalate hemihydrate (AHO; $NH_4HC_2O_4.\frac{1}{2}H_2O$). The first is soft with respect to elasticity, for the second the elasticity is higher and more anisotropic. A list of symbols used in this paper is given in Table 1.

The formulae used in the present paper contain a number of approximations among which the following are of fundamental importance: (a) the atoms are assumed to vibrate (pseudo)harmonically, (b) second and higher order phonon scattering is neglected and only acoustic modes are considered, (c) the frequency of an acoustic mode is assumed to be proportional to its wave vector, thus

$$\omega_j(\mathbf{g}) = 2\pi v_j(\hat{\mathbf{e}})g ,\qquad(1)$$

and for expressions of type exp $(-2\pi i \mathbf{g} \cdot \mathbf{a}_i)$ we use the approximation

$$\exp(-2\pi i \mathbf{g} \cdot \mathbf{a}_i) = 1 - 2\pi i \mathbf{g} \cdot \mathbf{a}_i .\qquad(2)$$

This corresponds to the method of long waves (Born & Huang, 1968, Ch. V) which can be used for $g \ll a^i$.

Theory

TDS distribution around a reflexion H

In the pseudo-harmonic approximation the distribution $I_1(\mathbf{S})$ of the first-order diffuse scattering around a point H in reciprocal space is given by (Cochran, 1963)

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