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Acta Cryst. (1985). B**41**, 425-431

The Effects of Extinction on the Refined Structural Parameters of Crystalline BeO: a Neutron and γ-Ray Diffraction Study

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(*Received* 17 *July* 1984; *accepted* 27 *June* 1985)

Abstract

Neutron and γ-ray diffraction data collected from the same single crystal of BeO were used in conventional crystal structure refinements. The very severely extinguished neutron data are adequately modeled with the Becker-Coppens anisotropic-extinction formalism. Although the thermal parameters are unreliable, the positional parameter is close to the best estimate obtained from the γ-ray results. The γ-ray (103 keV) data are much less extinguished than the neutron data. Refinements utilizing high-order γ-ray data with neutral-atom and spherical generalized scattering factors are virtually identical.

0108-7681/85/060425-07$01.50

Introduction

The diffracted intensities of elastic scattering by many crystals are severely affected by extinction. This is particularly true for many simple inorganic compounds and most minerals of geophysical interest. Several models have been proposed to correct Bragg intensities for extinction (see Hamilton, 1957; Zachariasen, 1967; Cooper & Rouse, 1970; Coppens & Hamilton, 1970; Becker & Coppens 1974*a*, *b*, 1975). Most of these formalisms are based on the mosaic model of the real crystal and the energy-transfer equations both ascribed to the early work of Darwin (1914*a*, *b*, 1922). These formalisms have been criticized by Werner (1969, 1974) since the energy-transfer equations attempt to describe a largely dynamical effect within the limits of kinematical theory. Although a more sophisticated formalism has been proposed by Kato (1976*a*, *b*, 1979, 1980*a*, *b*, *c*) and Kawamura & Kato (1983) the earlier formalism remains more computationally tractable. In fact, the formalism of Becker & Coppens (1974*a*, *b*, 1975) has become particularly popular and is incorporated into many modern crystallographic least-squares refinement programs.

In most cases it has been found that atomic positional parameters are unaffected by the details of the model for extinction (Becker, 1977). Thus, in many conventional crystal structure refinements extinction corrections serve merely to lower the agreement factors and estimated standard deviations of the refined parameters. However, if the details of the thermal motion or the valence electron distribution are sought from the data, an accurate accounting of extinction is absolutely necessary.

As part of an effort to deduce experimentally the electron distribution in BeO, accurate neutron and γ-ray data were sought from the same crystal. It was hoped that the neutron data would be accurate enough to warrant a detailed examination of thermal motion, including possible anharmonicity. Furthermore, it was hoped that the γ-ray data would be nearly extinction free and thus be useful for charge density analysis. However, due to the severity of extinction in both data sets neither of these goals was realized.

In this paper we report the results of conventional structure refinements using these two data sets. Because of the simple structure of BeO, these results provide a straightforward example of how severe extinction can affect the positional and thermal parameters obtained during a conventional refinement.

Previous work on BeO

It was McKeehan (1922) who first suggested that BeO was isostructural with ZnO which was known to adopt the wurtzite structure (hexagonal ZnS) originally solved by Bragg (1920). McKeehan's suggestion was later confirmed by the single-crystal work of Aminoff (1925).

BeO crystallizes in space group $P6_3mc$ with cell parameters at room temperature of $a = 2{\cdot}6979$ (2) and $c = 4{\cdot}3772$ (2) Å, reported by Bellamy, Baker & Livey (1961). The crystal structure may be considered as two interpenetrating hexagonal close-packed (h.c.p.) arrays of Be and O atoms displaced relative to one another along the z direction. Since the space group is polar, the lighter Be atom is traditionally fixed at the origin leaving the O z parameter as the only structural variable. Since Be and O both occupy special positions with site symmetry $3m$, thermal ellipsoids are constrained such that the only unique elements of the mean-square displacement matrix are U_{11} and U_{33}. These ideally measure the mean-square amplitudes of motion along the x and z directions respectively.

The 'ideal' wurtzite structure is that in which the atoms of one h.c.p. array occupy the exact center of the tetrahedral voids of the other array yielding a c/a ratio of 1·633 and a z parameter of 0·375. BeO is compressed along the z axis relative to the ideal structure. Be metal, also h.c.p., exhibits a similar z-axis compression.

The first structure refinement of BeO accurate enough to determine the deviation of the O z parameter from the ideal value was carried out by Jeffrey, Parry & Mozzi (1956) using single-crystal X-ray techniques. Their early results are of exceptional quality and were later confirmed by Smith, Newkirk & Kahn (1964). Later refinements have included neutron diffraction studies on powders by Pryor & Sabine (1964) and single-crystal neutron work by Sabine & Hogg (1969). Refinements from powder X-ray data were completed by Sabine & Dawson (1963).

Experimental methods and data reduction

Several crystals of synthetic BeO were obtained from the National Museum of Natural History, Smithsonian Institution (USNM#117861). A colorless, doubly terminated crystal was mounted in a general orientation on a silica-glass capillary with epoxy. The crystal was elongated along the hexagonal axis with approximate maximum dimensions 2·0×2·0×3·6 mm. Since the anisotropy of this polyhedral crystal was less than 2, the use of the pseudospherical treatment in the extinction model of Becker & Coppens (1975) was believed to be justified.

Single-crystal neutron diffraction profiles were measured at room temperature using θ–2θ step scans with 0·05° per step and 40–60 steps per scan. Data were collected on the computer-controlled four-circle diffractometer 2XE at the University of Missouri Research Reactor facility. After an orientation matrix was obtained from 20 automatically centered reflec-

tions, all intensities within the sphere of reflection consistent with space group $P1$ were measured out to $\sin\theta/\lambda = 0{\cdot}69$ Å^{-1}. The ranges of values for h, k, and l were -3 to 3, -3 to 3, and -5 to 5 respectively. The neutron wavelength was 1·075 Å and was obtained from the 220 reflection of a Cu monochromator crystal. The counting time for each step was controlled by a direct-beam monitor, while the scattered neutrons were detected with a BF_3 detector. Three standard reflections were measured every 75 observations, and no significant variation was observed in their intensities.

Peak profiles were reduced to integrated intensities using the algorithm of Lehmann & Larsen (1974) as embodied in the profile-analysis program of Blessing, Coppens & Becker (1974). These intensities were then treated for Lorentz and absorption effects ($\mu = 0{\cdot}854$ cm^{-1}), values for the absorption cross-sections being taken from *International Tables for X-ray Crystallography* (1962). Although the agreement factor among symmetry-equivalent observations given by the relation $R(|F_o|^2) = \sum |F_o|^2 - |F_{avg}|^2 / \sum |F_o|^2 = 0{\cdot}019$ for the neutron data the 254 data were not averaged in anticipation of the refinement of anisotropic-extinction parameters.

After reduction of the neutron data it was noticed that 5 of the 28 unique observations violated the diffraction conditions of space group $P6_3mc$ for spherical scatterers vibrating in harmonic potentials of site symmetry $3m$. It is unknown whether these reflections were due to multiple scattering, anharmonicity, or both. Nonetheless, these data were rejected prior to refinement since the level of extinction did not warrant the inclusion of anharmonic terms in the atomic probability density function. Since the 003 reflection was among those observed and is strictly forbidden, even in the presence of anharmonic vibrations, those observations were assumed to be due to multiple scattering.

γ-ray diffraction data were obtained from the same crystal used for the neutron study and were taken at the University of Missouri γ-ray scattering facility (MUGS). The γ-ray source was neutron-activated Sm_2O_3 powder which produces ^{153}Sm with its characteristic 103 keV γ-ray of wavelength 0·12 Å (1 eV = $1{\cdot}60 \times 10^{-19}$ J). The use of this source at the University of Missouri has been described in detail by Yelon, Alkire & Schupp (1979) and by Alkire & Yelon (1981). γ-ray diffraction using the 412 keV γ-ray of ^{198}Au has been reviewed by Schneider (1983).

Prior to the collection of γ-ray intensity data an orientation matrix from 20 automatically centered reflections was obtained. Peak profiles were measured using step scans on ω with 0·005° per step, 48 steps per scan, and a fixed counting time of 11 s per step. 472 reflections consistent with space group $P1$ were scanned throughout the sphere of reflection with $\sin\theta/\lambda \leq 1{\cdot}09$ Å^{-1} ($2\theta = 15{\cdot}03°$). Values of h, k, and l ranged from -6 to 6, -6 to 6, and -9 to 9 respectively. Only those reflections found to be above background during a quick preliminary scan were fully step-scanned. These reflection profiles were reduced to integrated intensities using a modified version of the Blessing, Coppens & Becker (1974) program. The resulting intensities were corrected for the exponential decay of the γ-ray source using the expression $I = I_0 \exp(-\alpha T)$, where I is the decay-corrected intensity, I_0 is the raw intensity from profile analysis, α is the decay constant, and T the time. The decay constant for the 103 keV ^{153}Sm γ-ray is 0·01498 h^{-1} with a half-life of 46·27 h. These data were corrected for Lorentz, polarization, and absorption effects. The mass-absorption coefficients were interpolated from tabulated values for $\lambda = 0{\cdot}10$ and 0·15 Å published by Philips Scientific Instruments. The minimum and maximum transmission factors were 0·931 and 0·932. The agreement among symmetry-related observations given by the relation $R = \sum |F| - |F_{avg}| / \sum |F|$ was 0·011. The unaveraged data set consisting of 354 observations was used in least-squares refinements.*

Neutron refinement

All refinements presented in this paper were completed using the method of least squares as coded in the program *LINEX* (Coppens, 1975), a modified version of *ORFLS* originally written by Busing, Martin & Levy (1962). The observations were in all cases weighted according to $w = 1/\text{var}(|F_o|^2)$ where $\text{var}(|F_o|^2) = \text{var}(|F_o|^2 \text{ count}) + P^2|F_o|^4$. The instrumental instability constant P was computed from the agreement among standard reflections and was 0·0057 and 0·0045 for the neutron and γ-ray data respectively. All refinements were based upon $|F_o|^2$ and the quantity minimized was $\varepsilon = \sum w(|F_o|^2 - k^2|F_c|^2)^2$ where $|F_o|$ is the observed structure factor modulus, on a relative scale, and k is the scale factor.

Values for the coherent neutron scattering lengths were taken from Koester (1977). Initial refinements of scale, positional, and thermal parameters failed to converge due to the severity of extinction in the neutron data. A type-I isotropic-extinction model of Becker & Coppens (1974*a*, *b*) with a Lorentzian mosaic distribution converged if the U_{33} terms were allowed to be negative. A type-II isotropic-extinction model failed to converge.

An anisotropic, type-I Lorentzian, extinction model incorporating the mosaic description after

* Lists of hkl, F_o^2, $\sigma(F_o^2)$, the absorption-weighted mean path length $\bar{T}$, and vector components necessary for anisotropic-extinction corrections for the neutron and γ-ray diffraction data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42257 (12pp.) Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Comparison of refined structural parameters*

	Neutron	IAM	GSF	IAM-HO	GSF-HO
Scale factor k	235 (8)	2·74 (1)	2·79 (1)	2·91 (3)	2·93 (3)
Be U_{11} (Å^2)	0·0093 (4)	0·0046 (2)	0·0045 (2)	0·0046 (1)	0·0045 (1)
U_{33} (Å^2)	0·0022 (6)	0·0035 (3)	0·0035 (3)	0·0042 (2)	0·0041 (2)
B_{eq}* (Å^2)	0·55	0·34	0·33	0·35	0·34
O z	0·377756	0·378201	0·378199	0·378341	0·378343
$\sigma(z)$	±0·000691	±0·000208	±0·000194	±0·000142	±0·000141
U_{11} (Å^2)	0·0074 (6)	0·0026 (1)	0·00282 (8)	0·0033 (1)	0·0033 (1)
U_{33} (Å^2)	0·0074 (8)	0·0024 (1)	0·0026 (1)	0·0031 (1)	0·0032 (1)
B_{eq} (Å^2)	0·58	0·20	0·22	0·25	0·26
sin θ/λ range (Å^{-1})	0·21-0·68	0·21-1·16	0·21-1·16	0·85-1·16	0·85-1·16
no	254	354	354	157	157
nv	12	12	12	12	12
ε†	3749	1360	1185	147·4	146·4
$R(\|F\|^2)$‡	0·0337	0·0353	0·0331	0·0224	0·0223
$wR(\|F\|^2)$§	0·0446	0·0393	0·0367	0·0274	0·0273
g.o.f.¶	3·936	1·994	1·861	1·008	1·005
$(\Delta/\sigma)_{max}$	0·0008	0·0003	0·0001	0·0031	0·0032
Apical (Å)	1·654 (3)	1·6555 (9)	1·6554 (8)	1·6561 (6)	1·6561 (6)
Basal (Å)	1·647 (1)	1·6464 (3)	1·6464 (3)	1·6462 (2)	1·6462 (2)

* $B_{eq} = (8/3)\pi^2(2U_{11} + U_{33})$.
† $\varepsilon = \sum w(|F_o|^2 - k^2|F_c|^2)^2$.
‡ $R(|F|^2) = (\sum \||F_o|^2 - k^2|F_c|^2|/\sum |F_o|^2)^{1/2}$.
§ $wR(|F|^2) = (\varepsilon/\sum w|F_o|^4)^{1/2}$.
¶ g.o.f. $= [\varepsilon/(\text{no} - \text{nv})]^{1/2}$.

Table 2. *Parameters of Becker–Coppens type-*I *Lorentzian anisotropic-extinction models [mosaic distribution according to Thornley & Nelmes ($Y_{ij} \times 10^8$)]*

	Neutron	IAM	GSF	IAM-HO	GSF-HO
Y_{11}	0·13 (4)	0·040 (3)	0·032 (2)	0·009 (2)	0·009 (2)
Y_{22}	0·15 (4)	0·043 (3)	0·034 (2)	0·018 (6)	0·018 (6)
Y_{33}	0·06 (2)	0·0074 (5)	0·0063 (4)	0·0022 (5)	0·002 (5)
Y_{12}	−0·004 (3)	0·004 (1)	0·0032 (9)	0·000 (1)	0·000 (1)
Y_{13}	0·001 (2)	−0·0082 (8)	−0·0063 (6)	−0·0001 (9)	−0·002 (9)
Y_{23}	−0·003 (3)	−0·0049 (8)	−0·0037 (6)	−0·003 (1)	−0·003 (1)
η_1''	1·7 (2)	1·00 (3)	0·89 (2)	0·55 (9)	0·56 (9)
a (°)	117	118	118	88	104
b* (°)	154	150	150	170	165
c (°)	89	81	82	81	83
η_2''	0·8 (1)	0·236 (7)	0·222 (6)	0·14 (1)	0·14 (1)
a (°)	93	80	80	88	94
b* (°)	88	86	86	80	82
c (°)	4	11	11	10	9
η_3''	1·1 (1)	0·52 (2)	0·47 (1)	0·29 (4)	0·29 (4)
a (°)	153	150	150	177	166
b* (°)	64	60	60	91	77
c (°)	94	84	84	88	95

Thornley & Nelmes (1974) was then introduced. Refinements were completed using both an unconstrained and a symmetry-constrained extinction ellipsoid. Both anisotropic-extinction models yielded positive-definite thermal parameters. An R-factor-ratio test after Hamilton (1965) based on R(constrained)/R(unconstrained) = 1·036 resulted in $\mathcal{R}_{4,242,0.005} = 1.022$ which suggests that we may reject the hypothesis that the axes of the extinction ellipsoid parallel the crystallographic axes at the 0·005 significance level. The results of the unconstrained refinement are given in Tables 1 and 2.

γ-ray refinements

Initial refinements using the γ-ray data were carried out with an independent-atom model (IAM) of neutral, spherical atoms using scattering factors taken from Doyle & Turner (1968). Since the photon energy of 103 keV is much greater than any ionization energy of Be and O, anomalous dispersion was assumed to be absent.

Refinements with a type-I, Lorentzian extinction model were completed for the isotropic, symmetry-constrained anisotropic and symmetry-unconstrained anisotropic cases. Tests of the R-factor ratio based upon $R_{\text{isotropic}}/R_{\text{anisotropic}}$ (constrained) = 1·998 yielded $\mathcal{R}_{1,346,0.005} = 1.012$ which indicated that an assumption that extinction is isotropic can be rejected at the 0·005 level. A similar test based on R(constrained)/R(unconstrained) = 1·239 with $\mathcal{R}_{4,342,0.005} = 1.022$ indicated that the statistical significance of the four additional parameters of the unconstrained model is greater than 99·5%. The unconstrained refinement is designated IAM in Tables 1 and 2. All subsequent refinements were completed with an unconstrained, type-I Lorentzian anisotropic-extinction model.

A first step toward a more realistic scattering model was to introduce spherical generalized scattering factors (GSF's) for Be and O. These were obtained from R. F. Stewart (personal communication) and consist of the monopole terms of a multipole expansion of the molecular form factor for the BeO diatomic molecule. These pseudoatoms correspond roughly to Be and O ions with charges of ±1·212. This refinement is labelled GSF in Tables 1 and 2.

Finally, both the IAM and GSF models were refined using only high-order data with sin $\theta/\lambda > 0.85$ Å^{-1}. These results are labelled IAM-HO and GSF-HO in Tables 1 and 2.

Discussion

The level of extinction in the γ-ray data is severe with $y < 0.40$ for 3·6% of the data and $y < 0.80$ for 20·3% of the data with the IAM model. The minimum extinction coefficient was $y = 0.30$ for the 002 reflection. The extinction level in the neutron data can be considered extreme with $y < 0.10$ for 11·4% and $y < 0.20$ for 50·4% of the data with none of the extinction coefficients being greater than 0·85. The minimum extinction factor was $y = 0.07$, again for the 002 reflection. If accurate, this corresponds to an attenuation of 93% on $|F|^2$ due to extinction. However, due to the high correlation between the scale factor and extinction parameters, the absolute values of these extinction factors may not be wholly reliable. Nevertheless, these data give us an opportunity to see how well structural parameters can be retrieved from data where extinction varies from moderate to extreme.

The structural parameters from the various refinements are listed in Table 1. The O z parameter increases slightly as the quality of the fit improves.

This causes a steady increase in the apical bond distance and a concomitant decrease in the basal bond length. The difference between the apical bond lengths obtained from the neutron refinement and the high-order GSF refinement is 0·0021 Å and is within one estimated standard deviation of the neutron result and four e.s.d.'s of the γ-ray result. The deviation of the neutron z parameter from the precise high-order γ-ray value is probably due largely to uncorrected anisotropic extinction in the neutron case. Thus, the z parameter crudely mimics the anisotropic-extinction parameters. However, in light of the apparent sensitivity of the z parameter to anisotropic extinction, the Becker–Coppens formalism appears to do a good job in the presence of such severe extinction.

Hutton, Nelmes & Scheel (1981) found remarkable agreement between lattice-dynamical thermal parameters and those obtained from highly extinguished neutron diffraction data from $SrTiO_3$ when the Becker–Coppens extinction model was applied. Their results show $y<0{\cdot}10$ for 2% and $y<0{\cdot}20$ for 9% of the data. The extinction encountered in the neutron data for BeO is seen to be significantly greater than that observed in $SrTiO_3$.

There is a slight decrease in the thermal parameters for Be and an increase for those of O when going from the IAM to the GSF refinement. This is consistent with the somewhat ionic model provided by the GSF's. The Be thermal motion estimated from the IAM and GSF refinements still appears too anisotropic compared to the more precise high-order values. In the γ-ray case, this discrepancy may be due to an inadequate electron density model of spherical atoms as well as to uncorrected extinction effects. The slightly improved fit of the GSF model relative to the IAM model indicates that the monopole GSF's appear to provide a more adequate description of bonded Be and O atoms than do neutral atoms.

The high-order γ-ray data with $0{\cdot}85\leq\sin\theta/\lambda\leq 1{\cdot}16$ Å^{-1} should emphasize the scattering from the 'core' region near the nucleus. The IAM and GSF high-order refinements are virtually identical. The slightly larger thermal parameters for Be and the smaller scale factor for the IAM high-order results is a reflection of the fact that the IAM scattering factors have a slightly greater amplitude at high values of $\sin\theta/\lambda$ than do the GSF's. Extinction is only moderate in the high-order data with $y>0{\cdot}80$ for all data and $y>0{\cdot}90$ for all but 5 reflections. We believe the parameters obtained from the high-order GSF refinement to be our most accurate results.

The elements of the anisotropic-extinction tensors for the various models are listed in Table 2. The tensors were diagonalized to yield the half-width misorientations of the perfect crystallites in seconds of arc about eigenvectors with angles given relative to **a**, **b***, and **c**. Extinction is expected to be greatest for those reflections whose scattering vectors lie closest to the smallest radius of the extinction ellipsoid.

The mosaic-spread parameters associated with the semi-major axes of the extinction ellipsoids attest to the anisotropic nature of the extinction for this sample of BeO. Extinction ellipsoids from the various refinements have similar orientations with the shortest axis nearly parallel to [001] and the longest axis close to $[\bar{1}\bar{1}0]$. This indicates that $00l$ reflections should be most affected by extinction.

The shapes of the extinction ellipsoids may be considered by plotting the ratio of the intermediate to large semi-axes against the ratio of the small to intermediate semi-axes as shown in Fig. 1. Since the extinction ellipsoids for the γ-ray refinements have virtually the same shape the results from the full-data GSF refinement are plotted as being representative. The dashed lines divide the figure into four fields, each labeled according to the type of ellipsoid which plots in that field. As one moves to the right across the plot ellipsoids become progressively more prolate, moving up they become more oblate, and toward the upper-right corner they become progressively more spherical. The extinction ellipsoid refined from the neutron data is seen to be somewhat more prolate and slightly more spherical than the ellipsoid from the γ-ray refinement. The shape of the extinction ellipsoid need not be constant as the wavelength is varied. However, the tendency for the extinction ellipsoid to be more isotropic in the neutron case may be traced to the tendency for the thermal and positional parameters to mimic the anisotropic-extinction parameters when extinction is severe.

There is a steady decrease in size of the extinction ellipsoids going from left to right across Table 2. Recall that for the Thornley & Nelmes (1974) description the radii of the extinction ellipsoid are directly proportional to the mosaic spread. The apparent decrease in the mosaic-spread parameters appears to contradict the fact that extinction decreases going from the neutron, to the full-data γ-ray, and to the

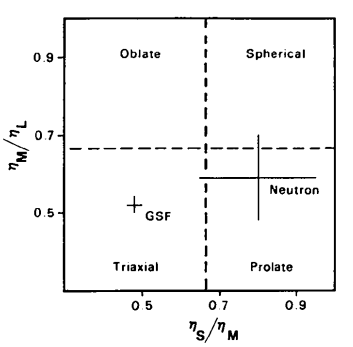

Fig. 1. The shapes of extinction ellipsoids are compared by plotting ratios of large η_L, medium η_M, and small η_S semi-axes. The four fields are labeled according to the general shape of the ellipsoids which fall within them. Error bars are two standard deviations in length.

Table 3. *Comparison of structure refinements on* BeO

	Jeffrey *et al.*	Smith *et al.*	Pryor & Sabine	Sabine & Dawson	Sabine & Hogg	This study‡
z	0·378	0·3786 (5)*	0·378 (1)	0·374 (2)	0·379 (2)	0·37834 (14)
B_{Be} (Å^2)	0·53	0·48†	0·35 (6)	0·23 (18)	0·27 (8)	0·34†
B_O (Å^2)	0·20	0·61†	0·27 (5)	0·63 (14)	0·53 (9)	0·26†
Apical (Å)	1·655	1·659 (3)	1·655 (4)	1·637 (9)	1·659 (9)	1·6561 (6)
Basal (Å)	1·647	1·645 (3)	1·647 (1)	1·652 (3)	1·645 (3)	1·6462 (2)

* E.s.d.'s given in parentheses refer to last decimal place.
† $B = (8/3)\pi^2(2U_{11} + U_{33})$.
‡ Refinement GSF-HO.

high-order γ-ray refinements. It must be emphasized that these data were collected on a relative scale and that the refined extinction parameters are highly correlated with the scale factor. Notwithstanding this fact, high-order data from the IAM-HO refinement equivalent to those from the IAM refinement have greater extinction corrections (*i.e.*, k^2y). Thus, it appears that the moderate extinction in the high-order data is slightly underestimated when the severely extinguished low-order data are included in the refinement.

The structural parameters of the high-order GSF refinement are compared with those of previous BeO structure refinements in Table 3. Note the rather wide range of z parameters and resulting bond distances. The thermal parameters also show a wide variation. Our results are in closest overall agreement with those obtained by Pryor & Sabine (1964) from powder neutron diffraction data. This agreement is not unexpected since the powder neutron data are presumably unaffected by secondary extinction or the ambiguity of scattering factors.

Hewat (1972) has calculated lattice-dynamical Debye–Waller parameters at 300 K for BeO and reports $B = 0{\cdot}27$ Å^2 for both Be and O. While the O value from this study and that of Pryor & Sabine compare favorably to Hewat's results, the Be values do not. We offer no explanation for this discrepancy.

Although the severely extinguished neutron data may be adequately handled using the Becker–Coppens extinction formalism, significant improvements in the quality of the results are obtained when the experiment is carried out using a short-wavelength γ-ray source. Traditionally, the way to eliminate extinction effects is to reduce the wavelength and the active volume of the crystal. γ-ray diffraction greatly reduces the wavelength. However, since neutron-activated γ-ray sources do not provide a large photon flux the active volume cannot be simultaneously reduced. It would be desirable to have a dedicated source of highly intense, high-energy (100 keV) photons for single-crystal diffractometry. Synchrotron radiation of this type could be obtained from bending magnets or high-field insertion devices in a high-energy electron or positron storage ring.

Much of this research was supported from NSF grant EAR-77-23114 awarded to GVG and P. H. Ribbe to study bonding in minerals. JWD wishes to acknowledge further the financial support during data collection of the University of Missouri Research Reactor (MURR). We thank Dr Randy Alkire for assistance in the collection of γ-ray data, Dr Mark Spackman for computing the GSF's, and Dr John White with the US Museum of Natural History for providing samples of synthetic bromellite (USNM#117861). The computing costs of the numerous refinements were defrayed by The Instructional and Research Computer Center (IRCC) of The Ohio State University. We thank Carolyn Gribbin for typing the manuscript and Karen Tyler for assistance in drafting.

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Water-Mediated Transformations in Protein Crystals

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(*Received* 8 *March* 1985; *accepted* 11 *June* 1985)

Abstract

Different crystal forms of bovine pancreatic ribonuclease A and hen egg white lysozyme, 2Zn insulin, 4Zn insulin and crystals of concanavalin A were examined under controlled environmental humidity in the relative humidity (r.h.) range of 100 to 75%. Many of them, but not all, undergo reversible structural transformations as evidenced by discontinuous changes in the diffraction pattern, the unit-cell dimensions and the solvent content. Tetragonal, orthorhombic and monoclinic lysozyme and a new crystal form of ribonuclease A show transformations at r.h.'s above 90%. Monoclinic lysozyme transforms at low r.h. to another monoclinic form with nearly half the original cell volume. The well known monoclinic form of ribonuclease A grown from aqueous ethanol solution undergoes two transformations while the same form grown from 2-methyl-2,4-pentanediol (MPD) solution in phosphate buffer does not transform at all. Soaking experiments involving alcohol solutions demonstrate that MPD has the effect of decreasing the r.h. at which the transformation occurs. Triclinic lysozyme, 2Zn insulin, 4Zn insulin and the crystals of cancanavalin A do not transform in the 100 to 75% r.h. range before losing crystallinity. The results obtained so far indicate that the crystal structure has a definite influence on water-mediated transformations. The transformations do not appear to depend critically on the amount of solvent in the crystals but the r.h. at which they occur is influenced by the composition of the solvent. The transformations appear to involve changes in crystal packing as well as conformational transitions in protein molecules. The present investigations and other related studies suggest that water-mediated transformations in protein crystals could be very useful in exploring conformational transitions in and the hydration of proteins.

Introduction

The role of water in biological systems can hardly be overemphasized. Proteins, like other biomolecules, almost invariably exist and function in an aqueous environment. Considerable progress has recently been made through X-ray studies in the understanding of the structure of water surrounding protein molecules (Blake, Pulford & Artymiuk, 1983; Finney, 1979; Watenpaugh, Sieker & Jensen, 1979; Sakabe, Sakabe & Sasaki, 1980; Teeter, 1984). The hydration of proteins and the effects of protein-water interactions have been studied in considerable detail by other techniques as well. Such studies had earlier indicated the dependence of protein conformation on the amount of water present in the sample (Kuntz & Kauzmann, 1974). Subsequent physicochemical and biochemical studies on lysozyme led to a hydration model that did not involve significant changes in protein conformation (Careri, Gratton, Yang & Rupley, 1980). More recently, there has been a spurt in the investigations on protein-water interactions and their consequences (Poole & Finney, 1983, 1984; Baker, Hansen, Bhaskara Rao & Bryan, 1983). Many of these investigations clearly show that a change in hydration is often accompanied by conformational changes. They also re-emphasize the importance of water in protein action.

The first and, as far as we are aware, only systematic attempt to study the effects of the amount and the composition of the aqueous solution surrounding protein molecules on crystal structure were made in the late nineteen forties and early fifties on haemoglobin (Boyes-Watson, Davidson & Perutz, 1947;

0108-7681/85/060431-06$01.50