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A revised method of operation of the single-crystal diamond cell and refinement of the structure of NaCl at 32 kbar

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Abstract

Revised operating techniques for the single-crystal diamond cell have been developed. Changes in operating procedures include an on-line correction for absorption in the diamond cell, automatic adjustment of the scan time to be inversely proportional to the peak-to-background ratio, and data collection with $\phi = 0$ rather than the normal mode with $\omega = 0$. These changes result in the measurement of up to 40 percent more reflections than obtained by previous methods. When the new techniques were applied to measurements of intensity data for NaCl, the structure refined to a weighted residual of 2.0 percent at 32 kbar.

Introduction

As a result of the modern developments in single-crystal diffractometry and high-speed computations, it is now possible for crystallographers to solve and refine the crystal structure of most materials. As the techniques have become more and more routine, mineralogist-crystallographers have devoted more effort to studying the structures of minerals under conditions that more closely approximate those of the formation of the phase. The use of the high-temperature furnace is well known (see the papers in the section on High-Temperature Crystal Chemistry, *Am. Mineral., 58,* 577–704, 1973) and has become a reasonably routine experimental technique, in spite of obvious difficulties in furnace design and calibration differences between laboratories. More recently, crystal structures of minerals at elevated pressures have been studied by Merrill and Bassett (1975), Hazen and Burnham (1974, 1975), and Hazen (1976a, 1976b), using techniques developed at the National Bureau of Standards (see review article by Block and Piermarini, 1976). The objectives of the present study are:

(1) to develop techniques for structural analysis of crystals when using pressure transmission fluids known to provide hydrostatic pressures up to 100 kbar,

(2) to investigate the procedures necessary to compute accurate factors for correction of the absorption in the cell,

(3) to develop techniques that maximize use of a computer-controlled four-circle diffractometer when collecting X-ray intensity data in the diamond cell, and

(4) to develop the software necessary to use the method of Hamilton (1974) for crystal centering.

Because the secondary pressure calibration using ruby fluorescence (Barnett *et al.,* 1973) was not yet available locally, it was necessary to choose a material for which the compressibility is known from previous studies. Accordingly, NaCl was selected as the material to be analyzed. The pressure was estimated using the NaCl volume equation of state (Decker, 1971).

Diamond cell absorption corrections

If a precise crystal-structure refinement for a crys-

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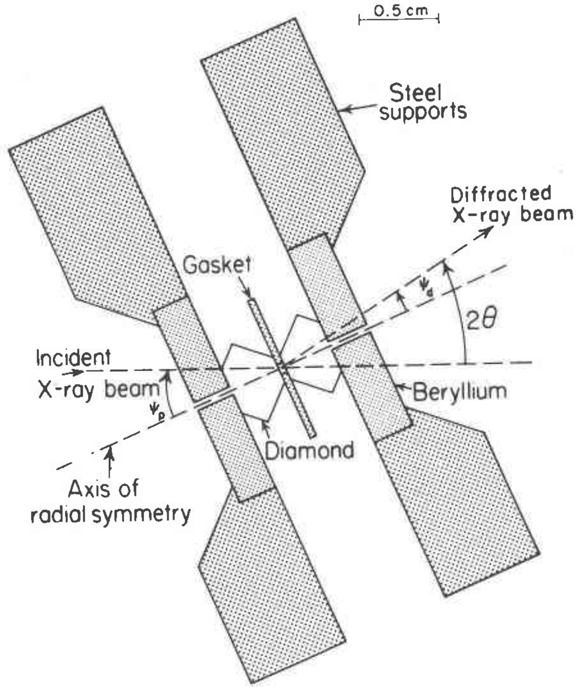

Fig. 1. Cross section of miniature diamond cell. (Figure adapted from Hazen, 1976a.)

tal mounted in a diamond cell is to be performed, Santoro *et al.* (1968) have shown that it is necessary to correct the measured intensities for the effects of absorption in the diamonds and other parts of the cell. In principle, the size and shape of the components of the cell could be measured and the transmission of the cell could be calculated. Hazen (1976a) however, found that this method failed to produce a satisfactory explanation of the observed absorption: he attributed the problem to inaccuracies in the measurements of the diamonds and metal parts and in the mass absorption coefficients of C and Be. In lieu of the analytical approach to the corrections, Hazen used two empirical methods. One involved a comparison between the integrated intensities measured for a crystal mounted in the cell and the same crystal mounted in the normal fashion. In the second method the attenuation of the direct beam was measured. Because one of the objectives of the present study was to develop techniques that could be standardized easily, the latter method was chosen.

Figure 1 shows the geometry of the diamond cell. If radial symmetry is assumed, only two angles are required to describe the relationship between the axis of the cell and the primary and diffracted beams. Using Hazen's notation, these angles are called ψ_p and ψ_d. The cell was mounted on the PDP-15 controlled, four-circle diffractometer system that is equipped with an X-ray tube with a silver target and a graphite primary-beam monochromator. The attenuation of the direct beam was measured with the count rate reduced to acceptable levels by an aluminum absorber. The count rate was measured for values of ω from −45° to 45° in steps of 0.5° for χ equal to 0°, 45°, and 90°. Because the diffraction experiment measures relative rather than absolute intensities, it is necessary to measure only the relative transmission factors for the cell; therefore, the intensity of the direct beam was not measured.

The ω traverses at the different values of χ gave nearly identical results, suggesting that the assumption of radial symmetry is not violated to a large degree. For each of the three traverses, the intensities for positive and negative ψ were averaged, and the data from the traverses were added and converted to relative attenuations. The resulting data set consists of measured attenuations for 91 different values of ψ from 0° to 45°.

If the shapes of the diamonds and the beryllium are approximated by a flat plate, the attenuation of the X-rays is described by a factor of $\exp(-\bar{\mu}_l t)$, where $\bar{\mu}_l$ is an average linear absorption coefficient and t is the path length. As a function of ψ, the path length is

$$t = 2t_0/\cos\psi,$$

where $2t_0$ is the thickness of the plate. The attenuation relative to the value for $\psi = 0$ is

$$I(\psi)/I(0) = \exp[-2\bar{\mu}_l t_0(1/\cos\psi - 1)] \qquad (1)$$

or

$$\ln[I(\psi)/I(0)] = -2t_0\bar{\mu}_l(\sec\psi - 1).$$

If the logs of the measured attenuation factors are plotted *vs.* ($\sec\psi - 1$), a pronounced curvature, as well as fine structure, is observed as a result of the nonideal shapes. Using least-squares regression techniques, a fifth-order equation was found to give the best fit to the data. Figure 2 shows the data points and line transformed into a plot of attenuation factors *vs.* ψ. Note that $I(\psi)/I(0)$ is roughly 0.3 at ψ = 45°. This attenuation is due to absorption within the cell as well as cutoff of the primary beam by the gasket. For crystals that are large relative to the hole in the gasket, the latter factor is very important; furthermore, if the crystal is not accurately centered in the gasket, the cutoff will not be radially symmetric. If the thickness of the gasket is t, cutoff will occur if any part of the crystal is less than $t \tan\psi_{\max}$

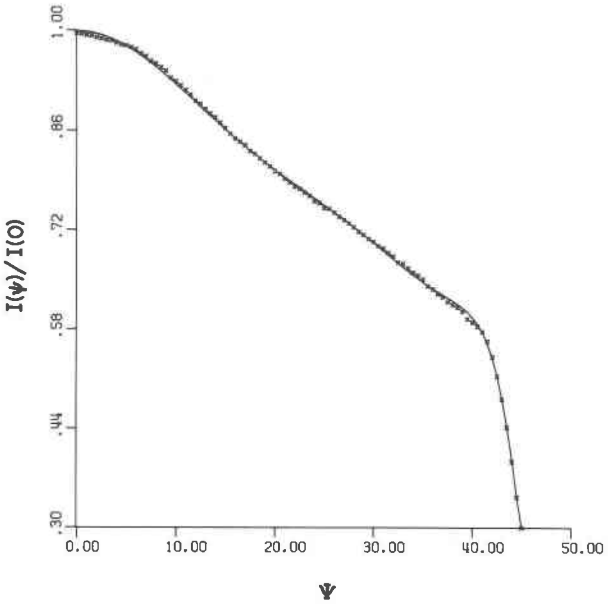

Fig. 2. Pressure cell attenuation as a function of angle.

from the edge, where $\psi_{\max}$ is the maximum angle used in the experiment.

The nonnegligible correction for the attenuation of the cell has been programmed into the data collection routine on the PDP-15 and is performed automatically on-line. Subsequent corrections for the absorption in the crystal under investigation may be made by standard routines in the normal fashion without regard for the diamond cell.

Calculation of optimum diffractometer angles

In their paper describing the use of the diamond-anvil pressure cell in a single-crystal X-ray diffractometer, Merrill and Bassett (1974) developed a set of equations that describe the volume of reciprocal space accessible when a crystal is mounted in the cell. The calculation, although correct, contains an assumption that reflections that initially lie above or below the equatorial plane of the instrument can be rotated into the diffracting position without tilting the radial symmetry axis of the cell out of the equatorial plane of the instrument. On a three-circle diffractometer such as employed by Merrill and Bassett and on four-circle instruments operated in the so-called *bisecting position* (Busing and Levy, 1967), this assumed condition is violated. The result is that fewer reflections can be measured than would be predicted by the equations of Merrill and Bassett (1974). Because only a small fraction of the reciprocal lattice points can be measured under the best of conditions (Fig. 5 of Merrill and Bassett, 1974), such further reduction in the number of observations should be avoided.

By recalculating the diffractometer settings with the symmetry axis of the diamond cell constrained to lie in the equatorial plane of the instrument, one can eliminate the extra reduction in accessible volume. If the coordinate and angle conditions of Busing and Levy (1967) are followed, the y-coordinate axis in the ϕ system is parallel to the radial symmetry axis of the diamond cell. As the goniometer is rotated through the Eulerian angles, the rotation of the ϕ system relative to the laboratory is given by **R** (Busing and Levy, eq. 47). The laboratory unit vector parallel to this radial axis will be given by the matrix product

$$\mathbf{R}\begin{bmatrix}0\\1\\0\end{bmatrix} = \begin{bmatrix}R_{12}\\R_{22}\\R_{32}\end{bmatrix}. \qquad (2)$$

The cosine of the angle between the laboratory z axis and the diamond-cell axis is equal to R_{32}; however, this angle is the complement of ϵ, the angle between the cell axis and the equatorial plane. Thus,

$$\sin\epsilon = \cos(\pi/2 - \epsilon) = R_{31} = -\sin\chi\sin\phi. \qquad (3)$$

This angle will be zero only if χ or ϕ is equal to zero.

Busing and Levy (1967) show that a reflection is in diffracting condition whenever the reciprocal lattice vector for that reflection is rotated parallel to the unit vector **u**, where

$$\mathbf{u} = \begin{bmatrix}\cos\omega\cos\chi\cos\phi - \sin\omega\sin\phi\\ \cos\omega\cos\chi\sin\phi + \sin\omega\cos\phi\\ \cos\omega\sin\chi\end{bmatrix}. \qquad (4)$$

The components of this vector may be calculated from the Miller indices, the orientation matrix, and the unit-cell metric for the crystal. Equation 4 does not yield a unique solution because one of these angles is redundant; therefore, when a reflection is in diffracting position, the angles ω, χ, and ϕ may be suitably changed while the conditions of diffraction are maintained. These changes correspond to rotating the crystal about the reciprocal lattice vector perpendicular to the Bragg plane being measured. Within certain limits, the investigator is free to choose any one of these angles. The other two will be determined by the crystal mounting and the plane to be measured. In an ordinary diffraction experiment, ω is usually chosen to be 0, which is the *bisecting position* referred to above. (In all equations it is assumed that ω is the deviation of the χ ring from the position bisecting the incident and diffracted beams.)

As shown in the previous paragraph, however, more observations could be measured if χ or ϕ were kept equal to zero, an operation that would keep the axis of the cell in the equatorial plane. When χ is zero, the ω and ϕ axes are redundant; therefore, this choice of a fixed axis is not useful. On the other hand, ϕ may be set to zero and the diffracting conditions obtained by changing ω and χ. These angles may be calculated by substituting $\phi = 0$ into equation 4 to obtain

$$\mathbf{u} = \begin{bmatrix} \cos\omega\cos\chi \\ \sin\omega \\ \cos\omega\sin\chi \end{bmatrix} \quad (5)$$

which may be solved for ω and χ. Because collisions between the χ ring and the tube housing or detector will occur on many diffractometers if ω is rotated outside a relatively restricted range, it may not be possible to satisfy equation 5. In that case, it is possible to use the mechanical constraints to determine the largest possible magnitude for ω and equation 5 to determine the appropriate sign. After ω is determined, χ and ϕ may be found from equation 4.

The effect of the *fixed phi* choice of angles is to reduce the sum of the angles ψ_p and ψ_d. As shown in Figure 1, this sum will equal 2θ whenever the axis of the cell lies in the equatorial plane; however, this sum will increase as the axis is rotated out of the plane. Because the steel mounting brackets of the cell separately limit ψ_p and ψ_d to be less than an angle of approximately 45°, the number of observable reflections is increased by holding ϕ equal to zero. In trial calculations, the number of reflections observable in the *fixed phi* mode is as much as 40 percent greater than the number that can be measured in the bisecting position. As an additional benefit, the path length of the X-rays in the diamonds is reduced, leading to increased peak-to-background ratios and an increased number of reflections with intensities significantly greater than the background. Note: the direction cosine equations of Hazen (1976a) must be modified for nonzero ω.

Data collection and refinement

To test the operation of the Stony Brook diffractometer system with the diamond cell mounted, a sample of NaCl crystallized from reagent-grade material was selected. A cube of approximately 150 μm on a side was mounted in the cell, using a gasket of hardened stainless steel of 0.25 mm thickness with a 250 μm hole. A 4:1 mixture of methyl and ethyl alcohol was used as the pressure-transmitting medium. When the pressure was increased to approximately 30 kbar, there was little doubt that the alcohol mixture remained fluid, as the crystal would not remain stationary, thereby preventing alignment of the crystal. This difficulty was overcome by using the alcohol-insoluble fraction of petroleum jelly to attach the crystal to the face of one of the diamonds. This material does not remain fluid at pressures above 15–20 kbar, as evidenced by the development of polygonal platelets in the petroleum jelly; because the bulk of the crystal is not enclosed, however, the resulting nonhydrostatic stresses are small.

After the crystal was mounted in the cell and the pressure was increased, the goniometer head holding the entire assembly was centered on the optical microscope and then transferred to the diffractometer. Reflections were located, the orientation matrix was determined, and this matrix and the unit-cell parameters were refined using the method of Tichý (1970). It became obvious that the errors in centering the crystal on the diffractometer were large enough to prevent determination of the unit cell with the precision required to use the volume as a pressure indicator. The method of Hamilton (1974), which uses the angles for the eight different diffracting positions for a reflection to determine crystal-centering errors and the zero errors of the diffractometer axes, was therefore used. An explanation of the details of this procedure and an extension of the equations for nonzero ω are presented elsewhere (King and Finger, in preparation).

The corrections in crystal centering are reported as the x, y, and z deviation of the crystal position from the center of the diffractometer. With the standard mounting bracket attached to an ordinary goniometer head, the corrections were easily made for the x and y axes, but were very difficult to make in the height or z adjustment. As a result, the goniometer head and the bracket mounting the diamond cell to it have been redesigned as shown in Figure 3 to facilitate this adjustment (plans for this assembly can be obtained from the authors). After the crystal was centered, the lattice constant was determined to be 5.4533(9) A, a value that corresponds to 32(2) kbar (Decker, 1971).

All accessible reflections with $l \geq 0$ and $2\theta \leq 90°$

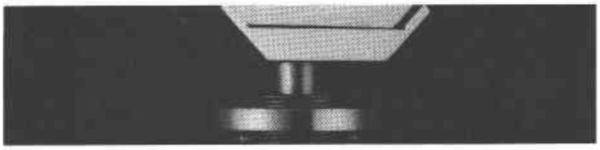

Fig. 3. Revised goniometer head and mounting assembly for miniature diamond cell.

for Ag radiation ($\lambda K\alpha_1$ = 0.55941 A) were measured using a θ–2θ scan with the correction for attenuation of the diamond cell automatically applied. Because the general scattering from the diamonds, beryllium plates, and steel gasket is relatively high, the background count rates are large. In addition, the attenuation of the diffracted beam leads to low peak-to-background values that make it difficult to observe a significant net intensity. With the small volume of reciprocal space accessible and the unfavorable peak-to-background ratios, the investigator is attempting to refine the structure with a very unfavorable observation-to-parameters ratio. One additional means of improving this ratio is to measure the intensities using the constant precision counting technique of Finger *et al.* (1973), that adjusts the total time to measure each reflection and the proportion of the time spent counting background to reach a particular value of σ_I/I. With the constant precision counting technique and the *fixed phi* mode of operation, a total of 296 reflections were measured. Corrections were applied for absorption in the crystal (μ_l = 8.8 cm^{-1}), and after the structure factors for reflections related by symmetry were averaged, a total of 60 reflections were obtained. Fifty-nine of these had integrated intensities greater than twice their standard deviation. By comparison, a total of 19 nonequivalent reflections would be measured in a "normal" experiment with Mo radiation and a maximum 2θ of 60°. Least-squares refinement was accomplished with the computer program RFINE4 (Finger and Prince, 1975).

In the sodium chloride structure, the sodium and chlorine ions are located at sites with symmetry $4/m\ \bar{3}\ 2/m$; consequently, the only variable parameter is an isotopic temperature factor for each atom. The results obtained in the refinement are listed in Table 1 with selected room-pressure data (Viswamitra and Jayalakshmi Ramanuja, 1972). The temperature factors for Na and Cl are equal to 1.46(3) and 1.18(2) A^2, respectively. When complex data reduction and correction procedures have been employed, as in this case, it is natural to question whether the temperature factors that result are indicative of a thermal vibration model or are an artifact of the calculation. For NaCl, the bonding may be modeled in a relatively rigorous fashion and the experimental results compared with the calculation.

The potential minimum for the sodium chloride molecule may be represented by an expression of the form

$$V(r) = Ae^{-ar} - \frac{q^2}{r} + V_\infty. \qquad (6)$$

The change in energy associated with an instantaneous displacement, u, from the equilibrium distance, r_e, has been shown by Karplus and Porter (1970, p. 249) to be

$$E = q^2[e^{-au}/ar_e^2 + 1/r_e - 1/(r_e + u)]. \qquad (7)$$

If $u \ll r_e$, the average energy is

$$\langle E \rangle \simeq \frac{q^2}{2r_e^3}(ar_e - 2)\langle u^2 \rangle. \qquad (8)$$

The isotropic temperature factor, B, however, is related to the mean-square displacement by

$$B = 8\pi^2 \langle u^2 \rangle; \qquad (9)$$

therefore,

$$\langle E \rangle = \frac{q^2 B}{16\pi^2 r_e^3}(ar_e - 2). \qquad (10)$$

If the Boltzmann statistical distribution is satisfied, the average energy should depend only on the temperature, not the pressure. If it is further assumed that the repulsion parameter, a, is independent of pressure, then the temperature factor at a given pressure would be

$$B_1 = B_0 \frac{(ar_{e_0} - 2)}{(ar_{e_1} - 2)}\left(\frac{r_{e_1}}{r_{e_0}}\right)^3. \qquad (11)$$

If a value of 3.47 A^{-1} is used for a (Karplus and Porter, 1970, p. 249), then the temperature factors for NaCl

Table 1. Crystal data and refinement results for NaCl at 32 kbar

	32 kbar	1 bar*
Space group	$Fm3m$	
Lattice constant (a_0)	5.4533(9) A	
Pressure	32(2) kbar	
Residuals (all data):		
R**	3.2%	
Wtd. R†	2.0%	
Temperature factors:		
B_{Na}	1.46(3) A^2	1.59(8) A^2
B_{Cl}	1.18(2) A^2	1.37(5) A^2
Root-mean-square displacements:		
Na	0.136(2) A	0.142(3) A
Cl	0.122(1) A	0.132(2) A

*Data from Viswamitra and Jayalakshmi (1972).

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

†Wtd. $R = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2\}^{1/2}$.

would change by a factor of 0.943 between 1 bar and 32 kbar. A comparison of the results of the present study with the 1 bar data from Viswamitra and Jayalakshmi Ramanuja (1972) gives observed ratios of temperature factors of 0.92(5) for Na and 0.86(9) for Cl, a close agreement. It is believed, therefore, that meaningful thermal parameters have been derived from the present study, in spite of the obvious difficulties associated with the high-pressure experiment.

The average linear compressibility of silicates is smaller than the corresponding value for NaCl by a factor of approximately 4; therefore, the compression will have a much smaller effect on the temperature factors of silicates.

Conclusions

This study has shown several important points regarding the collection of single-crystal intensity data at high pressure. The foremost of these conclusions is that data of sufficient quality for a precise refinement, including meaningful thermal parameters, can be collected if certain precautions are observed. First of all, it is essential to correct the intensity data for attenuation by the diamond cell. Secondly, the ratio of observations to parameters in the least-squares refinement can be greatly increased by operating the diffractometer in the *fixed phi* mode and using the constant precision method of peak integration.

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