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Mean-Square Atomic Displacement and Antisymmetric Atomic Vibrations in Beryllium at Room Temperature Determined from Short-Wavelength Neutron Data*

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Abstract

The atomic vibrations in metallic beryllium at 295 K are determined from single-crystal neutron diffraction data corrected for thermal diffuse scattering, second-order contamination and extinction effects. Full sets of data were collected from two single crystals of volumes 8 and 27 mm^3, using wavelengths of 0·525 and 0·425 Å, respectively. Data extend to $\sin\theta/\lambda = 2{\cdot}1$ Å^{-1}. The room-temperature values of the principal components of the mean-square atomic displacement are $\langle u_x^2\rangle$ = 0·00594 (3) Å^2 in the basal plane and $\langle u_z^2\rangle$ = 0·00537 (3) Å^2 along the 6_3 axis of the hexagonal cell. These values are compared with earlier and very recent X-ray determinations. The vibrational anharmonicity expressed as the third cumulant is $C_{112} = 0{\cdot}0008\,(1)$ Å^3.

Introduction

The electron-density distribution in beryllium was studied by Brown (1972) from Ag $K\alpha$ X-ray diffraction data and evidence of covalent bonding, which could be correlated with the anisotropy in the physical properties of metallic beryllium, was established. Brown's X-ray structure factors were used in further analyses of the electron-density distribution by Stewart (1977) and Yang & Coppens (1978).

Stewart applied his rigid pseudo-atom model, fitting by a least-squares technique an atom-centred spherical-valence monopole plus three higher multipoles to the experimental data, and finally calculated the valence density from the multipole functions. A conclusion of the refinements was that 'the high-angle residuals imply a rather complicated deformation of the static charge density near the nucleus and/or anharmonic motion of the nucleus'. Yang & Coppens in their study calculated valence and deformation-density maps by Fourier methods using thermal parameters determined by least-squares refinement of reflexions with $\sin\theta/\lambda \geq 0{\cdot}5$ Å^{-1}.

Weiss (1978) calculated the cohesion energy of beryllium from experimental X-ray Compton-profile data and found a discrepancy with the experimentally determined value. He concluded that the core-electron charge distribution is expanded relative to the free-atom configuration. Such an expansion in metallic beryllium would reduce the X-ray scattering factor relative to the free-atom scattering factor in much the same manner as does the atomic thermal motion. Resolution of these two effects calls for an independent determination of the atomic mean-square amplitude, which can be obtained from a neutron diffraction study. In non-magnetic materials, neutrons are almost exclusively diffracted by the nuclei. The nuclear scattering factor for neutrons, the scattering length, is independent of scattering angle. We undertook a neutron diffraction study of metallic beryllium with the aim of determining accurately the mean-square amplitude of atomic thermal motion in order to give a better basis for the interpretation of the X-ray diffraction data.

Experimental

Beryllium single crystals have many desirable properties for neutron monochromators and efforts are made to grow and prepare big beryllium single crystals of uniform mosaic structure (Aldinger & Freund, 1977). We obtained two good single crystals from Dr Aldinger, grown by the zone-refinement technique

* A preliminary account of this work has been given in the Institut Laue–Langevin Annual Report 1978, Annex 1, experiment 5-11-67.

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(Wilhelm & Aldinger, 1975). One crystal of 3·0 × 3·0 × 3·0 mm was arc-cut from a three-pass zone-refined crystal bar of starting material, high-purity electrolytic-origin beryllium (~99·85 wt % Be) and the other crystal of 2·0 × 2·0 × 2·0 mm was arc-cut from a ten-pass zone-refined crystal (wt % Be > 99·99). The small crystal cube was cut with one face parallel to the basal plane (0001); the best simple indexing of the two other sets of planes is $(\bar{2},10,\bar{8},0)$ and $(4\bar{1}\bar{3}0)$. It was mounted with the [0001] axis near, but not parallel to, the φ axis of the diffractometer. The big crystal had one face of the cube parallel to the basal plane (0001) and the two others parallel to $(10\bar{1}0)$ and $(\bar{1}2\bar{1}0)$. It was mounted with the $[10\bar{1}0]$ axis near, but not parallel to, the φ axis of the diffractometer.

Neutron diffraction data were collected at room temperature on the four-circle diffractometer D9 located at the hot source of the Institut Laue–Langevin high-flux beam reactor. Measurements were carried out using wavelengths of 0·525 Å for the 8 mm^3 crystal and 0·425 Å for the 27 mm^3 crystal. The monochromatic neutron beam was obtained by reflexion from the (200) planes of a Cu crystal in transmission geometry. Coupled ω–2θ step scans were used to record the reflexion profiles in the bisecting geometry and the number of steps in each profile was 41. The step length was varied as a function of the Bragg angle so that approximately half the points were recordings of background. The total scan width ranged from 5° at low angle to 10° at 140° in 2θ. Most reflexions were measured at two symmetry-related positions. The stability of the recording equipment was monitored by measurement of one standard reflexion, 103, at intervals of 25 reflexions, and no long-term systematic trend in intensity was observed.

Profiles were reduced to F^2 values with the minimal $\sigma(I)/I$ criteria including a correction of the known bias in the method (Lehmann & Larsen, 1974), where I is the integrated intensity and $\sigma(I)$ its standard deviation. Absorption corrections, although very small, were applied by the Gaussian numerical-integration method. A Hf filter was employed to remove most of the second-order contamination. An estimated remaining 0·25% contamination was corrected for by calculation.

Thermal diffuse scattering (TDS) by acoustic modes of lattice vibrations peaks under the Bragg peaks. The relative contribution of the thermal inelastic scattering to the total integrated intensity, the so-called 'TDS correction factor', α, increases with $\sin\theta/\lambda$. The beryllium data sets extend to the very high value of $\sin\theta/\lambda = 2{\cdot}1$ Å^{-1}, so we may anticipate an appreciable contribution of TDS in the high-order reflexions even though beryllium is a very hard material. Correction for TDS is crucial when we want to determine parameters describing the atomic vibrations, since neglect of TDS will cause an apparent decrease, $\Delta(\langle u^2\rangle)$, of the mean-square amplitude of vibration determined from uncorrected integrated intensities, which can be evaluated by the approximate expression (Cooper, 1970)

$$(1+\alpha) = \exp\{16\pi^2\Delta(\langle u^2\rangle)[\sin\theta(hkl)/\lambda]^2\}.$$

For 0·525 Å neutrons, all phonon velocities were faster than the neutron velocity, whereas, at 0·425 Å, phonon velocities both larger and smaller than the neutron velocity were found. This difference does not affect the basic expressions for the scattering cross sections, but it does affect the scattering surfaces. For phonons which are slow relative to the incoming neutrons, as in the 0·425 Å case, the scattering surfaces for one-phonon processes are hyperboloids which approach the Ewald sphere as the ratio, β, between the phonon velocity and the neutron velocity goes to zero. We can then approximate our correction with the standard X-ray correction where the scattering surface is nearly identical to the Ewald sphere. For β larger than 1, the scattering surfaces are ellipsoids and, if these are sufficiently small, the full scattering surface may be seen during the whole scan and the TDS contribution to the scattered intensity will be constant (Willis, 1970; Cooper, 1971). Normal background subtraction will then correct for TDS. The width of the plateau, δ, in the TDS profile can easily be estimated (Cooper, 1971); it is a function of the ratio β, the detector aperture size and the Bragg angle $\theta(hkl)$. In the present case with $\beta \simeq 1{\cdot}2$ for transverse phonons, typical values for δ were 1·25 and 2·35° for $\theta(hkl)$ 10 and 70°, respectively, which are much smaller than the observed peak widths of 2·3 and 7·5° at the two Bragg angles. We are, therefore, far from the above-mentioned situation, even if we include resolution effects. Indeed, the situation resembles well the case for $\beta < 1$ where the detector sees a small, rather flat bit of scattering surface. We, therefore, choose to include in the calculations all phonons for which the plateau in the TDS profile was smaller than the width of the Bragg peak. A computer program for anisotropic one-phonon TDS correction (Merisalo & Kurittu, 1978) was modified slightly to take this into account. Corrections were then carried out for the data of the two wavelengths using elastic constants given by Smith & Arbogast (1960). Corrections at the two wavelengths were of the same order of magnitude. The relative contribution of thermal inelastic scattering to the total integrated intensity, the TDS correction factor α, at $\sin\theta/\lambda = 1$ has the average value 0·05 for both sets of data and at $\sin\theta/\lambda = 1{\cdot}75$ has the average values of 0·22 and 0·19 for the 0·425 and 0·525 Å data, respectively.

As the thermal motion in beryllium is nearly isotropic, a good estimate of the thermal parameter and the general quality of the data can be obtained from a Wilson (1942) plot. The crystal structure of beryllium at room temperature is hexagonal close-packed with two atoms in the unit cell in positions of point

symmetry $\bar{6}m2$ with coordinates $\pm(\frac{1}{3},\frac{2}{3},\frac{1}{4})$. The structure factor takes the form

$$F(hkl) = 2b_{\mathrm{Be}} \cos 2\pi[(h + 2k)/3 + l/4]T(hkl)$$
$$= b_{\mathrm{Be}} C(hkl)T(hkl).$$

The trigonometric factor $C(hkl)$ has one of four values 0, 1, $\sqrt{3}$, 2, thus giving three groups of non-zero reflexions. b_{Be} is the nuclear scattering factor [0·774 × 10^{-14} m (Bacon, 1972)] which is independent of scattering angle. Under the assumption of isotropic thermal movement the temperature factor $T(hkl)$ can be written

$$T(hkl) = \exp\{-8\pi^2 \langle u^2 \rangle [\sin \theta(hkl)/\lambda]^2\}.$$

The isotropic temperature factor $\langle u^2 \rangle$ can thus be deduced from a plot of the following function, the Wilson (1942) plot:

$$\ln[F_o(hkl)/C(hkl)] = \text{constant} - 8\pi^2 \langle u^2 \rangle \sin^2 \theta(hkl)/\lambda^2.$$

Fig. 1 shows the Wilson plot of the 0·425 Å data corrected for TDS. The general slope of the curve of points gives an estimated value of the mean-square amplitude of vibration $\langle u^2 \rangle$ = 0·00565 (5) Å^2. Extinction is noticed for this 27 mm^3 crystal, especially in the strongest low-order reflexions, the points of which fall below a straight line through all the points. On the figure, a line is drawn through the outermost extinction-free $00l$ points and a similar line through the $hk0$ points. The '$00l$' line has a smaller slope than the '$hk0$' line indicating $\langle u_x^2 \rangle > \langle u_z^2 \rangle$. The Wilson plot of the 0·525 Å data is even straighter than that of the 0·425 Å data and indicates hardly any extinction effects for the 8 mm^3 crystal.

Refinements

Refinements were carried out using a full-matrix least-squares program developed by R. G. Hazell of the Department of Chemistry, Aarhus University, to refine thermal parameters in the form of a cumulant expansion of the probability distribution function which describes the time-averaged vibrational displacement of the beryllium atom (Johnson, 1969, 1970). The quantity minimized was $\sum w(F_o^2 - k^2F_c^2)^2$ with $w = 1/[\sigma(\text{counting}) + pF_o^2]^2$. k is the scale factor and the summation is over all sets of observed and calculated structure factors F_o, F_c. In a weighting analysis, a value of p = 0·01 was found to give the flattest distribution of $\langle w(F_o^2 - k^2F_c^2)^2 \rangle$ as a function of both $\sin\theta$ and F_o. The program corrects for isotropic extinction following the theory of Becker & Coppens (1975). The results of the refinements are given in Table 1.*

In the general case, the second, third and fourth cumulant tensors have six, ten and fifteen independent elements, respectively, but the site symmetry of the atom may reduce the number of its independent cumulant parameters. Be atoms sit on special positions of $\bar{6}m2$ site symmetry which gives the constraints $b_{11} = b_{22} = 2b_{12} \neq b_{33}$, $b_{13} = b_{23} = 0$ for the second cumulant. In Table 1, the harmonic thermal parameters are listed as mean-square displacements in Å^2, $b_{11} \rightarrow \langle u_x^2 \rangle$ and $b_{33} \rightarrow \langle u_z^2 \rangle$. Note that their values determined from the two sets of data are almost identical although the degree of extinction is quite different for the two crystals. The smallest values of the inverse extinction correction factors, E, found in the refinements of each

* Lists of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34837 (6 pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

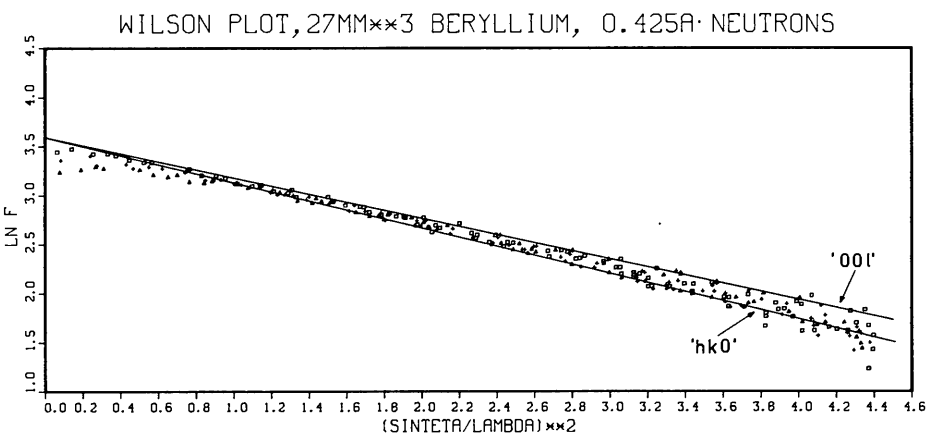

Fig. 1. Wilson (1942) plot, $\ln[F_o(hkl)/C(hkl)]$ = constant − $8\pi^2\langle u^2\rangle[\sin\theta(hkl)/\lambda]^2$ for the 0·425 Å neutron data. The three groups of non-zero reflexions are entered with separate marks. △ for the strongest, *i.e.* $C(hkl)$ = 2, + for $C(hkl) = \sqrt{3}$ and □ for the weakest, *i.e.* $C(hkl)$ = 1. The '$00l$' line is drawn through $00l$ points of $\sin\theta/\lambda > 1{\cdot}0$ Å^{-1}. The similar '$hk0$' line has smaller slope indicating $\langle u_x^2 \rangle > \langle u_z^2 \rangle$.

Table 1. *Crystal data for beryllium with thermal parameters from final refinements of neutron data*

The agreement factors are defined by $R(F^2) = (\sum |F_o^2 - F_c^2|/\sum F_o^2)^{1/2}$ and $wR(F^2) = (\sum w|F_o^2 - F_c^2|^2/\sum wF_o^2)^{1/2}$
$a = 2{\cdot}2858 \pm 0{\cdot}0002$, $c = 3{\cdot}5843 \pm 0{\cdot}0003$ Å at 293·5 K (Mackay & Hill, 1963).
Space group $P6_3/mmc$, hexagonal close-packed, two atoms per unit cell, positions $\pm(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$.

Crystal volume (mm³)	8·0	27·0
Neutron wavelength, λ (Å)	0·525	0·425
$\langle u_x^2 \rangle$ (Å²)	0·00586 (3)	0·00601 (3)
$\langle u_z^2 \rangle$ (Å²)	0·00536 (3)	0·00537 (3)
C_{112} (Å³)	0·00078 (14)	0·00083 (15)
$R(F^2)$	0·014	0·030
$wR(F^2)$	0·023	0·039
Number of observations	132	246
Number of variables	5	5
Goodness of fit	0·83	1·02
Smallest E	0·94	0·49

set of data are also shown in Table 1. The averaged values of the mean-square amplitudes are $\langle u_x^2 \rangle = 0{\cdot}00594$ (3) and $\langle u_z^2 \rangle = 0{\cdot}00537$ (3) Å². Fig. 2 shows atoms as the 99·9% probability distribution boundary ellipsoids in the harmonic approximation including only the second cumulants. The nearest and next-nearest neighbour surrounding of an atom is shown relative to the outlined hexagonal unit cell.

In order to test the hypothesis of anharmonicity of the thermal motion of beryllium even in room-temperature data (Stewart, 1977), the single third-cumulant parameter was included in the refinement. $C_{112} = -C_{222} \neq 0$; the rest of the ten C_{ijk}'s = 0 because of site symmetry. Introduction of the third cumulant which describes the antisymmetric behaviour of the probability distribution function gave a significant improvement in the agreement factor relative to that of the refinement in the harmonic approximation and resulted in small but significant third cumulants which, furthermore, were identical for the two sets of data. Inclusion of fourth cumulants gave inconclusive results. Agreement factors changed insignificantly and only the 0·525 Å data showed just-significant fourth cumulants which are very small in any case. The implication of the third cumulant can be illustrated in an Edgeworth map which displays the probability-distribution function represented by all the cumulants included. Fig. 3 is a section through the hexagonal basal plane and shows that there is an excess of thermal motion along the $[\bar{1}\bar{2}30]$ direction. It means that the atomic potential is softened towards the side which is part of the rectangular configuration of neighbouring atoms and hardened against the side which is part of the triangular configuration of neighbouring atoms. The deviation at room temperature from harmonic thermal vibration is small, as noted in the modest deviation from the circular 99·9% harmonic contour of the probability distribution function drawn in Fig. 3 as a broken line. This picture of the antisymmetric component of the thermal vibration is identical to our observations in a study of the room-temperature thermal vibrations in zinc (Merisalo & Larsen, 1979), which is also a hexagonal close-packed metal. However, in contrast to zinc, beryllium shows insignificant fourth cumulants at room temperature. The development with temperature of the thermal vibrations in beryllium is the subject of a subsequent neutron diffraction study.

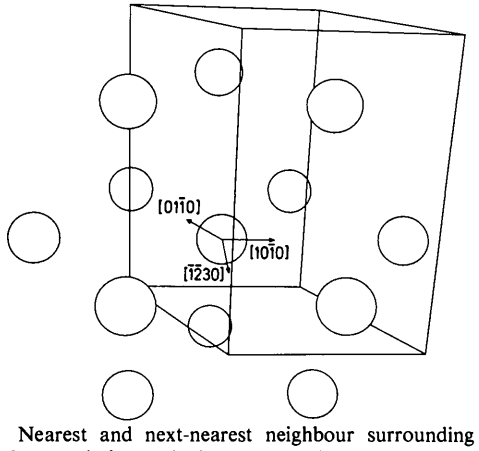

Fig. 2. Nearest and next-nearest neighbour surrounding a Be atom drawn relative to the hexagonal unit cell. Atoms are shown as the 99·9% harmonic probability distribution boundary ellipsoids.

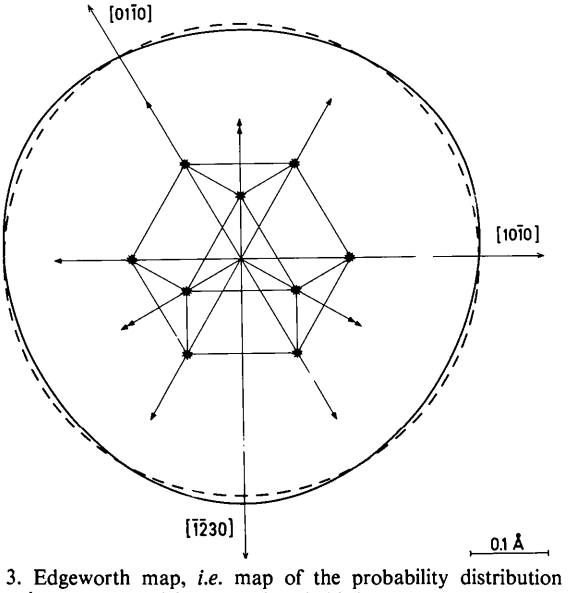

Fig. 3. Edgeworth map, *i.e.* map of the probability distribution function represented by second and third cumulants. A section through the hexagonal basal plane is shown. The central part of the figure, the stars interconnected with thin lines, is a projection of the shrinking (1/20) of the nearest and next-nearest neighbour atoms surrounding a Be atom, which is also indicated as arrows with one tip in the direction of nearest neighbours and arrows with two tips in the direction of next-nearest neighbours. The 99·9% probability distribution boundary contour is shown as a full line and indicates excess of thermal motion in the $[\bar{1}\bar{2}30]$ direction relative to the harmonic 99·9% probability distribution boundary contour, which is the broken line.

Table 2. *Comparison of mean-square amplitudes of vibration determined by neutron and X-ray diffraction*

Data	0·525, 0·425 Å neutrons	Ag $K\alpha$ X-rays extended crystal slabs Brown (1972)		Ag $K\alpha$ X-rays extended crystal slab	Ag $K\alpha$ X-rays small crystal
Refinements	This study	Stewart (1977)	Yang & Coppens (1978)	Manninen & Suortti (1979)	This study (FKL)
$\langle u_x^2 \rangle$ (Å^2)	0·00594 (3)	0·00724 (8)	0·00759 (12)	0·00583 ± 13	0·00611 (4)
$\langle u_z^2 \rangle$ (Å^2)	0·00537 (3)	0·00662 (15)	0·00686 (10)	0·00526 ± 13	0·00538 (4)

Conclusion

Table 2 summarizes the determinations of room-temperature mean-square displacements of beryllium obtained by neutron and X-ray diffraction. The difference between our neutron values and the values based on Brown's (1972) X-ray data is striking. A straightforward explanation would be that core electrons in the metallic form of beryllium are significantly expanded relative to those of the free atom. This observation supports the similar claim by Weiss (1978) based on an interpretation of Compton-profile data. However, the discrepancies between neutron and X-ray results were so substantial that redeterminations of the X-ray studies were initiated for both the thermal parameters (Manninen & Suortti, 1979) and the Compton profile (Manninen & Suortti, 1979; Hansen, Pattison & Schneider, 1979). The very recent X-ray study of the thermal parameters was performed on extended crystal slabs as in Brown's (1972) study. Absolute intensities of $h0l$ reflexions only were measured, but measurements were extended to larger scattering vectors ($0{\cdot}74 < \sin\theta/\lambda < 1{\cdot}40$ Å^{-1}) than in Brown's study ($\sin\theta/\lambda < 0{\cdot}88$ Å^{-1}). Furthermore, one of us (FKL) has collected a full set of Ag $K\alpha$ data extending to $\sin\theta/\lambda \leq 1{\cdot}44$ Å^{-1} using a small piece of crystal arc-cut and etched to the dimensions 0·1 × 0·25 × 0·30 mm. A refinement based on the 82 reflexions with $\sin\theta/\lambda > 0{\cdot}6$ Å^{-1} gives the thermal parameters $U_{11} = 0{\cdot}00611$ (4) and $U_{33} = 0{\cdot}00538$ (4) Å^2 for the agreement factors $R(F^2) = 0{\cdot}013$ and $wR(F^2) = 0{\cdot}012$. The two new X-ray determinations of the mean-square amplitudes are, as seen in Table 2, in excellent agreement with our neutron values, so we must conclude that the electron-density distribution of the core electrons is very similar for free-atom and metallic beryllium, which is also the conclusion from analysis of the new Compton-scattering results.

Since the valence-electron distribution is very diffuse, it contributes to the very-lowest-angle reflexions and so is only slightly affected by the thermal motion of the beryllium atom; therefore, we do not necessarily expect that our revised values for the mean-square amplitudes will change the picture of the valence-electron distribution presented by Brown (1972). In order, however, to extend our knowledge of the valence- and core-electron distribution, a further analysis of the small-crystal X-ray measurements is in progress.

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