The Electron Density and Bonding in Beryllium Metal as Studied by Fourier Methods*

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The bonding in Be metal is studied by calculation of valence and deformation density maps from data collected by Brown [*Philos. Mag.* (1972), **26**, 1377–1394]. The deformation maps show clearly that the predominant interaction is bonding through the tetrahedral holes of the h.c.p. lattice. The valence-density maps generally agree with least-squares-model maps published by Stewart [*Acta Cryst.* (1977), A**33**, 33–38], though differences in detail exist which may result from incomplete space filling of the least-squares model functions. The experimental densities are interpreted in terms of the hybrid-orbital model of Altmann, Coulson & Hume-Rothery [*Proc. R. Soc. London Ser. A*, (1957), **240**, 145–155] as corresponding to $(sp^2)^a(sp)^b$ hybridization of the Be atoms with $b > a$. Agreement with a theoretical density obtained by the augmented plane wave calculation of Inoue & Yamashita [*J. Phys. Soc. Jpn.* (1973), **35**, 677–683] supports both theoretical and experimental procedures.

Introduction

Beryllium in its metallic state has a hexagonal close packed (h.c.p.) structure. Though the appearance of this structure in $3d$ transition metals is correlated with an increasing participation of d orbitals in bond formation (Altmann, Coulson & Hume Rothery, 1957), this explanation is obviously not applicable in the case of Be. Brown (1972) from an analysis of 27 carefully measured absolute-scale structure factors concluded that tight binding must contribute to the bonding in crystalline Be in addition to metallic bonding. Brown's data were recently reanalyzed by Stewart (1977) who fitted an atom-centered spherical-valence monopole plus three higher multipoles to the experimental data and subsequently obtained the valence density as a plot of the multipole functions. This multipolar density analysis is attractive as it provides an analytical description of the density which in addition to its other merits, may also contain less noise than a regular Fourier map. Unlike Fourier methods, the technique may also be applicable in cases where the data set does not contain all reflections within a certain reciprocal radius. On the other hand, some of the features observed in the model maps (*i.e.* the plot of the least-squares functions) may be artifacts due to the nature of the functions selected, or to the possible incompleteness of the function set. In the case of Be, Stewart fitted the density with a set of three functions selected by a systematic search of all triples of surface harmonic

functions, y_{lm} with $l < 7$ which obey the $6m2$ site symmetry of the h.c.p. structure. But higher functions may be of importance and the radial description may be too restrictive, so a comparison with Fourier results is appropriate.

The present study is the first comparison of valence and deformation densities obtained by Fourier methods with densities obtained from least-squares refinement models. Preliminary reports of subsequent studies on tetracyanoethylene, *p*-nitropyridine *N*-oxide and ammonium thiocyanate have been presented elsewhere (Hansen & Coppens, 1976; Price, Hansen & Coppens, 1977). A second aim of this work is a more detailed analysis of the covalent contribution to the bonding in metallic Be.

Least-squares refinement and calculation of density maps

The valence and deformation densities calculated here are respectively defined as

$$\rho_{\text{valence}} = \rho_{\text{exp}} - \sum_{\substack{\text{all} \\ \text{atoms}}} \rho_{i,\text{core}}$$

and

$$\rho_{\text{deformation}} = \rho_{\text{exp}} - \sum_{\substack{\text{all} \\ \text{atoms}}} \rho_{i,\text{free atom}}$$

and obtained by Fourier transform of the difference structure factors $(F_{\text{obs}} - F_{\text{core}})$ and $(F_{\text{obs}} - F_{\text{free atom}})$, where the sign of F_{obs} is as calculated for $F_{\text{free atom}}$. Calculation of the structure factor requires knowledge of the positional and thermal parameters of the Be atoms. The former are fixed by symmetry, while the latter are obtained in a refinement using 17 reflections

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Table 1. *Results of spherical-atom least-squares refinements*

Crystal data: Space group $P6_3/mmc$; $a = 2.2858$ (2); $c = 3.5843$ (3) Å (Mackay & Hill, 1963). Be at $\frac{1}{3},\frac{2}{3},\frac{1}{4}$ and the symmetry-equivalent position $\frac{2}{3},\frac{1}{3},\frac{3}{4}$.

	Isotropic	Anisotropic		
$\sin\theta/\lambda$ (Å^{-1})	0·50–0·90	0·00–0·90	0·50–0·90	0·60–0·90
U_{11} (Å^2)*	0·00743 (7)	0·0080 (3)	0·00768 (13)	0·00759 (12)
U_{33} (Å^2)*		0·0071 (3)	0·00689 (12)	0·00686 (10)
Number of observed parameters n_o	18	27	18	13
Number of variables n_v	1	2	2	2
$R(F)$ (%)	1·5	3·2	1·3	1·0
$R_w(F)$ (%)	1·3	3·2	1·2	0·8
G†	4·11	10·22	3·31	2·75

* Values from the multipole refinement: $U_{11} = 0.0072$ (1); $U_{33} = 0.0066$ (2) Å^2 (Stewart, 1977).

† G = goodness of fit defined as $G = \left[\sum w \dfrac{(F_o - |kF_c|)^2}{n_o - n_v} \right]^{\frac{1}{2}}$

with $\sin\theta/\lambda > 0.5$ Å^{-1} ($\sin\theta/\lambda_{max} = 0.90$ Å^{-1}), and Hartree–Fock atomic form factors as given by Fukamachi (1971).* It may be noted that this cut-off would not be adequate to eliminate bonding effects in strongly covalent crystals where valence scattering persists much beyond this limit, but comparison with

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* Copies of the Be scattering factors used are available from the authors on request.
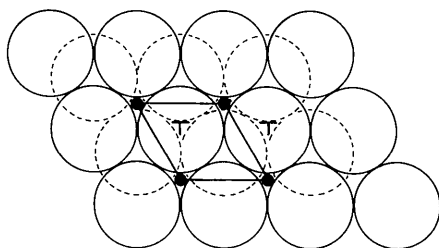

Fig. 1. The hexagonal close-packed structure indicating the positions of the tetrahedral (T) and octahedral (O) holes.

results using higher cut-off values shows it to be satisfactory in the case of Be metal. Results are summarized in Table 1. The goodness of fit is considerably improved in the high-order refinement in comparison with the full-data treatment, as may be expected when the free-atom model is inadequate in the low-order region. But the relatively high value of G even in the range 0·60–0·90 Å suggests that Brown's experimental standard deviations may have been underestimated by a factor of perhaps 1.5. As found by Stewart (1977), the anisotropy of the thermal motion is not significant when all data are included in a spherical-atom refinement. This result is not confirmed by the high-order refinement which indicates a smaller thermal motion along the c axis in agreement with Stewart's multipole analysis, though the present temperature factors are about 5% higher than those given by Stewart (Table 1). As illustrated by the density maps discussed below, part of the apparent isotropy in the full-data refinement is due to an accumulation of charge in the tetrahedral holes of the h.c.p. structure which are located above and below each of the Be atoms (Fig. 1).
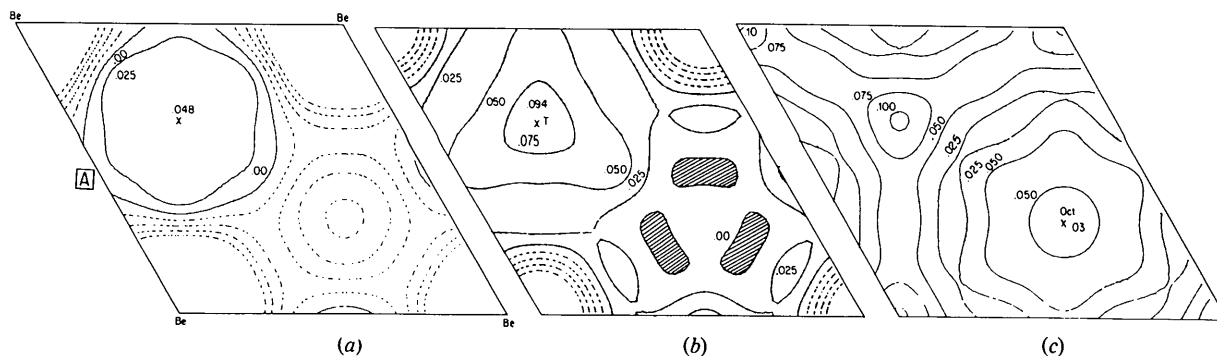

Fig. 2. Deformation-density maps in sections parallel to (001). Contours at 0·025 e Å^{-3}. Negative contours broken. Contours below −0·10 e Å^{-3} have been omitted. Cross-hatched areas are slightly negative. (a) $z = \frac{3}{4}$, the positions of four Be atoms are indicated. (b) $z = \frac{5}{8}$. T: tetrahedral site. (c) $z = \frac{1}{2}$. Oct: octahedral site.
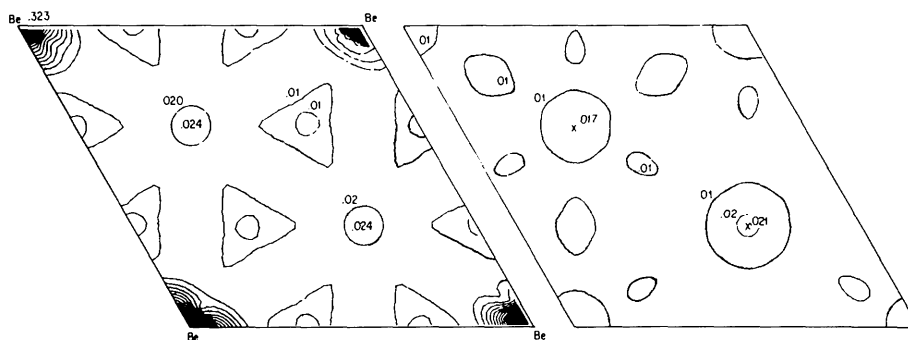
Fig. 3. Deformation-density error-distribution maps in sections parallel to (001). Contours at 0.01 e $Å^{-3}$. (a) $z = \frac{3}{4}$. (b) $z = \frac{1}{2}$.
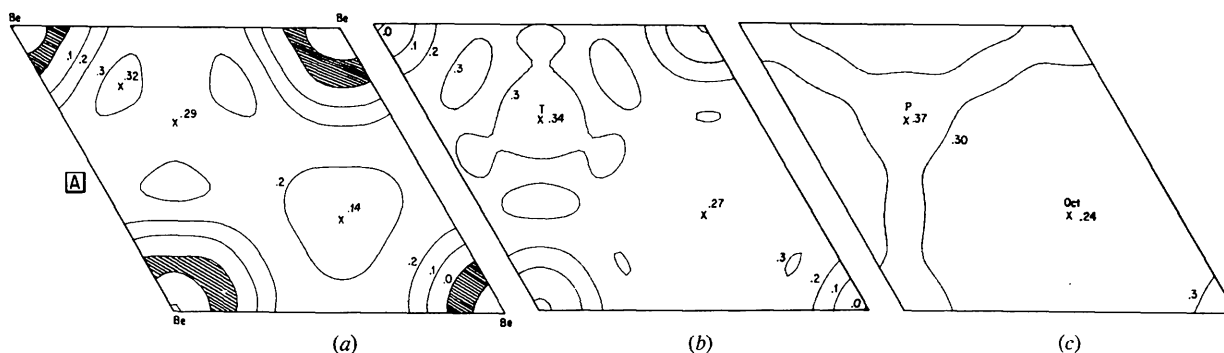

Fig. 4. Valence-density maps in sections parallel to (001). Contours at 0·10 e $Å^{-3}$. Negative areas cross-hatched (note that these negative areas are not statistically significant). (a) $z = \frac{3}{4}$. (b) $z = \frac{5}{8}$. (c) $z = \frac{1}{2}$.

The deformation density in three sections parallel to (001) are given in Fig. 2, while error maps, calculated as described elsewhere [Stevens & Coppens 1976; equations (5), (11) and (12)] are given in Fig. 3. The

Fig. 5 Valence density in the (110) plane. Contours as in Fig. 4. The tetrahedral, octahedral and Be sites are indicated, as are the positions of the density maxima (P).

sections shown are at (a) $z = \frac{3}{4}$ which is the hexagonal close-packed plane containing the Be atoms; (b) at $z = \frac{5}{8}$ which contains the tetrahedral sites (marked T); and (c) at $z = \frac{1}{2}$ which contains the octahedral sites (marked O). The errors in the deformation maps are smaller than 0·024 e $Å^{-3}$, except at the nuclear positions (about 0·32 e $Å^{-3}$) where the experimental density is notoriously unreliable. But, features in other regions are clearly significant. Noticeable are the accumulation of density in the tetrahedral hole as opposed to the octahedral holes and the low value of the deformation density in the plane through the Be atoms parallel to (001). These features are much clearer than in the valence maps (Figs. 4 and 5) in which the octahedral hole also receives density from each of the unperturbed valence shells of the six adjacent Be atoms so that the ratio ρ(tetrahedral)/ρ(octahedral) which is 0·094/ 0·03 = 3·1 in the deformation function is reduced to 0·37/0·24 = 1·5 in the valence density. Because the deformation function exclusively represents the redistribution of electrons on bond formation it is often more suitable for analysis of bonding than the valence density.
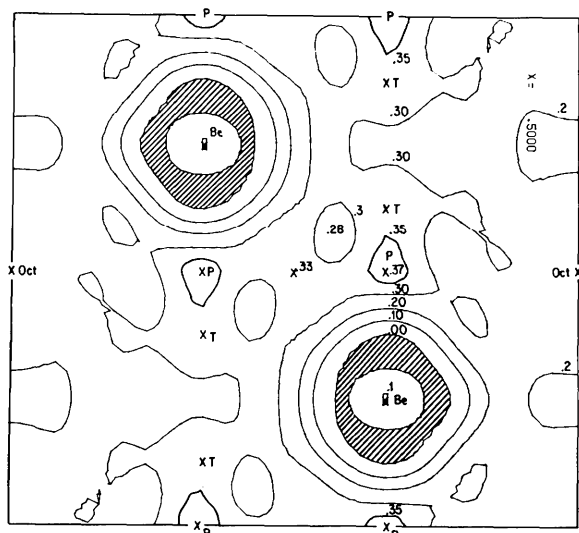
Comparison of least-squares and Fourier methods

Stewart (1977) has constructed the static valence-electron-density maps from the atomic deformation

functions (which are a monopole plus three harmonic functions): P_5^3 (cos θ) sin 3φ, P_6^0 (cos θ) and P_7^3 (cos θ) sin 3φ. Because the thermal parameters are not included, the maps correspond to an extrapolation of the experimental information to zero thermal motion and infinite resolution. But in the case of Be with its diffuse valence density and low thermal motion we may expect the main features in the least-squares model density (LSMD) and the experimental valence density (EVD) to be similar. The maximum valence-density peaks appear at the same position in the tetrahedral holes in both maps and are comparable in height (LSMD: 0·33 e Å⁻³, EVD: 0·37 e Å⁻³), but a peak of about 0·29 e Å⁻³ is found at the octahedral site in the model map which is only a saddle point at 0·24 e Å⁻³ in the experimental density. The ratio of the peak height in the tetrahedral hole to $\rho_{\text{octahedral}}$ is about 1·13 in the LSMD vs 1·5 in the EVD. Thus, the evidence for preferential bonding through the tetrahedral hole is much stronger in the present study. Such differences may be a result of incomplete space filling of the least-squares-model functions. In general, however, the two methods give comparable results and the experimental valence densities support the validity of the least-squares procedure.

The nature of bonding in Be

Although it is often stated that the metallic bond is non-directional in character, the bonding in metals may be more directional than has commonly been admitted. This view was adopted by Altmann, Coulson & Hume-Rothery (1957) who developed a theory linking the crystal structures of transition metals with appropriate hybrid atomic orbitals. The hexagonal close-packed structure is described as $(spd^4)^a(pd^5)^b(sd^2)^c$ where a, b, c are the relative populations of each of the hybrid orbitals. Such an explanation is, of course, not relevant to the Be structure where d orbitals cannot participate, but the principle of partially occupied atomic hybrids is useful in describing bonding in electron-deficient systems where the number of atomic neighbors far exceeds the number of available electron pairs.

Beryllium has two valence electrons in its atomic $2s$ level; thus a crystal of N atoms would have a completely filled valence band with N levels populated by $2N$ electrons, and accordingly be an insulator. The conductivity of Be metal has been explained by Inoue & Yamashita (1973) by the overlap of the $2s$ and $2p$ atomic levels which becomes important when Be atoms are brought closer than about 1·6 times the interatomic distance in beryllium. Thus, physical properties indicate mixing of the s and p orbitals in Be crystals. According to the deformation and valence maps, the bonding scheme in terms of overlap of partially populated hybrid orbitals for Be may be described as $(sp^2)^a(sp)^b$. The sp^2 hybrids account for the bonding to the in-plane
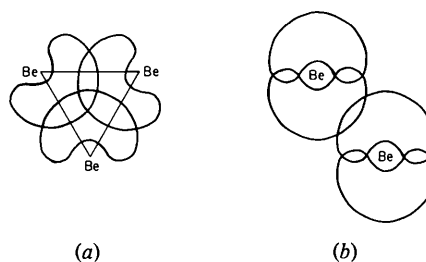

Fig. 6. Schematic representation of hybrid bonding (a) in the plane of the hexagonal close-packed layers, (b) between layers.

neighbors and are represented by the three peaks surrounding each Be atom in the plane parallel to (001), and thus form a multi-center bond in this plane. The two sp hybrids are in the direction of the c axis into the tetrahedral hole and can overlap sideways with sp hybrids pointing down from the subsequent layer and with the triple of sp^2 hybrids at the triangles which form the base of the tetrahedral hole (Fig. 6). Since each atom has two sp hybrids, one pointing up and one pointing down, the stacking sequence $ABAB\cdots$ of the h.c.p. lattice is logically accounted for. The density maps further show that the sp hybrids have more density than the sp^2 orbitals, i.e. $b > a$. This is in full agreement with the observation that the c/a ratio in Be is smaller than the value of 1·633 for the ideal hexagonal close-packed structure, indicating stronger bonding between than within layers.

An augmented plane wave (APW) calculation of beryllium has been performed by Inoue & Yamashita (1973). The position and peak height (0·32 e Å⁻³) of the maximum in the tetrahedral hole are in very satisfactory agreement with both Stewart's least-squares-model map and with the experimental maps presented here. The ratio of the maximum densities in the tetrahedral and octahedral holes is 1·4, which is quite close to its experimental value of 1·5. The almost quantitative agreement between theory and experiment is quite remarkable and suggests that further insight into bonding in metals and alloys may be obtained by analysis of either experimental or theoretical charge distributions.

References

ALTMANN, S. L., COULSON, C. A. & HUME-ROTHERY, W. (1957). Proc. R. Soc. London Ser. A, 240, 145–155.
BROWN, P. J. (1972). Philos. Mag. 26, 1377–1394.
FUKAMACHI, T. (1971). Tech. Rep. of the Institute for Solid State Physics, Univ. of Tokyo, Series B, No. 12.
HANSEN, N. K. & COPPENS, P. (1976). ACA Progr. Abstr. Ser. 2, 4, 54.

INOUE, S. T. & YAMASHITA, J. (1973). *J. Phys. Soc. Jpn.* **35**, 677–683.

MACKAY, K. J. H. & HILL, N. A. (1963). *J. Nucl. Mater.* **8**, 263–264.

PRICE, P. F., HANSEN, N. K. & COPPENS, P. (1977). *ACA Progr. Abstr. Ser.* 2, **5**, 28.

STEVENS, E. D. & COPPENS, P. (1976). *Acta Cryst.* A**32**, 915–917.

STEWART, R. F. (1977). *Acta Cryst.* A**33**, 33–38.

Modeling of Face-Centered Cubic Solid Solutions*

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A computer program has been written to simulate binary face-centered cubic solutions by interchanging the atoms until the populations in 18 shells are in agreement with the short-range order parameters obtained from diffuse X-ray measurements. Comparisons are made between the intensity maps from the model and from the data for most of the published work. We conclude that the published data are of reasonable quality, although sometimes the alphas are somewhat too large or the intensity maps contain artifacts. Computer simulation can be useful in rectifying errors in the experimental parameters.

Introduction

Since it is known that all the diffuse scattering that occurs solely as the result of the nonrandomness in solid solutions is representable in terms of the Warren–Cowley short-range order parameters, it follows that only these parameters can be calculated from the observations of diffuse scattering. These parameters, called alphas, are related to the average composition within a given shell around a given central atom. Thus, they are expressible in terms of conditional probabilities. Having obtained a set of alphas, one normally wants to answer certain questions about the nature of the solution, questions that cannot be answered directly from the alphas but which could be addressed by use of a physical model. The problem of translating the alphas into a model that will reproduce them is a rather formidable task because of the large number of atoms that must be used to obtain the desired statistical accuracy.

Gehlen & Cohen (1965) first solved this problem by devising a computer program that rearranged the two kinds of atoms until the desired populations were obtained in the first three shells. The author devised a similar program (Williams, 1970) and over the years kept including more and more shells in the simulation without necessarily ever getting entirely satisfactory agreement between the data and the model. In particular, in the case of a copper-base aluminum alloy,

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seven shells were not sufficient (Williams, 1974). Because of this continuing frustration of not being able to obtain the desired level of agreement, we decided to rewrite our program to model 18 shells in the hope that this would always be sufficient. Because of the large number of sites involved, we implemented the most efficient algorithm that we could devise. The possible small differences of the results produced by the new algorithm are masked by the effect of the inclusion of many more shells. The new program has been documented in a recent report (Williams, 1976).

As an extensive test of this new program, we have modeled most of the reasonably complete sets of data for face-centred cubic solutions. This was done not only to obtain a good base of experience with the new program, but also to determine the extent to which such simulation can identify and remove deficiencies in data sets. We have also included some information that characterizes the modeling process.

Model generation

The documentation report (Williams, 1976) gives the complete program along with the details of how it operates. Our comments here are limited to those required to made the present paper self-contained.

For a given model, one can calculate the number of 1–1 pairs for each shell that will agree with a prescribed set of alphas. (The minor species is identified as 1, the major as 0.) A pair is formed by a central 1 atom and a 1 atom in a shell. Further, at any stage of modeling one