Ab initio study of structural and electronic properties of beryllium

M. Y. Chou, Pui K. Lam, and Marvin L. Cohen

Department of Physics, University of California, Berkeley, California 94720
and Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720
(Received 18 May 1983)

An *ab initio* calculation of the structural and electronic properties of beryllium is presented. The calculational method used is the self-consistent pseudopotential approach within the local-density-functional scheme. The calculated lattice constants, cohesive energy, bulk modulus, Poisson's ratio, electronic band structure, density of states, and charge density are all in good agreement with the experimental measurements.

I. INTRODUCTION

Beryllium has attracted a lot of theoretical and experimental interest because of its simple atomic electronic configuration and anomalous physical properties. The crystal structure is hexagonal close packed with only two valence electrons per atom. The experimental c/a ratio is 1.586,[1,2] which is smaller than the ideal ratio of 1.633 by 3%. The Debye temperature is very high[3] (1440 K) compared with close neighbors in the Periodic Table, e.g., lithium (344 K) and magnesium (400 K). Poisson's ratio is extraordinarily small (about 0.05), 1 order of magnitude smaller than those of other common metals. It has been suggested that the electronic structure of beryllium metal deviates substantially from that of a free-electron-gas model.

Several *ab initio* calculations on beryllium have been performed. Janak *et al.*[4] used the augmented-plane-wave (APW) method in the local-density-functional formalism to study the thermomechanical properties. However, their calculation assumes that beryllium is in the fcc structure. Dovesi *et al.*[5] employed a Hartree-Fock (HF) linear combination of atomic orbitals (LCAO) self-consistent-field (SCF) method. The agreement between the calculated lattice constants and those measured is good, but the static structural properties are not calculated.

The present work presents an *ab initio* calculation of various properties of beryllium. The pseudopotential method[6] in the local-density-functional scheme[7] is employed. This first-principles approach has been applied to a wide range of systems, such as Si,[8] Ge,[8] C,[9] Sn,[10] and Al,[11] and it has been very successful in predicting the lattice constants, static structural properties, and phase transitions. The only input needed is the atomic number and information about the crystal structure. The calculational results include both structural and electronic properties. A brief report on the static structural properties has been published.[12] By minimizing the total energy, the predicted lattice constants a and c are in good agreement with the experimental values. The bulk modulus and Poisson's ratio are also in reasonably good agreement with experiment. The electronic properties, such as the band structure, the density of states, and the charge density, are also

presented in this paper. From the angular-momentum-projected density of states, we find that the amount of p-like character of the electrons in the crystal is about twice as much as s-like character. In other words, when the crystal is formed, a large fraction of the $2s$ valence electrons of the beryllium atom are promoted to p states. The role these p-like electrons play in the crystal binding is under investigation.

The rest of this paper is organized as follows: The calculational method is described in Sec. II, the structural properties are discussed in Sec. III, the electronic properties are examined in Sec. IV, and the conclusion is given in Sec. V. The computed Compton profiles, which are closely related to the electron-momentum distribution, are reported in detail in a separate paper.[13]

II. CALCULATIONAL METHODS

This calculation is based on the pseudopotential approach[6] within the local-density-functional formalism.[7] The core electrons are assumed to be frozen, i.e., to be atomiclike, and only the valence electrons are allowed to respond to the change in the chemical environment. The pseudopotential used is angular momentum dependent and is required to reproduce the results of all-electron calculations in the atomic limit, including the energy eigenvalues, eigenfunctions (outside the core region), and also the excitation energies in various electronic configurations. In the density-functional scheme a Schrödinger-type equation is obtained in varying the ground-state energy functional and it is solved self-consistently.[7] The advantages and limits of this approach have been discussed previously.[8]

In this work the norm-conserving pseudopotentials[14] are generated from the atomic configuration of Be $(1s^2 2s^1 2p^1)$. These pseudopotentials can reproduce the all-electron energy eigenvalues to within 10^{-3} Ry and excitation energies to within 10^{-4} Ry. The Hedin-Lundqvist[15] formula for the correlation energy is employed for both the atomic and solid calculations. We have also checked the effect of changing the correlation term by performing the calculation using the Wigner correlation formula,[16] which gives bulk modulus and cohesive energy slightly closer to the experimental values

than the Hedin-Lundqvist formula, but the lattice constants and Poisson's ratio are about the same. A plane-wave basis set is used to expand the crystal wave functions and the energy per unit cell is calculated in the momentum-space representation.[17] This energy is the total crystal energy for the system consisting of valence electrons and ionic cores. By investigating the total energy, it is possible to predict theoretically the static structural properties, crystal stability, and phase transitions.[8-11] Since beryllium is in the hexagonal close packed structure, there are two independent lattice parameters a and c. By examining the change in total energy with respect to the lattice parameters, the theoretical lattice constants, the cohesive energy, Poisson's ratio, and the bulk modulus can be obtained. The band structure, the density of states, and the charge density are also computed assuming the experimental lattice constants.

III. STRUCTURAL PROPERTIES

A. Lattice constants and cohesive energy

In the present work, the energy minimum is found for lattice constants $a = 4.255$ a.u. and $c = 6.75$ a.u. The cohesive energy is computed as the difference between the crystal energy and the energy of the pseudoatom. Since beryllium has the highest Debye temperature of the elements other than carbon ($\Theta_D = 1440$ K),[3] the correction due to the zero-point vibrational energy cannot be ignored. It is estimated to be $\frac{9}{8} k_B \Theta_D$ in the Debye model,[18] which is of the order of 0.14 eV. The cohesive energy in the calculation is found to be 3.86 eV/atom. If the Wigner correlation formula is used, the calculated lattice con-

stants are almost the same as these computed using the Hedin-Lundqvist functional, but the cohesive energy (3.60 eV/atom) is closer to the experimental value 3.32 eV/atom.[19] A comparison of the theoretical and experimental values is given in Table I. The lattice constants a, c, and the c/a ratio are in good agreement with the measured values; the deviations from experimental values are about 1–2%, which is of the same order as other previous local-density-functional calculations.[8-11] Beryllium has the smallest c/a ratio among hexagonal close packed elements, and this result is also predicted successfully. The theoretical cohesive energy is less accurate, about 8% larger than that observed, which is also consistent with previous local-density-functional calculations.[8-11] A possible explanation could be that the local-density functional is not accurate for the atom where the electronic density varies very rapidly. In fact, the calculated total energy of the pseudoatom is -27.19 eV, while the experimental ionization energy of Be^{2+} is 27.53 eV.[3] This difference is consistent with the 0.3-eV deviation of the cohesive energy from the observed value in this calculation.

Janak et al.[4] calculated the thermomechanical properties for beryllium using the APW method in the local-density-functional approach where the fcc structure is assumed for the crystal. They obtained an atomic volume 4.5% smaller that observed, and a larger cohesive energy of 4.00 eV/atom (see Table I). Dovesi et al. have also reported an ab initio calculation for beryllium in the hcp structure, using the HF SCF LCAO method.[5] The calculated lattice constants are listed in Table I. The agreement with experiment for the lattice constants is about the same as in the present calculation. However, other properties of beryllium were not calculated in the HF calculation.

TABLE I. Comparison of the calculated lattice structural properties with experimental values and previous calculations.

	Experiment	Present work	Calculations Janak et al. (Ref. 4)	Dovesi et al. (Ref. 5)
a (Å)	2.2850 ± 5,[a] 2.2858 ± 2[b]	2.25	3.14 (fcc)	2.29
c (Å)	3.5847 ± 5,[a] 3.5843 ± 3[b]	3.57		3.59
c/a	1.569,[a] 1.568[b]	1.586		1.568
Cohesive Energy (ev/atom)	3.32[c]	3.60	4.00	
Bulk Modulus (10^{12} dyn/cm^2)	1.27[d] 1.14,[e] 1.10[f]	1.31	1.35	
Poisson's ratio	0.05,[e] 0.02[f]	0.05		

[a]Reference 1.
[b]Reference 2.
[c]Reference 19.
[d]Reference 24.
[e]Reference 21.
[f]Reference 22.

B. Poisson's ratio

With the total energy as a function of lattice constants a and c, it is possible to determine Poisson's ratio theoretically. Poisson's ratio is defined[20] as the negative ratio of the transverse strain to the corresponding axial strain in a body subject to uniaxial stress, and can be written as

$$\sigma = -\frac{\Delta a/a}{\Delta c/c} = -\frac{d\ln a}{d\ln c} \; . \tag{1}$$

Therefore, we are interested in the change of lattice constant a when the crystal is compressed or expanded along the c axis. For a given lattice constant c, the value of the lattice constant a, with the lowest energy, is determined.[12] These points, a vs c, are plotted on a logarithmic scale and a straight line is expected (Fig. 1). Poisson's ratio is the negative of the slope, which is found to be 0.05. This result has a very small dependence on the correlation formulation used.

For most materials, Poisson's ratio is similar and ranges from 0.3 to 0.4. Beryllium is an anomalous material having the minimum's ratio, 1 order of magnitude smaller than the standard value. Experimental values for Poisson's ratio of beryllium vary from 0.02 to 0.05.[21,22] Although our calculated Poisson's ratio is not as accurately determined as the lattice constants due to the accuracy of the total energy, it is still within the experimental limits (Table I).

C. Bulk modulus

The bulk modulus B^0 is given by

$$B^0 = V_0 \frac{\partial^2 E}{\partial V^2} \; , \tag{2}$$

where V_0 is the equilibrium volume. For every volume the minimum energy and the corresponding c/a ratio are found.[12] The energy-versus-volume curve is shown in Fig. 2 where the solid line is a nonlinear least-squares fit using Murnaghan's equation of state.[23] The fit is better than 1.5×10^{-4} Ry and the bulk modulus is found to be 1.37×10^{12} dyn/cm^2. If the Wigner correlation functional is used the bulk modulus is 1.31×10^{12} dyn/cm^2. The experimental bulk modulus, which is computed from the
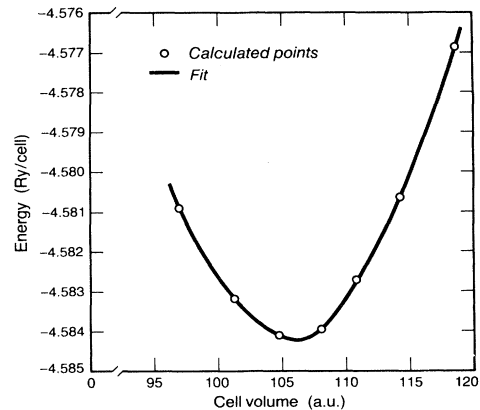
FIG. 2. Total energy per cell as a function of volume. Solid curve is obtained by fitting Murnaghan's equation of state to the calculated values.

measured elastic constants, ranges from 1.10×10^{12} to 1.27×10^{12} dyn/cm^2.[21,22,24] It appears that the Wigner correlation gives better results. The bulk modulus reported in the APW calculation by Janak *et al.*[4] is 1.35×10^{12} dyn/cm^2; they also employed the local-density-functional method with the Hedin-Lundqvist expression for the exchange-correlation potential. The similarity of the results obtained by the APW calculation and our pseudopotential calculation indicates that the deviation from the experimental values is not a result of the pseudopotential scheme. Also it cannot be concluded that the discrepancy between the experimental and calculated bulk modulus is caused by the local-density-functional method owing to the large range of experimental values.

IV. ELECTRONIC PROPERTIES

A. Band structure

A ball-and-stick model of the hcp structure is given in Fig. 3(a) and the first Brillouin zone is shown in Fig. 3(b) with symmetry points specified. Several band-structure calculations of beryllium have been reported.[5,25–29] The Fermi surface has also been studied extensively using different methods.[30–34] It is suggested that the Fermi surface consists of two parts: (1) a six-cornered hole surface known as a "coronet" in the second Brillouin zone, and (2) six equivalent electron surfaces, known as "cigars" in the third Brillouin zone, with the axes along the $H-K$ symmetry direction.

The band structure from the present calculation (Fig. 4) is quite similar to the results from previous calculations. The topology of the Fermi surface is consistent with experiment. The first energy band does not deviate too much from that obtained assuming a free-electron gas, but higher bands split and generate crossings and other complexities. Since the local-density-functional approach is strictly applicable to ground-state properties only, the optical properties of beryllium are not discussed in the present work.
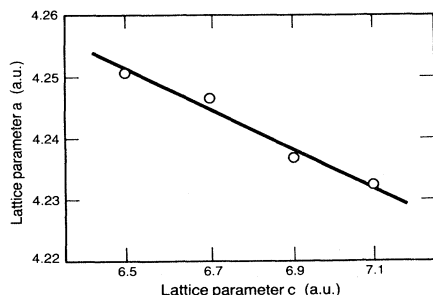

FIG. 1. Lattice constant a which gives the minimum total energy for a fixed lattice constant c. Plot is based on a logarithmic scale. Negative slope is Poisson's ratio which is found to be 0.05.
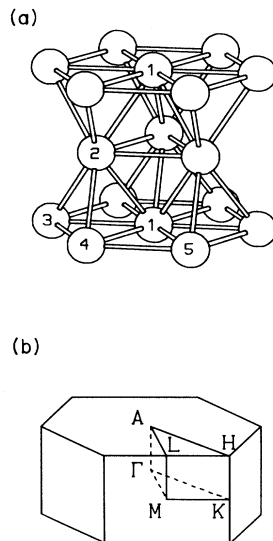
(a)

(b)

FIG. 3. (a) Ball-and-stick model for the hcp structure. Charge-density maps containing these labeled atoms are shown in Figs. 6 and 7. (b) First Brillouin zone of the hcp structure with symmetry points specified.

FIG. 5. Total density of states per atom for beryllium in the hcp structure. Fermi energy (0.82 Ry) is shown by a vertical line. (b) The contributions to the density of states from different angular momenta of the wave functions. Contribution from p_y, which is not shown in this figure, is the same as that of p_x.

B. Density of states

The total density of states is shown in Fig. 5 together with the individual contributions from different angular momenta of the wave function. The characteristic feature of the total density of states is the dip near the Fermi level. This dip appears in both s and p bands. According to the decomposition, the numbers of electrons with characters s, p_x (or p_y), and p_z are 0.63, 0.41, and 0.44 per atom, respectively, where z is chosen to be along the c axis. Although the atomic valence configuration of beryllium is $2s^2$, a large amount of electrons appear to have p character in the solid. The p_x (or p_y) component is very similar to the p_z component; there is no strong anisotropy in the density of states. However, the small difference between p_x (or p_y) and p_z density of states at about 0.6 Ry may be important for the observed small c/a ratio. For the ideal c/a ratio, we find that the p_x, p_y, and p_z components are almost indistinguishable below the Fermi level. Higher angular-momentum components ($l = 2$ and above) are not
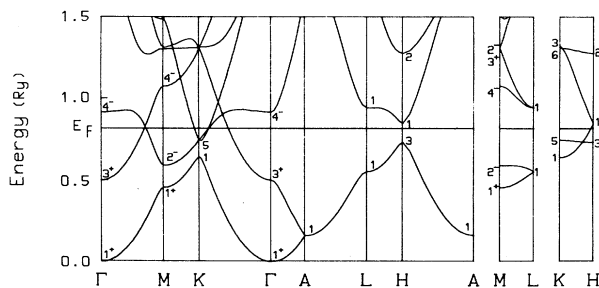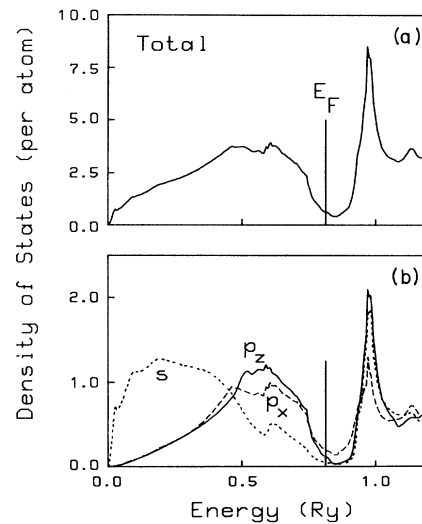
shown in Fig. 5; they contribute to the density of states mainly through the unoccupied states above the Fermi level. Below the Fermi level, the s band and p band overlap to a large extent. Both the band structure and the density of states suggest that there is a large deviation from the free-electron model near the Fermi level.

C. Charge density

The valence charge density is obtained directly from the self-consistent calculation. A contour plot of the valence
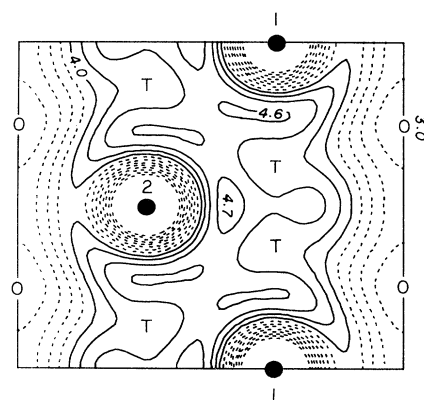

FIG. 6. Contour plot of the calculated valence charge density for beryllium in the $(11\bar{2}0)$ plane passing through the two nearest-neighbor atoms, atom 1 and 2. Atoms are denoted by filled circles. Numerical labels are the same as in Fig. 3(a). Units are electrons per cell volume. Contours are plotted in intervals of 0.2. Contours with a charge density smaller than 4.0 (the average charge density) are shown with dashed lines. Contours with a charge density smaller than 2.8 are not shown. Tetrahedral holes are marked by T and the octahedral holes by O.

FIG. 4. Calculated band structure for hcp beryllium. Fermi energy is 0.82 Ry. First Brillouin zone is shown in Fig. 3(b).

charge density in the $(11\bar{2}0)$ plane, parallel to the c axis and passing through the nearest-neighbor atoms, is shown in Fig. 6, with corresponding atoms labeled in Fig. 3(a). The contours are in intervals of 0.2 electrons per cell volume with dashed lines representing a charge density smaller than the average charge density, 4.0 electrons per cell volume. The departure from the free-electron model is also evident here. Charge is accumulated in the region near the atoms. The charge binds the nearest-neighbor atoms and two successive A planes in the packing form *ABAB* of the hcp structure. Another important feature is that the charge variation is much larger along the horizontal direction than along the c axis. A similar plot in the (0001) basal plane is shown in Fig. 7. The charge accumulates in the triangular region between atoms 1, 3, and 4, where there is an atom above and another atom below the center of the triangle. The p character of electrons makes the charge transfer possible. It has been claimed that the bonding is stronger along the c axis than in the basal plane.[28] According to the charge-density maps we find that the highest peaks in the (0001) basal plane and in the $(11\bar{2}0)$ plane are of the same order. However, unlike semiconductors, the highest peaks (with a charge density of 4.7 electrons per cell volume) do not depart dramatically from the uniform charge density (4.0 electrons per cell volume).

X-ray-diffraction studies of beryllium have been performed by Brown[35] and more recently by Larsen and Hansen.[36] The two sets of structure factors are quite different from each other, and there have been doubts about the extinction problem and absolute scale in Brown's data.[36,37] The present calculated charge density does not agree with that reconstructed from Brown's data by Stewart[38] and Yang and Coppens,[39] with the main discrepancy lying in the region near the octahedral sites. But the agreement is quantitatively good in that region compared with the experiment by Larsen and Hansen.[36]

The calculated valence structure factors are listed in Table II. The choice of different formulas for the correlation energy functional has very minor effect on the structure factors. To compare with the observed values, the contribution from the 1s core and the correction due to the thermal vibration are included. The 1s-core contribution is taken from the HF LCAO SCF calculation[5,40] and the thermal-motion parameters ($B_{11} = 0.469$ Å^2 and

$B_{22} = 0.424$ Å^2) are suggested by neutron-scattering data.[41] Table II shows the theoretical values compared with the recent observed x-ray structure factors.[36] The agreement is fairly good.

D. Compton profiles

The momentum distribution of electrons can be examined experimentally using Compton profiles which measure the integrated electron-momentum distribution over a plane perpendicular to a specific direction. We have performed a detailed calculation of the profiles and have reported the results earlier.[13] The agreement between the calculated and experimental profiles is excellent. As an example, the anisotropy of Compton profiles in $\langle 0001 \rangle$ and $\langle 11\bar{2}0 \rangle$ directions compared with experiment and other calculations is shown in Fig. 8. This agreement suggests that the theoretical approach used here can also give an accurate detailed description of the valence wave functions.[13]

V. CONCLUSION

In conclusion, we have shown that both the structural and electronic properties can be obtained using a single *ab initio* approach. The lattice constants for beryllium have been predicted accurately by calculating the total structural energy. The calculated Poisson's ratios are within the range of the measured values; this is satisfying because of the anomalously low value of this parameter. The bulk modulus is in fair agreement with experiment. In addition, the charge density, the topology of the Fermi surface, and the Compton profiles are in good agreement with experiments. The overall results for beryllium indicate that the static structural and electronic properties of crystalline solids can be obtained using a density-functional pseudopotential method with no input information beyond the atomic number of the constituent atoms and the crystal structure.
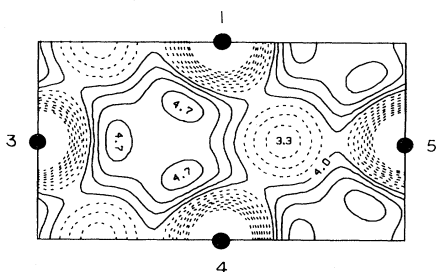

FIG. 7. Contour plot of the calculated beryllium valence charge density in the (0001) basal plane. The numerical labels are indicated in the ball-and-stick model shown in Fig. 3(a). Details are given in the caption for Fig. 6.
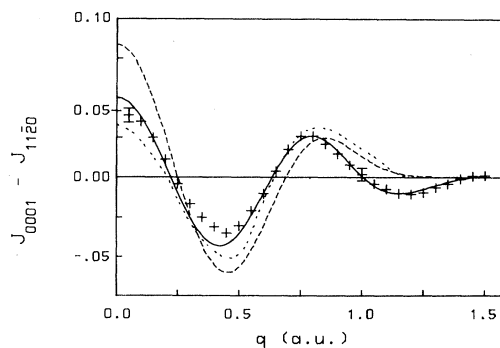

FIG. 8. Comparison between calculated and measured anisotropy of the Compton profile for $\langle 0001 \rangle$ and $\langle 11\bar{2}0 \rangle$ directions. Convoluted theoretical results are present calculation (solid line), LCAO (Ref. 42) (dotted line), and pseudopotential calculation by Rennert (Ref. 43) (dashed line). Crosses represent the experimental data by Hansen *et al.* (Ref. 44).

TABLE II. Comparison of the calculated structure factors with the recent x-ray measurements (Ref. 36). First column lists the calculated valence structure factors. Second column lists the total structure factors including the contribution from the $1s$ core (Refs. 5 and 40) and the correction due to the thermal motion (Ref. 41). Third column is the absolute values of the structure factors obtained from experiment (Ref. 36), where the estimated standard deviations are shown in parentheses.

hkl	Valence	Total	Experiment (Ref. 36)
002	0.0664	−3.330	3.348(29)
004	−0.0215	2.173	2.216(19)
006	0.0005	−1.184	1.212(3)
100	−0.0888	−1.829	1.839(16)
101	0.0880	−2.816	2.815(24)
102	−0.0534	1.442	1.473(13)
103	−0.0539	2.105	2.151(19)
104	0.0036	−0.977	0.995(8)
105	0.0018	−1.280	1.307(3)
106	−0.0000	0.539	0.551(1)
110	−0.0843	2.621	2.668(23)
112	0.0434	−2.303	2.335(20)
114	−0.0029	1.582	1.606(3)
200	0.0316	−1.168	1.188(10)
201	−0.0306	1.975	2.007(17)
202	−0.0091	1.036	1.044(9)
203	0.0037	−1.534	1.550(4)
204	0.0012	−0.714	0.727(2)
205	−0.0001	0.956	0.977(2)
210	0.0019	−0.854	0.863(2)
211	0.0030	−1.434	1.449(3)
212	−0.0012	0.755	0.762(1)
213	−0.0009	1.129	1.142(2)
214	0.0000	−0.535	0.541(2)
220	0.0000	1.041	1.056(2)
300	−0.0016	1.390	1.408(3)
302	0.0007	−1.238	1.251(3)

[1]V. M. Amonenko, V. Ye. Ivanov, G. F. Tikhinskij, and V. A. Finkel, Phys. Met. Metallog. 14, 47 (1962).

[2]K. J. H. Mackay and N. A. Hill, J. Nucl. Mater. 8, 263 (1963).

[3]American Institute of Physics Handbook, 3rd ed. (McGraw-Hill, New York, 1972), Tables 4e-10 and 7b-1.

[4]J. F. Janak, V. L. Moruzzi, and A. R. Williams, Phys. Rev. B 12, 1257 (1975).

[5]R. Dovesi, C. Pisani, F. Ricca, and C. Roetti, Phys. Rev. B 25, 3731 (1982).

[6]M. L. Cohen and V. Heine, in Solid State Physics, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1970), Vol. 24, p. 37.

[7]P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964); W. Kohn and L. J. Sham, ibid. 140, A1133 (1965).

[8]M. T. Yin and M. L. Cohen, Phys. Rev. Lett. 45, 1004 (1980); Phys. Rev. B 26, 5668 (1982).

[9]M. T. Yin and M. L. Cohen, Phys. Rev. B 24, 6121 (1981).

[10]J. Ihm and M. L. Cohen, Phys. Rev. B 23, 1576 (1981).

[11]P. K. Lam and M. L. Cohen, Phys. Rev. B 24, 4224 (1981).

[12]M. Y. Chou, P. K. Lam, and M. L. Cohen, Solid State Commun. 42, 861 (1982).

[13]M. Y. Chou, P. K. Lam, M. L. Cohen, G. Loupias, J. Chomilier, and J. Petiau, Phys. Rev. Lett. 49, 1452 (1982); M. Y. Chou, P. K. Lam, and M. L. Cohen, Phys. Rev. B 28, 1696 (1983).

[14]D. R. Hamann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. 43, 1494 (1979).

[15]L. Hedin and B. I. Lundqvist, J. Phys. C 4, 2064 (1971).

[16]E. Wigner, Phys. Rev. 46, 1002 (1934).

[17]J. Ihm, A. Zunger, and M. L. Cohen, J. Phys. C 12, 4409 (1979); 13, 3095(E) (1980).

[18]M. Born and K. Huang, Dynamical Theory of Crystal Lattices (Oxford University Press, London, 1956).

[19]C. Kittel, Introduction to Solid State Physics, 5th ed. (Wiley, New York, 1976), p. 74, Table I.

[20]Metal Handbook, 8th ed. (American Society of Metals, Cleve-

land, 1961), p. 10.

[21]J. F. Smith and C. L. Arbogast, J. Appl. Phys. 31, 99 (1960).

[22]D. J. Silversmith and B. L. Averbach, Phys. Rev. B 1, 567 (1970).

[23]F. D. Murnaghan, Proc. Natl. Acad. Sci. U.S.A. 30, 244 (1944); O. L. Anderson, J. Phys. Chem. Solids 27, 547 (1966).

[24]S. K. Joshi and S. S. Mitra, Proc. Phys. Soc. (London) 76, 295 (1960).

[25]T. L. Loucks and P. H. Cutler, Phys. Rev. 133, A819 (1964); T. L. Loucks, *ibid.* 134, A1618 (1964).

[26]J. H. Terrell, Phys. Rev. 149, 526 (1966).

[27]M. Taut, Phys. Status Solidi B 54, 149 (1972).

[28]S. T. Inoue and J. Yamashita, J. Phys. Soc. Jpn. 35, 677 (1973).

[29]S. Chatterjee and P. Sinha, J. Phys. F 5, 2089 (1975).

[30]B. R. Watts, Phys. Lett. 3, 284 (1963); B. R. Watts, Proc. R. Soc. London Ser. A 282, 521 (1964).

[31]J. H. Tripp, P. M. Everett, W. L. Gordon, and R. W. Stark, Phys. Rev. 180, 669 (1969).

[32]L. R. Testardi and J. H. Condon, Phys. Rev. B 1, 3928 (1970).

[33]T. A. Kennedy and G. Seidel, Phys. Rev. B 6, 3906 (1972).

[34]E. F. Vozenilek and R. W. Reed, Phys. Rev. B 12, 1140 (1975); R. W. Reed and E. F. Vozenilek, *ibid.* 13, 3320 (1976).

[35]P. J. Brown, Philos. Mag. 26, 1377 (1972).

[36]F. K. Larsen and N. K. Hansen (unpublished).

[37]N. K. Hansen, J. R. Schneider, and F. K. Larsen (unpublished).

[38]R. F. Stewart, Acta Crystallogr. Sect. A 33, 33 (1977).

[39]Y. W. Yang and P. Coppens, Acta Crystallogr. Sect. A 34, 61 (1978).

[40]We have also calculated the 1s-core charge density from the beryllium atom using the local-density-functional method, assuming that the core is frozen in forming the solid. The 1s contribution obtained this way is very similar to that taken from Ref. 5. However, the total structure factors with the 1s contribution taken from Ref. 5 are slightly closer to the measured values.

[41]F. K. Larsen, M. S. Lehmann, and M. Merisalo, Acta Crystallogr. Sect. A 36, 159 (1980).

[42]O. Aikala, Philos. Mag. 33, 603 (1976).

[43]P. Rennert, Phys. Status Solidi B 105, 567 (1981).

[44]N. K. Hansen, P. Pattison, and J. R. Schneider, Z. Phys. B 35, 215 (1979).