Elastic properties of the bcc structure of bismuth at high pressure

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First-principles calculations of the single-crystal elastic constants of the body-centered cubic phase of bismuth are carried out in the pressure range of 31–191 GPa. The calculations are performed in the framework of density functional theory with generalized gradient approximation using a plane wave basis set and pseudopotential scheme. These results confirm the conclusions drawn in a recent study based on the x-ray diffraction data under nonhydrostatic compression. The calculated unit cell volumes and the bulk moduli as a function of pressure agree well with the experimentally measured values.

The study of matter at high pressure is of considerable current interest, particularly in the case of elements.[1] The knowledge of material elastic properties at high pressure is important for a variety of scientific and technological applications, including the physics of planet interiors, materials strength and stability, and design and modeling of dynamic compression experiment. At a more fundamental level, the study of a material behavior at high compressions provides a better understanding of the interplay between the structural, dynamical, and electronic properties.[2]

Bismuth and $Bi_{1-x}Sb_x$ alloys are promising materials for thermoelectric devices[3] and their electronic structure has been subject of study for more than 60 years. In addition, because of the high compressibility of bcc-Bi, its use as a pressure marker in high-pressure x-ray experiments has been suggested. Interestingly, bismuth is one of the most studied elements at high pressure. It presents a rhombohedral structure (A7) at ambient pressure, and up to 7.7 GPa, Bi undergoes a number of structural phase transition, acquiring some nontrivial structures, only recently determined.[4,5] At pressure above 7.7 GPa, bismuth has a body-centered cubic phase, and according to recent measurements, this structure is stable at least up to 222 GPa,[6] confirming a previous theoretical calculation and experimental work up to 40 GPa.[7]

However, in contrast to the progress made in order to determine the high-pressure structure of Bi, the measurements of their single-crystal elastic properties at high pressure remain a challenge. Experimental determination of single-crystal stiffness C_{ij} (or compliance S_{ij}) constants, which provide a complete description of the macroscopic elastic properties,[8] has been feasible only at low to moderate pressures. The analysis of the powder diffraction data under nonhydrostatic compression offers the only way of estimating single-crystal elastic moduli of the reversible high-pressure phases.[9–11] However, this method requires diffraction data taken with the radial or perpendicular geometry.[9,11,12] Several examples[10–15] of such studies can be found in the literature.

The diffraction experiments on bcc-Bi conducted earlier[6] used the conventional geometry that does not give the range of data required for the estimation of elastic moduli. However, recently, by analyzing the line shift and linewidth data obtained earlier[6] we were able to constrain[16] two combinations of elastic compliances, $S=(S_{11}-S_{12}-S_{44}/2)$ and S/S_{11}, up to 222 GPa.

In this letter we report the first-principles calculations of the single-crystal elastic constants of the bcc-Bi carried out by using density functional theory (DFT).[17] These results are compared with those obtained in a recent study[16] based on the x-ray diffraction data under nonhydrostatic compression. The calculated unit cell volumes and the bulk moduli as a function of pressure are compared with the corresponding values determined from the high-pressure x-ray diffraction experiments.

We have performed calculations of the electronic structure in the framework of the DFT, using a plane wave basis set, with the Perdew-Burke-Ernzerhof parameterization of the generalized gradient approximation and replacing the core electrons by a Troullier-Martins norm-conserving pseudopotential, as implemented in the package ESPRESSO.[18] The pseudopotential was generated with the package due to P Giannozzi, which was included in the ESPRESSO distribution. As reference atomic configurations we used $[Xe]4f^{14}5d^{10}6s^{2}6p^{3}$ for the $s/p/d$ channels, and $[Xe]4f^{14}5d^{10}6s^{2}6p^{2}5f^{1}$ for the f channel, with the matching radii 1.79/2.30/1.88/2.41 bohr for the $s/p/d/f$ projectors. Scalar relativistic effects for the core electrons are included within the pseudopotential.

For the solid state calculations we have used a cutoff of 80 Ry for the plane wave expansion of the wave functions and 360 Ry for the charge density, which guarantees a convergence[19] within 0.002 Ry/at. in energy and 1 GPa in the hydrostatic stress. The geometry was specified using the conventional two-atom bcc unit cell. To obtain a smooth density of states, the first Brillouin zone was sampled with a Monkhorst-Pack $20\times20\times20$ k mesh centered at the Γ point.

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TABLE I. Calculated unit cell volume and single-crystal elastic constants (GPa) of bcc-Bi as a function of pressure. Combination of elastic compliances that were constrained for the x-ray diffraction studies are also given.

V_{cal} (Å^3)	V_{exp} (Å^3)	P	C_{11}	C_{12}	C_{44}	S[a]	S/S_{11}	A[b]
48	46	31	203	163	73	0.0182	1.049	3.65
46	44	39	238	191	85	0.0154	1.046	3.62
44	42	49	281	226	99	0.0131	1.044	3.60
42	40	61	333	268	116	0.0111	1.041	3.57
40	38	77	395	319	136	0.0095	1.043	3.58
38	37	96	471	382	160	0.0081	1.045	3.60
36	35	120	565	459	188	0.0068	1.040	3.55
34	33	151	685	557	223	0.0056	1.033	3.48
32	31	191	837	682	265	0.0046	1.025	3.42

[a] $S=(S_{11}-S_{12}-S_{44}/2)$. S_{ij} are elastic compliances in units of GPa^{-1}.
[b] Anisotropy factor $A=2C_{44}/(C_{11}-C_{12})$.

Unphysical oscillations of the density of states due to the finiteness of the k-space grid have been eliminated using a Fermi smearing of 0.02 Ry.

The independent elastic stiffness constants C_{ij} in cubic phase are C_{11}, C_{12}, and C_{44}. They were calculated (at zero temperature) at nine different pressures, from 31 GPa to 191 GPa, by using the definition of the stiffness constants in terms of the stress (σ_{ij}) and strain tensors (ε_{ij}),

$$c_{ijkl}=\frac{\partial\sigma_{ij}}{\partial\varepsilon_{kl}}, \quad (i,j,k,l=x,y,z), \tag{1}$$

where we follow the usual convention $C_{11}=c_{xxxx}$, $C_{12}=c_{xxyy}$, and $C_{44}=c_{xyxy}$. For the constants C_{11} and C_{12} we deformed the unit cell as defined by the lattice vectors (in cartesian coordinates) $\mathbf{a}_1=a(1+\varepsilon_{xx},0,0)$, $\mathbf{a}_2=a(0,1,0)$, and $\mathbf{a}_3=a(0,0,1)$.

The derivatives in Eq. (1) were evaluated numerically by making a series of calculations with $\varepsilon_{xx}=\{0.00,\pm0.01,\pm0.02,\pm0.03\}$, and fitting the calculated σ_{xx} and σ_{yy} to quadratic polynomial in ε_{xx}, the linear terms of which provide the elastic constants. The value of σ_{xx} at $\varepsilon_{xx}=0$ provides the pressure, which is controlled through the lattice parameter a.

To obtain C_{44} we calculated σ_{xy} using the unit cell $\mathbf{a}_1=a(1,0,0)$, $\mathbf{a}_2=a(2\varepsilon_{xy},1,0)$, and $\mathbf{a}_3=a(0,0,1)$.

The derivative in Eq. (1) was evaluated by the same procedure, using $\varepsilon_{xy}=\{0.00,\pm0.005,\pm0.010,\pm0.015\}$.

In Table I we show the calculated elastic stiffness constants and two combinations of the elastic compliances, S and S/S_{11}, at nine different pressures P between 31 and 191 GPa. There are no measurements of the elastic constants of bcc-Bi for a comparison with the calculated values. However, many other measured parameters can be compared with those calculated. For example, the calculated and measured[6] unit cell volumes, also given in the Table I, agree within a few percent. A recent analysis[16] of the x-ray diffraction line shift and linewidth data suggested that S values are positive and $S/S_{11}\simeq1$ in the pressure range of 10–222 GPa. It is seen that the calculated elastic constants support both these conclusions drawn. Both S and A are measures of elastic anisotropy but for comparison of elastic anisotropies of different materials, it is convenient to use the dimensionless parameter A. The values in Table I indicate that bcc-Bi has high elastic anisotropy that is comparable to that of highly anisotropic elemental metals such as Fe, Au, Ag, Cu, and Pb with the anisotropy factors 2.4, 2.85, 3.1, 3.2, and 4.1, respectively.

The isotropic elastic properties of the polycrystalline aggregate containing randomly oriented crystallites can be calculated from the single-crystal elastic constants. Such calculations are complicated by the complex nature of the stresses and strains across the grain boundaries separating differently oriented elastically anisotropic crystallites. Two averaging schemes, one suggested by Voigt[20] based on the assumption strain continuity and the other by Reuss[21] based on the stress continuity across the grain boundaries, are available for calculating the elastic properties of polycrystalline aggregate from single-crystal elastic constants. For the cubic symmetry, the relations for the bulk and shear moduli are[22]

$$B=\frac{1}{3}(C_{11}+2C_{12}), \tag{2}$$

$$G_V=\frac{1}{5}(C_{11}-C_{12}+3C_{44}), \tag{3}$$

$$G_R=\frac{5C_{44}(C_{11}-C_{12})}{3(C_{11}-C_{12})+4C_{44}}, \tag{4}$$

with $B=B_V=B_R$. The suffixes V and R denote the values under Voigt and Reuss averaging, respectively. It is shown that G_V and G_R are the upper and lower bounds of the shear modulus G and it is the average of the two that closely corresponds to the measured value.[23] The B and G at different pressures are given in Table II. It is seen that the bulk modulus derived from the high-pressure x-ray diffraction experiments[6] is in excellent agreement with the calculated values. The Young's modulus E and Poisson's ratio ν were calculated from the following standard relations:

$$E=\frac{9BG}{3B+G} \text{ and } \nu=\frac{3B-2G}{2(3B+G)}. \tag{5}$$

Figure 1 shows the calculated and the measured equation of state. Fitting the Birch-Murnaghan[24] equation of state to

TABLE II. The bulk modulus B, shear modulus G, Young's modulus E, and Poisson's ratio ν of the polycrystalline aggregate of bcc-Bi. Elastic moduli are in GPa. G and E represent Voigt-Reuss-Hill average.

P	B_{cal}	B_{exp}[a]	G	E	ν
31	176	182	44	121	0.39
39	207	213	51	141	0.39
49	244	252	59	165	0.39
61	290	297	70	194	0.39
77	344	357	82	228	0.39
96	412	426	96	268	0.39
120	494	512	114	316	0.39
151	600	619	136	378	0.39
191	734	751	162	454	0.40

[a]Based on data from Ref. 6.

the calculated data gives V_0=64.8 Å^3, B_0=52 GPa, and B_0'=4.6, where V_0, B_0, and B_0' are the unit cell volume, bulk modulus, and the pressure derivative of bulk modulus at zero pressure, respectively. These values compare well with V_0=60.4 Å^3, B_0=54.7 GPa, and B_0'=4.9 which are derived from the measured equation of state.[6] With B_0=31 GPa,[25] the rhombohedral A7 structure, which is stable between ambient pressure and 2.55 GPa, is much more compressible than the bcc-Bi.

In summary, we have calculated the elastic stiffness constants corresponding to the high-pressure bcc phase of Bi using an *ab initio* pseudopotential method. So far, there is no experimental data about these individual elastic constants under pressure, and this calculation provide theoretical results in this respect. However, it is possible to obtain some constraints of the elastic constants from measurements on polycrystalline sample, and both theoretical and experimental results are in good agreement each other. Also, from the calculated elastic constant we evaluate the elastic properties that have been measured in polycrystalline samples of Bi, obtaining a good agreement. We hope the present work will provide useful information that encourage new theoretical and experimental work for this important material.

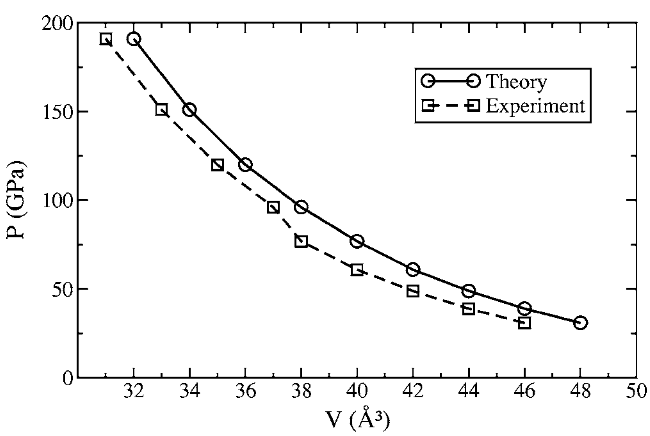

FIG. 1. Equation of state for bcc-Bi. Experimental data are from Ref. 6.

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