

# Cesium under pressure: First-principles calculation of the bcc-to-fcc phase transition

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In this paper we present the *ab initio* calculation of the structural properties of cesium under pressure. The calculation of the total energy is done in the local-density approximation of density-functional theory, using a nonlocal pseudopotential including the nonlinear core corrections proposed by Louie *et al.* The calculation of the pressure-volume diagram for both bcc and fcc structures allows us to prove that the transition from bcc to fcc structure is a first-order transition. [S0163-1829(99)00617-7]

## I. INTRODUCTION

The structural transition of metals under pressure has been a challenging problem for a long period of time. Any of the *d*-transition metals under pressure exhibits a fcc structure as the *d* band becomes filled. At high pressure also simple metals, such as the alkali metals, exhibit structures different from their usual bcc structure. Lithium becomes fcc at 69 kbar.<sup>1</sup> Potassium shows two transitions, one at 114 kbar and the other at 188 kbar.<sup>2</sup>

The most interesting phase transitions are present in cesium. In the Cs metal the *d* states are lying just above the Fermi level and an external pressure can push the *d* levels down below the Fermi energy. At room temperature and under hydrostatic pressures, x rays, neutron-scattering, and optical reflectivity measurements<sup>2-5</sup> show that there are several discontinuities in the pressure-volume diagram. The first discontinuity occurs at  $P=23.7$  kbar and  $V/V_0=0.63$ . At this pressure Cs undergoes a transition from bcc (CsI) to fcc (CsII) with a small reduction of volume. The second one is an isostructural transition from fcc (CsII) to fcc (CsIII) with a large reduction of volume (9%). At  $P=42.7$  kbar there is a transition to tetragonal Cs. At high pressures more complicated phases appear. Many theoretical investigations have been devoted to the study of the isostructural transition where a large drop in the volume is present.<sup>6-8</sup> The transition CsI to CsII was qualitatively predicted by Bardeen<sup>9</sup> and energy band calculations were performed by Skriver.<sup>8</sup>

In this paper using the pseudopotential approach we evaluate the  $P$ - $V$  diagram to study the bcc-fcc transition. In the pseudopotential we will include the core corrections, which are important for heavy alkali metals. The calculation is outlined in Sec. II and the results are discussed in Sec. III, where the conclusions are also drawn.

## II. CALCULATIONS

The electron-ion interaction has been evaluated using the nonlocal pseudopotential model which is the most appropriate for the study of the nearly free-electron metals. The nonlocal pseudopotential that we have used is a norm-conserving one, constructed in a way to reproduce the all-

electrons valence wave functions and energies:

$$V_{ps}(\mathbf{r}, \mathbf{r}') = V_{loc}(r) \delta(\mathbf{r} - \mathbf{r}') + \sum_l V_l(\mathbf{r}, \mathbf{r}'), \quad (1)$$

where

$$V_l(\mathbf{r}, \mathbf{r}') = V_l(r) P_l(\hat{\mathbf{r}} \cdot \hat{\mathbf{r}}') \delta(\mathbf{r} - \mathbf{r}'), \quad (2)$$

with  $P_l$  the Legendre polynomial of degree  $l$ . We have chosen the local and nonlocal terms as suggested by Bachelet *et al.*<sup>10</sup> with the local term

$$V_{loc}(r) = -\frac{Ze^2}{r} \sum_{i=1}^2 c_i \text{erf}[(\alpha_i)^{1/2} r], \quad (3)$$

and  $l$ -dependent terms

$$V_l(r) = e^2 Z \sum_{i=1}^3 (A_i + r^2 A_{i+3}) e^{-\beta_i^l r^2}. \quad (4)$$

All the coefficients  $c_i$ ,  $\alpha_i$ ,  $A_i$ , and  $\beta_i^l$  have been evaluated for the electronic configuration of the cesium atom with one valence electron.

For the exchange and correlation energy in the local-density approximation we have used the Ceperly and Alder<sup>11</sup> form.

The pseudopotential method implies a linearization of the exchange and correlation energy. This procedure gives a poorly transferable pseudopotential if the core and valence charge are not well separated in space. For cesium we include core corrections in the one valence electron pseudopotential to take into account the “semicore states”  $5s$  and  $5p$ .<sup>12</sup> The idea underlying the nonlinear core correction approximation<sup>13</sup> (NLCC) is to use the total charge instead of the valence charge to compute the nonlinear exchange and correlation energy

$$E_{xc}[n] = \int \epsilon_{xc}(n_v + n_c)(n_v + n_c) d\mathbf{r}, \quad (5)$$

where  $n_c$  is the charge density of the core electrons, computed as a superposition of the atomic core charges, and  $n_v$  is

TABLE I. In the first column are reported the equilibrium lattice parameter for Cs bcc, the bulk modulus and its derivative obtained by fitting the total energies with the Murnaghan curve (Ref. 17), while the second column contains the experimental data from Swenson *et al.* (Ref. 5).

	Calc.	Expt.
$a_0$ (a.u)	11.39	11.43
$B_0$ (kbar)	22.0	21.5
$B'_0$	4.87	3.76

the valence charge. Following Louie<sup>13</sup> we evaluate the core charge as a superposition of partial core charges fitted by

$$n_c(\mathbf{r}) = (a_{cc} + b_{cc}r^2)e^{\alpha_{cc}r^2}, \quad (6)$$

where  $a_{cc}$ ,  $b_{cc}$ ,  $\alpha_{cc}$  are parameters determined by the norm-conserving condition.

The total energy of the solid can be written as

$$E_{\text{tot}}[n] = E_k[n] + E_{e-\text{ionl}}[n] + E_H[n] + E_{\text{xc}}[n] + E_{i-i}[n], \quad (7)$$

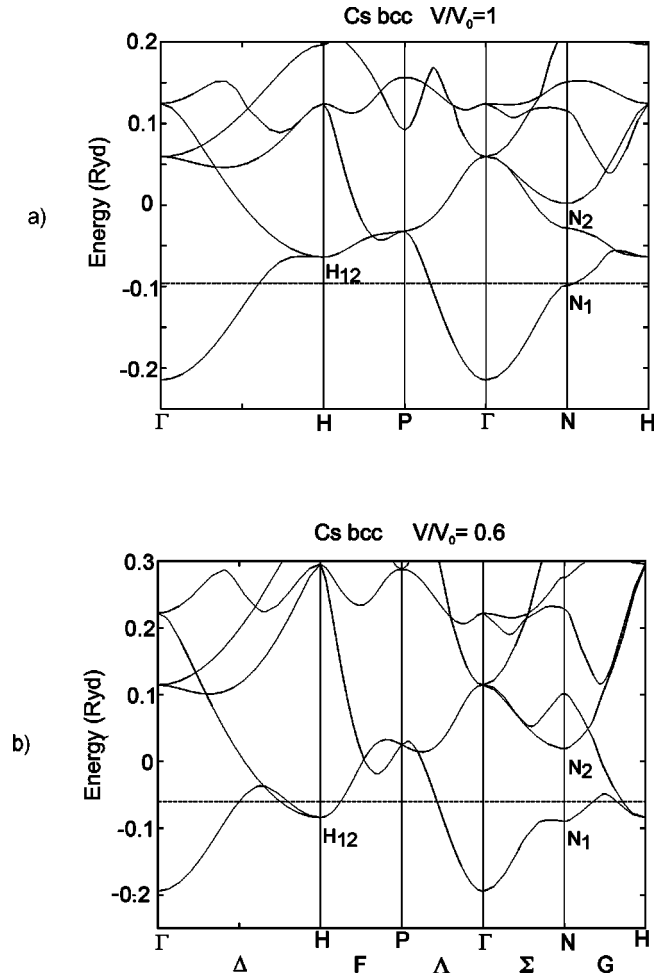


FIG. 1. The electronic bands along the bcc bulk high symmetry directions at equilibrium volume  $V_0$  and at  $V/V_0=0.6$  are shown in panels (a) and (b), respectively. The dashed line indicates the Fermi level.

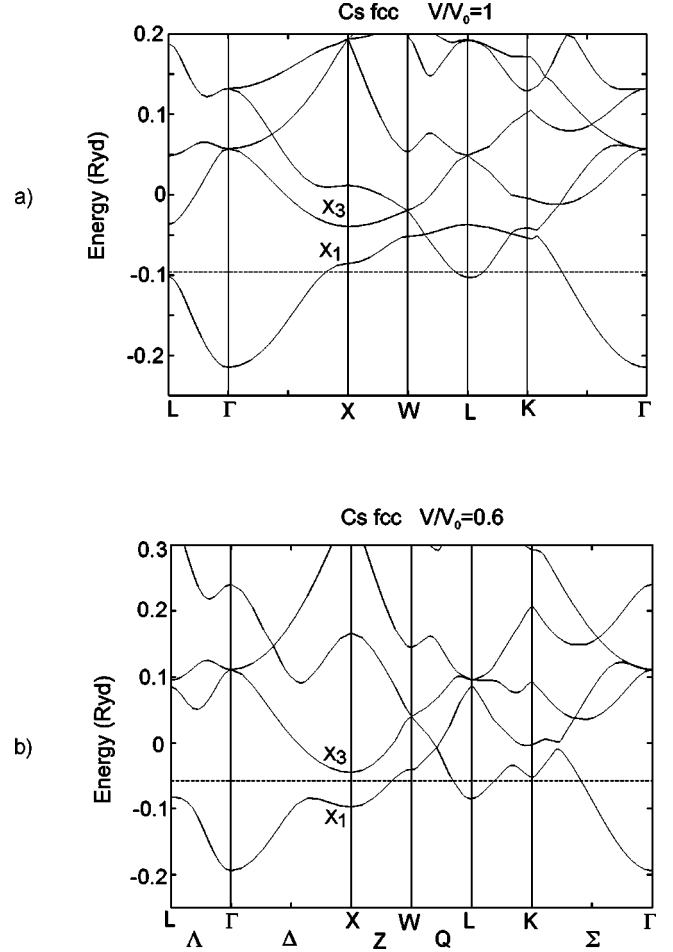


FIG. 2. As Fig. 1, but for the fcc structure.

where  $E_k[n]$  is the kinetic energy,  $E_{e-\text{ionl}}[n]$  is the interaction between electrons and ions evaluated by the pseudopotential method,  $E_H$  is the Hartree energy,  $E_{\text{xc}}$  is the exchange and correlation energy given by Eq. (5) and the last term represents the ion-ion interaction. The total energy per unit cell  $V_a$ , in the plane-wave representation, is given by

$$E_{\text{cell}} = \frac{2}{N} \sum_{\mathbf{k}j} f_{\mathbf{k}j} \epsilon_{\mathbf{k}j} - \frac{v_a}{2} \sum_{\mathbf{G} \neq 0} n_v(\mathbf{G}) V_H(\mathbf{G}) + v_a \sum_{\mathbf{G}} n_v(\mathbf{G}) \times [\epsilon_{\text{xc}}(\mathbf{G}) - V_{\text{xc}}(\mathbf{G})] + v_a \sum_{\mathbf{G}} n_c \epsilon_{\text{xc}}(\mathbf{G}) + \gamma_{\text{Ewald}} + \alpha_1 Z, \quad (8)$$

where  $N$  is the number of atoms  $\epsilon_{\mathbf{k}j}$  is the Kohn-Sham eigenvalue,  $\alpha_1$  is the nonsingular part of the bare pseudopotential,<sup>14</sup>  $\gamma_{\text{Ewald}}$  is the ion-ion interaction evaluated with the Ewald summation method.<sup>15</sup>

### III. RESULTS

We have solved the Kohn-Sham equations in the plane-wave basis and calculated the ground-state energy. The number of reciprocal-lattice vectors kept in the expansion was determined by keeping all those that fulfill the condition

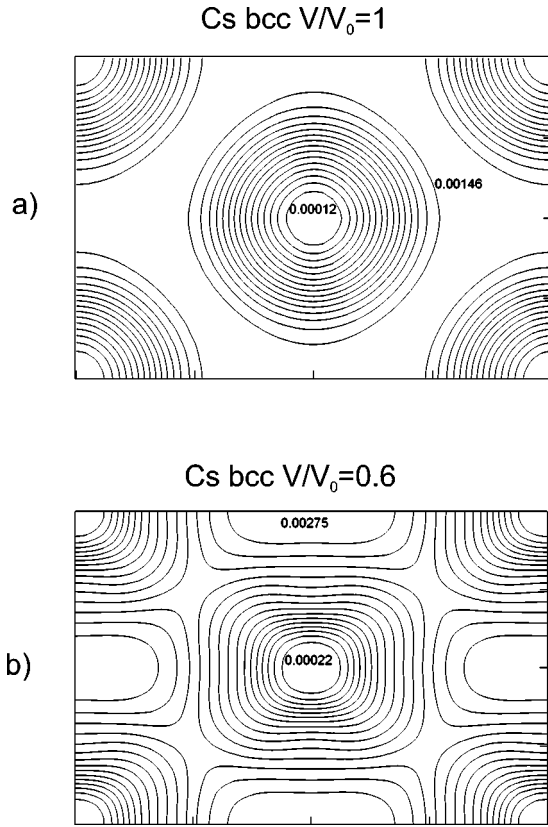


FIG. 3. In panels (a) and (b), respectively the valence charge at volume  $V_0$  and the valence charge at  $V/V_0=0.6$  are plotted for a bcc structure. The charge density values are in a.u. and the charge is projected in the (110) plane.

$$\frac{\hbar^2}{2m}(\mathbf{q} + \mathbf{G})^2 \leq E_{\text{cut}}, \quad (9)$$

where we have taken  $E_{\text{cut}} = 10$  Ryd. This cutoff corresponds to about 3000 plane waves at the experimental equilibrium condition. In the evaluation of the energy a sum over points in the Brillouin zone (BZ) is required. We deal with it using the tetrahedron method.<sup>16</sup> To get convergence in our numerical calculation we take in the irreducible part of the BZ 444  $\mathbf{k}$  points, which corresponds to about 21 000  $\mathbf{k}$  points in the full BZ.

The equilibrium lattice constant  $a_0$  at zero pressure is determined by minimizing the total-energy of the solid. Because the total energy requires the self-consistent solution of the Kohn-Sham equations, it is not possible to evaluate the total energy for every value of  $a_0$ . We evaluate the total energy value for a several values of  $a_0$ , fit these data with an equation of state, then find the minimum from the functional form of the equation of state. For the equation of state we have chosen the Murnaghan curve<sup>17</sup> which has the form

$$E_{\text{tot}} = \frac{V_0 B_0}{B'_0} \left[ \frac{1}{B'_0 - 1} \left( \frac{V_0}{V_a} \right)^{(B'_0 - 1)} + \frac{V_a}{V_0} \right] + C, \quad (10)$$

where  $B_0$  and  $B'_0$  is the bulk modulus and its volume derivative and  $V_0$  is the equilibrium volume to be determined from the fitting procedure.

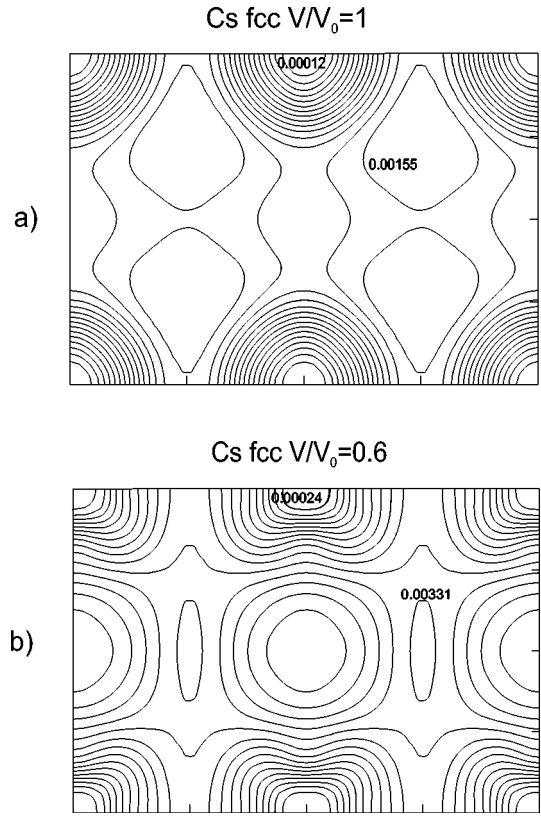


FIG. 4. As Fig. 3, but for fcc structure.

The equilibrium lattice parameters for Cs bcc, the bulk modulus and its derivative, obtained from the fit, are compared in Table I with the experimental data of Swenson *et al.*<sup>5</sup> The equilibrium volume determined by the fitting procedure is  $V_0 = 739$  a.u.<sup>3</sup> As shown in Fig. 1(a), at the equilibrium volume for the bcc structure only the  $s$  band is full. In Fig. 1(b) the same calculations have been performed for  $V/V_0 = 0.6$ , around the transition volume. In this case the  $d$  bands along the  $\Delta$ ,  $\Sigma$ , and  $G$  directions of the bcc bulk Brillouin zone are already dropped below  $E_f$ . The calculations performed for the fcc structure present a similar behavior, as shown in Fig. 2. For  $V/V_0 = 1$  [Fig. 2(a)] only the  $s$  bands are filled, while, as shown in Fig. 2(b), for  $V/V_0 = 0.6$  the  $X_1$  band at the zone border of the  $\Delta$  and  $\Lambda$  directions are already dropped below the Fermi energy.

The valence charge density of cesium bcc and fcc, projected into the (110) plane, at equilibrium lattice parameter and at  $V/V_0 = 0.6$ , are plotted in Figs. 3 and 4. At equilibrium the contribution to the valence charge is only given by the  $s$  electrons and the charge around the nuclei has a spherical symmetry, as shown in Figs. 3(a) and 4(a). For  $V/V_0 = 0.6$  the charge around the nuclei is no longer spherical, as shown in Fig. 3(b), and this is the indication that the  $s$ - $d$  electronic transition has occurred. After the transition, since the  $d$  bands are partially filled, the  $d$  electrons give their contribution to the valence charge distribution. During the compression, the charge overlap grows in the interatomic zones. For this reason the density is increased in that region which would be occupied by atoms in the fcc structure. This is consistent with the calculations presented in Fig. 4(b) for the valence charge of cesium fcc at  $V/V_0 = 0.6$ . One sees that the charge density has the same shape as the one plotted in Fig. 3(b).

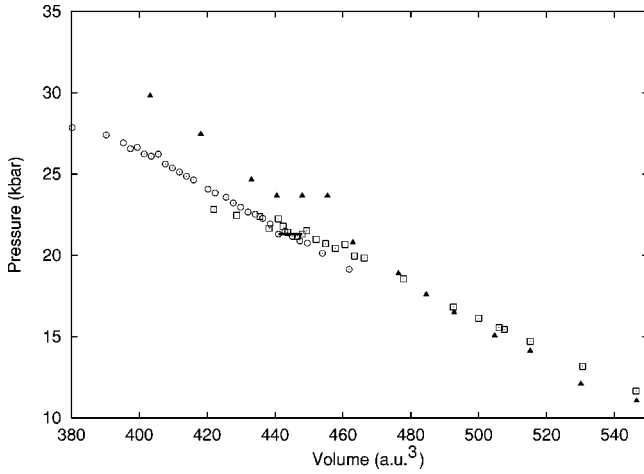


FIG. 5.  $P$ - $V$  diagram for cesium. Open squares represent bcc structure results, while open circles are the fcc calculations. Full triangles show experimental data from Swenson (Ref. 5). The heavy horizontal line indicates the estimated first-order transition plateau.

This is again an indication that cesium exhibit a bcc to fcc transition around  $V/V_0=0.6$ . We have also evaluated the energy difference between the two structures. We found that for  $V/V_0>0.6$  the bcc structure is more stable, while the opposite occurs for  $V/V_0<0.6$ .

To investigate the transition region we have constructed the  $P$ - $V$  diagram. The pressure has been evaluated numerically by using the expression

$$P = - \left( \frac{1}{V} \frac{\partial E_{\text{tot}}}{\partial V} \right)_{T=0}. \quad (11)$$

The phase diagram for the bcc and fcc structures are reported in Fig. 5. We have investigated the origin of the transition by assuming, as suggested by the experiments, that it occurs at fixed  $P$  and  $T$ , namely is a first-order phase transition. In this case the Gibbs free energy for the bcc phase should be equal to that of the fcc phase. Since we are working at  $T=0$  K, we should have

$$E_{\text{bcc}}(V_{\text{bcc}}) + pV_{\text{bcc}} = E_{\text{fcc}}(V_{\text{fcc}}) + pV_{\text{fcc}}. \quad (12)$$

The fulfillment of this equation has been checked numerically. Our calculations show that for  $p=21.3$  kbar,  $V_{\text{bcc}}$

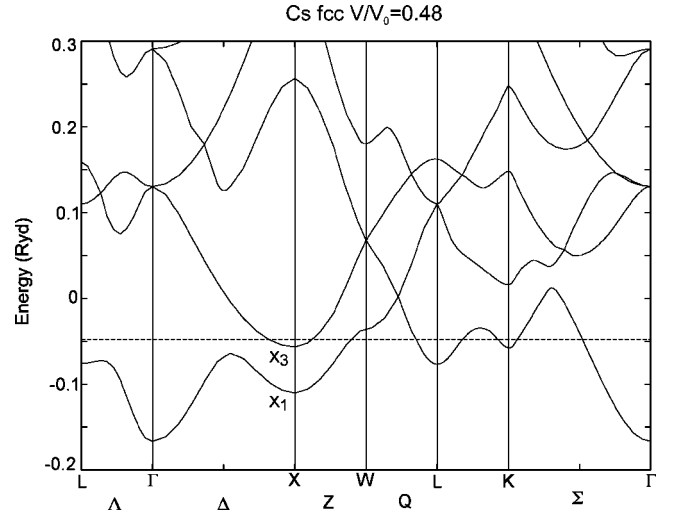


FIG. 6. The electronic bands along the fcc bulk high symmetry directions at  $V/V_0=0.48$ , in the region of the isostructural fcc to fcc transition. The dashed line indicates the Fermi level.

$=448$  a.u.<sup>3</sup>, and  $V_{\text{fcc}}=441$  a.u.<sup>3</sup>, Eq. (12) is satisfied. This proves that the bcc-fcc transition around  $V/V_0=0.6$  is a first-order transition. Our results, however, underestimate the experimental volume variation by a factor of 2, while our value of the pressure agrees up to 10% with the experimental one. We have also investigated the second isostructural phase transition occurring experimentally at  $V/V_0=0.46$ . The calculated band structure, drawn in Fig. 6, for the fcc phase at  $V/V_0=0.48$  shows that the  $X_3$  band has been pushed below  $E_f$ . Increasing the pressure the  $d$  bands become progressively filled and cesium exhibits the characteristics of transition metals in agreement with the general idea of Skriver<sup>8</sup> that most metals become transition metals at high pressures.

In summary we show that *ab initio* calculations of cesium using a nonlocal pseudopotential including the NLCC is able to prove that the bcc-fcc change of structure is a first-order transition. This approach allows us not only to calculate the bands, the valence charge density and the total energy of the solid, but also to study ordering phenomena, evaluating the  $P$ - $V$  diagram. The results are in good agreement with the experimental measurement of the CsI to CsII phase transition and agree with previous theoretical band calculations.

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