

Calculation of the Total Energy and Pressure of Compressed Cesium[†]

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The results of a self-consistent $X\alpha$ augmented-plane-wave calculation of the cohesive energy, pressure, and enthalpy of bcc and fcc cesium metal are presented. The exchange factor used was approximately the one which made the total atomic $X\alpha$ energy equal to the total atomic Hartree-Fock energy. The maximum value of the cohesive energy was calculated to be 0.062 ± 0.0015 Ry, and it occurs when the volume of the primitive unit cell is 780 ± 30 cubic atomic units. These results can be compared with the experimental values of 0.062 Ry and 745 cubic atomic units. The computed pressure and enthalpy predict that the isomorphic transition of the fcc phase of cesium should occur at 26 ± 2 kbar at 0°K. The computed isomorphic transition is accompanied by severe distortion of the Fermi surface, as suggested by Yamashita and Asano and by Kmetko.

Cesium metal at room temperature is known to undergo a transformation from the bcc to the fcc structure at a pressure of 23 kbar.¹ At 42 kbar, the metal experiences an isomorphic transition in which the fcc structure is retained but the volume is discontinuously reduced by 9%.¹ The collapsed fcc lattice is stable over a pressure range of only 0.5 kbar, above which it loses the cubic form and assumes an as yet unknown structure.¹ The first theoretical explanation of the isomorphic transition was given by Sternheimer.² Based upon the results of an energy-band calculation for cesium by the Wigner-Seitz method, he proposed that as the pressure is increased, the bottom of the unoccupied $5d$ band is pushed down relative to the partially occupied $6s$ band. Ultimately, the valence electronic charge begins to assume a more compressible $5d$ -like character, and the crystal collapses. Modern calculations of the one-electron energy levels^{3,4} tend to support the essence of Sternheimer's explanation, although they criticize it as an oversimplification. In Refs. 3 and 4, the Fermi surfaces of compressed fcc cesium were calculated, and the authors, independently and for different reasons, reached the conclusion that the isomorphic transition should be accompanied by considerable distortion of the Fermi surface. Unfortunately, the Fermi surface of compressed cesium is not experimentally known, and not since the work of Sternheimer has there been an attempt to calculate the total energy and pressure of the metal. As a consequence, neither of these later papers has been able to make a direct connection between their results and the experimentally observed isomorphic transition.

Recent developments,^{5,6} however, have now made it possible to calculate the total energy and pressure of a metal from a self-consistent energy-band calculation. The purpose of this paper is to present

the results of such a calculation for cesium and to relate these results to the previous work in Refs. 3 and 4.

The numerical methods used are essentially the same as those used by Ross and Johnson⁷ on aluminum. The one-electron $X\alpha$ equation⁸ is solved self-consistently within the muffin-tin approximation by use of the augmented-plane-wave (APW) method, and the resulting one-electron energies and charge densities are then used to calculate the total $X\alpha$ energy per primitive unit cell of the crystal. By performing the above procedure at a number of different lattice constants, one can determine the volume dependence of both the total energy and the energy bands. The exchange factor used in both the atomic and crystalline calculations was the one which makes the atomic $X\alpha$ and "Hartree-Fock"⁹ energies equal. Using this criterion, the exchange factor for cesium was determined to be equal to 0.69941.

The calculation required an unusually high degree of numerical accuracy which made it necessary for great care to be exercised in the solution of the one-electron equation. The Herman-Skillman radial mesh¹⁰ was used in all calculations. This mesh was of sufficient density such that the radial numerical integration error in the total energy of the cesium atom was of the order of 0.0005 Ry. The core electron wave functions were calculated self-consistently using a computer program which integrates inward and outward in the manner of the Schrödinger subroutine of the Herman-Skillman program.¹⁰ The calculations were begun on an IBM 360/65 computer, but the last two iterations of the self-consistent crystalline calculations were performed on a CDC 6700 computer to obtain greater accuracy. It is estimated that within the model employed, the crystalline total energies presented in this paper are numerically accurate to about

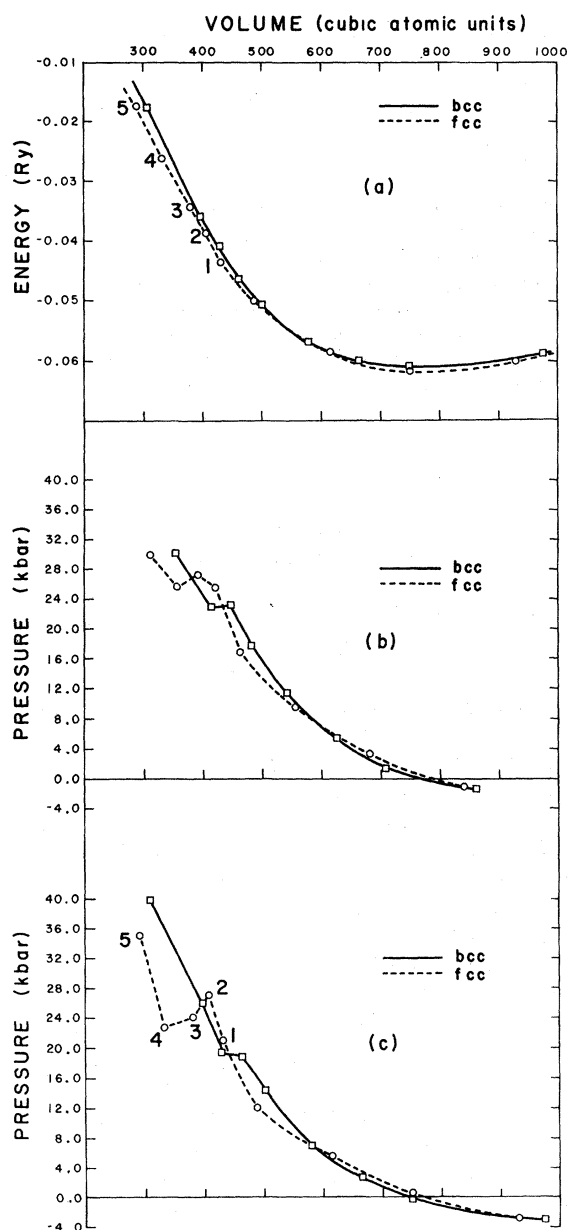


FIG. 1. (a) Calculated total energies of bcc and fcc cesium metal relative to the separated atom limit, as functions of the volume of the primitive unit cell. Squares and circles are data points of the bcc and fcc lattices, respectively. In order to facilitate the comparison of figures in this paper, some of the fcc data points have been numbered. (b), (c) Theoretical pressures of bcc and fcc cesium metal as functions of the volume of the primitive unit cell. In (b) the pressure was obtained as the negative of the numerical volume derivative of the total energy given in (a). Value of the pressure given in (c) was calculated by use of the virial theorem (see Refs. 5 and 6).

0.0015 Ry, and the calculated pressures are in error by no more than 2 kbar.

The results are presented in Figs. 1 and 2. Fig-

ure 1 is a plot of the pressure and total energy of both bcc and fcc cesium as functions of the volume of the primitive unit cell. The total energy of the metal is given relative to the calculated $X\alpha$ energy of the cesium atom which is $-15\,107.7719 \pm 0.0005$ Ry. Experimentally, bcc cesium is known to have zero pressure, zero temperature volume of 745 cubic atomic units (c. a. u.)¹¹ and a cohesive energy of 0.062 Ry per atom.¹² The results can also be compared to the theoretical values obtained by Sternheimer of 869 c. a. u. and 0.051 Ry.² The close agreement between the pressure, as determined by taking the volume derivative of the total energy and by applying the virial theorem to the computed results [Figs. 1(b) and 1(c)], lends confidence to the numerical accuracy of the calculation. The most striking feature of Fig. 1 is the region of instability in the fcc lattice between the volumes of 350 and 400 c. a. u. Somewhat similarly, the bcc lattice has a momentary cessation in the decrease in the compressibility between the volumes of 425 and 450 c. a. u.

To understand these results from the thermodynamic point of view and to determine the most stable lattice and volume at a given pressure and 0°K , requires knowledge of the enthalpy as a function of the pressure. Figure 2 is a plot of the calculated enthalpy of the fcc lattice in the pressure range between 20 and 35 kbar. The figure clearly shows that the volume of the fcc cesium lattice should decrease discontinuously at a pressure of about 26 kbar. Unfortunately, the numerical accuracy of the calculation is not great enough at the present time to allow any conclusions as to which lattice, the fcc or bcc, is more stable at a given pressure.

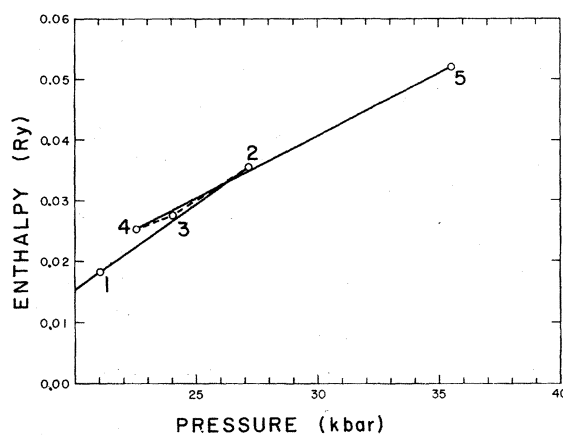


FIG. 2. Theoretical enthalpy of fcc cesium as a function of the calculated pressure. Enthalpy as defined in this figure is equal to $E + PV$, where E is the energy of the fcc cesium given in Fig. 1(a) at volume V , and P is the pressure of fcc cesium given in Fig. 1(c) at volume V .

The energy bands resulting from this calculation are in qualitative agreement with those presented in Ref. 3, and it is therefore unnecessary to reproduce them in this paper. The connection between this paper and the work of Refs. 3 and 4 can best be made by describing the characteristic features of the Fermi surfaces obtained at volumes near those at which the compressibility is seen to increase in Fig. 1. At a volume of about 580 c. a. u., the bcc Fermi surface has developed a pocket of electrons about the symmetry point H , and at a volume of 425 c. a. u., that pocket includes $\frac{1}{4}$ of the Δ symmetry axis. The changes taking place in the fcc Fermi surface are somewhat similar. At a volume of 450 c. a. u., the fcc Fermi surface includes most of the XU symmetry line, although the point U is still outside the surface (see Fig. 3 of Ref. 3). When the volume is 375 c. a. u., the U symmetry point is inside the Fermi surface (Fig. 4 of Ref. 3), and as the volume is further decreased to 325 c. a. u., the additional Fermi sheet begins to develop about the symmetry point X . Thus, as suggested by Yamashita³ and Kmetko,⁴ the dip in the fcc pressure vs volume curve and the corresponding isomorphous transition are seen to be closely correlated with the occurrence of these topological changes in the fcc Fermi surface. Similarly, the brief leveling off of the bcc pressure curve is correlated with topological changes of the Fermi surface for that structure.

Based upon the information found in Figs. 1(c) and 2, one would predict that at 0°K the fcc lattice would discontinuously decrease in volume from 410 to 320 c. a. u. at a pressure of 26 kbar. There is no experimental data on the transition at or near

0°K with which to compare. However, experiments at room temperature have shown that the isomorphous phase transition occurs at a pressure of 42 kbar with the volume changing from about 362 to 329 c. a. u.¹ The quantitative differences are obvious, but it is not clear how much of the difference is due to temperature effects and how much is due to approximations of the model. In the calculation, the zero-point motion of the lattice has been ignored. By use of the Grüneisen model,^{7,13} it is easy to show that the error in the total energy and pressure introduced by this approximation is less than the estimated numerical accuracy. However, if the calculation was to be extended to nonzero temperatures, it would no longer be satisfactory to neglect the lattice in this manner. Also, at temperatures greater than zero, it is the Gibbs free energy rather than the enthalpy which determines the relative stability of a system. This quantity has not as yet been calculated and it is, as a result, not possible to make a quantitative comparison between the results and the experimentally observed isomorphous transition.

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