

Calculation of the electronic transition in cesium

A. K. McMahan

University of California, Lawrence Livermore Laboratory, Livermore, California 94550

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The behavior of cesium under compression is unusual not only because of the isostructural transition at 4.25 GPa, but also because of the abnormal softness of the isotherm at lower pressures. Self-consistent augmented-plane-wave $X\alpha$ calculations of the $T = 0$, fcc cesium pressure-volume isotherm are reported which suggest that both phenomena may be due to the electronic s - d transition in this material. It is demonstrated that in the vicinity of an electronic transition, such techniques are very poorly convergent with the number of points taken in the Brillouin zone, and that great care must be exercised to insure that the results are physically meaningful.

I. INTRODUCTION

It is well known that room-temperature cesium metal undergoes a first-order isostructural (fcc to fcc) transition under 4.25 GPa (42.5 kbar) of pressure, with a volume decrease of about 9%.¹⁻⁵ According to the original suggestion of Fermi,⁶ the transition occurs because the 6s electrons collapse into more-localized 5d orbitals which become energetically favorable as the solid is compressed. While this picture is certainly oversimplified, electron band-structure calculations do show the empty 5d band to drop down through the half-filled 6s band as the solid is compressed.⁷⁻¹² Using estimates of the total energy against volume as obtained from the Wigner-Seitz method, Sternheimer⁷ first argued that such band crossing could lead to a first-order transition. This contention is apparently supported by self-consistent augmented-plane-wave (APW) calculations reported by Averill,¹² although these results are complicated by numerical problems as will be discussed in this paper.

Experimental evidence indicates that the shift in valence electrons from 6s to 5d states is actually already underway at zero pressure. This can be judged from a relatively larger distortion (3%) in the Fermi surface of cesium, presumably due to admixture of 5d states, than is found in the other alkali metals.¹³ The band-structure calculations are in qualitative agreement,^{9,11} and show that the shift from 6s to 5d is continuous and not completed until very high compressions.¹¹ Completion occurs at pressures quite likely in excess of 10 GPa. Given this continuous and extended character of the s - d transition, McWhan *et al.*⁵ have recently argued that it is most likely responsible for the unusual softness of the observed isotherm below 4.25 GPa and not perhaps for the first-order transition itself. The size of the bulk modulus and its rate of increase with pressure are considerably

smaller for the low-pressure cesium isotherm than would be expected from trends apparent in the other alkali metals.¹⁴

The purpose of the present paper is to report self-consistent APW calculations of the $T = 0$ fcc cesium pressure-volume isotherm which suggest that the s - d transition may indeed lead to *both* the first-order transition and to the overall softening of the low-pressure isotherm. The isostructural transition is seen to be associated with only a small part of the 5d band, namely the subband in the vicinity of the X point which includes the X_3 state. These states are of a symmetry character not found in the 6s band, and thus cross through the 6s band without hybridization in very much the manner initially conceived by Sternheimer. This aspect of the s - d transition appears to lead to the first-order transition. However, the lowest-energy 5d states nearby and including the X_1 state are of a symmetry character which is present within the 6s band. The first encounter of the two bands is thus not in fact band crossing, but rather a continuous distortion of the predominantly s -like valence band as it gradually assumes increasing d character via hybridization. It is this initial part of the s - d transition which determines the character of the low-pressure isotherm. The essential point is that the mechanism responsible for the isostructural transition and the softening mechanism discussed by McWhan *et al.* pertain to qualitatively different aspects of the prolonged s - d transition and are not therefore in conflict.

Numerical calculations in the vicinity of an electronic transition are complicated by pronounced convergence problems with the number of points taken in the Brillouin zone. This fact does not appear to have been appreciated before, and indeed Averill's calculations¹² using 256 points in the Brillouin zone are far from converged. The basic problem is that approximation of the band structure by a finite sampling of the Brillouin zone leads

in the vicinity of an electronic transition to large and spurious discontinuities in the computed pressure-volume isotherm, which may be mistakenly identified as real first-order transitions. Increasing the number of points in the Brillouin zone results in more, but smaller discontinuities, as the curve approaches a continuous and physical limit. Only in this limit can a real first-order transition be detected in the computed pressure-volume isotherm as a region of negative bulk modulus, i.e., a Van der Waals loop.¹⁵ These facts are demonstrated in the present paper by comparing separate calculations of the cesium isotherm as obtained with the self-consistent APW- $X\alpha$ method using 32, 256, and 2048 points in the Brillouin zone. The isotherm appropriate to 16384 points is also obtained by a slightly different method. The 16384-point calculations are very nearly converged, and exhibit a well-defined shoulder in the pressure-volume isotherm. The trend evident with increasing number of points in the zone suggests that this feature will indeed evolve into a Van der Waals loop in the fully converged result. The 16384-point isotherm is already sufficiently converged, however, to permit for the first time a clear identification of that specific part of the $5d$ band which is responsible for the isostructural transition, as mentioned above. The numerical convergence problems and this identification are the two principal new points made in this paper. They are considered in detail in Secs. II and III.

II. CALCULATIONS

Bulk properties of solids have by now been rather successfully calculated using self-consistent electron band theoretical techniques in which the Brillouin zone is sampled at only a relatively small number of points (typically 256 or 2048 for an fcc lattice). If there is band crossing at the Fermi level, however, this approximation can lead to large and spurious discontinuities in the computed pressure-volume isotherm. This fact does not appear to be generally appreciated, and is documented here. It is not a serious obstacle, and simply means that an unusually large number of points in the Brillouin zone must be used for accurate calculations in the vicinity of an electronic transition. Methods exist for such calculations.¹⁶ Another method is used here for cesium in order to more clearly illuminate the nature of these convergence problems, and at the same time to yield an isotherm which appears to be nearly converged.

In one-electron self-consistent-field methods, the total energy, pressure and number of electrons at $T = 0$ may be written

$$E(V) = f(V) + \sum_i w_i n_i \epsilon_i(V), \quad (1)$$

$$P(V) = -f'(V) - \sum_i w_i n_i \epsilon_i'(V), \quad (2)$$

$$N = \sum_i w_i n_i, \quad (3)$$

where $f(V)$ contains potential energy terms, $\epsilon_i(V)$ are one-electron eigenvalues, and the primes in Eq. (2) signify volume derivatives. According to Fermi statistics, the n_i are unity and then zero working up from the lowest eigenvalue. (In the approximation to be discussed, the uppermost occupied state may have n_i a fraction.) Whereas the sums in Eqs. (1)–(3) should be replaced by integrals over the Brillouin zone, it is possible in practice to solve the one-electron equation for only a *finite* number of eigenvalues as indicated. This is usually done over a grid in the irreducible part of the zone, with w_i giving the appropriate symmetry weighting, multiplied by a fixed macroscopic number to simulate all of the states which are omitted. It is this macroscopic weighting of the finite number of calculated states that can lead to significant discontinuities in the sum in Eq. (2), when there is band crossing at the Fermi level. The discontinuities occur at volumes where the uppermost occupied state suffers an abrupt change in its occupation, because its eigenvalue has been crossed by that of another state. At the point of crossing, the volume derivatives of the two eigenvalues are of necessity different. The difference between these derivatives multiplied by the change in occupation and by the macroscopic weighting factor gives a discontinuity in the sum in Eq. (2), and thus in the pressure. This mechanism is the predominant source of the spurious discontinuities in the pressure. The present work indicates that any discontinuities induced in the function $f'(V)$ or in the eigenvalue derivatives $\epsilon_i'(V)$ due to the abrupt changes in composition of the Fermi sea are relatively unimportant by comparison. In any case, as more and more points are calculated in the Brillouin zone, and the weight factors w_i are correspondingly reduced, the discontinuities in all functions will decrease in size as the functions approach continuous limits.

Numerical calculations were performed using the self-consistent APW- $X\alpha$ method, which has been fully described elsewhere.¹⁷ The muffin-tin approximation was assumed, and is likely to be quite good. Simple estimates¹⁸ indicate very small corrections to the pressure, less than 0.1 GPa and negative below the isostructural transition. The exchange-correlation parameter α was taken to be 0.69941. This is the same value as used by Averill,¹² and was chosen so that the $X\alpha$ atom cal-

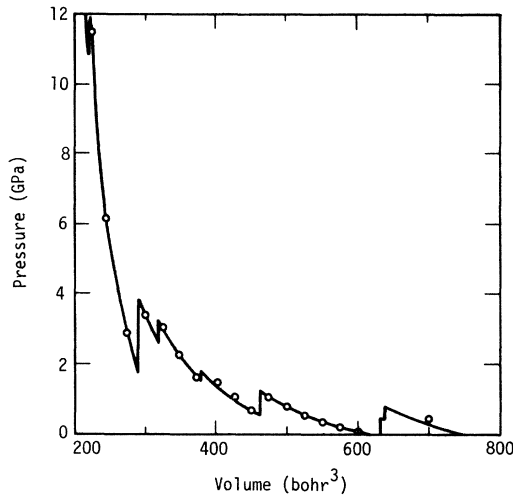


FIG. 1. $T=0$ pressure-volume isotherm of fcc cesium as obtained with a 32 points per Brillouin-zone treatment of the valence bands. The data points are the results of self-consistent APW- $X\alpha$ calculations; the curve was obtained from Eq. (2) as described in the text. The discontinuities are spurious, and arise from sampling the Brillouin zone at only a finite number of points. Increasing the number of points in the Brillouin zone results in more, but smaller discontinuities, as the curve approaches a continuous and physical limit.

ulation would give the same total energy for the cesium atom as the Hartree-Fock method. All electrons were included and treated self-consistently, although the core electrons could be handled in a self-consistent atomic fashion. The $5s$ and $5p$ bands were computed with the equivalent of 32 points in the Brillouin zone, which is fully adequate for these filled, narrow bands. The $6s$ - $5d$ bands were treated in three separate sets of calculations with 32, 256, and 2048 points in the Brillouin zone, respectively. Pressures were obtained by the virial theorem.¹⁷ In general, each calculation was iterated until the total energy and pressure were converged to within ± 0.0005 Ry and ± 0.03 GPa, respectively.

The results obtained for the fcc cesium $T=0$ pressure-volume isotherm using the self-consistent APW- $X\alpha$ method are presented as data points in Figs. 1-3. The solid curves were calculated by another method to be explained below. The three figures correspond to 32-, 256-, and 2048-point treatments of the $6s$ - $5d$ bands, respectively. The 32-point results shown in Fig. 1 are especially useful, since the data points are sufficiently dense so as to clearly illustrate the spurious discontinuities. For example, it is clear that there are two discontinuities in the region 325-600 bohr³, and that these do correlate with abrupt

changes in occupation of the states. The volumes at which these changes in occupation occur are conveniently indicated by the breaks in the solid curve. Values of the total energy and pressure at the 12 volumes in the range 325-600 bohr³ can be fitted within the convergence tolerances of 0.0005 Ry and 0.03 GPa, respectively, by a piecewise function (composed of three smooth analytic curves) and its negative derivative. The virial theorem is thus still satisfied in spite of the discontinuous behavior. The 256-point results shown in Fig. 2 are in close agreement with Averill's calculations.¹² Indeed, his virial theorem pressures fall exactly on the curve shown in the figure, and the 2.6-GPa transition that he reported is the structure suggestive of a Van der Waals loop which lies between 300 and 400 bohr³. Even the 2048-point results shown in Fig. 3 are not yet adequately converged, as is clear from the significant changes which have occurred throughout this sequence of three figures. Nevertheless, the approach towards continuity is evident in these figures, as the number of points in the Brillouin zone is increased.

The slow convergence seen in Figs. 1-3 is principally due to the changing character (number, location, and magnitude) of the spurious discontinuities, and not to pronounced sensitivity of the potential energy integrals or one-electron eigenvalues to the number of points taken in the Brillouin zone. To demonstrate this fact, the solid curves appearing in Figs. 1-3 were all calculated

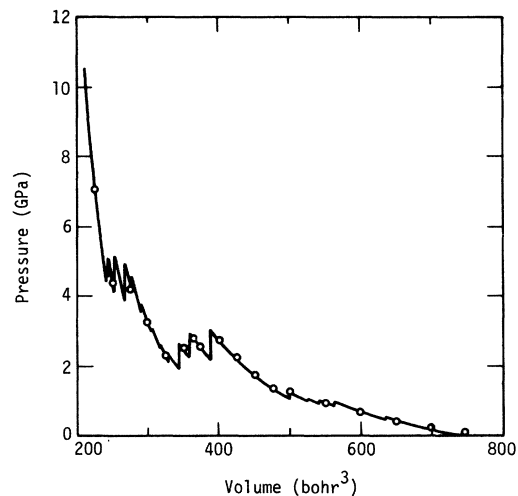


FIG. 2. $T=0$ pressure-volume isotherm of fcc cesium as obtained with a 256 points per Brillouin-zone treatment of the valence bands. The data points are the results of self-consistent APW- $X\alpha$ calculations; the curve was obtained from Eq. (2) as described in the text.

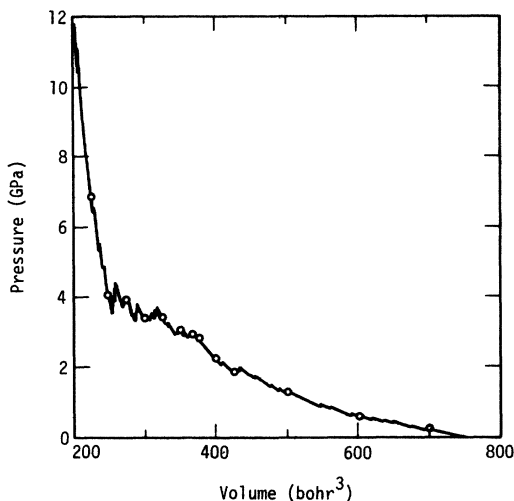


FIG. 3. $T=0$ pressure-volume isotherm of fcc cesium as obtained with a 2048 points per Brillouin-zone treatment of the valence bands. The data points are the results of self-consistent APW- $X\alpha$ calculations; the curve was obtained from Eq. (2) as described in the text.

using Eq. (2) with the same function $f'(V)$ and with eigenvalues obtained from the same set of potentials. To be more specific (i) the self-consistent 2048-point potentials (one for each volume) were used to generate sets of eigenvalues appropriate to 32-, 256-, and 2048-point grids in the full Brillouin zone; (ii) analytic fits to these eigenvalues $\epsilon_i(V)$ were used to obtain their volume derivatives. The fits were made at 11 volumes with an rms deviation of less than 0.1% of the extent of the volume variation. Since the discontinuities arise from the crossing of eigenvalues at the Fermi level, only the 6s-5d valence states were included in the sum, and the remainder was considered lumped in with $f'(V)$; (iii) $f'(V)$ was taken to be the same, analytic function in each case. Tabular values of this function were first obtained using the appropriate sets of eigenvalues and the 32-, 256-, and 2048-point APW pressures. These values were generally found to differ by less than 0.1 GPa in the three cases. The analytic form of $f'(V)$ was then fit to the average of the three tables. The evident success of this prescription (the solid curves) in accounting for the APW results (the data points) in Figs. 1-3 appears to verify the interpretation given above for the slow convergence of the cesium isotherm. In addition it seems quite likely that these curves are to a good approximation the full predictions of the self-consistent APW- $X\alpha$ method when used with 32, 256, and 2048-point samplings of the Brillouin zone. Discontinuities in the curves were connected with vertical lines for visual clarity.

The method just described permits calculation of an isotherm appropriate to an arbitrarily large number of points in the Brillouin zone. The function $f'(V)$ is already known, and the 2048-point potentials can be used to get the appropriate eigenvalues. This has been done for a grid corresponding to 16384 points in the Brillouin zone, and the resultant isotherm is shown in Figs. 4 and 5 (the solid curves). As a comparison, the number of distinct eigenvalues (in the irreducible part of the zone) used in calculation of the curves in Figs. 1-4 were 7, 21, 91, and 491, respectively. Viewing the full sequence of the four figures it is evident that the isotherm in Fig. 4 is very nearly converged, although it still contains residual unphysical structure of about 0.2 GPa in amplitude (see Fig. 5). The most dramatic structure in the curves is tending to coalesce, and has formed a shoulder in the vicinity of 300 bohr³ in the 16834-point isotherm. This trend suggests that the fully converged result is likely to show a Van der Waals loop, i.e., an isostructural transition, at a pressure of 3.5 GPa.¹⁹

The present $T=0$, fcc calculations are compared directly with room-temperature experiment²⁰ (the dashed curves) in Figs. 4 and 5. Thermal corrections to the calculated isotherm are likely to be small (~ 0.1 GPa)²¹; and zero-point corrections,

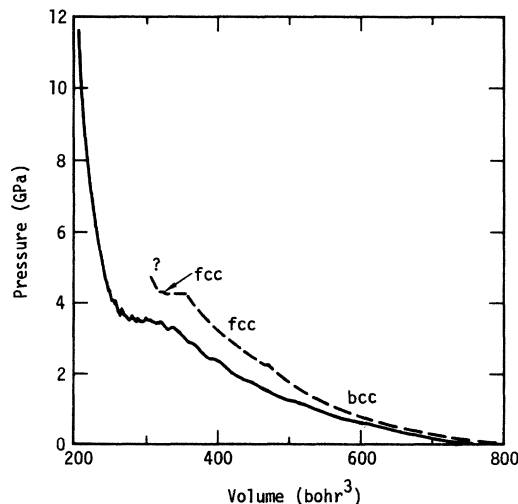


FIG. 4. $T=0$ pressure-volume isotherm of fcc cesium as obtained with a 16384 points per Brillouin-zone treatment of the valence bands (solid curve), and room-temperature experiment (dashed curve, see Ref. 20). The calculated isotherm was obtained from Eq. (2) as described in the text. Considering the trend in Figs. 1-4 with increasing number of points in the Brillouin zone, it is likely that the shoulder at 3.5 GPa seen in the solid curve will evolve into a Van der Waals loop in the fully converged result.

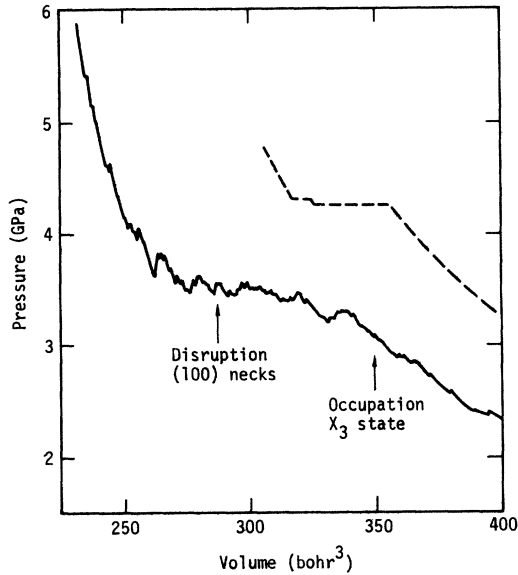


FIG. 5. Results presented in Fig. 4 are shown here in more detail near the isostructural transition. The shoulder in the calculated curve is correlated with two topological changes in the Fermi surface, as shown.

negligible. While cesium exists in the bcc phase below 2.25 GPa,² Averill's results suggest this difference is on the order of the 0.1-GPa computational uncertainty.¹² Examination of Fig. 4 shows that while approximately the correct zero pressure density is found,²⁰ the calculated pressure increases too slowly with compression, leading to the apparent transition at 3.5 GPa rather than the observed 4.25 GPa. Furthermore, the shoulder in the calculated isotherm is displaced to smaller volumes by about 12% in comparison with experiment. These results are nevertheless fairly good for the following reason: In the vicinity of an electronic transition, computed bulk properties are extremely sensitive to details of the electron band structure. A decrease in the $5d$ - $6s$ separation of only 0.02 Ry, for example, would be sufficient to move the shoulder of the theoretical curve in Fig. 4 to within the experimentally observed volume range. This sensitivity to the band structure makes accurate calculation of the cesium isotherm quite difficult, especially in light of the generally poor agreement with experiment achieved by theoretical calculations of the normal density, bcc phase Fermi surface.²² It may be that adjustments in the band structure due to relativistic effects, neglected here and generally neglected in cesium calculations, will lead to better results for both the Fermi surface and the bulk properties.²³ However in the case of the bulk properties, there is possibly another more subtle problem. Local ex-

change-correlation potentials do not simultaneously give accurate results for both bulk properties and band structure.²⁴ In the case of an electronic transition the two are so interconnected that such approximate potentials may be inadequate. Indeed, while the present work used the $X\alpha$ approximation, selected tests with both the Hedin-Lundqvist²⁵ and Kohn-Sham potentials did not significantly improve overall agreement with experiment.²⁶

III. DISCUSSION

The isostructural transition in cesium is due to only one aspect of the prolonged s - d transition in this material. Before focusing on this aspect in detail, it is important to have some idea as to the full extent and complexity of the s - d transition itself. The present fcc calculations will suffice for qualitative observations, in spite of the fact that the stable phase of cesium is not fcc everywhere in this range.²⁷ Figure 6 shows the electron band structure of fcc cesium at two volumes. In rough essence, the crossing of the $5d$ and $6s$ bands results in the population of d -like states about X at the expense of s -like states about Γ . There are in fact two pockets of electrons about X which arise in qualitatively different ways according to the different symmetries (X_1 and X_3) of the two subbands which constitute the $5d$ band near this

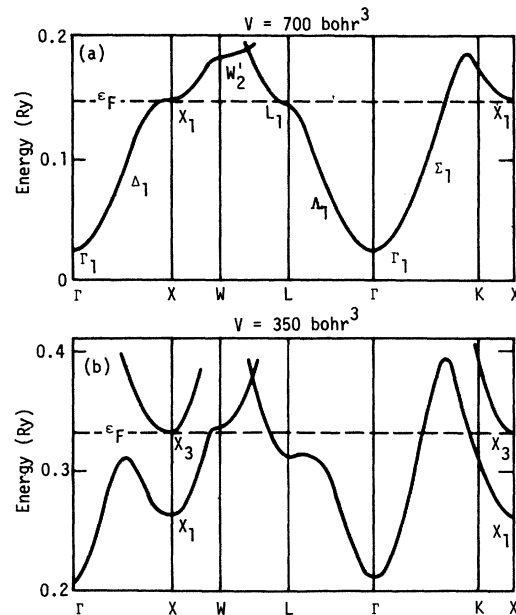


FIG. 6. Electron band structure of $T=0$, fcc cesium at two volumes: (a) at 700 bohr^3 , and (b) at 350 bohr^3 . Energies are relative to the muffin-tin zero. The softness of the low-pressure isotherm and the isostructural transition are likely due to the development of electron pockets at X_1 and X_3 , respectively.

point. The lower energy X_1 subband is of the same symmetry as the $6s$ band. Its effect is thus manifest via hybridization in a growing distortion of the originally s -like valence band as states in the vicinity of the X point assume increasing d character and are depressed in energy. Compare Figs. 6(a) and 6(b). This process is already underway in Fig. 6(a), roughly normal density, as can be deduced from the presence of significant distortion in the Fermi surface. The higher energy X_3 subband is characterized by a symmetry not present in the $6s$ band, and so will cross through the $6s$ band without hybridization. Figure 6(b) shows that these nearly pure $5d$ states begin to pass below the Fermi surface at $V = 350 \text{ bohr}^3$. With further compression both X_1 and X_3 states continue to drop in energy relative to the rest of the band structure, until at $V = 220 \text{ bohr}^3$ the Γ_1 state rises above the Fermi surface, and the s - d transition is completed.

There are two anomalous features in the experimental cesium isotherm—the isostructural transition, and the unusual softness of the isotherm below this phenomenon. McWhan *et al.*⁵ have suggested that the later effect is due to the lower electron pocket at X_1 . According to their argument the kinetic energy is reduced by dividing the electrons between this pocket of states and the original pocket at Γ_1 . The present paper shows that the isostructural transition is probably due to the upper electron pocket at X_3 . The flat portion of the 16 384-point isotherm coincides with the population of these states largely at the expense of states along the $\langle 100 \rangle$ necks of the original Fermi surface. The process begins at $V = 350 \text{ bohr}^3$ when the X_3 state passes beneath the Fermi level, and terminates at $V = 287 \text{ bohr}^3$ when the $\langle 100 \rangle$ necks are disrupted. Indeed the electron density of states at the Fermi energy, taken as a function of volume, shows a peak centered about the region where the isotherm is flat. The initial 30% rise and the subsequent decay of this peak are due, respectively, to the gain of states at X and to the loss of states through disruption of the necks. One may ask why the two $5d$ subbands near X should lead to such qualitatively different features in the isotherm. A tentative answer is that the effects of hybridization involved in the first case lead to a more gradual form of s - d transition, whereas in the second case

one actually has abrupt band crossing in the sense initially considered by Sternheimer.⁷

The locations of the two topological changes in the Fermi surface do not coincide exactly with the flat portion of the calculated isotherm, as may be seen in Fig. 5. This is easily understood in terms of the analysis of Lifshitz.²⁸ When the new electron pocket appears at the X point as the volume is reduced below $V_1 = 350 \text{ bohr}^3$, the functional dependence of the pressure is abruptly changed by addition of a correction $\delta P_1(V)$, whose leading term can be shown to be $\propto (V_1 - V)^{3/2}$ and negative. As the volume is further reduced below $V_2 = 287 \text{ bohr}^3$, and the $\langle 100 \rangle$ necks are disrupted, there is another correction $\delta P_2(V)$ with leading term $\propto (V_2 - V)^{3/2}$, but now positive. The singular behavior of $\partial^2 P / \partial V^2$ at these critical volumes is not the important issue. Rather it is that systematic changes in the pressure are *initiated* at these volumes. Furthermore, these changes start with zero value and slope, and so the effects may not be immediately apparent. Thus it is to be expected that the flat area of the 16 384-point isotherm should appear displaced to lower volumes relative to the critical volumes, as is the case. However it must be emphasized that while topological changes in the Fermi surface do play an important role as Kmetko²⁹ and others^{11,5} have suggested, their existence alone does not explain the isostructural transition. What is important is the rate at which each such change occurs as the volume is reduced, i.e., the coefficients of the $\frac{3}{2}$ -power pressure corrections. (Parameters extracted from the band structure do show these coefficients to be appropriately large for the two cases discussed above.) Thus in last analysis, the isostructural transition in cesium occurs because the rate at which the X_3 eigenvalue approaches the Fermi energy is sufficiently large so as to drive the bulk modulus negative.

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- ¹⁸See Appendix in A. K. McMahan, B. L. Hord, and M. Ross, *Phys. Rev. B* **15**, 726 (1977).
- ¹⁹It may be that the amplitude of the anticipated Van der Waals loop is so small as to still appear as a shoulder on the scale of Fig. 5. A simple-minded consideration of the Van der Waals liquid-gas model suggests that the local maxima of loops in the pressure-volume isotherms should lie beneath the coexistence curve. In cesium there is no critical point for the isostructural transition, presumably because it is obscured by the liquid. However, in the case of the other known electronic isostructural transition in cerium, $T_c \sim O(10^3)$ K [A. Jayaraman, *Phys. Rev.* **137**, A179 (1965)]. Presume this to apply to cesium, and suppose that the amplitude of the loop in the $T=0$ isotherm is, say a third of the difference between the critical pressure and the $T=0$ transition pressure. Taking 0.1 GPa thermal pressure per 300 K in temperature, one then estimates an amplitude ~ 0.1 GPa.
- ²⁰The room-temperature experimental isotherm has been taken from Refs. 2 and 5 as pressure vs relative volume, V/V_0 . There is some small disagreement as to V_0 . However the extensive piston-displacement work of Ref. 14 and the single-crystal x-ray work of C. E. Weir, G. J. Piermarini, and S. Block [*J. Chem. Phys.* **54**, 2768 (1971)] both suggest that at 300 K, $V_0 = 70.5 \text{ cm}^3/\text{mole} = 117 \text{ \AA}^3 = 790 \text{ bohr}^3$. This value was chosen. Reference 14 shows that at $T=0$, $V_0 = 66.5 \text{ cm}^3/\text{mole} = 745 \text{ bohr}^3$.
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- ²²See Refs. 9 and 11. Improved agreement with experiment has been achieved only through very careful adjustments of the one-electron potential, cf. S. D. Mahanti and T. P. Das, *Phys. Rev.* **183**, 674 (1969).
- ²³Relativistic shifts for cesium can easily be as large as 0.02 Ry. See F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, N.J., 1963), Chap. 2.
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- ²⁶The Hedin-Lundqvist potential gave pressures in close agreement with those obtained with the $X\alpha$ potential. The Kohn-Sham potential, $\alpha = \frac{2}{3}$, gave pressures in considerably better agreement with experiment in the vicinity of the isostructural transition. Unfortunately this choice worsens agreement with experiment at normal density, cf. F. W. Averill, *Phys. Rev. B* **6**, 3637 (1972).
- ²⁷At room temperature, cesium is bcc below 2.25 GPa (Cs-I), and of unknown structure above about 4.3 GPa (Cs-IV) (see Ref. 2). At zero temperature the fcc to fcc isostructural transition (Cs-II-Cs-III) is in fact bypassed in a direct transition from Cs-II to Cs-IV (see Ref. 4). This is a complication which goes beyond the scope of the present work. Nevertheless, the volume change in the low-temperature Cs-II-Cs-IV transition is comparable to that of the higher-temperature isostructural transition, and so the electronic effects studied in this paper are likely to still play an essential role in this low-temperature counterpart of the isostructural transition.
- ²⁸I. M. Lifshitz, *Zh. Eksp. Teor. Fiz.* **38**, 1569 (1960) [*Sov. Phys.-JETP* **11**, 1130 (1960)].
- ²⁹E. A. Kmetko (private communication).