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Relativistic effects, phonons, and the isostructural transition in cesium

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Relativistic linear-muffin-tin-orbital calculations of the fcc cesium 0-K pressure-volume isotherm are reported which indicate that the isostructural transition in this material is a more complicated phenomenon than has been thought to be the case. It is shown that the effect of relativistic shifts on the electron bands serves to eliminate the possibility of obtaining such a transition in the $T = 0$ isotherm for the static lattice. Thermal effects must therefore play an essential role in the observed isostructural transition at room temperature. In particular, it is suggested on the basis of simple model calculations that an anomaly in the lattice vibrational contribution to the pressure, which is in fact intimately connected with the electronic transition in cesium, is a possible mechanism for the observed transition.

I. INTRODUCTION

Room-temperature (298 K) cesium metal exhibits an unusual first-order phase transition, from an fcc to an fcc lattice, under 4.22 GPa (42.2 kbar) of pressure.[1–6] Fermi[7] originally suggested that the cause of this isostructural transition was the collapse of the outermost $6s$ electrons in the Cs atoms into more localized $5d$ orbitals. Indeed, early Wigner-Seitz calculations by Sternheimer[8] and others[9] showed a Van der Waals loop in the pressure-volume isotherm, i.e., a first-order transition, due to the empty $5d$ band passing down through the initially half filled $6s$ band. Subsequent more rigorous band-structure calculations[10–15] show the situation to be more complicated, although they still appear to verify the essential electronic nature of the isostructural transition. The evolution of valence electrons from $6s$ to $5d$ states occurs over a rather extended range in pressure, from zero up to about 10 GPa. McMahan[15] has argued that only one aspect of this prolonged change in electronic structure leads to the isostructural transition, namely, that due to a small pocket of $5d$ states including that of X_3 symmetry. These states are incapable of hybridizing with the $6s$ band and thus pass down through the Fermi level in much the abrupt manner described by Sternheimer. Elsewhere the effects of the electronic s-d transition appear to be considerably softened due to hybridization between the two bands. McWhan *et al.*[6] have suggested that this milder form of electronic transition may explain the abnormal softness observed in the low-pressure Cs isotherm.[16]

It would seem that the isostructural transition in Cs is now understood. However, all of the calculations described above have been nonrelativistic, and yet it is known that such effects on the band structure can be important for the heavier elements in the Periodic Table. We report here relativistic calculations of the $T = 0$, fcc Cs pressure-volume isotherm using Andersen's linear-muffin-tin-orbital (LMTO) method.[17,18] These calculations indicate that relativistic shifts of the bands have totally removed the possibility of a Van der Waals loop in the $T = 0$ isotherm, as obtained for the static lattice.[19] The effect of the X_3 pocket of $5d$ states is still significant, but it is not now sufficient to drive the bulk modulus negative, and thus yield a Van der Waals loop. The important implication of these results is that the 298-K isostructural transition in Cs must then arise at least partially from thermal effects, either lattice vibrational or of electronic character.

The most likely source of interesting thermal effects at 298 K is from the lattice vibrational or phonon excitations. The electronic density of states is devoid of sufficiently dramatic structure to permit very significant effects from electronic excitation at such a low temperature. On the other hand, Fermi's idea of a collapsing Cs atom is suggestive of a temporary *decrease* with compression in the lattice vibrational frequencies in the vicinity of the collapse. This would imply a negative phonon contribution to the total pressure in this volume range, which might conceivably induce a Van der Waals loop into the total pressure. Essentially this same idea is implicit in explanations[20–22] of the dramatic decrease observed[2,4] in the Cs melting temperature in the vicinity of the isostructural transition. The decreasing phonon frequencies near the collapse lead to larger amplitude thermal vibrations, which according to the Lindemann criteria will depress the melting temperature.

To lend some credence to the suggestion that the isostructural transition in Cs might be caused by an anomally in the phonon contribution to the pressure, we report a simple Grüneisen model calculation of 298-K isotherm. In the high-temperature limit, the phonon contribution to the total pressure may be expressed in terms of the lattice Grüneisen parameter. There are approximate expressions for this parameter which involve derivatives of the static lattice pressure-volume curve.[23] These expressions do in fact yield a Grüneisen parameter which is consistent with both the existence of a Van der Waals loop in the 298-K pressure, and also with the melting curve anomaly. Furthermore, this behavior is related to the s-d transition in Cs. The important structure in the Grüneisen parameter comes from a region of negative curvature in the $T=0$ static lattice pressure-volume curve, which is the reduced effect of the X_3 pocket of $5d$ states in the new relativistic calculations. Although suggestive, these Grüneisen parameter calculations are still far too approximate to be conclusive. A rigorous calculation of the phonon frequencies will be needed to substantiate these ideas about the Cs isostructural transition. Direct calculation of phonon frequencies from first-principles band theory is at present a relatively new and difficult area of research. It is hoped that the present work will stimulate further effort in this area for the case of Cs.

II. RELATIVISTIC LMTO CALCULATION

To calculate the band structure, we have used the linear-muffin-tin-orbital (LMTO) method of Andersen[17,18] in the atomic-sphere approximation (ASA). In this approximation the LMTO method is some hundred times faster than conventional augmented-plane-wave (APW) or Korringa-Kohn-Rostocker (KKR) techniques, with little loss of accuracy. Thus we were able to calculate the band structure self-consistently on a rather fine grid of $\vec{k}$ points (715 in the irreducible wedge of the fcc Brillouin zone) and avoid the convergency problems encountered in recent APW calculations for Cs.[15] The rigid core approximation was used for all inner shells, including the $5s$. The $5p$ states were treated self-consistently as bands. Their bandwidth was found to be strongly volume dependent, and at about 8 GPa, when Cs is compressed to one third of its equilibrium volume, it amounts to 3 eV. This is within 5% of the result found in nonrelativistic APW calculations,[15] which also showed the $5s$ band at this volume to be 1 eV wide and located 21 and 9 eV, respectively, below the bottoms of the $6s$ and $5p$ bands. The $5s$ bandwidth should get rapidly smaller at the larger volumes of principal concern here, and as will be argued shortly, we anticipate no significant effect of our non-self-consistent treatment of the $5s$ states on the conclusions reached in this paper.

In the angular momentum expansions of the muffin-tin orbitals, we included terms up to $l=3$ in the two- and three-center terms, for $5p$ and conduction bands. Relativistic effects, apart from spin-orbit coupling, have been treated in a scalar relativistic equation[24] which keeps the Darwin and the mass-velocity term to all orders in $1/c$. For exchange and correlation, we applied the local-density (LD) approximation and the prescription of Hedin and Lundqvist.[25] Previously, this approximation has been shown to account for the cohesive properties of simple and transition metals[26] and, therefore, seems adequate also for the near transition metal Cs.

The electronic pressure may be expressed as a surface integral over the unit cell, and in the ASA[27]

$$3PV=\sum_l \int^{E_F} dE\, N_l(E)\, s\,\phi_l^2(E,s) \times[(D_l-l)(D_l+l+1) +(E-\epsilon_{xc})s^2]\,, \tag{1}$$

where $N_l(E)$ is the projected density of states (DOS) of angular momentum l and $\phi_l(E,s)$ is the amplitude at the sphere radius s of the normalized radial function at energy E. The logarithmic derivative is defined by $D_l(E)=s\phi_l'(E,s)/\phi_l(E,s)$, and $\epsilon_{xc}(n_s(s))$ is the density of exchange-correlation energy at the sphere radius in the local approximation. To evaluate Eq. (1), we need only the self-consistent electron potential and density at a given volume. This avoids the calculation and numerical differentiation of large numbers and, at the same time, provides a bonding analysis in local angular momentum.

The intercellular Coulomb interaction beyond the ASA may be included as a muffin-tin correction to the total energy, namely, $\Delta U/\text{atom}=\alpha q_s^2/s$, where α is a constant and equals 8.25, 8.14, and 8.34 mRy for the fcc, bcc, and hcp lattice, and q_s is the charge per atom corresponding to a constant density $n_s(s)$ in the unit cell. The resulting pressure correction is

$$\Delta P=\frac{\alpha q_s^2(s)(1-2sq_s'/q_s)}{3Vs}\,. \tag{2}$$

A derivation of this correction term may be found in Ref. 28, and, there, it has been shown that it considerably improves the calculated cohesive properties of simple and transition metals over their ASA values.

In Fig. 1, we compare the present relativistic results (solid line) for the $T=0$ static lattice pressure-volume isotherm of fcc Cs to the recent nonrelativistic calculation of McMahan[15] (dashed line), which has been smoothed. The muffin-tin correction, Eq. (2), has been included. It increases from 0.1 GPa at $V/V_0 = 0.7$, where $V_0 = 745$ a.u.^{3} is the low-temperature equilibrium volume of Cs, to 1.4 GPa at $V/V_0 = 0.3$. On the whole, the relativistic calculation is much steeper, and the Van der Waals loop, which may or may not exist in the nonrelativistic calculation near $V/V_0 = 0.4$, is reduced to a negative curvature in this region. To make sure that this drastic difference is not an artifact of the approximations inherent in either band-structure program, we also performed nonrelativistic LMTO calculations over the important region, $V/V_0 = 0.35-0.5$, and confirmed McMahan's results to within a few kbar. Since this test, nonrelativistic LMTO calculation treated the $5s$ states in the same non-self-consistent manner as the present relativistic calculation, the difference between the two curves reflects only the effects of relativity, and not possible inaccuracies caused by treatment of the core. We expect such inaccuracies to be quite small for $V/V_0 > 0.35$. They should be most notable in the case of the larger nonrelativistic core, and yet as noted there is good agreement in this region between the test LMTO calculation and McMahan's nonrelativistic APW work which not only treated all core states self-consistently, but also included the $5s$ states amongst the bands. While core corrections will eventually be needed at smaller volumes, this is beyond the range of interest in this paper.

In Fig. 2, the pressure is analyzed into angular momentum components according to Eq. (1). The dominant bonding contribution ($P < 0$) derives from $5d$ partial waves, and even at equilibrium the now only hybridized $5d$ contribution is responsible for bonding. The theoretical equilibrium atomic distance ($P = 0$) is about 3.4% too small; similar agreement has been found in LMTO-ASA calculations for simple and transition metals.[28] The $6s$ and $6p$ conduction electrons are increasingly repulsive under compression and, after the anomaly, the hard $5p$ core determines the slope of the pressure isotherm. The $5p$-bonding contribution is grossly overestimated in the nonrelativistic calculation (dashed line in Fig. 2) and accounts for part of the discrepancy in Fig. 1. The remaining difference is due to the continuous s-d transition, which occurs much slower in the relativistic case.

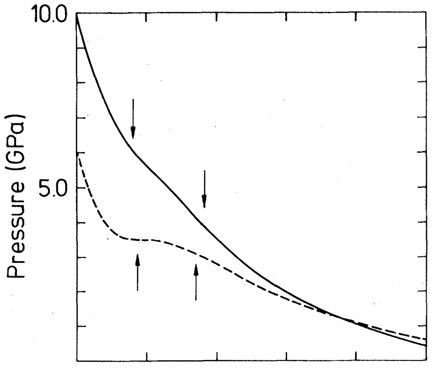

FIG. 1. Calculated static lattice pressure-volume isotherm of fcc Cs at $T = 0$. Solid line: relativistic calculation, applying Eq. (1) and muffin-tin correction, Eq. (2). Dashed line: smoothed nonrelativistic calculation of Ref. 15. $V_0 = 745$ a.u.^{3}.

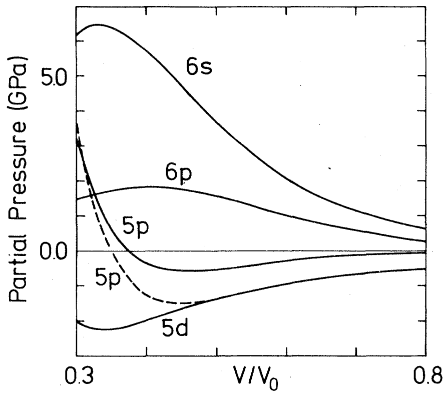

FIG. 2. Electronic pressure of fcc Cs decomposed with respect to angular momentum [Eq. (1)] as function of volume. Solid lines: relativistic calculation for conduction electrons ($6s$, $6p$, and $5d$) and the outermost core electrons ($5p$). Dashed line: nonrelativistic $5p$ pressure.

The relativistic s-d transition is shown in detail in Figs. 3 and 4. The amount of $6s$ and $6p$ charge within the atomic sphere, $n_s + n_p$ (solid lines in Fig. 3), decreases from 0.8 electrons at $V/V_0 = 0.8$ to 0.2 at $V/V_0 = 0.3$. The $5d$ electrons predominate at this relative volume with $n_d = 0.76$, the missing few percent of charge being f-like. These features are accompanied by rapid increases (van Hove singularities) in the d-like density of states at the Fermi energy, N_d (dashed line in Fig. 3), as first the X_1—and then the X_3—subbands of the $5d$ band near X pass below the Fermi level (see also Fig. 4). Finally, at $V/V_0 = 0.38$, the top of the Γ_1-X_1 band rises above the Fermi energy, so that the [100] necks of the Fermi surface disrupt. This yields a negative square-root contribution to the s- and p-like density of states, N_s and N_p (dashed lines in Fig. 3), thereby accelerating the depopulation of the s band. In Fig. 4, we show various band energies, the Fermi energy, and the potential at the atomic sphere as functions of volume, all with respect to the Coulomb potential at the sphere radius. All levels move up under compression due to increasing kinetic energy, especially Γ_1 and X_4', the bottoms of the $6s$ band and of the unoccupied $6p$ band. The Fermi energy moves almost parallel to C_{5d}, the center of gravity of the $5d$ band. One could extrapolate the volume $V/V_0 = 0.25$, where the s

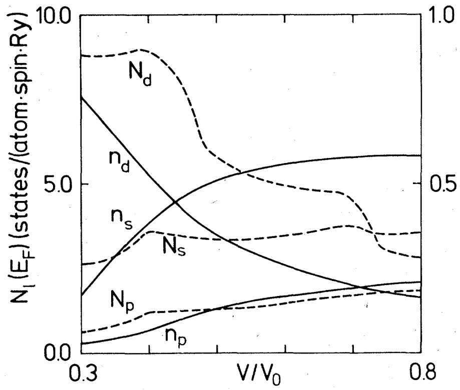

FIG. 3. Projected numbers of state (solid) and densities of state (dashed) at E_F for 6*s*, 6*p*, and 5*d* electrons as function of volume. Note the van Hove singularities crossing the Fermi energy at $V/V_0=0.73$ and $V/V_0=0.48$, respectively (see Fig. 4).

band is compeltely empty, but due to numerical difficulties, we were not yet able to further investigate the low-volume region.

The main features of the continuous *s*-*d* transition in fcc Cs, as analyzed by McMahan,[15] are confirmed by the present relativistic calculation; yet the *s*-*d* transfer happens much more gradually in the relativistic case. This is due to the smaller size of the relativistic atom core and the 6*s* orbital, and therefore the difference in volume between the occupation of the X_3 level and the disruption of the Fermi-surface necks (marked by arrows in Fig. 1) is much larger in the relativistic case. The nonrelativistic calculation gets rid of the antibonding 6*s* electrons much faster and, with the aid of overestimated 5*p* bonding, can almost produce a Van der Waals loop for the $T=0$ static lattice.

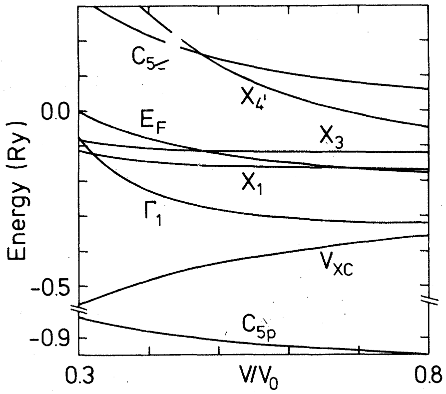

FIG. 4. Band energies of fcc Cs as function of volume. C_{5p} and C_{5d} are the centers of gravity of the 5*p* and 5*d* band, and Γ_1 the bottom of the conduction band. The 5*d* levels of symmetry X_1 and X_3 successively cross the Fermi energy under compression. The accompanying van Hove singularities produce a dramatic increase in 5*d* character at E_F (see Fig. 3).

III. GRÜNEISEN MODEL CALCULATION

We suggest here that the *s*-*d* transition in Cs may lead to an anomaly in the phonon contribution to the total pressure, and that this phenomenon may be responsible for the isostructural transition at 298 K. To best understand this possibility, consider the following expression for the pressure, neglecting electronic excitation and electron-phonon coupling:

$$P(V,T)=P_0(V)+3Nk_BT\gamma(V)/V\ . \tag{3}$$

$P_0(V)$ is the $T=0$ static lattice pressure calculated in Sec. II. The second term is the contribution from quasiharmonic phonons[29] evaluated in the high-temperature limit, which should be adequate at 298 K given the very low Debye temperature in Cs.[30] Note that the Grüneisen parameter depends on the volume derivatives of the phonon frequencies, $\omega_{\vec{k}\lambda}$, according to

$$\gamma(V)=-\frac{1}{3N}\sum_{\vec{k}\lambda}\left(\frac{\partial\ln\omega_{\vec{k}\lambda}}{\partial\ln V}\right)_{T=0}. \tag{4}$$

Thus while $P_0(V)$ does not exhibit a Van der Waals loop, the total pressure may exhibit such a loop should the phonon frequencies dramatically change their volume dependence in some particular volume range.

An approximation to the Grüneisen parameter may be obtained from derivatives of the static lattice pressure. Three expressions are commonly used, based on a Debye model and different assumptions about the volume dependence of Poisson's ratio.[23] They may be summarized by a single equation

$$\gamma(V)=\tfrac{1}{2}\eta-\tfrac{2}{3}-\tfrac{1}{2}V\left(\frac{d^2}{dV^2}[P_0(V)V^\eta]\Big/\frac{d}{dV}[P_0(V)V^\eta]\right), \tag{5}$$

where $\eta=0$, $\frac{2}{3}$, and $\frac{4}{3}$. Any dependence of γ on η may be taken as a measure of the uncertainty in this approach. The function $P_0(V)$ calculated in Sec. II has been analytically fit,[31] and the results for $\gamma(V)$ taking $\eta=\frac{2}{3}$ are shown in Fig. 5. In spite of the large dependence on η shown by the error bars, these results are sufficient for the qualitative observations intended here. Note that γ actually becomes negative in the vicinity of $V/V_0=0.43$, signifying phonon frequencies which are decreasing with compression. This feature is due to the region of negative curvature in $P_0(V)$, which as mentioned earlier arises from the passing of the X_3 pocket of 5*d* states below the Fermi energy. The peak of γ for $V/V_0\sim0.35$

follows from the relatively large positive curvature in $P_0(V)$ as this curve stiffens in response to the contribution from the $5p$ core. Both this peak and the negative minimum in γ are consistent with the observed minimum in the Cs melting temperature. The Lindemann law within the Debye approximation is[32]

$$\frac{d\ln T_m}{d\ln V}=\frac{2}{3}-2\gamma\ . \tag{6}$$

Thus the overall oscillation in γ corresponds, respectively, to a rapid decrease and then subsequent increase in the melting temperature as volume is decreased. Actual numerical integration of Eq. (6) based on the values for γ in Fig. 5 yields a melting temperature in qualitative, but only about factor of 2 agreement with experiment.

The 298-K isotherm calculated from Eq. (3) with the $\eta=\frac{2}{3}$ choice for γ is shown in Fig. 6 (solid curve). A Van der Waals loop does arise from the negative region in γ for this choice of η, and is shown in more detail in Fig. 7 along with the Maxwell construction for the two-phase region (dotted line). At and below the isostructural transition, there is reasonable agreement between the calculated isotherm (solid curve) and the experimental 298-K isotherm[33] (dash-dot curve) shown in the figures. The 0.2–0.4-GPa offset between the two curves is consistent with the accuracy shown by other LMTO-ASA calculations.[28] Although the experimental pressure-volume results shown above the isostructural transition are not entirely reliable,[33] the discrepancy between theory and experiment in this region is more likely due to the uncertainties in our simple Grüneisen parameter calculations. Even so, these calculations suggest a region of negative curvature in the 298-K isotherm, arising from the positive peak in γ, as can be seen near $V/V_0\sim 0.39$ in Fig. 6. The onset of such behavior, i.e., bulk modulus decreasing with compression, was observed by Bridgman[1] near 9 GPa.

An interesting consequence of the present Grüneisen model calculations is the possible disappearance of the first-order fcc-fcc transition *below* some critical temperature. Given the $\eta=\frac{2}{3}$ choice for γ, this critical temperature is about 220 K, suffi-

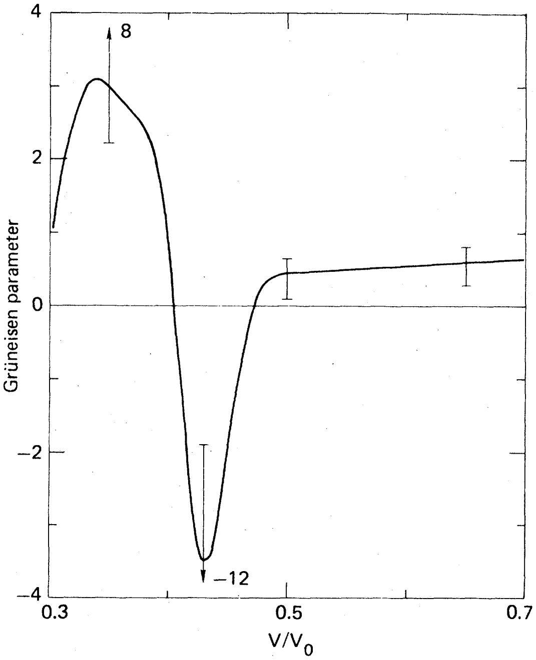

FIG. 5. Grüneisen parameter, γ, as a function of relative volume, V/V_0. Error bars show the uncertainties due to the choice of η. Note that a negative value of γ signifies a region in which the phonon frequencies are decreasing with compression.

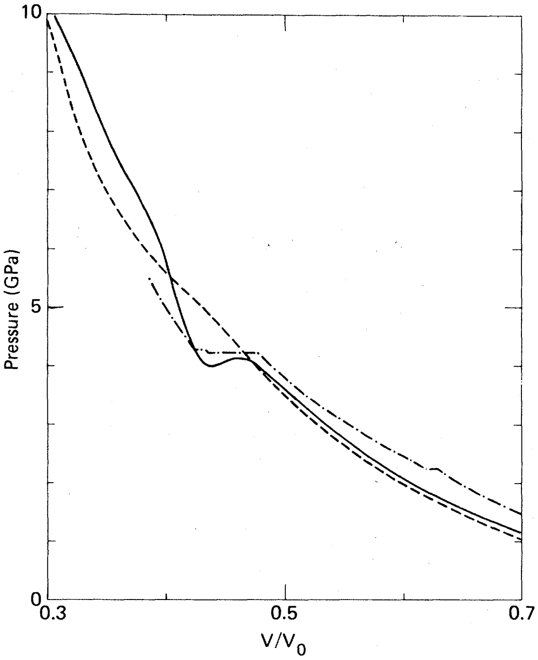

FIG. 6. Cs 298-K pressure as a function of relative volume, V/V_0. In qualitative agreement with experiment (dash-dot curve, Refs. 3 and 6), the theoretical calculation (solid curve) shows an isostructural transition, i.e., the Van der Waals loop. The difference between the solid curve and $P_0(V)$ (dashed curve) is proportional to γ. Thus the Van der Waals loop may be seen to originate from the negative minimum in γ shown in Fig. 5. The positive peak in γ leads to the region of negative curvature seen near $V/V_0\sim 0.39$ for the solid curve, i.e., a region of decreasing bulk modulus with compression.

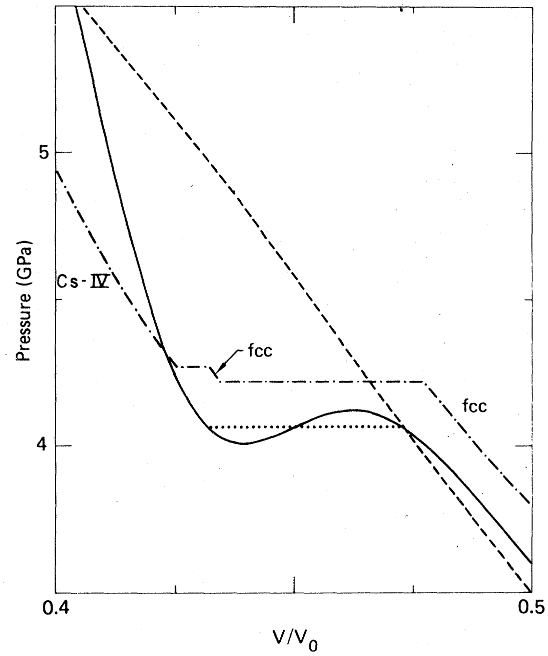

FIG. 7. Cs 298-K pressure as a function of relative volume, V/V_0. The region around the isostructural transition in Fig. 6 is shown in more detail. The Maxwell construction for the two-phase region (dotted line) is shown for the theoretical 298-K isotherm.

ciently larger than the 70–100-K Debye temperature in the transition region[30] to still permit use of the high-temperature expansion, Eq. (3), for an estimate. Such an inverted critical point is unusual, but thermodynamically possible, and has an analogy in the lower consolute temperatures of certain binary mixtures.[34] It is known experimentally that below about 270 K, the isostructural transition in Cs is in fact bypassed,[5] with Cs transforming from the low-pressure fcc phase directly to the high-pressure phase referred to as Cs-IV.[33] The critical temperature indicated by the present simple model might have some bearing on this behavior, and warrants further investigation based on more rigorous calculations of γ.

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[19] Band-theory calculations yield a $T=0$ isotherm for a lattice of immobile atoms, the static lattice. These results must be corrected for zero-point lattice vibrations to obtain the actual $T=0$ isotherm. The appropriate pressure correction within the Grüneisen model is $\gamma\Delta E/V$, where ΔE may be taken as the zero-point phonon energy, $(\frac{9}{8})k_B\Theta_D$. Given the results for the Grüneisen parameter, γ, and the Debye temperature, Θ_D, discussed in Sec. III of this paper, it seems unlikely that the actual $T=0$ isotherm will contain an isostructural transition.

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which is to be used in Eq. (5).

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[29] By quasiharmonic we mean that the harmonic force constants are taken to be volume dependent, while thermal anharmonic effects are ignored.

[30] Based on resistivity data, McWhan and Stevens [Ref. 5, Fig. 1(d)] estimate the Debye temperature for Cs for pressures up to about 6 GPa. Throughout this range they find this quantity to be less than about 120 K. Their low-pressure results are in good agreement with the 1-atm heat-capacity value of 38 K [D. L. Martin, Phys. Rev. 139, A150 (1965)].

[31] Fit used to obtain the results in Figs. 5–7 was

$$P_0(V)=[a+\exp(b+cV)-\exp(d+eV+\cdots+hV^4)]/V .$$

Eight parameters were chosen to fit 22 calculated values of $P_0(V)$ from $V/V_0=0.3$ to 0.8 with an rms deviation of 0.015 GPa. Uncertainties in γ and $P(V,T)$ due to the choice of fitting function were estimated by trying a number of different analytic forms, and found to be considerably smaller than those due to the choice of η. In all cases some value of η between $\frac{2}{3}$ and $\frac{4}{3}$ would yield a first-order transition of the same ΔV as seen in Fig. 7. With η selected according to this criterion, the different analytic fits led to variations of about 9 and 2%, respectively, in the transition pressure and in the location of the transition. In the region most sensitive to the positive peak in γ, $V/V_0\sim 0.37$, pressures as much as 14% larger than shown in Fig. 6 were found with some fits.

[32] S. N. Vaidya and E. S. Raja Gopal, Phys. Rev. Lett. 17, 635 (1966).

[33] The data in Fig. 6 have been taken from x-ray (Ref. 3) and neutron (Ref. 6) diffraction experiments. Note that at 298 K, Cs is bcc below 2.37 GPa, and transforms to an as yet unknown structure, Cs-IV, at 4.27 GPa. This occurs only slightly above the fcc-fcc isostructural transition at 4.22 GPa. The data above 4.27 GPa in the figure are from Ref. 3, and presume Cs-IV to be approximately close packed in order to get the volume from the diffraction pattern.

[34] W. J. Moore, *Physical Chemistry,* 3rd ed. (Prentice-Hall, Englewood Cliffs, 1962), p. 144.