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# Negative thermal expansion coefficient and isostructural transition in fcc cesium

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The equation of state of solid cesium in the face-centered-cubic (fcc) structure is examined theoretically by means of *ab initio* calculations. The electronic energy is calculated within density-functional theory, whereas vibrational contributions to energy and entropy are calculated within the quasiharmonic approximation. The thermal expansion coefficient is predicted to be negative for pressures above 3.5 GPa and up to the end of the stability range of the fcc phase for *all T*. The fcc phase becomes unstable around 4.3 GPa, where a transverse phonon mode with a wave vector along (110) becomes soft. According to the calculations an isostructural transition does *not* occur.

Cesium undergoes a number of structural phase transitions under pressure. Six phases are known to exist at room temperature: I (bcc), II (fcc), III (fcc ??), IV (tetragonal), V (orthorhombic), and VI (double hexagonal close packed).[1–5] The pressure-driven electronic $s\rightarrow d$ transition[6] in cesium is believed to play a major role in the structural behavior, at least for pressures up to about 15 GPa corresponding to fourfold compression.[7–10] One of the remarkable features of the structural sequence is the occurrence of the tetragonal phase IV (4.4–12 GPa) which is only eightfold coordinated.[2] The unusual decrease of the coordination number with increasing pressure from 12 in fcc to 8 in Cs-IV has been interpreted in terms directional bonding induced by the $s$-$d$ transition.[10,11] Beyond phase IV the coordination number increases with pressure. The recently determined orthorhombic structure of Cs-V (12 to ≈70 GPa) has two nonequivalent crystallographic sites with coordination numbers of 10 and 11, respectively,[3] and this $Cmca$ structure is the same as that of Si-VI.[12,13]

The Cs-II phase, which is the one studied here, was found experimentally to exist[1] from 2.3 GPa up to 4.2 GPa. The following phase, Cs-III, exists only in a narrow pressure range, 4.2–4.4 GPa, and until recently it was believed to have the fcc structure. The experiments by Hall *et al.*[1] indicate that an isostructural fcc→fcc transition occurs, and theoretical calculations seemed to confirm this.[9,11] Recent experiments[3] have not been able to confirm that Cs-III has the fcc structure. The existence of an isostructural transition would be interesting, in particular because this would imply that the ‘‘normal’’ metal, Cs, would undergo a transformation similar to the $\alpha\rightarrow\gamma$ transition in Ce, which is due to the $4f$ electrons (see, for example, Ref. 14 and references therein).

Previous calculations,[9,11] as well as the present, show that the $s\rightarrow d$ transition in Cs does not produce a van der Waals loop in the pressure-volume relation for fcc-Cs obtained from total-energies of the electrons alone. But such effects could be caused by the phonons, and therefore their contributions to the free energy must be included. The work in Ref. 9 used a Debye model for the phonons together with an approximative description of the overall Grüneisen parameter in order to estimate the phonon contribution to the pressure. For certain choices of parameters in the model, a van der Waals loop did occur. However, an evaluation of the rather small phonon contributions requires much better precision. Therefore we calculate full phonon spectra for all relevant volumes, and together with the electronic energies this then leads to free energies as functions of pressure $(P)$, volume $(V)$, and temperature $(T)$. This allows not only a study of the phase transition, but also calculations of thermodynamical quantities, like the thermal expansion coefficient. Furthermore, using the present methods, we can examine the *dynamical* stability of the structure vs $P$ and $T$. The earlier calculations[9,11] used electronic total energies obtained within the atomic-spheres approximation[15] (ASA) (with spherical charge distributions inside atomic spheres) which cannot yield energy changes associated with symmetry-breaking distortions. Therefore, such calculations could neither be used to obtain elastic shear constants nor phonon frequencies. This requires methods without shape approximations to potentials and charge densities. Specifically, the ASA calculations would not predict the dynamical instability of fcc-Cs as we describe below. Furthermore, the Debye model cannot lead to the peculiar variation of the thermal expansion coefficient with $P$ and $T$ which is predicted here for fcc-Cs.

The electronic energy of the electrons for a given choice of atomic coordinates is calculated within approximations to the density-functional theory, the local approximation (LDA) as well as a generalized gradient approach (GGA). The LDA calculations lead to a non-negligible overbinding in Cs. The results presented here were obtained with the GGA, and we used the Perdew-Burke-Ernzerhof scheme.[18] We did, however, choose the parameter $\kappa$ to be 0.45 (in accordance with

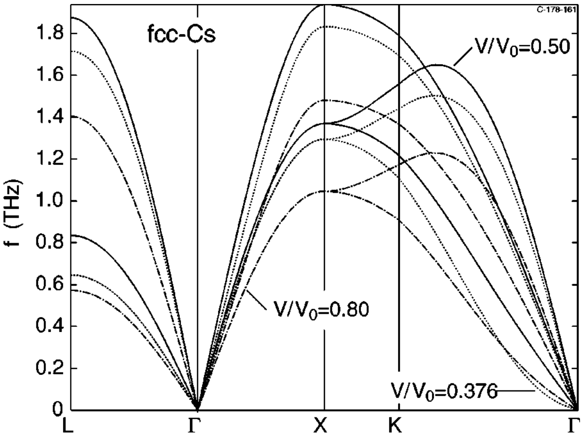

FIG. 1. Phonon-dispersion relations for fcc-Cs for the volumes $V/V_0=0.376$ (dotted curve), $V/V_0=0.50$ (full line), $V/V_0=0.80$ (dash-dotted curves).

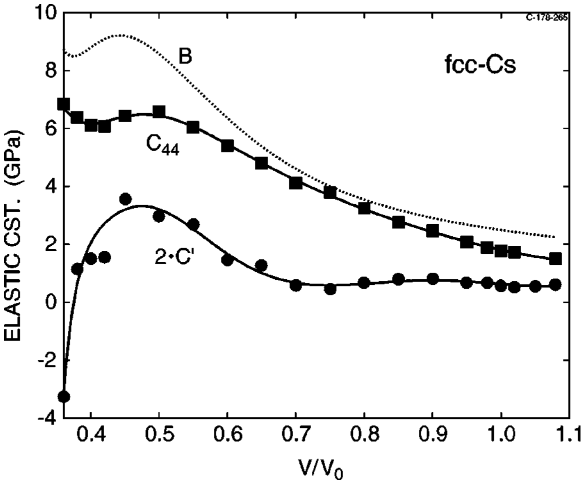

FIG. 2. The elastic constants of fcc-Cs. The lines are least-squares fits to a series of functions of $V$. $B$ is the bulk modulus, squares denote the calculated $C_{44}$ value, while those of $2C'=C_{11}-C_{12}$ are denoted by circles. [Note that Cs is a very soft metal, and the elastic constants are particularly small. The total-energy changes associated with the imposed strains are thus very small (10 $\mu$Ry range), and we needed to include $\approx$14 000 points in the irreducible Brillouin zone. Still some scatter remains, and the curves drawn represent least-squares fits to a series of functions of $V^{-1/3}$.]

previous estimations[19]), i.e., smaller than the "standard value," 0.806,[18] and applying that we found[20] for bcc-Cs a theoretical equilibrium volume at $T=300$ K only slightly larger (by $\approx$2%) than observed.

The solution of the effective one-electron equations was performed by means of the linear muffin-tin orbital (LMTO) method[15] in the full-potential version.[16,17] The semicore states, Cs-5$s$ and $-5p$, were treated as *local orbitals*[21,22] in the same energy window as the valence states. The band-structure calculations were scalar relativistic, i.e., all relativistic effects, except spin-orbit splitting, were included. Concerning the band-structure method, approximations to exchange correlation, and basis set, the present calculations are then similar to, and consistent with, those used earlier[13,5,20] for the high-pressure phases of Cs.

We have estimated the finite-$T$ contributions to the electronic free energy (energy as well as $TS$ terms, $S$ being the entropy), and found that they can be neglected in comparison to the phonon terms. The phonon contributions to the free energy are calculated within the quasiharmonic approximation, i.e., the dispersion relations are derived as in usual harmonic approximations, but the force constants (and thus frequencies) vary with volume. We decided to use a method quite similar to the one suggested by Sharma and Joshi,[23] in which the elements of the dynamical matrix are related to the elastic shear constants. These are obtained from electronic total-energy calculations as described above and in Refs. 24 and 20. (Our final equations and arguments leading to them differ somewhat from those of Ref. 23. For example, the dynamical matrix fulfills in our version the symmetry requirements in $\mathbf{q}$ space.[25,20]) The phonon-dispersion functions, $f(\mathbf{q})$, are calculated on a dense mesh of volumes, and in terms of the phonon density-of-states functions we obtain the contributions to the thermodynamical functions, $F$, $E$, and $S$, Helmholtz free energy, the energy, and the entropy, respectively.

Figure 1 shows three examples of the dispersion relations obtained for fcc-Cs. It is seen that a compression of the lattice from $V/V_0=0.80$ (dash-dotted lines) to $V/V_0=0.50$ (full lines) leads to an increase of the frequencies in all modes. This is the "normal" behavior, since usually a crystal hardens under compression. ($V_0$ is the experimental equilibrium volume of bcc-Cs at room temperature, and it corresponds to a lattice constant $a_{bcc}=6.05$ Å.) The dotted curves in Fig. 1 show that at $V/V_0=0.375$ all frequencies are *lower* than those found for $V/V_0=0.50$ (full lines). In addition we find that one mode, the lowest transverse mode with wave vector $\mathbf{q}$ along (110) becomes soft in the long-wavelength limit. At $V/V_0=0.375$ it already drops below the corresponding curve for $V/V_0=0.80$, and further compression would (formally) lead to imaginary frequencies. This is the volume range where the fcc structure of Cs becomes unstable, and it transforms to Cs-III and then on to Cs-IV, etc. The softening of fcc-Cs under compression is also clearly seen in the calculated elastic constants, see Fig. 2.

Having calculated both electron and phonon contributions to $F(V)$ for various temperatures, we derived $P(V,T)$, and the thermal (volume) expansion coefficient, $\alpha$, was then calculated as a function of both $P$ and $T$. Figure 3 shows that $\alpha$ decreases if, at a fixed temperature, the pressure is increased, and it goes through zero at a single value of $P$ (3.5 GPa) *irrespective* of the temperature. This is a consequence of all mode-Grüneisen parameters vanishing at a specific volume[20] in fcc-Cs. At this volume the phonon contribution to the pressure vanishes. This is also evident from the calculated isotherms, Fig. 5, which coalesce near $V/V_0=0.5$.

Yet another way of illustrating the extremal behavior of the phonon frequencies consists in examining the zero-point-motion energy, $E_{zp}$, and the Debye temperature, $\Theta_D$, as functions of $V$, as is done in Fig. 4.

The full line in Fig. 4 shows $E_{zp}$ as derived from the limit of $F$ or $E$ as $T\rightarrow 0$. The dashed curve was obtained from

$$E_{zp}=\frac{9}{8}k_B\Theta_D, \tag{1}$$

where $\Theta_D$ is obtained from the low-$T$ limit of the specific heat (phonons only):

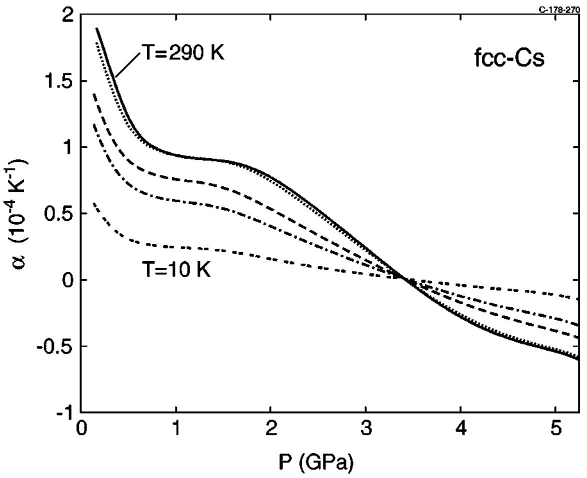

FIG. 3. Thermal-(volume) expansion coefficient of the fcc phase for the temperatures 10, 20, 30, 200, and 290 K.

$$C_V = \frac{12\pi^4}{5} n k_B \left( \frac{T}{\Theta_D} \right)^3, \tag{2}$$

where $n = N/V$ is the concentration of atoms. A comparison of the two sets of results in Fig. 4 further shows that the frequently used approximate relation Eq. (1) yields a rather good estimate of the zero-point energy.

Neither the isotherms shown in Fig. 5, nor any other isotherms which we calculated for fcc-Cs exhibit a van der Waals loop even down to $V/V_0 = 0.37$. We do find that the phonons cause a softening of the lattice leading finally to thermodynamical instability, but we do not find a first-order fcc→fcc transition.

The phonon contribution to the pressure as calculated in Ref. 9 is

$$P_{ph} = 3 n k_B T \gamma(V), \tag{3}$$

where $\gamma(V)$ is the *overall* Grüneisen parameter. This was not easily estimated[9] within the Debye model. From our calculations we can estimate $\gamma$ as a function of $V$ from its relation to $\alpha$ (note: volume expansion coefficient, i.e., three times the linear coefficient) and the bulk modulus, $B$:

$$\alpha = \frac{\gamma C_V}{B}. \tag{4}$$

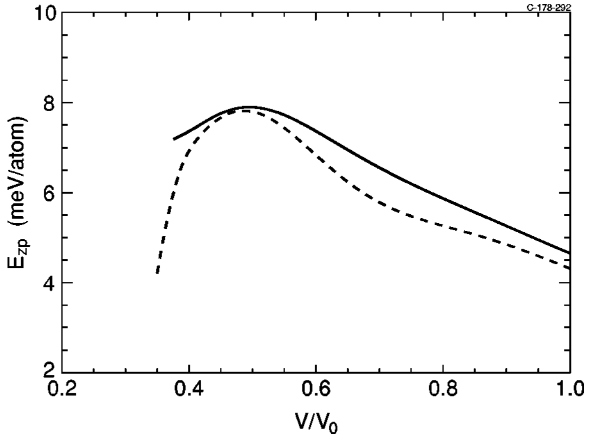

FIG. 4. Energy, $E_{zp}$, associated with the atomic zero-point motion in fcc-Cs vs volume. The results shown with a full line were obtained directly from the $T \rightarrow 0$ common limit of $F$ and $E$ [Eq. (1)], whereas the dashed line represents those calculated in a Debye model [Eq. (1)] with $\Theta_D$ deduced from the low-temperature limit of the phonon contribution to the specific heat.

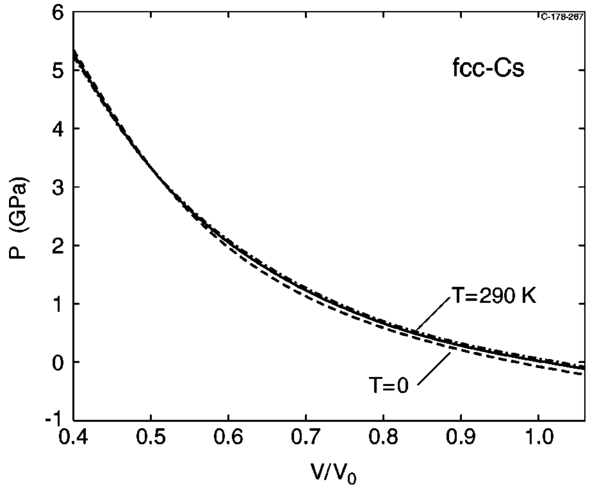

FIG. 5. Isotherms for the fcc phase for the temperatures 0, 200, and 290 K.

Using the high-temperature values of $\alpha$ (Fig. 3, 290 K), together with Eq. (4), one obtains (with $C_V = 3 n k_B$) the $\gamma$ vs $V$ as shown in Fig. 6. This can be compared to Fig. 5 of Ref. 9, where a minimum in $\gamma$ is found near $V/V_0 = 0.4$, the minimum value being between $-2$ and $-12$ depending on approximation. This should be compared to the value $-0.5$ in Fig. 6 here. Inserting this value in the model of Ref. 9, the van der Waals loop would also disappear. But the present calculations also differ from those of Ref. 9 with respect to the prediction that $\gamma$ should increase when $V/V_0$ is reduced below 0.4. Such an increase is necessary in order to stabilize an fcc structure with smaller volume. Our calculations show that $\gamma$ almost exhibits a minimum at $V/V_0 = 0.4$, but just below $V/V_0 = 0.4$, $\gamma$ decreases rapidly, and below 0.37 the fcc phase becomes *dynamically* unstable, and also unstable towards shears ($C'$ becomes negative).

Solids with negative thermal-expansion coefficients are not unknown. Diamond- and zinc-blend-type semiconductors

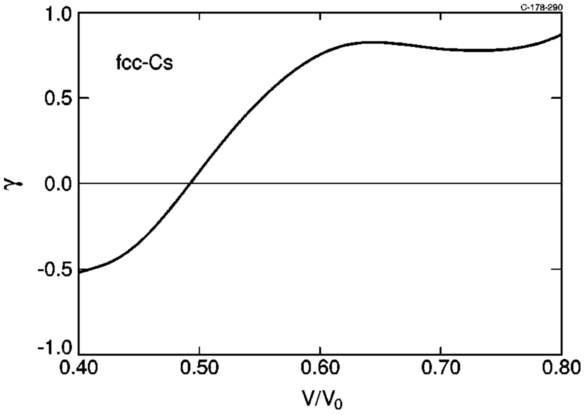

FIG. 6. Overall Grüneisen parameter, $\gamma$, as a function of $V$.

exhibit negative $\alpha$ at about 100 K; see for example Ref. 26 and the theoretical analysis by Biernacki and Scheffler.[27] The behavior found here for fcc-Cs is different because $\alpha$ is predicted to be negative at *all* temperatures for pressures above 3.5 GPa and up to the pressure at which the fcc structure is dynamically unstable (around 4.3 GPa). So far no experiments have been performed against which this prediction can be tested. As some evidence for reliability of the present results, it is mentioned that the thermal-expansion coefficient calculated[20] for bcc-Cs at ambient conditions is $3.0 \times 10^{-4}\ \mathrm{K}^{-1}$. This agrees with experimental values cited in standard tabulations, and the Debye temperature of bcc-Cs at $V=V_0$, 39.5 K, agrees with the value 39 K obtained from the calorimetric data by Filby and Martin.[28]

Thus, Cs-II (fcc) softens as the applied pressure exceeds 3 GPa, but according to the present calculations a van der Waals loop does not form in the isotherms for two reasons: (i) the decrease in phonon pressure upon compression near $V/V_0=0.4$ is too small to compete with the increase in electronic contribution, and (ii) at the volumes where an upturn of the phonon pressure should have stabilized an fcc structure with ‘‘collapsed’’ volume, we find that fcc-Cs has become *dynamically* unstable. This would suggest that Cs-III has a structure different from fcc.

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[1] H. T. Hall, L. Merrill, and J. D. Barnett, Science **146**, 1297 (1964).

[2] K. Takemura, S. Minomura, and O. Shimomura, Phys. Rev. Lett. **49**, 1772 (1982).

[3] U. Schwarz, K. Tawemura, M. Hanfland, and K. Syassen, Phys. Rev. Lett. **81**, 2711 (1998).

[4] K. Takemura, O. Shimomura, and H. Fujihisa, Phys. Rev. Lett. **66**, 2014 (1991).

[5] K. Takemura, N. E. Christensen, D. L. Novikov, K. Syassen, U. Schwarz, and M. Hanfland (unpublished).

[6] R. Sternheimer, Phys. Rev. **78**, 235 (1950).

[7] S. G. Louie and M. L. Cohen, Phys. Rev. B **10**, 3237 (1974).

[8] A. K. McMahan, Phys. Rev. B **17**, 1521 (1978).

[9] D. Glötzel and A. K. McMahan, Phys. Rev. B **20**, 3210 (1979).

[10] A. K. McMahan, Phys. Rev. B **29**, 5982 (1984).

[11] N. E. Christensen, Z. Pawlowska, and O. K. Andersen (unpublished).

[12] M. Hanfland, U. Schwarz, K. Syassen, and K. Takemura, Phys. Rev. Lett. **82**, 1197 (1999).

[13] N. E. Christensen, D. L. Novikov, and M. Methfessel, Solid State Commun. **110**, 615 (1999).

[14] L. Z. Liu, J. W. Allen, O. Gunnarsson, N. E. Christensen, and O. K. Andersen, Phys. Rev. B **45**, 8934 (1992).

[15] O. K. Andersen, Phys. Rev. B **12**, 3060 (1975).

[16] M. Methfessel, Phys. Rev. B **38**, 1537 (1988).

[17] M. Methfessel and M. van Schilfgaarde (unpublished)

[18] J. P. Perdew, K. Burke, and M. Ernwerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[19] E. L. Peltzer y Blancá, C. O. Rodriguez, J. Shitu, and D. L. Novikov (unpublished).

[20] N. E. Christensen, D. J. Boers, J. L. van Velsen, and D. L. Novikov (unpublished).

[21] D. J. Singh, *Planewaves, Pseudopotentials and the LAPW Method* (Kluwer Academic Publishers, Boston, 1994).

[22] M. van Schilfgaarde (unpublished).

[23] P. K. Sharma and S. K. Joshi, J. Chem. Phys. **39**, 2633 (1963).

[24] N. E. Christensen, A. L. Ruoff, and C. O. Rodriguez, Phys. Rev. B **52**, 9121 (1995).

[25] See, for example, Problem 26.1 in N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Saunders College, Philadelphia, 1976).

[26] G. Dolling and R.A. Cowley, Proc. Phys. Soc. London **88**, 463 (1966).

[27] S. Biernacki and M. Scheffler, Phys. Rev. Lett. **63**, 290 (1989).

[28] J. D. Filby and D. L. Martin, Proc. R. Soc. London, Ser A **284**, 83 (1965).