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Theoretical confirmation of the high-pressure orthorhombic phase in strontium

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The recent experimental observation of a new phase (Sr III) at high pressure in strontium metal, with a base-centered orthorhombic crystal structure, is investigated theoretically by means of a full-potential linear muffin-tin-orbital method. Our calculations reproduce the observed transition volume very well. The occurrence of the phase III in Sr is calculated to take place at around 0.4 Mbar, to be compared with the experimental value of around 0.3 Mbar. The increasing occupation of the *d* band is found to be the mechanism driving the transition to the Sr III phase. The simple cubic phase observed at high pressure in Ca is investigated for Sr and found not to be a stable phase at any pressure. [S0163-1829(98)01237-5]

I. INTRODUCTION

The question about the structural stability of materials and the consequences of the detailed atomic arrangement on materials properties have fascinated physicists and chemists for a long time. The structural behavior of the alkaline-earth metals has over the years, by careful experimental and theoretical work, been demonstrated to be quite intricate. For instance, under compression Ca has been demonstrated to transform to a simple cubic structure[1,2] as well as to a yet unknown structure. In a similar way, compressed Ba displays two unknown complex structures, called Ba III and Ba IV, respectively.[1] Another example of the rich structural properties shown by divalent alkaline-earth metals is provided by strontium which shows an interesting phase diagram under pressure.[1] At ambient conditions strontium is well known to be stable in the face-centred-cubic (fcc) structure.[3] Skriver[4] carried out calculations and found a fcc → bcc transition and he derived a transition pressure of 4.0 GPa. The driving force for this crystallographic change was argued to be the number of *d* electrons, which, as is now well established, increases when the metal is compressed. On the experimental side Olijnyk and Holzapfel[1] confirmed that Sr undergoes a structural phase transition to the bcc phase at 3.5 GPa, in good agreement with the prediction. Most recently still another phase was found to be stable for highly compressed Sr.[5] At around 0.3 Mbar the bcc structure was observed to transform to a body-centered-orthorhombic (bco) phase with four atoms in the unit cell. It was shown that the latter phase, called the Sr III phase, can be considered as a small distortion of the β-tin structure. The Sr III phase was also demonstrated to transform first to the Sr IV and then to the Sr V phase. However, the detailed structural properties of the latter two phases have unfortunately not been determined, making a theoretical treatment of them almost impossible. However, the known Sr III structure should be of interest to study theoretically, but to our knowledge no theoretical work which considers the stability of this structure for Sr has been published. In the present work we report on such a theoretical investigation.

II. DETAILS OF CALCULATIONS

In order to study the electronic structure and total energy of strontium metal we have used the full-potential linear muffin-tin-orbital (FPLMTO) method.[6] The calculations were based on the local-density approximation and we used the Hedin-Lundqvist[7] parametrization for the exchange and correlation potentials. Basis functions, electron densities, and potentials were calculated without any geometrical approximation.[6] These quantities were expanded in combinations of spherical harmonic functions (with a cutoff $l_{max}=8$) inside nonoverlapping spheres surrounding the atomic sites (muffin-tin spheres) and in a Fourier series in the interstitial region. The muffin-tin sphere occupied approximately 70% of the unit cell. The radial basis functions within the muffin-tin spheres are linear combinations of radial wave functions and their energy derivatives, computed at energies appropriate to their site, principal as well as orbital atomic quantum numbers, whereas outside the muffin-tin spheres the basis functions are combinations of Neuman or Hankel functions.[8,9] In the calculations reported here, we made use of pseudocore $4s$ and $4p$ and valence band $5s$, $5p$, and $4d$ basis functions with corresponding two sets of energy parameters, one appropriate for the semicore $4s$ and $4p$ states and the other appropriate for the valence states. The resulting basis formed a single, fully hybridizing basis set. This approach has previously proved to give a well-converged basis.[6] For sampling the irreducible wedge of the Brillouin zone we used the special k-point method.[10] In order to speed up the convergence we have associated each calculated eigenvalue with a Gaussian broadening of width 20 mRy.

III. RESULTS AND DISCUSSION

In Fig. 1 we show as a function of volume the difference in total energy between the orthorhombic bco phase, tetragonal (β-tin) phase, simple cubic (sc), and the bcc crystal structure. The energy of the bcc structure has been chosen as the zero-energy reference level. Here we have also considered the sc phase because Ca, which is isoelectronic to Sr, transforms to the sc phase at high pressure,[1] which recently was confirmed theoretically.[2] As can been seen the bcc structure is stable up to $V/V_0=0.36$ where V_0 is the experimental equilibrium volume. Further compression leads to a transition from the bcc structure to the orthorhombic phase whereas the β-tin structure is higher in energy than the orthorhombic phase (0.5 mRy). The theoretically calculated

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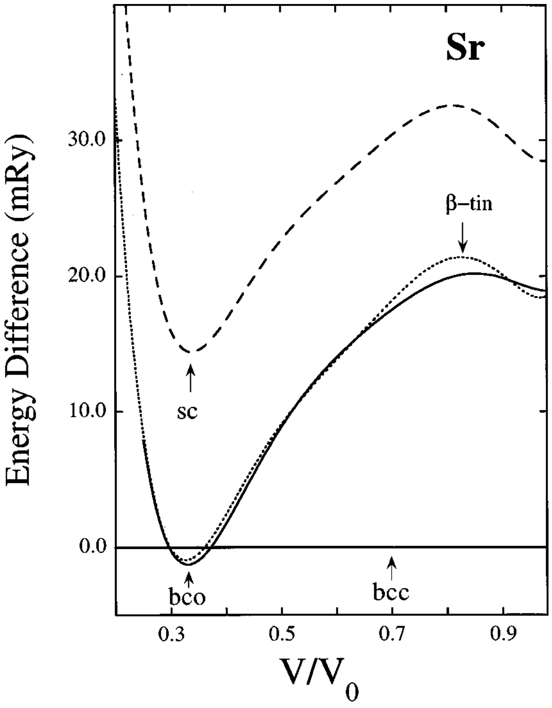

FIG. 1. Energy difference between the bcc, sc, β-tin, and orthorhombic crystal structures (bco) for Sr as a function of volume (V/V_0, V_0= equilibrium volume). The bcc structure is used as the zero-energy reference level.

transition pressure for the bcc → bco phase transformation is 0.4 Mbar. Experimentally[5] this transition is observed to take place at around $V/V_0=0.36$, corresponding to a pressure of 0.3 Mbar. The volume collapse at the transition was determined to be 1.6% in the experiments, which should be compared with our theoretical value of 1.7%. Thus the calculated properties for the bcc → bco transition are in good agreement with the experimental values except perhaps the calculated transition pressure. As can be seen from Fig. 1, upon further compression, we calculate a new transition back to the bcc phase. However, this cannot be compared with experiments since, as mentioned in the Introduction, experimentally the bco phase transforms to a yet unknown structure (Sr IV). It should also be noticed from Fig. 1 that the simple cubic structure is never stable in the studied volume range. This is in contrast to Ca which undergoes a phase transition to a simple cubic phase.[1,2] However, we remark that at a volume of about $V/V_0=0.4$ the sc phase comes down in energy relative to the bcc phase but not enough for a crystallographic change.

In order to analyze the reasons for the onset of the bco structure we display in Fig. 2 the density of states (DOS) for the bcc and bco structures at two widely different volumes. At the larger volume the bcc structure is stable whereas at the lower volume the bco structure is stable. As is clear from Fig. 2 the occupied DOS changes quite dramatically under compression. This is due to the fact that at ambient pressure the d band is essentially empty and most of the occupied levels have sp character, whereas under compression the d band moves down and becomes occupied. The difference in energy dispersion characteristics of the s and d states results in a quite pronounced change in the DOS under compression. As is clear from Fig. 2 the shape of the DOS also depends on the crystal structure, and this is more pronounced at the compressed volumes where d states are more dominating. At ambient conditions the valence electrons in Sr behave more or less as independent free electrons which results in a rather feature-less free-electron-like DOS. In contrast, at elevated pressures, where the d-electron states have moved down in energy and become partially occupied, the energy dispersions are better understood from a tight-binding approach, where the atomic arrangement influences quite strongly the electronic structure. As a result, the DOS in Fig. 2 is clearly strongly structure dependent at compressed volumes.

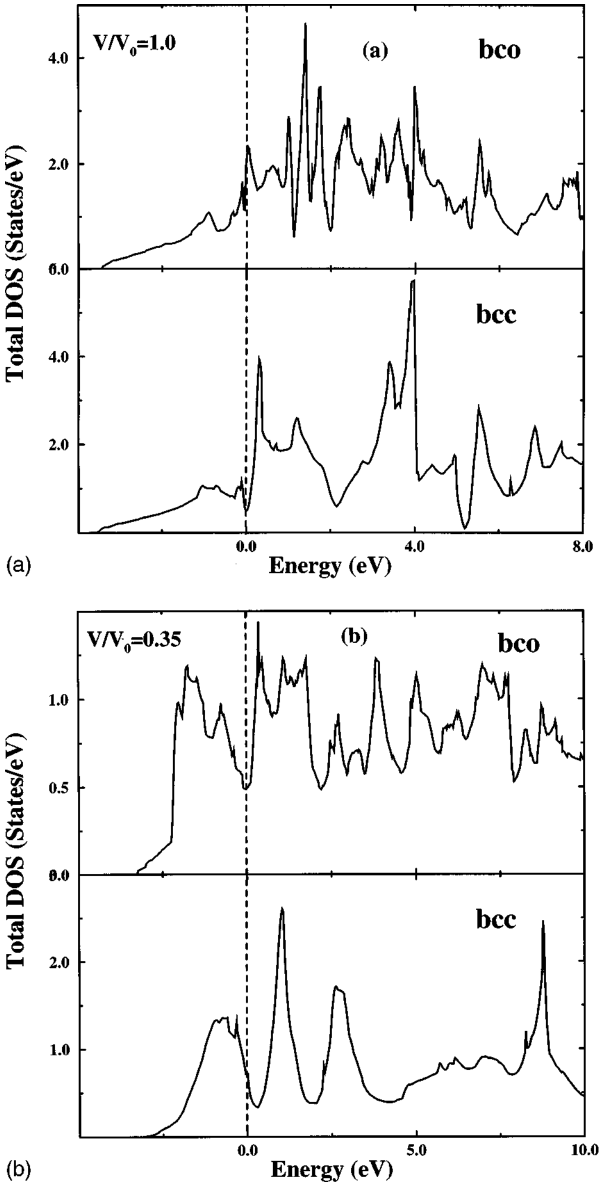

FIG. 2. Calculated total density of states (DOS) for Sr in bcc and bco structure (a) at experimental volume and (b) at compressed volume. The Fermi level is set at zero energy and marked by a vertical dashed line.

We can now isolate the mechanism which makes the bco structure stable at compressed volumes. When the d occupation starts to increase, the occupied part of the DOS is to a larger extent influenced by the atomic arrangement, and structural transitions may occur. As has been observed previously,[11] an important term is provided by the sum of the one-electron eigenvalues, although one should be careful to remember that this term is not the only one of importance in the total energy expression. However, it certainly is one of the most structure-dependent terms and for this reason is necessary to consider. Another term which depends on the structural arrangement and the detailed atomic distances, and which in self-consistent calculations is included in the sum of the eigenvalues, is the overlap repulsion. A third term, most important in the present context, is the electrostatic Madelung contribution. A useful comparison between the different terms was recently given by Pettifor.[11] The eigenvalue sum is now minimized by two competing mechanisms: a structural rearrangement from high coordination, with equal bond lengths with the nearest neighbors, to a lower coordination, where some bond lengths are shortened and others are lengthened, which most often increases the atomic overlap repulsion and increases the splitting between the antibonding-bonding band states. These two effects clearly compete and in addition to this the Madelung energy is known to favor the high-symmetry structures. If we now look at the DOS curve in Fig. 2, we notice that for compressed Sr the bco structure has a considerably larger d-band width than the bcc phase. This may, among other things, be seen from the occupied part of the DOS which starts at -3.5 eV which is to be compared to -2.9 eV for the bcc structure. Thus this is in line with the analysis of Ref. 11 showing that the reduced interatomic distances in the bco structure result in a larger bandwidth. Hence Fig. 2 shows that compressed Sr is stabilized in the bco structure due to the fact that the sum of one-electron eigenvalues is lowered. A further compression will increase the overlap repulsion between the core states, stabilizing the bcc (or generally a high-symmetry structure) over the bco structure. In order to further elaborate on this we have performed LMTO atomic sphere approximation calculations using self-consistently calculated potentials parameters for the fcc structure at two volumes, one close to the equilibrium volume and one close to where the bco phase is stable. We then made use of the structural energy difference theorem[11] and compared the energy difference between the bcc and bco structures. In agreement with the full-potential calculations we find that this simplified model gives the correct structural trend, with the bcc phase being lower in energy at larger volume and the bco phase at lower volume.

IV. CONCLUSION

By means of first principles theory we have reproduced most of the observed aspects of the bcc → bco phase transition in Sr. We argue that the transition is driven by the increased d occupation. The d electrons stabilize the bco structure due to the one-electron term,[11] and an analysis of the DOS shows that an increase of the number of d electrons takes place for compressed Sr. The bco structure is geometrically very close to the β-tin structure[5] and accordingly we find that the energy difference between these two structures is extremely small. Hence, it may be possible that experimentally both the β-tin and bco phases may be found. The bco structure in Sr is in our calculations found not to remain stable upon further compression, but rather the crystal returns to the bcc arrangement. This is also understood from the fact that at very small volumes the overlap repulsion of the pseudocore states and Madelung term will favor a symmetric geometry (like bcc) rather than distorted structures. This line of argumentation also leads us to predict that Sr should ultimately return to a closed-packed crystal structure.

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