

Stability of the Anomalous Large-Void CoSn Structure

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The crystal structure of CoSn represents a highly peculiar intermetallic structure type because of the presence of a large void and highly nonspherically coordinated tin atoms. Voids in crystal structures of intermetallic compounds are most unusual and always give rise to speculations whether the observed phase is the ground state or not. Here we examine this problem by means of *ab initio* calculations and show that the void structure of CoSn is indeed the stable phase. With pressure we predict the following sequence of structural transformations: CoSn type \rightarrow FeSi type \rightarrow CsCl type. The structural properties of CoSn are understood in terms of competition between covalent and metallic bonding in the system. [S0031-9007(97)03781-2]

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The problem of structural stability of intermetallic compounds has fascinated physicists and chemists since the early days of this century [1]. A wealth of experimental and theoretical work has been done in this field and, in particular, the determination of the crystal structures of a great number of intermetallic compounds has led to an increased knowledge about the structural building principles behind this class of compounds [2]. For example, binary intermetallic compounds of the simple stoichiometry AB are expected to crystallize in structure types which provide high space filling and a homogeneous, approximately spherical coordination of the atoms on the different sites [3].

The hexagonal structure of CoSn, for the first time described more than 50 years ago [4], is strikingly different. It can be divided into two different kinds of planar layers which are stacked alternately in the z direction (Fig. 1). The layer at $z = 0$ contains all the Co atoms and one sort of Sn atoms (Sn1) in the ratio 3:1. Each Sn1 atom is surrounded by six Co atoms and together they form a close-packed layer. The second layer at $z = \frac{1}{2}$ represents a honeycomb net consisting exclusively of the other sort of Sn atoms (Sn2). Compared to the close-packed layer the honeycomb net contains only half as many atoms, which results in a large void centered at $(0,0,\frac{1}{2})$. The CoSn structure type, though rare, does occur among binary intermetallic compounds and in addition to CoSn the representatives FeSn, NiIn, PtTl, and RhPb are known [5].

The peculiarity of the CoSn structure stimulated high-pressure experiments [6]. Surprisingly the compound CoSn remained stable in the void-containing CoSn structure type at pressures up to 26 GPa, corresponding to a volume decrease of about 12%. This experimental finding gives rise to two immediate questions. First, is the CoSn structure a genuine ground state? For instance, it could be possible that CoSn contains hydrogen on the site of the voids. This could stabilize the void structure and

prevent its transformation to a structure of higher density when compressed. It is well known that hydrogen can accidentally be introduced when synthesizing intermetallic compounds [7] and it is almost impossible to detect hydrogen in a structure determination from x-ray diffraction. Second, provided that the void structure of CoSn is the genuine ground state, at which pressure can one expect a phase transition (obviously above 26 GPa) and what would be the appropriate high-pressure modification? In this Letter we investigate these questions by means of the *ab initio* full-potential linear muffin-tin orbital (LMTO) method [8,9], which has proven to be a powerful tool for calculating different properties of elements and compounds and has turned out to be especially suitable for studies of structural transitions [10]. The calculations were based on the local-density approximation (LDA), and we used the Hedin-Lundqvist parametrization for the exchange and correlation potentials [11]. Basis functions, electron densities, and potentials were calculated without any shape approximation. We made use of pseudocore d states of Sn and valence band s , p , and d basis functions with two corresponding sets of energy parameters: one appropriate for the semicore d states and

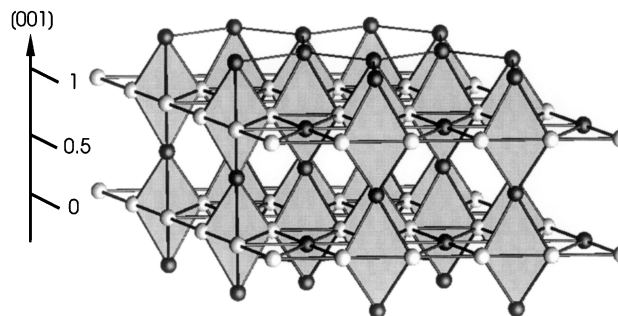


FIG. 1. The hexagonal structure of CoSn. Common view. Light circles are Co atoms, dark circles represent Sn atoms.

the other appropriate for the valence states. The resulting basis formed a single, fully hybridizing basis set. This approach has previously been proven to give a well-converged basis [9]. For sampling the irreducible wedge of the Brillouin zone (BZ) we used the special k -point method [12] with a Gaussian function of width 20 mRy. In order to ensure convergency several tests were performed, such as the effect of increasing the number of k points used in the summation over the BZ.

The actual problem may be analyzed by a search for energetically favorable structures for the CoSn system over a wide range of atomic volumes. We selected possible alternative structures to the CoSn type by inspecting the empirical Pettifor structure map for AB compounds [3]. We found the structure types NiAs, MnP, CoGe, FeSi, and CsCl to be closest situated to CoSn. Further, we considered the WC, NbAs, NaCl, and CrB structure types in order to cover most of the structures of the known pd -bonded intermetallic AB compounds [5]. The structure types NaTl and CuAu are not typical of pd -bonded systems but were included as possible high pressure modifications because they are ordered close-packed structures. We did not consider any structures which can be derived by a simple distortion or transformation of one of the structures above (e.g., CoAs being closely related to MnP; FeB and MoB being closely related to CrB) expecting their total energies to lie very close. The calculated total energies versus volume for those structures which have total energies closest to the ground state are shown in Fig. 2. Notice that these structures correspond to the closest situated to CoSn structures, according to the Pettifor structure map, and that the total energies of the other structure types are far above the total energies of this group. This gives a nice theoretical confirmation of the

usefulness of the empirical structure map as an adequate representation of the structural trends among binary compounds. From Fig. 2 it is clearly seen that the CoSn type is the most stable structure at ambient pressure and, therefore, represents the genuine ground state structure for CoSn. Its total energy at the equilibrium volume lies about 15 mRy/atom lower compared to the closest competing structures.

Our results, therefore, confirm a high stability of the void CoSn structure which is not compatible with a purely metallic-bonded system as which pd -bonded intermetallics are often regarded [13]. This suggests a much more complex character of bonding. In Figs. 3(a) and 3(b) we show calculated charge density distribution plots for the layers at $z = 0$ and $z = \frac{1}{2}$. The difference between Figs. 3(a) and 3(b) is remarkable because the closed-packed layer ($z = 0$) exhibits a typical metallic picture with undirected bonding (spherical regions around the atomic sites and more or less flat regions in the interstitial areas), while, on the other hand, the honeycomb

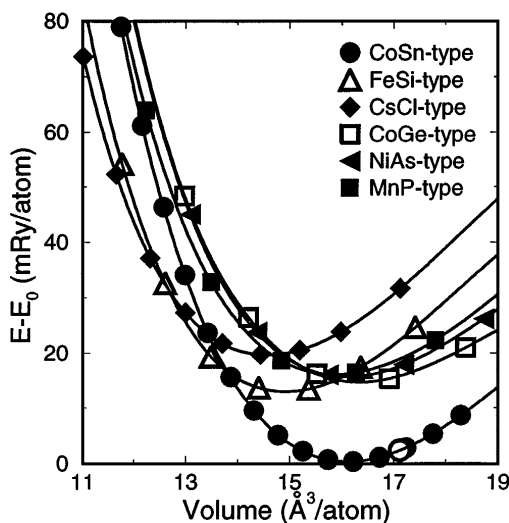


FIG. 2. Calculated total energy versus volume for the most competitive structures. E_0 is the energy of the ground state. The open circle corresponds to the experimental equilibrium volume.

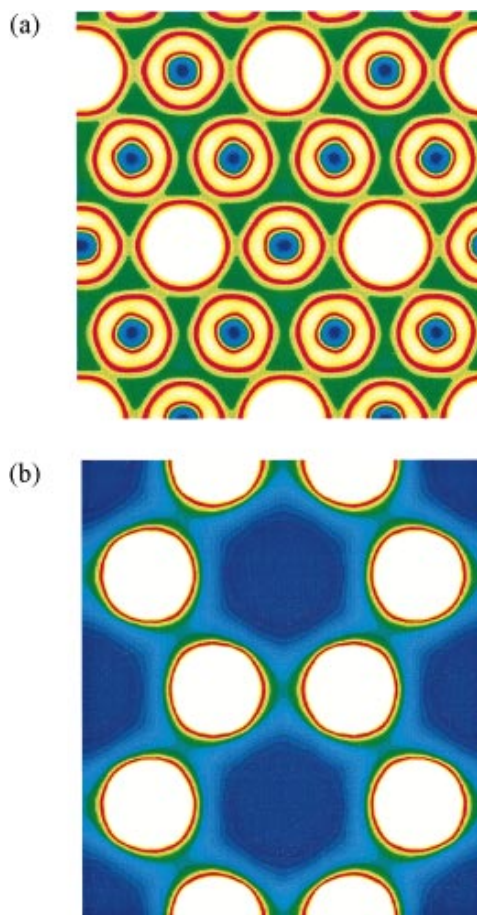


FIG. 3(color). Calculated valence charge density distribution ρ in the close-packed layer at $z = 0$, where Sn1 atoms are surrounded by Co atoms (a) and in the graphitelike layer consisting of the Sn2 atoms at $z = \frac{1}{2}$ (b). Increasing ρ scale: dark blue (<0.01); green, red, yellow, white (>0.1).

net reveals a bonding picture similar to graphite layers. In order to analyze this bonding picture in more detail we have calculated the so-called electron localization function (ELF) [14,15], which has been developed into a useful tool for the characterization of bonds in solids and molecules [15,16]. Furthermore, it has been shown that the spatial organization of this scalar function provides a basis for a well-defined classification of bonds [17]. ELF is defined as $[1 + (D/D_h)^2]^{-1}$, with D being the excess of the local kinetic energy due to the Pauli principle. Thus D is given by $D = \tau - t_W$, where τ is the Kohn-Sham local kinetic energy, $\tau = \frac{1}{2} \sum |\nabla \varphi_i|^2$ (φ_i are the Kohn-Sham orbitals), and t_W is τ in the absence of the Pauli principle ($\sim |\nabla \rho|^2/\rho$, where ρ is the charge density). D_h represents D for the corresponding uniform electron gas ($\sim \rho^{5/3}$). According to this definition ELF can take values in the range between 0 and 1, where 1 corresponds to perfect localization. Figure 4(a) depicts ELF in the honeycomb layer at equilibrium volume. ELF has a local maximum with a value of 0.65 between two Sn2 atoms and this shared-electron character of interaction together with a rather high value of ELF is a characteristic feature of the covalent bonding [17,18]. The bonding situation in CoSn is indeed peculiar with a covalent bonded tin substructure embedded into metallic bonded environ-

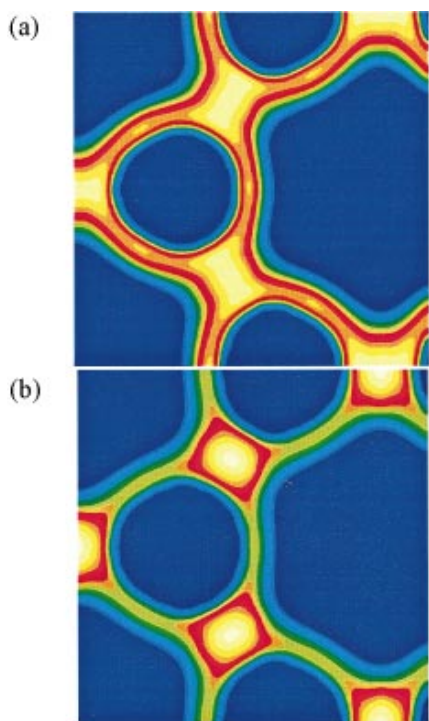


FIG. 4(color). Calculated valence electron localization function in the graphitelike layer consisting of the Sn2 atoms at $z = \frac{1}{2}$ at the equilibrium volume (a) and at the volume corresponding to the transition pressure (transition CoSn-structure type \rightarrow FeSi-structure type) (b). Increasing ELF scale: dark blue (<0.4); green, red, yellow, white (>0.65). ELF is calculated using [19].

ment (i.e., metallic bonded close-packed layers). In other words, this compound may be considered as an intrinsic multilayer system composed of layers with different character of bonding. The structure is then a result of an interplay between two opposite tendencies: the tendency of the Sn atoms to form covalent bonds with each other and the normal tendency of pd -bonded intermetallic compounds to adopt a more close-packed structure with homogeneous coordination of the atoms. Notice that the application of high pressure must suppress the former and favor the latter. Figure 4(b) shows ELF in the honeycomb layer under pressure. It may be seen that the spatial regions of relatively high localization diminish with pressure indicating the decreasing strength of the covalent bonding.

From the above considerations it follows that under pressure one should expect a transition from the CoSn-structure type into a structure with a, for intermetallic compounds, more typical bonding. The calculated equation of state is presented in Fig. 5 together with the experimental data [6]. The CoSn structure type remains stable up to ≈ 26 GPa, i.e., up to the highest pressure applied in the experiment [20]. From Fig. 5 we can also predict two structural transitions (CoSn type \rightarrow FeSi type \rightarrow CsCl type) which occur above 26 and 36 GPa, respectively.

The calculated transformations under high pressure are well explained as a path towards closer packing accompanied by a tendency of the atoms to be surrounded exclusively by atoms of the other kind in the first coordination sphere. Then the highest possible coordination number is 8 as realized in the CsCl structure, whereas in the FeSi structure this nearest neighbor coordination number is limited to 7. Co and Sn atoms in both these high pressure modifications have a crystallographically identical environment, i.e., an equal coordination polyhedron. In the CoSn structure all three kinds of atoms (Sn1, Sn2, and Co) are differently coordinated. As regards the first coordination sphere both the Sn1 and Sn2 atoms are six-coordinated by Co atoms, in the case of Sn1 in a very unusual planar way. The Co atoms have, besides six Sn

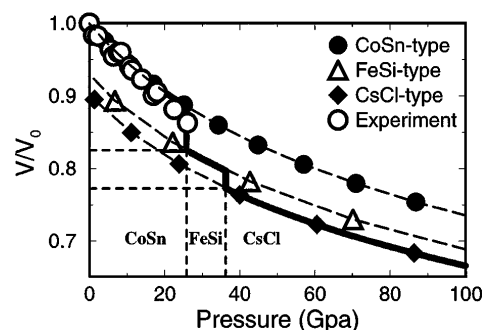


FIG. 5. Equation of state for the CoSn system. Experimental data were taken from Ref. [6]. V_0 is the observed equilibrium volume for the experimental data and the calculated equilibrium volume for the theoretical data. The regions of stability of the CoSn, FeSi, and CsCl structures are indicated.

atoms, additional Co atoms as nearest neighbors. Thus in the CoSn system the structural changes to the modifications with higher density are predicted to increase stepwise the coordination number of atoms of opposite kind to the maximum possible value of 8 yielding at the same time equal coordination polyhedra for Co and Sn atoms.

In summary, we have studied the structural stability of the CoSn intermetallic compound by performing *ab initio* calculations for numerous structure types over a wide pressure range up to about 100 GPa. We have shown the unusual void-containing CoSn structure type to be the ground state structure of this system, stable up to 26 GPa. We predict two structural phase transitions (CoSn type \rightarrow FeSi type \rightarrow CsCl type) at about 26 and 36 GPa, respectively. The stability and high pressure behavior of the CoSn structure is explained as an interplay between the tendency of Sn atoms to form covalent bonds with each other and the tendency of *pd*-bonded intermetallic compounds to form more close-packed structures where the atoms are surrounded by atoms of the other kind in the first coordination sphere.

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