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Calculated properties of high-pressure phases of ‘simple metals’

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Abstract

X-ray diffraction experiments carried out on alkali metals under high pressure have provided new insight into pressure-induced structural transformations. New structures have been identified, and some of these have surprising similarities, such as low coordination numbers. The present *ab initio* calculations of electronic and structural properties provide theoretical support for the analysis of these experiments, and may also serve to predict new properties, such as superconductivity, of the materials when exposed to high pressures.

1. Introduction

The alkali metals, often considered as *simple* metals with band structures that differ only slightly from those of free-electron systems, have attracted considerable interest because application of external pressure changes the bonding properties fundamentally. It was remarkable that Neaton and Ashcroft [1] predicted that compressed Li might assume a structure where the atoms form *pairs*, and that this phase is semi-insulating. This is in sharp contrast to the intuitive expectation that application of hydrostatic pressure should favour highly coordinated metallic phases. Siringo *et al* [2] predicted that a charge density wave instability could cause the light alkali metals to become insulating at high pressure. At lower pressure Li may be a superconductor [3].

The compressibility of the alkali metals is very large, and the large volume reduction with application of pressure affects significantly the otherwise free-electron-like electronic structure. As a consequence, these metals undergo several pressure-induced structural transformations. These have been studied experimentally (see for example [4–9]) as well as by theoretical methods (see [1, 3, 4, 9–14]). Among several interesting results of this research are the observation [4] of new high-pressure phases of lithium, Li-*hR1* and Li-*cI16*, and the identification [7, 15] of the structure of Cs-V and Rb-VI as being the orthorhombic *Cmca* structure with 16 atoms in the orthorhombic cell (*oC16*). The same structure type, with almost the same relative atomic coordinates, is found in Si and Ge [8, 12, 16, 17]. This *Cmca* structure contains two types of atom, say Cs₁ and Cs₂, with Cs₁ in planar arrangements separating Cs₂

double layers. The atoms in the single planes form a dense packing of *dimers* [12]. This has some similarity with the *Cmca* structure predicted for Li by Neaton and Ashcroft [1]. In that structure (*oC8*), however, the double layers of type-2 atoms are absent.

The pressure-driven electronic $s \rightarrow d$ transition [18] plays a major role in the structural behaviour of caesium [11], in particular for the occurrence of the tetragonal Cs IV phase which is only eightfold coordinated [6]. The s - d transition also leads to a softening and a dynamical instability in Cs-II (*fcc*), and causes the thermal expansion coefficients of Cs to be negative at all temperatures in a certain pressure range [13]. The light alkali metals are similarly strongly influenced by an $s \rightarrow p$ transition.

2. Structures and methodology

The simplest close-packed structures, *bcc*, *fcc*, *hcp* *dhcp*, are well known. The *hcp* stacking sequence in the c -direction is ABA. Similarly, *fcc* and *bcc* can be built by stacking (111) layers in the sequence ABCA. In this representation, *fcc* has $c/a = \sqrt{6}$ and for *bcc* the axial ratio is $c/a = \sqrt{3/8}$. The omega structure appears if the B and C layers in *bcc* are shifted so that they coalesce at $z = c/2$.

The *dhcp* structure has an ideal c/a ratio which is twice that of *hcp*, and the stacking is ABACA. The ‘samarium type structure’, *9R*, is a nine-layer hexagonal structure, stacking ABABCBCACA. The primitive rhombohedral cell contains only three atoms. Also A7 (space group 166 in the international tables, arsenic structure) has a rhombohedral primitive cell with two atoms. For special parameters, A7 becomes the simple cubic, *sc*, structure. The simple rhombohedral structure, *hR1*, is obtained by straining the *fcc* structure along a body diagonal. The structure which is called *cI16* belongs to the space group *I43d* (number 220). This was found experimentally for Li under pressure [4]. The atoms are located in the 16c Wyckoff positions, and the structure is defined by a single distortion parameter x . The *oC8* structure is of *Cmca* symmetry, and it resembles that of alpha-gallium, but can also be viewed as that of black phosphorus compressed perpendicularly to its double layers.

Some of the high-pressure phases have structures similar to the cation sublattices of binaries [4], and the structure of Cs IV [6] is an example of this. Cs IV forms in a tetragonal structure with *I4₁/amd* symmetry, SG 141, and the atoms are placed in the positions of Th in ThSi₂ [19]. The *cI16* structure described above is in fact that of the cation sublattice in Eu₄As₃ and Yb₄As₃. The *BC8* structure can be considered as a special setting of the structural parameters of the *R8* structure [20].

The total energy is calculated within the density functional theory using the generalized gradient approach (GGA) in the Perdew–Burke–Ernzerhof scheme [21]. The solution of the effective one-electron equations is performed by means of the linear muffin-tin-orbital (LMTO) method [22] in the full-potential version [23]. The semi-core states, Li 1s, Na 2s and Na 2p, are treated as *local orbitals* [24] in the same energy window as the valence states.

The structural optimization required in all cases except for the *bcc* and *fcc* structures is made at each of 21 volumes, V , in the range $0.10 \times V_0$ to $1.10 \times V_0$, where V_0 is the (experimental) equilibrium volume of *bcc* Na at ambient pressure, 37.7073 \AA^3 . The energy optimization of the structural parameters is done by means of a steepest-descent method.

3. Results

Having calculated the optimized total energies, E , versus volume for all structures, and applying a least-squares fit to a power series in $X = (V/V_0)^{1/3}$ (positive as well as negative powers), we derive pressure (P) and enthalpy, $H = E + PV$. The calculated P - V relations

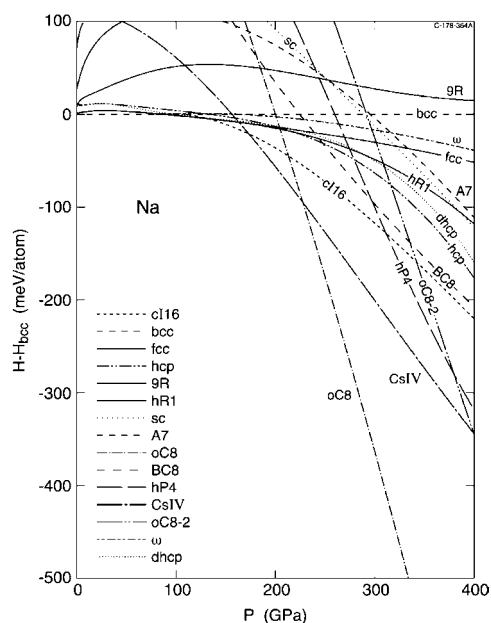


Figure 1. Enthalpies of 15 Na phases versus pressure. The enthalpy of *bcc* Na is used as a reference.

are then used to calculate $H(P)$, and the results are summarized in figure 1 for sodium. At low pressures we find that the *bcc* structure is favoured in sodium. The calculation predicts that this remains the stable structure up to ~ 80 GPa, where it transforms to *fcc*. The instability of *bcc* Na is also reflected in the volume dependence of the elastic shear constants. As found by Katsnelson *et al* [10] and also in the calculations [13] for Cs, C' and C_{44} soften and become negative under compression. Another distortion of the *bcc* structure of sodium could be possible, namely that to the omega-phase. The *fcc* structure remains stable up to ~ 130 GPa, where it becomes unstable against a rhombohedral shear. C_{44} becomes negative, and the *fcc* lattice becomes dynamically unstable. This signals the transition to the distorted structure, *hR1*, but the *cI16* structure starts to be energetically favoured in the same pressure regime. Until recently lithium was the only [4] element for which the *cI16* structure had been observed, but now it has also been found for Na near 100 GPa [25]. Near 170 GPa Na-Cs IV rapidly lowers its free energy with pressure so much that it becomes the lowest among those examined up to ~ 220 GPa, where Na-*oC8* takes over.

For Li it was demonstrated that the distortion (finite x value in figure 2 of [4]) of the *bcc* structure into *cI16* causes the formation of a pseudo-gap, and thus to a downshift in an appreciable number of filled states. The one-electron energy sum is similarly reduced in Na-*cI16* as x becomes non-zero. A similar effect is found in the Cs IV and the BC8 structures. Again the formation of a pseudogap near E_F tends to stabilize the structure. In all cases the increasing occupation of p states with pressure is essential for the formation of the new structures, and this is most spectacular in Na-*oC8*, the phase which is clearly the lowest in energy among those examined in the high end of the pressure range of figure 1. At the smallest volume examined, $V/V_0 = 0.10$, its DOS at (E_F) vanishes. In fact a very small, finite gap has formed (see figure 2). In Li-*oC8* it was also found [1, 4] that DOS(E_F) vanishes at a very high pressure, but the energy-optimized structure did not exhibit a finite gap. We find that Li-*hP4* (graphite structure) has lower enthalpy than Li-*oC8* for P above 300 GPa. In a small pressure range this phase appears to be a zero-gap semimetal, but as in Li-*oC8* a non-zero gap does not develop.

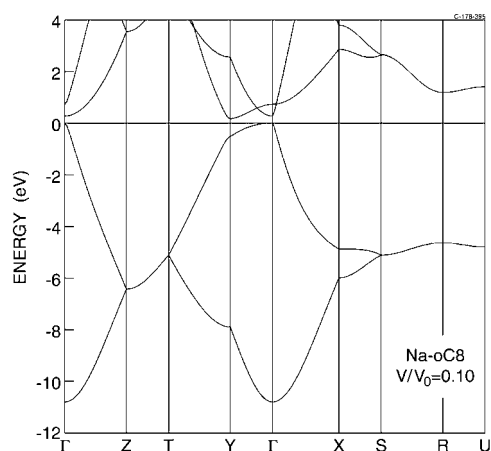


Figure 2. Band structure of Na-*oC8* at one-tenth of the zero-pressure volume. The horizontal line marks the valence band maximum.

In Li the s–p transition has been associated with the orthogonality requirement keeping the 2s electrons away from the 1s core regime, combined with the fact that Li has no core p electrons imposing similar constraints to p valence states. A similar argument cannot be applied to Na. In that case the atomic core contains s as well as p states (2p), and a weaker s → p transition should then be expected. But the behaviour in sodium is as that of lithium. Hybridization is very strong in the compressed alkali metals. If we consider a hypothetical Na-*fcc* crystal at the smallest volume, $V = 0.1V_0$, considered here, its interatomic distance is 1.73 Å. This is the same as the distance from the nucleus of the free Na atom to the outer maximum of the Na-3s wavefunction [26]. Consequently, a 3s wavefunction from a nearest neighbour atom in the compressed solid will, when expanded in around the local site, yield a very large p component. Only s states have non-vanishing amplitudes on the nucleus, and the crystal structure adjusts so that there are interstitial regimes where the valence charge can pile up. This means that the coordination number is reduced to a lower value than in for example *fcc*.

4. Conclusion

The ‘simple metals’ considered here are not simple at all as pressure is applied. Some phases may even be non-metallic. The peculiar behaviour under pressure is associated with a softening of the interatomic bonds following the pressure-induced s–p transition. The high-pressure phases have structures with low coordination numbers, and the valence electrons pile up in the interstitial regime. The structural energy differences calculated here do not include thermal effects, i.e. the vibrational contributions to energy and entropy are neglected. This adds to the error bars, and for example we cannot safely predict the zero-pressure structure of Na.

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