Origin of the complex crystal structures of elements at intermediate pressure

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Abstract. We present a unifying theory for the observed complex structures of sp-bonded elements under pressure on the basis of nearly free electron picture. In the intermediate pressure regime, the dominant contribution to crystal structure arises from Fermi-surface Brillouin zone interactions—structures which allow this are favoured. This simple theory explains the observed crystal structures, transport properties and the evolution of internal and unit cell parameters with pressure and appears to hold for elements in groups I–VI. We illustrate it with experimental data for these elements and ab initio calculations for Li.

Recent experimental high-pressure investigations of metallic elements have yielded surprising and intriguing results. Simple metals, which adopt close-packed crystal structures at both high and low pressures exhibit low coordination and increasing crystal complexity at intermediate pressures (figure 1). Moreover, these phases are associated with low conductivity at normal temperatures and superconductivity at high temperatures.

These anomalous features—the minima of coordination and conductivity—are also observed in the liquid phases. A similar behaviour is seen in many s-band elements, e.g. Li, Na, K, Rb, Cs, Ca, Sr and Ba.

This behaviour can be reproduced by ab initio calculations based on the density functional plane wave pseudopotential method (DFPP), which represents a sufficient theoretical understanding of the problem: there is no need for physics ‘beyond’ DFPP, as is required in the f-metal localization transitions.

1 We use the term ‘intermediate’ since the actual pressures involved vary from element to element. In general, pressures are in the GPa range, with lighter elements having larger absolute values of ‘intermediate’ pressure.
However, DFPP calculations are sufficiently complex that no simpler theoretical principles emerge. Moreover, DFPP calculations require plausible candidate structures—in simple cases, picking the ‘usual suspects’ and symmetry-breaking distortions from them has worked, but when very complex structures are contenders, a more systematic approach is needed. Here, we demonstrate the general principles that contribute to complex crystal structures, and deduce heuristics from which to choose candidate structures.

DFPP gives the enthalpy of various structures, the lowest enthalpy structure being stable. Under pressure, the total enthalpy comprises a band structure term (the eigenvalues of non-interacting electrons moving in an effective field), an Ewald sum, pressure $\times$ volume, exchange correlation and Hartree energies. The dependence on volume ($\Omega$) is as follows: $\Omega^{-1/3}$ for the coulombic terms (Hartree, ion–ion, ion–electron), $\Omega^0$ for the exchange correlation (neglecting ‘non-linear core corrections’) and $\Omega^{-2/3}$ for kinetic energy. Thus, under pressure, materials become more free-electron-like. We note two aspects of DFPP. Firstly, the fact that pseudopotentials work indicates that repulsion between core electrons can be neglected. Secondly, energy minimization in DFPP codes is hugely improved by preconditioning [12]: assuming that the contribution from a plane wave basis state is primarily its free-electron-like kinetic energy.

Two further effects are not explicit here: imperfect screening of ionic charge as ions approach closely and the Fermi-surface Brillouin zone (FSBZ) energy splitting from interaction between plane waves and ionic potentials [13]:

$$\Delta E = \pm \int_{\Omega} e^{i\mathbf{k} \cdot \mathbf{r}} V(\mathbf{q} \cdot \mathbf{r}) e^{i\mathbf{k}^{\prime} \cdot \mathbf{r}} d^3 \mathbf{r}. \quad (1)$$
$V(\mathbf{q} \cdot \mathbf{r})$ depends on the scattering at $\mathbf{q} = \mathbf{k} + \mathbf{k}'$ which, for elements, is strongly peaked at the Bragg reflections as revealed by x-ray diffraction. If $\mathbf{k}$ falls near the Fermi level, the state with increased energy is unoccupied, while the other is occupied. Thus FSBZ interaction gives a first-order change in energy with crystal structure, while, at other $\mathbf{k}$, the energy gained and lost cancels. FSBZ effects scale as $\Omega^{-1}$.

It is important to distinguish the terms contributing most to the total energy from those contributing to energy differences between crystal structures. The latter are the screened ion–ion potential and the perturbation of the free electrons from FSBZ interactions. Given its $\Omega^{-1}$ scaling with volume, FSBZ interaction may dominate at intermediate pressures with the $\exp(-\Omega^{1/3})$ dependence of imperfect screening being important at the highest pressures.

The central result of this paper is the demonstration that the complex elemental crystal structures at intermediate pressures can be simply understood using the NFE picture. This theory also gives a way of picking plausible trial structures for total energy calculation and explains a number of observed properties. To ease comparison with experiments, we will refer to specific interactions between the Fermi surface (FS) and particular points in the Brillouin zone (BZ) (diffraction peaks) rather than the equivalent description in terms of the BZ planes containing these points.

Under pressure, group I and II metals transform from simple structures, bcc and fcc, to more complex structures. The striking similarity between the Cs-oC84, Rb-oC52 and Li-cI16 structures [1, 3, 4] is shown in figure 2 and in the diffraction patterns (figure 5): all are derivatives of bcc.

Complex phase stability in Rb and Cs [3, 4] has been described by s–d electron transfer, allowing directional bonding and hence open structures. This was justified by the now-discredited isostructural phase transition in Cs [3], which cannot be explained in a free-electron picture. Although, in a localized basis picture, s–d transfer exists, it offers no insight into the detailed structures and cannot explain the Li-cI16 structure (figure 2) as Li has no d-orbitals available.

DFPP calculations for cI16 Li provide an ideal testbed for the alternate FSBZ picture (figure 5): FSBZ effects scale strongly as $\Omega^{-1}$ with decrease in volume, causing increases in internal parameter $x$, (211) band gap opening and diffraction peak intensity. At very high pressure, this is overcome by imperfect screening of ionic charges (exponential in $x/\Omega^{1/3}$).

Figure 3 shows that the variation in total energy with atomic position parameter $x$ in cI16 Li for various volumes is due to Ewald and band structure contributions only. Band energy is reduced with increase in $x$, but, ultimately, Ewald energy increases faster and dominates. Since fcc and bcc structures are extremely close in energy for Li, the energy gain for bcc distortion is sufficient to bring the cI16 lower in energy than fcc. Of course, the actual phase transformation does not proceed by a soft-mode mechanism since the physical transition is from fcc.

Figure 4 shows the development of the pseudogap due to FSBZ effects as the $x$-parameter is increased. This shows conclusively that the band structure energy is the driving force for

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2 Strictly, FSBZ energy from second-order perturbation theory requires an integral between pairs of occupied and unoccupied orbitals in adjacent BZs. This integral is complicated enough to obscure the simple picture, yet quantitatively less accurate than DFPP calculation—since its value varies with the interaction at the diffraction peak, we use the latter for qualitative discussion.

3 Boettger and Trickey [14] considered s–p transfer and concluded that it was ‘not a sufficient mechanism to induce an fcc–bcc transition’.
Figure 2. Crystal structures of Li-cI16 (left), Cs-III (middle) and Rb-III (right) viewed along the [100] axis of the C2221 unit cell. Interatomic distances up to 2.5 Å (Li), 4.7 Å (Cs) and 4.1 Å (Rb) are shown as solid lines. True symmetry operators normal to the plane of projection are shown by solid symbols and pseudo-symmetry operators by open symbols. The cI16 structure can be viewed as a simple distortion of body-centred cubic structure, in which each atom is shifted by $x$ along the bcc [111] directions [1]: in this projection we find eight-atom layers. For Cs-III and Rb-III [4], identical eight-atom layers exist interspersed with ten-atom layers (black), which can be considered as eight-atom layers with (001) dumbbell interstitials inserted. (Layers are inclined at about $\pm 35^\circ$ to the conventional $b$-axis [4]. The angle of 35$^\circ$ originates as the angle between the bcc planes (110) and (111) and it does not change in the bcc–CI16 transformation.) Thus, the Cs-oC84 and Rb-oC52 structures are the same as Li-cI16, with the density increased by interstitial atoms every fifth (Cs) or third (Rb) layer.

complex structure stability in Li [1], [16]–[18]. The experimental signature of FSBZ effects in powder diffraction is the appearance of diffraction peak(s) with wavevectors slightly below the free electron $k_F$. They are lower because the actual Fermi energy will lie slightly lower than the free-electron value.

In DFPP, some high-$k$ components are mixed into low-energy states, so the free-electron-like states at $E_F$ will have wavevectors below the free electron $k_F$. For maximum BZFS effect, $k_F$ should lie just above the relevant diffraction peak. s–d transfer arguments give a similar picture by assuming fewer free electrons.

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Figure 3. Upper panel: \textit{ab initio} phonon dispersion relation \cite{15} showing dynamic instability for bcc-Li at 40 GPa. Frequencies below zero are imaginary, corresponding to negative-energy eigenvectors. Bottom panel, right: Li-DFPP energy difference between bcc and cI16 for various $x$ over a range of volumes ($V_0 = 146.4$ A$^3$, the volume at which cI16 is first observed). cI16 is energetically stable between 42 and 50 GPa, $V/V_0 = 1–0.85$. Symbols are the total energy and lines are the Ewald and bandstructure contributions only. The thick line indicates the lowest energy $x(V)$. Bottom panel, left: band structures and integrated density of states along the [2$x$, $x$, $x$] direction for $V_0$; $x = 0$ (lower) and $x = 0.05$ (upper), showing pseudogap due to FSBZ interactions: the FS touches the 24 (211) BZ planes. Elsewhere in the BZ, bcc and cI16 band structures are similar.
Figure 4. Density of electron states as a function of distortion $x$ in Li-c116. The legend indicates colours of various $x$-values—the effect of $x$ in opening a pseudogap at the Fermi level is evident.

Precisely, this signature exists in Cs and Rb (figure 5), indicating similar physics. The interstitial atoms reduce the volume per atom at the expense of splitting the diffraction peak near the Fermi level. In a real space picture, the sequence of first increasing then decreasing the interstitial number seems inexplicable. In the FSBZ picture, the FS is more easily deformed at large $Z$. For Li, the PV enthalpy gained from interstitials cannot compensate for the loss of FSBZ interaction from peak splitting. Rb has FSBZ interactions with three of the four split peaks, while Cs deforms to touch all four.

This gives us the desired heuristic in the search for candidate ‘complex’ structures for DFPP calculation: multiple strong diffraction peaks at the Fermi energy. It also suggests that a simple model of interatomic interactions in such materials should concentrate on a particular wavenumber in reciprocal space: a condition somewhat encapsulated long ago by Friedel oscillations.

With the FSBZ picture established for alkali metals, it is instructive to turn to other elements. Recently, complex Li-type distorted bcc structures have been reported in gallium [19]. This extraordinary confluence of monovalent and trivalent materials would appear to contradict the FSBZ picture. However, figure 5 reveals the (310)$_{Li}$-type diffraction peak just below the Fermi level.

In Rb, Ba and Sr, a new principle emerges: in real space, BaIV-type forms self-hosting ‘hotel’ structures, which can only be described using two interpenetrating crystal structures (the ‘host’ and chains of ‘guests’) [5], [20]–[22]. The structures can be incommensurate, giving rise to two distinct BZ and the consequent additional possibilities for FSBZ interactions. Again, their stabilities are well reproduced by DFPP [20].

Figure 6 shows their diffraction patterns—once again strong diffraction peaks lie near the Fermi level, and the FSBZ picture is dominant. Significantly, while, in Ba and Sr, there is interaction with the (201) guest, there is no guest reflection (with non-zero $k_z$) near the BZ in
Figure 5. Calculated diffraction patterns for the bcc complex structures of Li, Cs, Rb and Ga. A major effect of the cI16 distortion in Li is to throw up a 211 peak just below the Fermi vector (see footnote 4), calculated assuming a free electron sphere to equate to \[2\theta = 2 \sin^{-1} \left( \frac{\lambda}{\sqrt{3N}} \right) \frac{\sqrt{3}}{64\pi V}.\]

Rb. Thus FSBZ interaction order the positions of adjacent chains in Ba and Sr, but not in Rb; indeed, interchain order is observed in Ba and Sr, but Rb undergoes a ‘melting’ transition at low pressure [11].

Other properties of complex crystal structures in alkali metals relate to the FSBZ interpretation.

The resistivity in liquid Li [23] rises 10-fold between 40 and 120 GPa, and a similar rise is observed in the crystal phases corresponding to the cI16 and other complex orthorhombic phases [1, 2]. A similar behaviour is observed in Cs (4 GPa, the Cs-III phase) and Rb (10 GPa, the Rb-II and Rb-III phases) [24]. Figure 5 shows that the FSBZ interaction opens pseudogaps at the Fermi level in Li-cI16, resulting in a much lower electron density at the Fermi level than in fcc and bcc phases.

One of the criteria for superconductivity is the coupling of electrons to low-frequency vibrational modes; we have not performed detailed calculations, but complex phases tend to exhibit superconductivity through the low-frequency phonons associated with FSBZ effects, and phasons of incommensurate phases. Superconductivity is observed in the complex structures of Li cI16 phase [1], Cs, Ba, Sr and Ga. In contrast, superconductivity is not detected in Rb up to pressures of 21 GPa [25], where the weak non-FSBZ interchain coupling melts the phason mode.
Figure 6. The calculated diffraction patterns for hotel structures of Ba-IV, Sr-V and Rb-IV. The tick marks show whether the reflection is from host (upper) or guest (lower) lattice. The insets show how the BZ maintains contact with the FS.

Projection of our wavefunctions onto atomic orbitals shows increase in $d$ character with pressure; however, the concept of FSBZ interactions provides a better, simple description for high-pressure ‘complex’ phases than s–d transfer. As with intermediate pressure phases of group IV and III–V compounds [26, 32, 33], a simple heuristic for stable phases is the existence of strong diffraction peaks just below the free-electron Fermi vector [26]. Monovalent elements achieve this.
by distortion of bcc with FSBZ at (211) peaks; divalent materials form host–guest structures with two BZ and trivalent gallium adopts distorted-bcc structures with FSBZ at (310) peaks. Unlike s–d transfer, the theory also accounts qualitatively for the chain-melting and pressure sensitivity of c/a in rubidium, pressure independence of c/a ratio in Ba and Sr, increased superconductivity transition temperature in complex phases and similarity of Li to other group 1 elements under pressure.

The incommensurate nature of the ‘hotel’ structures appears again in the group VI elements. The hexavalent crystal structures of S, Te and Se evolve with increase in pressure from covalently bonded, insulating chain and layered structures into low-coordination metals, with incommensurate distortions arising from FSBZ effects, onto high-coordination metals dominated by close packing [27, 28].

The FSBZ principle is also evident in the crystal structures of group IV elements and group III–V compounds. Here, the stable structures have a simpler crystalline, which opens up a pseudogap for a tetravalent, based on β-tin and its binary equivalents [26]. This shows that the trend in intermediate pressure structures is not necessarily towards complexity per se, rather complexity appears as a solution to the problem of minimizing enthalpy via the FSBZ effect.

It is worth noting that the physics underlying FSBZ interactions due to ionic distortion is exactly the same as a charge density wave. It is simply a matter of taste whether one regards the electronic distortion as fundamental, with the ions following it, or vice versa.

In sum, we present a simple picture of the bonding of elements with increase in pressure. Low-pressure forms are best described by the conventional chemical picture of covalent or metallic bonding (ions floating in a free-electron gas, avoiding each other through screen repulsion). High-pressure forms arise from efficient packing of near-spherical atoms. Intermediate pressure crystal structures are those which maximize FSBZ interactions.

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