Fermi surface effects in solid-solid phase transitions in simple metals under pressure

G.J. Ackland

School of Physics and Centre for Science at Extreme Conditions, The University of Edinburgh, Mayfield Road, Edinburgh, EH9 3JZ, UK

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Abstract

We discuss the behaviour of Group 1 and 2 elements under pressure, describing crystallography based on diamond anvil pressure cell experiments and electronic structure calculations. In addition to these precise methods, we discuss more intuitive pictures of both the electronic driving force for the transitions, and the structural motifs which optimise the electronic energy by opening pseudogaps at the Fermi energy.

Introduction

Phase transitions occur when the relative stability of two putative phases changes. The stable phase is the one with lowest Gibbs free energy \( G \), and in most familiar temperature-driven cases the transitions arises due to the relative importance of energy \( U \) and entropy \( S \), \( G = U - TS \).

Transitions may also be caused by external strain and magnetic field, however because of the ability of a crystal to support a shear, or to screen a magnetic field, such transitions lead to formation of domain microstructure, and the transformation is dominated by interface effects between parent and daughter phase, which may co-exist. Such transitions are still described by the Gibbs free energy, with additional terms describing the strain and/or magnetic energies, which compete with the internal energy and entropy: \( G = U - TS + \sigma \epsilon + \mu B \).

Now additional complications arise from the fact that the strain field is a tensor, and the magnetic field is a vector.

Under isotropic pressure, the relative importance of various contributions to cohesion varies continuously. It is therefore possible to find phase transitions between structures with different electronic structures, and for these transitions to be induced by an externally applied field (the pressure) rather than arising from phase separation. Because the phase separation necessarily involves diffusion, the possibility that a diffusionless transition between crystal phases may be possible is suppressed. Thus pressure transitions give us a way to study structural transitions driven by changes in the electronic structure, without the complicating factor of diffusion.

Experimental pressures in the GPa range can routinely be obtained, thus the free energy contribution from the PV term can be much larger than that arising from TS. As a consequence, temperature effects are routinely ignored when considering high-P phase transitions, and we minimise the enthalpy \( G \approx H = U + PV \).

Extensive experimental and theoretical studies on the alkali and alkaline earth elements reveals a similar theme to the sequence of transitions with pressure. Typically the materials have a low-pressure, close-packed structure (either fcc or bcc - both have very similar energies), then a range of less-densely packed structures at intermediate pressure, and finally a return to close packing at the highest pressures. This
apparently counter-intuitive behaviour, with phases going from close-packed to open and back to close packed, is also associated with low-T superconductivity and a drop in the conductivity in the intermediate regime. It can be intuitively understood as follows: the low temperature "close packed" phases actually represent atoms being as far apart as possible, minimising their electrostatic repulsion in a delocalised free-electron gas. The atoms have relatively high entropy, manifested as very low phonon frequencies and elastic moduli. As pressure increases, the stronger interactions between atoms and electrons favours structures which maximise this effect, in particular those which open a pseudogap at the Fermi energy. At still higher pressures the Pauli repulsion between the core electrons becomes dominant, and again close packed structures are obtained. Thus the interesting region crystallographically lies at “intermediate” pressure.

We use the term “intermediate” because the actual pressures involved vary from element to element, i.e. the absolute GPa value is system dependent with lighter elements having larger absolute values.

The band structure stabilisation of certain crystal structures by interactions between the Fermi surface and Brillouin zone has been known for many years is familiar in many metallic compounds, from Hume-Rothery phases to quasicrystals, at special values of the number of valence electrons. It is only one of the competing effects, and the advent of total energy calculation has blurred the distinction between them, however, the Kohn-Sham Hamiltonian comprises a band structure term (the eigenvalues of non-interacting electrons moving in an effective field), an Ewald sum, exchange correlation and Hartree energies. The dependence on density ($\rho$) is as follows: $\rho^{1/3}$ for the coulombic terms (Hartree, ion-ion, ion-electron), $\rho^0$ for the exchange correlation (neglecting “non-linear core corrections”), $\rho^{2/3}$ for kinetic energy. Aside from the exclusion force from orthogonalisation, the only energy term which increases linearly with density is that due to energy splitting from interaction between plane waves and the lattice at the Fermi level. $\Delta E = \pm \int_{\Omega} e^{i\mathbf{k}\cdot\mathbf{r}} V(q) e^{i\mathbf{k}\cdot\mathbf{r}} d^3\mathbf{r}$

For group 1 and 2 elements the relative importance of this effect varies continuously with application of pressure. Although one cannot easily continuously vary the valence electron density in a sample chemically, pressure provides an external field enabling us to find and traverse the region where Fermi surface effects dominate.

How elements maximise Fermi surface Brillouin zone interactions

Having established that the total energy can be reduced by finding structures which maximise Fermi-surface effects, there remains the problem of determining exactly what kind of structure arises. There are close parallels with the powder crystallography experimental situation here - we know theoretically which scalar Bragg vectors would be favoured ($2k_F$), and the problem is to reconstruct a crystal which optimise these. While some structures can be guessed as distortions of simple structure, it turns out that nature has some admirably complex structures which are solutions to the FSBZ optimisation problem.

Distortions of simple structures

The bcc structure provides a close packed reciprocal lattice, and is therefore a good starting point to hunt for FSBZ-optimising structures. Lattice dynamics calculations enable us to determine mechanical instabilities of bcc, or other high-symmetry structures. Lithium provides a good example - Figure shows a phonon spectrum calculation for bcc lithium under pressure, showing that the structure is unstable, and the stable structure associated with allowing this instability to relax. These calculations are done using density functional
theory and the plane wave pseudopotential method PW-DFT \[17\] with phonons calculated by finite displacements \[18\], full details are given elsewhere \[11\].

The distorted structure turns out to be the cI16 crystal structure observed in lithium \[1\] at intermediate pressures. The energy gained in the distortion comes from opening a pseudogap at the Fermi level. The mechanism by which such a structure can be reached from bcc is straightforward.

Figure 1: Calculated phonon spectrum for bcc Li at 40GPa. The “negative” frequency phonons correspond to unstable modes, i.e. distortions which lower the energy of the crystal.

Spontaneous interstitial formation

The distorted bcc structure of Li may provide the option of multiple FSBZ interactions. However, it may prove impossible to match the necessary crystal density with the required number of atoms. Nature’s ingenious solution here is to incorporate interstitial atoms onto the distorted bcc structure. Figure 2 shows the relationship between the intermediate crystal structure of lithium and that of caesium, found both experimentally \[3\] and theoretically \[12\] and confirmed by our own PW-DFT calculation. This shows that the Cs structure can be thought of as being created from the distortion of the bcc structure into the cI16 structure, combined with the formation of planes of interstitials (black layers). No work has been done on the mechanism for this transformation, in particular whether the distortion can occur in a diffusionless manner while the interstitial array takes longer due to being diffusive.

Incommensurate structures

Another way to increase FSBZ interactions is to increase the dimensionality of the reciprocal space. This is observed when an incommensurate structure (sometimes called a charge density wave) is formed. This conventional type of structure is a modulation of a simple
crystal structure, as observed in high-pressure selenium. Simple elemental metals have a far more complex modulation: the “hotel” structure. Some “host” atoms form a zeolite-like crystal structure, with sizable, usually linear, pores. The remaining atoms then form “guest” chains inside the pores. Such structures can then be described by two inter-penetrating lattices, incommensurate in one axis, which then require a four dimensional reciprocal space to describe. By transferring atoms between “guest” and “host” structures, the shape of the 4D reciprocal lattice can be moulded to fit the Fermi surface, and thus lower the energy.

**What about s-d transfer?**

The traditional picture of the complex intermediate phases is one in which electrons transfer from “delocalised, large, spherical” s-orbitals to “localised, compact, angular” d-orbitals. It is important to realise that both this and the FSBZ model are just pictures - one can of course make projections of the electronic wavefunctions onto localised orbitals and find that as pressure increases there is a transfer from s to d. Historically, the key experimental “proof” of this was the report isostructural fcc-fcc transition in Cs, which of course cannot introduce extra FSBZ effects. However, this is undermined by the recent experimental determination that there is no such transition - the intermediate phase was simply misidentified. In favour of the FSBZ picture are:

- that the energetics can be described by density functional theory (which is known to fail for strongly localised electrons)
- the similarity between the structures in high pressure Li and those in Cs and Rb (despite the absence of a 2d electron shell!)
- the drop in conductivity in the intermediate phases associated with opening of the pseudogap
- the experimental observation of structures with multiple strong diffraction peaks around $2k_F$.
- The calculation of dips in the density of states at the Fermi level for complex structures.

**Consequences for transition mechanisms**

The phase transition mechanisms between complex phases of the elements cannot be done by simple displacements in all cases, however in simple metals the metallic binding and low melting point/shear moduli mean that the transitions do occur on the timescale of at most few hours after pressurization. Since no composition change is required for an element, relatively small atomic motions could effect the transitions, however to my knowledge there has been no work in this area, either experimentally or theoretically.

It is interesting to note that the FSBZ energy reduction comes from long range periodic interactions of delocalised distortion and delocalised electrons. It is therefore unclear whether this would be approached by a localised nucleation and growth process, as envisaged in most continuum mechanics approaches, or whether the nucleation should be thought of in reciprocal space, and the “growth” as the freezing in of a single in-phase long range mode.
Conclusions

We have shown that from scaling relations one might expect a pressure regime in which Fermi Surface-Brillouin zone interactions dominate the energy differences between crystal structures of similar density. We have then shown how experimental and density-functional theory data from our own work and the literature support this picture for the complex intermediate phases of the group I and II elements. The mechanism by which these phase transformations occur is as yet unknown.

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Figure 2: Relationship between intermediate pressure crystal structures in Li (top, with black diamond showing doubled, distorted bcc cell)) and Cs bottom. Four interstitial dumbbells (two atoms on one site, pointing along the longer axis) have been inserted in the black layers, Rubidium shows similar behaviour.
Rubidium, potassium and sodium show similar guest-host behaviour. Figure 3: Schematic incommensurate crystal structure in barium IV, showing inter-penetrating “guest” and “host” structures (a) shows chains end-on fitting into the host structure (b) shows incommensurate guests and hosts along the c-axis. The guest chains are regularly arranged with respect to each other, but incommensurate with the hosts. Rubidium, potassium and sodium show similar guest-host behaviour.