

# Symmetry breaking and restoring under high pressure: the amazing behaviour of the “simple” alkali metals

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**Abstract.** We argue that an ionic lattice surrounded by a Fermi liquid changes phase several times under pressure, oscillating between the symmetric phase and a low-symmetry dimerized structure, as a consequence of Friedel oscillations in the pair potential. Phase oscillations explain the tendency towards dimerization which has been recently reported for the light alkali metals under high pressure. Moreover, a restoring of the symmetric phase is predicted for such elements at an even higher density.

**PACS.** 71.20.Dg Alkali and alkaline earth metals – 62.50.+p High-pressure and shock-wave effects in solids and liquids – 64.70.Kb Solid-solid transitions

## 1 Introduction

Some years ago we predicted [1] that under high pressure the light alkali metals should be unstable towards less symmetric phases. We also argued that the lowering of symmetry could give rise to a metal-insulator transition. We did not attempt to predict the structure of the high pressure phase, and unfortunately any such theoretical prediction is quite difficult, because of the small energy differences which separate most phases. Our result followed the early suggestion that electron correlation in the alkalis could give rise to broken symmetry of the charge density wave (CDW) type, albeit incommensurate with the lattice [2]. The role of core repulsion in stabilizing the high pressure phases of the alkali had been also emphasized by McMahan *et al.* [3,4].

The prediction of a symmetry lowering was quite unexpected, as it is usually believed that an increase of pressure should give rise to an increase in the symmetry of the system. Actually, under very high pressure the most likely state of matter is a uniform plasma, so that any system is expected to raise its symmetry at a sufficiently high pressure. However, many “simple” metals are still far from such a limiting behaviour, and their path towards the ultimate metallization may contain oscillations of their degree of symmetry.

More recently, both theoretical calculations [5] and experimental findings [6–8] have confirmed the tendency of the light alkali metals to lower their symmetry under high pressure. Low symmetry phases have been observed for

Li [7] and Na [9] (see also Ref. [10]), whereas the eventual occurrence of a metal-insulator transition has not been observed yet [8]. According to recent calculations [11], both Li and Na show a tendency towards the formation of atomic pairs, and a dimerized *oC8* structure would be the most stable phase above 165 GPa for Li, and above 220 GPa for Na.

The physical reason for dimerization is not evident. *Ab initio* electronic structure calculations [12] indicated a tendency towards “distance alternation”, due to a sizeable overlap of  $p\pi$  orbitals in the interstitial regions. On the other hand, it has been noticed [11] that the increase of *s-p* hybridization could give rise to a low coordination number. However, even the fully dimerized phase is far from any standard covalent solid: the electron density is uniformly spread and almost constant, while the first and second neighbours distances are comparable. Such a dimerized phase is better described as a charge density wave in a high density metal rather than a molecular solid. Now, at zero pressure both Li and Na are already well described by a simple degenerate Fermi liquid where the kinetic energy is the most relevant energy term [13]. At high density all the interactions should become smaller and smaller compared to the kinetic energy, and if all the energy terms are assumed to be monotonic functions of density, then nothing relevant is expected to happen. On the other hand, the high density limit is where the Fermi liquid model should work better, thus it remains to be explained why a Fermi liquid should be unstable towards a charge density wave.

In this paper we address such a problem and show that an ionic lattice, surrounded by a Fermi liquid, oscillates

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between a simple metal and a charge density wave, several times with increasing density. We start in Section 2 by reviewing the evaluation of the structural energy of a solid lattice within linear response theory. In Section 3, we later discuss the case of lithium and other alkali metals under high pressure, where the presence of Friedel oscillations in the screened pair interactions can justify the occurrence of an instability towards a broken-symmetry phase. We eventually summarize in Section 4.

## 2 Structural energy of solids close to a phase instability

The basic idea is foreshadowed in the seminal works of Pettifor *et al.* [14,15], who discussed the possible existence of phase oscillations. The physical motivation is related to Friedel oscillations [16], which characterize the screened interactions and give rise to a non-monotonic oscillating behaviour of the structural energy terms. A dimerization of the lattice can be regarded as a broken-symmetry phase described by an order parameter  $y$  which vanishes in the symmetric phase. In most cases,  $y$  can be taken to be the difference between first and second neighbours distances, and  $y = 0$  yields the monoatomic lattice. The total structural energy of the system must be an even function of  $y$  and can be expanded as  $U(y) \approx U(0) + \frac{1}{2}U''(0)y^2$ . Its main contribution comes from screened pair interactions which oscillate with a wavevector  $q = 2k_F$ , where  $k_F$  is the Fermi wavevector (Friedel oscillations). Thus the sign of the second derivative  $U''(0)$  is dominated by the sign of the second derivative of the pair interaction with respect to the pair distance. But an oscillating pair interaction yields oscillating derivatives, so that  $U''(0)$  is expected to change sign as the pair distance decreases. A positive sign  $U''(0) > 0$  corresponds to having a minimum for  $y = 0$  (symmetric phase); a negative sign  $U''(0) < 0$  corresponds to having a relative maximum for  $y = 0$ , thus indicating that the symmetric phase is unstable towards a dimerized phase. Moreover, we expect that with increasing density the sign of  $U''(0)$  could change several times, thus giving rise to phase oscillations between a symmetric and a dimerized lattice.

In order to make the above idea more quantitative, let us specialize to the light alkali metals. We start by expressing the total energy per atom of a metal lattice in real-space formulation as [17]:

$$U = U_0 + \frac{1}{2} \sum_{i \neq j} \Phi(R_{ij}), \quad (1)$$

where the pair potential  $\Phi(R_{ij})$  measures the interaction between two ions located at sites  $i$  and  $j$  in the lattice,  $R_{ij}$  being their mutual distance, and  $U_0$  summarizes all the contributions independent of the lattice structure. Within second order local pseudopotential theory, the pair potential can be written as [15,18]:

$$\Phi(R) = \frac{Z^2}{R} \left( 1 + \frac{2}{\pi} \int_0^\infty h(q)v^2(q) \frac{\sin qR}{q} dq \right), \quad (2)$$

where  $Z$  is the atomic number,

$$h(q) = -\frac{\kappa^2 \chi(q)}{q^2 \epsilon(q)} = -\kappa^2 \frac{\chi(q)}{q^2 + \kappa^2 [1 - G(q)] \chi(q)}, \quad (3)$$

with  $\epsilon(q)$  the dielectric screening function,  $\kappa^2 = 4k_F/\pi$  is the Thomas-Fermi screening parameter,  $\chi(q)$  is the normalized Lindhard susceptibility [ $\chi(0) = 1$ ], and  $G(q)$  takes into account for exchange and correlation corrections (local field corrections) to the electron-electron interaction [19]. In the following, we shall take  $Z = 1$  for simplicity, which is a good approximation for the light alkali at ambient conditions. In equation (2) we assume the ‘empty core’ model for the ionic pseudopotential [20],

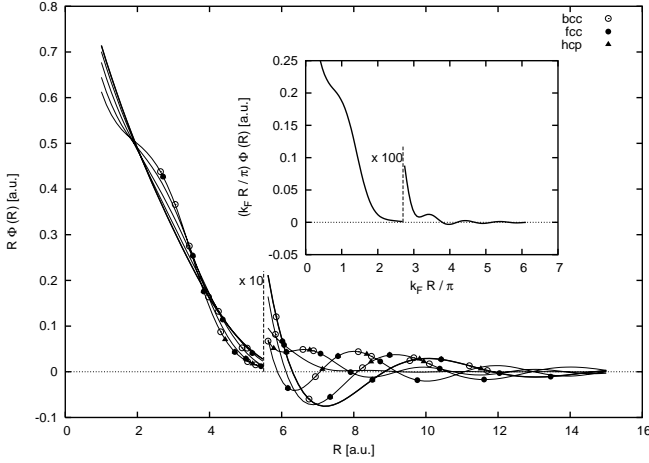
$$v(q) = \cos qR_c, \quad (4)$$

where  $R_c$  defines the radius of the atomic core. The core radius  $R_c$  is usually obtained by fitting equation (4) against the value of the band gap  $2|v(\mathbf{g})|$ . We have checked that equation (4) is also consistent with the calculated band structure of lithium both in the bcc [21] and in the fcc structure [22]. However, different sources of experimental data result in slightly different values of  $R_c$  for a given element [23]. Moreover, the value of  $R_c$  can be effectively altered by chemical substitution (*e.g.* in alloys). Therefore, in the following we will regard  $R_c$  as a parameter ranging within given bounds for each element of interest. The other independent parameter of the model is the electron spacing  $r_s$ , defined as  $4\pi r_s^3/3 = N/V$ , where  $N/V$  is the conduction electron density. Such parameter enters equation (2) through the Fermi momentum  $k_F$  in the Thomas-Fermi parameter  $\kappa^2$ , and can be used as a measure of pressure, with  $r_s$  decreasing as pressure increases. Moreover, for a given lattice structure, all inter-site distances  $R_{ij}$  in equation (1) scale with  $r_s$ .

As a result of the singular behaviour of  $h(q)$  at  $q = 2k_F$ , which in turn arises from the logarithmic discontinuity in the derivative of the Lindhard function  $\chi(q)$ , the Fourier transform in equation (2) endows the pair potential  $\Phi(R)$  with an oscillating behaviour, with a characteristic length  $\sim \pi/k_F$  (Friedel oscillations, see Fig. 1, inset). The analytical properties of the pair potential  $\Phi(R)$  have been analyzed further in reference [18]. The actual value of the total energy  $U$  in equation (1) then depends on whether the distances of nearest and farther neighbours in the lattice lay close to maxima or minima in the plot of  $\Phi(R)$  (Fig. 1). For a fixed value of the pseudopotential parameter  $R_c$ , such distances can be actually shifted to lower values by decreasing  $r_s$ , *i.e.* by means of an applied pressure. On the basis of such considerations, the stability of the crystal structures of several elements under pressure has been discussed in the past [24].

## 3 The case of lithium and other light alkali metals under high pressure

The phase diagram of the alkali at low pressure has been extensively addressed both experimentally and theoretically, with lithium crystallizing in the 9R phase at zero

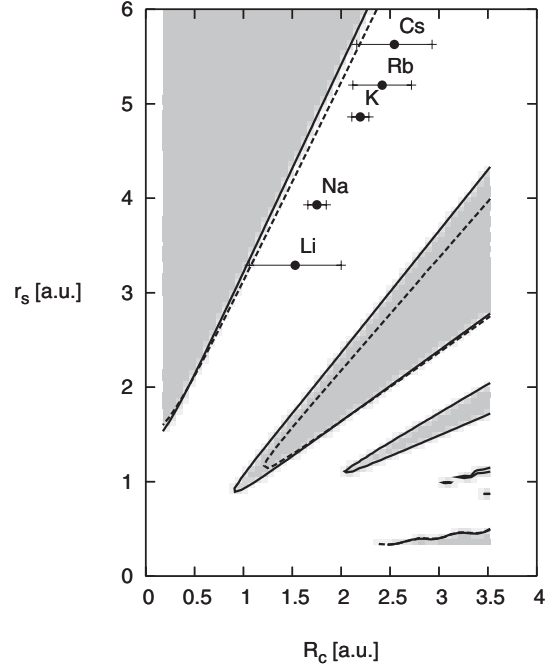


**Fig. 1.** Scaled pair potential  $R\Phi(R)$  versus interatomic distance  $R$ . *Main plot:*  $R_c = 1.76$  a.u.,  $r_s = 1.5 - 3.326$  a.u., with thicker line corresponding to  $r_s = 3.326$  a.u. Symbols correspond to nearest and farther neighbours locations in the bcc (open circles), fcc (full circles), and hcp (triangles) lattices, respectively. *Inset:* Same as main plot for  $R_c = 1.76$  a.u.,  $r_s = 1.5$  a.u., but now with distances scaled by  $k_F R / \pi$ . Notice that minima in  $R\Phi(R)$  occur close to integer values of  $k_F R / \pi$  (Friedel oscillations).

temperature and pressure [22,25–27]. At high pressure ( $\sim 39$  GPa), a new structural phase (Pearson symbol *cI16*) has been recently detected [7]. Hanfland *et al.* [9] have recently observed bcc  $\rightarrow$  fcc  $\rightarrow$  *cI16* transitions in Na. Thus we can regard the *cI16* phase as our starting point for the following discussion on alkali metals. Such a high-pressure phase is characterized by a bcc primitive cell, with an 8-atom basis [11], and can be thought of as a distorted bcc phase, with a distortion parameter  $x = 0.045 - 0.060$  [7]. The *cI16* phase formally reduces to the bcc structure (‘supercell’ with eight usual cubic cells) for  $x = 0$  [11]. In the undistorted bcc phase, the lattice is composed of two interpenetrating cubic sublattices, *A* and *B*, say. Such classification applies to the *cI16* structure as well, after distortion from the parent bcc lattice, but now with a basis of four atoms for each sublattice. The *cI16* phase by itself is not dimerized, and it has been recently predicted to be even superconducting [28,29]. We would like to test its stability with respect to a dimerized phase obtained by rigidly shifting the two sublattices each other of a tiny amount  $y$  along the (111) direction. Here,  $y$  plays the role of the order parameter discussed above. For a fixed value of the distortion parameter  $x$ , one can then think of expanding the total energy per atom equation (1) in powers of our ‘dimerization’ parameter  $y$ ,

$$U[x, y] = U_0 + U_y[x, 0]y + \frac{1}{2}U_{yy}[x, 0]y^2 + O(y^3), \quad (5)$$

where  $U_y = \partial U / \partial y$  etc. Due to crystal symmetry, it can be proved analytically that  $U_y[0, 0] = 0$  exactly, whereas we numerically checked that  $|U_y[x, 0] / U_{yy}[x, 0]| \ll 1$ , for  $x \ll 1$  [30]. Therefore, an indication of instability towards



**Fig. 2.** Shaded regions in the plane of parameters  $(R_c, r_s)$  are characterized by the condition  $U_{yy}[x, 0] < 0$ , which signals an instability towards dimerization. The regions corresponding to instability towards dimerization in the undistorted bcc phase ( $x = 0$ ) and in the *cI16* phase ( $x = 0.05$ ) are bounded by continuous and broken lines, respectively. Data for  $(R_c, r_s)$  pairs for the light alkali metals at ambient pressure have been taken from references [23,24]. Different methods of fitting pseudopotentials to the experimental data result in a rather wide range for  $R_c$ , which is here displayed as an error bar.

‘dimerization’ is provided by the condition  $U_{yy}[x, 0] < 0$ . From equations (1, 2),  $U_{yy}[x, 0]$  can be expressed as

$$U_{yy}[x, 0] = \frac{1}{4} \sum_{\mathbf{n}\mu\nu} \left[ \left( \Phi''(R_{\mathbf{n}\mu\nu}^0) - \frac{1}{R_{\mathbf{n}\mu\nu}^0} \Phi'(R_{\mathbf{n}\mu\nu}^0) \right) \times \left( \frac{\partial R_{\mathbf{n}\mu\nu}^0}{\partial y} \right)^2 + \frac{3a^2}{R_{\mathbf{n}\mu\nu}^0} \Phi'(R_{\mathbf{n}\mu\nu}^0) \right], \quad (6)$$

where  $\mathbf{n}$  labels lattice points in the primitive bcc lattice, with lattice parameter  $a$ ,  $\mu$  and  $\nu$  label the basis vectors in sublattice *A* and *B*, respectively [11], and  $R_{\mathbf{n}\mu\nu}^0$  denotes the mutual distances between lattice points for  $y = 0$ . Equation (6) has been evaluated on a finite lattice, large enough to reach full convergence. Figure 2 displays our numerical results for  $U_{yy}[x, 0]$  as a function of parameters  $(R_c, r_s)$ , for  $x = 0$  (undistorted bcc phase) and  $x = 0.05$  (representative value of the high-pressure *cI16* phase according to Refs. [7,11]).

In the plane of parameters  $(R_c, r_s)$  we find regions of instability towards dimerization where  $U_{yy}[x, 0] < 0$  (Fig. 2, shaded areas). It is remarkable that at ambient pressure all the alkali metals are predicted to be stable

in the symmetric phase. As the core radius  $R_c$  is related to the band gap, one would in general expect  $R_c$  to be a (monotonic) function of the density parameter  $r_s$ . More generally, a more quantitative analysis would require a non-local pseudopotential, with a density-dependent range in reciprocal space. However, within linear response theory, the long wavelength behaviour of the pseudopotential is what actually matters. Indeed, the first zero of equation 4 occurs at  $q = \pi/2R_c$ , which is very close to the smallest reciprocal lattice vector of most metals. Therefore, at the level of approximation implied by the present calculation, we can safely neglect the density dependence of  $R_c$ , without qualitatively alter our main conclusions. In this way, the effect of applied pressure on the phase point corresponding to each alkali metal in Figure 2 can be tracked as a vertical shift at constant  $R_c$ , with increasing density. However, the error bars for  $R_c$  under normal conditions grossly provide order of magnitude boundaries for the generally expected variation of  $R_c$  with density.

A sign change in  $U_{yy}$  for a given alkali metal then corresponds to a critical density. The uncertainty on  $R_c$  lends a wide window for the critical densities of Li and Na: the largest values (still compatible with the core radius data of references [24,23]) are  $r_s \sim 2 - 2.2$  a.u., which are not too far from the values observed by Hanfland *et al.* [7] for the onset of a dimerized phase for Li ( $r_s \approx 2.1$  a.u. and  $P = 165$  GPa) and predicted by Christensen and Novikov [11] for the onset of a dimerized phase for Na ( $r_s \approx 2.3$  a.u. and  $P = 220$  GPa). However, we caution that such a critical density occurs for  $r_s \sim R_c$ , *i.e.* close to the limits of applicability of the empty-core pseudopotential approximation, thus suggesting that more refined pseudopotentials should be employed in more realistic calculations. The phase diagram of Figure 2 also suggests that, with a further increase of density, both Li and Na should drop below the instability area, and a second transition would eventually restore the symmetry of the lattice. This oscillating behaviour, from a symmetric phase to a less symmetric one and back to a restored symmetric phase, seems to be a general effect due to the presence of Friedel oscillations in the interatomic distance dependence of the pair potential. Such oscillations in turn are a consequence of the existence of a Fermi surface at  $k = k_F$ . Thus the tendency towards the formation of atomic pairs would be a signature of the Fermi liquid behaviour of the alkali metals.

Our method relies on linear response theory, which contains the Thomas-Fermi approximation as a long wavelength limit [31]. Both such methods are known to be reliable if the density gradients are not too strong. In large atoms, the Thomas-Fermi method yields results which only differ by 8% from Hartree-Fock calculations, in space regions where the density gradient  $\nabla\rho/\rho \approx 2.5/a_0$  ( $a_0$  is the Bohr radius) [32]. Here, the typical density gradients are  $\nabla\rho/\rho < 0.5/a_0$ , as reported by reference [11] for the high pressure phase of Li at 165 GPa. Thus, we expect linear response to be reliable in the high pressure range, where eventual second order corrections are very small (for these gradients even the simple Thomas-Fermi

approximation would deviate less than 1% from Hartree-Fock calculations).

## 4 Conclusions

In summary, we have shown that a distorted bcc lattice (*cI16* phase), surrounded by a Fermi liquid, undergoes several structural transitions under high pressure, oscillating between a symmetric phase and a broken-symmetry dimerized phase. These phase oscillations seem to be a direct consequence of the non monotonic behaviour of the pair potential which is characterized by a Friedel wavelength  $\pi/k_F$  in the presence of a sharp Fermi sphere. Such findings could be relevant for the understanding of the tendency towards the formation of atomic pairs, which has been recently reported for the light alkali metals. We furthermore predict that a restoring of symmetry should take place at some stage under higher pressure, which would be signalled by a reentrant metallic character.

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