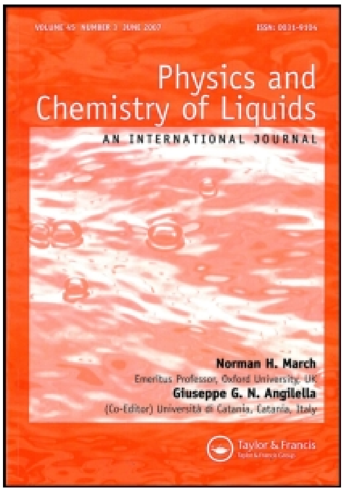

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Low-coordination phases of both crystalline and fluid states of alkali metals under extreme conditions of high and low densities, respectively

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LETTER

Low-coordination phases of both crystalline and fluid states of alkali metals under extreme conditions of high and low densities, respectively

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After a brief summary of early work, involving the present authors, relating to low coordination phases of some alkalis in either dense crystalline states at high pressure (e.g. Li) or low density metallic fluids near criticality (Cs and Rb), contact is made with the very recent density functional study by Pickard and Needs (Phys. Rev. Lett. **102**, 146401 (2009)). Whereas these authors predict three- and four-fold coordination numbers for extremely high pressure crystalline phases of Li, we stress here the remarkable behaviour of the heavy alkali metallic fluids Cs and Rb along the liquid–vapour coexistence curve towards the critical point. Coordination numbers $\sim 8-10$ near melting then reduce, as the density is lowered, to 2 at or near the critical point.

Keywords: fluid alkalis; high pressure; liquid–vapour coexistence

Both the authors have been involved in early work on some of the alkali metals, in different phases and under somewhat extreme conditions. Thus, in [1], light crystalline alkali metals were studied theoretically by using the extended Hubbard Hamiltonian. In this work, the prediction was made that under high pressure the body-centred-cubic (bcc) light alkali metals should be unstable towards less symmetric phases. Subsequently, the same authors [2] stressed that experimental findings [3–5] have confirmed the tendency of the light alkali metals to lower their symmetry under sufficient compression.

In contrast, in the highly expanded heavy alkalis Cs and Rb, but now in the liquid metallic phase, one of us [6,7] considered their behaviour along the liquid–vapour coexistence curve (LVCC) towards the critical point. This work utilised the neutron diffraction measurements of Hensel *et al.* [8,9] to represent their experimental data on the mass density d, for coordination number z, by

$$d = az + b. \tag{1}$$

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For the dense metallic fluid Cs, along the LVCC towards the critical density $d_c = 380\,\mathrm{kg\,m^{-3}}$, Freeman and March [10] record the values $a = 230\,\mathrm{kg\,m^{-3}}$ and $b = -80\,\mathrm{kg\,m^{-3}}$. The relative constancy [9] of the nearest neighbour (NN) bond length as the density d is lowered lends strong support to the viewpoint that a chemical bond is the basic building block in Cs, and also in Rb, in these highly expanded fluid metals. Freeman and March [10] refer in these cases to a rather constant bond length ~0.54–0.57 nm.

This brings us to the basic motivation for reopening the low coordination numbers inferred in the early references [1] and [2] for light solid alkalis, and for the highly expanded fluid metals Cs and Rb, represented by Equation (1). Near $d = d_c$, z tends to 2 for Cs using the values of d_c, a and b cited above. This Letter is then motivated by the very recent density functional (DFT) study by Pickard and Needs [11] on dense low-coordination phases of crystalline metallic Li. In particular, using DFT plus a structure-searching technique, these authors predict low-coordination crystals under high pressure. More specifically, their predictions are: (a) for three-fold coordinated structures to be stable in the pressure range 40–450 GPa; and (b) for four-fold coordination at higher pressures.

In more detail, to summarise the findings of Pickard and Needs [11], their theoretical predictions as to the characteristics of the ground-state electron density in the high-pressure Li structures they advocate, are as follows. The valence electrons appear to move away from the ions and take up interstitial locations which are rather isolated from each other. Also, the occupied valence band widths of the high-pressure crystalline phases are narrower than the corresponding free-electron predictions, which accords with the viewpoint expressed by Rousseau and Ashcroft [12].

In concluding this Letter, we find remarkable the fact that while at ambient pressure, there is a high coordination number for both crystalline (bcc) Li and also for the heavy metallic fluids Rb abnd Cs near their melting temperatures T_m, one gets, if one adopts the theoretical solid-state predictions of [11], low-coordination numbers $z \sim 3$ or 4 for Li under extreme high pressures and z reducing from high values ~8–10 for fluid Rb and Cs near T_m to ~2 for Cs near the critical point. The formation of chains has been proposed by one of us [6,7] as leading to a Peierls instability coincident with the critical point. It is relevant in this context to mention, following Freeman and March [10], that, subsequent to the experiments of Hensel *et al.* [8,9] focused on above, Whitman *et al.* [14] have reported the structural properties of Cs adsorbed on room temperature GaAs(110) and InSb(110) surfaces, as observed by means of scanning tunnelling microscopy. These authors demonstrate that Cs initially forms long, one-dimensional (1D) zig–zag chains on both surfaces. For example, their Figure 1a [14] shows in particular a large-area image of

Table 1. Critical constants: pressure, number density, temperature and compressibility ratio, $Z_c = p_c/\rho_c R T_c$, for the alkali metals (after [13]).

Element	p_c (MPa)	ρ_c ($10^{-4}\,\mathrm{m^{-3}\,mol}$)	T_c (K)	Z_c
Li	30.4	1.701	3344	0.064
Na	25.22	0.917	2.497	0.132
K	15.95	0.490	2239	0.175
Rb	12.45	0.341	2017	0.217
Cs	9.25	0.285	1924	0.203

Cs chains on GaAs(110), including chains extending over ~100 nm. For further details, reference can be made to [10] and [14]. The final comment concerns future experimental studies. It would, of course, be interesting to extend the experiments of Hensel *et al*. [8,9] to other alkalis. Some progress should be possible for say K, along the LVCC, but as Table 1 shows, the critical regimes become less accessible experimentally for the lighter alkalis than for Rb and Cs.

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