## Low density observations of Rb and Cs chains along the liquid-vapour coexistence curves to the critical point in relation to quantum-chemical predictions on the metal-insulator transitions in Li and Na rings

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# LETTER

# Low density observations of Rb and Cs chains along the liquid–vapour coexistence curves to the critical point in relation to quantum-chemical predictions on the metal-insulator transitions in Li and Na rings

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Recent *ab initio* predictions concerning the metal-insulator (MI) transition in rings of the light alkali atoms, Li and Na, are compared and contrasted with experimental facts concerning diluted Rb and Cs alkalis. The main focus here is on the local coordination number as a function of density as these two heavy alkali metallic fluids are taken along the liquid–vapour coexistence curve towards the critical point, which in these cases coincides with the MI transition. Also recorded are the results of experiments in which Cs chains are observed at large interatomic spacing outside semiconducting substrates of InSb and GaAs.

## 1. Introduction

In a recent work, Paulus *et al.* [1] have reported *ab initio* calculations relating to the metal-insulator (MI) transition in Li rings. Subsequent studies by Alsheimer and Paulus [2] have embraced both the Na rings, as well as some mixed Na–Li systems.

Our purpose here is to note that in the heavier alkalis Rb and Cs, chains are observed under two very different physical areas. The first area is when one takes these two alkali metal fluids along the liquid–vapour (LV) coexistence curve towards the critical point. From neutron diffraction studies of Jüngst *et al.* [3], it is known that high coordination number $z$ in these metallic liquids near the freezing point is reduced greatly as the

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Table 1.  Bulk alkali metal equilibrium nearest-neighbour separation, $R_e$, compared with some results at separations larger than those required to induce the metal-insulator transition.

| Alkali | $R_e$ for bcc (Å) | Non-metallic separations (Å) | |
|---|---|---|---|
| Li rings | 3.03 | ~4.6 | [1] |
| Na rings | 3.66 | ~4.8 | [2] |
| K linear chains | 4.52 | | see figure 4 of Ref. [8] |
| Rb linear chains | 4.83 | | see figure 5a of Ref. [8] |
| Cs linear chains | 5.2 | | see figure 5b of Ref. [8] |
| Cs zig-zag chains on InSb(110) surface | 5.2 | 8.0 | [6] |
| Cs zig-zag chains on GaAs(110) surface | 5.2 | 6.9 | [6] |

density $d$ is lowered along the LV coexistence curve. One of us [4] has fitted the experimental data by

$$d = az + b \qquad (1)$$

where $a = 230$ and $b = -80$, both in kg/m$^3$ (see also [5]). Cs having a critical density of 380 kg/m$^3$, the conclusion is that $z \to 2$ as the critical point is approached. To present experimental accuracy, in these two heavy alkalis, Cs and Rb, the MI transition and the critical point coincide for these fluids.

The second area we wish to draw attention to in the present study is that of Cs outside semiconducting surfaces, and in particular, InSb(110) and GaAs(110) [6]. Here, the atom spacings in the Cs chains, which were observed experimentally, were dictated dominantly by the geometry of the semiconducting substrates. The spacing of Cs atoms is then substantially larger than for Cs body-centred cubic metal at atmospheric pressure (see table 1).

## 2. *Ab initio* studies of Paulus *et al.* on Li and Na rings

Recently, Paulus *et al.* [1] have applied *ab initio* quantum-chemical techniques to Li rings, with the aim of studying the analogue of a metal-insulator (MI) transition. By varying the interatomic distance, these authors have analyzed the character of the many-electron wave function. In particular, the importance of the *s–p* orbital quasi-degeneracy within the metallic regime has been emphasized. Parallel work embracing now both Na rings and mixed Na–Li systems has subsequently been reported [2].

## 3. Experimental studies on the heavy alkalis Rb and Cs: in relation to the formation of chains

Though the *ab initio* studies above [1,2] were on rings of some 10 alkali atoms, reference was also made to less accurate mean field studies of finite linear chains. It is this aspect that has prompted us to reopen older studies, dominantly but not wholly experimental, on chains of the heavy alkalis Rb and Cs.

Let us begin with a brief summary of the experimental findings of Jüngst *et al.* [3]. These authors used neutron diffraction to study the structure of several thermodynamic states of fluid Cs, lying along the liquid–vapour coexistence curve towards the critical point.

One important conclusion was that the near-neighbour 'bond' distance remained relatively constant ($\sim 5.4 - 5.7\,\text{Å}$) as the density was lowered towards the value at the critical point. The obvious implication is that this density reduction must come about for Rb and Cs largely by the lowering of the local coordination number $z$ [see equation (1)] as the critical point is approached [see again equation (1)]. The other important point to be stressed here is that whereas in a divalent metal like Hg, there is a MI transition in the originally metallic fluid well before the critical point is reached, in the monovalent heavy alkalis Rb and Cs, experimental accuracy does not presently allow the critical point and the MI transition to be separated.

Therefore, it is of interest to turn to a second, very different, area, in which chains of Cs atoms have been detected experimentally. Thus Cs has been adsorbed on room temperature semiconducting substrates. This is then found, under suitable experimental conditions, to lead to the formation of quite long Cs chains outside, both InSb and GaAs [6], as observed with scanning tunneling microscopy. Taking the example of GaAs, one-dimensional zig-zag chains, more than $1000\,\text{Å}$ in length, were observed by Whitman *et al.* [6].

## 4. Summary and future directions

We have compared and contrasted (see also table 1) the behaviour of configurations consisting of a (relatively small) number of light alkali atoms having low local coordination number $z$ (e.g., a ring-like $\text{Li}_{10}$ studied by *ab initio* quantum-chemical methods in [1]) with some experimental observations where $z$ is small ($\sim 2$) on the heavy alkalis Rb and Cs: especially as these metallic liquids approach the critical point, along the LV coexistence curve. Paulus *et al.* [1] stress for Li metal the substantial contribution of $p$ electrons to the conduction band. They point out that with increasing interatomic separation the ratio of $p$ and $s$ electrons alters and in particular in the atomic limit, one is dealing with a $1s^2 2s$ atomic state.

Of course, in the heavy alkalis Rb and Cs, one must expect to deal with more angular momentum quantum numbers, and this will most probably affect the character of the MI transition. However, as experiments employing neutron scattering show, Rb and Cs retain a rather constant near-neighbour distance along the LV coexistence curve out to the critical density, and the MI transition to present experimental accuracy coincides with the critical point, where the local coordination number $z \sim 2$. It was proposed therefore in [4] that a Peierls transition occurred in Cs and Rb at the critical point. Also invoked is data for Cs adsorbed on semiconducting substrates, where chains are observed on both InSb and GaAs. Whitman *et al.* [6] invoke, at a semiquantitative level, the model of Ferraz *et al.* [7] in which, in general terms, the dissociation of $H_2$ embedded in an electron liquid is observed to occur as the electron density of the background fluid is increased. This model has some features in common with the observations of Whitman *et al.* [6].

Obviously, for the future, it would be of considerable interest if the *ab initio* quantum-chemical studies of [1] and [2] could be extended to the heavy alkali Rb,

though already K would be of interest (see also the density functional work of March and Rubio [8]: this could be extended, as it was under compression to date, to lower conduction electron density). We note also the likely relevance of cluster studies, such as that recently reported on $Li_8$ by Grassi *et al.* [9], motivated by experimental determination of the geometry of the lowest isomers of such light alkali atom clusters [10]. Finally, it seems of interest to return briefly to table 1 above. There it is recorded first for Na rings that the interatomic separation has to be increased by a factor of $\sim 1.3$ from the equilibrium distance in bcc Na to induce a MI transition in the ring. Moving to the final entry in table 1, the non-metallic separation recorded for GaAs(110) is also 1.3 times the equilibrium spacing in bcc Cs metal. It is tempting therefore to conjecture that, in the case of GaAs, one is quite near the MI transition. In contrast, the formation of the same one-dimensional Cs zig-zag chains observed in InSb(110), the III-V semiconductor with the largest lattice constant, seems well into the insulating chain regime.

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