On the constitution of sodium at higher densities

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Abstract

Using density functional theory the atomic and electronic structure of sodium are predicted to depart substantially from those expected of simple metals for \( r_s < 2.48 \) \((p > 130 \text{ GPa})\). Newly-predicted phases include those with low structural symmetry, semi-metallic electronic properties (including zero-gap semiconducting limiting behavior), unconventional valence charge density distributions, and even those that raise the possibility of superconductivity, all at currently achievable pressures. Important differences emerge between sodium and lithium at high densities, and these are attributable to corresponding differences in their respective cores.

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In their classic papers *On the Constitution of Metallic Sodium*, Wigner and Seitz [1] successfully described ground state properties of sodium invoking the notion of a nearly-free electron metal, one whose valence electrons are only weakly perturbed by an underlying periodic arrangement of ions. An assumption central to their conclusions (and important to the developing concept of the simple metal) was that the tightly bound core electrons remain largely unaltered with respect to those in the free atom. At its stabilizing (atmospheric) density, this assumption is valid because the ion cores occupy an exceedingly small fraction of the overall volume of the solid. But as we show in this Letter, if the overall density (and hence relative core volume) is increased by pressures that are currently achievable, the core states come in to play and the electronic structure of sodium departs quite significantly from this simple metal paradigm.

Recently it was predicted [1] that the ground state of steadily compressed lithium, also a prototypical “simple” metal, would be unstable to less symmetric, semi-metallic structures beginning at pressures near 50 GPa; and remarkably, it was suggested that the tendency toward less metallic behavior with increasing pressure would culminate in a nearly-insulating, paired ground state [2] at around 100 GPa. Two groups, using diamond-anvil cells, have since reported that lithium gradually loses its Drude-like luster under compression, first becoming grey and then finally black (i.e., strongly absorbing) at around 50 GPa [3,4]. Another group, using dynamical shock methods, observed a declining conductivity with increasing density [4], broadly consistent with these results. Recent structural measurements by Hanfland et al. [6] find a complex cubic, 16-atom unit cell with space group *I43d* in lithium near 50 GPa and 200 K. Interestingly enough although Ref. [6] reports a decline in reflectivity against diamond it is suggested that the general characteristics remain notably metallic. The companion first-principles calculations [6] also predict near-insulating behavior with minimal optical reflectivity at higher pressures and a subsequent transition to the paired *Cmca* phase [2] above 150 GPa. Though the possibility of broken electronic symmetry states in the light alkalis has been raised earlier [7], such states are of a very different physical character from what is now being found, especially as we show for sodium.
The striking departure from the simple, nearly-free electron-like behavior conventionally associated with lithium under standard conditions is attributed in Ref. [2] to an electron-ion interaction (or pseudopotential) which, on the length scales of relevance, becomes increasingly repulsive with density; it originates with the combined effects of Pauli exclusion and orthogonality. Given the novel structural and electronic properties predicted to result from these growing effects under compression, it is natural to examine the stability of other metals at higher densities often regarded as “simple”. In this Letter we report results of first-principles calculations indicating that some low-coordinated structures first predicted for lithium [2,6] are also found to be favored in sodium beginning near 130 GPa. Further, as in lithium, these unexpected transitions are accompanied by significant departures from nearly-free electron-like behavior and should be accessible through optical response. Differences in the cores of lithium and sodium result in complementary differences in ground state atomic and electronic structures; yet sodium is also predicted to finally take up the paired Cmca phase with nearly zero-gap semiconducting electronic properties.

To study the structural and electronic behavior of sodium over a wide range of densities, we use a plane-wave implementation [8] of density functional theory within the local density approximation [9] and the projector-augmented wave (PAW) method [10, 11]. As the equation of state will be affected by increasing core overlap at high densities, we treat the 3s, 2p, and 2s electrons as valence and incorporate only the tightly-bound 1s state into an effective frozen core. Previous first-principles calculations of standard low- and high-pressure structural and electronic properties of dense sodium [13-16] appear to be limited to the monatomic lattices BCC, FCC, and HCP. Experimentally it is well known that sodium undergoes a martensitic transformation below 35 K, possibly to the 9R phase (as in lithium) [17], illuminating the role of dynamics in its stabilization at one atmosphere; our static calculations predict that HCP is very slightly favored over BCC, FCC, and also 9R at one atmosphere, but by energies less than 1 meV/ion (quite small compared with dynamical energies and about equal to the accuracy of our calculations) and consistent with previous work [15]. The equilibrium density we calculate for Na in both the FCC and BCC
structures ($r_s = 3.78$) is also in excellent agreement with previous LDA results [14, 15], overestimating that found in experiment ($r_s = 3.93$ [18]) by slightly more than 10%. (Here $r_s = (3V/4\pi N_e)^{1/3}$, where $V$ is the volume (a.u.$^3$) per ion and $N_e$ corresponds to one electron/atom throughout.) Above 5 GPa the BCC structure emerges with lowest enthalpy, and then remains stable after an additional 3-fold reduction in volume. It has generally been expected that BCC should eventually be preferred at the highest densities (the “free electron” limit) because of its favorable Madelung energy, and while it might be suggested that this limit could be reached early for sodium with minimal compression, we find instead that BCC is actually unstable to FCC for $r_s \leq 2.66$ ($p \geq 71$ GPa), again consistent with the results of a previous study [16].

Under atmospheric conditions, the ground state electronic structure of sodium therefore conforms to the classic nearly-free electron system of Wigner and Seitz [1] having a single valence electron and an equilibrating density where the core volume is certainly an exceedingly small fraction of the cell volume. The pseudopotential for sodium at this density is quite well approximated as local, and under moderate compression a purely local picture also continues to suffice: the primary Fourier component of the pseudopotential $V_G$ diminishes relative to the growing bandwidth. But beyond an approximately 3-fold compression in volume this simple interpretation no longer holds. In Fig. 1 we plot the band structure of FCC sodium at $r_s = 2.3$ and compare it with that of lithium at the same density. The bands near points $K$, $W$, and $L$ of Na are quite different from those of Li, and, interestingly, the Fermi surface does remain nearly spherical in Na at these elevated densities. Further, the site-projected partial density of states (DOS) of Na has a growing $d$ character; in Li, only $s$ character and $p$ character are observed at $r_s = 2.3$ [19, 20]. However despite these differences (which, as we will emphasize, are related to the different electronic configurations of their cores), the energy bands of sodium and lithium are both appreciably less free electron-like at high densities: both exhibit sizable gaps at $X$ and, in contrast to the predictions of the nearly-free electron model, these gaps are now growing in magnitude with increasing density.

For lithium the departure from nearly-free electron behavior has evidently been predicted
to result in relatively low-coordinated and open atomic structures [2,6]. Likewise for sodium
when the same non-Bravais lattices are in fact considered, we find that it is also unstable
to the formation of these lower-coordinated phases for densities greater than \( r_s = 2.48 \). A
plot of their enthalpies versus pressure appears in Fig. 2. The newly-observed cubic \( I\bar{4}3d \)
phase in lithium [6] is also found to be favored over FCC in Na at \( p \sim 130 \text{ GPa} \) (~3.5-fold
compression): in it, each sodium atom has essentially five neighbors (three at a distance
of 2.18 Å and two at 2.23 Å at a density of \( r_s = 2.4 \)) [21]. Before reaching \( r_s = 2.3 \),
however, our calculations predict that sodium should transform to Cs-IV at \( p \sim 190 \text{ GPa} \)
\( (r_s = 2.32) \). The Cs-IV phase, in which each ion is coordinated by four others [20, 23], can
be obtained by a tetragonal distortion of the diamond structure along \([001]\). Finally, for
densities above \( r_s = 2.24 \) (\( p \sim 280 \text{ GPa} \)), a transition to \( Cmca \) is predicted, and we find
this phase to be favored to the highest pressures allowed by our PAW potentials (\( p \sim 900 \)
GPa). In each primitive cell of \( Cmca \), two pairs of ions lie in adjacent (100) planes displaced
with respect to one another by half of a lattice vector in the [010] direction [2, 24]. These
predictions are clearly limited by our choice of structures, and for this reason experiment
will again play a crucial role (as in lithium [6]). It is clear from Fig. 2, however, that simple,
monatomic structures are not stable above 130 GPa [16]. Going beyond LDA we find that
gradient corrections [26] result in an expanded equilibrium volume and shift the Cs-IV to
\( Cmca \) transition to \( \sim 260 \text{ GPa} \), but do not change transition pressures at lower densities. In
addition, spin polarization effects are found to be insignificant.

Sodium remains metallic in both the \( I\bar{4}3d \) and Cs-IV phases, and notably the transition
into each is accompanied by additional shifts of \( p \) and \( d \) states below the Fermi energy. The
Cs-IV phase was not predicted to precede the \( Cmca \) phase in lithium, and the difference here
may be understood by observing that the \( d \) states descend under compression in sodium (as
in dense Cs [25]) but not in lithium (where they remain far above the Fermi energy to the
highest pressures theoretically examined [20].) Once in \( Cmca \), sodium becomes increasingly
less metallic as the density rises; the total and site-projected DOS are plotted in Fig. 3 for
the predicted \( Cmca \) phase near the highest density achieved, and most strikingly, at these
extremely high pressures (above 800 GPa), sodium, as with lithium before it, approaches a zero-gap semiconducting phase despite considerable differences in core physics. As a direct result of the minimal DOS at the Fermi energy, dense sodium should become increasingly absorbing in the visible and its resistivity should increase dramatically [27]. Once again the combined effects of Pauli exclusion and orthogonality result in an increasing valence electron density in the interstitial regions with density; we observe that the valence charge density in $^{I43d}$, Cs-IV, and Cmca is minimal near and between the ions (in regions of maximum core overlap) and maximal in the interstitial regions [23]: the valence electrons are evidently forced away from the cores (and regions of significant core overlap, i.e., the regions between neighboring ions) into the roomier interstitial space, resulting in significant benefits for both kinetic and exchange energies.

The exclusionary effects mentioned above, arising from core overlap, and also the nature of the cores themselves, strongly influence the atomic and electronic structure of compressed sodium, which we find to have growing $p$ and $d$ character with density. At low densities large kinetic energy costs prevent these bands from dropping below the Fermi energy. But at higher densities rising core overlap will favor less symmetric charge distributions, and the associated Bloch wave functions have an angular momentum character that depends on the details of core itself. Sodium’s core, for example, contains both $s$ and $p$ states. Bloch states with these angular momentum components (i.e., $3s$ and $3p$) are largely excluded from the core region (where their attraction to the bare nuclear potential $-11e/r$ is greatest), raising their electrostatic energy. Bloch states with $d$ character in sodium (and $p$ character in lithium, as its core contains only the $1s$ state), however, are able to sample the full nuclear potential. (The more asymmetric $3p$ states in sodium will have a lower kinetic energy and therefore continue to be important as well.) Thus in sodium the $3d$ bands rapidly drop and increasingly hybridize with the $3p$ bands under sufficient compression, even though they remain nominally above the unoccupied $3p$ bands at normal densities. Similarly the $2p$ bands descend in lithium [19, 20] because they are absent from its core.

We have seen here that at the relevant length scales the electron-ion interaction in sodium
is no longer weak under compression (again as in lithium), and its putative “simple” metallic behavior at low densities appears to be an accident of the relative core and unit cell volumes present at one atmosphere. Whether exclusionary effects actually culminate in an eventual transition to an insulating state [7] in sodium remains to be resolved by future experiments. Since the interstitial charge build-up is a consequence of general quantum mechanical arguments, the underlying effects revealed here should be evident in other elements and compounds under sufficiently large compressions. In addition, the dramatic changes in the atomic and electronic structure revealed here and in Ref. [2] indicate a large electron-phonon interaction, enhancing the possibility for observation of a significant superconducting transition temperature (a possibility also noted for lithium in Ref. [2]). Up to this point, superconductivity has not been observed in sodium at normal densities; but a comprehensive study of its pressure dependence—both experimentally and theoretically—remains to be performed. Finally since the calculations presented above are carried out for static lattices, the temperature dependence of the structural transformations predicted here will also be a matter of considerable experimental interest.

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FIG. 1. Band structures and partial densities of states (s, p, and d) at $r_s = 2.3$ for FCC (a) lithium ($p \sim 60$ GPa) and (b) sodium ($p \sim 245$ GPa). Solid horizontal lines denote the Fermi energies. The free electron value for the Fermi energy at this density is 9.47 eV. The 2s and 2p bandwidths in sodium at this density are 1.25 and 3.5 eV, respectively; the 1s bands in lithium are 0.7 eV wide.
FIG. 2. Enthalpy difference $H - H_{FCC}$ (meV) vs. pressure $p$ (GPa) for competitive structures of dense Na. The inset illustrates the calculated low pressure BCC-FCC transition described in the text. The A7, $Fmmm$, simple cubic, $\beta$-Sn, and 9R phases (all lower in enthalpy than FCC above 250 GPa but uncompetitive with $Cmca$) are omitted from the figure for clarity. $R3m$ is the space group of the primitive rhombohedral phase (see [6]). The Monkhorst-Pack k-meshes appear in the legend and resulted in convergence of the total energy to $\sim 1$ meV/ion. For densities below $r_s = 2.4$ we use a PAW potential with a 37 Ry plane wave cut-off and maximum core radius of 1.16 Å; for higher densities the distance between neighbors becomes exceedingly small and we use a potential having a 90 Ry cut-off and maximum core radius of 0.76 Å. (Results at low densities are independent of the potential.) $E(V)$ is well fit to $\sum_{n=-2}^{2} a_n V^{n/3}$. Previous static compressions of Na reached only 30 GPa [19].
FIG. 3. Valence band (a) total and (b) partial density of states of Na in the $\text{Cmca}$ structure at $r_s = 1.9$ ($\sim$880 GPa). The partial wave $l$ character of the DOS is primarily $p$, but there is also a significant amount of $d$ character which is growing with increasing density. At lower pressures ($p \sim 300$-600), the DOS also exhibits a minimum at the Fermi energy (though it is not zero, as it nearly is above); the state density at the Fermi energy is found to steadily decline with increasing pressure. A solid black vertical line denotes the Fermi energy. The $l$-projected partial DOS are determined within a 0.75 Å sphere.
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neighbors 11% further away. The $c/a$ ratio is found to decrease from 1.38 at $r_s = 2.2$ to 1.15 at $r_s = 1.9$.

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