

# Diamond, diamond cells, and the structure of element 11

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Almost exactly 200 years ago, sodium was isolated as an elemental metal during electrolysis of molten sodium hydroxide (caustic soda). This was announced on November 19, 1807, by Sir Humphry Davy, in the Bakerian Lecture of the Royal Society, along with another new alkali metal, potassium (from molten caustic potash). Sodium made its initial appearance as liquid metal "... globules having a high metallic lustre" (1), and Davy established an approximate "fusion" (or freezing) point from liquid to solid between 120°F and 180°F, now accepted as 208°F (371 K). The article by McMahon *et al.* (2) in a recent issue of PNAS concerns the structure of a solid phase of sodium, not at the one atmosphere conditions of Davy, but at pressures corresponding to almost 4-fold relative compression. For homogeneous densification, this corresponds to reductions in average near-neighbor separations by upward of 40% that are sufficient to bring into play the hitherto mostly passive core states of the sodium ion. The arrangements assumed by the ions are surprisingly complex, and the implications for our understanding of the physics of sodium and other metals variously described as "simple" in the electronic context but now at higher densities may be considerable.

## Sodium's Structural Legacy

Davy presciently observed that solid sodium is "... exceedingly malleable, and is much softer than any of the common metallic substances." Although later diffraction studies readily revealed the body-centered-cubic (BCC) structure at one atmosphere, they also often indicated the presence of a variety of defects or faults, these somewhat impeding the determination of the structure, especially at lower temperatures. Similar difficulties were encountered in lithium, and a low-temperature structure was not established until 1984, by Overhauser (3); it belonged to the rhombohedral class and was of the delta-*Sm* (or 9R) arrangement in particular. As it transpired, the situation for sodium at low temperatures, again at one atmosphere was somewhat indecisive, with neutron (4) and x-ray (5) studies at  $\approx 30$  K revealing several possible rhombohedral stackings.

These transformations are of the Martensitic type, and their presence at low

temperatures indicates that static considerations may not suffice for the structural physics issues raised by the measurements in dense sodium, often within typical thermal ranges. As gauged by its thermal de Broglie wavelength,  $\lambda$ , quantum effects are not easily ignored, likewise in lithium. At absolute temperature  $T$ [K] (in Kelvin) and for mass number  $A = 23$ , this characteristic wavelength is given by  $\lambda = 32.85/(AT[\text{K}])^{1/2}$  in Bohrs (0.529 Å) and for sodium is 1.25 at  $T[\text{K}] = 30$  (the near-neighbor separation is typically 6.95 Bohrs). From

## The enthalpic differences between competing phases of sodium, a light element, are quite slight.

this, it is anticipated, and observations of low-temperature transitions confirm, that the quantum aspects of the ions are important (6). They may become progressively more demonstrable if the density could be increased at low temperatures, extensions that are reasonably proposed in the article by McMahon *et al.* (2).

## Pressure and Emerging Complexity

For room temperatures and above, the current phase diagram for sodium is shown in figure 1 of ref. 2. As pressure and density increase, sodium passes from its familiar BCC arrangement to face-centered-cubic (FCC), but only after the curve separating the solid from liquid phases (the melting curve) has passed through an entirely unanticipated maximum. This extraordinary behavior was discovered in 2005 by Gregoryanz *et al.* (7), and strikingly evident is a succeeding and quite low minimum in the melting curve, near, it appears, a structure identified as "CI16." The elucidation of the complete ionic arrangement of this phase is the primary result reported by McMahon *et al.* (2), and in pursuit of this, they have manifestly benefited from some highly favorable beam characteristics of Diamond, the new British third-generation light source.

The CI16 structure was also discovered in compressed lithium by Hanfland *et al.* (8) (in 2002); and notably, Syassen

(9) also reported that a phase with this general symmetry was appearing in compressed sodium. From figure 1 of ref. 2, it is apparent that in a range of pressures  $\geq 105$  GPa, the melting temperature of sodium has remarkably declined and is close to room temperature. Accordingly, sodium can be brought close to conditions that significantly promote annealing processes but in a high-pressure environment. This is a central and appealing point in the article by McMahon *et al.* (2): The authors are able to grow fine crystals of compressed sodium, and *in situ*.

The lower-pressure BCC arrangement is a Bravais lattice in its own right but may also be viewed as a simple cubic with a two-ion basis, one at the corner and the other at the center of a primitive cube. The high-pressure CI16 arrangement is also in the cubic class; it too may be regarded as simple cubic but with a 16-ion basis. With considerable accuracy, the basis vectors are given by McMahon *et al.* (2) (in their figure 2), and when set against BCC, the emergent complexity is all too evident. But what is its likely physical origin?

## Structure and Its Origins

Under the thermodynamic conditions prescribed by the experiment, the structure taken up by sodium, whether solid- or liquid-phase, will be such as to minimize an appropriate thermodynamic function (for example, the Gibbs free energy). For a metallic state of matter, this will contain contributions depending entirely on volume (not structure) and contributions that depend on the average arrangement of ions, and their dynamics. In a crystalline context, these might comprise electron, phonon, and electron-phonon terms, all determined self-consistently for proposed structures. Within the adiabatic approximation, pair- and higher-center ion-ion interactions will reflect the distribution of electrons, both valence and core. At the traditional level of linear electronic response, the concept of screened interactions arises with an expectation of

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plausibly short-range rather than long-range Coulombic characteristics, at least on the energy scales typical of any ensuing dynamics. If sufficiently short-ranged, these ion-ion interactions might begin to approach those of the historical rigid-sphere view of an atom, and the issue then devolves on how these might be expected to pack to form a crystal, overall volume now being significantly adjusted by experiment.

Although the most efficient packing of space by truly rigid and identical spheres is thought to be FCC, at one atmosphere sodium instead takes up the familiar BCC arrangement. The immediate inference is that features in the interactions beyond repulsive short-range regions remain significant. But these are functions of state and alterable by pressure. The associated electronic densities are governed by a growing electron-ion pseudopotential, reflecting not only the charge of the nucleus but also the charges of core electrons, the role of orthogonality of valence and core states, and the role of particle identity. Increasingly, the “valence” electron density, generally expelled from the core, tends to occupy interstitial (rather than nuclear-centric) locations. Nonlinear corrections to ion-ion interactions and enhancements of the longer-range Friedel structure can be significant (10). Furthermore, for the high-density situations attained in ref. 2 and elsewhere, changes in electronic densities arising from the core states themselves can also be increasingly involved. Pseudopotentials (and the implicit core-valence separation underlying them) are being driven from their familiar “weak” paradigms at these densities, and the structural consequences may be considerable.

### Core Issues

Accurate determinations of structure and associated dynamics can therefore be expected to establish links to the quite basic quantum many-body problem presented by a macroscopic Coulombic assembly of  $N$  nuclei (here of charge  $11e$ ) and an assembly of  $11N$  Fermionic electrons (charges  $-e$ ), both assemblies occupying a common macroscopic volume  $V$ . This well recognized and fundamental

problem (11) can be further probed through increasing capabilities that permit confining volumes  $V$  to be substantially altered, and to progressively engage core states as well as valence.

Determination of the spectrum of energy levels, or bands, of the valence electrons of sodium was a major early focus of condensed matter physics. “On the constitution of metallic sodium” by Wigner and Seitz (12, 13) is one of the founding papers of the still rapidly emerging fields of electronic structure and quantum chemistry. In what are now termed first principles calculations, the element sodium has also continued to attract considerable attention, both under normal conditions and at higher densities (see, for example, ref. 14). That the many-body problem embodied by the light alkali metals might, however, be susceptible to symmetry breaking is not an entirely unheralded suggestion. In 1968, Overhauser (15) proposed the possibility of charge-density-wave instabilities, and more recently, Siringo *et al.* (16) suggested that ionic-charge rearrangement in the alkalis could occur at fixed structure. The notion that lithium could engage in symmetry lowering structural transitions at higher densities was also put forward in 1999 (17) (and the suggestion was made that compressed lithium could also exhibit significant superconducting order).

Similar arguments were later advanced for sodium (18); it may be noted *a priori* that because the core states in  $\text{Na}^+$  are quite extended and the anticipated experimental reductions in near-neighbor separations also quite significant, some care might well be exercised in choosing a physically meaningful valence-core division. Indeed, at the higher densities, the  $2p$  electrons of the traditional sodium core actually take up bands whose widths begin to rival those of the  $3s$ -derived electrons (18) (effects going considerably beyond the traditional Born–Mayer descriptions of core–core repulsions); and as in lithium, the standard “valence” bands actually began to narrow at high densities (18). These are interesting physical consequences of the overlap of core states now being brought about by the capabilities of the diamond cell and probed with some

clarity by the Diamond source. Because the “core” bands are determined by (and partly determine) the ensuing structures, it is clear that the transferability of pseudopotentials may not be quite so clear cut for these conditions. In principle, some of these effects are embodied in recent simulation methods where ions and electrons are treated on the same footing; Raty *et al.* (19) show that, by such approaches, sodium can indeed exhibit a melting-point maximum, and it is immediately interesting to ask how general this behavior might be.

### Pressing On ...

Both in the elements and the elements in combination (using anomalous diffraction), extensions of these single-crystal diffraction techniques to higher pressures and to even more complex structures promise instructive further developments and insights (2). The unexpected structural complexities of the heavier alkalis at high pressures, including partial incommensurabilities (see ref. 20), already sustain these expectations, and they might well be expanded to include even higher complexities resulting from the inevitable conflicts of length scales presented in these systems. The rich history of the structure of the light alkalis and their quantum characteristics clearly points to additional studies at low temperatures and high pressures. Further observations at just above the melting line are also indicated; for the solid that emerged from Davy’s “globules” did so from a liquid that is now regarded as “simple,” and yet it also had an average coordination of  $\approx 9$  (21) (for a BCC crystal it is 8). Deductions about the forms of the ion-ion interactions pertinent to the translationally invariant phase just above the melting line may yet have much to say about the crystalline structure (and by implication the electronic structure) just below. Finally, it is obvious that the results present a very considerable challenge to the theories of melting (whether classical or quantal) and the various “melting laws” that have been developed over the years. Complex crystalline phases may be developing from quite complex liquid phases, and of course vice versa.

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