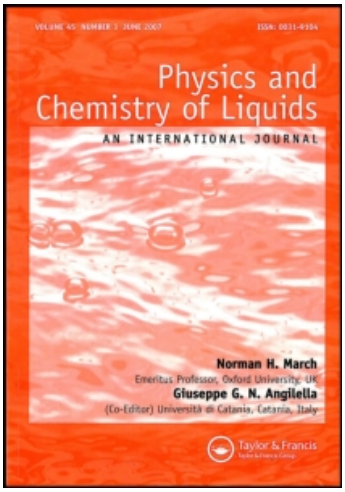

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Melting curve $T_m(p)$ of sodium under pressure p: transition from a Wigner-like nuclear bcc structure near 30 GPa to lower symmetry states with negative dT_m / dp at higher pressures

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Melting curve $T_m(p)$ of sodium under pressure p: transition from a Wigner-like nuclear bcc structure near 30 GPa to lower symmetry states with negative dT_m/dp at higher pressures

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It is known experimentally that the melting temperature $T_m(p)$ of Na as a function of pressure p increases with p out to ~ 20 GPa and then passes through a maximum. Here, we interpret the behavior as passing from classical Wigner-like bcc nuclear structure at low pressures to a structure out to about 60 GPa where the melting is mediated by topological defects.

Keywords: Melting of Na; Low-p Wigner-like structure; Crossover to dislocation-mediated melting

It has been recognized for some time that near 30 GPa metallic Na can be modeled on its melting curve as a one-component plasma characterized by its customary parameter $\Gamma \simeq 180$ (equation (1)) at the liquid–solid phase transition. Going back to Brush, Sahlin and Teller [1] one has a transition of (classical) nuclei in a uniform background of electrons where T_m is proportional to the cube root of the number density n. Evidently then, in such a regime, dT_m/dp is positive, and the nuclei reside on a body-centered cubic lattice, as found by computer simulation [1,2]. Such an attractive picture of freezing of Na is now known to have a quite limited range of validity as a function of pressure (see figure 1, where experimental results out to $\sim$120 GPa are displayed).

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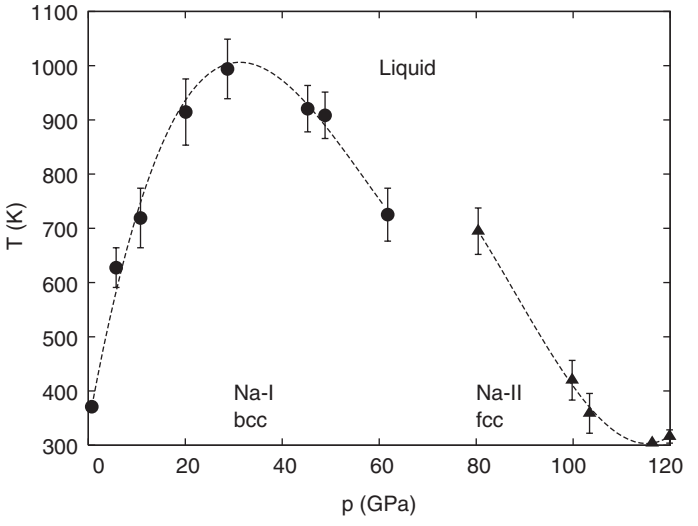

Figure 1. Melting curve of Na up to 120 GPa. Redrawn after reference [3].

In a little more detail, the so-called one-component plasma (OCP) model is characterized by a single parameter Γ, which for a monovalent metal like Na is defined by

$$\Gamma = \frac{e^2}{r_s k_B T}. \tag{1}$$

This parameter measures the ratio of Coulomb potential energy (e^2/r_s), with r_s the mean charge–charge separation, to the thermal energy $k_B T$, with k_B denoting Boltzmann's constant. What has emerged from further detailed studies of the classical OCP model, following Brush *et al.* [1], is that there is a liquid–solid phase transition when $\Gamma \sim 180$, at first sight a very surprisingly large ratio of potential to (thermal) kinetic energy.

The study of the melting curve of Na is also motivated by the unconventional behavior of the alkalis at high pressure. Early theoretical work [4] predicted that the alkalis should undergo an electronic instability at high pressure, thus deviating from their almost ideal metallic behavior. First-principles calculations then demonstrated a pressure-induced structural instability towards closely packed structures [5]. These were indeed followed by the observation of low-symmetry structures in Li at pressures greater than 40 GPa [6]. At such high pressures, Li exhibits an anomalous electronic behavior, with some evidence of a metal-insulator transition in the high-pressure, high-temperature phase [7], and even superconductivity in the high-pressure, low-temperature phase [8–10]. Oscillations between the symmetric and low-symmetry phases are expected for the alkalis as a function of increasing pressure, with a re-entrant metallic character at higher densities, as a consequence of Friedel oscillations in the pair potential [11].

We shall adopt below for Na and $30 < p < 120$ GPa a model of melting which has a relatively long history, going back at least to proposals by Kuhlmann-Wilsdorf [12]. Later work by Cotterill [13,14] has a prominent place also in this area.

However, we here appeal directly to the recent discussion of Matthai and March [15]. These authors appeal, as in the above references, to a melting scenario based on topological defects, and in particular on dislocations. Matthai and March write the melting temperature T_m as

$$T_m \sim \Omega FS \tag{2}$$

where Ω is the atomic volume, F is a function of elastic constants, and S is a structure-dependent factor depending relatively weakly on the local coordination number c of the lattice under consideration.

For present purposes, we want to contrast the appearance of the atomic volume Ω in equation (2) in a linear fashion with the classical Wigner crystal dependence on $\Omega^{-1/3}$, which is useful near 30 GPa. Of course, one will eventually need to estimate the volume dependence of F and S in equation (2). As to S, the work of e.g. Burakovsky *et al.* [16] gives in S a factor of $\log(c-1)$, so the dependence on c is expected to be pretty weak. As to F, Kleinert and Jiang [17] give a fairly comprehensive but then inevitably somewhat complicated phonon theory of how F in equation (2) depends on the elastic constants. Though involving, of course, additional assumptions beyond those made by Kleinert and Jiang [17], Burakovsky *et al.* [16] effectively approximate F by the shear modulus G.

But we stress that in such a topological defect-mediated melting mechanism, which we propose as appropriate to the low-symmetry structures, we foresee no difficulty in understanding a decrease in $T_m(p)$ as p increases from $\sim$30 GPa to $\sim$120 GPa.

In summary, the studies of Gregoryanz *et al.* [3,18] on $T_m(p)$ in Na can, we propose, be understood in terms of a crossover from the melting of a bcc crystalline phase near 30 GPa which grossly is a classical OCP transition first predicted by Brush *et al.* [1] and in which T_m under compression varies roughly as $\Omega^{-1/3}$, with Ω the atomic volume, to a melting in low symmetry structures in which the mechanism is the one mediated by topological defects.

As to future directions, it would be of obvious interest in low-symmetry structures to study the way elastic constants, and especially the shear modulus, vary with pressure in the regime between say 40 GPa and 100 GPa, both experimental and theoretical studies of this kind being, we suggest, highly worthwhile areas.

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