

# Thermal Effects on the Electronic Properties of Sodium Electride Under High Pressures

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Despite being one of the simplest alkali metals at ambient pressure and temperature conditions, sodium exhibits a remarkably complex behavior under compression. The transition from lower-pressure metallic phases to the electride hP4 phase commences at approximately 160 GPa. This phase is structurally similar to a double hexagonal close-packed (dhcp) structure but has a higher compression along the  $c$  axis ( $c/a = 1.391$ ) compared to the ideal dhcp ( $c/a = 3.266$ ) at 320 GPa (Ref. 1). Due to the existence of a band gap, this phase has been described as a transparent insulator, deviating from the reflective metallic behavior observed at lower pressures. However, all diamond-anvil-cell (DAC) experiments performed on sodium at such pressures have been along the  $T \approx 300$  K isotherm, while accompanying calculations were performed for static, nonthermalized crystals. To address the lack of systematic studies on the effects of thermal excitations on the electronic properties of electride sodium, we used density functional theory (DFT) to perform molecular dynamics (MD) and electro-optical calculations.

Canonical ensemble MD simulations were performed along different isochores while gradually increasing the ensemble temperature. This is termed as the “heat-until-melt” method, and the temperature regulation was attained using a Nosé–Hoover thermostat. The resulting melt curve for the tI19- and hP4-to-liquid transition demonstrates a monotonically increasing behavior as pressure increases, as can be seen in Fig. 1(a). Formerly, in order to establish the insulator nature of the phase, the orthonormalized single-particle Kohn–Sham orbitals  $\Psi_n^{KS}$  were used to construct the one-particle density operator, which in turn was used to create the real-space, one-particle density matrix  $\rho(\mathbf{r}, \mathbf{r}') \sim \langle \exp(-\gamma|\mathbf{r} - \mathbf{r}'|) \rangle$ . For normal insulators  $\gamma \propto E^{1/2}$  and for semiconductors  $\gamma \propto E$ , where  $E$  is the band-gap energy.<sup>2</sup> Along the  $\rho = 5.872\text{-g/cm}^3$  isochore, our analyses indicate that  $\rho(\mathbf{r}, \mathbf{r}')$  varies with a band-gap exponent  $\gamma$  of 0.460, 0.438, 0.421, and 0.414 at  $T = 300$  K, 700 K, 1200 K, and 1800 K, respectively. Therefore, the hP4 phase of sodium behaves like an insulator and not a semiconductor, when quantitatively analyzed using the *nearsightedness* of the density matrix as a criterion.

The band gaps obtained from the electronic density-of-state (DOS) calculations show a gradual decrease with increasing temperatures along the  $\rho = 5.872\text{-g/cm}^3$  isochore until it abruptly decreases to zero upon melting, as shown in Fig. 1(b) for various exchange-correlation functionals. At  $T = 300$  K, the calculated band gap was in the range of 1.54 eV (SCAN-L) to 1.84 eV Perdew–Burke–Ernzerhof (PBE), which corresponds to a photon wavelength of 673.83 nm (PBE) to 805.09 nm (SCAN-L). For wavelengths shorter than this threshold, hP4 sodium would exhibit reflectivity resembling that of an optical insulator.

Taking a closer look into the electronic charge distributions, it can be seen that one exceptional feature of high-pressure electrides is the localization of electrons in the interstices between ions, which leads to the formation of pockets with an electron localization function (ELF) value of near unity existing as pseudoanions. The hP4 phase of sodium exhibits such features, resulting in an insulating behavior owing to the band gap that develops from such an electronic distribution. This is true all the way up to the melt point, beyond which, using *a priori* knowledge from the band gap, one would expect these localization features to almost completely disappear and the system to transform into a near free electron (NFE)-type metallic liquid with  $\text{ELF} \approx 0.5$ . This is not seen to be the case, however, and even though the liquid phase is metallic, electron bubbles with paired localization exist in

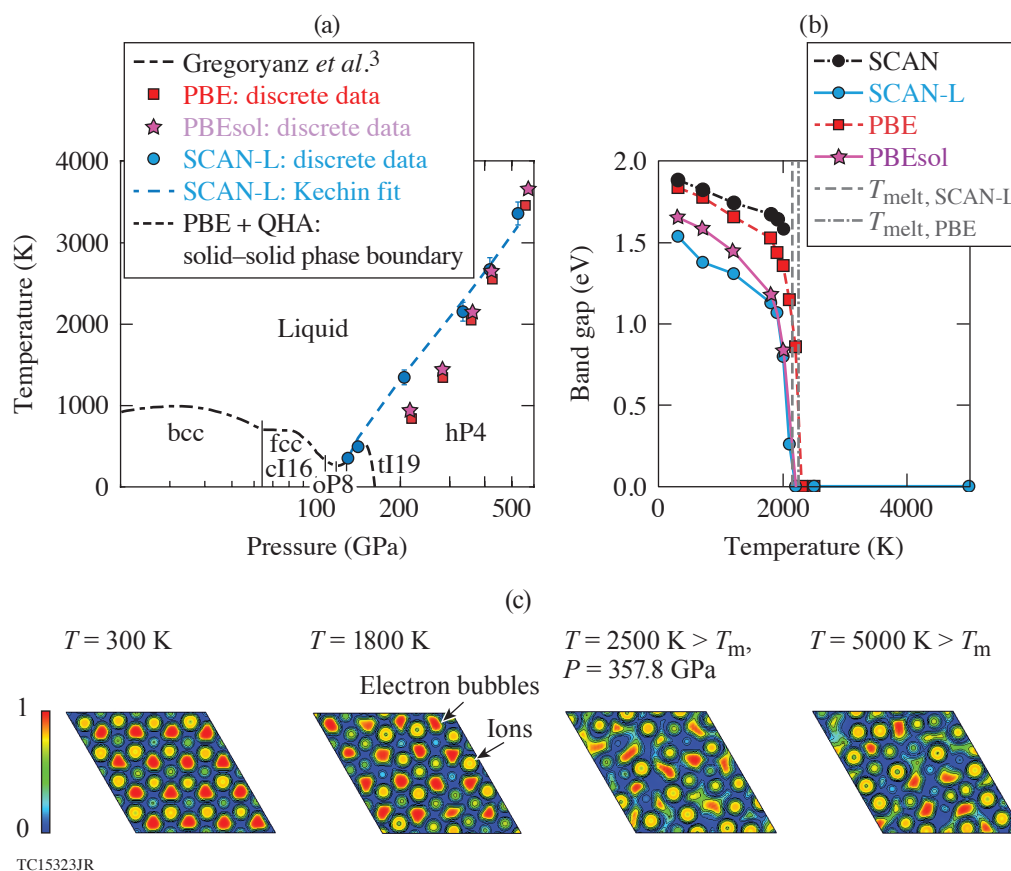


Figure 1

(a) The  $T$ - $P$  phase diagram of sodium from literature<sup>3</sup> combined with our work, with the existing melt curve data plotted. The tI19-hP4 phase boundary was constructed by comparing the Gibbs free energy computed by combining DFT and quasiharmonic approximated (QHA) phonon calculations. The uncertainty for the six isochoric melt data points, calculated using SCAN-L, are 20, 35, 90, 115, 145, and 140 K, respectively, calculated using five separate sets of MD calculations, with differing starting solid geometry, for each isochore. (b) The evolution of the band gap with temperature during heating along the  $\rho = 5.872\text{-g/cm}^3$  isochore demonstrates the abrupt closing of the band gap on melting at  $T_m \sim 2100$  to  $2200$  K, corresponding to an insulator-to-metal transition. Four sets of data corresponding to different exchange-correlation functionals: PBE, PBEsol, SCAN, and SCAN-L have been shown. (c) Planar static ELF on the (001) plane along the  $\rho = 5.872\text{-g/cm}^3$  isochore, which shows the existence of paired interstitial electron bubbles (red) even beyond the melt point ( $T_m \sim 2100$  to  $2200$  K).

tandem with a NFE distribution. The (001) planar ELF along the  $\rho = 5.872\text{-g/cm}^3$  isochore clearly exhibits localized clusters of paired electrons, in the form of electron bubbles with  $0.8 < \text{ELF} < 1.0$ , that persist even beyond the melt point, as can be seen in Fig. 1(c). Rough estimation of the total number of electrons in certain pseudoanionic attractor regions yields a value of 1.91 to 2.0 in the solid phase and 1.77 to 1.94 in the liquid phase. This implies that the ELF attractors in the liquid phase are paired as well. Since planar cross-sectional representation of volumetric data can be misleading, we also calculated the all-volume, charge-weighted ELF histograms. Such an analysis also showed an abundant existence of regions with  $\text{ELF} > 0.8$  in the liquid phase. However, increased temperatures along any isochore gradually dissipates these electron bubbles and the liquid ultimately reverts back to a NFE liquid beyond  $5000$  K.

Whereas in the solid state, interstitial electrons are predominantly  $p$ - $d$  hybridized, two separate phenomena take place upon melting: (a) the thermal disorder in the ionic configuration in liquids, vis-à-vis solids, leads to delocalization of the  $p$  electrons from the  $p$ - $d$  hybridized ELF attractors, alongside drastically increasing the  $s$  character and (b) delayed plasmon onset for the  $d$  electrons, compared to  $s$  and  $p$  electrons, due to higher effective mass caused by more localization. The combination of these

two effects reduces the contribution of the localized  $d$  electrons in the liquid-phase electron bubbles, despite being coalescent, to electro-optical properties and prevents such electrons from hybridizing. This also results in a change in hybridization from  $p-d$  to  $s-p$  upon melting. Electro-optical properties calculated using the Kubo–Greenwood formula also show this insulator-to-metal transition upon melting. In essence, the hP4 phase of sodium exhibits a decrease in band gap with thermalization, culminating in an insulator-to-metal transition upon melting, accompanied by the formation of residual electron bubbles and a change in electronic hybridization.

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