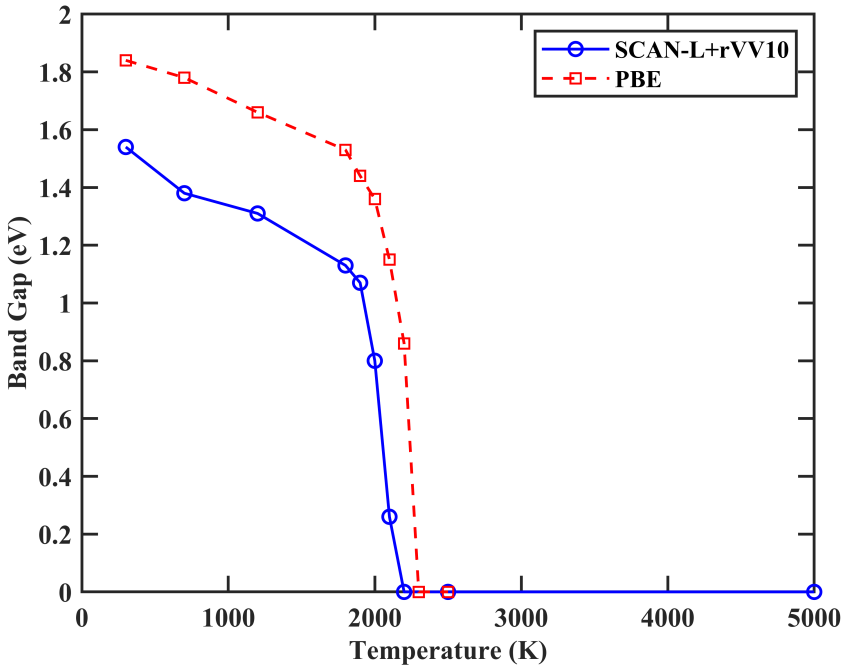
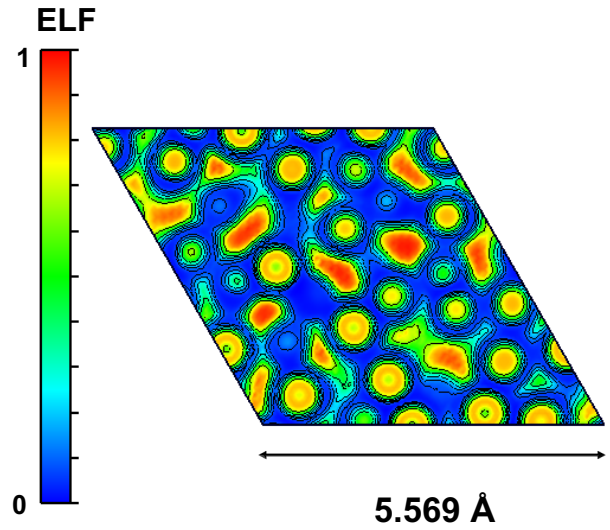
Temperature-induced changes in hP4-Sodium Electride: An *Ab Initio* Study





R. Paul
University of Rochester
Laboratory for Laser Energetics

61st Annual Meeting of the American Physical Society
Division of Plasma Physics
Fort Lauderdale, FL
21-25 October 2019

Summary

High-pressure dynamics of the hP4 electride* phase of sodium exhibit an unconventional insulator-to-metal transition: upon melting localized electrons become bubbles

UR LLE

- We have used density-functional theory (DFT) based methods to investigate the finite-temperature effects on the electride phase of Na under extreme conditions
- Our *ab initio* results indicate that the band gap of Na-electride at ~320 GPa gradually decreases with increasing temperature, until it abruptly becomes zero upon melting, due to an insulator-to-metal transition
- Melting is accompanied by coalescent dynamic electron bubbles rather than conventional uniform electron gas, as is the case for metallic liquids

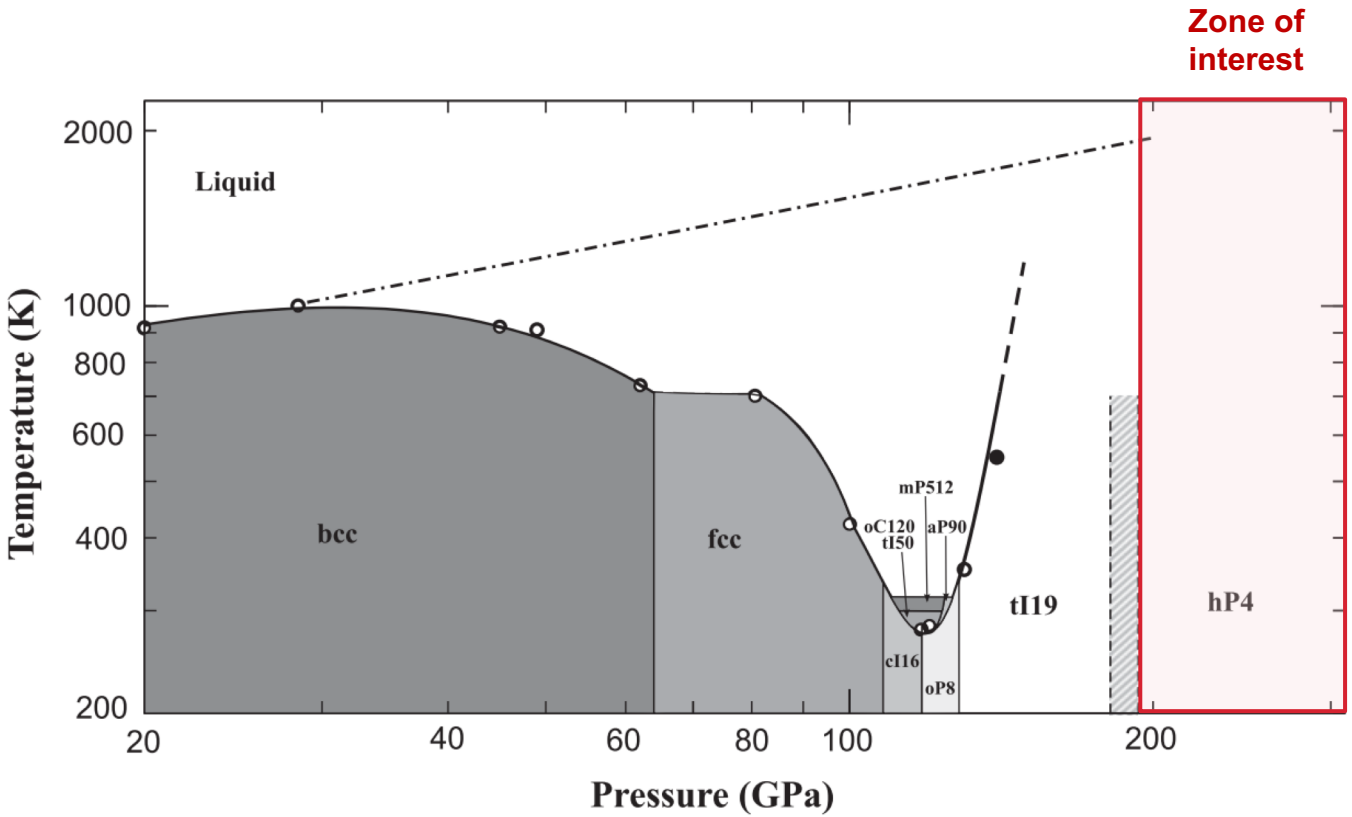
* Y. Ma *et al.*, Nature 458, 182-184 (2009)

Collaborators

Suxing Hu and Valentin Karasiev
Laboratory for Laser Energetics (LLE)

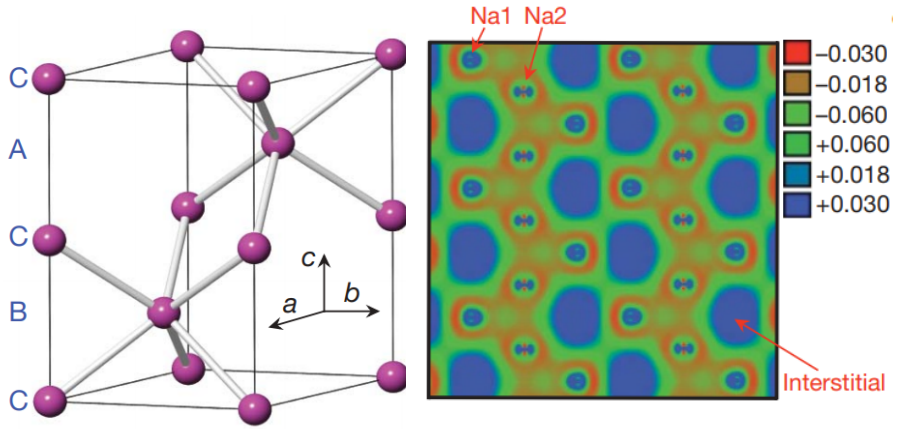
Stanimir Bonev
Lawrence Livermore National Laboratory (LLNL)

Upon high-pressure compression metallic Na has been observed to become an insulator – the electride phase (hP4) – at room temperature



*

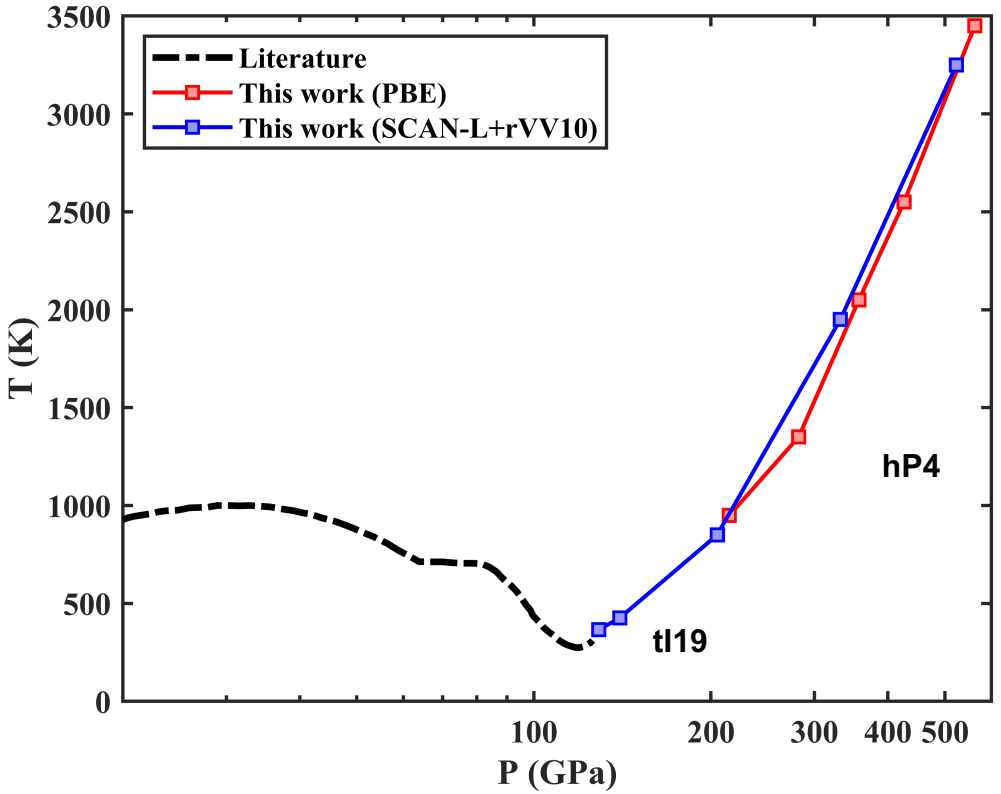
**

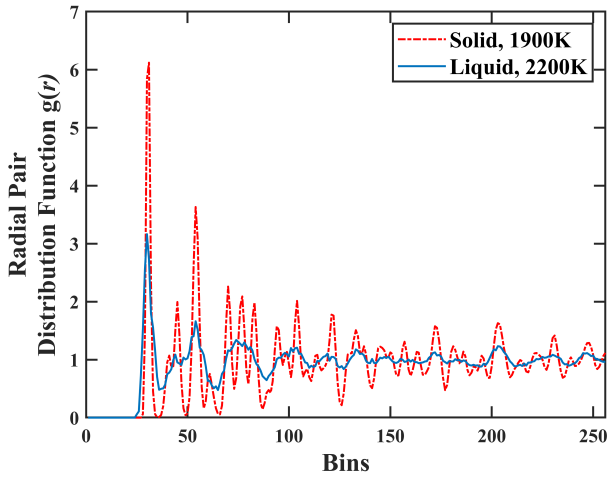


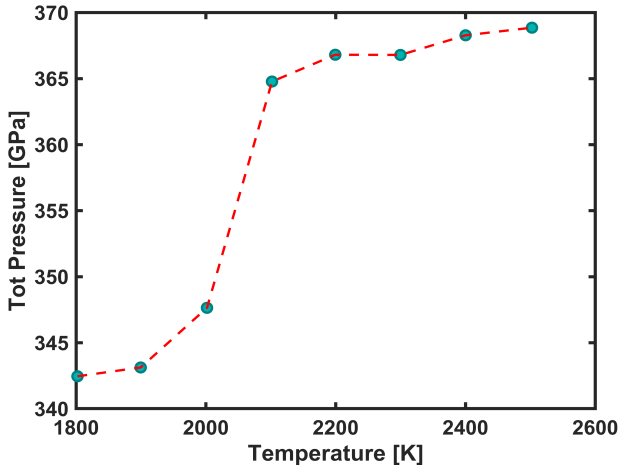
Na-hP4 : Hexagonal conventional unit cell with an axial (c/a) ratio approximately 1/2 that of double hexagonal close packed (dhcp)

* E. Gregoryanz *et al.*, Science 320, 1054 (2008)
M. Marqués *et al.*, Phys. Rev. B 83, 184106 (2011)
D. Polsin *et al.*, APS SCCM (2019)
** Y. Ma *et al.*, Nature 458, 182-184 (2009)

The melt curve for Na-hP4 monotonically increases between 200 and 500 GPa





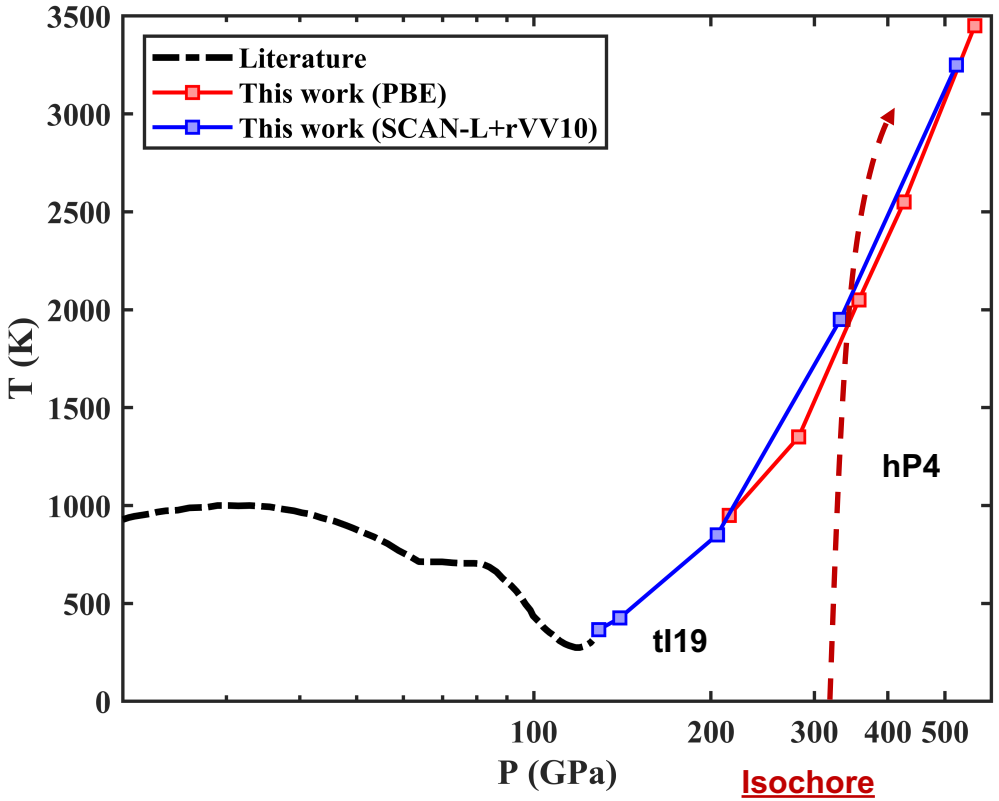


NVT-MD* Simulation details
No. atoms = 256
K-mesh = 1x1x1 (Γ-point)
Energy cutoff = 800 eV
Simulation time ≈ 1.2 ps

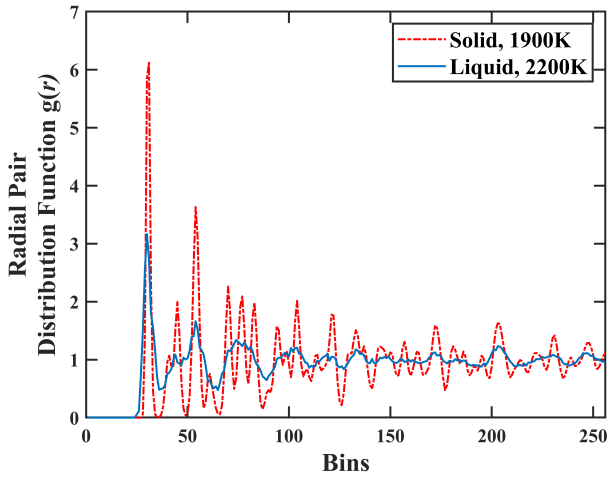
Results from calculations using PBE and SCAN-L+rVV10 xc agree within 100 K**

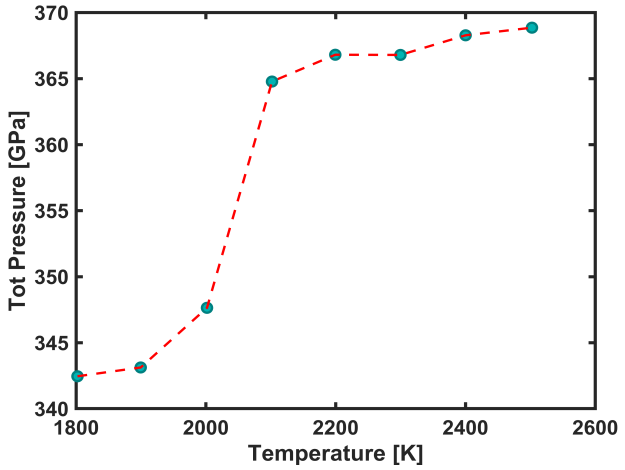
* MD – Molecular Dynamics
R. Paul *et al.*, PRL 122, 125701 (2019)
**xc – exchange-correlation

The melt curve for Na-hP4 monotonically increases between 200 and 500 GPa



Isochore
(*P* = 320 GPa, *T* = 0 K)



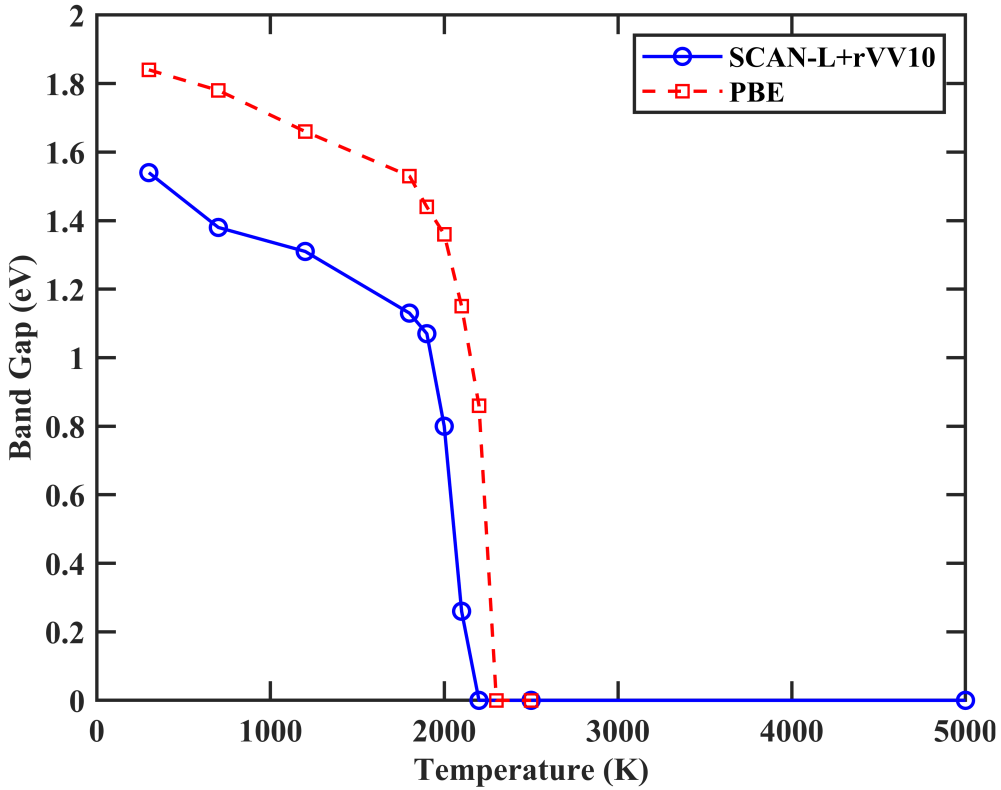


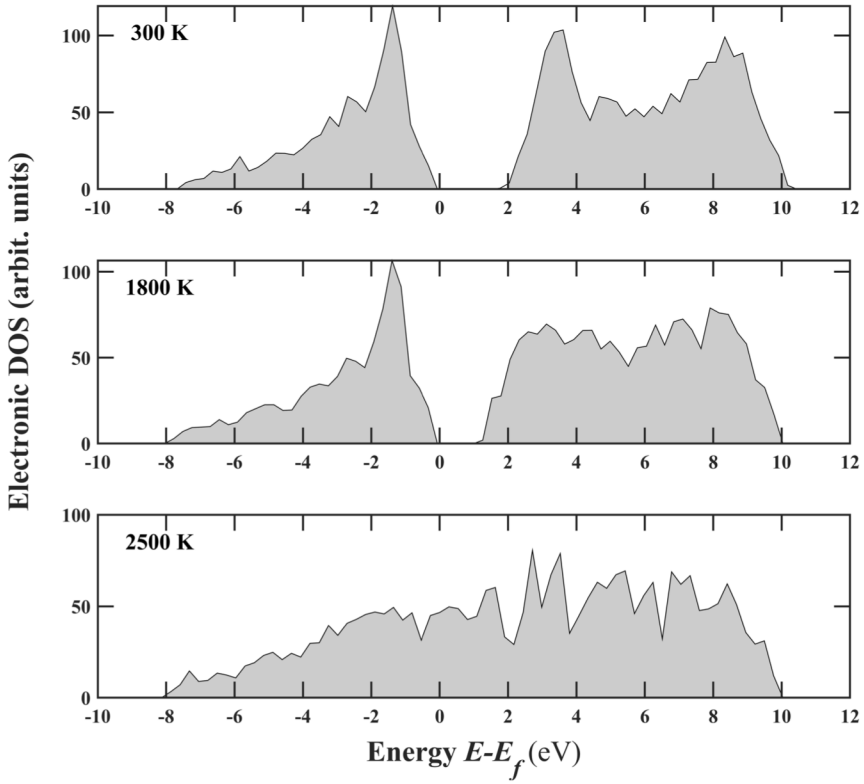
NVT-MD* Simulation details
No. atoms = 256
K-mesh = 1x1x1 (Γ-point)
Energy cutoff = 800 eV
Simulation time ≈ 1.2 ps

Results from calculations using PBE and SCAN-L+rVV10 xc agree within 100 K**

* MD – Molecular Dynamics
R. Paul *et al.*, PRL 122, 125701 (2019)
**xc – exchange-correlation

The band gap along the (P = 320 GPa, T = 0 K) isochore gradually closes with increasing temperature demonstrating an abrupt insulator solid–to–metallic liquid transition

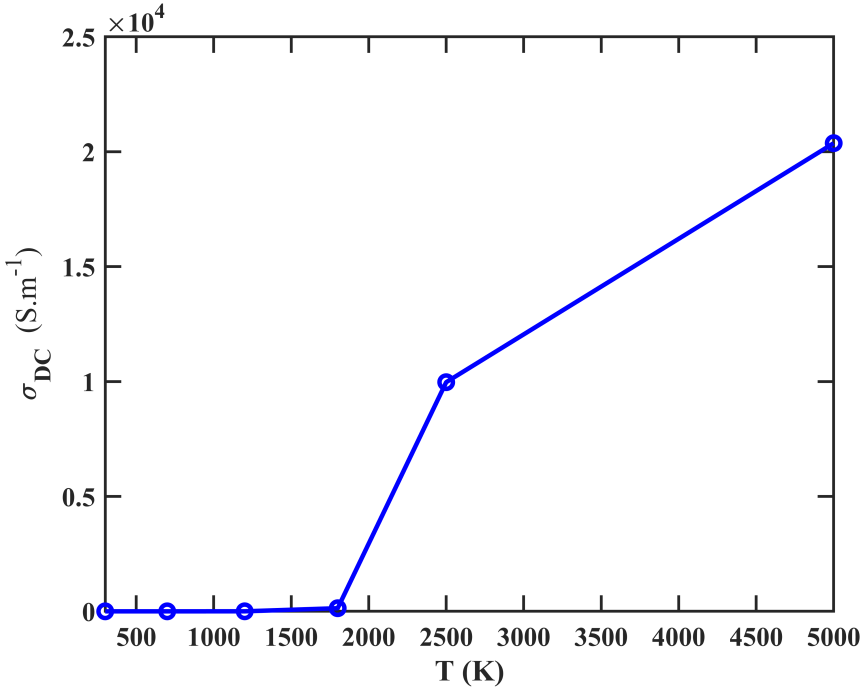


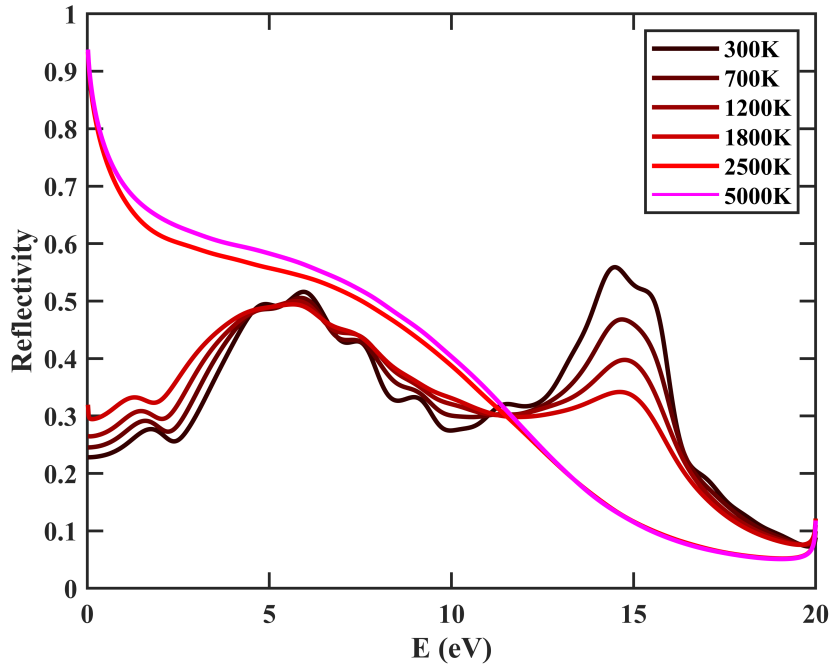


Electronic Density of States

- Band gap from PBE consistently different from SCAN-L+rVV10
- Calculated from averaging 6 snapshots
- Liquid phase is metallic with no band gap

The optical properties along the (P = 320 GPa, T = 0 K) isochore also show abrupt change upon melting as a further confirmation of metallization

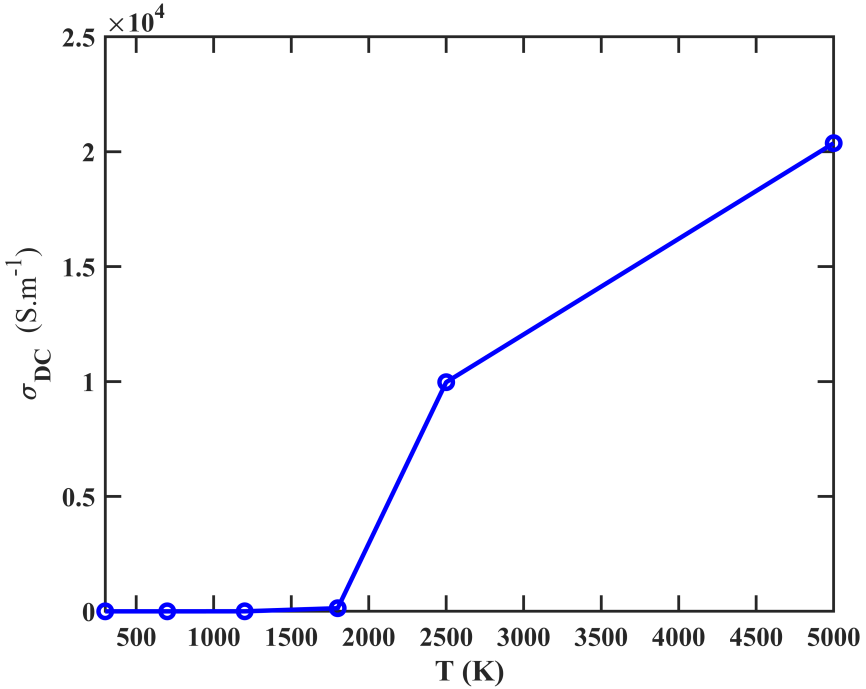


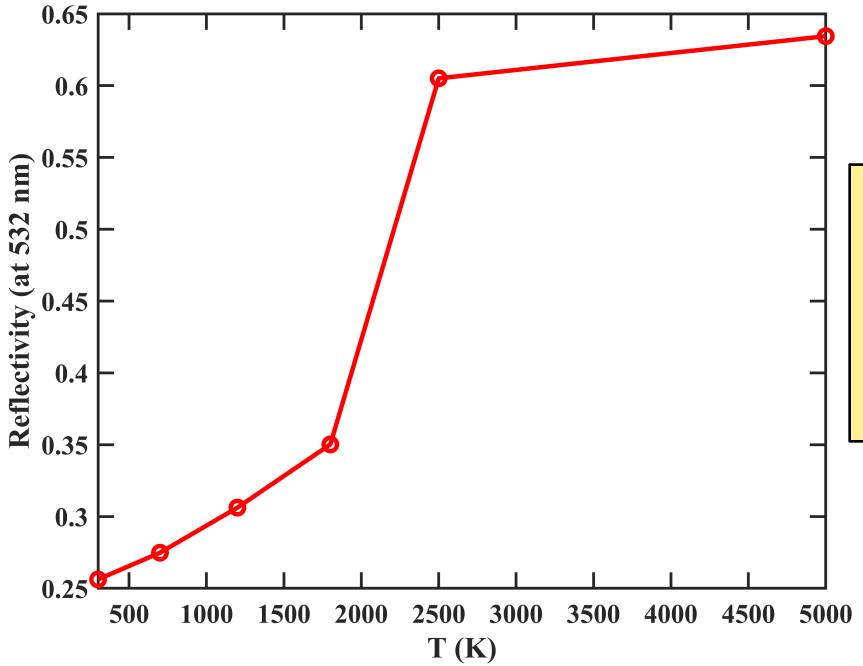


Simulation details (SCAN-L+rVV10)
No. atoms = 256
K-mesh = 2x2x2 (Monkhorst-Pack)
Energy cutoff = 800 eV
Simulation time ≈ 1.0 ps
No. snapshots = 4 (with Δt=80-100 fs)

Characteristic changes in optical properties observed upon melting (T_m ~ 2000 K), calculated using DFT with the Kubo-Greenwood formulation

The optical properties along the (P = 320 GPa, T = 0 K) isochore also show abrupt change upon melting as a further confirmation of metallization

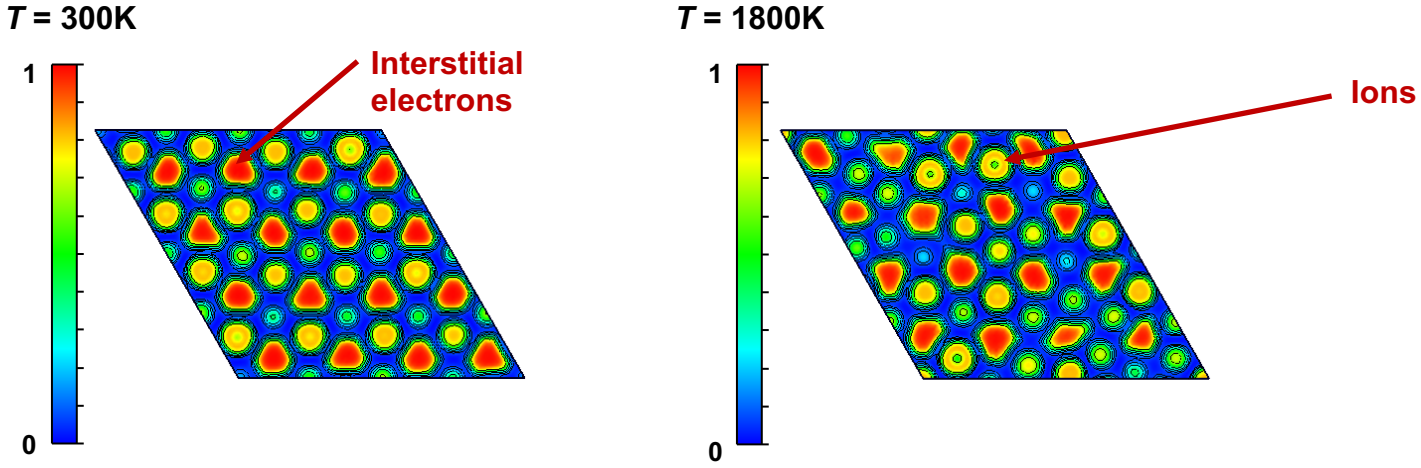




Simulation details (SCAN-L+rVV10)
No. atoms = 256
K-mesh = 2x2x2 (Monkhorst-Pack)
Energy cutoff = 800 eV
Simulation time ≈ 1.0 ps
No. snapshots = 4 (with Δt=80-100 fs)

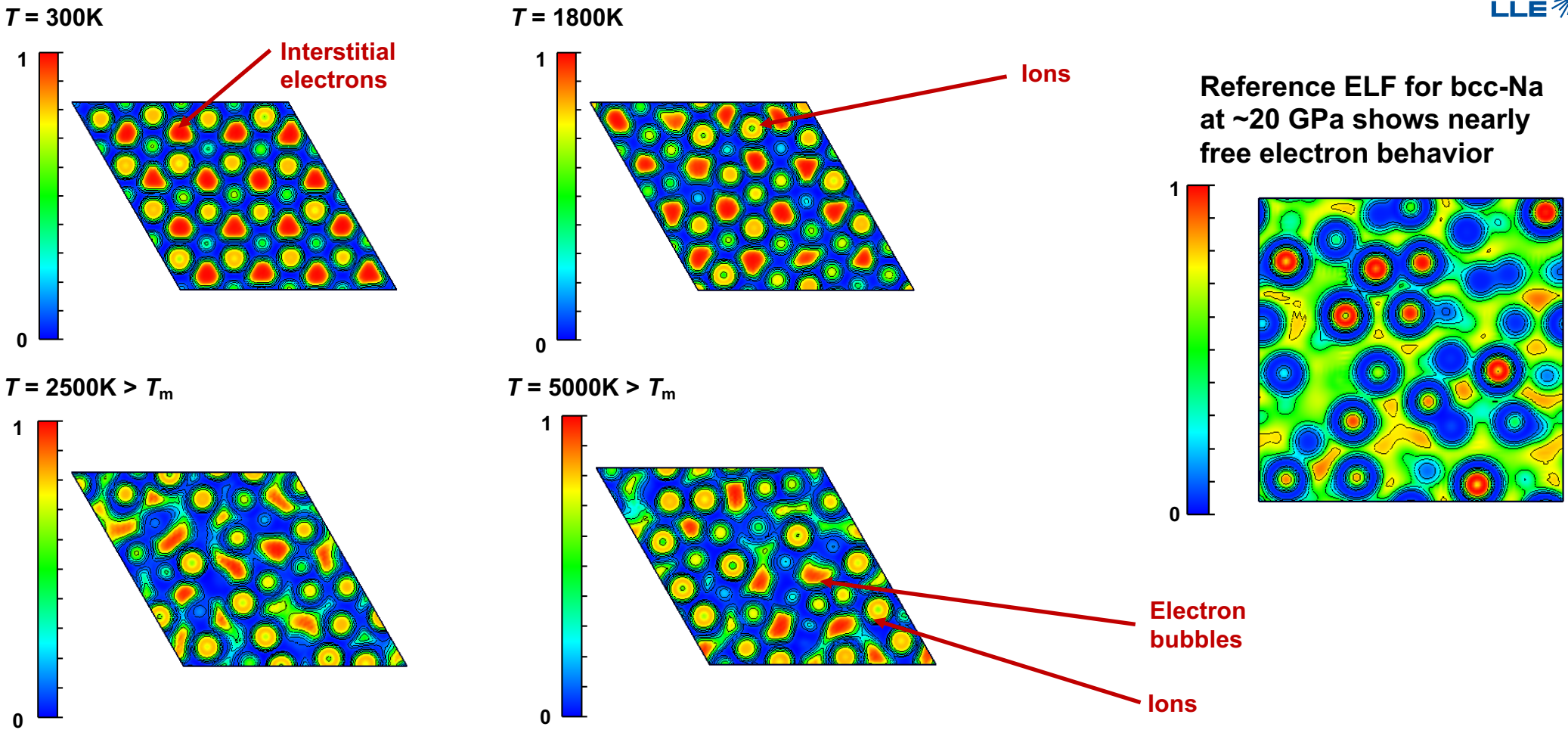
Characteristic changes in optical properties observed upon melting (T_m ~ 2000 K), calculated using DFT with the Kubo-Greenwood formulation

The static Electron Localization Function (ELF) along the (P = 320 GPa, T = 0 K) isochore exhibits paired and localized interstitial electrons in solid phase



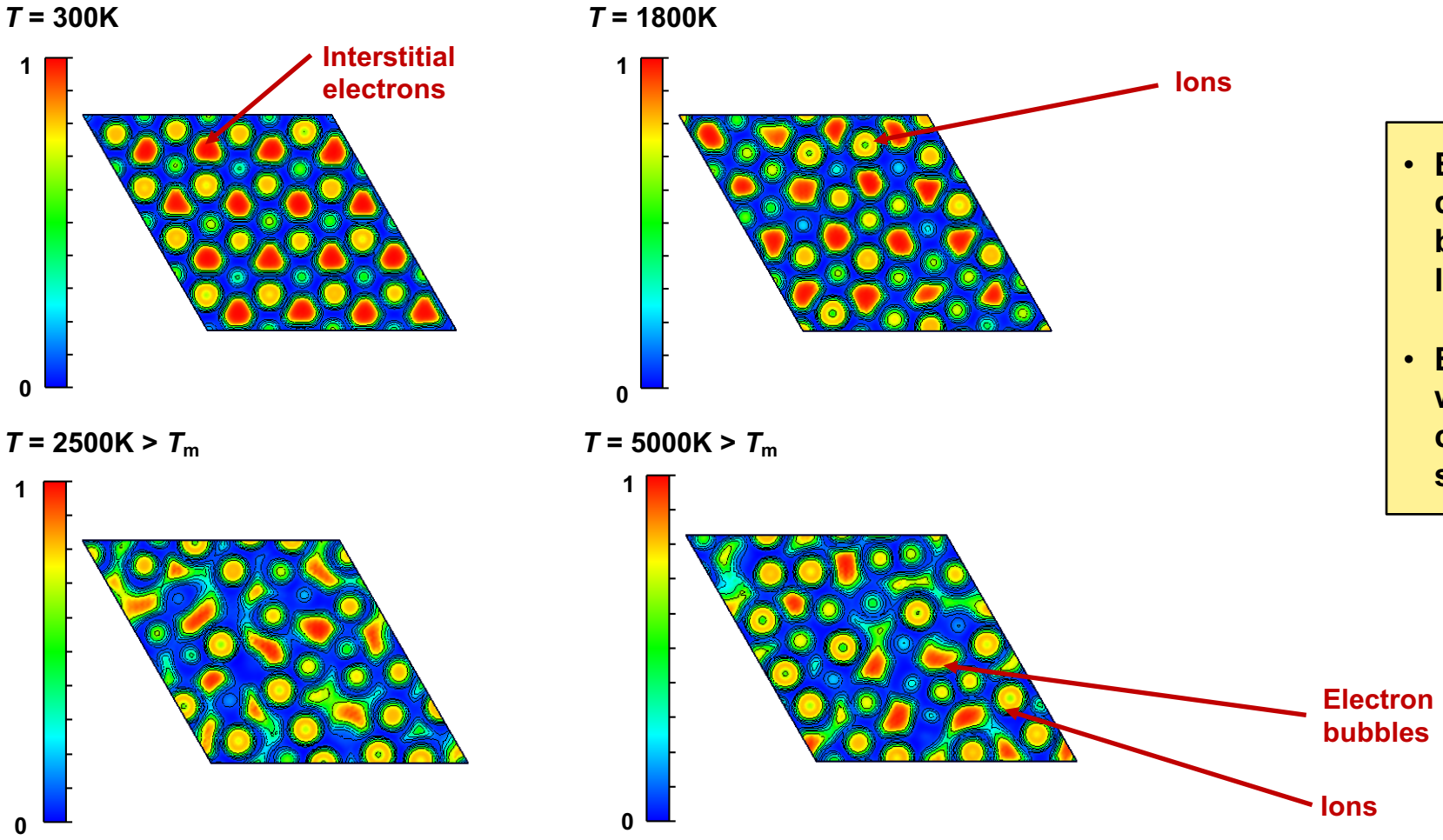
All ELF plots are on the (001) plane

The static Electron Localization Function (ELF) along the (P = 320 GPa, T = 0 K) isochore exhibits dynamic electron bubbles in liquid phase



All ELF plots are on the (001) plane

The static Electron Localization Function (ELF) along the (P = 320 GPa, T = 0 K) isochore exhibits dynamic electron bubbles in liquid phase



- Electron bubbles are dynamic and move between dynamic ions in liquid phase
- Electron bubbles interact with each other, exhibiting coalescence, making the system conducting

All ELF plots are on the (001) plane

Summary/Conclusions

High-pressure dynamics of the hP4 electride* phase of Sodium exhibit an unconventional insulator-to-metal transition: upon melting localized electrons become bubbles

- We have used density-functional theory (DFT) based methods to investigate the finite-temperature effects on the electride phase of Na under extreme conditions
- Our *ab initio* results indicate that the band-gap of Na-electride at ~320 GPa gradually decreases with increasing temperature, until it abruptly becomes zero upon melting, due to an insulator-to-metal transition
- Melting is accompanied by coalescent dynamic electron bubbles rather than conventional uniform electron gas, as is the case for metallic liquids

* Y. Ma *et al.*, Nature 458, 182-184 (2009)

Electron Localization Function

$$\mathrm{ELF}_\sigma(r) = \frac{1}{1 + \chi_\sigma^2(r)}$$

$$\chi_\sigma(r) = \frac{D_\sigma(r)}{D_\sigma^0(r)}$$

$$D_\sigma(r) = \sum_{i=1}^{N_\sigma} |\nabla \Psi_i(r)|^2 - \frac{1}{4} \frac{|\nabla \rho_\sigma(r)|^2}{\rho_\sigma(r)}$$