Probing a New Regime of Extreme Chemistry at High-Energy-Density Conditions: Na as a Prototypical Example

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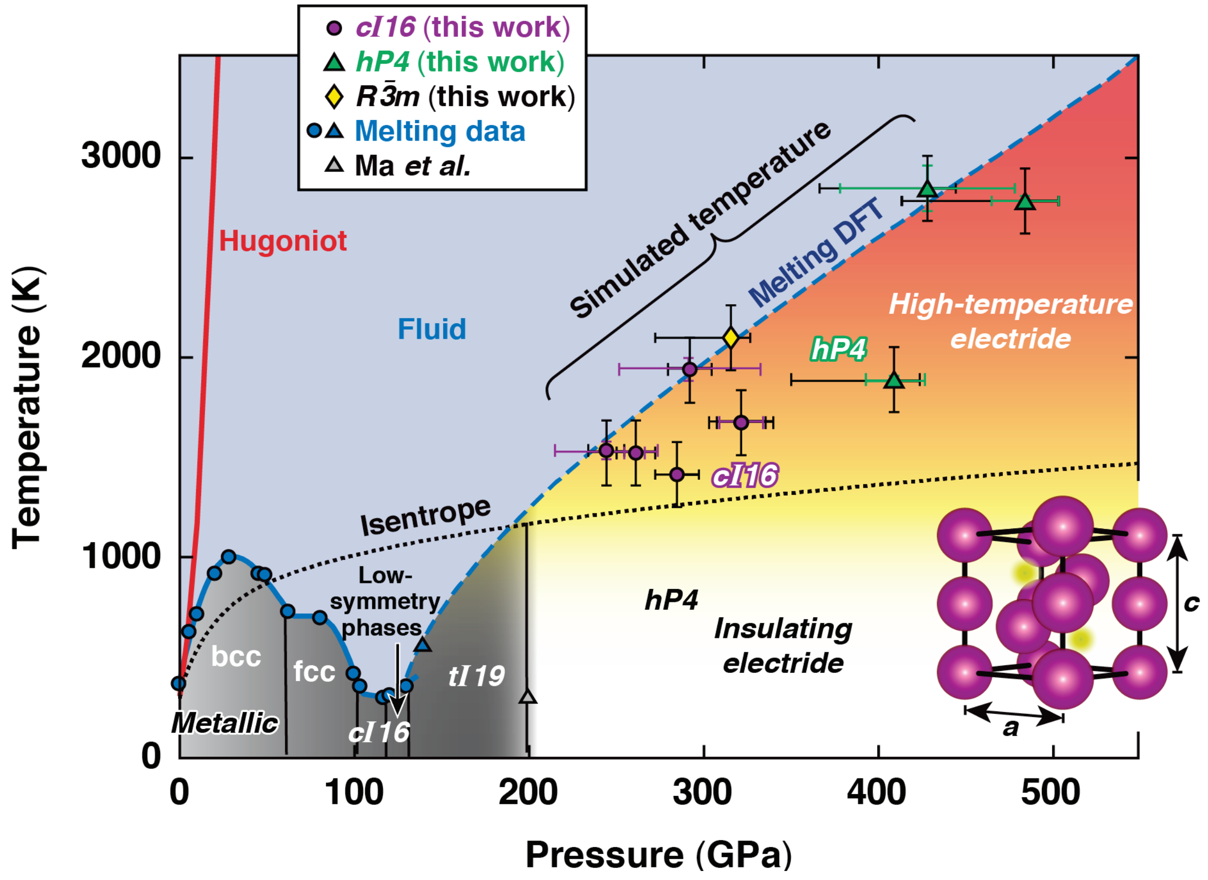

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UNIVERSITY of ROCHESTER

For the first time, we have created an electride using laser-driven compression

- Laser-driven experiments allow access to unprecedented pressures (484 GPa) and temperatures (~3000 K) in ramp-compressed Na
- Although 0-K calculations predict that the *hP4* phase is stable from 0.2 to 1.75 TPa,* a series of phase transitions were observed upon recrystallization with the *hP4* phase only appearing at the highest compressions
  - we observe the *cI16* phase forming from the liquid, a potential confirmation of the prediction that the liquid has transformed to a *cI16*-like local order**
- Simultaneous reflectivity measurements show a decrease throughout the liquid and solid phases—consistent with predictions that the alkali metals undergo continuous free-electron to electride liquid transitions†

Pressure

*Y. Li *et al.*, Phys. Rev. Lett. 114, 125501 (2015).
**J.-Y. Raty, E. Schwegler, and S. A. Bonev, Nature 449, 448 (2007).
† H. Zong *et al.*, Nat. Phys. 17, 955 (2021).

Collaborators

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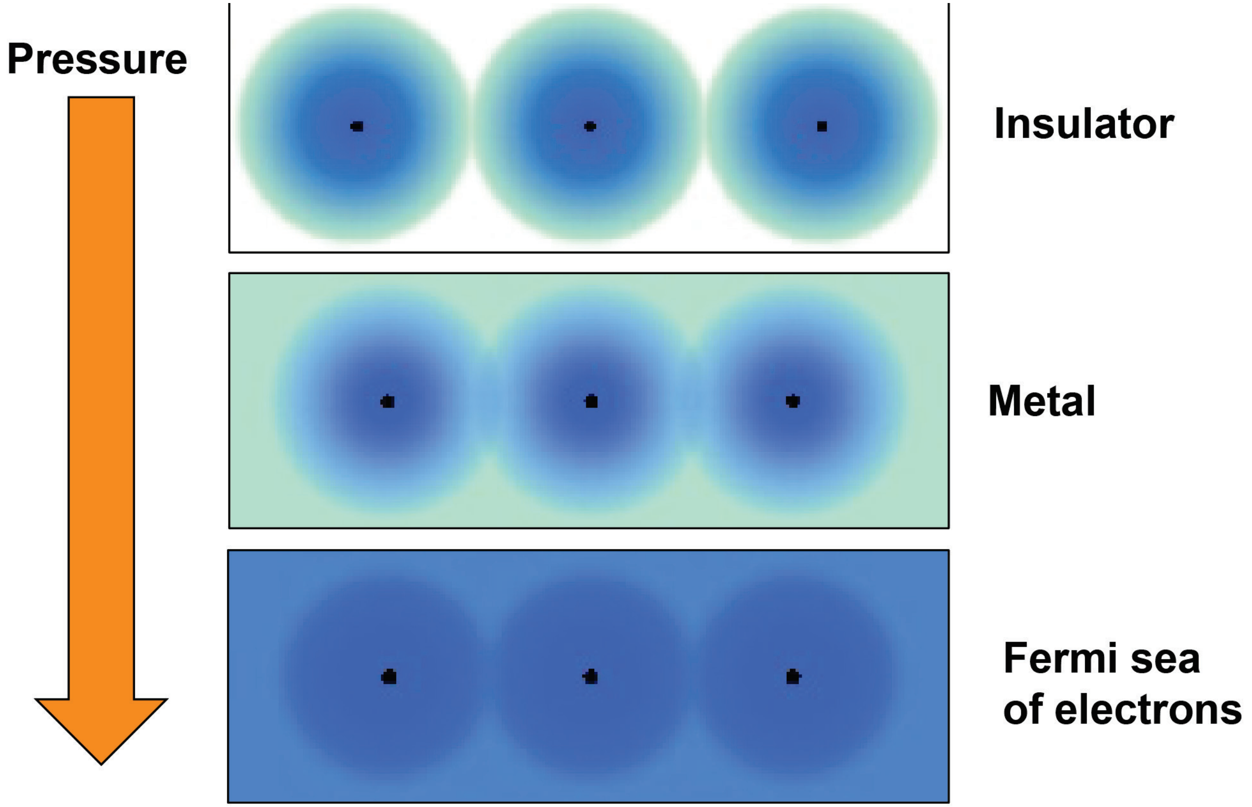
X. Wang, K. Hilleke, and E. Zurek
University of Buffalo

Application of pressure: Rules of thumb

- **Under high pressure, the structures of solid compounds tend to***
  - **become more homogeneous (long and weak bonds get compressed)**
  - **assume close-packed structures**
  - **increase coordination numbers**
  - **have higher symmetry**
  - **exhibit more delocalized electronic states, which bring about insulator–metal transitions**



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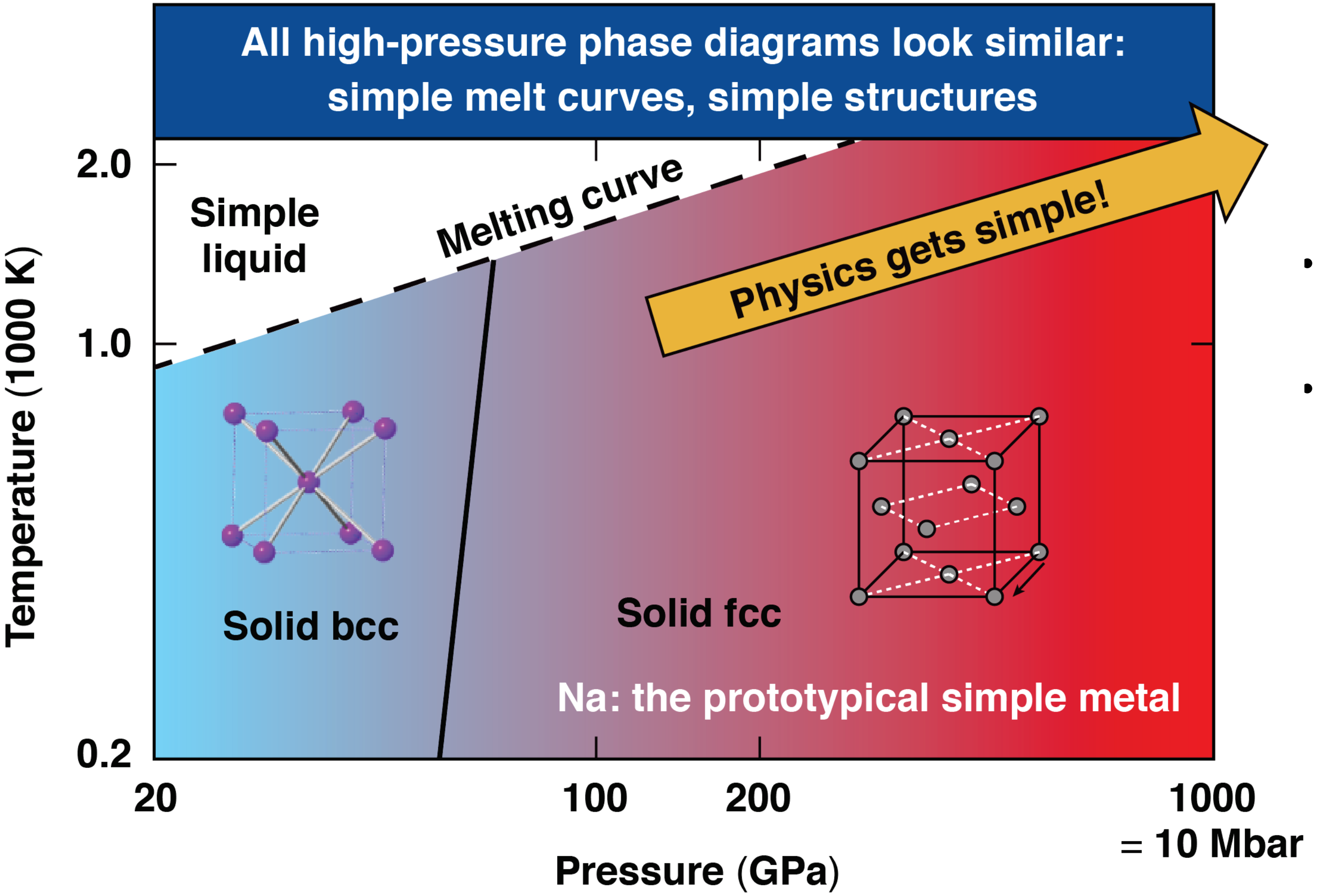
* M. Miao *et al.*, Nat. Rev. Chem. 4, 508 (2020);
C. T. Prewitt and R. T. Downs, in *Ultrahigh Pressure Mineralogy: Physics and Chemistry of the Earth's Deep Interior*, edited by R. J. Hemley (De Gruyter, Boston, MA, 1998), Vol. 37, Chap. 9, p. 283.
Based on slide by Martin Gorman

The Thomas–Fermi model has long been used to describe the limiting high-pressure behavior of matter



- Thomas–Fermi: the limiting high-pressure behavior of matter
- The band gap is predicted to close under pressure—free-electron behavior

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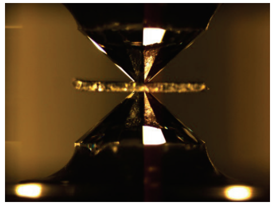
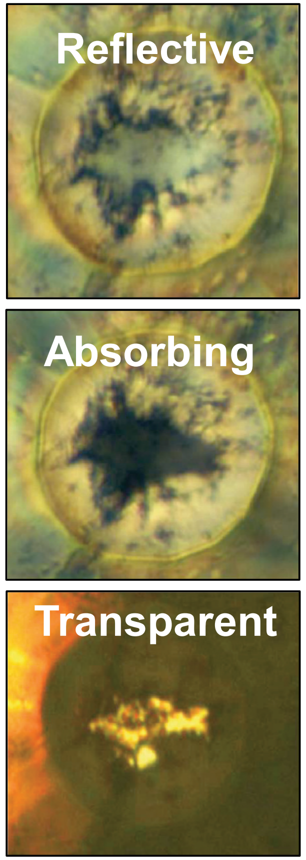
Application of pressure: Defying intuition

- In some cases, the “rules” do not apply*
  - deviation from close packing of spheres may be used to achieve higher density
  - electrons detach from atoms
  - repopulation of the atomic orbitals might change the chemical identity of the atoms



Pressure



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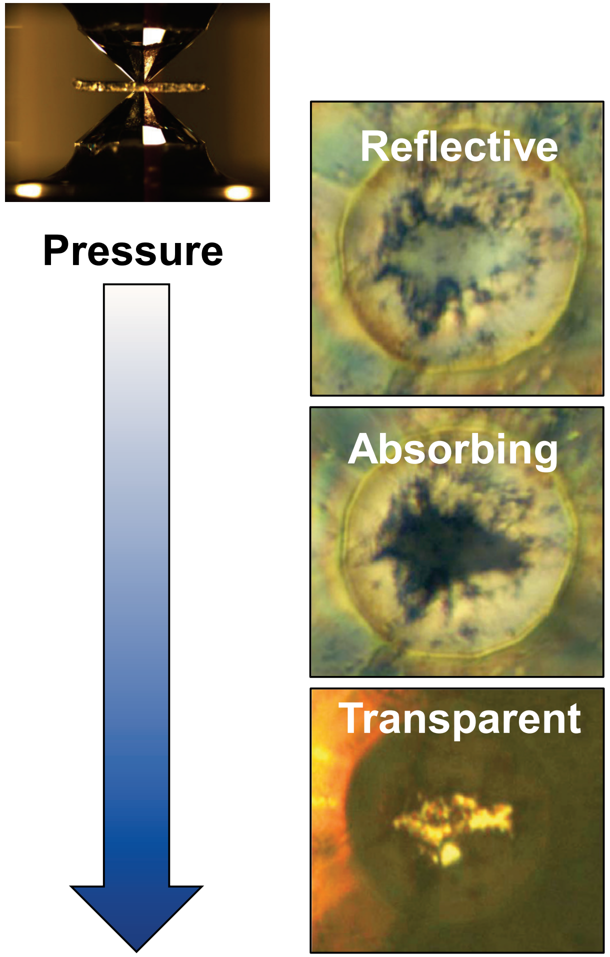

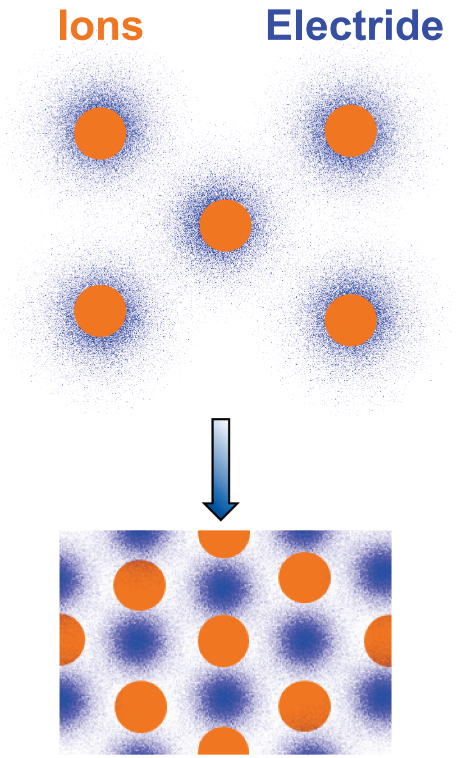

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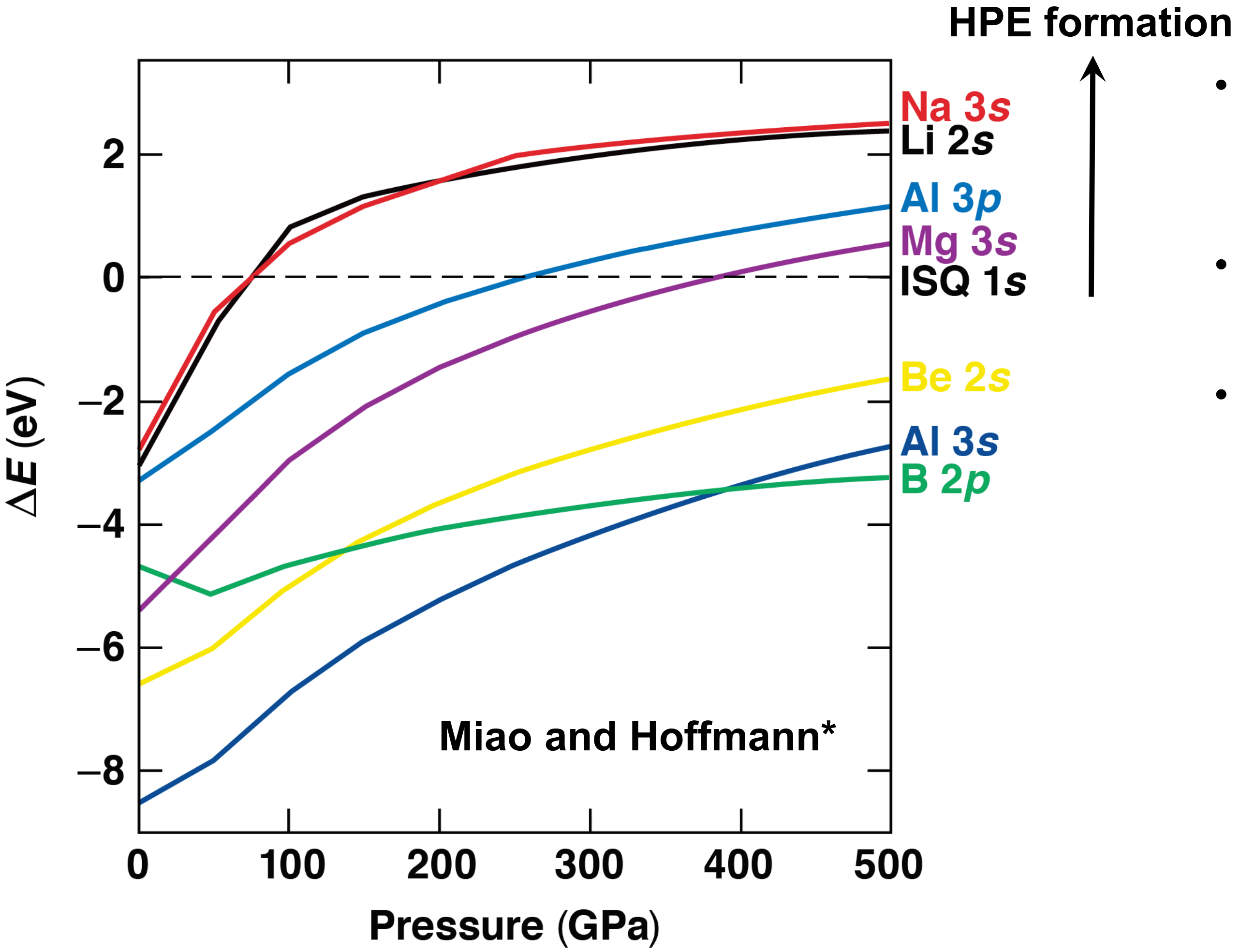
The formation of high-pressure electrides can be understood by realizing the interstitial space in a crystal lattice can accommodate quantum orbitals



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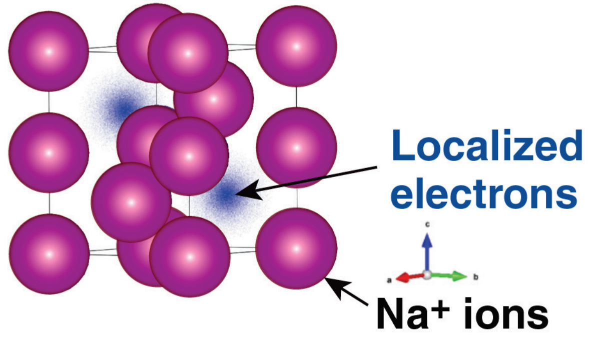
- An electride phase is one where the electrons are squeezed into the spaces between the atoms, creating an insulating behavior
- The interstitial space can accommodate quantum orbitals
- Model calculations* show that under pressure the energies of atom-centered orbitals increase more quickly than the interstitial space because of repulsion from the core electrons



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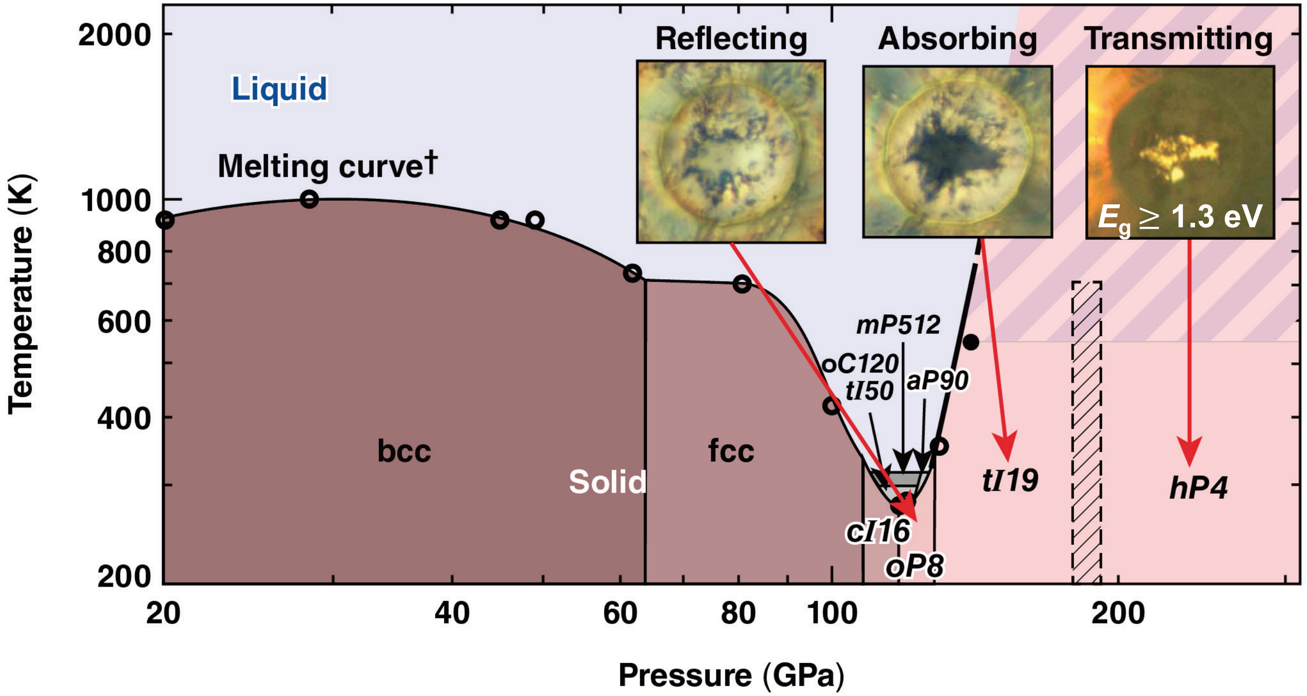
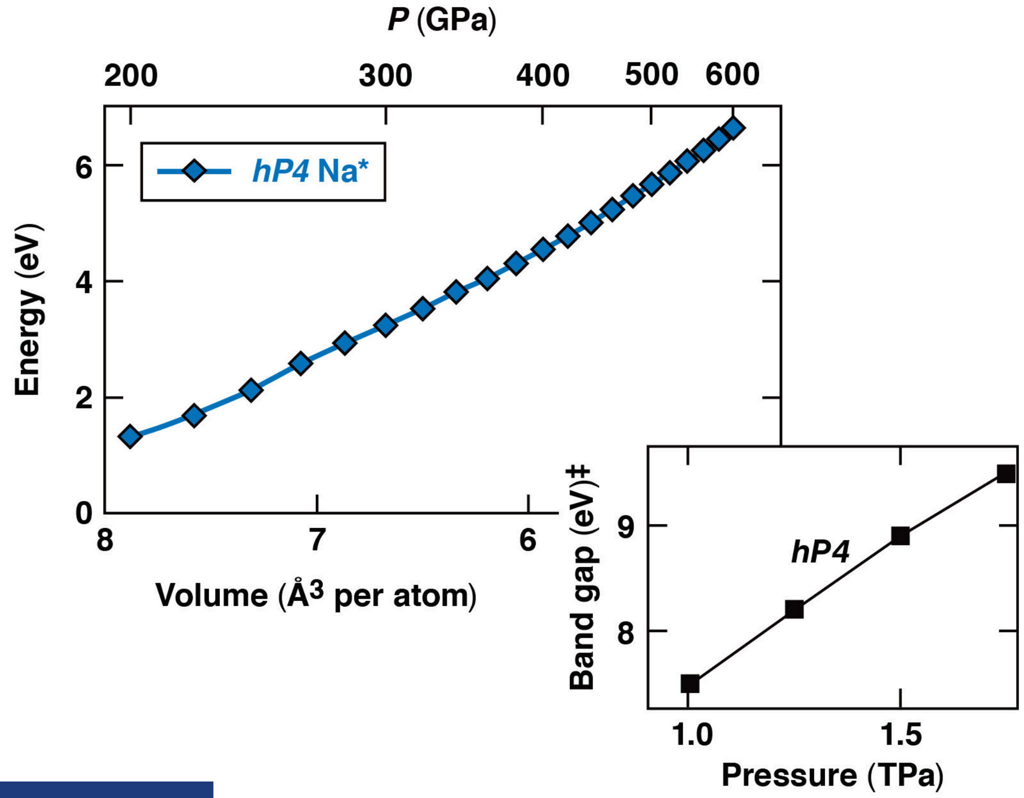
* M.-S. Miao and R. Hoffmann, Account. Chem. Res. 47, 1311 (2014).
HPE: high pressure electride
ISQ: interstitial quasi-atom

Diamond-anvil cell (DAC) experiments* show that Na transforms into an optically transparent electride at 200 GPa and room temperature

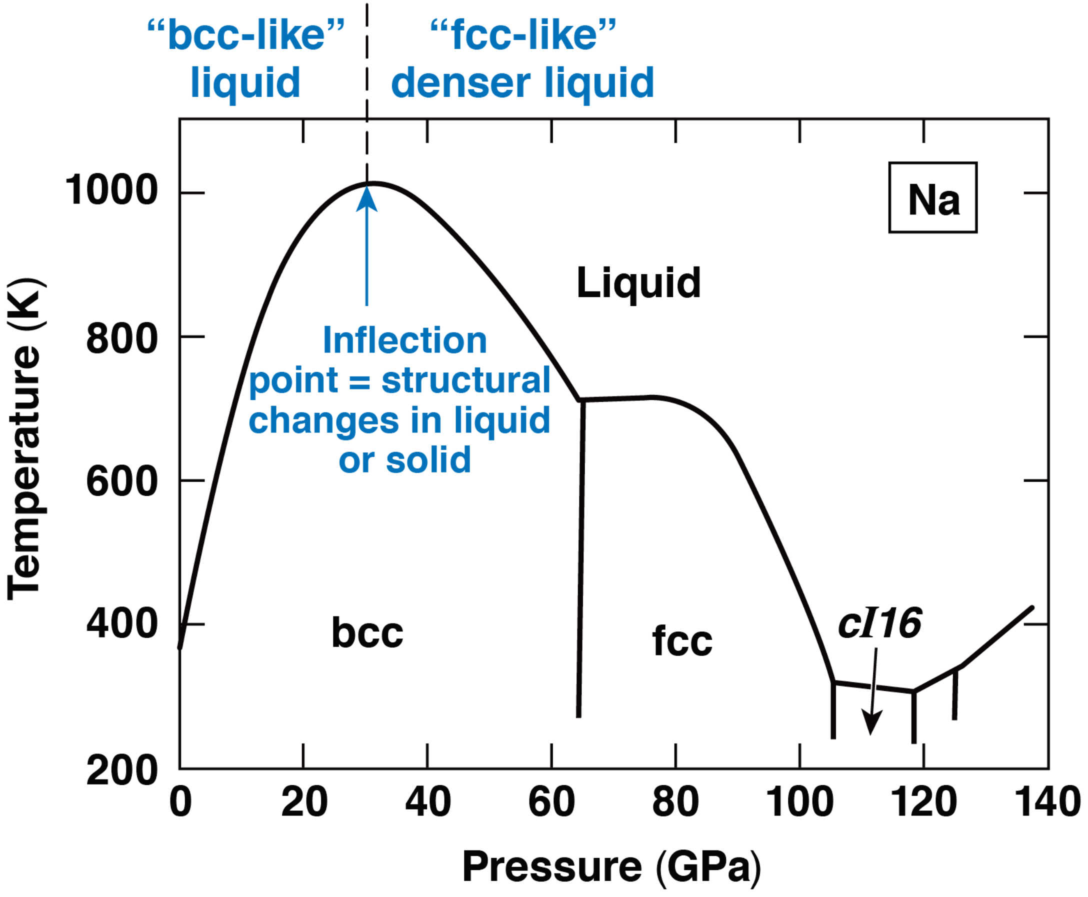




Density functional theory predicts that the *hP4* structure is stable up to 1.75 TPa at 0 K.**

* Y. Ma *et al.*, Nature 458, 182 (2009).
** Y. Li *et al.*, Phys. Rev. Lett. 114, 125501 (2015).
† E. Gregoryanz *et al.*, Science 320, 1054 (2008).
‡ M. Marqués *et al.*, Phys. Rev. B 83, 184106 (2011).

One common feature of most alkali metals is complex melting behavior



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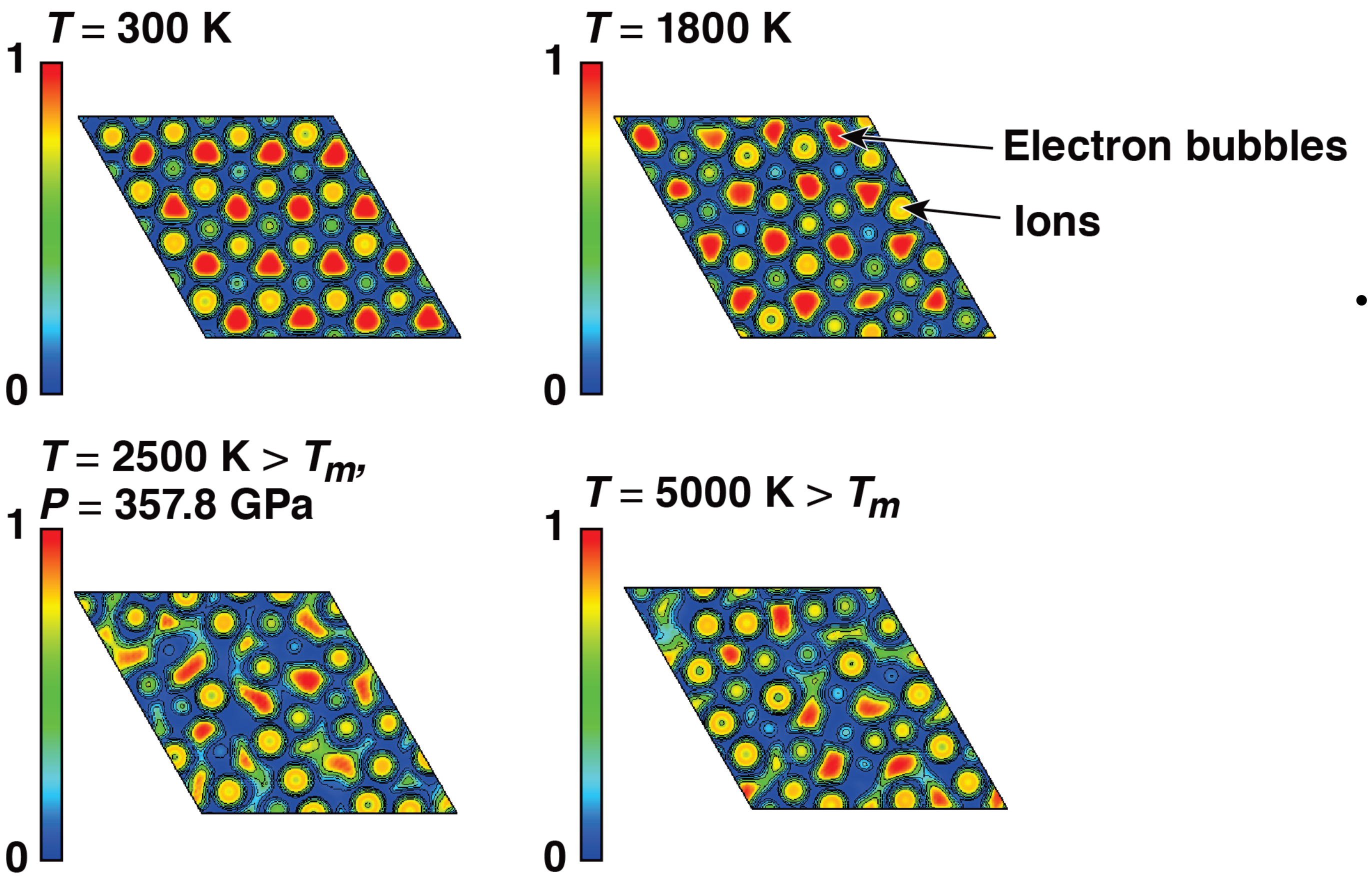
- According to the Clausius–Clapeyron equation, a change in the gradient of the melting curve slope suggests a change in the relative densities of the solid and liquid phases
  - no solid transition, so it must be in the liquid!
- Molecular dynamic simulations of liquid and solid Na showed changes in the second coordination shell of the liquid phase above 30 GPa*
- Some argue more subtle changes in local order** or that the liquid phase is more compressible than the solid†

* J.-Y. Raty, E. Schwegler, and S. A. Bonev, Nature 449, 448 (2007).
** M. Marqués, D. J. González, and L. E. González, Phys. Rev. B 94, 024204 (2016).
† V. F. Degtyareva, Cogent Phys. 4, 1327697 (2017).

Recent theoretical work* has predicted that electride character persists up to and into the liquid phase, and similar predictions have been made for Li** and K†

DFT calculations



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- Upon melting, electron localization persists in *hP4* Na in the form of dynamic electron bubbles and a change in hybridization from *p–d* to *s–p* occurs*

* R. Paul *et al.*, Phys. Rev. B 102, 094103 (2020).
** I. Tamblyn, J.-Y. Raty, and S. A. Bonev, Phys. Rev. Lett. 101, 075703 (2008).
†H. Zong *et al.*, Nat. Phys. 17, 955 (2021).

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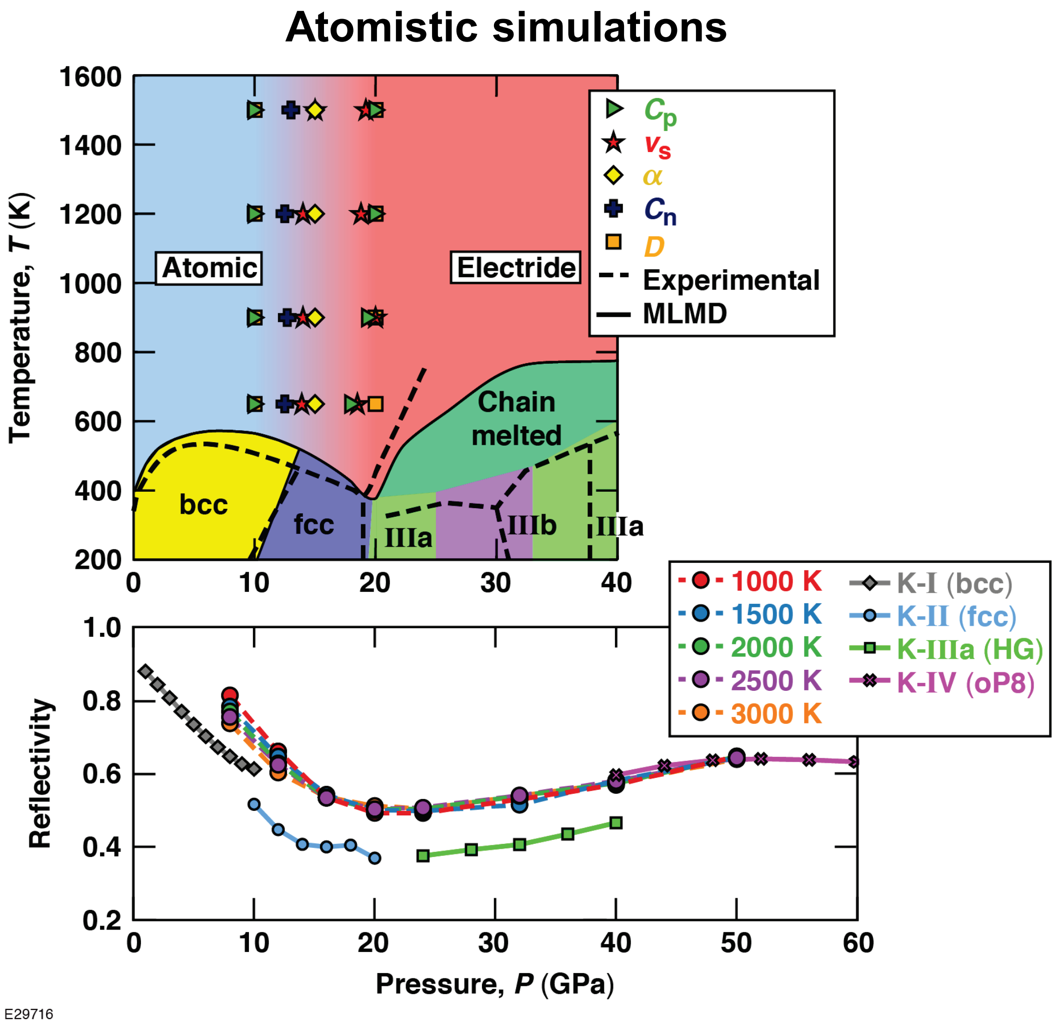
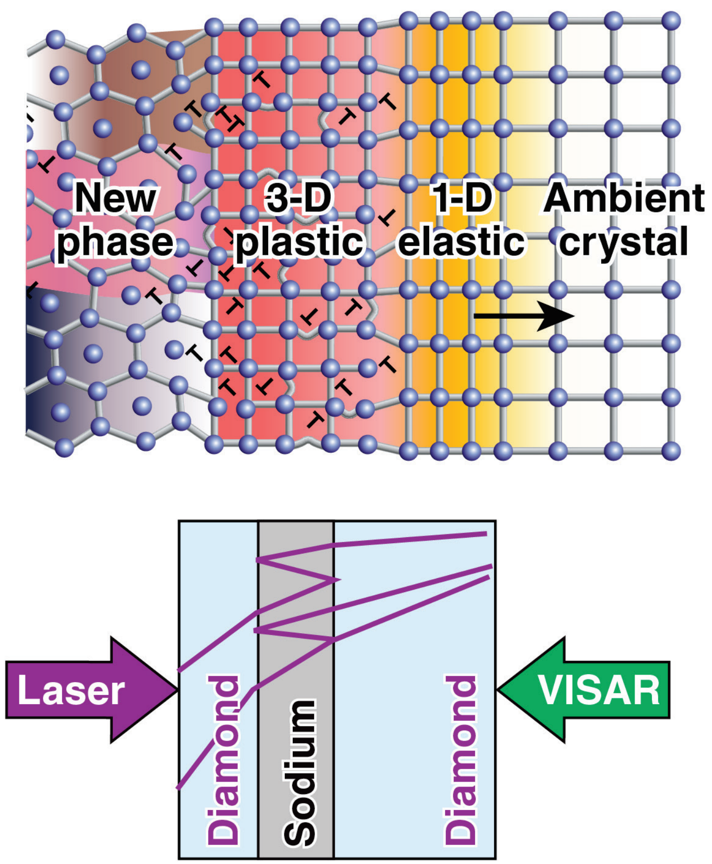
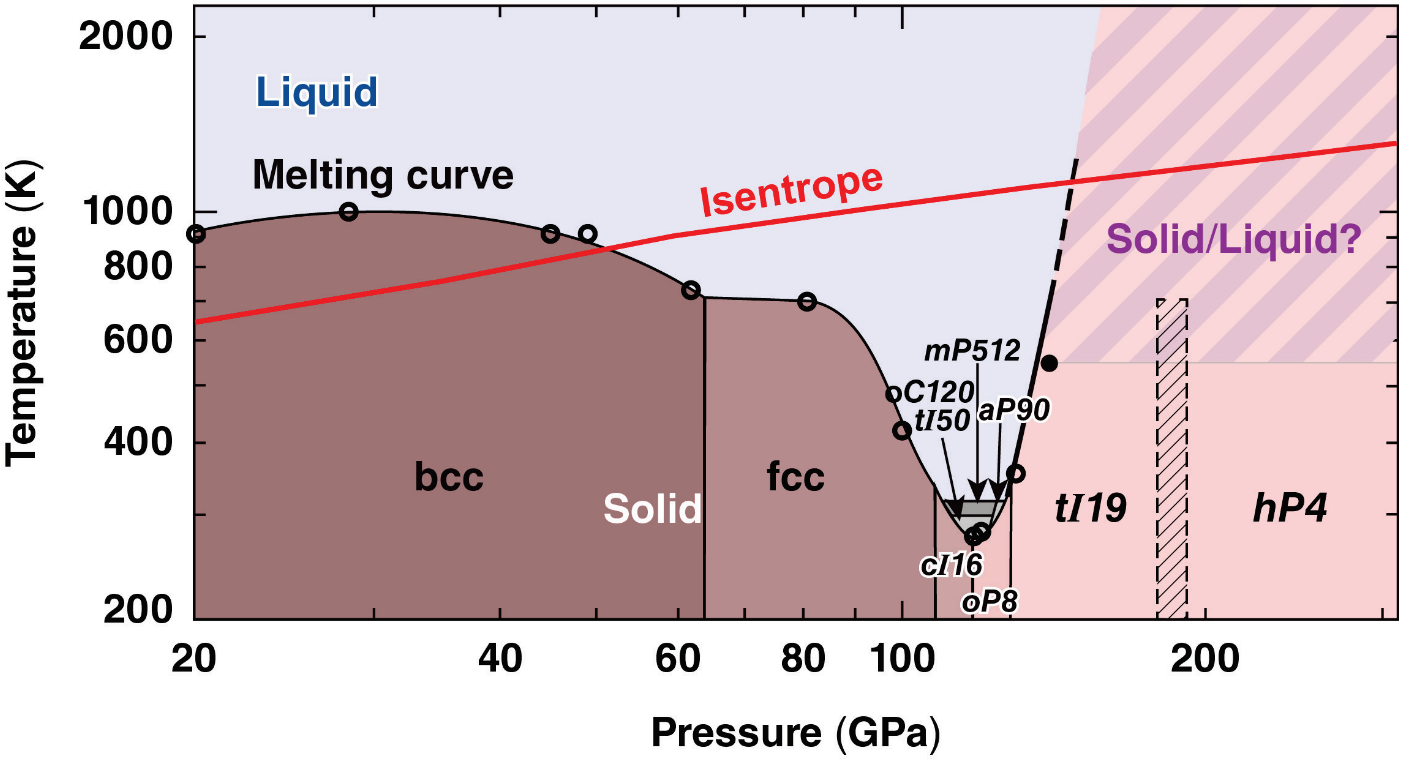


- **Atomistic simulations of liquid potassium show evidence of a liquid–liquid continuous transformation from free electron to electride behavior**
  - **the negative Clapeyron slope in the fcc phase is due to a larger electride fraction in the liquid**

* R. Paul *et al.*, Phys. Rev. B 102, 094103 (2020).
** I. Tamblyn, J.-Y. Raty, and S. A. Bonev, Phys. Rev. Lett. 101, 075703 (2008).
† H. Zong *et al.*, Nat. Phys. 17, 955 (2021).
MLMD: machine-learned molecular dynamics

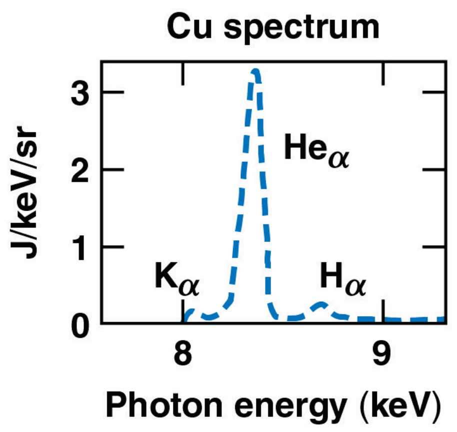
Assuming isentropic compression, Na first melts in the bcc phase before recrystallizing at high pressures as it crosses the melting curve again

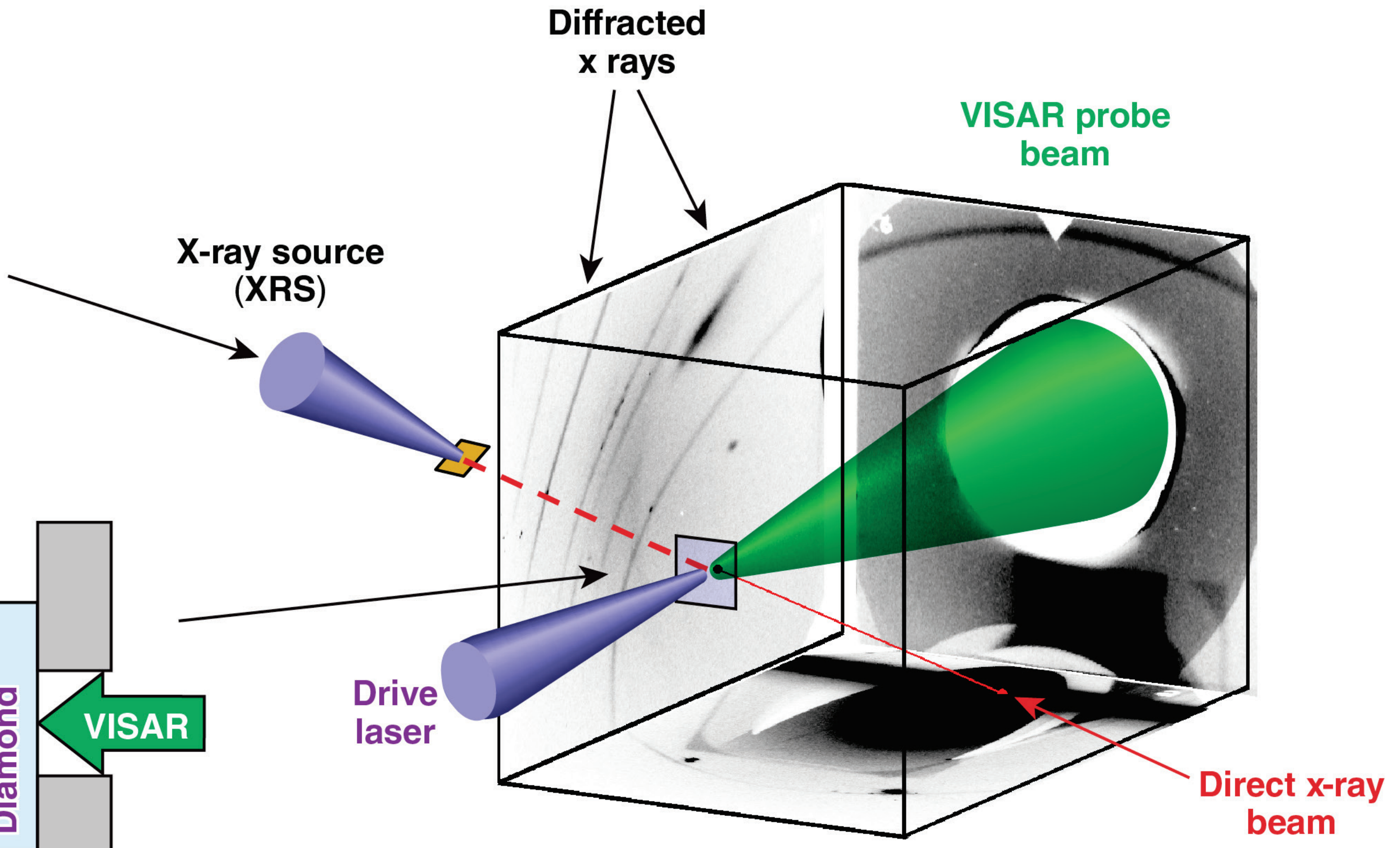


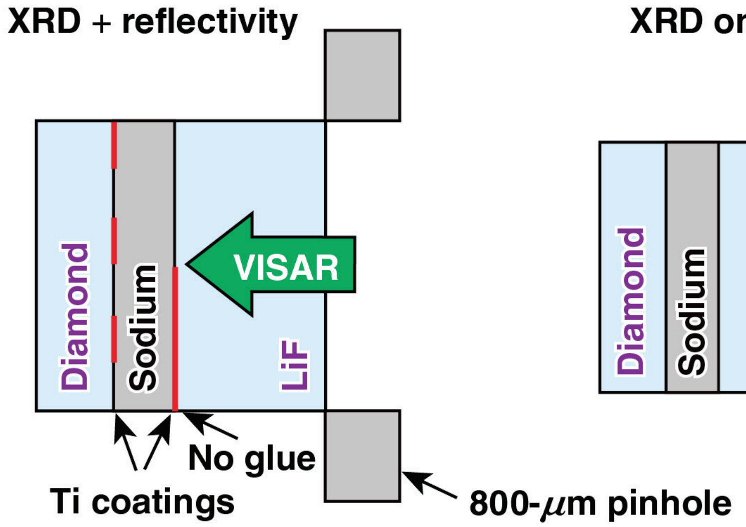


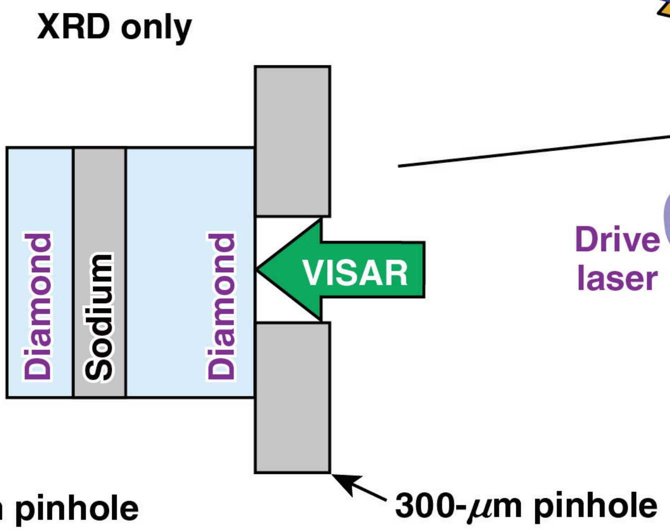
M. Marqués *et al*., Phys. Rev. B 83, 184106 (2011).
VISAR: velocity interferometer system for any reflector

Using the PXRDIP* platform, simultaneous x-ray diffraction (XRD) and reflectivity measurements were performed on ramp-compressed Na to 480 GPa









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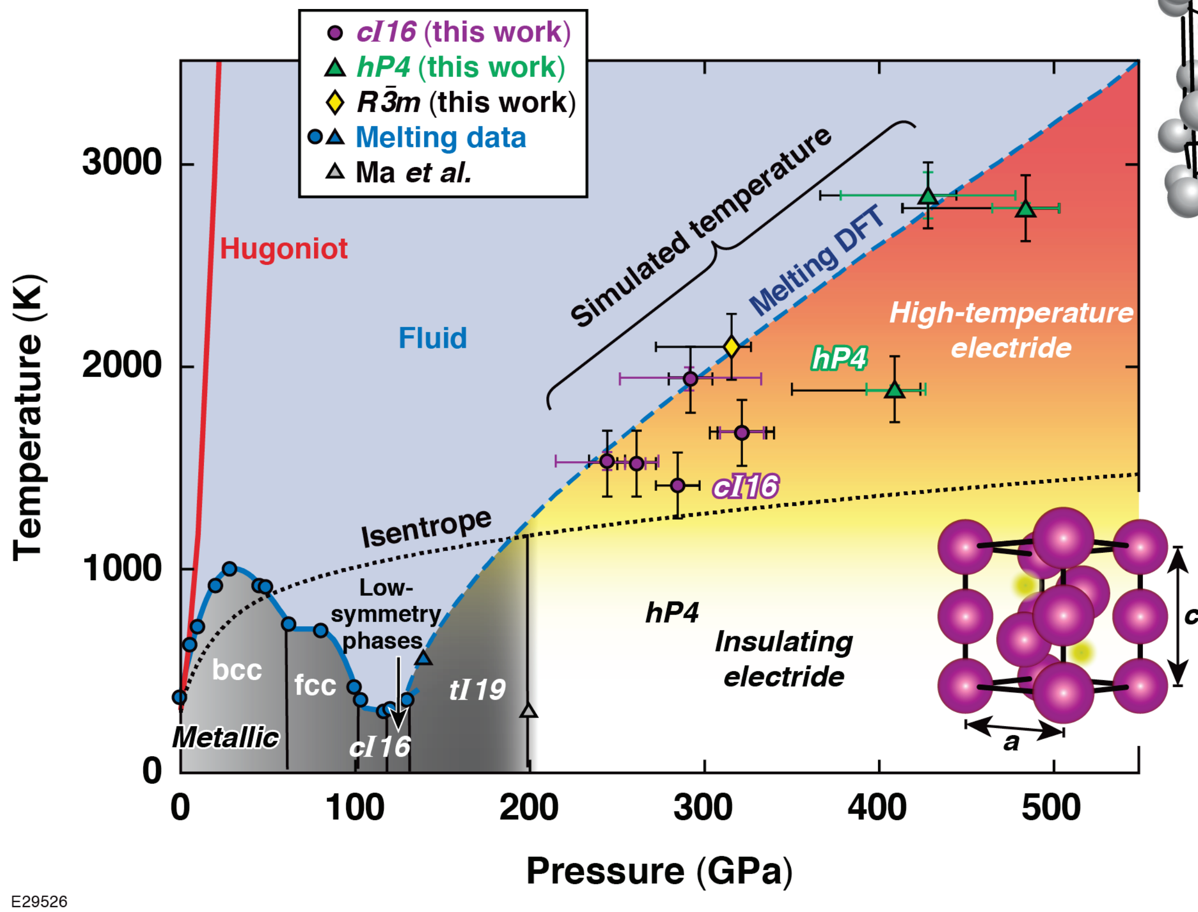
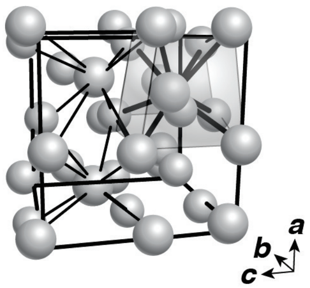
* J. R. Rygg *et al.*, Rev. Sci. Instrum. 83, 113904 (2012);
J. R. Rygg *et al.*, Rev. Sci. Instrum. 91, 043902 (2020).
PXRDIP: powder x-ray diffraction image plate

X-ray diffraction and reflectivity data for ~sevenfold compressed Na reveal a series of phase transitions upon recrystallization

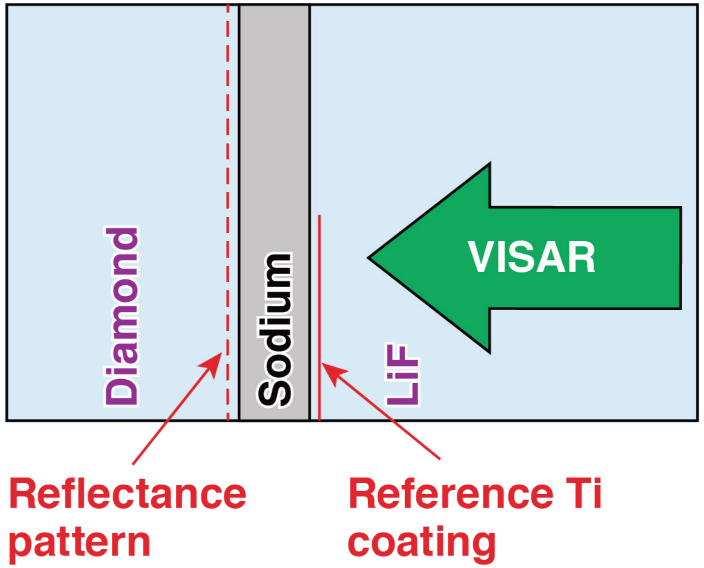


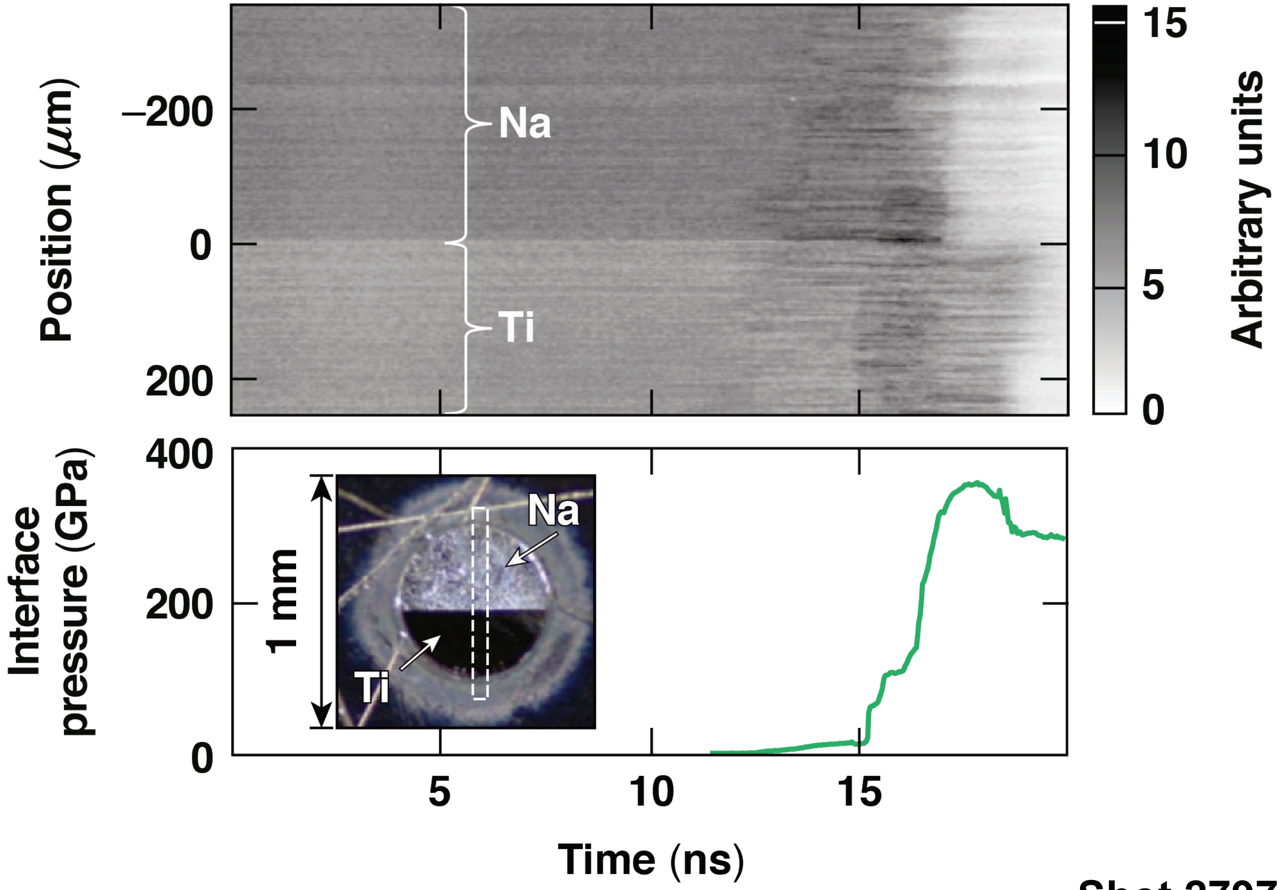


- We observe *cI16* forming from the liquid
  - a potential confirmation that the liquid has transformed to *cI16*-like local order*
- In one experiment, we observe a rhombohedral structure, *R*$\bar{3}$*m*
  - isostructural to that observed in As, Sb, and Bi

* J.-Y. Raty, E. Schwegler, and S. A. Bonev, Nature 449, 448 (2007).

The first measurements of the high-pressure Na liquid reflectivity were made using a novel target design





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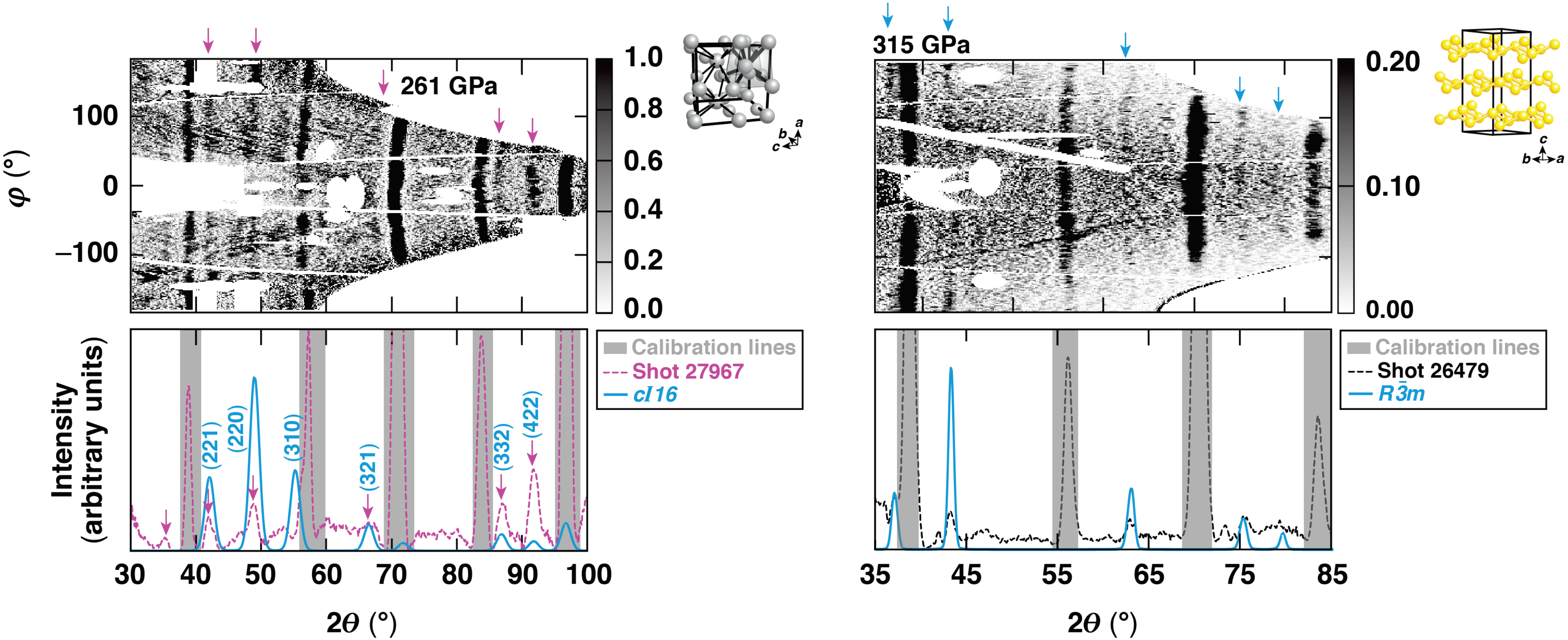
LLNL *AnalyzeVISAR* code (Marius Millot) was used to process the *VISAR* data

At intermediate pressures, we observe two new phases



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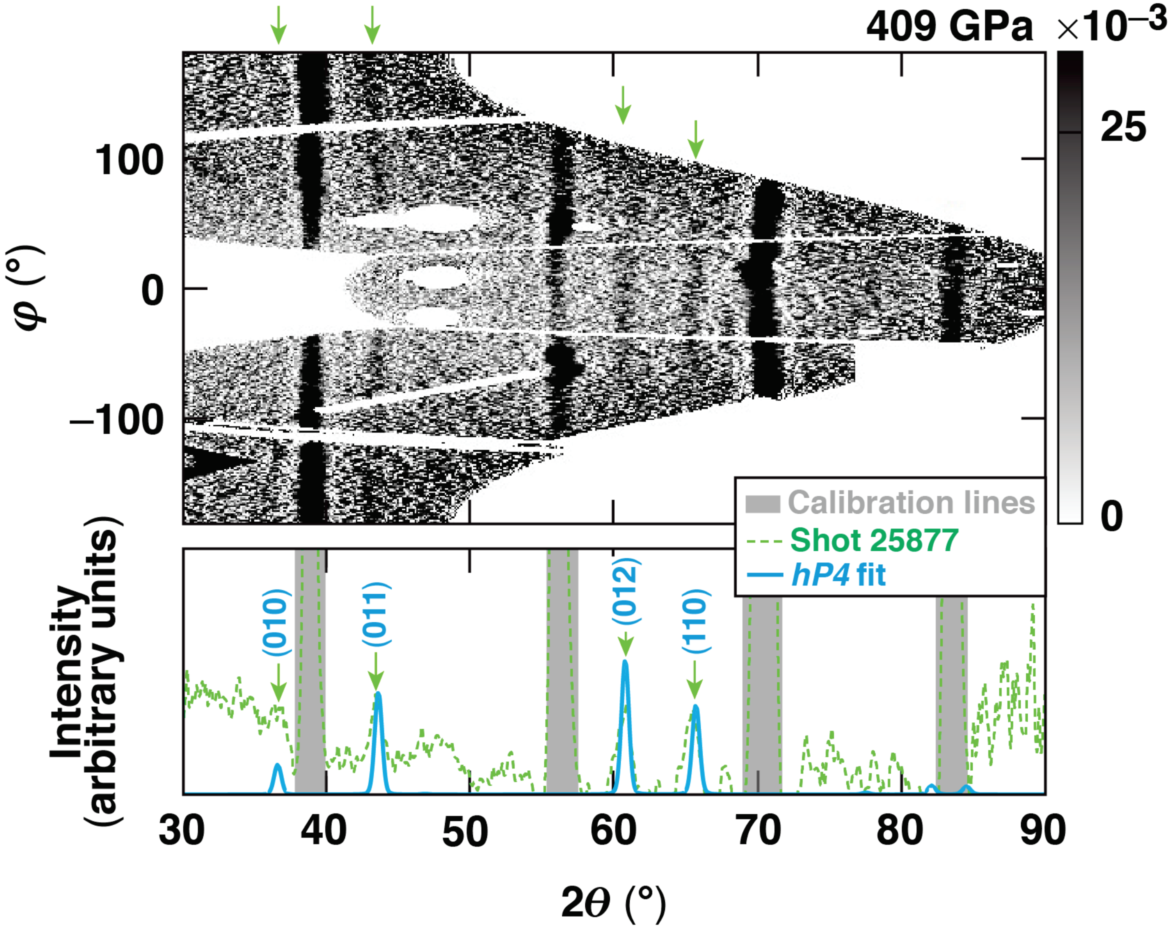
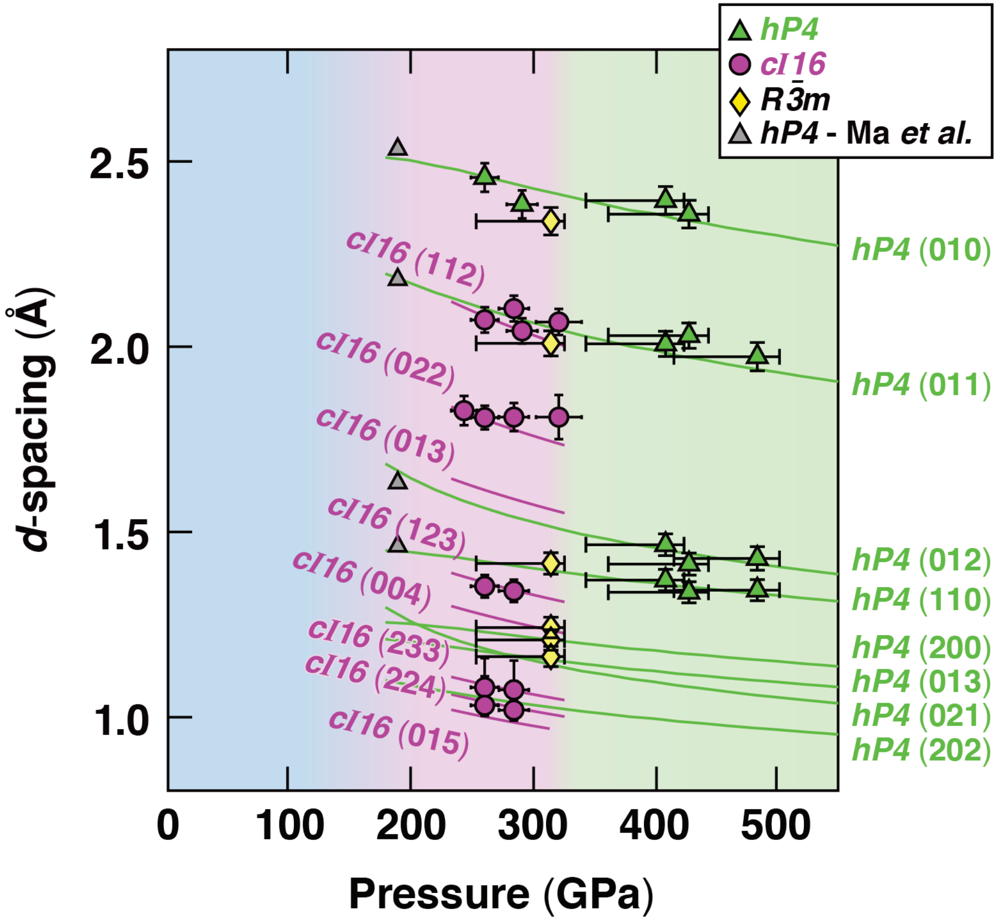
At the highest pressures, we observe the *hP4* electride phase





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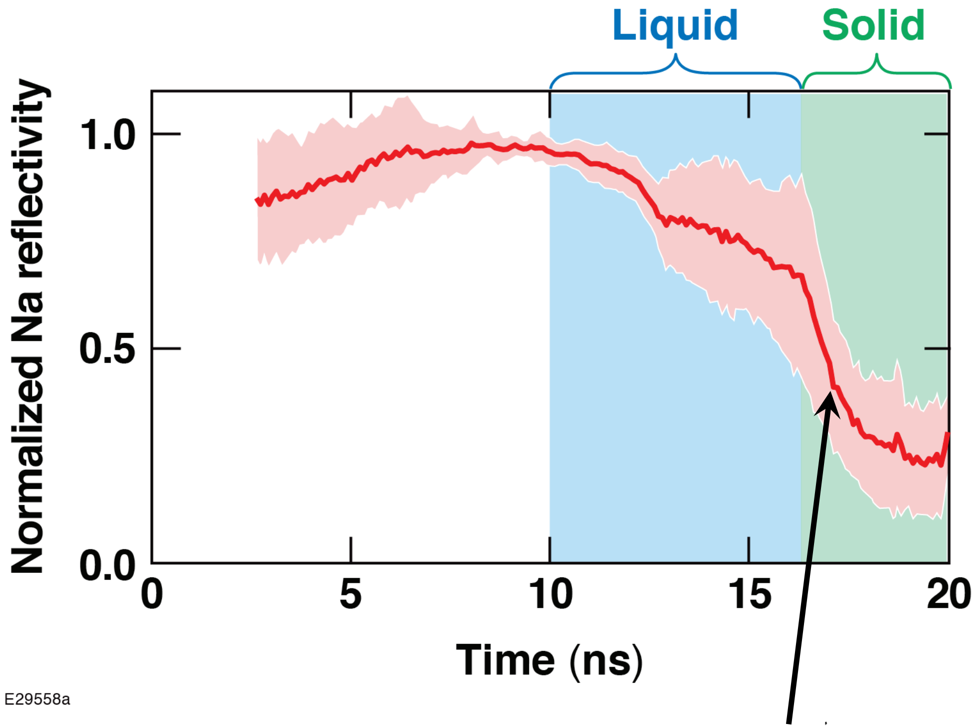
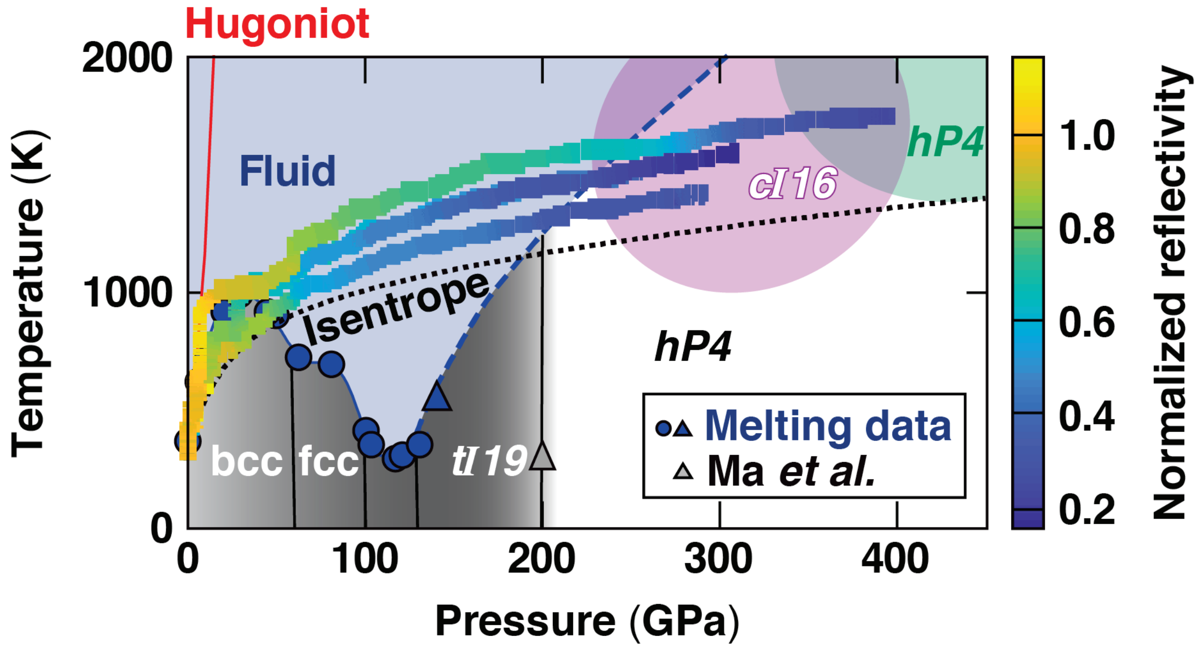
The reflectivity is tracked through the bcc phase into the fluid phase, and at the highest pressures, in the *cI16* phase and approaching the *hP4* phase





Reflectivity drop –
electron localization*,**,†

* J.-Y. Raty, E. Schwegler, and S. A. Bonev, Nature 449, 448 (2007).
** H. Zong *et al.*, Nat. Phys. 17, 955 (2021).
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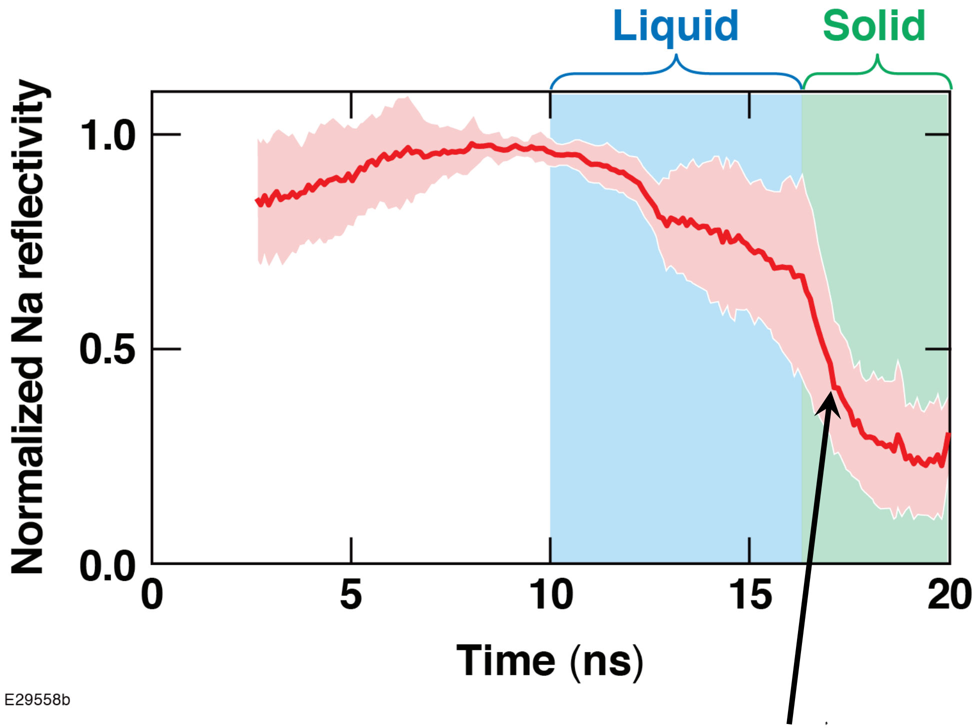
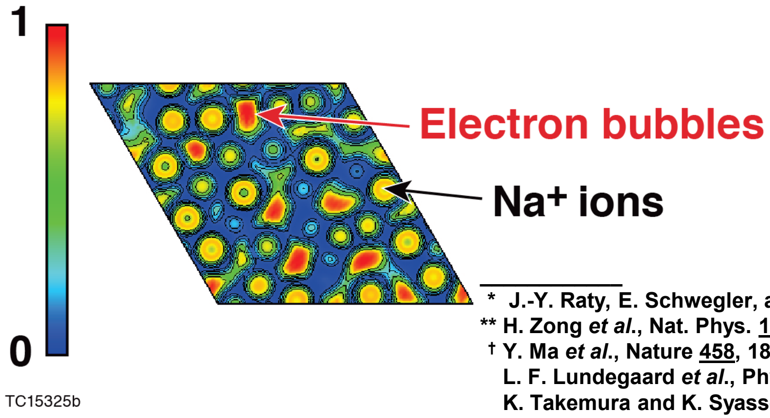
K. Takemura and K. Syassen, Phys. Rev. B 28, 1193(R) (1983).

At the highest pressures, the Na reflectivity drops to about 23% of its initial value



- A threefold drop in electrical conductivity is expected in the low-coordinated liquid sodium between 40 and 80 GPa*
- In liquid K, a liquid–liquid phase transition is expected to manifest as a dip in the reflectivity, similar to that observed here**
- Reduced reflectance is consistently observed in host–guest structures in Na and K at lower pressures†



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