Electronic Structures and Physical Properties of Uranium Hydride under Shock Compression

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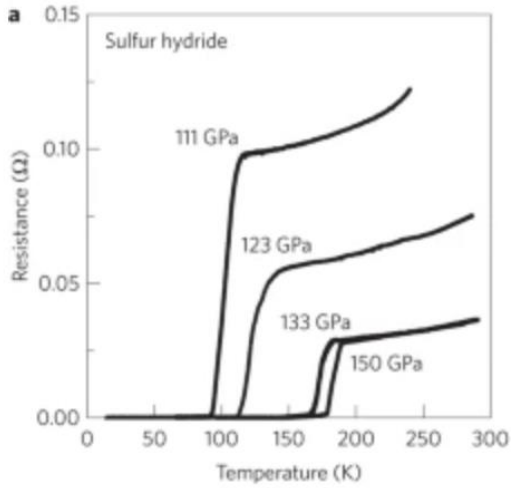
Outline

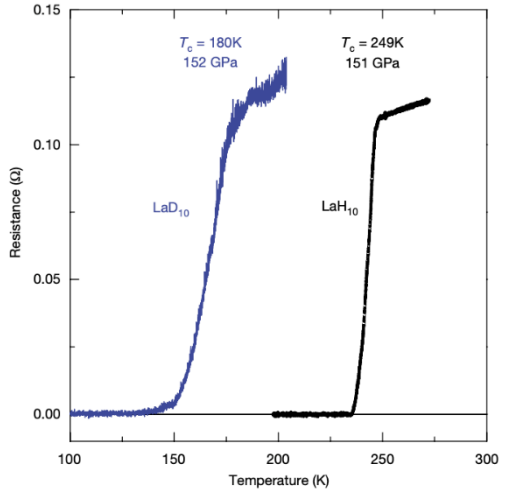
1. Background
2. Method
3. Discussions
4. Conclusions

1. Background

Superconductivity of Hydrides

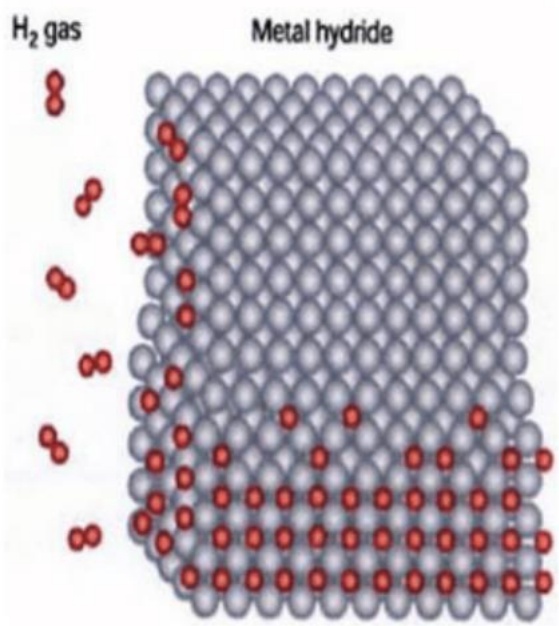


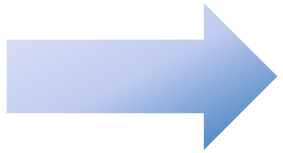
M. Einaga *et al.*, Nature Physics (2016)



A. P. Drozdov *et al.*, Nature (2019)

Metal hydrides for hydrogen storage



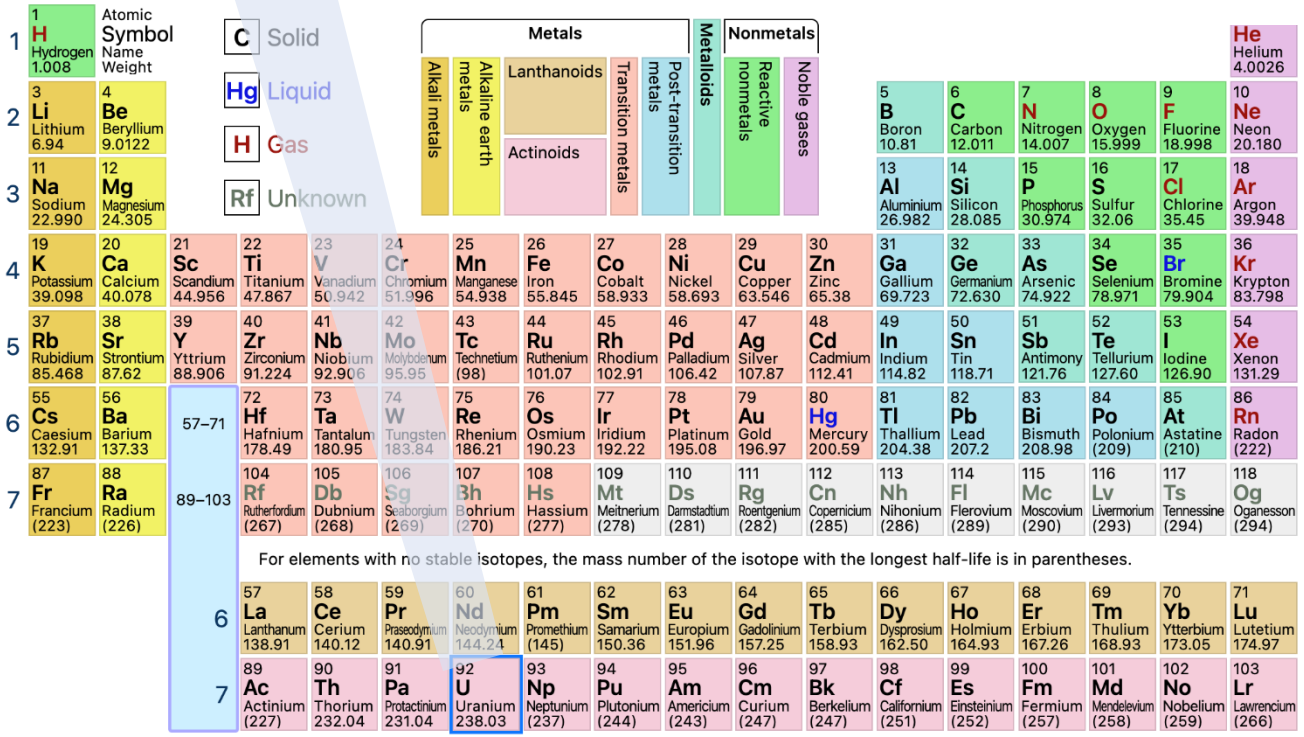


Physical & thermodynamic properties

$$M + H_n \leftrightarrow MH_n$$

- M = Ti, Fe, Mn, Ni, Cr etc. that can react with H_2 in a reversible reaction.
- The forward reaction is slightly exothermic. To release hydrogen, a small amount of heat must be supplied.
- H_2 is stored at a modest pressure and release at ambient pressure.

1. Background



$$2U + 3H_2 \leftrightarrow 2UH_3$$

➢ **Disadvantages:**

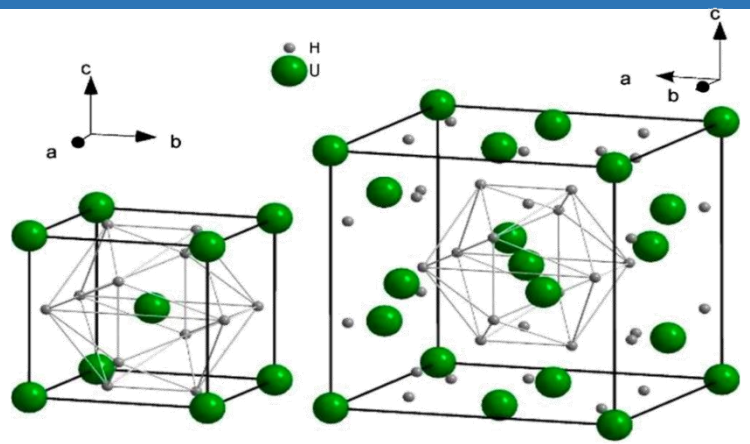
- Heavy, not suitable for portable storage.
- Hard to handle the uranium hydride. (due to its radioactivity and high pyrophoricity with oxygen)

➢ **Advantages:**

- Low equilibrium pressure (< 0.1 Pa) at room temperature for less tritium loss;
- Low release temperature (400~450 ℃) that can reduce the permeation loss of tritium through containment;
- Fast gas uptake/release rate that is desired for emergency use;

Properties of Uranium hydride

1. Background



α-UH_3 β-UH_3

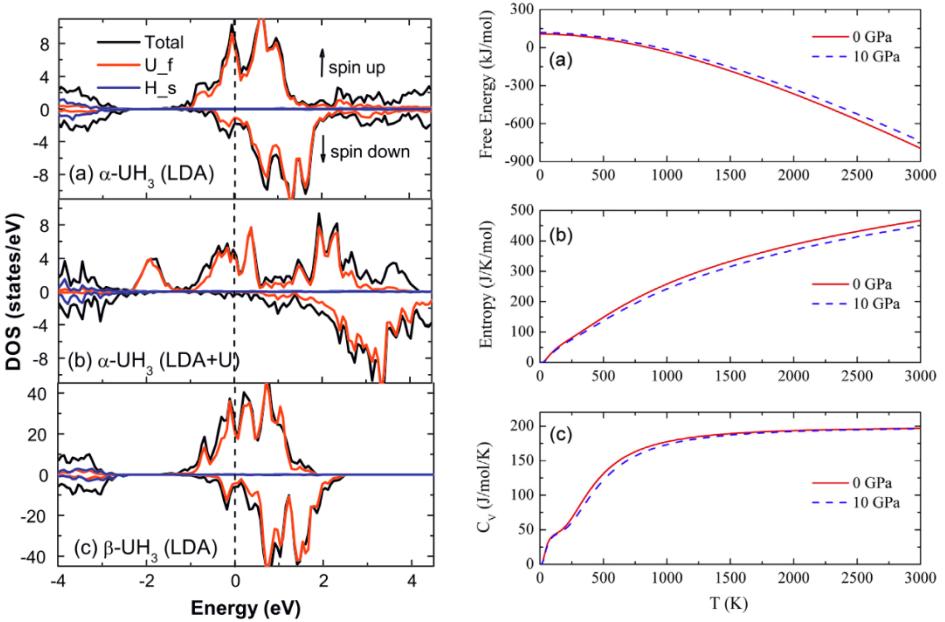
Table 1
The different phases and structural properties of uranium and uranium hydride. U [18,19], UH_3,UD_3 [20–22] and UT_3 [23].

Metal/ compound	Symmetry	Lattice cell parameter (Å)	Density (g/cm^3)
α-UH_3	Cubic	4.160 ± 0.001	11.12
α-UD_3	Cubic	4.150	11.33
α-UT_3	Cubic	4.142 ± 0.002	11.55
β-UH_3	Cubic	6.645	10.92
β-UD_3	Cubic	6.620 ± 0.002	11.11
β-UT_3	Cubic	6.625 ± 0.003	11.29

A. Banos *et al.*, Corrosion science (2018)

➢ Difficuties in investigation:

- Complex behaviors of 5f electronic states;
- Limited experimental data on physical properties of uranium compounds, such as, phase diagram, magnetic properties and phonon dispersions.

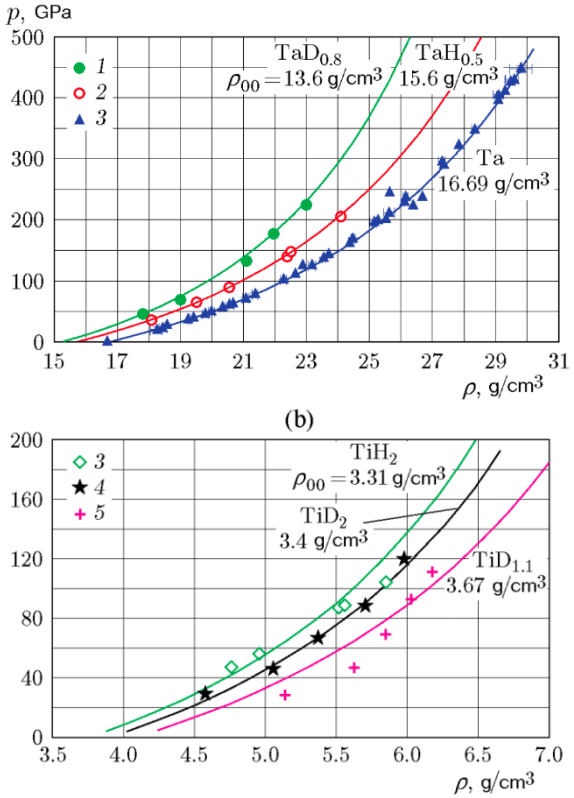


Zhang *et al.*, Journal of Nuclear Materials （2012）
Zhang *et al.*, Journal of Alloys and Compounds (2014)

1. Background

Shock compression

- Fast
- Non-equilibrium
- Structural phase transition may exist



Golubkov et al. Combustion, Explosion, and Shock Waves (2021)

URANIUM HYDRIDE

Average ρ_0 = 10.920 g/cm³.

ρ_0 (g/cm³)	U_s (km/s)	U_p (km/s)	P (GPa)	V (cm³/g)	ρ (g/cm³)	V/Vo	Exp
10.920	2.766	.416	12.565	.0778	12.853	.850	im1 o
10.920	2.706	.416	12.293	.0775	12.904	.846	im1 o
10.920	2.747	.424	12.719	.0774	12.913	.846	im1 o
10.920	2.651	.428	12.390	.0768	13.022	.839	im1 o
10.920	2.688	.432	12.680	.0769	13.011	.839	im1 o
10.920	2.622	.454	12.999	.0757	13.207	.827	im1 o
10.920	2.982	.637	20.743	.0720	13.886	.786	im1 o
10.920	3.022	.638	21.054	.0722	13.842	.789	im1 o
10.920	2.906	.646	20.500	.0712	14.041	.778	im1 o
10.920	2.925	.664	21.209	.0708	14.127	.773	im1 o
10.920	3.119	.682	23.229	.0716	13.976	.781	im1 o
10.920	2.914	.687	21.861	.0700	14.289	.764	im1 o
10.920	3.002	.704	23.078	.0701	14.265	.765	im1 o
10.920	3.164	.715	24.704	.0709	14.108	.774	im1 o
10.920	3.124	.741	25.279	.0699	14.316	.763	im1 o
10.920	3.288	.892	31.832	.0666	15.020	.727	im1 o
10.920	3.301	.918	33.091	.0661	15.127	.722	im1 o
10.920	3.237	.930	32.874	.0653	15.322	.713	im1 o
10.920	3.338	.943	34.373	.0657	15.220	.717	im1 o

S. P. Marsh, *Lasl Shock Hugoniot Data* (1980)

- Experiment shock compression data of UH_3 are available for pressure up to 35 GPa.

2. Method

- **Computational method:**
- First-principles molecular dynamics（FPMD)
- The Rankine-Hugoniot equation:

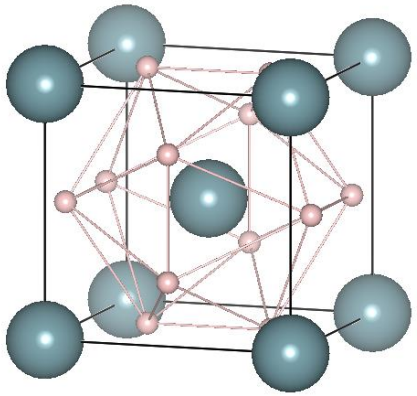
$$(E_1 - E_0) + 1/2\,(V_1 - V_0)(P_0 + P_1) = 0$$

$$V_1 = V_0(1 - u_p/u_s)$$

$$P_1 - P_0 = \rho_0 u_s u_p$$

Hugoniots

- Electronic structures: PCF, DOS, ELF
- Physical properties: Electrical conductivity (σ), thermal conductivity (κ), and optical reflectivity



2×2×2 cubic supercell

- **FPMD details**
- NVT ensemble; pressure range up to 200 GPa;
- Starting at ρ_0=11.12 g/cm^3 (α-UH_3) and ρ_0=11.33 g/cm^3 for α-UD_3 at 300 K;
- Time steps of 0.8 fs; 8000 steps totally
- The final 4000 steps equilibrated for property calculations
- GGA and GGA+U with U_{eff} = 2 and 4 eV (U_{eff} = U – J)

3. Results

Hugoniots

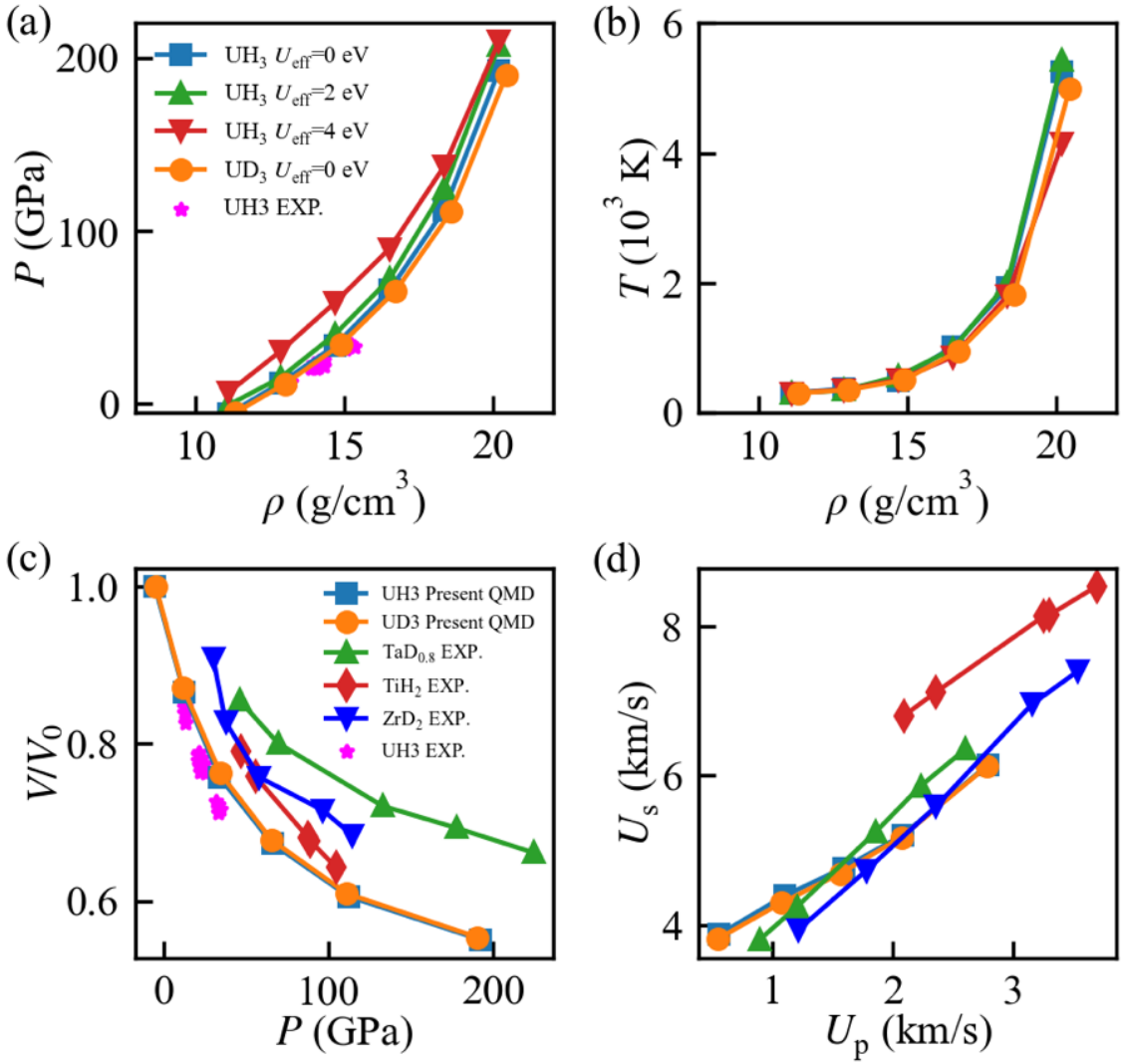


FIG. (a-b) Principal Hugoniot of UH_3 and UD_3 calculated with DFT+U method where U_{eff}= 0, 2, and 4 eV, respectively. (c) Normalized molar volumes of hydrides and deuterides as a function of pressure along the Hugoniot curve. (d) The velocity of the shock wave front versus the particle velocity.

- UH_3 and UD_3 have a similar equation of state along the Hugoniot;
- The pressure is higher with a larger U_{eff} for the same density;
- Standard PBE calculations are more reasonable in this study according to the experimental Hugoniot.
- The behavior of UH_3 (UD_3) under shock compression is similar to that of TiH_2, which might be associated with their similar cubic structures.

3. Results

Atomic structure

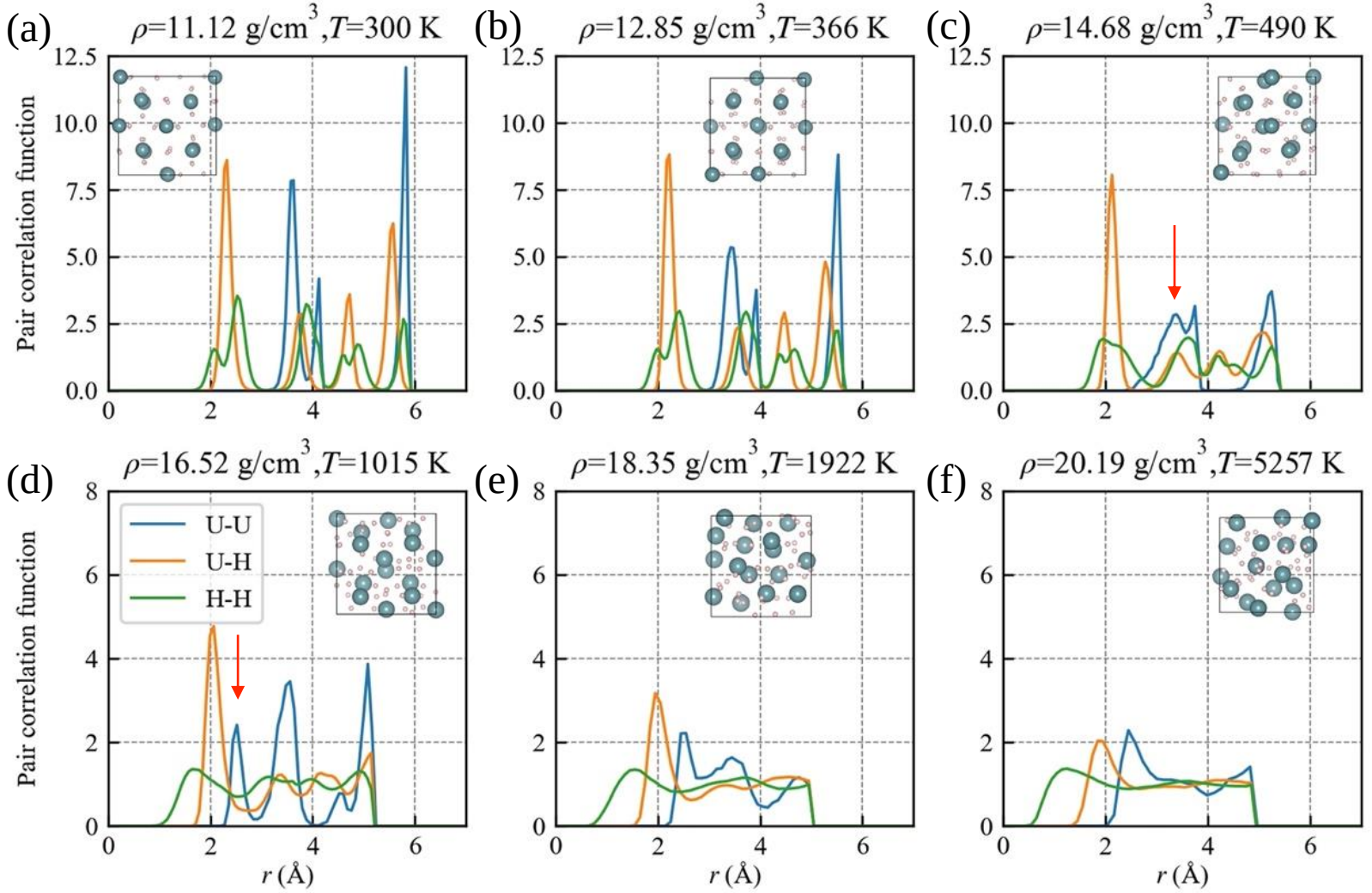


FIG. Pair-correlation functions for U-U (blue line), U-H (orange line), and H-H (green line) along the principal UH_3 Hugoniot.

- (a)→(b): Peaks are clearly split and most peak values decrease slightly;
- (b)→(d): Peaks are lowered and broadened. In (d), peaks of H-H vanish. The first peak of U-H at about r=2.1 Å is obviously higher than other U-H peaks; The first U-U peak at 3.36 Å for ρ =14.68 g/cm^3 moves to 2.5 Å suddenly.
- (d)→(f): Peaks of U-U vanish gradually; No peak at the equilibrium distance of the hydrogen molecule at 0.75 Å.

3. Results

Density of states & Fermi weight

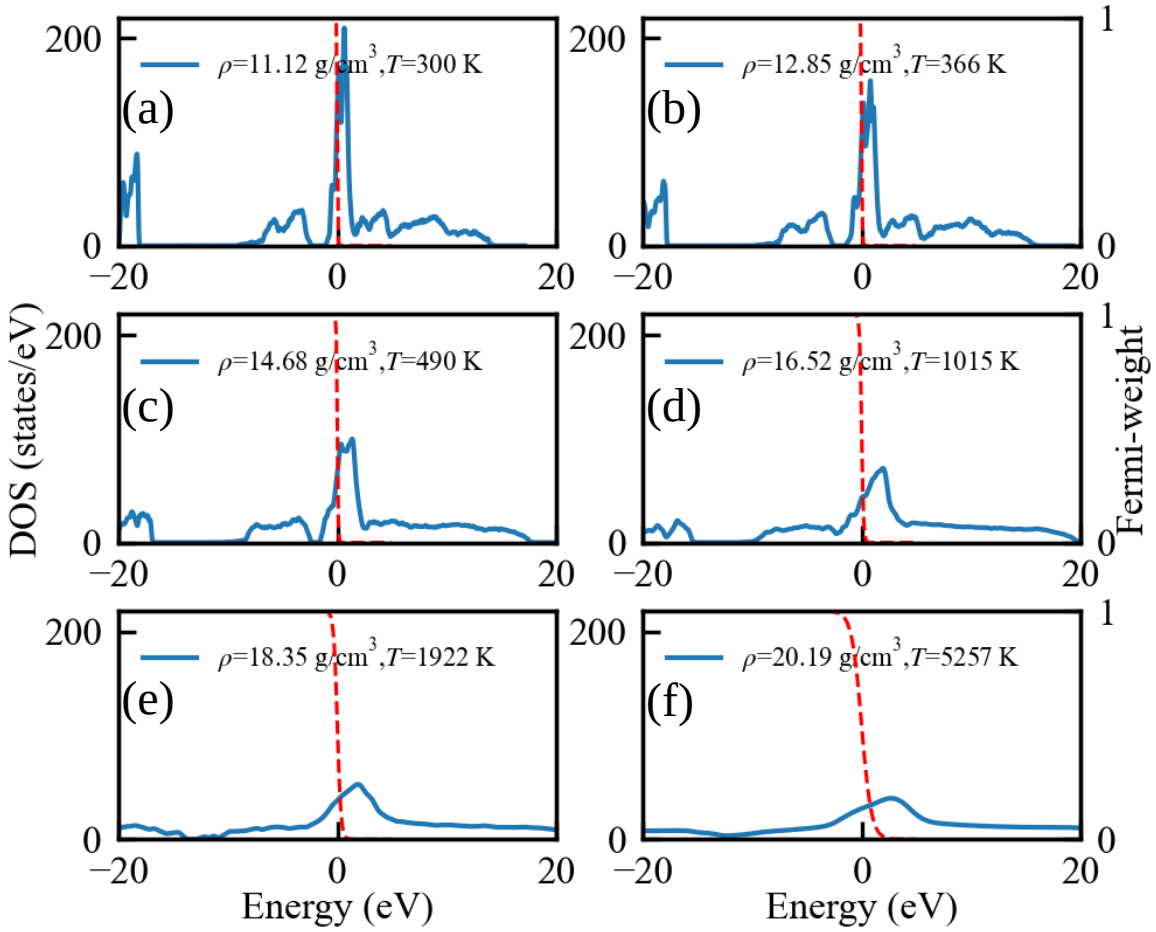
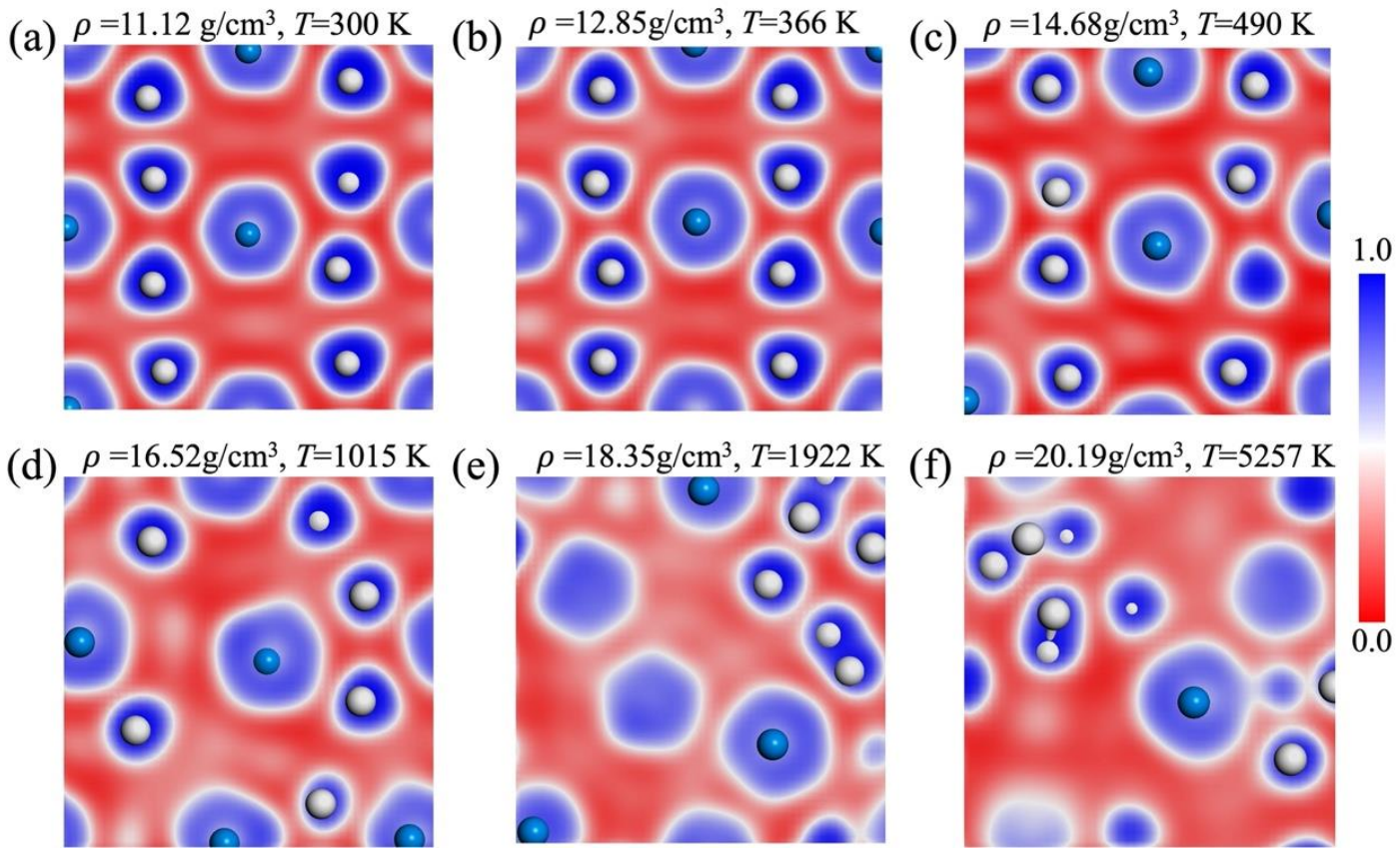


FIG. Electron density of states of α-UH_3 along the principal Hugoniot (blue solid line). The red dashed line shows the Fermi-weights $f(\varepsilon-\mu)$ for corresponding temperatures.

- (a)→(b): The electrons are relatively localized in the energy range of -10 ~ 15 eV ;
- (b)→(e): The DOS peak near the Fermi level is broadened, DOS gaps disappear due to the disordered structure after dissociation, which causes the energy levels to be continuous.
- (e)→(f): The shape of DOS is almost unchanged but slightly smoothed and the Fermi weight change obviously due to the increase in temperature.

3. Results

Electron localization function (ELF)



- U and H atoms are bonded ionically;
- H atoms deviate from the equilibrium position and show liquid-like feature in Fig. 6(d), while U atoms deviate from the equilibrium position in Fig. 6(e) at a higher density and temperature.

FIG. The electron localization functions (ELF) of (1 0 0) plane of α-UH_3 along the principal Hugoniot. The uranium and hydrogen atoms are denoted by blue and white balls, respectively.

3. Results

Dynamic electrical conductivity

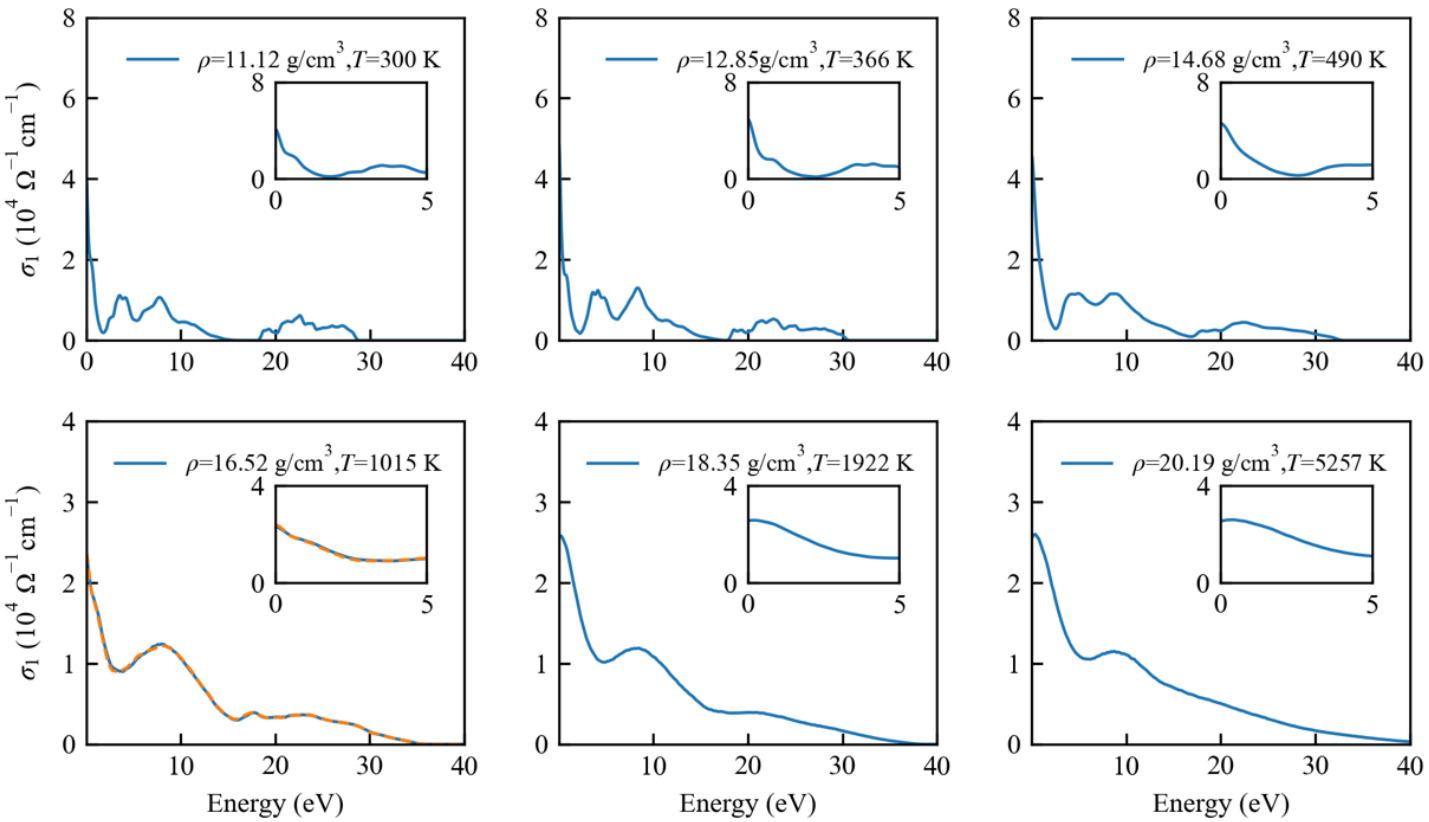


FIG. The real part of the dynamic electrical conductivity along the principal Hugoniot.

- The Kubo-Greenwood formula :

- $\sigma_1(\omega) = \frac{2\pi}{3\omega\Omega}\sum_{\boldsymbol{k}} W(\boldsymbol{k}) \sum_{j=1}^{N}\sum_{i=1}^{N}\sum_{\alpha=1}^{3}\left[f\left(\epsilon_{i,\boldsymbol{k}}\right) - f\left(\epsilon_{j,\mathbf{k}}\right)\right] \times \left|\left\langle\Psi_{j,\boldsymbol{k}}\middle|\nabla_{\alpha}\middle|\Psi_{i,\boldsymbol{k}}\right\rangle\right|^{2}\delta\left(\epsilon_{j,\boldsymbol{k}} - \epsilon_{i,\boldsymbol{k}} - \hbar\omega\right)$
- $\sigma_{dc} = L_{11} = \lim_{\omega\to 0} L_{11}(\omega)$
- $\kappa_e = L_{22} - \frac{L_{12}L_{21}}{L_{11}}$

➢ Drude-like shape in the low-frequency regime with the maximum located at zero frequency that is classical for liquid metals ;

➢ The curve of $\sigma_1(\omega)$ becomes smoother due to the distortion of the atomic structure and the temperature-induced broadening of the Fermi-Dirac distribution function, which lead to continuous density of states

3. Results

Transport properties

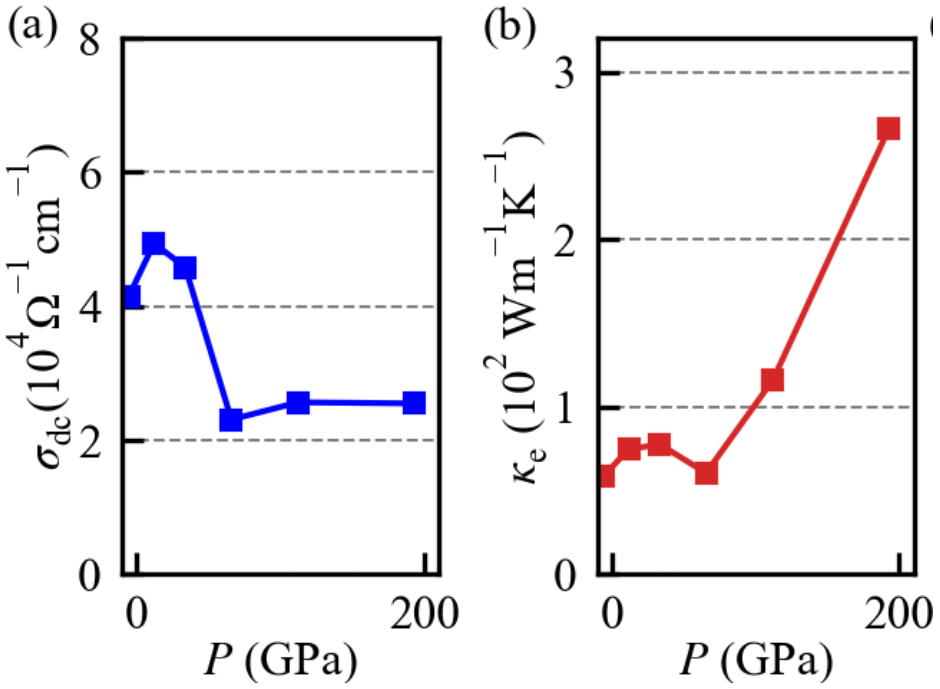


FIG. (a) The dc conductivity along the principal Hugoniot. (b) The electrical thermal conductivity along the principal Hugoniot.

- According to σ_{dc}, the status of α-UH_3 could be devided into three period:
  - 1) P < 12 GPa;
  - 2) 12 GPa ~ 66 GPa;
  - 3) P > 66 GPa.
- $\kappa_e$shows a similar trend with σ_{dc} for the pressures below 66 GPa ;
- For P > 66 GPa, κ_e obeys the Wiedermann-Franz law, $L = \frac{\kappa_e}{\sigma T} = Constant$, the dramatic increase should be owing to the huge temperature increase from 1015 K to 5257 K.

3. Results

Reflectivity

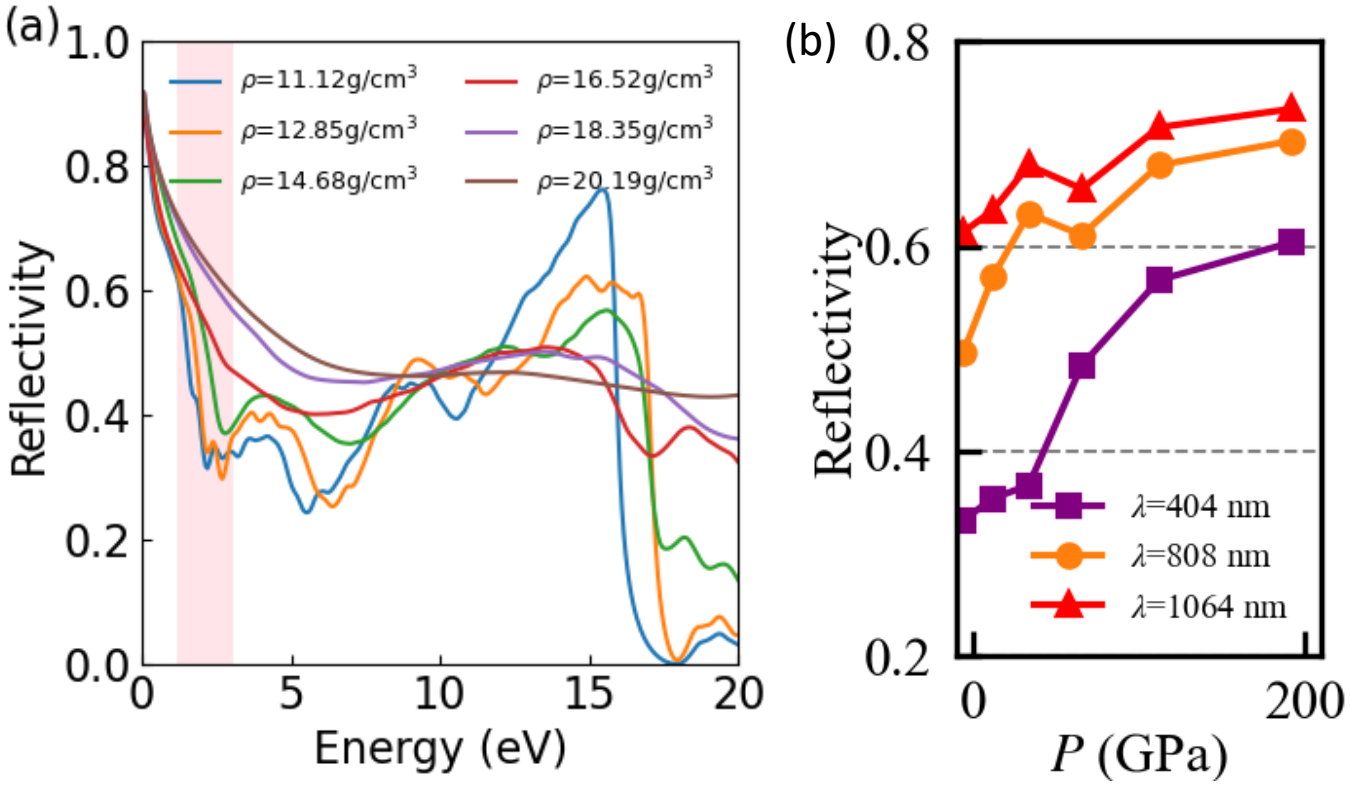


FIG. (a) Reflectivity as a function of photon energy for different UH_3 densities along the principal Hugoniot. (b) Optical reflectivity of shocked UH_3 for wavelengths 404 (purple square), 808 (orange circle), and 1064 nm (red triangle) along the Hugoniot.

- Kramers-Kronig relation :

$$\sigma_2(\omega) = -\frac{2}{\pi} P \int_0^\infty \frac{\sigma_1(\nu)\omega}{\nu^2-\omega^2} d\nu \; ; \varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$$

$$\varepsilon_1(\omega) = 1 - \frac{\sigma_2(\omega)}{\omega\varepsilon_0}; \; \varepsilon_2(\omega) = \frac{\sigma_1(\omega)}{\omega\varepsilon_0} \; ;$$

$$optical\ refraction: \; n(\omega) + ik(\omega)$$

$$n(\omega) = \frac{1}{\sqrt{2}}\sqrt{|\varepsilon(\omega)| + \varepsilon_1(\omega)} \; ; \; k(\omega) = \frac{1}{\sqrt{2}}\sqrt{|\varepsilon(\omega)| - \varepsilon_1(\omega)}$$

$$r(\omega) = \frac{[1-n(\omega)]^2+k(\omega)^2}{[1+n(\omega)]^2+k(\omega)^2}$$

➢ The reflectivities corresponding to different wavelengths become closer under compression.

4. Conclusions

- The variation of structures and properties under shock compression can be generally divided into three periods: the density increase of solid crystal that dominated by pressure increase (<12GPa), bond dissociation process caused by both pressure and temperature increase (12~66 GPa), and the activity increase of dense fluid atoms dominated by temperature increase (66~193GPa).

- The structure of U atoms is not dissociated below 66 GPa according to the PCF. No hydrogen molecule forms which implies that U is excellent in stable storage of hydrogen under shock compression up to 66 GPa.

- Experimentally measurable dc conductivity, electrical thermal conductivity, and optical reflectivity are all associated with the structural change, providing several ways to probe the dynamic compression process.

Thank you very much!

Q & A

Appendix

Convergence test for EOS

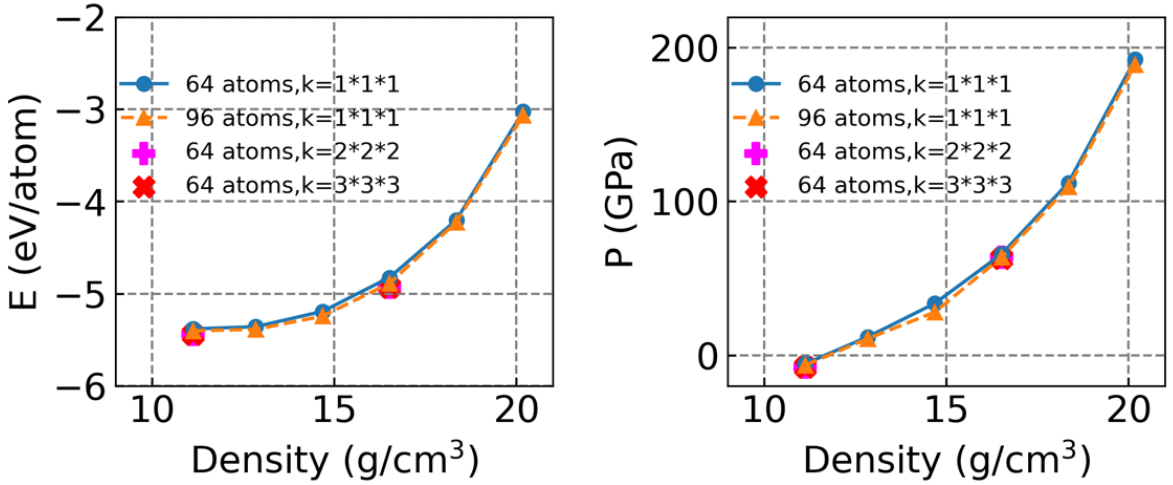


FIG. The energy per atom (left panel) and the pressure along the Hugoniot curve (left panel) obtained from first-principles MD simulations with different particle numbers and *k*-points meshes.

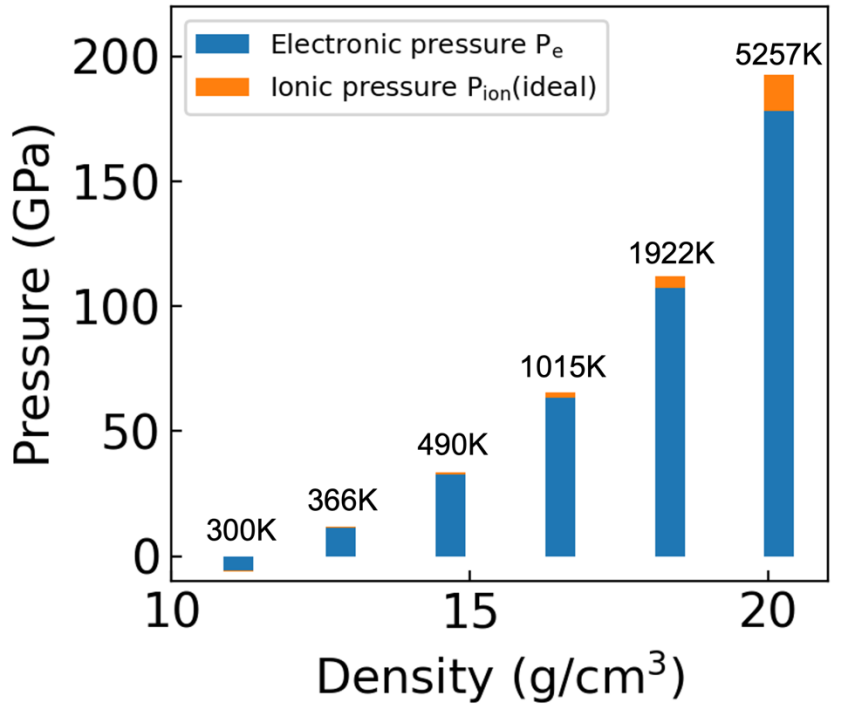


FIG. The electronic pressure and ionic pressure for UH_3 at different densities along the Hugoniot curve.

Appendix

Convergence test for K-G formula

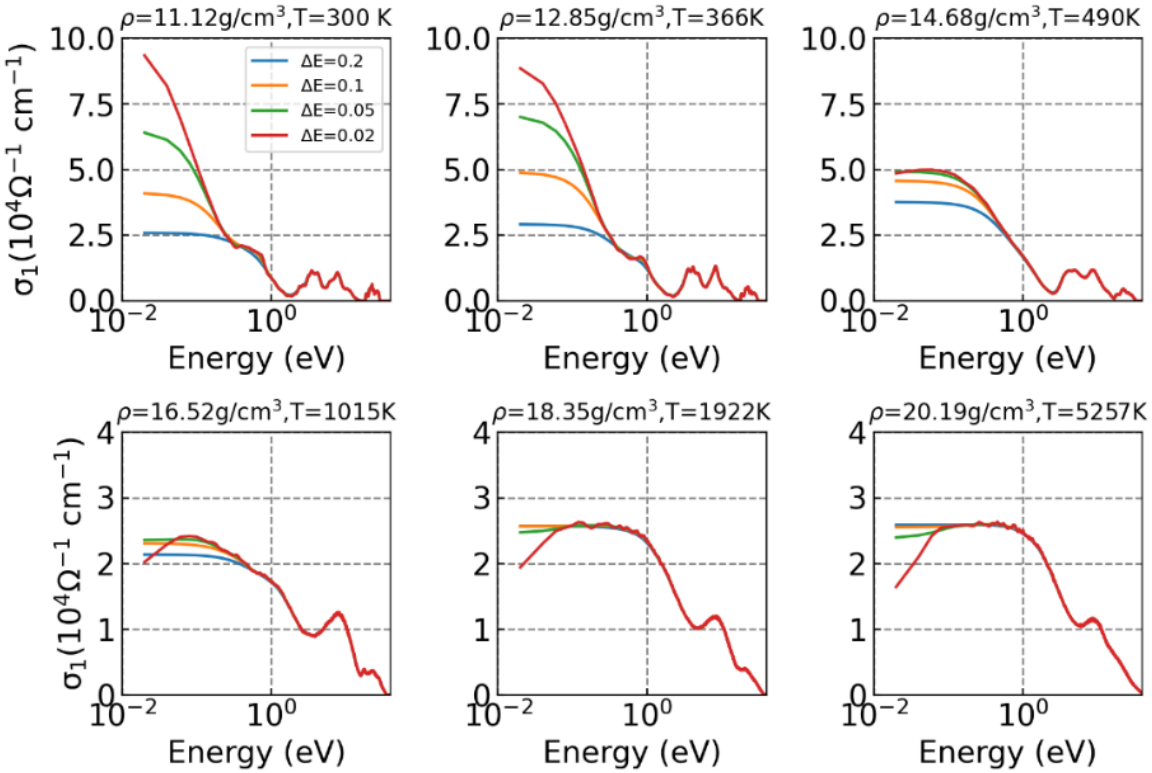


FIG. The real part of the dynamic electrical conductivity along the principal Hugoniot curve calculated with different ΔE values. Data have been averaged over 5 uncorrelated MD configurations.

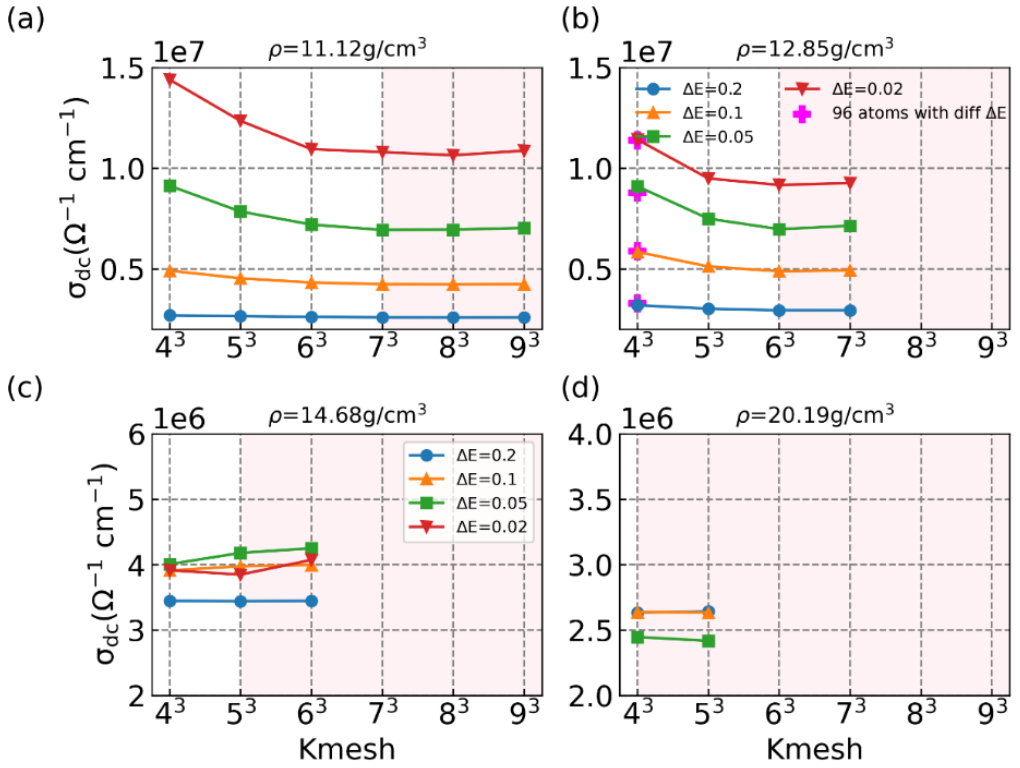
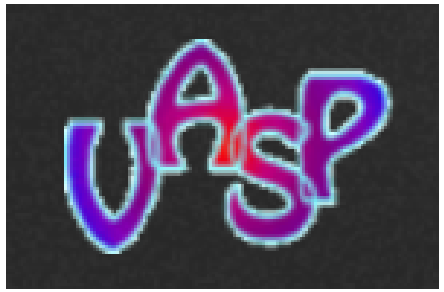


FIG. Dc conductivity versus k-mesh density for densities along the principal Hugoniot. The calculations were performed with different ΔE. The pink shaded area indicates the convergence of σ_{dc}.

Packages



https://www.vasp.at/

GreeKuP (GREEnwood-KUbo Program) code

https://github.com/dvknyazev/GreeKuP