13th International Conference on Physics of Non-Ideal Plasmas
Chernogolovka, September 13 – 18, 2009

Ab initio modeling of solids with hot electron subsystem

V.V. Stegailov

Joint Institute for High Temperatures of Russian Academy of Sciences

Moscow Institute of Physics and Technology

Ultrafast energy deposition into the condensed phase

↓

Electronic excitation

↓

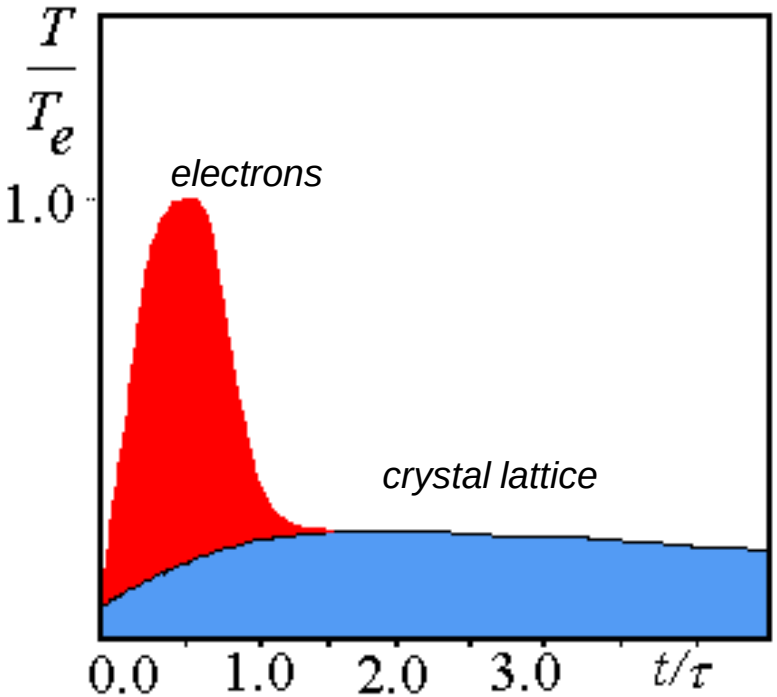
Relaxation of a transient non-equilibrium state on a fs-ns timescale

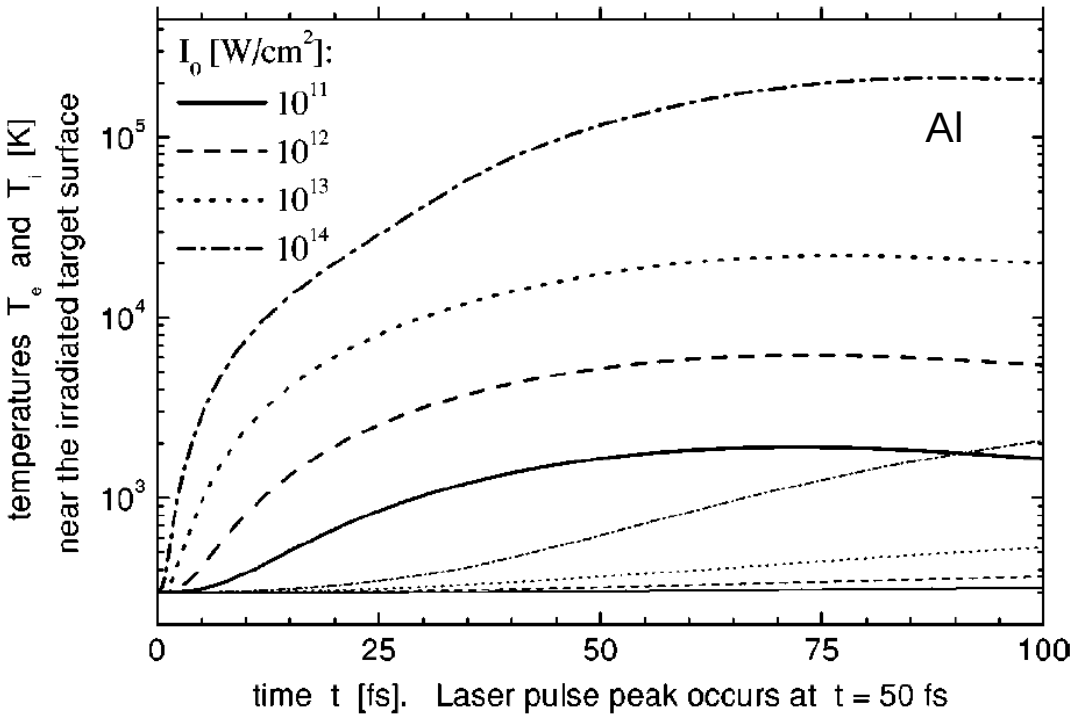
Goal: atomistic description based on first principles

Influence of the electronic system excitation on crystal lattice stability

Dynamics of the crystal lattice after femtosecond pulse irradiation

Two-temperature system
«cold» lattice – hot «electrons»





Fisher et al., 2001

Electronic density functional theory

Density Functional Theory

N-electron wave function

$$\Psi(\vec{r}^{\,N})$$

$$\Downarrow$$ Hohenberg-Kohn theorem

One-electron density

$$n(\vec{r})$$

$$\Downarrow$$ Kohn-Sham scheme

N one-electron orbitals

$$\Phi_1(\vec{r}),\ldots,\Phi_N(\vec{r})$$

Connection:

$$N\int d\vec{r}_2\ldots d\vec{r}_N\left|\Psi(\vec{r},\vec{r}_2\ldots\vec{r}_N)\right| = n(\vec{r}) = \sum_{i=1}^{N}\left|\Phi_i(\vec{r})\right|^2$$

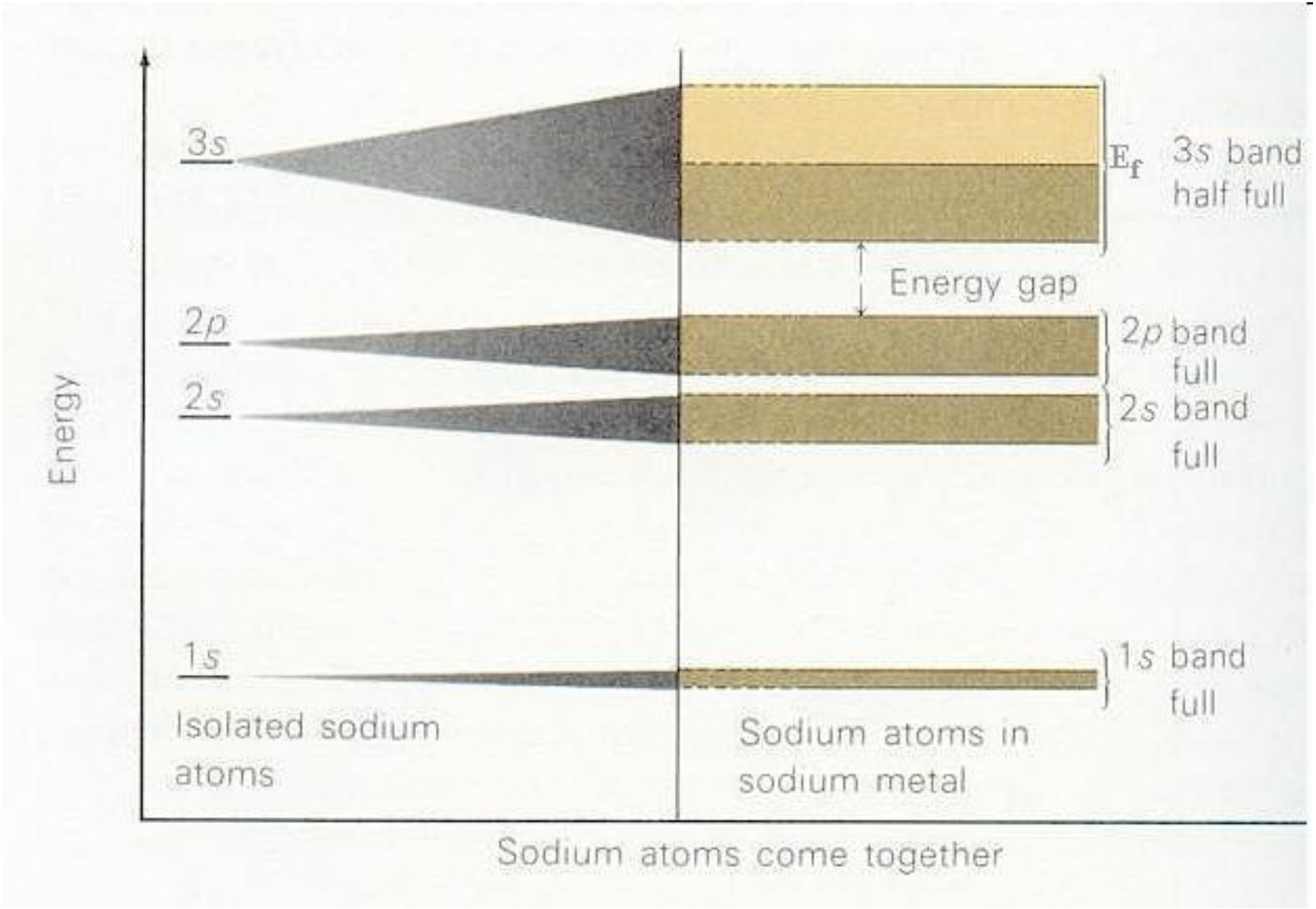
Density Functional Theory

$$E[n] = T_s[n] + V_H[n] + E_{xc}[n] + \int d\vec{r}\, n(\vec{r}) v(\vec{r})$$

$$T_s[n] = -\frac{1}{2}\sum_{i=1}^{N} \left\langle \Phi_i \middle| \nabla^2 \middle| \Phi_i \right\rangle$$

$$\left(-\frac{1}{2}\nabla^2 + \frac{\delta V_H[n]}{\delta n(\vec{r})} + \underbrace{\frac{\delta E_{xc}[n]}{\delta n(\vec{r})}} + v(\vec{r}) \right) \Phi_i = \varepsilon_i \Phi_i$$

approximations to the exchange-correlation term
LDA, GGA etc.


3s
2p
2s
1s
Energy
E_f
3s band half full
Energy gap
2p band full
2s band full
1s band full
Isolated sodium atoms
Sodium atoms in sodium metal
Sodium atoms come together

T>0: Mermin functional

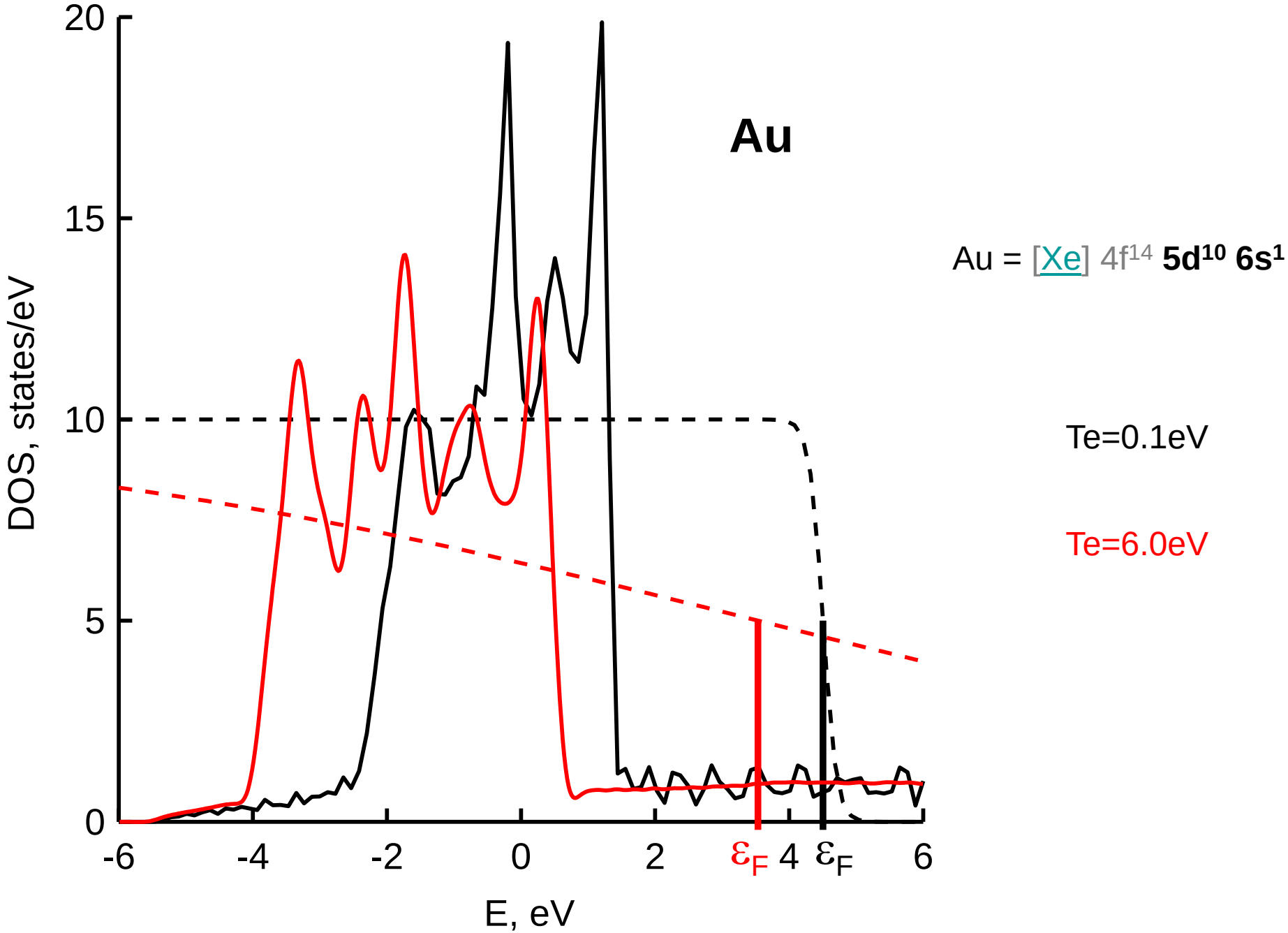
$$f_i(\beta) = \frac{1}{1 + \exp\left[\beta\left(\varepsilon_i - \mu\right)\right]}$$

$$n(\vec{r}) = \sum_{i=1}^{N} f_i(\beta) \left|\Phi_i(\vec{r})\right|^2$$

$$\Omega[n] = T_s[n] + V_H[n] + \Omega_{xc}[n] + \int d\vec{r}\, n(\vec{r}) v(\vec{r})$$

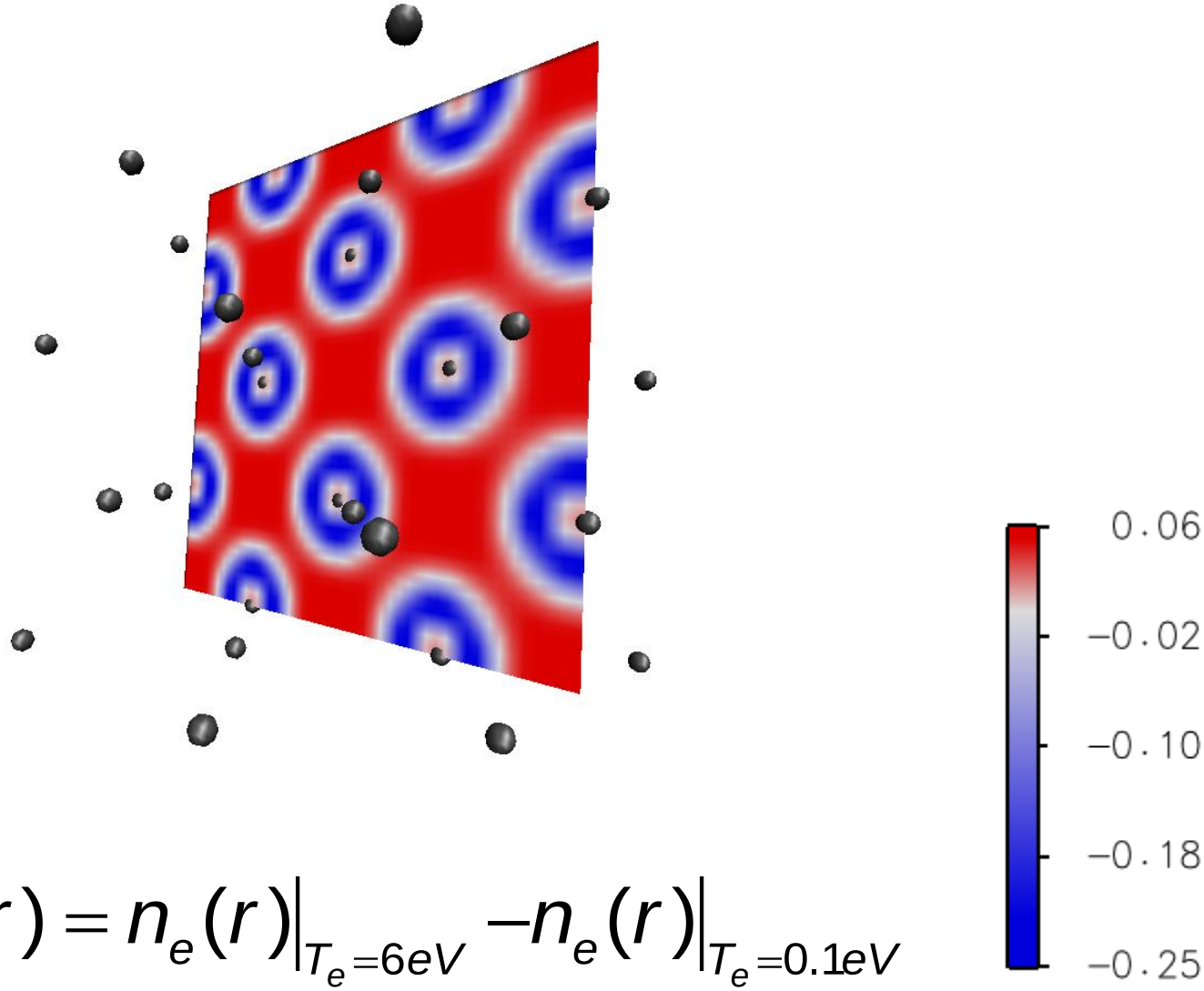
Mermin, 1965

Gold: electron DOS (d- and s-electrons)



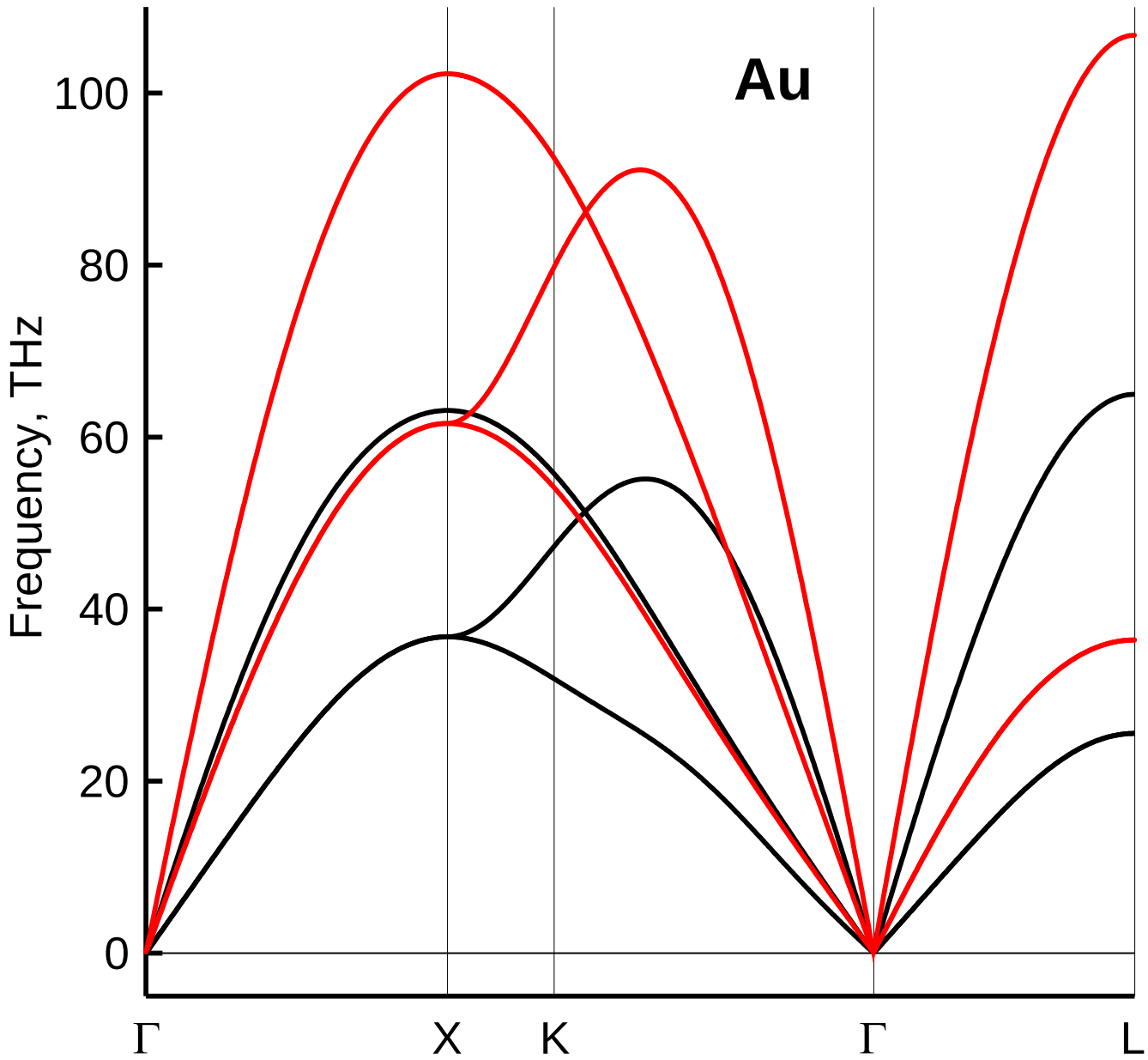
Redistribution of the electron density after the electron temperature increase

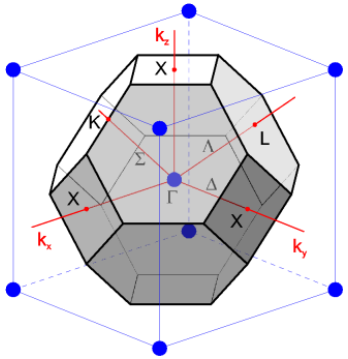
f.c.c. Au



$$\Delta n_e(r) = n_e(r)\big|_{T_e=6eV} - n_e(r)\big|_{T_e=0.1eV}$$

FCC gold phonon spectrum after pulse irradiation



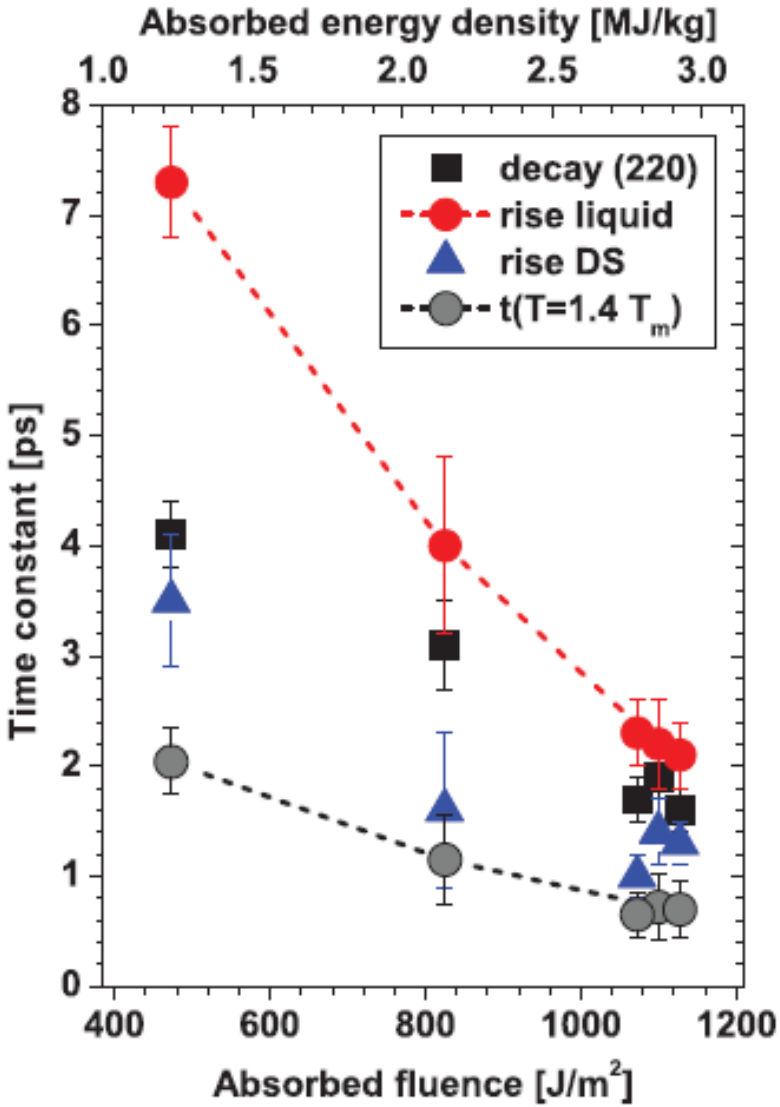


Te=0.1eV

Te=6.0eV

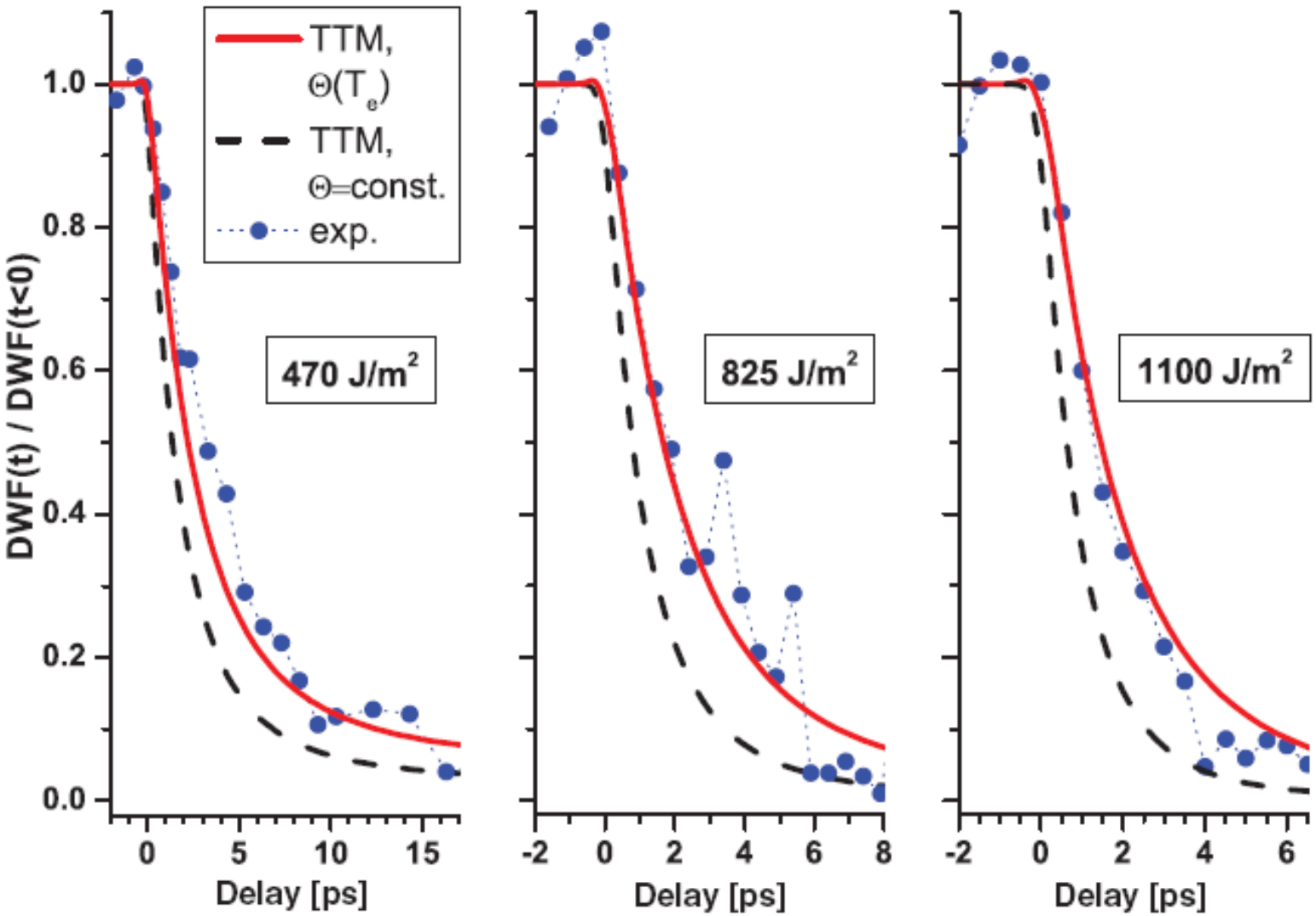
In agreement with
V. Recoules et al.
PRL 96 055503 2006

Experimental evidence for electronic bond hardening in gold



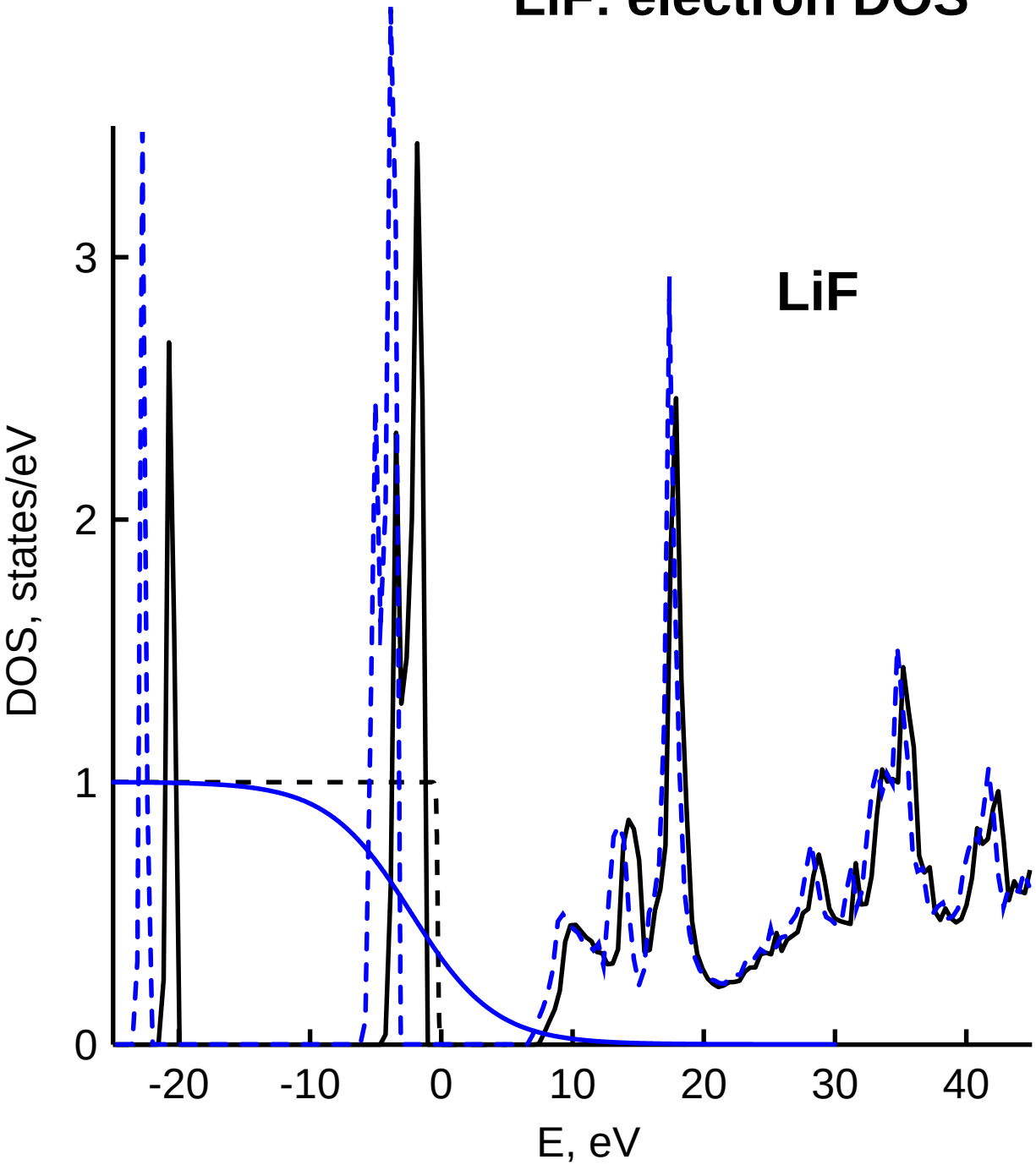
J. Edwards et al., Science, vol. 323, p. 1037, 2009

Experimental evidence for electronic bond hardening in gold



J. Edwards et al., Science, vol. 323, p. 1037, 2009

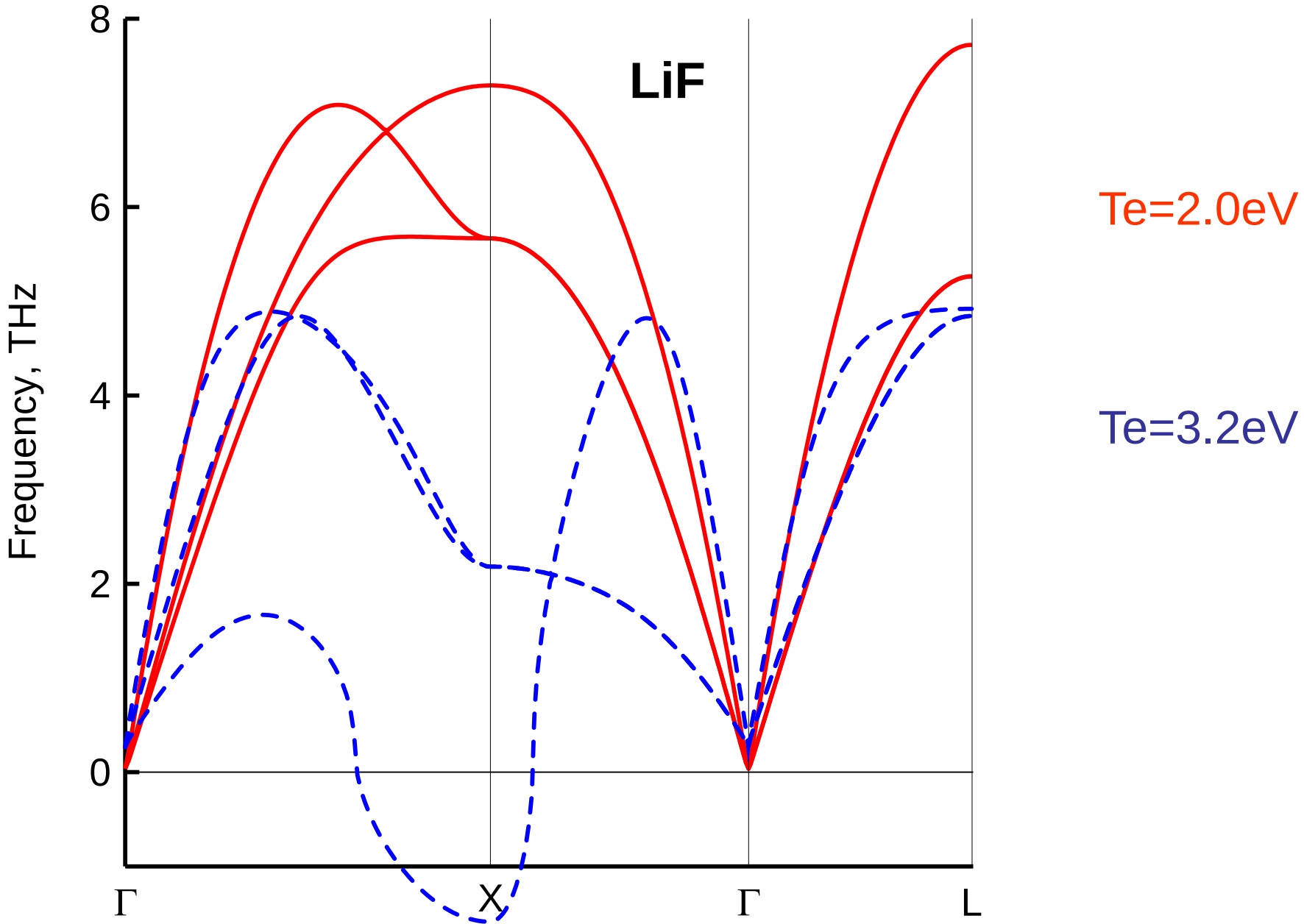
LiF: electron DOS



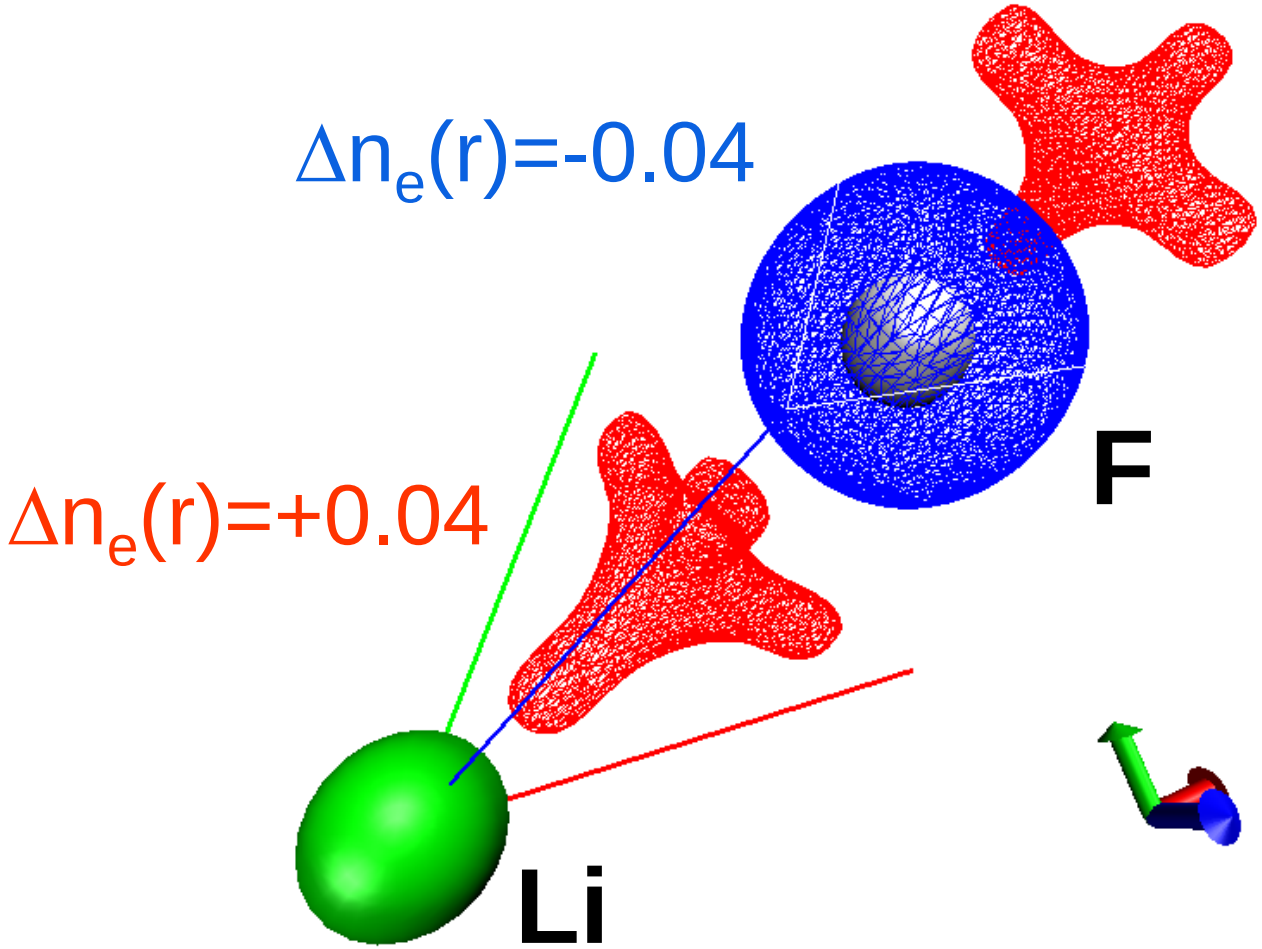
Te=0

Te=3.2eV

Phonon dispersion in LiF



Redistribution of the electron density due to the heating of the electron subsystem in the LiF crystal unit cell



Conclusions

The predictions of the bond hardening in d-metals made using the finite-temperature DFT calculations are now confirmed by experiments.

The excitation of the electronic subsystem results in the loss of mechanical stability of the fcc LiF lattice that is manifested as an appearance of the soft acoustic phonon mode. The corresponding redistribution of the electronic density implies that the originally strongly ionic interatomic interaction becomes more of covalent character with the rise of electronic temperature.