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Dynamics of Electron and Phonon Spectra, the Structural Phase Transitions and Melting of Sodium at *P*=0-100 GPa

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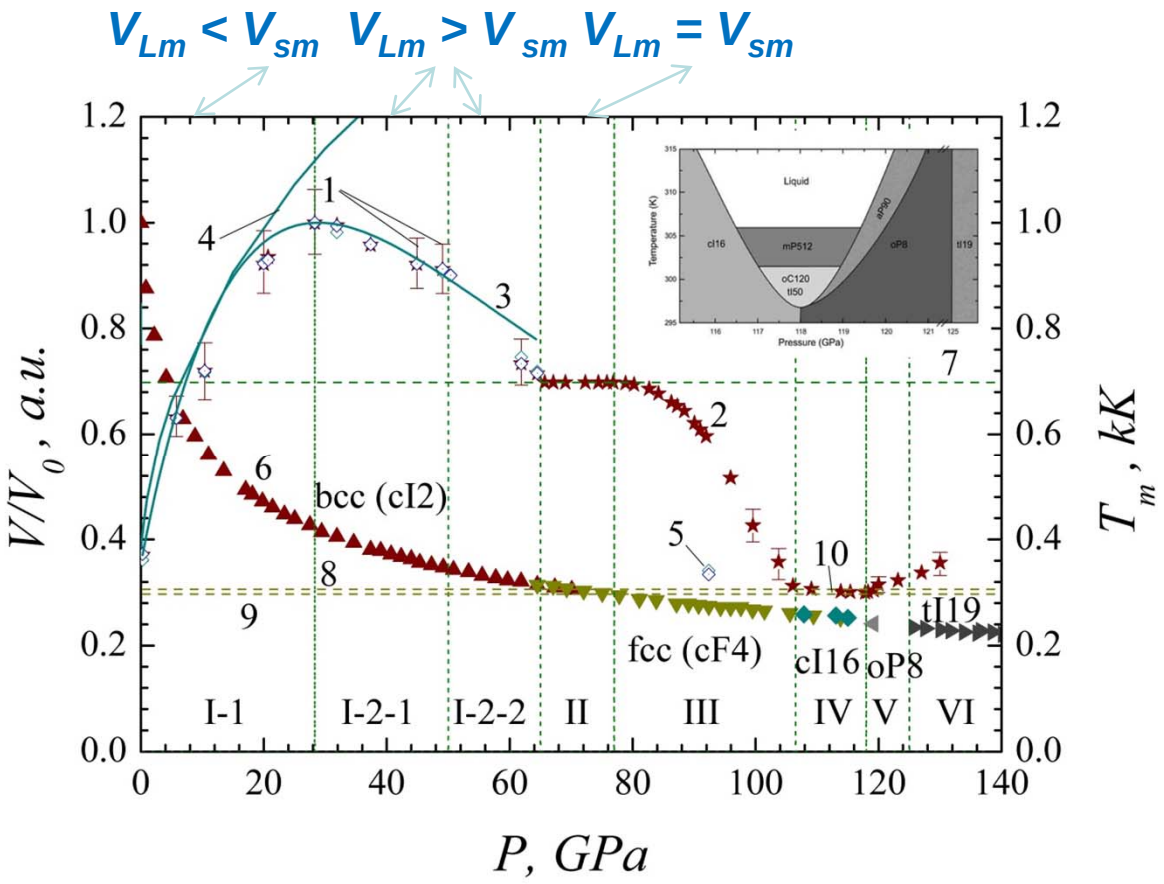
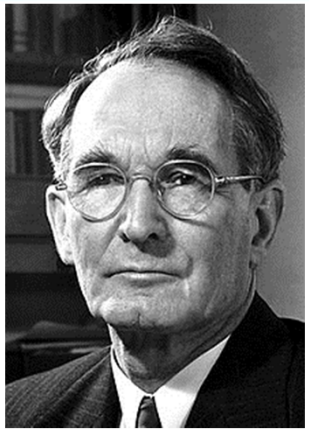
Outline

1. Motivation;
2. Some experimental facts;
3. Our results;
4. Discussion and conclusion;
5. Future work.

Motivation

The ultra-fast intense processes simulation within mechanics and electrodynamics of continuum media at local thermodynamic equilibrium requires equations of matter states and electronic transport coefficients for its determination. These coefficients are defined by charged particles scattering on density fluctuations, which within long-wave approximation are dependent of isothermal compressibility, i.e. equations of states for matter in different phases.



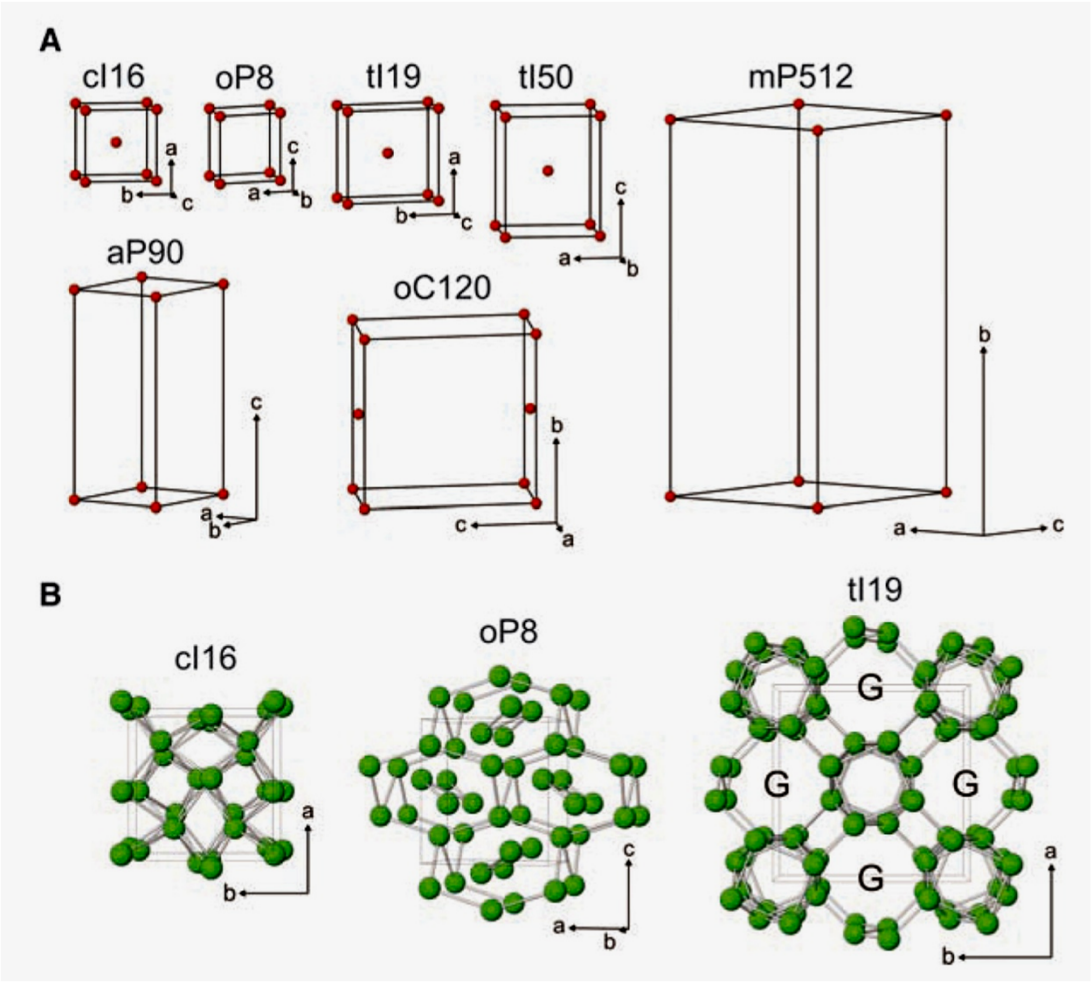

P.W. Bridgman


E. Gregoryanz

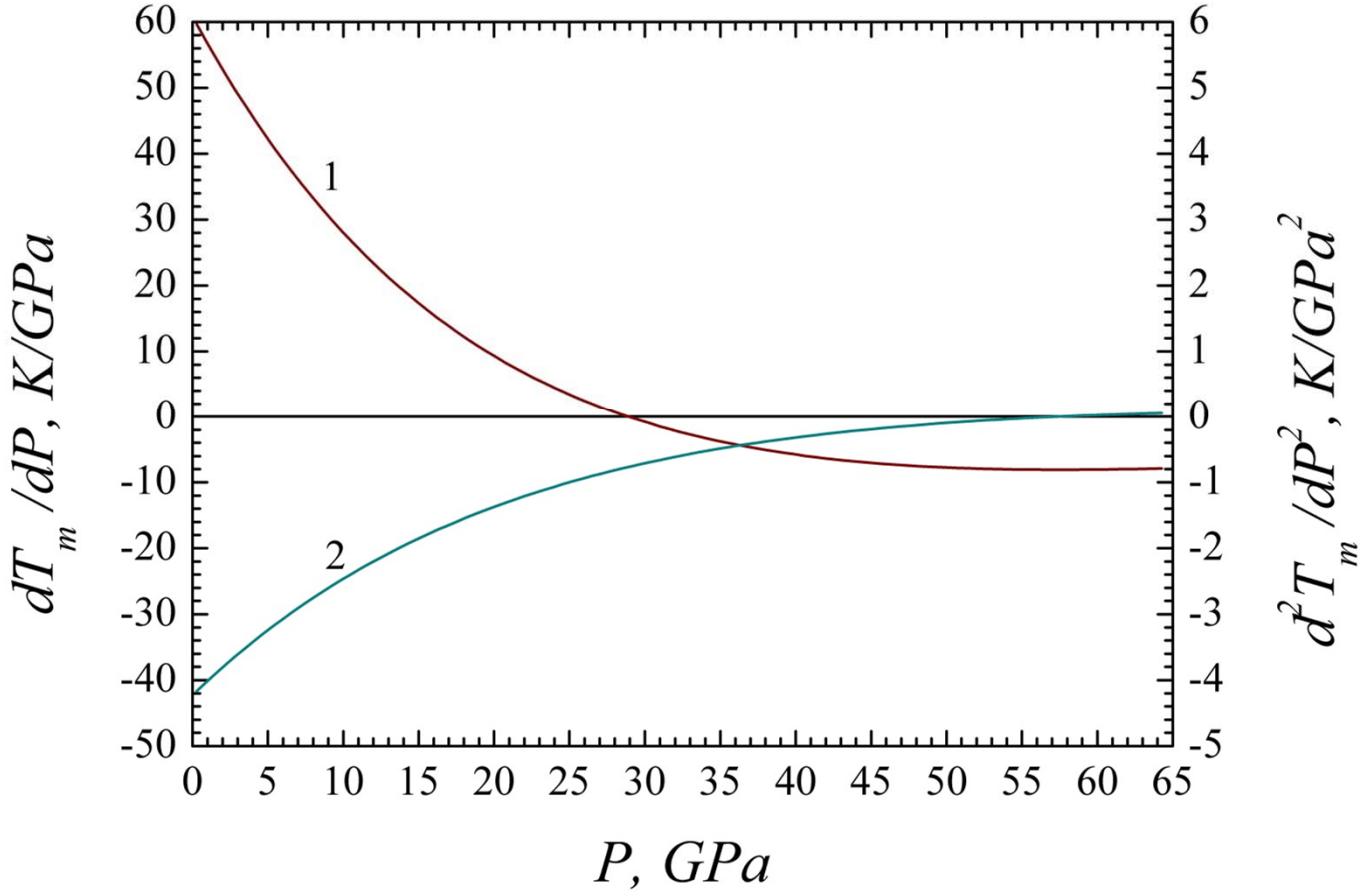

R.J. Nelmes


M.I. McMahon

Fig. 1. Experimental (1, 2) [E. Gregoryanz et al. // *PRL*, 2 $_{005}$, **94**, 185202] and theoretical (4) [N.B. Volkov and E.A. Chingina. //*J. of Phys.: Conf. Series*, 2015, **653**, 012084], (3, 5-diamonds) [present work] melting curves; (6) experimental curve of *V/V0* [C. L. Guillaume et al., *Nature Physics*, **7**, 211-214 (2014)]. On an insert the crystal structures corresponding a minimum of the melting curve are shown [E. Gregoryanz et al. // *Science*, 2008, **320**, 1054].



The unit cells and some crystal structures corresponding to minimum on sodium melting curve [E. Gregoryanz et al., *Science*, 320, 1054 (2008)].**



The first and second derivatives of the curve 3 on Fig. 1 (present work).

The Klayperon-Klausis equation:

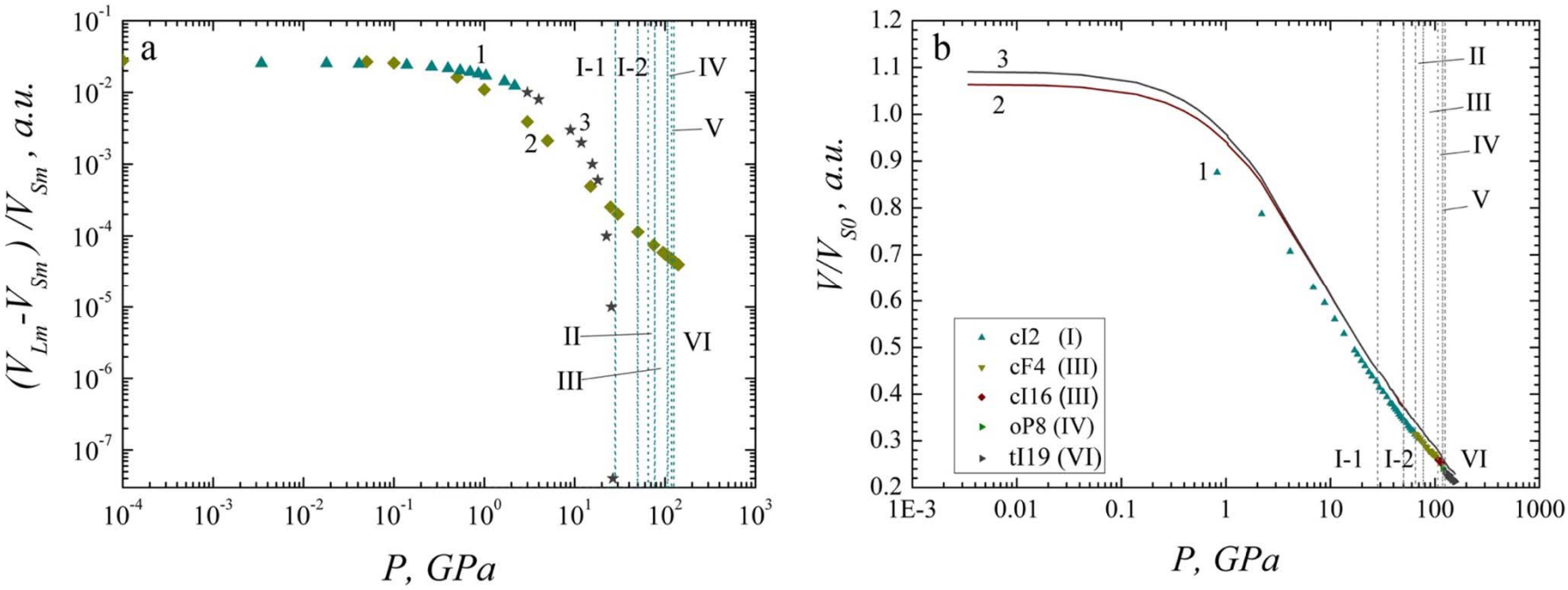
$$\frac{dT_m}{dP} = \frac{T_m \Delta_m V}{\Delta_m H} = \frac{T_m \Delta_m V}{T_m \Delta_m S} = \frac{\Delta_m V}{\Delta_m S} = \frac{V_{Lm} - V_{sm}}{S_{Lm} - S_{sm}}.$$

In points of a maximum and a minimum of the melting:

$$\frac{dT_m}{dP} \equiv 0, \text{ i. e. } \Delta_m V = V_{Lm} - V_{sm} \equiv 0, \Delta_m S = S_{Lm} - S_{sm} > 0.$$

$$\text{If } \frac{dT_m}{dP} < 0, \text{ then } \Delta_m V = V_{Lm} - V_{sm} < 0, \Delta_m S = S_{Lm} - S_{sm} > 0.$$

Why? Growth of the cold energy and/or increase of the crystal lattice anharmonizm with pressure growth? Or other reasons?



Left: Sodium volume-jump on the melting curve vs pressure: 1 (triangles) – experimental data [S.M. Stishov // *Sov. Phys. Usp.*, 1975, **17**, 625]; **2 (diamonds) -** [N.B. Volkov and E.A. Chingina. //*J. of Phys.: Conf. Series*, 2015, **653**, 012084]; **3 (stars)** – our extrapolation of the experimental data.

Right: Qualitative picture of change of relative volume of solid and liquid sodium on the melting curve: 1 - change of volume of solid sodium far from the curve (experiment); curves of volume solid (2) and liquid (3) sodium on the melting curve.

In our opinion, the point of *P*=28.3 GPa represents a critical point of the orientation transition "an order-disorder" (phase transition of the II sort) that shapes in with the melting (phase transition of the I sort). According to Patashinsky A. Z. with coauthors the order parameter of an orientation transition for lattices of the cubic singoniya has an appearance:

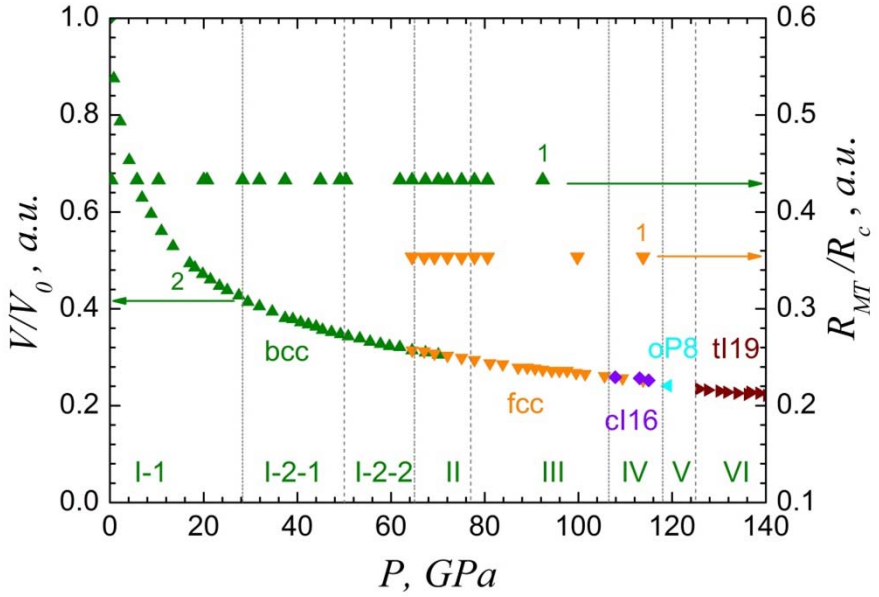
$$T^{ijkl}(\mathbf{r}) = \sum_{\alpha=1}^{3} U^{i\alpha}(\mathbf{r}) U^{j\alpha}(\mathbf{r}) U^{k\alpha}(\mathbf{r}) U^{l\alpha}(\mathbf{r}) - \frac{1}{5}\left(\delta^{ij}\delta^{kl} + \delta^{ik}\delta^{jl} + \delta^{il}\delta^{jk}\right).$$

The matrix $U^{ij}(\mathbf{r})$ representing a rotation operator $\hat{g}(\mathbf{r})$ sends the local coordinate axes into the basis vectors of global coordinate systems. Then at *P*=28.3 Gpa and *P*=64.5-77.8 Gpa

$$\left\langle T^{ijkl}(\mathbf{r}) \right\rangle \begin{cases} = 0 \text{ for } T \geq T_m \\ \neq 0 \text{ for } T < T_m \end{cases}.$$

For description of the orientation transition order-disorder can be used the well-known mathematical apparatus of theory of the phase transitions of the II sort (see, for example, the book: Yu. A. Izyumov, V. I. Syromyatnikov. Phase transitions and crystals symmetry).

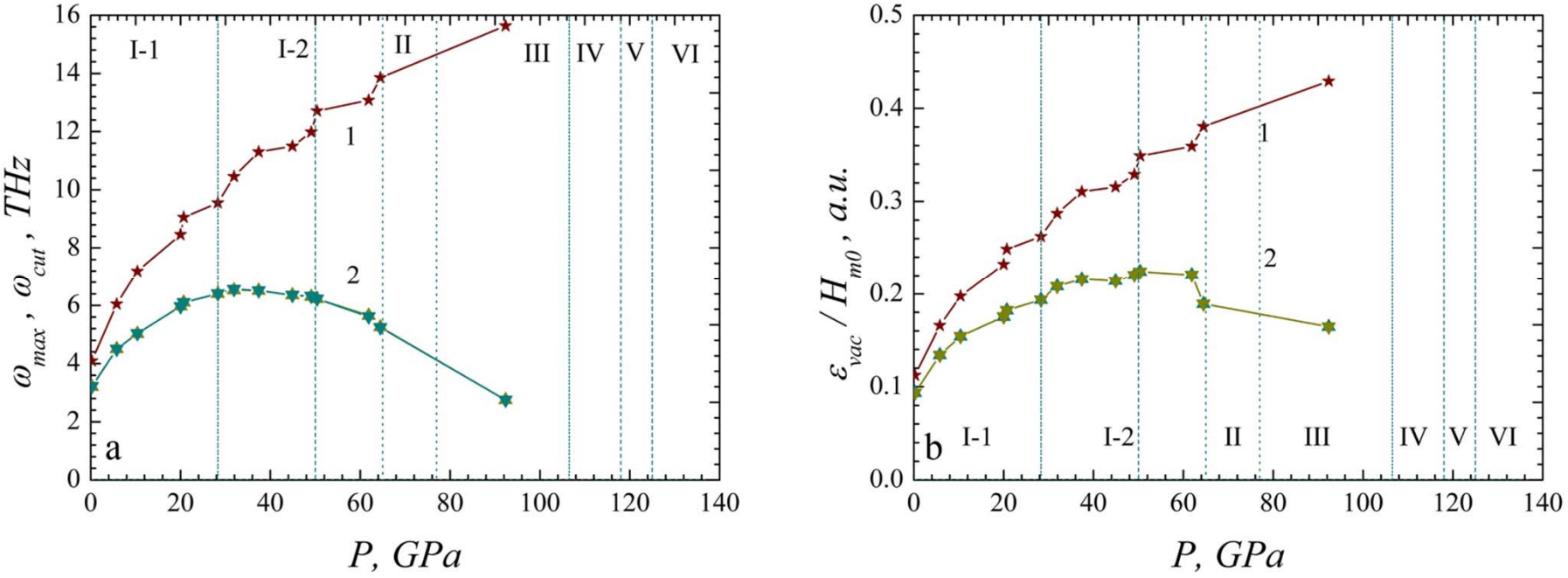
We used the software package of LMTART-7 (Savrasov, 1996; 2004] for *ab initio* finding of phonon and electron spectra, as well as of a total interaction energy between electrons and sodium nuclei. Dynamics of a lattice was computed using linear response method within well-known density functional theory by LMTART-7. The exchange-correlation potential (Vosko-Wilk-Nussair, 1980) was considered in a generalized gradient approximation (Perdew-Burke-Ernzerhof, 1996). We used a pseudo-potential method in plane wave expansion (PLW). The PLW expansion is a full potential approximation which uses non-overlapping muffin-tin spheres, where the potential is represented via spherical harmonics, expansion, and the interstitial region where the potential is expanded in plane waves. The full potential regime provides the best accuracy at the price of increasing computational time (Savrasov, 1996; 2004). The number of plane waves was used 14146, the plane-wave energy cutoff was 138.1 Ry (up to 250 Ry). Integration on Brillouin zone was carried out on a grid 32*32*32 special (Monkhorst--Pack) k-points. Phonon spectra were calculated by means of the interatomic power constants on the basis of 35 basic q-vectors in the irreducible Brillouin zone (a grid 8*8*8).



Relative radius of the MT sphere and volume both vs pressure.

We use well-known Lindeman measure for finding the melting temperature of sodium:

$$\sqrt{\left\langle\left\langle u^2(T_m)\right\rangle\right\rangle} = L\cdot d_{NN} \Rightarrow \begin{cases} \left(Ld_{NN}\right)^2 - \dfrac{\hbar}{2M}\displaystyle\int_{\omega_{cut}}^{\omega_{\max}} \frac{g_{ph}(\omega)}{\omega}\coth\frac{\hbar\omega}{2T_m}d\omega = 0; \\ T_m = \left(Ld_{NN}\right)^2 M\left(\displaystyle\int_{\omega_{cut}}^{\omega_{\max}} \frac{g_{ph}(\omega)}{\omega}d\omega\right)^{-1} \quad \text{for } T_m \gg \hbar\omega. \end{cases}$$



The boundary (1) and cutoff (2) frequencies (left) and energy of the vacuum oscillations (the curve 1 is received with use of boundary frequency and 2 – with help of LMTART-7) (right) both vs pressure.

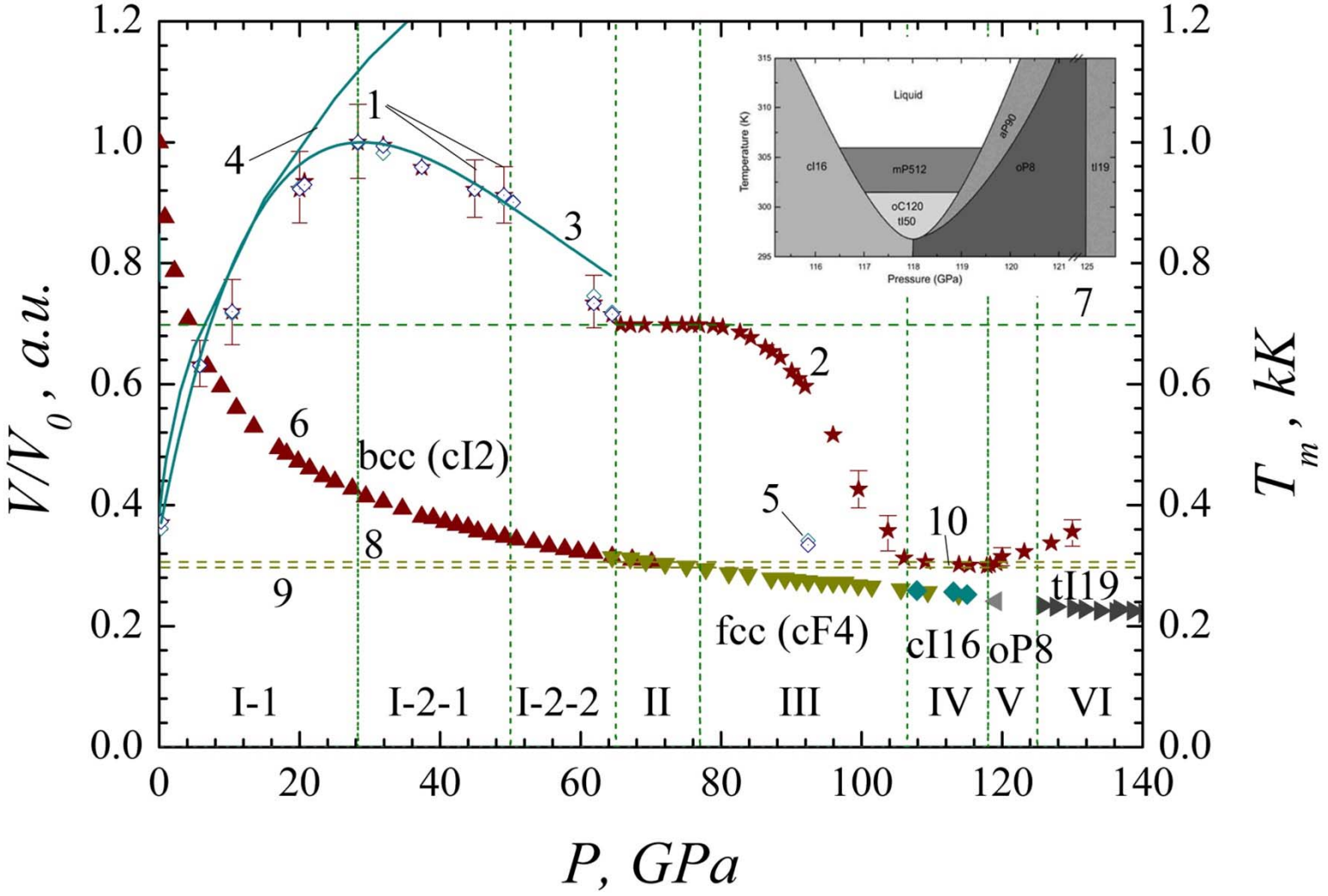
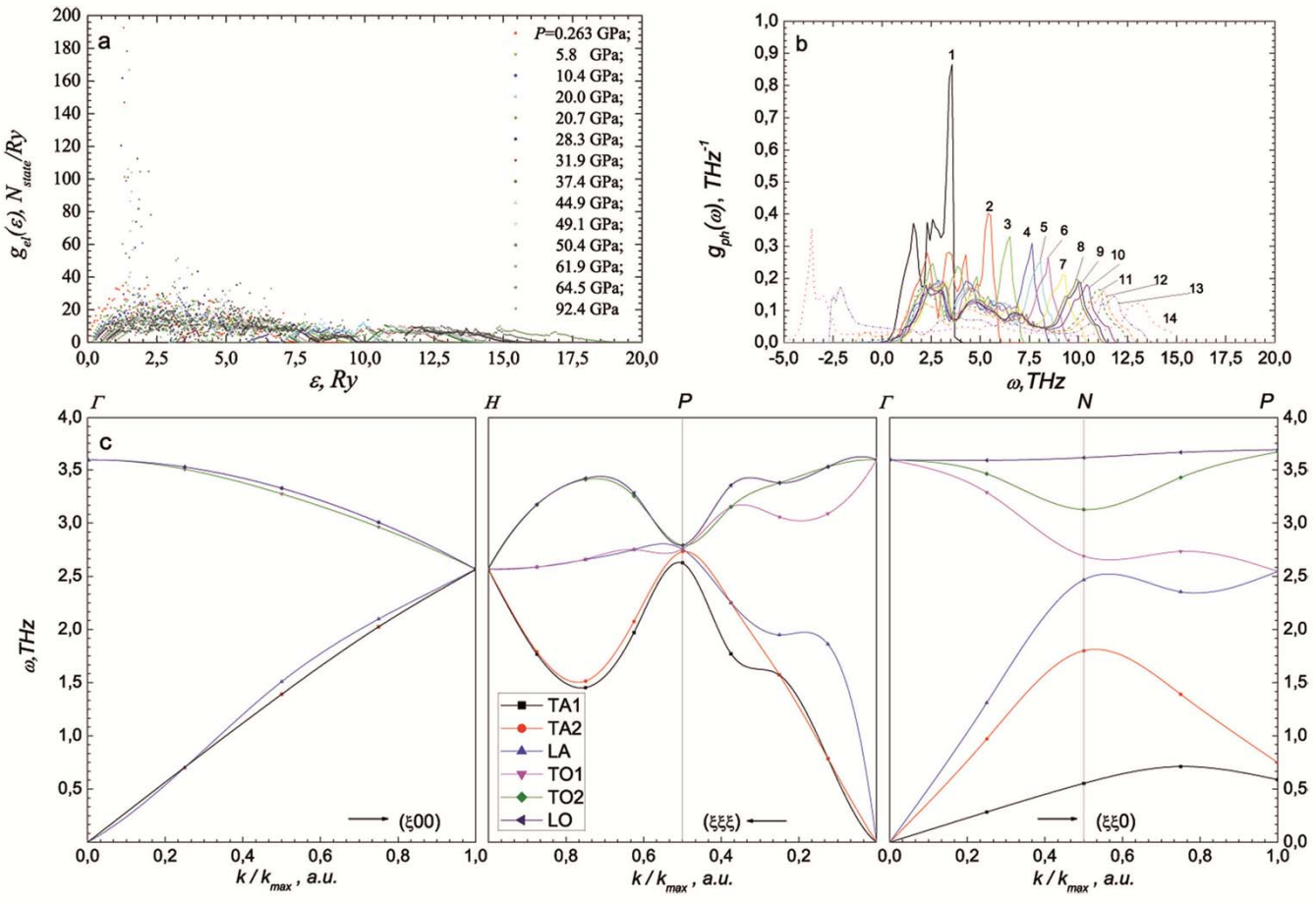
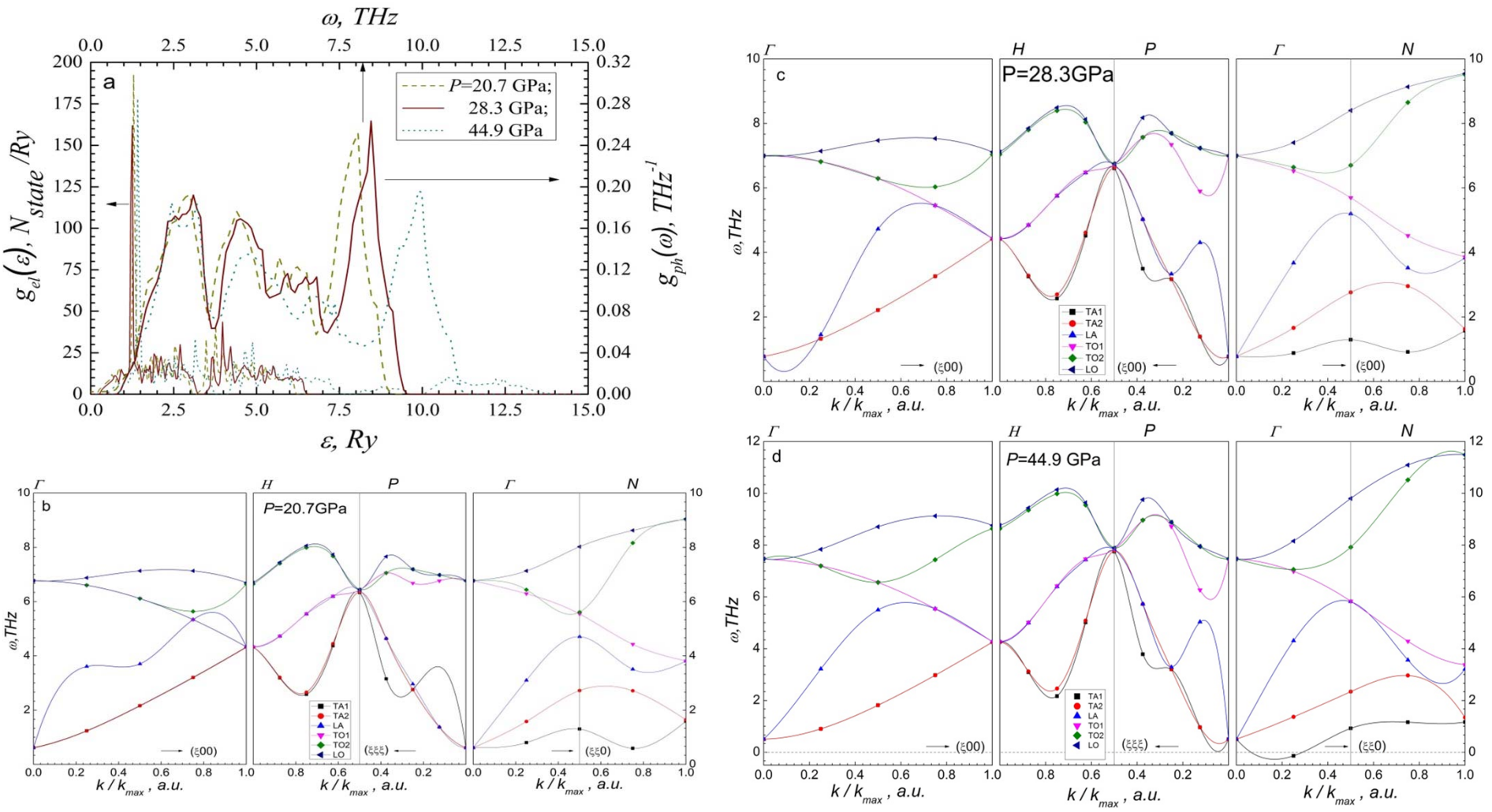

V/V0, a.u.
Tm, kK
P, GPa
bcc (cI2)
fcc (cF4)
cI16
oP8
tI19
I-1
I-2-1
I-2-2
II
III
IV
V
VI
Liquid
cI16
mP512
oC120
tI50
aP90
oP8
tI19
Temperature (K)
Pressure (GPa)

Fig. 1a

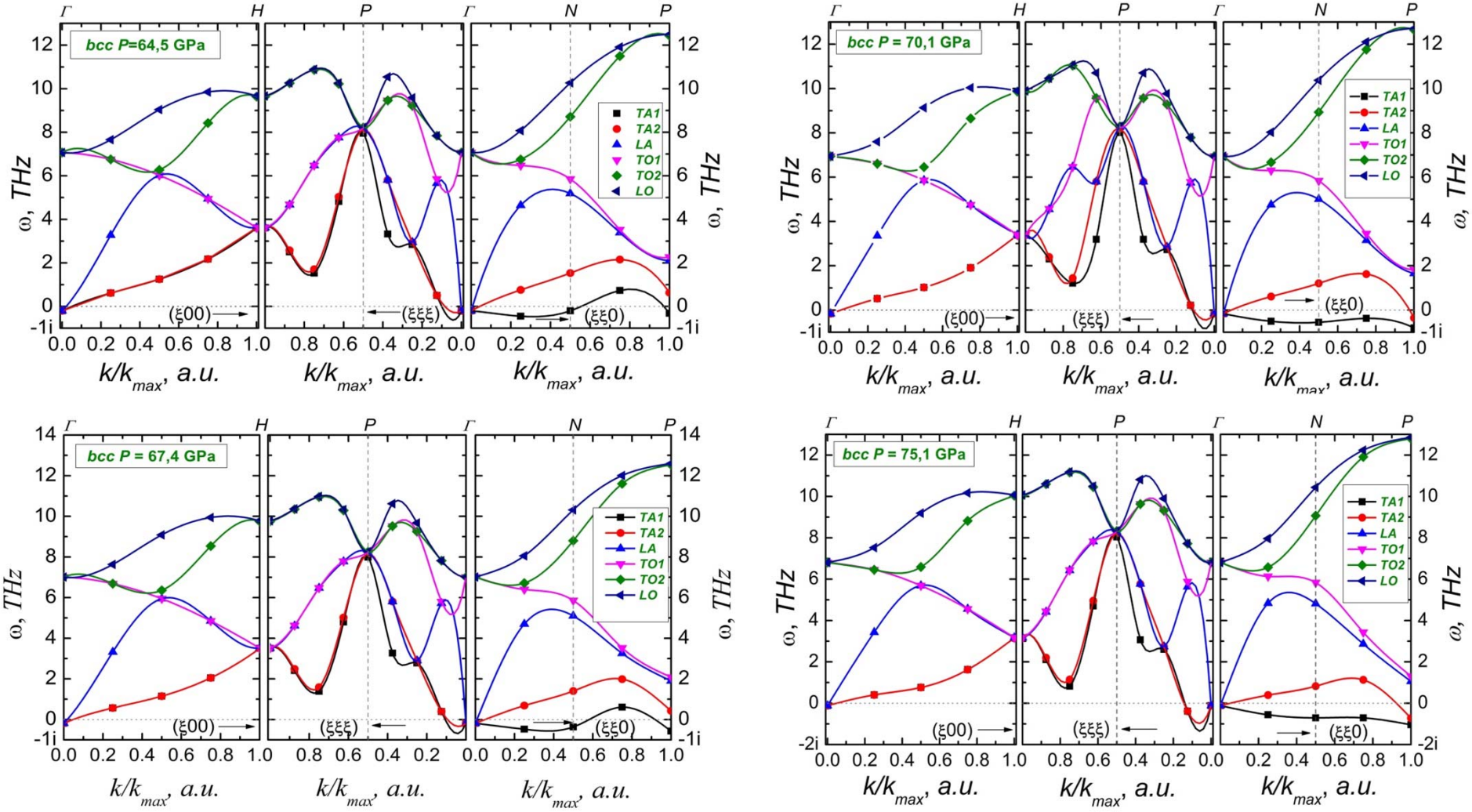


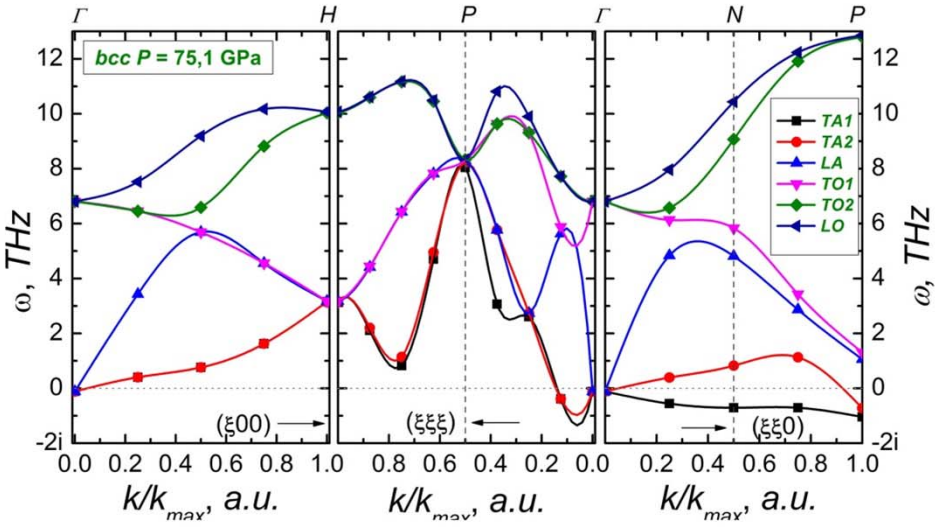
Densities of electron (a) and phonon (b) states, as well as the phonon spectrum at P = 0.263 GPa (c).



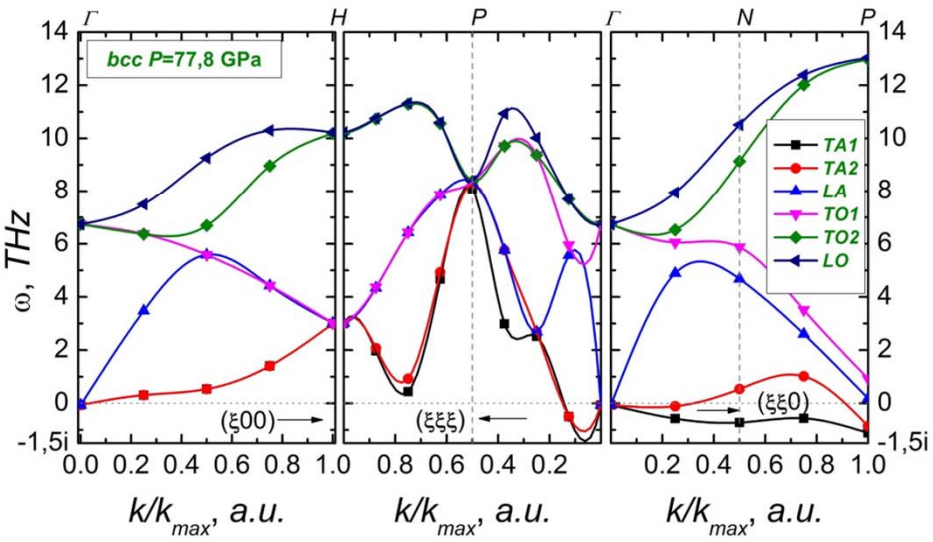
Densities of electron and phonon states (a), as well as phonon spectrum (b, c, d) both near maximum of the melting curve for Na.

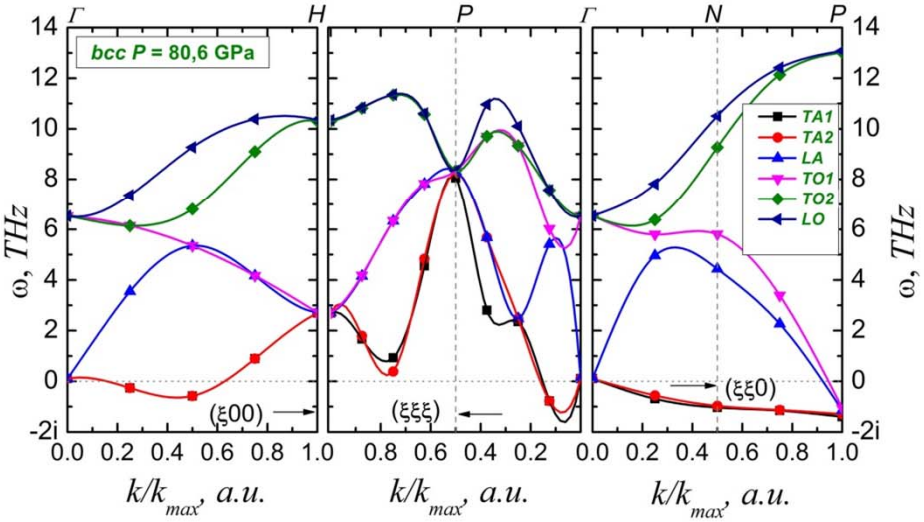
Phonon spectrum of the bcc sodium for cI2->cI4 transition



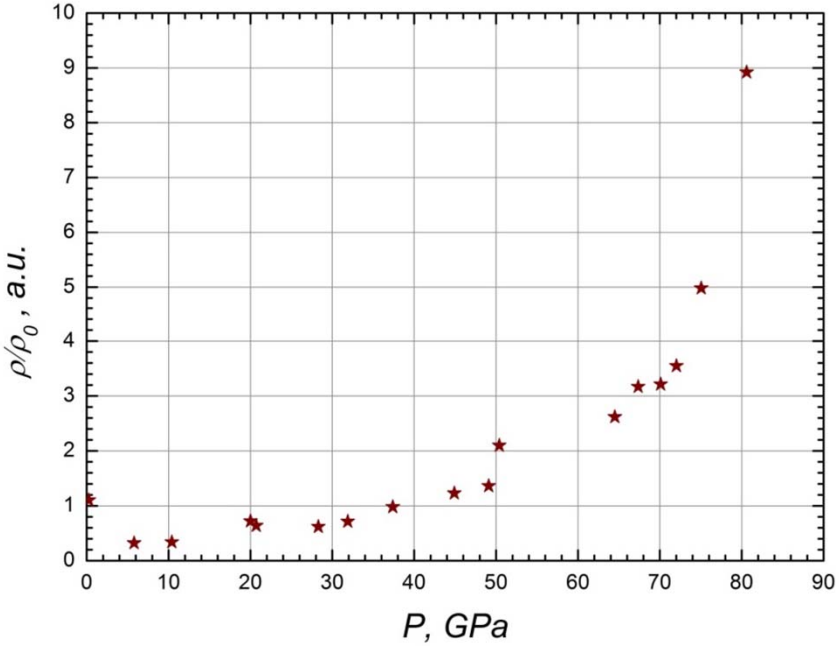


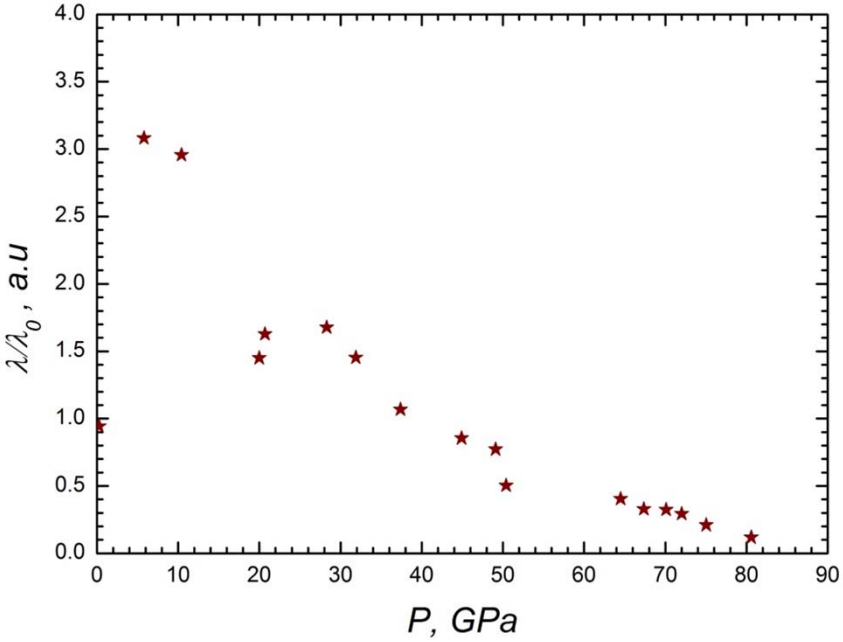
Phonon spectrum of the bcc sodium for cI2->cI4 transition





Relative resistivity at 295 K and thermal conductivity at 300K both via pressure





Resistivity growth and thermal conductivity decrease at *P*>6 GPa testify both in favor of increase in structural changes of sodium with pressure growth.

Conclusion

Thus, in the present work we have calculated a power spectrum of electrons and phonons, and also density of their states for all experimental points in the field of sodium-bcc-lattice existence. With their help and with use of single-phase Lindeman measure values of melting temperature, well agreed with experimental data are designed. Energy of zero fluctuations of a sodium lattice is designed and necessity of the account of its contribution to dynamics of electron and phonon spectra is shown. Features of volume-jump behavior at sodium fusion with pressure growth are discussed.

Many thanks for attention!!!