Thermal expansion anisotropy of compounds predicted using DFT calculations

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Introduction

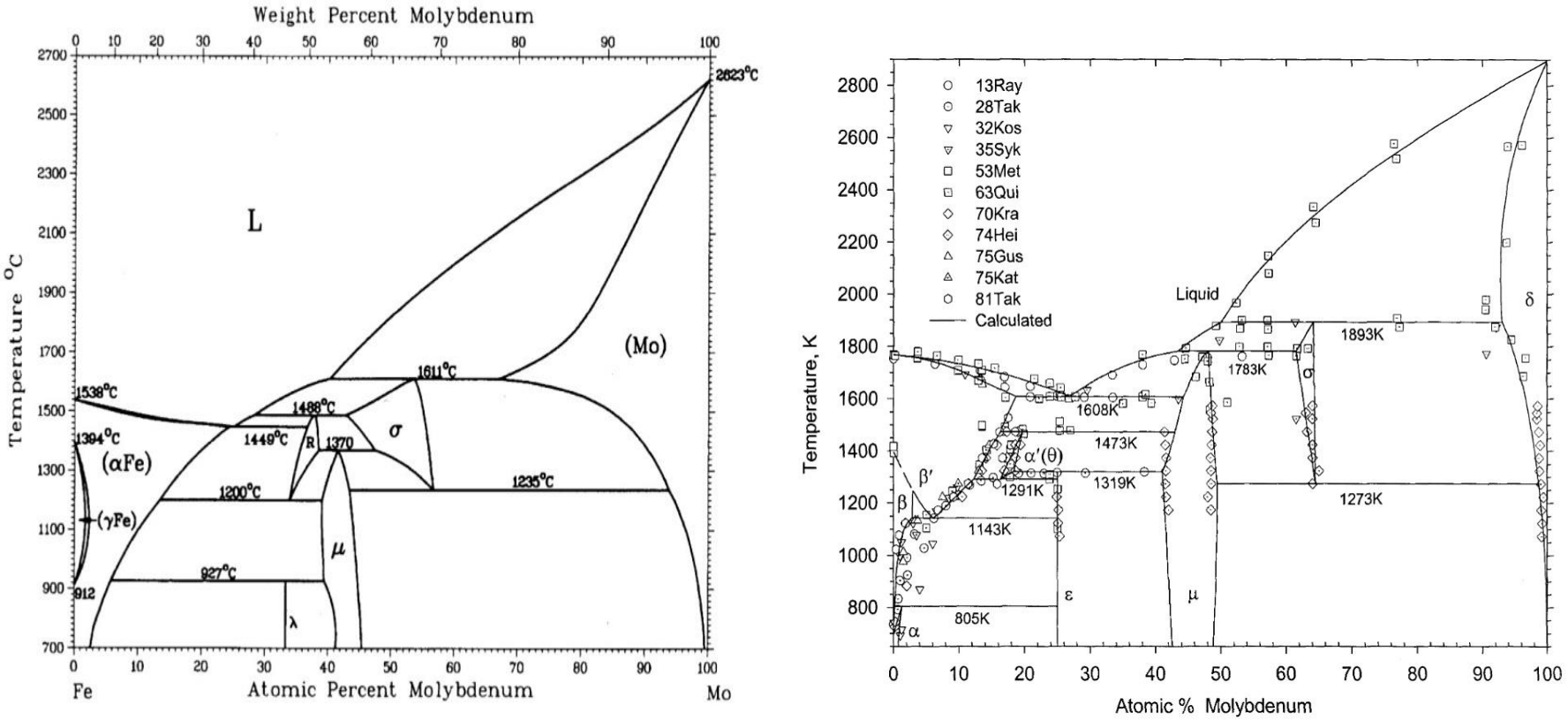


Fig. 1. Phase diagrames: a) Fe-Mo system according T. Massalski et al.; and b) Co-Mo system evaluated by A. Davydov et al.

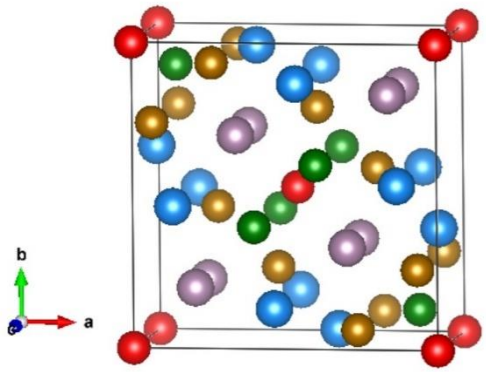
Topologically close-packed (TCP) model binary phases: Laves (λ-), σ - and μ- phases

Fe_7Mo_8 σ-phase

Lattice	atom	number
1 (2a)	Fe	2
2 (4f)	Fe	4
3 (8i)	Mo	8
4 (8i')	Mo	8
5 (8j)	Mo	8

a = 8.765, c = 4.768 (A)

α = β = γ = 90

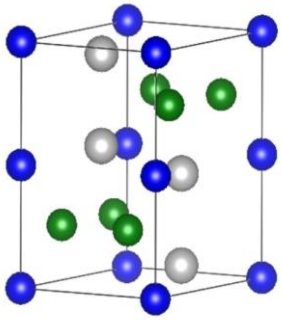


C14 Fe_2Mo λ-phase

Lattice	atom	number
1 (2a)	Fe	2
2 (6h)	Fe	6
3 (4f)	Mo	4

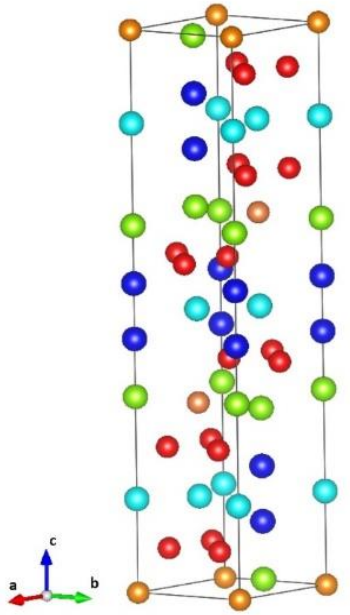
a = 4.765, c = 9.243 (A)

α = β = 90, γ = 120



Co_7Mo_6, Fe_7Mo_6 μ-phase

Lattice	atom	number
1 (3a)	Fe	3
2 (18h)	Fe	18
3 (c)	Mo	6
4 (c')	Mo	6
5 (c'')	Mo	6



a = 4.765, c = 25.768 (A)

α = β = 90, γ = 120

Difficulties in modeling the thermal expansion of a solid

Quasi-harmonic approximation:

$$F(T,V) = E_{tot}(V) + F_{el}(T,V) + F_{vib}(T,V) + F_{mag}(T,V) \quad (1)$$

$$E_{el}(T,V) = N_A \int_{-\infty}^{\infty} n(\varepsilon,V) f(\varepsilon,T) \varepsilon d\varepsilon - N_A \int_{-\infty}^{\varepsilon_F} n(\varepsilon,V) d\varepsilon \quad (2)$$

$$\gamma = -1 - \frac{V}{2} \frac{\partial^2 P/\partial V^2}{\partial P/\partial V}$$

$$F_{phonon}(V,T) = k_B T \int_0^{\infty} ln \left[2 \cdot sinh \frac{\hbar\omega}{2k_B T} \right] g(\omega,V) d\omega \quad (3)$$

$$\theta_D(V) = \theta_{Do} \left(\frac{V_0}{V} \right)^{\gamma}$$

$$S_{vib}(T,V) = 3N_A k_B \left[\frac{4}{3} D\left(\frac{\theta_D}{T} \right) - ln\left(1 - exp\left(-\frac{\theta_D}{T} \right) \right) \right] \quad (4)$$

Murnoghan equation of state:

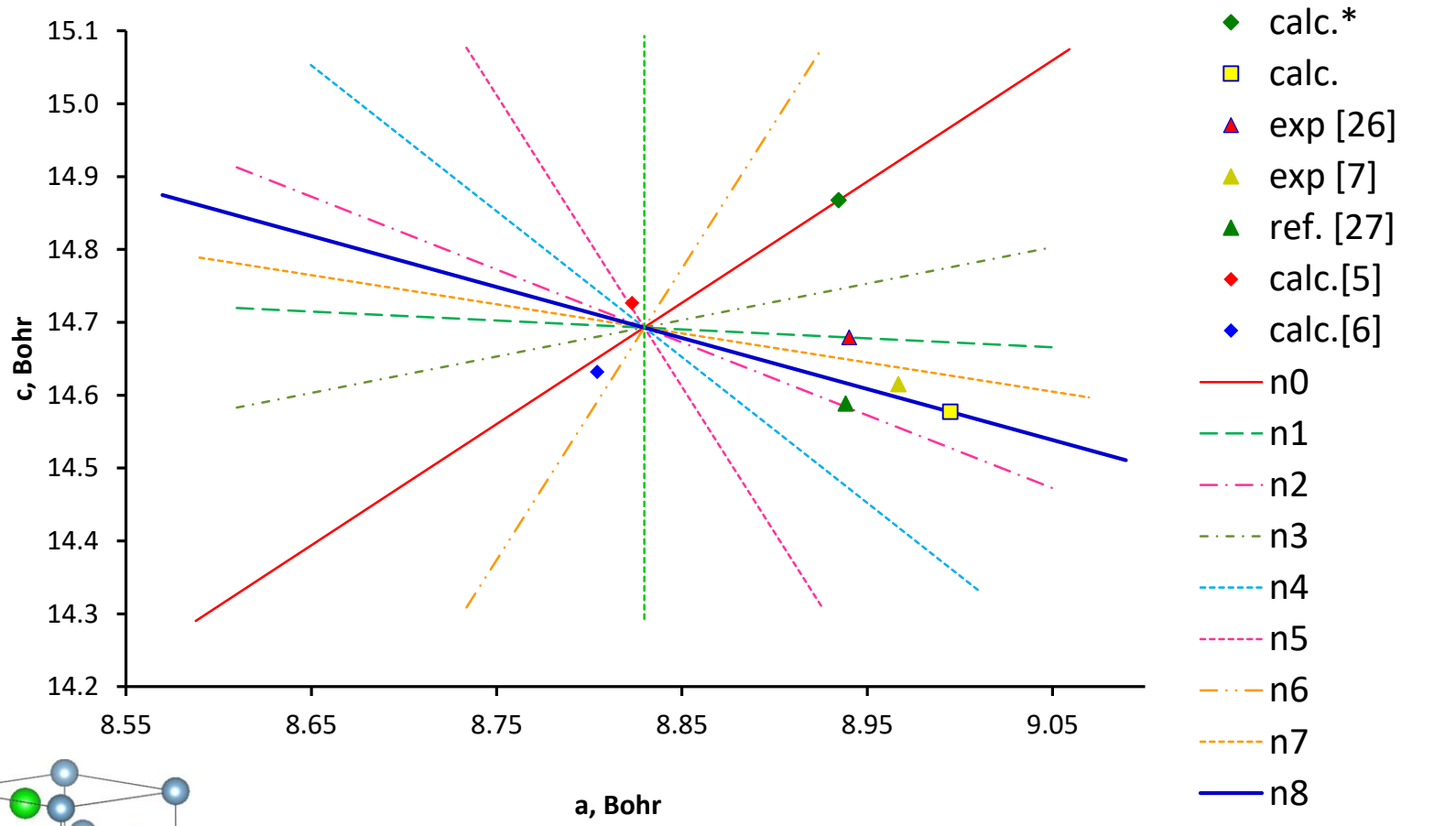
$$E(V) = \frac{BV}{B'(B'-1)} \left[B'\left(1 - \frac{V_o}{V}\right) + \left(\frac{V_o}{V}\right)^{B'} - 1 \right] + E(V_o) \quad (5)$$

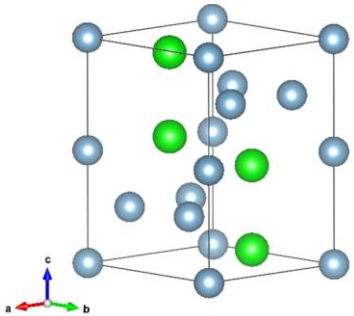
Modification of equations are required :

$$V(a,c) = \frac{\sqrt{3}}{2} a^2 \cdot c \quad (6)$$

$$P(a,c) = -\frac{dE}{dV} = -\frac{1}{\frac{\sqrt{3}}{2} a^2 \cdot c} \left[\frac{2}{a \frac{\partial E(a,c)}{\partial a}} + \frac{1}{c \frac{\partial E(a,c)}{\partial c}} \right]^{-1} \quad (7)$$

Search of Thermal Expansion Path (STEP) method, application to Laves phase C14 Fe_2Mo





The n0 is a path of the isotropic expansion and contraction where the *c/a* ratio remains constant.

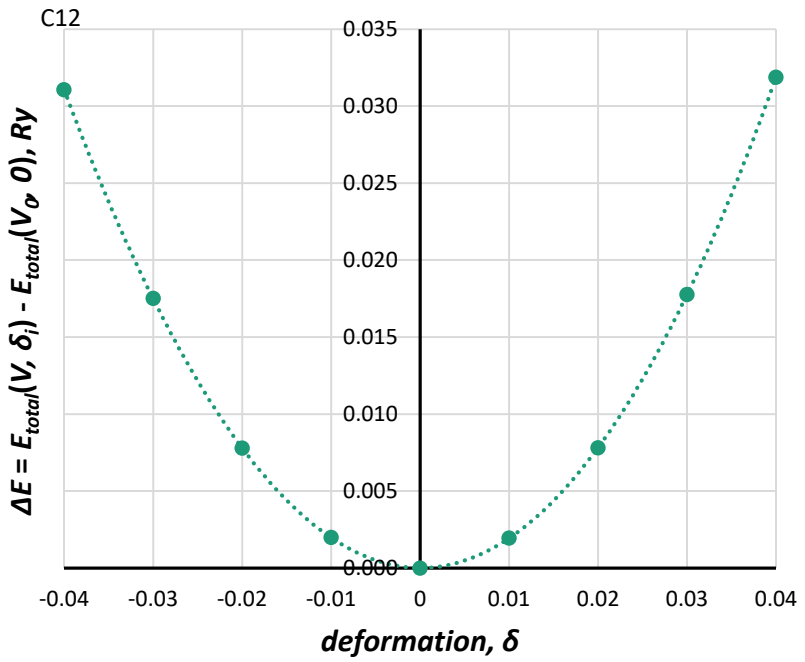
* calculated in this work at T = 1073 K by applying the quasi-harmonic Debye - Grüneisen theory without accounting magnetic contributions to the free energy.

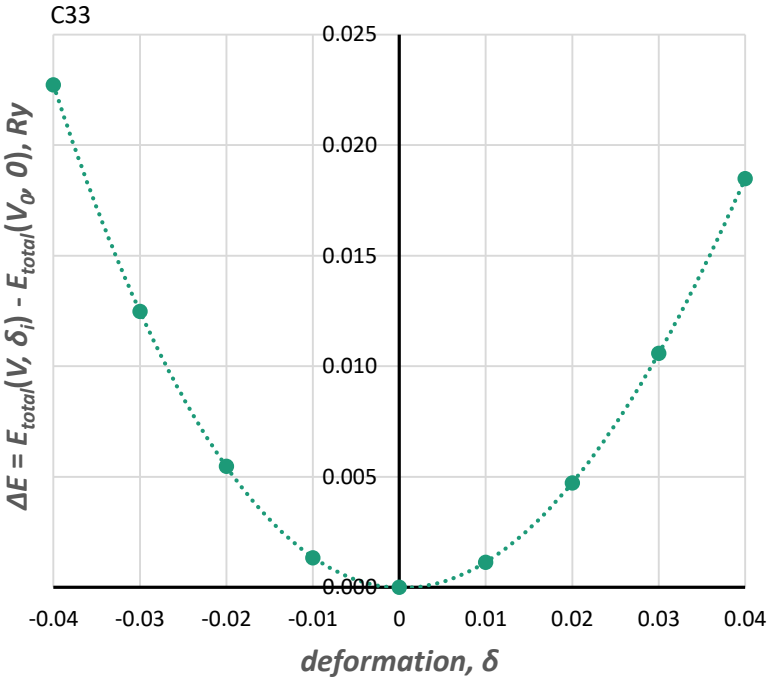
[1] D. Vasilyev, Physica B: Condensed Matter 621 (2021) 413307

Distortion matrices for calculating elastic constants *Cij*

Distortion matrices*	Energy change due to applied deformation
$`D_1 = \begin{pmatrix} 1+\delta & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\Delta E = V_0(\tau_1\delta + \frac{C_{11}}{2}\delta^2)$
$D_2 = \begin{pmatrix} \frac{1+\delta}{(1-\delta^2)^{1/3}} & 0 & 0 \\ 0 & \frac{1-\delta}{(1-\delta^2)^{1/3}} & 0 \\ 0 & 0 & \frac{1}{(1-\delta^2)^{1/3}} \end{pmatrix}$	$\Delta E = V_0\left[(\tau_1-\tau_2)\delta + \frac{1}{2}(C_{11}+C_{22}-2C_{12})\delta^2\right]$
$D_3 = \begin{pmatrix} \frac{1+\delta}{(1-\delta^2)^{1/3}} & 0 & 0 \\ 0 & \frac{1}{(1-\delta^2)^{1/3}} & 0 \\ 0 & 0 & \frac{1-\delta}{(1-\delta^2)^{1/3}} \end{pmatrix}$	$\Delta E = V_0\left[(\tau_1-\tau_3)\delta + \frac{1}{2}(C_{11}+C_{33}-2C_{13})\delta^2\right]$
$D_4 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1+\delta \end{pmatrix}$	$\Delta E = V_0(\tau_3\delta + \frac{C_{33}}{2}\delta^2)$
$D_5 = \begin{pmatrix} \frac{1}{(1-\delta^2)^{1/3}} & 0 & 0 \\ 0 & \frac{1}{(1-\delta^2)^{1/3}} & \frac{\delta}{(1-\delta^2)^{1/3}} \\ 0 & \frac{\delta}{(1-\delta^2)^{1/3}} & \frac{1}{(1-\delta^2)^{1/3}} \end{pmatrix}$	$\Delta E = V_0(2\tau_4\delta + 2C_{44}\delta^2)$

An example of calculating the strain tensor coefficients C_{12} and C_{33} for Fe_7Mo_6

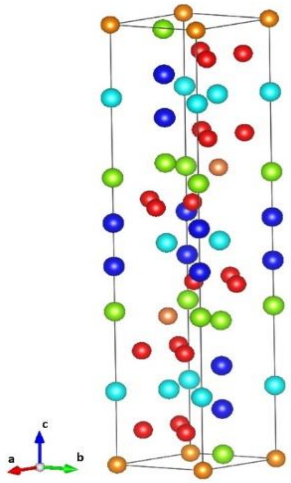




$$\Delta E = V_0\left[(\tau_1-\tau_2)\delta+\frac{1}{2}(C_{11}+C_{22}-2C_{12})\delta^2\right]$$

$$(C_{11}+C_{22}-2C_{12})=\frac{2}{V_0}d*k$$

$$\begin{pmatrix}\frac{1+\delta}{(1-\delta^2)^{1/3}} & 0 & 0\\ 0 & \frac{1-\delta}{(1-\delta^2)^{1/3}} & 0\\ 0 & 0 & \frac{1}{(1-\delta^2)^{1/3}}\end{pmatrix}$$



$$\Delta E = V_0\left(\tau_3\delta+\frac{C_{33}}{2}\delta^2\right)$$

$$C_{33}=\frac{2}{V_0}d*k$$

$$\begin{pmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1+\delta\end{pmatrix}$$

The calculation of the elastic properties of the Fe_7Mo_6 polycrystal was carried out from the elastic constants C_{ij} of the single crystal using the Voigt-Reuss-Hill (VRH) approximation*

$$B = \frac{1}{2}(B_V + B_R), G = \frac{1}{2}(G_V + G_R) \quad (1)$$

$$E = \frac{9GB}{3B+G}, \quad \nu = \frac{3B-E}{6B} = \frac{E-2G}{2G} \quad (2)$$

$$B_V = \frac{1}{9}(2(C_{11} + C_{12}) + 4C_{13} + C_{33}) \quad (3)$$

$$B_R = \frac{(C_{11}+C_{12})C_{33}-2C_{13}^2)}{C_{11}+C_{12}+2C_{33}-4C_{13}} \quad (4)$$

$$G_V = \frac{1}{30}(C_{11} + C_{12} + 2C_{33} - 4C_{13} + 12C_{44} + 12C_{66}) \quad (5)$$

$$G_R = 15/(14S_{11} + 4S_{33} - 8S_{13} - 10S_{12} + 6S_{44})$$

*R. Hill, The Elastic Behaviour of a Crystalline Aggregate, Proc. Phys. Soc. A 65 (1952) 349-354

Elastic coefficients of the Fe_7Mo_6 compound

Calculated elastic coefficients C_{ij} (in GPa) of a single crystal of the Fe_7Mo_6.

Compound	Elastic coefficients of Fe_7Mo_6					
	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}
Fe_7Mo_6	424.57	191.73	136.27	393.86	103.55	116.42
Calc. [1]	433	216	144	389	102	109

As can be seen from the table, C_{ij} satisfy the criterion of mechanical stability:

$$C_{11} > 0,\ C_{11} - |C_{12}| > 0,\ (C_{11} + C_{12})\, C_{33} > 2C_{13}^2,\ C_{44} > 0$$

and, as a consequence, Fe_7Mo_6 is mechanically stable at zero pressure and T = 0K.

[1] Persson, Kristin. 2016. "Materials Data on Fe7Mo6 by Materials Project"

Calculated elastic moduli (in GPa) and Poisson's ratio ν of a polycrystalline Fe_7Mo_6 aggregate

Compound	B_V	B_R	B	G_V	G_R	G	E	ν	B/G
Fe_7Mo_6	241.3	239.4	240.3	116.7	99.1	107.8	281.4	0.30	2.33

The ratio B/G > 1.75 indicates that the polycrystalline Fe_7Mo_6 aggregate is a ductile material.

Calculated average (V_m), shear (v_s) and longitudinal (v_l) velocities of elastic waves (in m/s); the predicted Debye temperature θ_D (in K) and the velocities of elastic waves in the [001] and [100] directions (in m/s) of the Fe_7Mo_6 μ-phase.

Compound	v_s	v_l	V_m	θ_D	[001]		[100]		
					V_l	V_s	V_l	V_{s1}	V_{s2}
Fe_7Mo_6	3369	6357	3765	**477**	6437	3301	6684	3500	3301

[1] O.L. Anderson, A simplified method for calculating the Debye temperature from elastic constants, J. Phys. Chem. Solids 24 (1963) 909-917.

Part II
Thermodynamic properties

5. Thermodynamic properties

$$F(T,V) = E_{tot}(V) + F_{mag}(T) + E_D(T,V) - TS_D(T,V) + E_{el}(T,V) - TS_{el}(T,V) \quad (5.1)$$

where $E_{tot}(V)$ – total energy obtained from ab initio calculations at T = 0 K

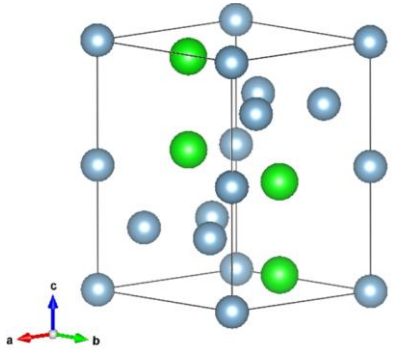
$F_{mag}(T)$ – magnetic contribution to free energy at equilibrium volume

$E_D(T,V)$ and $S_D(T,V)$ – vibrational and entropy contributions

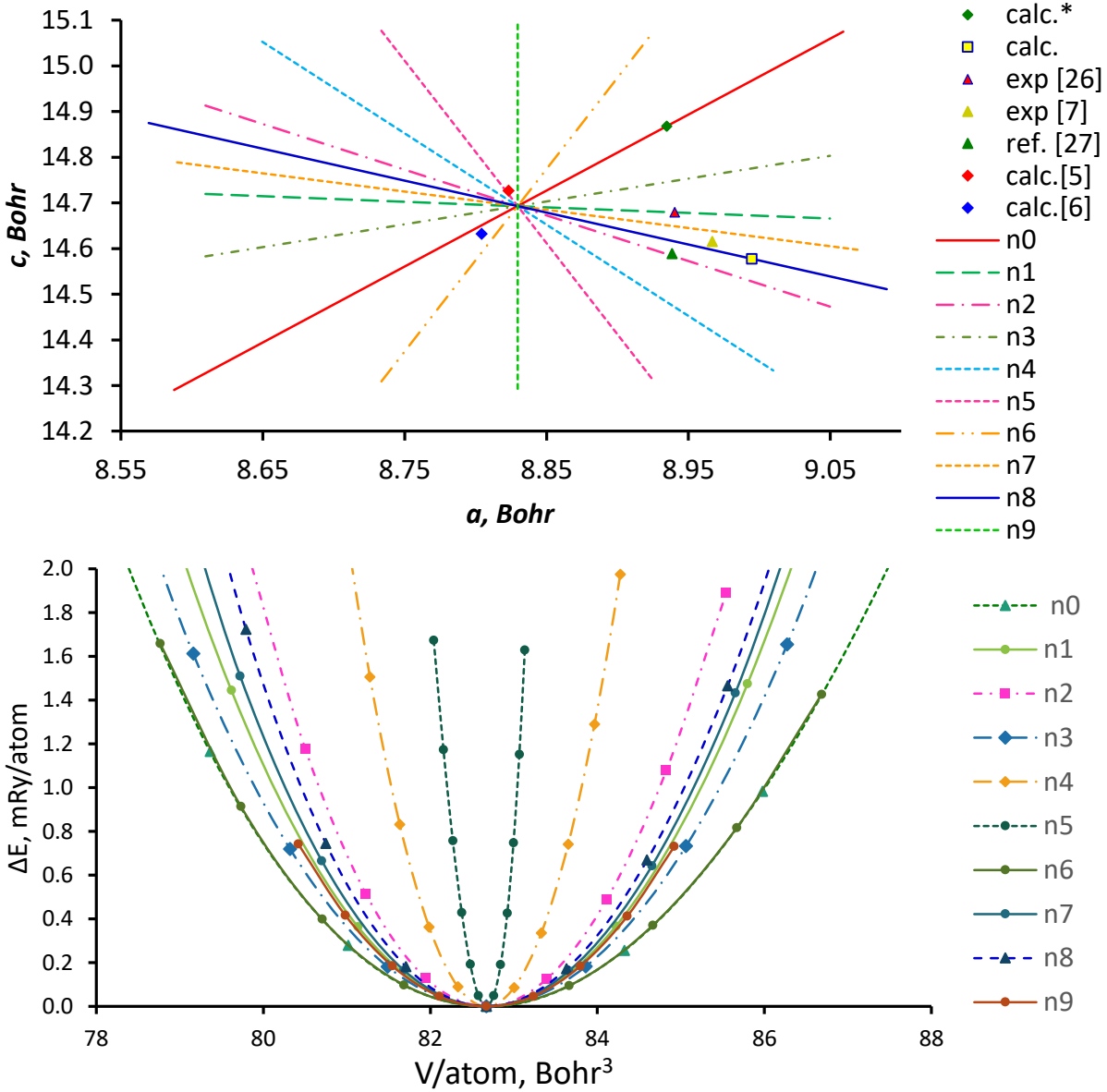
$E_{el}(T,V)$ and $S_{el}(T,V)$ – contributions due to thermally excited electrons

Scheme for calculating the path of thermal expansion of C14 Fe_2Mo [1]

Paths (directions) n0 ÷ n9 along which the calculations were carried out. The intersection point is the parameters (a_0 , c_0) of Fe_2Mo obtained at T=0K by DFT.



Total energies E(V) calculated for different paths, n0 ÷ n9



[1] D. Vasilyev, Physica B: Condensed Matter 621 (2021) 413307

Fe_2Mo Laves phase electron energy

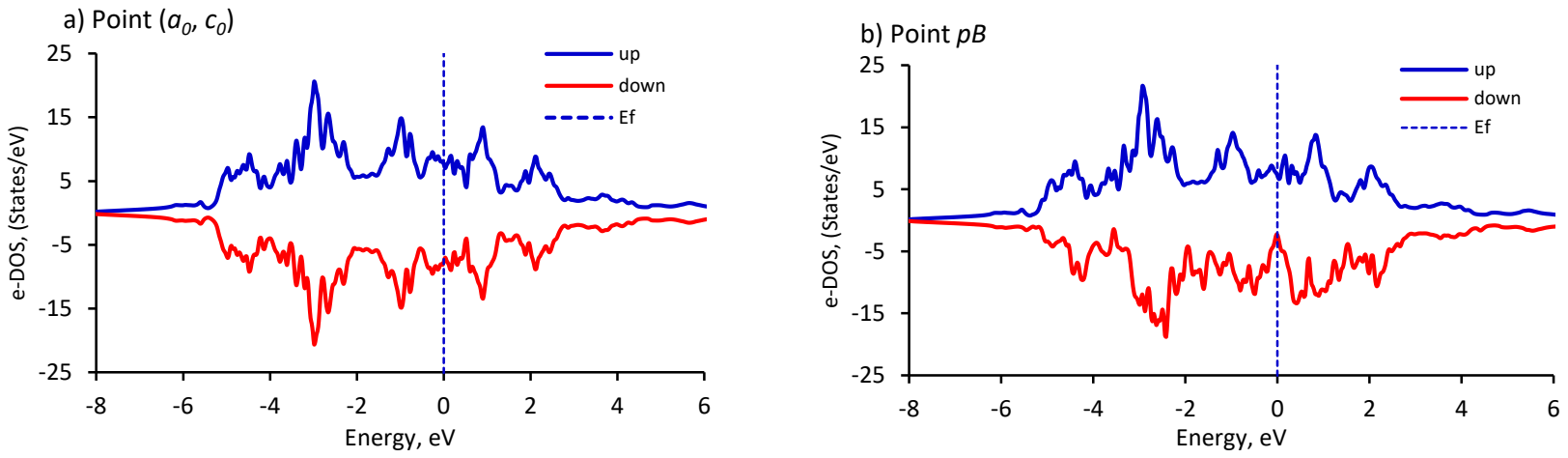


Fig. 4. Total electronic density of states (e-DOS) for Laves phases of Fe2Mo, calculated a) at point (a0, c0) and b) at point pB.

$$E_{el}(T,V) = N_A \int_{-\infty}^{\infty} n(\varepsilon,V) f(\varepsilon,T) \varepsilon d\varepsilon - N_A \int_{-\infty}^{\varepsilon_F} n(\varepsilon,V) d\varepsilon \tag{5.6}$$

$$S_{el}(T,V) = -N_A k_B \int_{-\infty}^{\infty} n(\varepsilon,V) \Big(f(\varepsilon,T) \ln(\varepsilon,T) + \big(1 - f(\varepsilon,T)\big) \mathrm{l\,n}\big(1 - f(\varepsilon,T)\big) \Big) d\varepsilon \tag{5.7}$$

where $n(\varepsilon,V)$ is the electron density of states, $f(\varepsilon,T)$ is the Fermi-Dirac distribution, $\boldsymbol{N_A}$ is Avogadro's constant

[1] C. Kittel Introduction to solid state physics. New York (NY): Wiley, 1996, p.152

[2] N.W. Ashcroft, N.D. Mermin, Solid State physics. Brooks/ Cole, Cengage Learning; 1976, p.54.

The vibrational energy of atoms of the compound

The vibrational and entropic contributions to the energy were calculated according to the Debye model using the formulas [1]:

$$E_D(T,V) - E_0 = 3N_A k_B T D\left(\frac{\theta_D}{T}\right) \qquad E_0 = \frac{9}{8} N_A k_B \theta_D \qquad (5.8)$$

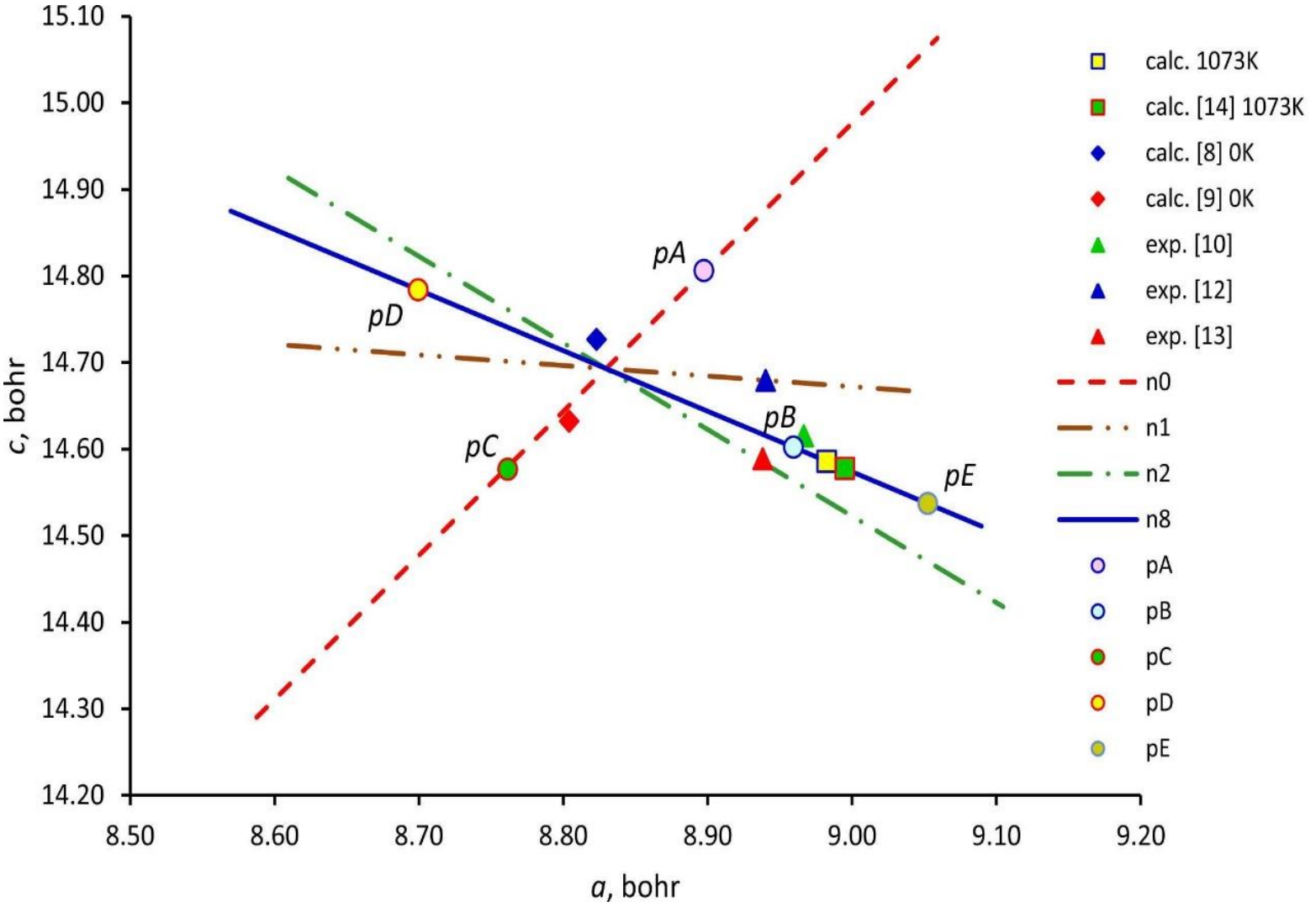
where D(θ_D/T) is the Debye function, θ_D is the Debye temperature, and k_B is the Boltzmann constant. Where E_0 is the energy of zero-point vibrations expressed in the Debye approximation

$$S_D(T,V) = 3N_A k_B \left[\frac{4}{3} D\left(\frac{\theta_D}{T}\right) - \ln\left(1 - \exp\left(-\frac{\theta_D}{T}\right)\right)\right] \qquad (5.9)$$

$$F_{phonon}(V,T) = k_B T \int_0^\infty ln\left[2 \cdot sinh\frac{\hbar\omega}{2k_B T}\right] g(\omega,V) d\omega \qquad (5.10)$$

[1] G. Grimvall, Thermo physical properties of materials. Amsterdam: North-Holland. 1999

Phonon energy calculations



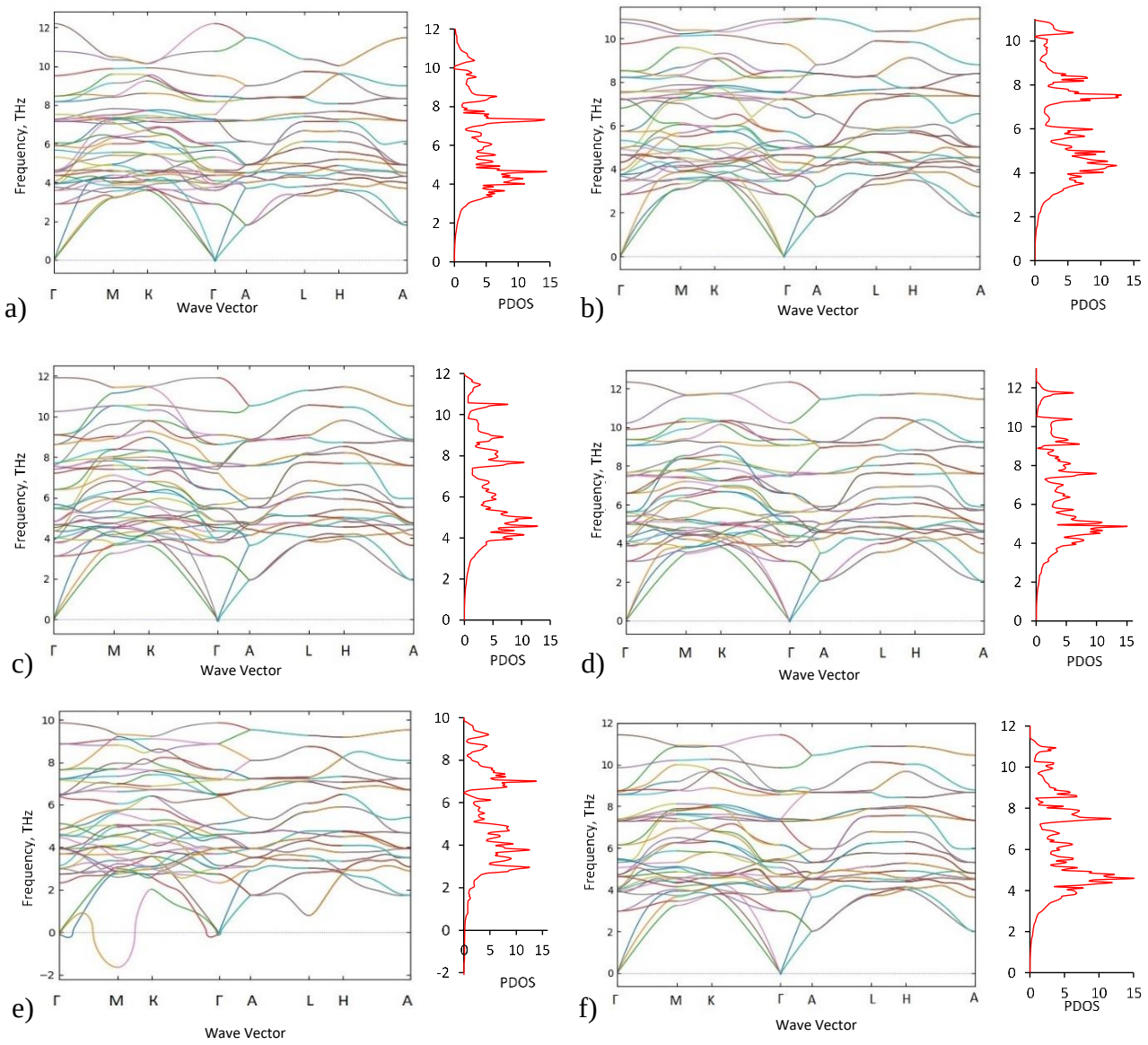
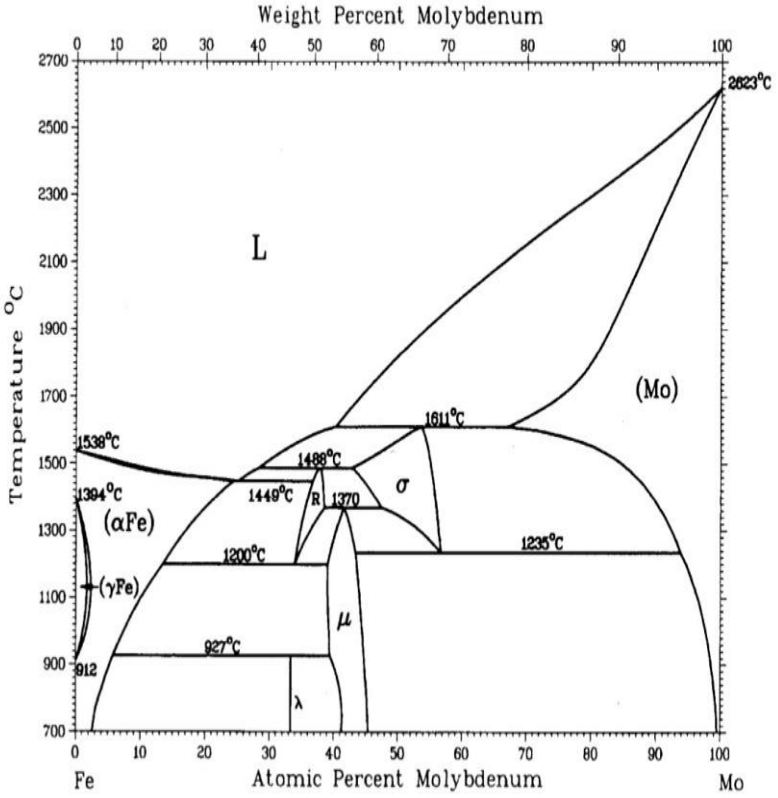
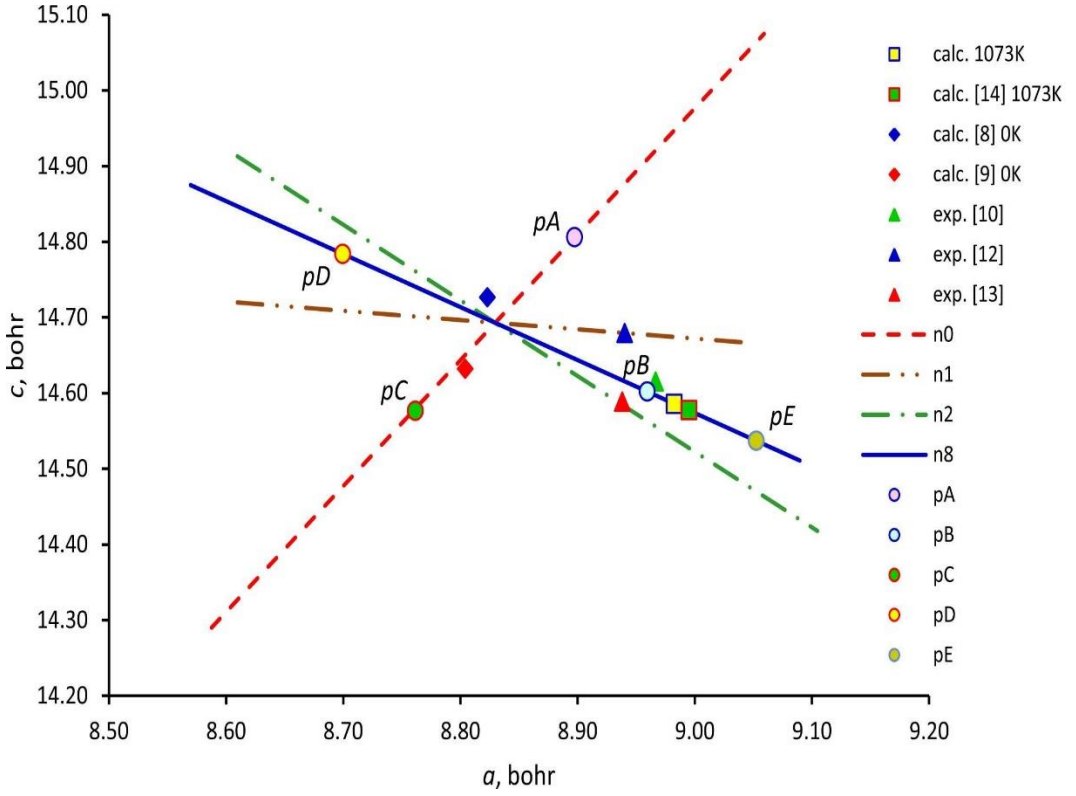


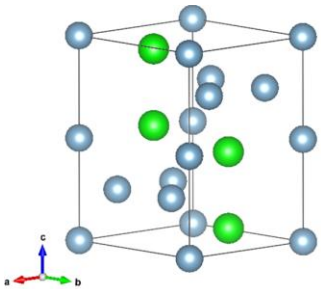
Рис. 1. The phonon dispersion curves and the phonon density of states (PDOS) for Fe_2Mo Laves phases calculated at points: a) *pA*; b) *pB*; c) *pC*; d) *pD*; e) *pE* and f) point (a_0, c_0), [1]

[1] D. Vasilyev, Materials Today Communications, 35 (2023) 105550.

Phonon energy calculations







[1] D. Vasilyev, Materials Today Communications, 35 (2023) 105550.

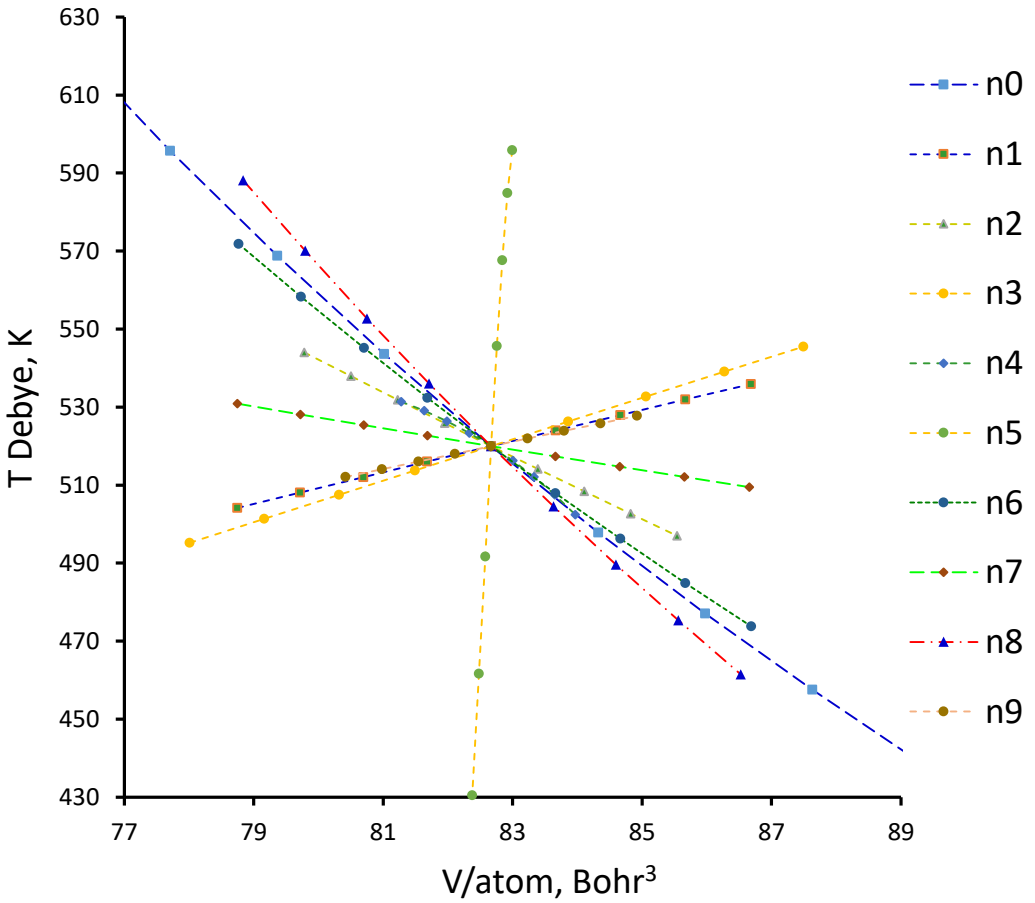
Debye temperatures calculated for different paths n0 ÷ n9 and Grüneisen parameter of Fe_2Mo compound

The Grüneisen parameter, γ, was calculated using the formulas

$$\gamma = -1 - \frac{V}{2}\frac{\partial^2 P/\partial V^2}{\partial P/\partial V}$$

Debye temperature, θ_D, was calculated as a function of volume

$$\theta_D = \theta_{Do}\left(\frac{V_0}{V}\right)^{\gamma}$$



[1] D. Vasilyev, Physica B: Condensed Matter 621 (2021) 413307

The magnetic component of the free energy of the system in the framework of the approximation of the Indene-Hillert-Jaerl model. [CALPHAD, 1978, p. 227-238]

$$F_{mag}(V,T) = [F'_{mag}(T) - F'_{mag}(0K)] - TS_{mag}(V) \quad (5.2)$$

$$S_{mag}(V) = N_A k_B \sum_{i=1}^{n} c_i ln\left(|\mu_i(V)| + 1\right) \quad (5.3)$$

$$F'_{magn}(x,T) = R \cdot T \cdot Ln\left[B_0(x)+1\right] \cdot \gamma\left[\tau(x)\right] \quad (5.4)$$

$$T_C = \frac{2}{3k_B}\left(E_{tot}^{PM}(V) - E_{tot}^{FM}(V)\right) \quad (5.5)$$

Calculated value of **Tc = 299** K

the mean magnetic moment B_0. **= 0.371** μB

$\tau(x) = T/T_c$

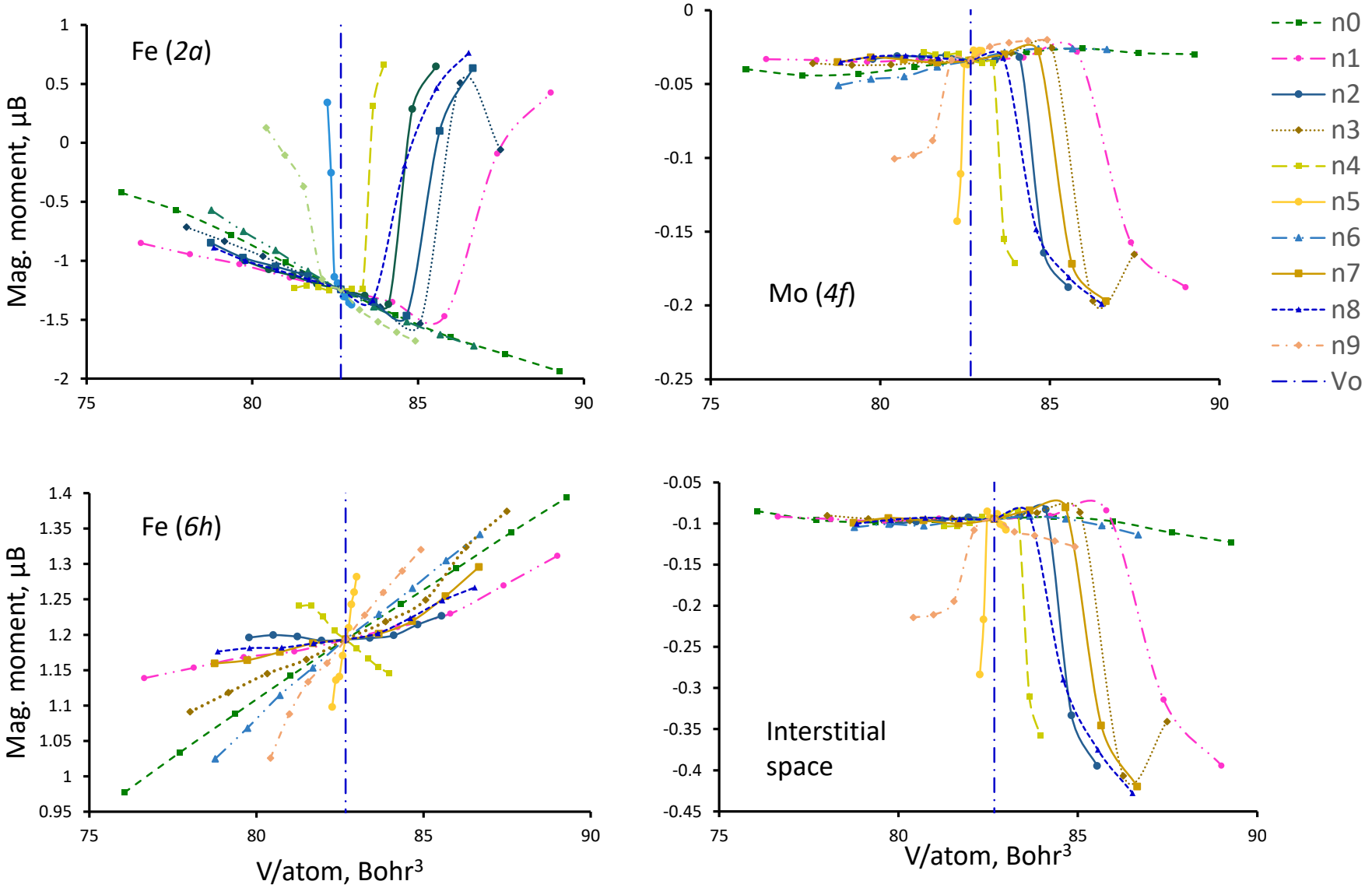
Data base, **A. Dinsdale [SGTE, 1991]** for the pure components

if τ ≤1 $\gamma(\tau) = 1 - \{79/(140*p*\tau)+[474*((1/p)-1)/497]*(\tau^3/6 + \tau^9/135 + \tau^{15}/600)\}/D$.

if τ >1 $\gamma(\tau) = -1*\{1/(10*\tau^5)+1/(\tau^{15}*315)+1/(\tau^{25})\}/D$.

[1] M. Hillert M. Jarl, A model for alloying in ferromagnetic metals, CALPHAD 2(3) (1978), 227-238.
[2] A.T. Dinsdale, SGTE Data for Pure Elements, CALPHAD, 15(4) (1991) 371- 425.

Distribution of local magnetic moments (μB) of Fe and Mo atoms on the sub-lattices of Fe_2Mo along n0 ÷ n9 paths



[1] D. Vasilyev, Physica B: Condensed Matter 621 (2021) 413307

The Helmholtz free energies of the C14 Fe_2Mo calculated along the n0 ÷ n9 paths

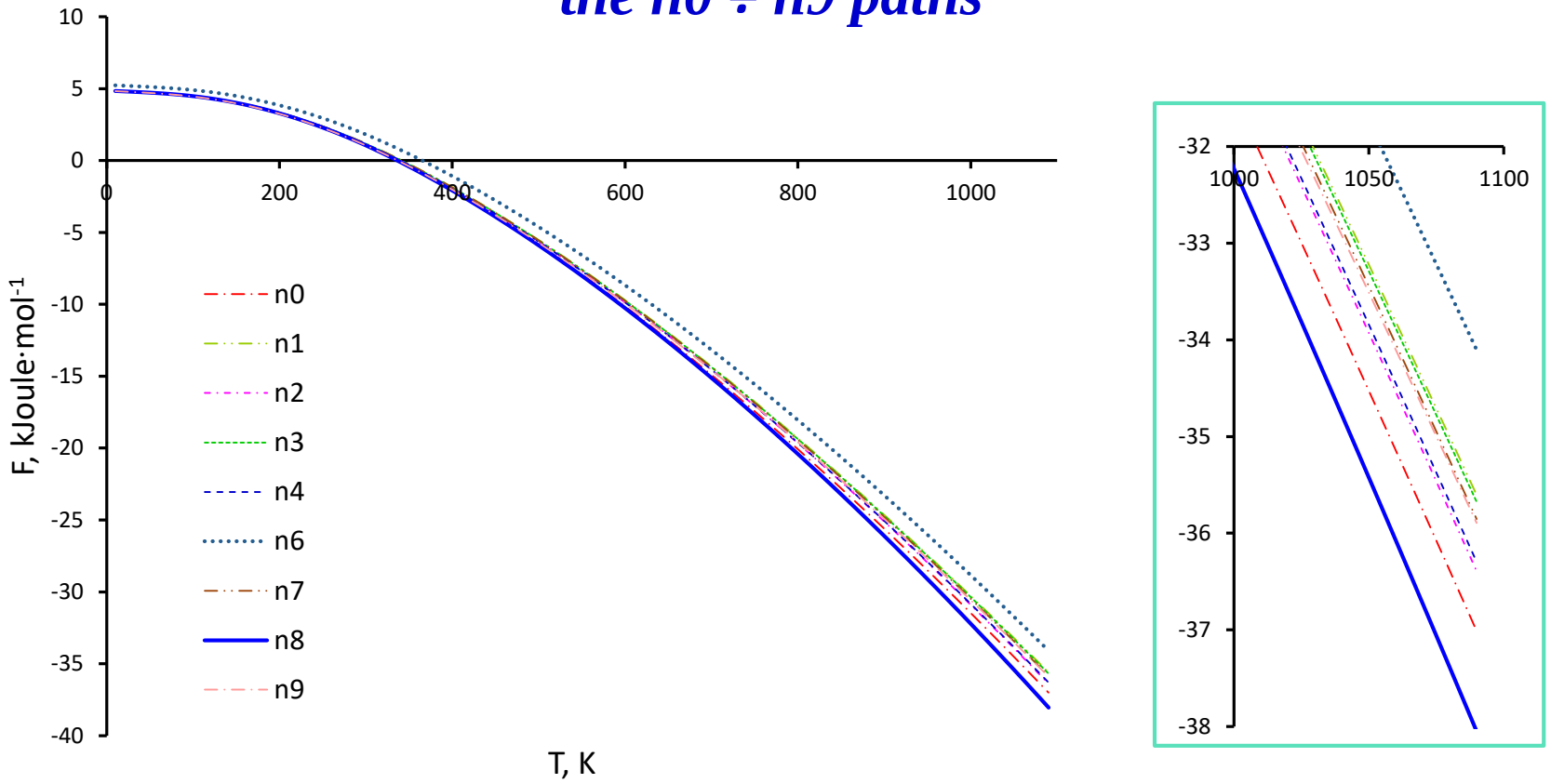
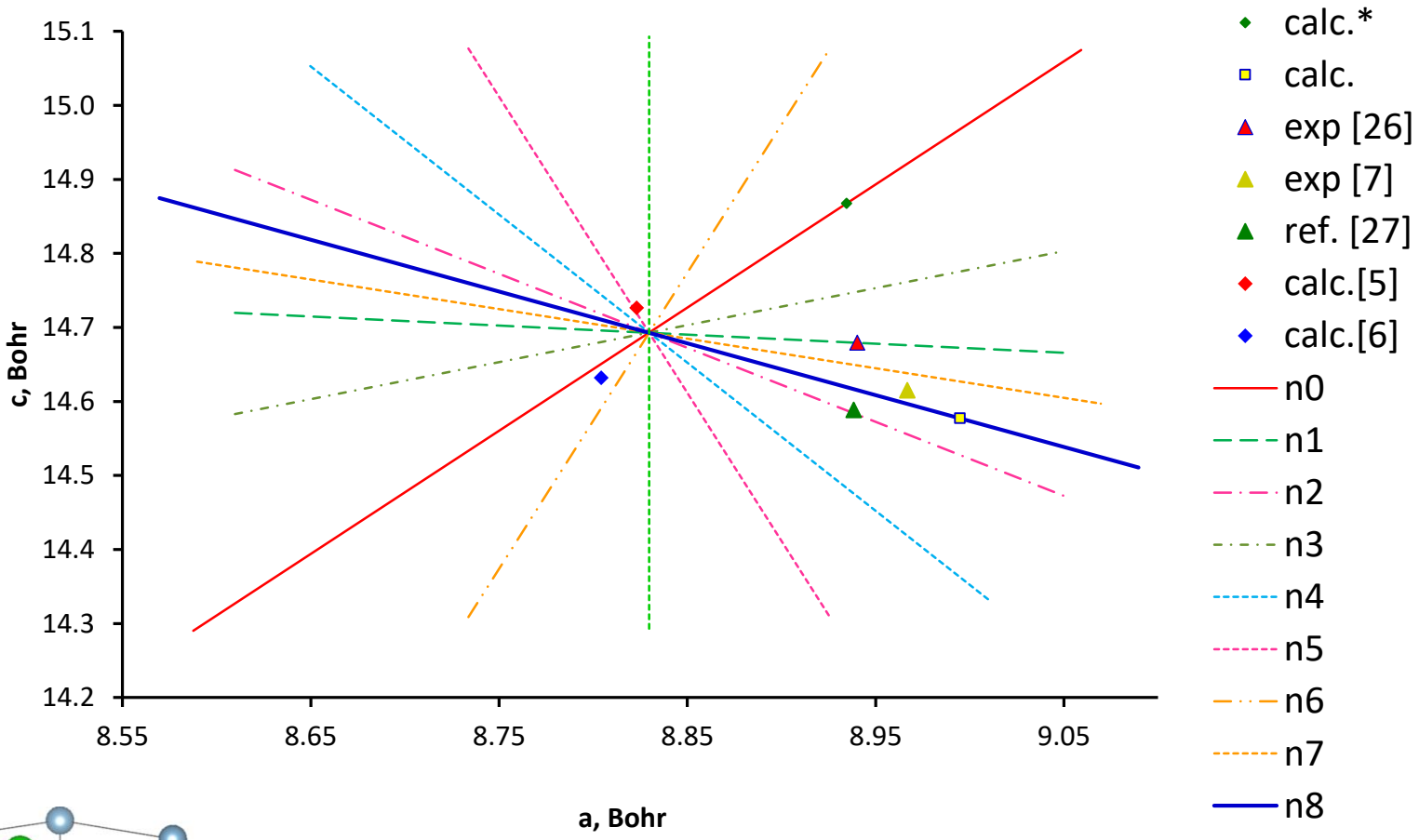
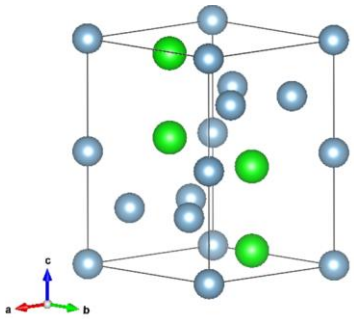


Figure. The Helmholtz free energy curves $F_{ni}(T)$ of Laves phase Fe_2Mo calculated along n0 ÷ n9 paths. **The *n8* is energetically most favourable path, it's a thermal expansion – contraction path of Fe_2Mo**.

[1] D. Vasilyev, Physica B: Condensed Matter 621 (2021) 413307

The n8 is the thermal expansion - contraction path of the Fe_2Mo

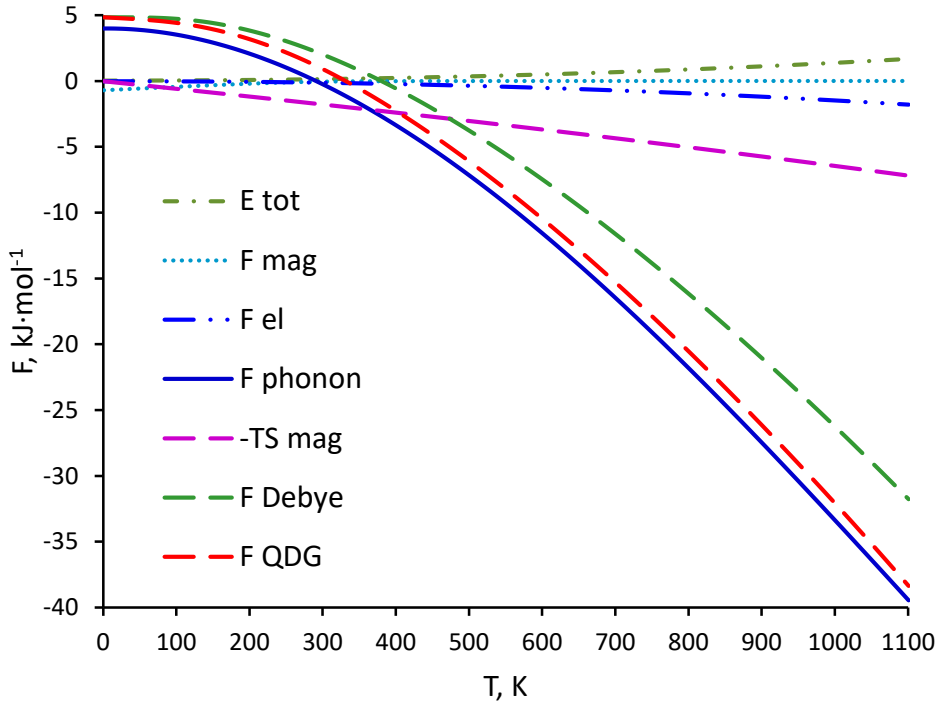


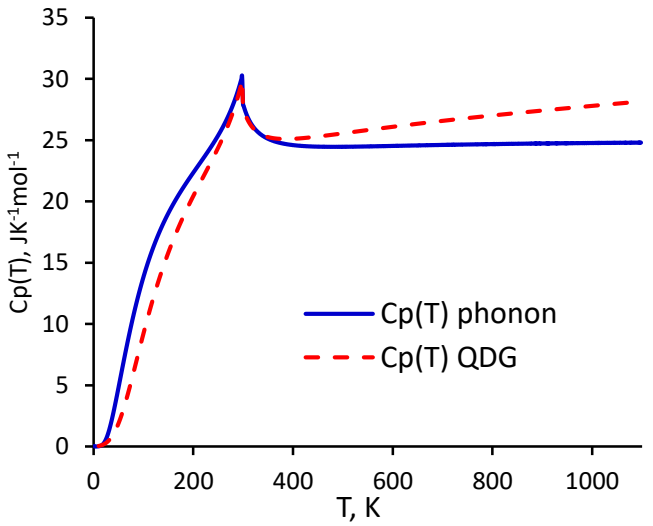


The n0 is a path of the isotropic expansion and contraction where the *c/a* ratio remains constant.

* calculated in this work at T = 1073 K by applying the quasi-harmonic Debye - Grüneisen theory without accounting magnetic contributions to the free energy.

Temperature dependences of the free energy and heat capacity of the Laves phase of Fe_2Mo, calculated along the thermal expansion – contraction path n8





$$F_{phonon}(V,T) = F_{Debye}(V,T) - T \cdot S_{mag}(V,T) - \delta$$

Fig. a) magnetic, vibrational, electronic parts; b) heat capacity Cp(T) of the Laves phase of Fe2Mo [1], jump in heat capacity - ferro-paramagnetic phase transition according to the applied model [M.Hillert].

[1] D. Vasilyev, Materials Today Communications, 35 (2023) 105550.

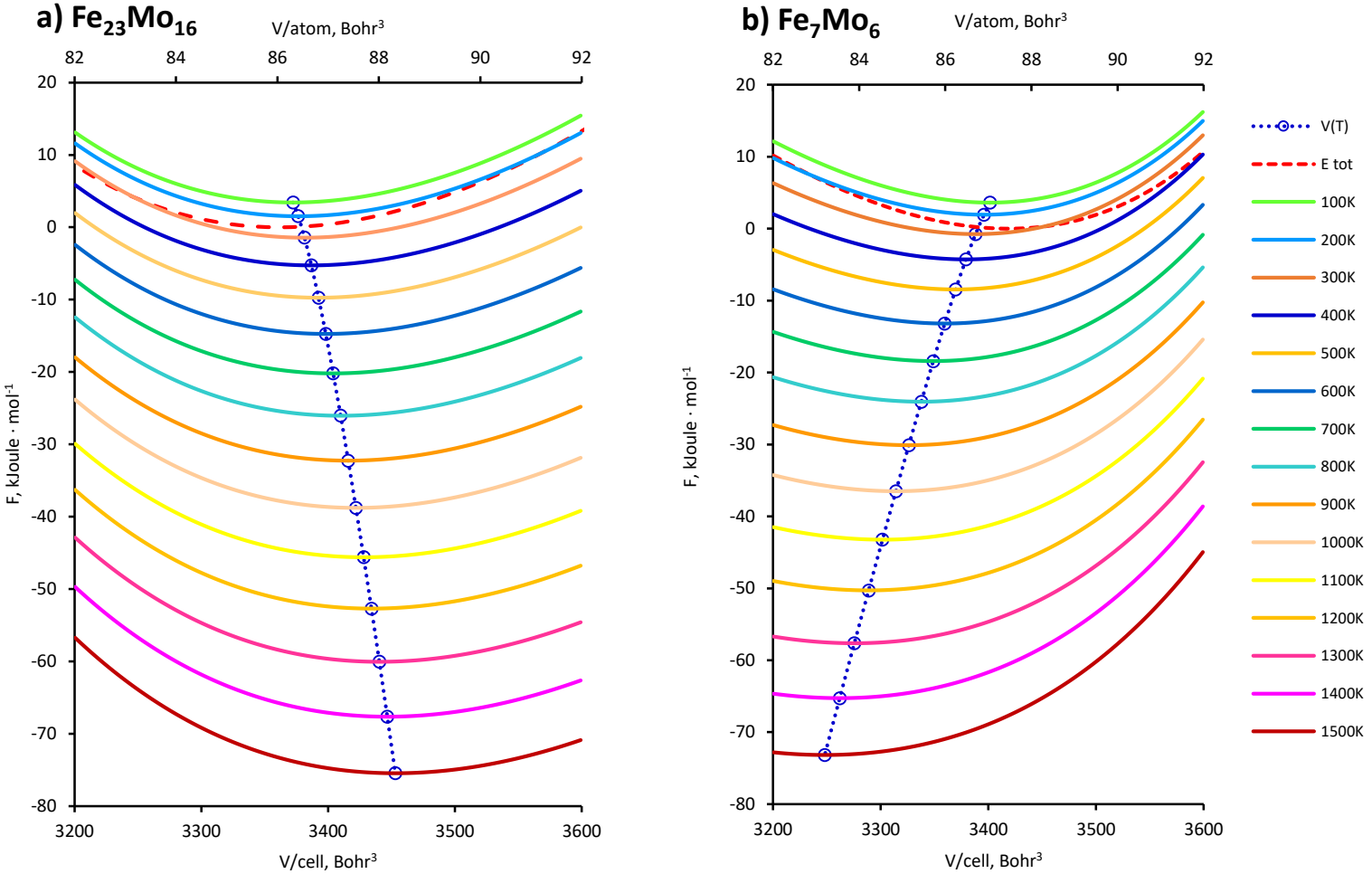


Figure 11. Functions of free energy *F(V,T)* calculated at finite temperatures for a) $Fe_{23}Mo_{16}$ along the *k3* pathway, and b) Fe_7Mo_6 along the *p3* pathway. The total static energies are shown by the red dashed lines. The equilibrium volumes $V_0(T)$ are presented by the blue dotted lines, open circles indicate the equilibrium volumes [1].

[1] D. Vasilyev, Physical Chemistry Chemical Physics, 26 (2024) 3482 – 3499, DOI: 10.1039/D3CP04266A

Elastic constants C_{ij} and modules B, G, E of Laves phase Fe_2Mo

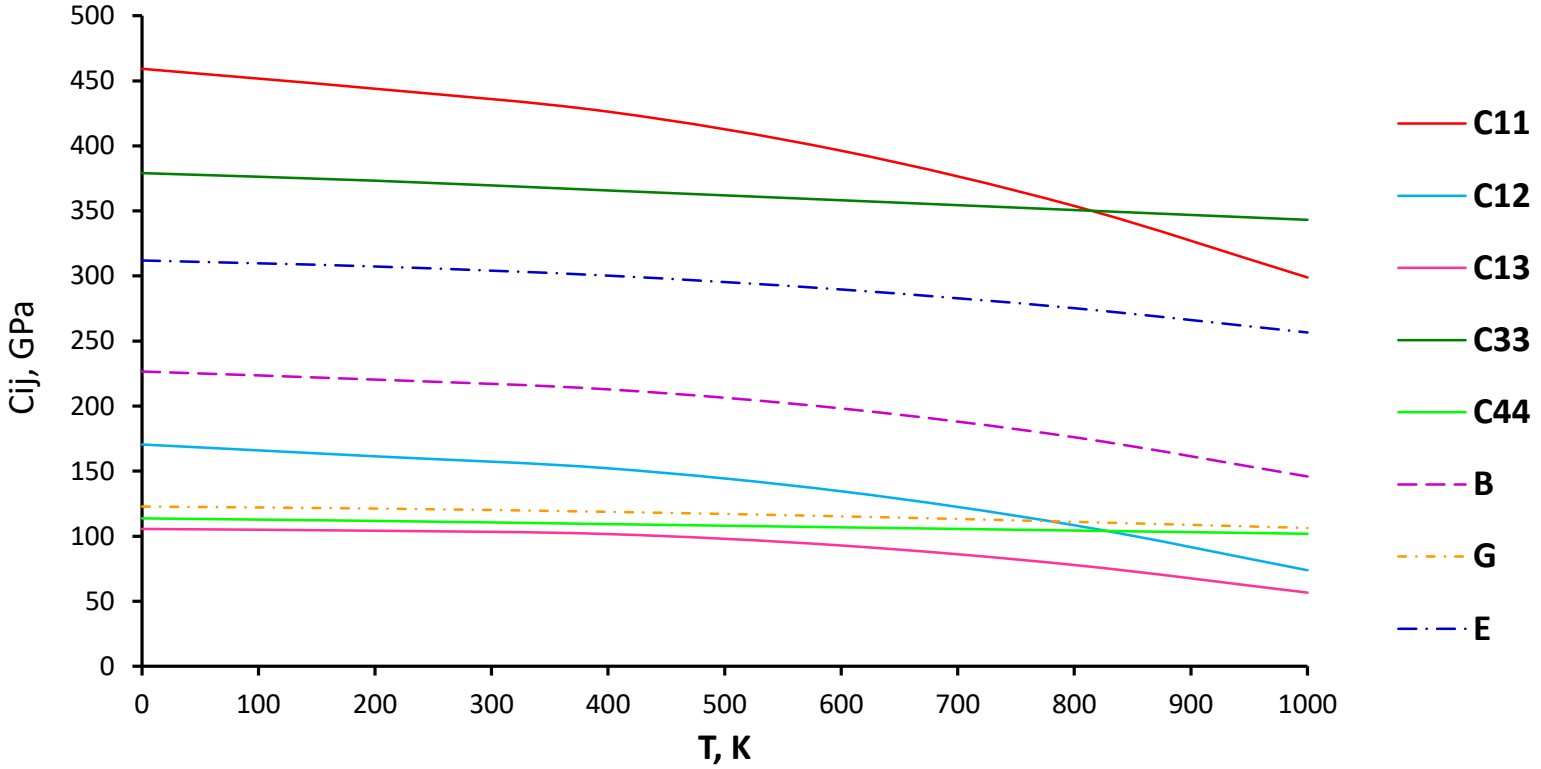


Figure. Elastic constants C_{ij} and modules *B*, *G*, *E* of Laves phase Fe_2Mo calculated as functions of temperature along the thermal expansion – contraction path, *n8*.

[1] D. Vasilyev, Physica B: Condensed Matter 621 (2021) 413307

Conclusions

1. **The independent coefficients of the elastic strain tensor are calculated, which show that Fe_7Mo_6 is a mechanically stable phase.**
2. **Polycrystalline parameters *B, G, E, v* were calculated from the elastic coefficients for a single crystal using the Voigt-Reuss-Hill approximation.**
3. **The Debye temperature and sound wave velocities of Fe_7Mo_6 were calculated.**
4. **A method for calculating the path of thermal expansion and contraction of compounds has been presented using the Laves phase Fe_2Mo example.**
5. **The temperature dependences of the free energy, lattice parameters and heat capacity C_p were calculated.**
6. **The influence of magnetic entropy on the stability of λ-phase is shown.**

Thanks for attention!