First-Principles Calculations of the Thermal Expansion Path of the Co$_7$Mo$_6$ μ-Phase

Dmitry Vasilyev

The thermal expansion path is calculated for the Co$_7$Mo$_6$ compound, with the structure of μ-phase, from $T = 0$ to 1500 K which is below its decomposition temperature. The method allowing to reduce the problem to a 1D case and considering the energy as depending on only one variable, the volume, is used. The thermodynamic properties of Co$_7$Mo$_6$ are studied using first-principles-based quasiharmonic Debye–Grüneisen approximation and by comparing the free energies calculated along different paths of thermal expansion. The electronic, vibrational, and magnetic energy contributions to the free energy are accounted. The thermal expansion of Co$_7$Mo$_6$ is not isotropic. The influence of electronic, magnetic, and vibrational entropy on the stability of Co$_7$Mo$_6$ is analyzed. The isobaric heat capacity, thermal expansion, elastic constants, bulk modulus, sound wave velocities, and Debye and Curie temperatures are reported. The calculated results are analyzed and are in agreement with the available experimental and theoretical data.

1. Introduction

The Co$_7$Mo$_6$ compound is the topologically close-packed (TCP) intermetallic phase existing in Co–Mo systems. In the Co–Mo phase diagram, the μ-phase has a homogeneity range from ≈45 to 50 at.% Mo as presented by Davydov et al.[1,2] Thus, Co$_7$Mo$_6$ with its stoichiometry composition of 46.2 at.% of Mo is a stable compound.

The Co$_7$Mo$_6$ compound is the model μ-phase which is used to study the effect of precipitation of TCP phases on mechanical properties of the cubic matrices of cobalt (or nickel)-based superalloys, because it is prone to precipitation during thermal exposure at high temperature. A large number of refractory elements have been added to superalloys to improve their creep and stability at elevated temperatures, but the drawback of it is the precipitation of TCP phases.[3]

The effect of the possible precipitation of TCP phases brings significant obstacles in the design of superalloys which are widely used in the production of turbine blades for aircraft engines. It’s because that these materials have excellent high-temperature mechanical properties, creep, and corrosion resistance.[4]

The μ-phase is a hard brittle compound and is detrimental because its precipitation induces local depletion of the matrix of superalloys and its needle morphology can easily initiate a rupture and influence in particular the creep resistance, yield strength, and ductility. Therefore, the range of the stability of μ-phase should be accurately investigated. Especially, Gibbs potentials, thermodynamic properties, and a path of thermal expansion of μ-phase must be calculated to model phase boundaries and simulate properties of superalloys.

In this work, the calculations are restricted to Co$_7$Mo$_6$ compound and does not take into account the disorder associated with possible deviation from the stoichiometry.

The μ-phase due to its technological importance attracts a lot of attention. A number of works studying the phase equilibria, structural properties, and lattice parameters of μ-phases were conducted over the last years. The phase boundaries of the μ-phase in the Co–Mo system were studied in the work.[1,2] The experimental calorimetric study of the Co$_7$Mo$_6$ was reported by Spencer et al.[5] The phase equilibria in the Co$_7$Mo$_6$ μ-phase were studied by Oikawa et al.[6] Zhao et al.[7] studied the precipitation of μ-phase in nickel-base alloys by scanning, transmission electron microscopy and X-ray diffraction. Qin et al.[8] investigated the response of μ-phase in the cast Ni-base superalloys to applied stress and long-term thermal exposure at $T = 800$ °C. The site occupation in the Ni–Nb μ-phase and configurational thermodynamic properties have been studied by Sluiter et al.[9] The formation enthalpies of the elements of Fe and Mo in metastable μ-phases were reported by Sluiter,[10] using density functional theory (DFT) calculations. Joubert et al.[11] studied the atom distribution on the five different sites of the crystal structure of μ-phases. The structure and lattice parameters of Co$_7$Mo$_6$ μ-phase have been studied by Forsyth et al.[12]

As one could see from earlier, these studies mainly focus on structure properties of μ-phases. However, the thermodynamic and physical properties of Co$_7$Mo$_6$ compound are not reported...
yet. The factors influencing the stability of μ-phase have not been investigated so far. However, Grabowski et al.\textsuperscript{[13]} have shown that magnetic entropy can significantly increase, up to 30%, the free energy of alloys, and it should be accounted in calculations. Moreover, the answer to the question of whether the thermal expansion of these compounds is isotropic or not is also unknown.

Insofar as answering these questions and obtaining these data are important for calculating the Gibbs potentials and predicting the properties of compounds at various temperatures, this was the motivation for this study.

In this work, the thermal expansion of the Co\textsubscript{7}Mo\textsubscript{6} μ-phase was studied by first-principles calculations based on DFT and combined with the quasiharmonic Debye–Grüneisen (QDG) approximation, as used in other studies\textsuperscript{[13,14]} As the crystal lattice of Co\textsubscript{7}Mo\textsubscript{6} has two parameters \(a\) and \(c\), and in order to find out how the lattice parameters of Co\textsubscript{7}Mo\textsubscript{6} change during heating, the method used to calculate the thermodynamic properties of Laves-phase Fe\textsubscript{2}Mo reported in another study\textsuperscript{[15]} was utilized. This method gives the formal right to use the equation of state \(\text{EOS}\) and the QDG approach in thermodynamic calculations related to crystal lattices having different parameters.

The electronic, vibration energies, and the magnetic entropy of local magnetic moments of atoms were accounted to study the thermodynamic properties. The physical factors affecting the stability of Co\textsubscript{7}Mo\textsubscript{6} are analyzed. The thermal expansion path, isobaric heat capacity, structural properties, elastic constants of the strain tensor, bulk, shear, Young’s modulus, Debye, and Curie temperatures are reported. The anisothermal expansion in the Co\textsubscript{7}Mo\textsubscript{6} compound is predicted. The results of this work can be useful for further modeling the Gibbs energies of the μ-phase as a function of composition, for calculating the phase diagrams and further theoretical and experimental research. In addition, it may provide valuable data which are difficult to obtain from experiments.

2. Method of Calculation

2.1. Thermodynamic Model

Helmholtz free energy \(F(V,T)\) was formulated according to\textsuperscript{[15,16]}

\[
F(V,T) = E_{\text{tot}}(V) + F_{\text{el}}(V,T) + F_{\text{vib}}(V,T) + F_{\text{mag}}(V,T) - TS_{\text{conf}}
\]

(1)

where \(E_{\text{tot}}(V)\) is the total energy obtained by DFT calculations at \(T = 0\) K. The other free energy terms are the electronic, \(E_{\text{el}}(V,T)\); vibrational, \(F_{\text{vib}}(V,T)\); magnetic, \(F_{\text{mag}}(V,T)\); and ideal configurational entropy, \(S_{\text{conf}}\).

2.2. Free Energy Subsystems

The electronic energy \(E_{\text{el}}(V,T)\) was described by\textsuperscript{[17]}

\[
E_{\text{el}}(V,T) = E_{\text{el}}(V) - TS_{\text{el}}(V,T)
\]

(2)

With the energy of electrons due to their excitations, \(E_{\text{el}}(V,T)\) is formulated by\textsuperscript{[18]}

\[
E_{\text{el}}(V,T) = \int_{-\infty}^{\infty} n(e,V)f(e,T) \text{d}e - \int_{-\infty}^{\infty} n(e,V) \text{d}e
\]

(3)

where \(n(e,V)\) is the electronic density of states DOS and \(f(e,T)\) is the Fermi–Dirac distribution. The electronic entropy \(S_{\text{el}}(V,T)\) takes the form

\[
S_{\text{el}}(V,T) = -k_B \int_{-\infty}^{\infty} n(e,V) f(e,T) \ln f(e,T)
\]

\[
+ (1 - f(e,T)) \ln (1 - f(e,T)) \text{d}e
\]

(4)

where \(k_B\) is the Boltzmann constant.

The vibrational free energy of the lattice ions under the QDG approximation is given by\textsuperscript{[13,14]}

\[
F_{\text{vib}}(V,T) = E_{\text{D}}(V,T) - TS_{\text{vib}}(V,T)
\]

(5)

where the energy of ions due to their vibrations \(E_{\text{D}}(V,T)\) is formulated by

\[
E_{\text{D}}(V,T) = \frac{9}{8} N_A k_B \theta_D + 3 N_A k_B T D\left(\frac{\theta_D}{T}\right)
\]

(6)

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

(7)

where \(D(\theta_D/T)\) is the Debye function. The Grüneisen parameter \(\gamma\) was expressed according to\textsuperscript{[14]}

\[
\gamma = -1 - \frac{V}{2} \frac{\partial^2 P}{\partial V^2}
\]

(8)

The Debye temperature \(\theta_D(V)\) was formulated as\textsuperscript{[14]}

\[
\theta_D(V) = \frac{\theta_D}{\left(\frac{V}{V_0}\right)^{\gamma}}
\]

(9)

where \(\theta_D\) is the Debye temperature obtained at \(T = 0\) K and equilibrium volume, \(V_0\), is shown in Table 5 and 1, respectively.

The magnetic energy \(F_{\text{mag}}(V,T)\) was described by the assumption

\[
F_{\text{mag}}(V,T) = \left[F'_{\text{mag}}(T) - F'_{\text{mag}}(0 K)\right] - TS_{\text{mag}}(V)
\]

(10)

Table 1. Ground-State properties of lattice constants (in Å), equilibrium volume \(V\) (in Å\(^3\)), and formation enthalpies \(\Delta H\) (kJ mol\(^{-1}\)) of Co\textsubscript{7}Mo\textsubscript{6} together with experimental and other theoretical values.

| Compound   | Method  | \(a\)   | \(c\)   | \(c/a\) | \(V\)  | \(\Delta H\) |
|------------|---------|---------|---------|---------|-------|-----------|
| Co\textsubscript{7}Mo\textsubscript{6} | This work | 4.744   | 25.423  | 5.359   | 495.524 | -4.43     |
|           | This work\textsuperscript{a} | 4.756   | 25.644  | 5.392   | 502.388 |           |
|           | exp\textsuperscript{[19, b]} | 4.761   | 25.59   | 5.375   | 502.34  |           |
|           | exp\textsuperscript{[20]} | 4.762   | 25.615  | 5.379   | 503.04  |           |
|           | calc\textsuperscript{[20]} |         |         |         |        | -2.51     |

\textsuperscript{a}Calculated in this work at \(T = 1423\) K; \textsuperscript{b}Experimental data obtained at \(T = 1423\) K after 912 h of annealing treatments.
where \( F_{\text{mag}}(T) \) is the magnetic energy term of Hillert and Jarl model as given in \([21]\)

\[
F_{\text{mag}}(T) = RT \ln(\beta + 1) f(\tau)
\]  

(11)

where \( \tau = T/T_C \); the function \( f(\tau) \) is defined in the study by Dinsdale;\([21]\) \( \beta \) is the average magnetic moment which was obtained at \( T = 0 \text{ K} \); it is equal to 0.172 (\( \mu_B \) atom\(^{-1} \)) for Co\(_7\)Mo\(_6\). The expression in square brackets of (10) is to compensate the constant contribution of magnetic internal energy persistently existing in the total energy.

The theoretical estimation of Curie temperature was calculated using the mean-field approximation, borrowing from ref. \([13]\)

\[
T_C = \frac{2}{3k_B} (E_{\text{PM}}^{\text{tot}}(V_0) - E_{\text{PM}}^{\text{tot}}(V_0))
\]  

(12)

where \( E_{\text{PM}}^{\text{tot}}(V_0) \) and \( E_{\text{PM}}^{\text{tot}}(V_0) \) are the total energies of the compound calculated at \( T = 0 \text{ K} \) for paramagnetic (PM) and ferromagnetic (FM) states at the corresponding equilibrium volumes \( V_0 \).

The magnetic entropy \( S_{\text{mag}}(V) \) and configurational entropy \( S_{\text{conf}} \) were calculated as follows

\[
S_{\text{mag}}(V) = k_B \sum_{i=1}^{n} c_i \ln(|\mu_i(V)| + 1)
\]  

(13)

\[
S_{\text{conf}} = k_B \sum_{i=1}^{n} c_i \ln c_i
\]  

(14)

where \( \mu_i \) is the local magnetic moment of atom \( i \) and \( c_i \) is the atomic concentration.

### 2.3. First-Principles Calculations

The calculations were carried out using the full-potential linear-augmented planewave (FP-LAPW) method\([22]\) within the DFT;\([23,24]\) as implemented in the WIEN2k package.\([22]\) The exchange-correlation effects were treated as a function within the generalized gradient approximation (GGA)\([25]\) and GGA along with Perdew–Brune–Erzerhof (PBE).\([26]\) The muffin-tin radii (\( R_{MT} \)) were set as \( R_{MT} = 2.05 \text{ for Co} \) and \( R_{MT} = 2.15 \text{ for Mo} \). The parameter \( R_{K_{\text{max}}} \) was set as 8. To model the Co\(_7\)Mo\(_6\) compound, the two kinds of cells, in hexagonal\([11]\) and rhombohedral\([12]\) notations of 39 and 13 atoms, were used with the 15 \( \times \) 15 \( \times \) 3 and 12 \( \times \) 12 \( \times \) 12 \( \text{k-point mesh} \) in the first irreducible Brillouin zone using the Monkhorst–Pack scheme.\([27]\)

The energy between successive iterations is converged to 1 \( \times \) 10\(^{-6} \text{eV atom}\(^{-1} \) and forces are minimized to 5 meV \text{Å}^{-1}.

### 3. Results and Discussion

#### 3.1. Ground State Properties

##### 3.1.1. Structural Properties

The crystal lattice of Co\(_7\)Mo\(_6\) \( \mu \)-phase belongs to the \( \text{R}3\text{m} \) space group and is typified by Fe\(_2\)W\(_6\) compound. The unit cell of Co\(_7\)Mo\(_6\) can be represented in rhombohedral\([12]\) and hexagonal notations,\([11]\) with 13 and 39 atoms per unit cell, respectively. The hexagonal notation of Co\(_7\)Mo\(_6\) is shown in Figure 1.

The computations in this work were carried out with spin-polarized calculations. The geometry optimizations and the full structural relaxation procedures were used to obtain lattice parameters and atoms positions of the Co\(_7\)Mo\(_6\) compound. The optimized lattice parameters are listed in Table 1 and Figure 3, together with the available experimental data.\([12,19]\) The lattice parameters of Co\(_7\)Mo\(_6\) calculated in this work at \( T = 1423 \text{ K} \) are close to the experimental data\([19]\) obtained at \( T = 1423 \text{ K} \) after 912 h of annealing treatments, as listed in Table 1 and shown in Figure 3. The enthalpy formation \( \Delta H \) of Co\(_7\)Mo\(_6\) was calculated by the following expression

\[
\Delta H_{\text{Co}_7\text{Mo}_6} = E_{\text{total}} - (x E_{\text{Mo}}^{\text{bcc}} + (1 - x) E_{\text{Co}}^{\text{hcp}})
\]  

(15)

where \( E_{\text{total}}^{\text{Co}_7\text{Mo}_6} \) is the total energy of Co\(_7\)Mo\(_6\) and \( E_{\text{Co}}^{\text{hcp}} \) and \( E_{\text{Mo}}^{\text{bcc}} \) are the energies of Co and Mo atoms in the hexagonal-close-packed (hcp) and the body-centered-cubic (bcc) lattice, respectively; \( x \) is the concentration of Mo atoms (\( x = 0.462 \)). \( \Delta H \) of Co\(_7\)Mo\(_6\) calculated in this work has a negative value; this
suggested that the compound is stable at T = 0 K; the obtained value is listed in Table 1 with the other theoretical values\(^\text{[20]}\) for comparison.

### 3.1.2. Elastic and Thermal Properties

The elastic constants \(C_{ij}\) of the strain tensor were determined by successively imposing distortion matrices \(D_i\), listed in Table A1 (in Appendix), on the lattice of Co\(_7\)Mo\(_6\), according to the expressions

\[
R \cdot D_i = R'
\]

\[
R = \begin{pmatrix}
\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\
-\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\
0 & 0 & 1
\end{pmatrix}
\]

where \(R\) is the lattice of \(\mu\)-phase in a matrix form described by the Bravais lattice vectors of a hexagonal crystal with parameters \(a\) and \(c\) and \(R'\) is the deformed matrix containing distorted lattice vectors.

For each type of lattice distortion, the corresponding energy dependences for various deformations \(\delta = \pm 0.01\)\(^\text{m}\) were obtained. The variations in total energies \(\Delta E(\delta)\) as functions of applied strains for the different types of distortions \(D_i\) are plotted in Figure 2. Then, five independent elastic constants \(C_{ij}\), which are inherent in the hexagonal nature of the Co\(_7\)Mo\(_6\) lattice, were calculated by solving the corresponding set of equations, reflected total energy change \(\Delta E\), listed in Table A1. The calculated elastic constants \(C_{ij}\) are listed in Table 2, together with the available theoretical data\(^\text{[20]}\) for comparison.

The obtained elastic constants \(C_{ij}\) can be used for checking the mechanical stability of Co\(_7\)Mo\(_6\) lattice, using the generalized criterion for hexagonal crystals, according to\(^\text{[28]}\)

\[
C_{11} > 0; \quad (C_{11} \cdot C_{33} - 2C_{12}^2 + C_{12} \cdot C_{33}) > 0; \\
C_{11} - |C_{12}| > 0; \quad C_{44} > 0
\]

Thus, as follows from Table 2, the criterion (18) is fulfilled. Therefore, Co\(_7\)Mo\(_6\) is a mechanically stable compound at zero pressure.

The elastic properties of a polycrystalline, namely, bulk modulus, \(B\); shear modulus, \(G\); Young’s modulus, \(E\); and Poisson’s ratio, \(\nu\), can be evaluated using the Voigt-Reuss-Hill (VRH) approximation\(^\text{[29]}\)

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

\[
E = \frac{9GB}{3B + G}, \quad \nu = \frac{3B - E}{6B} = \frac{E - 2G}{2G}
\]

where \(B_V\) is the Voigt model which calculates the upper assessment of mechanical modulus, and \(B_R\) is the Reuss model, it brings their lower evaluation. The moduli of Co\(_7\)Mo\(_6\) were calculated as follows\(^\text{[30]}\)

\[
B_V = \frac{1}{9} (2(C_{11} + C_{12}) + 4C_{13} + C_{33})
\]

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

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

\[
G_R = \frac{15}{(14S_{11} + 4S_{33} - 8S_{13} - 10S_{12} + 6S_{44})}
\]

where \(C_{ij}\) are the elasticity constants and \(S_{ij}\) are the elastic compliances of the elasticity and compliance tensors, respectively. The obtained elastic compliances \(S_{ij}\) of a single crystal of Co\(_7\)Mo\(_6\) are listed in Table 3.

The modulus of the polycrystalline aggregate of Co\(_7\)Mo\(_6\) calculated by (19–24) is listed in Table 4 together with data\(^\text{[20]}\) for comparison.

In order to separate the plastic behavior of a material from a brittle one, it was proposed in works\(^\text{[31,32]}\) to use the values of \(B/G = 1.75\) and Poisson’s ratio \(\nu = 0.26\). If a value of \(B/G \geq 1.75\) or \(\nu \geq 0.26\), then elastic properties of such a material

### Table 2. Ground-state elastic constants \(C_{ij}\) (in GPa) of Co\(_7\)Mo\(_6\) with theoretical values taken from the study by Persson et al.\(^\text{[20]}\) for comparison.

| Compound    | Method    | \(C_{11}\) | \(C_{12}\) | \(C_{13}\) | \(C_{22}\) | \(C_{23}\) | \(C_{33}\) | \(C_{44}\) | \(C_{66}\) |
|-------------|-----------|------------|------------|------------|------------|------------|------------|------------|------------|
| Co\(_7\)Mo\(_6\) | This work | 478.67     | 174.25     | 141.55     | 520.11     | 105.07     | 152.21     |            |            |
|              | calc.\(^\text{[20]}\) | 464        | 191        | 149        | 470        | 103        | 136        |            |            |

### Table 3. Elastic compliances \(S_{ij}\) (T Pa\(^{-1}\)) of single crystals of Co\(_7\)Mo\(_6\) calculated at \(T = 0\) K.

| Compound    | \(S_{11}\) | \(S_{12}\) | \(S_{13}\) | \(S_{33}\) | \(S_{44}\) |
|-------------|------------|------------|------------|------------|------------|
| Co\(_7\)Mo\(_6\) | 2.59       | -0.69      | -0.85      | 3.93       | 9.52       |

\(\Delta E = E_{tot}(V, \delta) - E_{tot}(V_0, 0), \) mRy atom\(^{-1}\) as a function of applied strains \(\delta\) occurring while imposing the distortion matrices \(D_1 - D_6\) on the lattice Co\(_7\)Mo\(_6\) are calculated at \(T = 0\) K. The dotted lines are approximations of polynomial functions.

Figure 2. The curves of differences in total energies (\(\Delta E = E_{tot}(V, \delta) - E_{tot}(V_0, 0), \) mRy atom\(^{-1}\)) as a function of applied strains \(\delta\) occurring while imposing the distortion matrices \(D_1 - D_6\) on the lattice Co\(_7\)Mo\(_6\) are calculated at \(T = 0\) K. The dotted lines are approximations of polynomial functions.
are considered as having a plastic character; otherwise, it is a brittle material. Thus, as follows from Table 4, in according to this criterion, Co7Mo6 can be classified as a material with ductile properties at T = 0 K.

The Debye temperature \( \theta_D \) is a fundamental parameter of thermodynamics and is used in material science to describe physical processes such as heat capacity, thermal expansion, elastic properties, vibrational entropy, and melting temperature that result from theories involving atomic vibrations. \( \theta_D \) is necessary to use the QDH to calculate the thermodynamic properties.

The Debye temperature \( \theta_D \) of Co7Mo6 was obtained using bulk \( B \) and shear \( G \) modulus, according the work by Anderson et al.\(^{[33]} \)

The \( v_s \) shear and \( v_l \) longitudinal elastic wave velocities were calculated by the following expressions.

\[
v_s = \left( \frac{G}{\rho} \right)^{1/2}, \quad v_l = \left( \frac{B + 4G/3}{\rho} \right)^{1/2}
\]

(25)

where \( \rho \) is a density of Co7Mo6. The average elastic velocity \( V_m \) in a polycrystalline aggregate is expressed as

\[
V_m = \left[ \frac{1}{3} \left( \frac{2}{v_s^2} + \frac{1}{v_l^2} \right) \right]^{-1/3}
\]

(26)

Debye temperature was calculated as follows.\(^{[33]} \)

\[
\theta_D = \frac{h}{k_B} \left[ \frac{3n}{4\pi} \left( N_A \rho \right) \right]^{1/3} V_m
\]

(27)

Calculations of the velocities of sound waves moving in the [001,100] directions of Co7Mo6 crystal were carried out using formulae taken from other studies.\(^{[34,35]} \) \( V_L \) longitudinal and \( V_S \) shear velocities of elastic waves moving along the [001] direction are formulated by

\[
V_L = \left( \frac{C_{11}}{\rho} \right)^{1/2}, \quad V_{S1} = V_{S2} = \left( \frac{C_{44}}{\rho} \right)^{1/2}
\]

(28)

whereas the velocities of elastic waves moving along the [100] direction are calculated as

\[
V_L = \left( \frac{C_{11}}{\rho} \right)^{1/2}, \quad V_{S1} = \left( \frac{C_{66}}{\rho} \right)^{1/2}, \quad V_{S2} = \left( \frac{C_{44}}{\rho} \right)^{1/2}
\]

(29)

The calculated sound waves velocities (\( v_s, v_l, V_m \)), Debye temperature calculated by Equation (27), Curie temperature \( T_C \) (12), and anisotropic sound waves velocities (28, 29) for Co7Mo6 are

Table 4. The elastic modulus (in GPa) and Poisson’s ratio \( \nu \) for Co7Mo6 calculated at \( T = 0 \) K together with theoretical values taken from the study by Persson et al.\(^{[20]} \) for comparison.

| Compound      | Method | \( B_V \) | \( B_E \) | \( B \) | \( C_V \) | \( C_E \) | \( C \) | \( E \) | \( \nu \) | \( B/G \) |
|---------------|--------|-----------|-----------|-------|----------|----------|-------|-------|--------|--------|
| Co7Mo6        | This work | 265.8     | 265.8     | 265.8 | 140.1    | 122.1    | 131.3 | 338.2 | 0.29   | 2.02   |
| calc.\(^{[20]} \) | 264   | 264       | 264       | 129   | 124      | 126      |       |        | 0.29   | 2.10   |

Table 5. Predicted ground-state average (\( V_m \)), shear (\( v_s \)), and longitudinal (\( v_l \)) sound wave velocities (in m s\(^{-1} \)); Debye temperature \( \theta_D \) (in K), Curie temperatures \( T_C \) (in K), and sound velocities along [001,100] crystallographic directions (in m s\(^{-1} \)) for Co7Mo6.

| Compound      | \( v_s \) | \( v_l \) | \( V_m \) | \( \theta_D \) | \( T_C \) [001] | \( T_C \) [100] | \( V_L \) [001] | \( V_S1 \) [001] | \( V_S2 \) [001] | \( V_L \) [100] | \( V_S1 \) [100] | \( V_S2 \) [100] |
|---------------|---------|---------|---------|-----------|-------------|-------------|--------------|---------------|---------------|--------------|---------------|---------------|
| Co7Mo6        | 3635    | 6651    | 4054    | 517       | 7235        | 3252        | 6941         | 3914          | 3252          |               |               |               |

Figure 3. The scheme of the calculations of Co7Mo6 compound. The intersection point of all paths corresponds to the optimized lattice parameters (\( a_0, c_0 \)) calculated in this work by DFT at \( T = 0 \) K. The red dashed line \( d0 \) corresponds to the isotropic thermal expansion of Co7Mo6; the blue solid line \( d12 \) is the calculated thermal expansion path of Co7Mo6. It was calculated in this work at \( T = 1073 \) K and \( T = 1423 \) K, and experimental lattice parameters of Co7Mo6,\(^{[12]} \) obtained at \( T = 1423 \) K,\(^{[19]} \) are presented as well.
listed in Table 5. The fastest propagation of sound waves was obtained along the [001] direction by longitudinal waves.

For the best knowledge, there are no experimental or theoretical studies on the Curie and Debye temperature and elastic wave velocities for Co\textsubscript{7}Mo\textsubscript{6}. So, the obtained predictions may be useful in further studies of the μ-phase.

3.2. Thermodynamic Properties at Finite Temperatures

3.2.1. Scheme of the Calculations

In order to investigate the stability of Co\textsubscript{7}Mo\textsubscript{6} with different lattice parameters and find out whether the thermal expansion path of this compound is isotropic or not, the approach of searching a thermal expansion path (STEP)\textsuperscript{[15]} was applied.

The layout used in these calculations is shown in Figure 3. The intersection point of the d\textsubscript{0}–d\textsubscript{13} paths (routes) corresponds to the coordinates (a\textsubscript{0}, c\textsubscript{0}), and these are the optimized parameters of Co\textsubscript{7}Mo\textsubscript{6} lattice obtained in this work by DFT at T = 0 K, which are listed in Table 1. A number of d\textsubscript{i} paths are presented here as an example, as shown in in Figure 3. d\textsubscript{0} corresponds to the direction of isotropic expansions of Co\textsubscript{7}Mo\textsubscript{6}, where the c/a = 5.359 ratio remains constant. The d\textsubscript{1} path passes through coordinates of the experimental point obtained at T = 1423 K after 912 h of annealing treatments\textsuperscript{[19]} as shown in Figure 3 by a blue triangle. Along the d\textsubscript{10} route, the a- parameter of Co\textsubscript{7}Mo\textsubscript{6} lattice remains constant, as shown in Figure 3.

As the volume of the μ-phase, $V(a,c) = (\sqrt{3}/2) a^2 \cdot c$, is a function of lattice parameters a and c, and in order to avoid dealing with the energy surface $E(a,c)$, the total energies $E(V)$ were calculated along the d\textsubscript{0}–d\textsubscript{13} routes, as shown in Figure 4. This approach simplifies the calculations and allows us to reduce the problem to a 1D case and consider the free energy as depending on one variable, the volume. On the one hand, it allows to avoid the differentiation of the total energy $E(a,c)$ with respect to

![Figure 4. Curves of total energies $E_{\text{tot}}(V)$ versus volumes obtained by DFT for Co\textsubscript{7}Mo\textsubscript{6} along the d\textsubscript{0}–d\textsubscript{13} routes.](image)

![Figure 5. Curves of Debye temperatures $\theta_D(V)$ versus volumes calculated for Co\textsubscript{7}Mo\textsubscript{6} along the d\textsubscript{0}–d\textsubscript{13} routes.](image)
variables $a$ and $c$, in order to obtain the pressure $P(a,c)$ and the other functions, like the bulk modulus $B(a,c)$. On the other hand, it allows to use the EOS, like the Vinet EOS, and apply the QDG model for each path $di$ to simulate the effect of temperature on the thermodynamic properties of compounds by calculating the free energies $F(V,T)$, depending only on the volume and temperature, calculated by Equation (1) along each route. Then, by comparing these free energies between themselves, one can find the most energetically favorable thermal expansion route with the lowest energy.

If adding more routes, one can improve an accuracy of the calculations by comparing the energies calculated along these extra routes. In effect, the thermal expansion route may turn out to be curved.

Figure 6. Distribution of local magnetic moments ($\mu_B$) on different sublattices and in the interstitial space of Co$_7$Mo$_6$ $\mu$-phase calculated for $d_0$ – $d_{13}$ routes: a) Co atoms on the first sublattice, Co (3a); b) Co atoms on the second sublattice, Co (18$h$); c) Mo atoms on the third sublattice, Mo (6$c$); d) Mo atoms on the fourth sublattice, Mo (6$c^0$); e) Mo atoms on the fifth sublattice, Mo (6$c^0$); f) in the interstitial space. $V_0$: equilibrium volume.
3.2.2. Calculations of the Debye Temperatures

To study the vibrational entropy contribution to the free energy of the Co7Mo6 compound, the Debye temperatures \( \theta_0(V) \) were calculated for the \( d0-d13 \) routes by Equation (9) and are shown in Figure 5. As follows from the Figure, all the \( \theta_0(V) \) curves have negative slopes at the equilibrium volume \( V_0 \) and at \( T = 0 \) K, except for the curve calculated along \( d4 \). The absolute value of the \( d4 \) slope is the smallest among the other, and because that the total energy \( E(V) \) calculated for \( d4 \) route has higher energy under expansion and contraction relative to other routes, as follows from Figure 4, therefore, according the Debye–Grüneisen model,[14] the contribution to the free energy along the \( d4 \) will be smallest. Along the \( d10 \) route the Debye temperature has the smallest value, but the total energy \( E(V) \) calculated along the \( d10 \) doesn’t have the smallest value at expansion. It is difficult to see in advance which route wins this peculiar competition. Thus, all these routes will compete with each other for the most energetically stable thermal expansion path of Co7Mo6.

3.2.3. Accounting for Magnetic Excitations

If the magnetic energy is not taken into account, then the thermal expansion, as was shown in the study by Vasilyev et al.[15] using the Laves-phase Fe2Mo as an example, will be isotropic, which contradicts the experimental data. So, to investigate the influence of magnetic entropy on the stability of Co7Mo6 compound the dependences of local magnetic moments, in Bohr magnetons, of Co7Mo6 on volumes were obtained along \( d0-d13 \) routes and shown in Figure 6.

Analyzing the curves of the distribution of magnetic moments over the sublattices obtained along different routes, it was found that at equilibrium volume \( V_0 \), which is related to \( T = 0 \) K, the largest contribution to the magnetic energy of Co7Mo6 is made by Co atoms located on the 18 \( h \) sublattice, about 35%; then follows Co atoms located on the 3\( a \) sublattice and the interstitial space, they contribute 28% each. The rest comes from Mo atoms accommodated on 6\( c \), 6\( c' \), and 6\( c'' \). These are 1%, 6% and 2% respectively.

3.2.4. Helmholtz Free Energy and Its Constituents

The calculations of free energies \( F(V,T) \) of Co7Mo6 were carried out by Equation (1) at finite temperatures along the \( d0-d13 \) routes shown in Figure 3. The example of free energies calculated along the \( d12 \) route, for \( T = 100 - 1500 \) K, is shown in Figure 7. Total energy \( E_{tot}(V) \) calculated by DFT at \( T = 0 \) K along the \( d12 \) route is shown in Figure 7 by the red dashed line together with equilibrium volume \( V_0(T) \) obtained at each temperature as the minimum value of the thermodynamic functions shown by blue dotted line. The thermal expansion can be seen as an increase of equilibrium volumes.

All the energy contributions to the Helmholtz free energy \( F(V,T) \), electronic, vibrational and magnetic, were calculated by Equation (2)–(14) at the corresponding equilibrium volumes \( V_0 \).

The graphs of electronic \( E_{el}(V_0(T)) \), vibrational energies \( E_{vib}(V_0(T)) \), magnetic entropies, \( -T \cdot S_{mag}(V_0(T)) \), multiplied by \( -T \), and the sum of free energies \( F(V_0(T)) \) calculated by Equation (1)–(14) versus temperatures for \( d0-d13 \) routes are shown in Figure 8.

By analyzing the graphs presented in Figure 8, one can conclude that the electron energy along the \( d7 \) route is the lowest electron energy among others, as follows from Figure 8a. The \( d10 \) route brings more vibrational energy to the free energy, as shown in Figure 8b. The magnetic contribution for \( F(V_0(T)) \) benefits from the \( d12 \) route, as presented in Figure 8c.

It’s essential to note that the configurational entropy \( S_{conf}(14) \) in the stoichiometry case, such as Co7Mo6, gives the same energy contribution for all the routes and does not affect comparative analysis. Therefore, by analyzing the free energies \( F(V_0(T)) \) of Co7Mo6 shown in Figure 8d, one can find out that the \( d12 \) route is the most energetically favorable one. Therefore, heating the lattice parameters of Co7Mo6 will be increased from \( (a_0, c_0) \), calculated at \( T = 0 \) K, toward values lying on the \( d12 \) route shown in Figure 3. Thus, this is the pathway of thermal expansion of Co7Mo6, in accordance with Figure 7.

The free energy \( F(V_0(T)) \) of Co7Mo6 and its energy terms, total, magnetic, electronic, vibrational, and magnetic entropy, calculated along the \( d12 \) route are shown in Figure 9.

Analysis shows that at heating, the spread of the magnetic energies of Co7Mo6 in different directions is about 5%, as shown in Figure 8c, while the electronic energy is about 2%, as shown in Figure 8a. Both the electronic and magnetic energies equally affect the stability of Co7Mo6. However, the main contributor in the free energy of Co7Mo6 compound is the vibrational energy. The calculation shows that all the energy contributions should be accurately accounted for the correct prediction of a thermal expansion path.

It follows from the obtained free energies of Co7Mo6 shown in Figure 8d that the other closest stable routes to the \( d12 \) are \( d10, d2, \) and \( d0 \); thus, these routes lose this peculiar competition.
Figure 8. The free energy curves $F(T)$ of Co-Mo$_6$ and its energy terms calculated for $d0–d13$ routes. a) Electronic energies, $F_{el}(V_0(T))$; b) vibrational energies, $F_{vib}(V_0(T))$; c) magnetic entropies, $-T\cdot S_{mag}(V_0(T))$; and d) free energies, $F(V_0(T))$. On the right sides of the graphs, in the insets, magnified values are shown for convenience.
3.2.5. Thermal Expansion and Heat Capacity

The thermodynamic properties of Co$_7$Mo$_6$ were obtained along the most energetically favorable thermal route $d_{12}$. The volume expansion $V(T)$ of Co$_7$Mo$_6$ is shown in Figure 10a together with the experimental result$^{[19]}$ obtained at 1423 K after 912 h of annealing treatments, for the sake of comparison. The heat capacity $C_p(T)$ of Co$_7$Mo$_6$ calculated along the route of thermal expansion $d_{12}$ is shown in Figure 10b together with the experimental data taken from the study by Spencer et al.$^{[5]}$ The figure also shows the upper and lower error of the experiment, which is given in the study by Spencer et al.$^{[5]}$. The heat capacity jump at $T_C$ shown in the graph, is the FM/PM phase transition in Co$_7$Mo$_6$ upon heating, as the used model$^{[21]}$ predicts. However, since the experimental data on Curie temperatures for Co$_7$Mo$_6$ are unknown, the search for the exact temperature value is necessary and it is a subject for further study.

3.3. Discussion

Thus, DFT calculations with the QDG approach and the STEP method$^{[15]}$ which, in essence, gives us the formal right to use Equation (1) in these calculations and compare free energies calculated along different routes of thermal expansion, can correctly predict the thermal expansion of Co$_7$Mo$_6$ compound.

The lattice parameters of Co$_7$Mo$_6$ calculated in this work at $T = 1423$ K are in good agreement with the experimental data reported in other studies$^{[12,19]}$ as shown in Figure 3, 10a, and listed in Table 1. The heat capacity calculated in this work and the experimentally estimated data reported in another work$^{[5]}$ as shown in Figure 10b, are in satisfactory agreement at $T = 800$ K; at the higher temperatures, the calculated heat capacity increases slowly than the estimated values.$^{[5]}$

The results of this work show that if we neglect the electronic and magnetic energies, then the $d_{10}$ route, along which the lattice parameter $a$ remaining constant, will be the most energetically favorable, as shown in Figure 8b and presented in Figure 5 by the most lower Debye temperature along $d_{10}$. However, the experimental data on the lattice parameters obtained in the study by Joubert et al.$^{[19]}$ after annealing at $T = 1423$ K and in the study by Forsyth et al.$^{[12]}$ show that this is not the case. The calculated $d_{12}$ path of thermal expansion passes close to the experimental data$^{[12,19]}$ as shown in Figure 3. Therefore, the electronic and magnetic entropies have an essential effect on the stability of this compound and in no case should they be neglected.

The QDG approximation is now considered as a classical theory, and, as experimental data show, its application with the STEP method can correctly predict the direction of the thermal
expansion path of compounds such as Fe₂Mo Laves phase, as reported in the study by Vasilyev et al.\textsuperscript{[13]}

A comparison between thermal expansion paths calculated based on phonon spectra and based on QDG approximation is necessary. In theory, these calculations should match each other. It may be a valuable argument for checking the results obtained in this work.

Such a similar comparative analysis was reported in the study by Vasilyev et al.,\textsuperscript{[37]} where the phonon spectra of Fe₂Mo Laves phase were calculated in the entire Brillouin zone. This analysis shows good agreement between the DFT-based phonon\textsuperscript{[37]} and QDG\textsuperscript{[15]} approaches for predicting the direction of thermal expansion of Fe₂Mo. These calculations show that the anisotropy of the shape of the total energy $E(a,\delta)$ surface is completely correlated with the Debye temperature curves calculated for different directions. Also, if the electronic and magnetic energies are carefully taken into account, then the free energy curves calculated using QDG completely coincide with the curves calculated using phonons. These outcomes are confirmed by the results of the present work, that is, the shape of the energy surface is indeed reflected by the curves of the Debye temperatures, as follows from Figure 4 and Figure 5, and it is necessary to take into account the electronic energy and magnetic entropy for correct prediction of properties. Therefore, as follows from the works, these two approaches can be equally applied to the calculations of the thermodynamics of TCP Laves and $\mu$-phases, which have similar hexagonal structures.

Owing to the fact that the phonon calculations are already including magnetic contributions, it is difficult to assess separately the influence of magnetic entropy. The advantage of the QDG approach with STEP method is that it allows one to separately evaluate the influence of the electronic, vibrational, and magnetic subsystems on the stability of a compound. Thus, this method can provide a complete picture of physical factors affecting the stability.

Finally, it needs to be mentioned that the QDG approach consumes much less computer power than the phonon method, and this difference increases as the crystal structures under study become more complex. Thus, the QDG approach with the STEP method may be preferable for modeling large supercells.

4. Conclusion

The finite-temperature DFT calculations have been carried out to calculate the electronic, vibrational, and magnetic free energy contributions for the Co₇Mo₆ $\mu$-phase. Using the approach of STEP of the compounds, the thermal expansion of Co₇Mo₆ is correctly calculated in accordance with the experimental data. The nature of the thermal expansion is not isotropic. The elastic constants, bulk modulus, elastic sound velocities, Curie, and Debye temperatures were calculated at ground state. The heat capacity calculated along the thermal expansion path of Co₇Mo₆ is in satisfactory agreement with the experimental data. Thus, the approach of searching the thermal expansion path of compounds may be used to study the thermodynamic properties of $\mu$-phase. The work shows that vibrational energy is the main factor influencing the stability of Co₇Mo₆, but the electronic and magnetic entropies should be accurately accounted for in the correct thermodynamic description of the $\mu$-phase.

Appendix

| $D_i$ matrices | Total energy change as a function of applied strains |
|----------------|------------------------------------------------------|
| $D_1 = \begin{pmatrix} 1 + \delta & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$ | $\Delta E = V_0 (\tau_1 \delta + \frac{C_{138}}{C_0} \delta^2)$ |
| $D_2 = \begin{pmatrix} \frac{1}{2} \delta & 0 & 0 \\ 0 & \frac{1}{2} \delta & 0 \\ 0 & 0 & \frac{1}{2} \delta \end{pmatrix}$ | $\Delta E = V_0 (\tau_1 \delta + \frac{1}{2} \delta)$ |
| $D_3 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 + \delta \end{pmatrix}$ | $\Delta E = V_0 (\tau_1 \delta + \frac{1}{2} \delta)$ |
| $D_4 = \begin{pmatrix} \frac{1}{2} \delta & 0 & 0 \\ 0 & \frac{1}{2} \delta & 0 \\ 0 & 0 & \frac{1}{2} \delta \end{pmatrix}$ | $\Delta E = V_0 (\tau_1 \delta + \frac{C_{138}}{C_0} \delta^2)$ |
| $D_5 = \begin{pmatrix} \frac{1}{2} \delta & 0 & 0 \\ 0 & \frac{1}{2} \delta & 0 \\ 0 & 0 & \frac{1}{2} \delta \end{pmatrix}$ | $\Delta E = V_0 (\tau_1 \delta + \frac{1}{2} \delta)$ |

Acknowledgements

The research was financially supported by the Russian Foundation for Basic Research as a part of scientific project 19-03-00530.

Conflict of Interest

The author declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

$\mu$-phase, Debye temperature, elastic properties, first-principles calculations, thermal expansion, thermodynamic properties

Received: May 20, 2022
Revised: August 19, 2022
Published online: September 4, 2022

[1] A. Davydov, U. R. Kattner, J. Phase Equilib. 1999, 20, 5.
[2] A. V. Davydov, U. R. Kattner, J. Phase Equilib. 2003, 24, 209.
[3] C. Rae, M. Karunaratne, C. Small, R. Broomfield, C. Jones, R. Reed, *Superalloys 2000*, 2000, 767.

[4] R. C. Reed, *The Superalloys: Fundamentals and Applications*, Cambridge University Press, Cambridge 2006.

[5] P. J. Spencer, F. H. Putland, *J. Chem. Thermodyn.* 1975, 7, 531.

[6] K. Oikawa, U. R. Kattner, J. Sató, T. Omori, M. Jiang, K. Anzai, K. Ishida, *Mater. Trans.* 2012, 53, 1425.

[7] K. Zhao, Y. H. Ma, L. H. Lou, Z. Q. Hu, *Mater. Trans.* 2005, 46, 54.

[8] X. Z. Qin, J. T. Guo, C. Yuan, G. X. Yang, L. Z. Zhou, H. Q. Ye, *J. Mater. Sci.* 2009, 44, 4840.

[9] M. Sluiter, A. Pasturel, Y. Kawazoe, *Phys. Rev. B* 2003, 67, 174203.

[10] M. H. F. Sluiter, *Calphad* 2006, 30, 357.

[11] J.-M. Joubert, N. Dupin, *Intermetallics* 2004, 12, 1373.

[12] J. B. Forsyth, L. M. d’Alte da Veiga, *Acta Cryst.* 1962, 15, 543.

[13] D. Ma, B. Grabowski, F. Körmann, J. Neugebauer, D. Raabe, *Acta Mater.* 2015, 100, 90.

[14] V. I. Moruzzi, J. F. Janak, K. Schwarz, *Phys. Rev. B* 1988, 37, 790.

[15] D. Vasilyev, *Physica B* 2021, 621, 413307.

[16] Y. Wang, L. G. Hector, H. Zhang, S. L. Shang, L. Q. Chen, Z. K. Liu, *Phys. Rev. B* 2008, 78, 104113.

[17] L. D. Landau, E. M. Lifshitz, *Statistical Physics*, Pergamon Press, Oxford, New York 1980.

[18] Y. Wang, Z. K. Liu, L. Q. Chen, *Acta Mater.* 2004, 52, 2665.

[19] J. Joubert, N. Dupin, *Intermetallics* 2004, 12, 1373.

[20] K. A. Persson, Materials Data on Co7Mo6 (SG:166) by Materials Project, https://doi.org/10.17188/1274024, https://materialsproject.org/materials/mp-567747/

[21] A. T. Dinsdale, *Calphad* 1991, 15, 371.

[22] P. Blaha, K. Schwarz, F. Tran, R. Laskowski, G. K. H. Madsen, L. D. Marks, *J. Chem. Phys.* 2020, 152, 074101.

[23] P. Hohenberg, W. Kohn, *Phys. Rev.* 1964, 136, B864.

[24] W. Kohn, L. J. Sham, *Phys. Rev. A* 1965, 140, A1133.

[25] J. P. Perdew, K. Burke, Y. Wang, *Phys. Rev. B* 1996, 54, 16533.

[26] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* 1996, 77, 3865.

[27] H. J. Monkhorst, J. D. Pack, *Phys. Rev. B* 1976, 13, 5188.

[28] J. F. Nye, *Physical Properties of Crystals*, Clarendon Press, Oxford 1964.

[29] R. Hill, *Proc. Phys. Soc. A* 1952, 65, 349.

[30] D. Tromans, *JIRAS* 2011, 6, 462.

[31] S. F. Pugh, *Philos. Mag. Ser. 7* 1954, 45, 823.

[32] J. J. Lewandowski, W. H. Wang, A. L. Greer, *Philos. Mag. Lett.* 2005, 85, 77.

[33] O. L. Anderson, *J. Phys. Chem. Solids* 1963, 24, 909.

[34] B. B. Karki, L. Stixrude, S. J. Clark, M. C. Warren, G. J. Ackland, J. Crain, *Am. Mineral.* 1997, 82, 51.

[35] W.-C. Hu, Y. Liu, D.-J. Li, X.-Q. Zen, C.-S. Xu, *Comput. Mater. Sci.* 2014, 83, 27.

[36] P. Vinet, J. H. Rose, J. Ferrante, J. R. Smith, *J. Phys.: Condens. Matter* 1989, 1, 1941.

[37] D. A. Vasilyev, arXiv:2208.04241.v1, 2022.