



Thermophysical properties of titanium and vanadium nitrides: Thermodynamically self-consistent approach coupled with density functional theory



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ABSTRACT

In this study, density functional theory (DFT) with a thermodynamically self-consistent (TSC) method are used to predict the thermophysical properties of metallic compounds. The TSC method used in this work is, in summary, an extension of the classical quasi-harmonic approximation satisfying the Maxwell relations and thus ensuring thermodynamic consistency. Electronic band structure and density of state (DOS) of titanium nitride (TiN) and vanadium nitride (VN) are calculated by generalized gradient approximation (GGA) and local density approximation (LDA) to reveal their metallic character. The electron contribution to the heat capacity and thermal expansion is deduced from the DOS and Fermi-Dirac distribution at temperatures above the ground state. The vibrational contribution to thermophysical properties at high temperatures is calculated using the TSC method as an alternative for the existing quasi-harmonic approximations. In addition, elastic and mechanical properties of TiN and VN are calculated. These results show that VN is more anisotropic than TiN, which is manifested in the calculated results. It has been shown that this anisotropic character is rooted in the electronic structure and charge distribution in VN. Thus, the electron localization function (ELF) is calculated to highlight the way in which electrons are localized and the nature of the chemical bonding between the atoms. The significance of the anharmonicity contribution, due to phonon–phonon interaction, for the thermal properties is discussed. Predicted heat capacities and thermal expansions by the TSC method accord well with experimental data. Overall, it has been shown that the TSC method, together with consideration of the electronic structure, is a powerful tool to predict the thermophysical properties of non-magnetic metallic systems, with a high accuracy.

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1. Introduction

An accurate description of the Gibbs energy of chemical compounds as a function of temperature is highly desirable in many materials science applications, e.g., to predict phase equilibria; or to understand nucleation, growth and the solidification processes. The Gibbs energy of a given stoichiometric compound as a function of temperature is fully defined by the energy of formation at 0 K, ΔE_{0K} ,

and the heat capacity at constant pressure, C_p , as a function of temperature:

$$G(T) = \Delta E_{0K} + \underbrace{\int_0^T C_p(T') dT'}_{\Delta H} - T \underbrace{\int_0^T \frac{C_p(T')}{T'} dT'}_{\Delta S} \quad (1)$$

The first integral represents the enthalpic contribution, ΔH , and the second one the entropic contribution, ΔS . Often, in thermodynamic databases, the heat capacity of elements and compounds are given in the form of empirical functions of temperature (e.g. polynomial) and in different temperature ranges. For many compounds, of different chemical nature, there is a considerable lack of

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data on heat capacity. To overcome this, and consequently provide an accurate prediction of the Gibbs energy, several methods are available. The most reliable is, so far, the quasi-harmonic approximation (QHA) model combined with DFT calculations for its parameterization [1–4]. Strictly speaking, the QHA describes the vibrational Helmholtz free energy, i.e. the characteristic thermodynamic function of the lattice vibration in the canonical (NVT) ensemble. According to the QHA method, the lattice vibration contribution to the heat capacity is given by the Debye model C_V^D [5], and so the lattice contribution to C_p is deduced by adding the lattice expansion contribution:

$$C_p^{latt}(T) = \underbrace{C_V^D(T)}_{\text{Harmonic}} + \underbrace{C_V^D(T) \cdot \alpha(T) \cdot \gamma(T) \cdot T}_{\text{Lattice expansion}} \quad (2)$$

where γ is the Grüneisen parameter and α the volumetric thermal expansion coefficient. The thermal expansion is calculated by the minimization of the Gibbs energy [1–4] and the Grüneisen parameter is derived from the volume dependence of the Debye temperature to express the anharmonicity in the solid. Thereafter a physical expression for C_p for non-magnetic solids is given by adding to the lattice C_p the other physical contributions: the electronic part and the thermal vacancy contribution:

$$C_p(T) = \underbrace{C_V^D(T)}_{\text{Harmonic}} + \underbrace{C_p^{Expn}(T)}_{\text{Lattice expansion}} + \underbrace{C_p^{Anh}(T)}_{\text{Anharmonic}} + \underbrace{C_p^{el}(T)}_{\text{Electronic}} + \underbrace{C_p^{Def}(T)}_{\text{Thermal vacancy defects}}$$

For a better prediction of phase equilibria, an attempt at physical representation of the Gibbs energy [6] was proposed and still is used by the “CALPHAD community”. However, in their representation, the lattice expansion and the anharmonic term are merged into the same anharmonic term by assuming that it deviates only slightly from linear behavior with temperature. However, from a physical point of view, this assumption gives an incorrect interpretation of the experimental data, by giving an incorrect large value to the anharmonic contribution of the lattice vibration.

Recently, Glensk et al. [7] proposed a DFT-based method which combines the QHA method with electronic and anharmonic contributions to predict the heat capacity of metallic elements. This methodology shows high predictive capacity. However, a large (negative) anharmonic contribution was found in order to compensate for the exponential increase in the quasi-harmonic C_p with temperature. However, in a recent paper [8] we have shown that the QHA overestimates the lattice vibration. This is owing to the parameterization procedure, which leads to violations of the Maxwell relations and thus to the thermodynamic consistency between the various properties directly derived from the Gibbs energy. These are heat capacity, entropy, thermal expansion and compressibility. The new thermodynamically self-consistent (TSC) method [8] was proposed in order to improve the classical QHA method with respect to the Maxwell relations. This method has shown, for oxides (CaO and K₂O), a good predictive capacity without anharmonic corrections.

The aim of this work is to extend the TSC method to the nonmagnetic and electrically conducting materials, and to discuss the role of the anharmonicity. To achieve this, we have considered titanium and vanadium nitrides (TiN and VN) instead of pure metals as has been done by Glensk et al. [7]. These two materials are of importance in many materials science applications because of their good mechanical, chemical and thermal properties. The rest of this paper is organized as follows: first the DFT computational

details are explained, then three different approaches for calculation of the elastic constants are described. Thereafter, the procedure for calculation of the relevant Debye temperatures are delineated. Finally, before results and discussion are presented, the TSC method and vibrational and electronic contributions to the thermal properties are described in detail.

2. Computational details

In this work, *ab initio* computations based on the Plane-Wave basis sets Density Functional Theory (DFT) is performed using the Vienna *ab initio* Simulation Package (VASP) [9–12]. The Projected Augmented Wave (PAW) approach [13,14] together with the Generalized Gradient Approximation (GGA) parameterized by Perdew, Burke and Ernzerhof (PBE) [15,16] are employed. The Local Density Approximation (LDA) is also used for comparison purposes. A cut-off energy of 520 eV and $31 \times 31 \times 31$ Γ -centered k-points grid with a Gaussian smearing parameter σ of 0.02 eV are used to ensure that force and energy convergence criteria be better than 0.02 eV/Å and 0.01 meV, respectively. For band structure calculations, a denser k-points sampling of 51 grids in each symmetrical direction is considered.

3. Calculation of elastic constants

In the present article, bulk modulus at ground state is calculated through three different approaches by using all elastic constants, an Equation of State (EOS) and simple parabolic energy curve fitting. It is shown that for an isotropic system all these approaches converge to the same value; however, when there is considerable anisotropy, a significant difference may be observed. The cubic structure with $Fm\bar{3}m$ space group is considered to describe TiN and VN. This structure in the conventional unit cell has only one lattice parameter a , with the Bravais lattice vectors of the matrix form

$$\mathbf{R} = a \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

DFT based *ab initio* computations implemented in VASP allows total energy calculation to be done for arbitrary crystal structures. Therefore, by applying small strains to the equilibrium lattice and calculating the relevant total energies, one would be able to deduce the elastic constants. Distortion applied to the equilibrium lattice must be small so that it remains in the elastic limit of the crystal. Thus, in this limit, elastic stiffness constants c_{ij} are identified as proportional to the second order coefficient in a polynomial fit of the total energy as a function of the strain ϵ . For a small strain, the total energy $E(V, \epsilon)$ of a crystal under strain ϵ , can be expanded in the following way:

$$E(V, \epsilon) = E(V_0, 0) + V_0 \left(\sum_i \sigma_i \xi_i \epsilon_i + 1/2 \sum_{ij} c_{ij} \xi_i \epsilon_i \xi_j \epsilon_j \right) \quad (4)$$

where V_0 and $E(V_0, 0)$ are the volume of the unstrained system and the corresponding total energy, respectively. Here σ_i represents elements of the stress tensor ($\sigma_i = c_{ij} \epsilon_j$). In this equation, Voigt notation is used to replace xx, yy, zz, yz, xz and xy by 1, 2, 3, 4, 5 and 6, respectively. In Voigt notation ϵ 's are symmetric, and ξ will take the value 1 for the indices 1, 2 and 3 and the value 2 for the indices 4, 5 and 6, to compensate this symmetry. The distorted lattice vectors, identified by the matrix \mathbf{R}' , is obtained according to the rule $\mathbf{R}' = \mathbf{R}\mathbf{D}$ in which \mathbf{D} is the distortion matrix. For the cubic crystal there are only three independent elastic stiffness constants:

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