



LETTER

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To cite this article: A. S. Bochkarev *et al* 2016 *EPL* **116** 16001

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A single-volume approach for vacancy formation thermodynamics calculations

A. S. BOCHKAREV^{1,2}, S. O. ZAMULKO^{3,4}, O. I. GORBATOV^{5,6,7}, S. I. SIDORENKO³, P. PUSCHNIG²
and A. V. RUBAN^{1,5}

¹ Materials Center Leoben Forschung GmbH (MCL) - Roseggerstraße 12, A-8700 Leoben, Austria

² University of Graz, Institute of Physics, NAWI Graz - Universitätsplatz 5, A-8010 Graz, Austria

³ Metal Physics Department, National Technical University of Ukraine “Kyiv Polytechnic Institute” Kyiv 03056, Ukraine

⁴ Centre for Materials Science and Nanotechnology, University of Oslo - P. O. Box 1048 Blindern, NO-0316 Oslo, Norway

⁵ Department of Materials Science and Engineering, KTH Royal Institute of Technology SE-100 44 Stockholm, Sweden

⁶ Institute of Quantum Materials Science - Ekaterinburg 620107, Russia

⁷ Magnitogorsk State Technical University - Magnitogorsk 455000, Russia

received 17 June 2016; accepted in final form 25 October 2016

published online 16 November 2016

PACS 61.72.jd – Vacancies

PACS 63.20.dk – First-principles theory

PACS 65.40.-b – Thermal properties of crystalline solids

Abstract – The vacancy formation Gibbs free energy, enthalpy and entropy in fcc Al, Ag, Pd, Cu, and bcc Mo are determined by first-principles calculations using the quasi-harmonic approximation to account for vibrational contributions. We show that the Gibbs free energy can be determined with sufficient accuracy in a single-volume approach using the fixed equilibrium volume of the defect-free supercell. Although the partial contributions to the Gibbs free energy, namely, the formation enthalpy and entropy exhibit substantial errors when obtained directly in this approach, they can be computed from the Gibbs free energy using the proper thermodynamic relations. Compared to experimental data, the temperature dependence of the vacancy formation Gibbs free energy is accounted for at low temperatures, while it overestimates the measurements at high temperature, which is attributed to the neglect of anharmonic effects.

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The vacancy formation energy is an important parameter which determines phase and structural transformations in solids at finite temperatures. Being difficult to measure [1–3], it is generally believed that it can be obtained relatively easily by first-principles calculations based on density functional theory (DFT) as has been done in the past in a large number of publications [4–28].

However, there are two major problems in such DFT calculations. First, it is not clear to what extent the inevitable approximations in the exchange-correlation functional affect the results. Even for metallic systems, where effective short-range screening of electrostatic interactions takes place, an accurate account of the large gradient of the electron density near the vacant site may still pose a problem [27,29–33]. The second problem arises if one

wishes to account for the temperature dependence of the vacancy formation energy.

On the one hand, most of the existing phenomenological models, which involve this quantity, assume that the vacancy formation energies and entropies are temperature independent, and, therefore, it is enough to determine the vacancy formation energy only at 0 K. On the other hand, it has been demonstrated in several *ab initio* calculations [10,23,24] as well as in a more approximate atomistic modeling [34,35] that the vacancy formation energy can change dramatically with temperature. For instance, first-principles molecular-dynamics (MD) simulations by Smargiassi and Madden [10] showed a decrease of the vacancy formation free energy in Na by a factor of two from 0 K to close to the melting point. In contrast to this

finding, Mattsson *et al.* [23] obtained a significant increase of the vacancy formation energy with temperature for Mo in first-principles MD simulations.

A similar increase has been obtained in ref. [24] for Al, while the more recent calculations by Glensk *et al.* [33] have demonstrated that the overall vacancy formation free energy substantially decreases if anharmonic contributions are taken into consideration, similarly to the results by Smargiassi and Madden [10]. In summary, this means that neither the vacancy formation energy nor the vacancy formation entropy can be considered to be temperature independent. The work by Glensk *et al.* [33] also demonstrates that the quasi-harmonic approximation substantially overestimates the vacancy formation free energy at high temperatures. Thus, in order to accurately reproduce the temperature dependence of the vacancy formation energy at high temperatures, one should account for anharmonic vibrations of the atoms next to the vacancy.

In this work, we establish a thermodynamically consistent approach which is based on quasi-harmonic calculations using one fixed equilibrium volume of a defect-free supercell. Being able to eliminate calculations of the equilibrium volume of the defected cell presents an important simplification in the computational algorithm, which allows one to study the temperature dependence of the vacancy formation energy by more elaborate methods such as *ab initio* molecular dynamics. We demonstrate our method for vacancies in fcc Al, Cu, Ag, Pd, and bcc Mo using PBEsol functional [29], which has been chosen as to minimise the error for the exchange-correlation energy near the vacancy. The numerical results support our single-volume approach. It should be noted that when comparing the so-obtained results to available experimental data, anharmonic effects beyond the quasi-harmonic approximation should be considered.

Thermodynamic properties of vacancies. – In pure metals, the free energy (per atom) related to the thermally induced vacancies can be defined as follows:

$$G_{\text{vac}} = cG_f - TS_{\text{conf}} \equiv c[H_f - TS_f] - TS_{\text{conf}}. \quad (1)$$

Here, c is the concentration of vacancies, G_f is the vacancy formation free energy associated with a single vacancy, H_f is the vacancy formation energy (enthalpy), S_f the vacancy formation entropy, and S_{conf} the configurational entropy related to the vacancies. Using the thermodynamic relation

$$\left(\frac{\partial G_{\text{vac}}}{\partial T}\right)_P = -S, \quad (2)$$

where $S = cS_f + S_{\text{conf}}$ is the total entropy of the system related to vacancy formation, assuming no interaction between vacancies one finds

$$c \left[\frac{\partial H_f}{\partial T} - T \frac{\partial S_f}{\partial T} \right] + \frac{\partial c}{\partial T} \left[H_f - TS_f - T \frac{\partial S_{\text{conf}}}{\partial c} \right] = 0. \quad (3)$$

If both H_f and S_f are temperature independent, one immediately finds the concentration of *noninteracting*

vacancies using the entropy of an ideal solution, $S_{\text{conf}} = -k_B[c \ln c + (1-c) \ln(1-c)]$, which is a well-known result:

$$c \approx \exp(S_f/k_B) \exp(-H_f/k_B T). \quad (4)$$

In general, the equilibrium concentration of vacancies is obtained from the corresponding minimization of G_{vac} at a fixed temperature, which leads to the following equation:

$$c \left[\frac{\partial H_f}{\partial c} - T \frac{\partial S_f}{\partial c} \right] + \left[H_f - TS_f - T \frac{\partial S_{\text{conf}}}{\partial c} \right] = 0. \quad (5)$$

However, as long as there is no interaction between vacancies, the first term in this equation vanishes and the concentration of vacancies is determined from the last term, which again leads to (4). Moreover, since in this case, the last term in (5) is zero, the first term in (3) should be also zero, and thus the following important relation between the vacancy formation enthalpy and entropy should be satisfied:

$$\frac{\partial H_f}{\partial T} = T \frac{\partial S_f}{\partial T}. \quad (6)$$

This means that if the vacancy formation enthalpy is temperature dependent, so should be the formation entropy, and they are connected via eq. (6).

Vacancy formation energy calculations require, in general, finding the equilibrium volume corresponding to the minimum of the Gibbs free energy of systems (supercells) without and with a vacancy denoted as G_0 and G_v , respectively. The difference in equilibrium volumes of those supercells with and without and with a vacancy, $\Omega_0(T)$ and $\Omega_v(c, T)$, (normalized by the number of sites) is related to the vacancy formation volume, ω_f :

$$\omega_f(T) = \frac{\partial \Omega_v(c, T)}{\partial c}. \quad (7)$$

Here, we have neglected the concentration dependence of ω_f , which should be insignificant. So, the equilibrium volume of the system with vacancies can be written as

$$\Omega_v(c, T) = \Omega_0(T) + c\omega_f(T). \quad (8)$$

In practical applications, however, it would be computationally advantageous to determine the thermodynamic properties of vacancies without the need of finding the equilibrium volume of the supercell with vacancy. In such an approach, one performs all supercell calculations, both with and without a vacancy for the equilibrium volume of the defect-free system. We refer to this approximation as the single-volume approach. The validity of this simplification arises from the fact that the difference in the equilibrium volume of two systems is usually small. As a consequence, the free energies of the systems with and without a defect exhibit small variations as a function of volume due to the fact that their first derivatives are zero at the equilibrium volume.

This approach can be particularly useful in calculations of the self- or substitutional impurity diffusion coefficients

at a certain temperature. Although the directly calculated vacancy formation entropy and enthalpy can be in error in this approach, they still obey relations (2) and (6). Below we demonstrate this approach in calculations of the vacancy formation free energy, enthalpy and entropy for five metals: Al, Ag, Cu, Mo and Pd. The following notations are used. Quantities corresponding to calculations in which the equilibrium volumes $\Omega_0(T)$ and $\Omega_v(c, T)$ are explicitly taken into account are denoted as G , S , H . Those numerical results in which a single volume $\Omega_0(T)$ has been used for both supercells, without and with vacancy, are abbreviated as \tilde{G} , \tilde{S} , and \tilde{H} , respectively.

Computational details. – In this work, the vacancy formation free energy $G_f(T)$, is obtained as a sum of three different contributions:

$$G_f(T) = H_f(T) + G_f^{el}(T) + G_f^{vib}(T). \quad (9)$$

Here, $H_f(T)$ is the vacancy formation energy (we consider the case of zero pressure) at the corresponding temperature T . $G_f^{vib}(T)$ and $G_f^{el}(T)$ are the contributions to the vacancy formation free energy from lattice vibrations and thermal one-electron excitations, respectively. In particular, the vacancy formation energy, H_f , is obtained as

$$H_f(T) = E_v(T) - \frac{N-1}{N}E_0(T), \quad (10)$$

where $E_v(T)$ and $E_0(T)$ are the total energies of the supercells with and without vacancy, respectively, and N is the number of atoms in the supercell without vacancy.

The contribution from the thermal one-electron excitations to the total energy, E_{el} , and free energy, G_{el} , has been determined as

$$E_{el}(T) = \frac{\pi^2}{3}N(E_F)k_B^2T^2, \quad (11)$$

$$G_{el}(T) = -\frac{\pi^2}{3}N(E_F)k_B^2T^2, \quad (12)$$

where $N(E_F)$ is the density of states at the Fermi energy, E_F , per supercell. We have neglected this contribution for Al, Cu and Ag due to its insignificant contribution to the total free energy of vacancy formation in these cases.

All *ab initio* calculations in this paper are performed by the frozen-core full-potential projector augmented wave (PAW) method [36,37] as implemented in the Vienna *ab initio* simulation package (VASP) [38–40]. The PBEsol generalized gradient approximation [29] has been utilized, which minimizes the error for open systems like surfaces and vacancies. Besides, this functional reproduces quite well the lattice constants of 4d metals (Ag, Pd, Mo), which is important for description of the first-principles thermodynamics of defect properties.

The size of the supercell for fcc Al, Ag, Cu and Pd was $2 \times 2 \times 2(\times 4)$ containing 32 atoms in the defect-free cell, and for bcc Mo the size of the supercell used was $3 \times 3 \times 3(\times 2)$ containing 54 atoms in the defect-free supercell. We have checked the convergence of the vacancy

formation energy in the case of copper with respect to the supercell size and found that the difference between the 0 K vacancy formation energies for supercells containing 32 and 108 atoms was less than 0.01 eV. Therefore, we conclude that the size of the supercell used in the present study is sufficient for obtaining reasonably accurate vacancy formation energies. All atoms were allowed to relax during calculations of the defected supercells. The plane-wave energy cutoff was 500 eV. The integration over the Brillouin zone has been done using a $10 \times 10 \times 10$ grid of the Monkhorst-Pack (MP) mesh [41] in the case of Cu, Pd, Mo, $12 \times 12 \times 12$ in the case of Al and $14 \times 14 \times 14$ for Ag. The convergence tolerance for the total energy was 10^{-8} eV/atom, while 10^{-3} eV/Å for forces on atoms during local lattice relaxations.

The free energy of lattice vibrations is calculated in the quasi-harmonic approximation using the phonopy code [42] where the dynamical matrix has been obtained by the small displacement method [43]. The unit cell was taken to be identical to the supercell while calculating phonon dispersion. Symmetry was considered while performing displacements reducing the number of displacements to one for defectless supercells and to 7 and 13 for supercells with a vacancy in the case of fcc and bcc materials respectively. The amplitude of displacements was 0.005 Å in the case of Al and 0.01 Å for the other metals. The linear dependence of the force with respect to the displacement amplitude was checked in the case of Cu. The linear regime preserves at least up to displacements of 0.07 Å.

Results. – As a first step, we have calculated the temperature dependence of the equilibrium lattice parameters of the five investigated metals for the defect-free supercells within the quasi-harmonic approximation. As can be seen from fig. 1, the calculated lattice parameters for Al, Ag and Pd are in very good agreement with the experimental data, especially at low temperatures. Somewhat worse agreement is observed for Cu and Mo which is attributed to a deficiency of PBEsol for these elements. Nevertheless, the character of the temperature dependence is still well described within the quasi-harmonic *ab initio* calculations. We have also performed quasi-harmonic calculations for supercells with a vacancy in order to find the respective equilibrium volumes. The obtained data is shown in fig. 1 as dashed lines.

Based on these results, we are able to compute all thermodynamic properties describing the vacancy formation as a function of temperature. We illustrate the effectiveness of the single-volume approach in fig. 2 using Al as an example. Here, we show the properly calculated values of the vacancy thermodynamic properties, G , S and H for Al, obtained in calculations with the corresponding equilibrium volumes together with their counterparts, \tilde{G} , \tilde{S} , \tilde{H} obtained for the single equilibrium volume of the defect-free supercells. First of all, one can see that G and \tilde{G} are very close to each other. This is to be expected

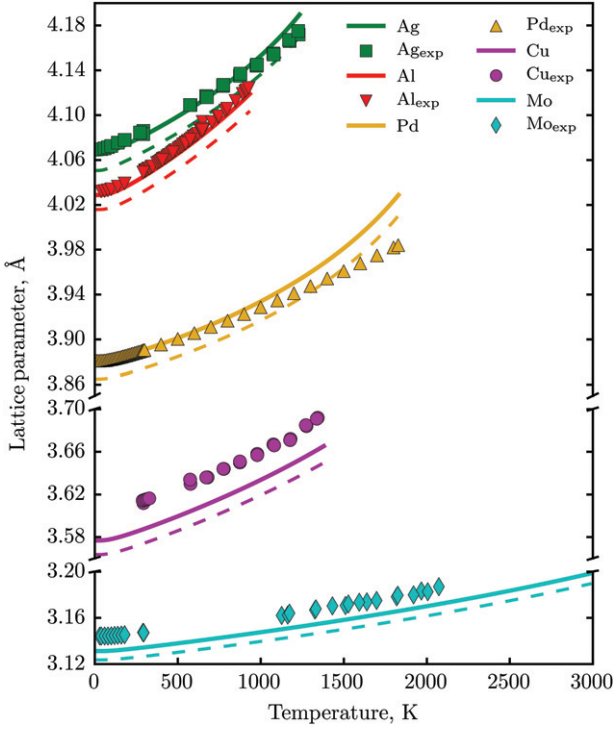


Fig. 1: (Color online) Calculated equilibrium lattice parameters of Ag, Al, Pd, Cu, and Mo obtained in the quasi-harmonic approximation as a function of temperature (full lines) compared to the experimental data (symbols) for Al [44–46], Ag [46,47], Cu [47,48], Pd [49], Mo [46,50,51]. Dashed lines show the equilibrium lattice parameters obtained for supercells with vacancy.

since the variation of the free energy of the supercells is small close to their equilibrium volume. Moreover, the close agreement of G and \tilde{G} provides the basis for using the thermodynamic relation (2) in order to determine formation enthalpies and entropies. The resulting entropy and enthalpy terms are shown in panels (b) and (c) of fig. 2 and are denoted as S' and H' , respectively.

One can see that S' and H' are very close to the directly calculated values, S and H . On the other hand, the difference between S and \tilde{S} as well as between H and \tilde{H} is significant. This implies that using the entropy and enthalpy of vacancy formation directly obtained for a single-volume of both supercells, one introduces a substantial error. It is interesting that the huge errors in \tilde{S} and \tilde{H} compensate each other and produce accurate result for the Gibbs free energy when summed up.

In fig. 3, we show analogous results for four other metals: fcc Cu, Ag, and Pd as well as for bcc Mo. Overall, the differences between the numerical values for G and \tilde{G} are reasonable small. In the case of Cu, it is negligible, while it is somewhat larger in the case of Ag, and is about 0.04–0.05 eV for Mo and Pd. However, it is mostly a constant shift. Moreover, the energy differences can be regarded as minor when taking into consideration typical errors related to various approximations for

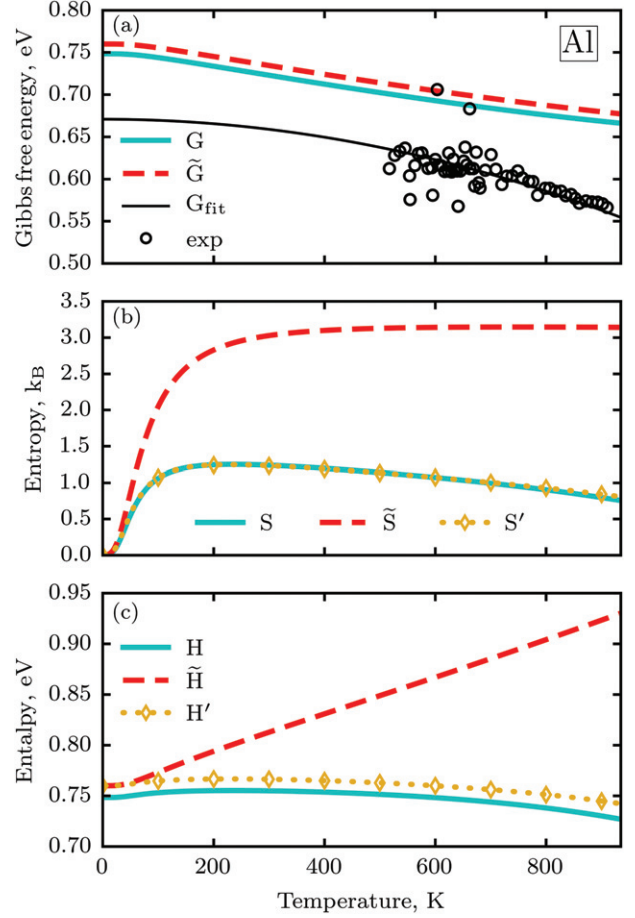


Fig. 2: (Color online) (a) The vacancy formation Gibbs free energy, (b) vacancy formation entropy and (c) vacancy formation enthalpy in Al. G , S , H correspond to the calculations done at the equilibrium volumes of supercells and they are plotted by solid lines. \tilde{G} , \tilde{S} , \tilde{H} are the vacancy formation free energy, enthalpy and entropy determined in the single-volume approach and plotted by dashed lines with diamonds. The vacancy formation entropy, S' , and enthalpy, H' , are obtained from \tilde{G} using relation (2). Black dots show available experimental data [52]. G_{fit} is the quadratic fit of the experimental temperature-dependent vacancy formation free energy shown by the black solid line.

the exchange-correlation potential. At the same time, the agreement of formation entropies, S and S' , is very good in all the cases showing that the single-volume approach is reasonably accurate for different metals. Regarding the temperature dependence of G , we notice a pronounced influence of the electronic free energy for Pd and Mo. In the case of Pd, G first decreases and then rises with the temperature, for Mo the decrease of G is much more pronounced than for all other metals. This is because a vacant site differently affects the density of states at the Fermi energy in these metals, increasing it in Mo and decreasing in Pd, leading according to (11) to the respectively negative and positive contributions to the vacancy formation free energy.

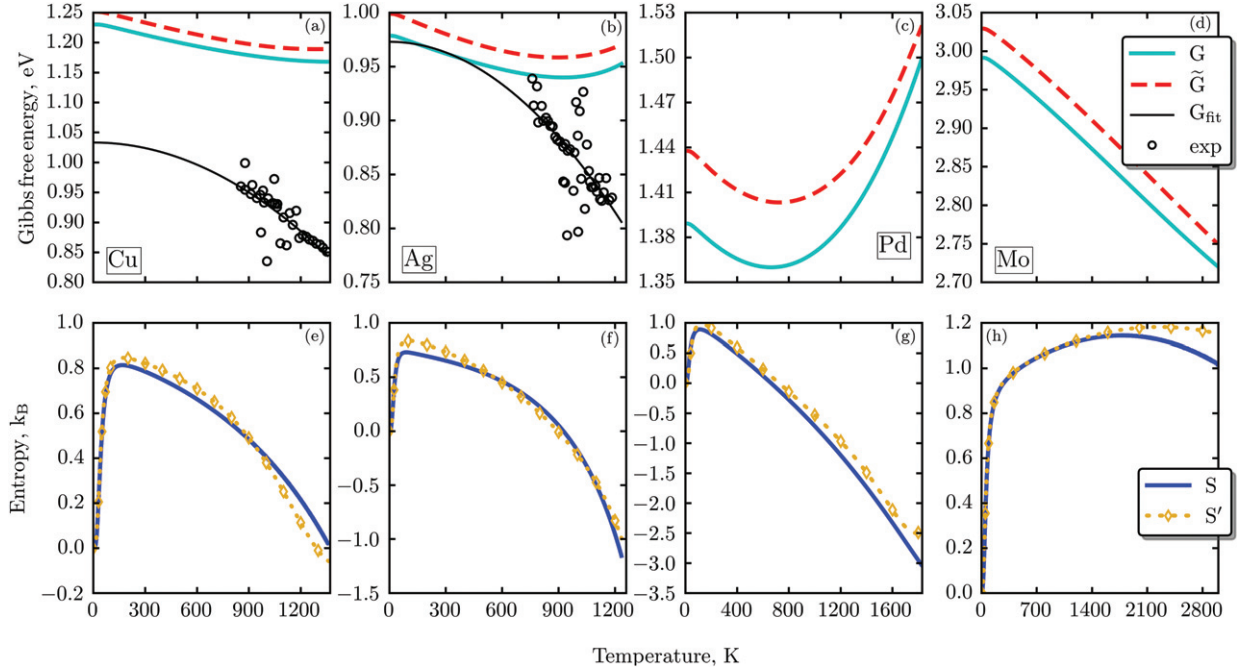


Fig. 3: (Color online) (a)–(d) The vacancy formation Gibbs free energy; (e)–(h) the vacancy formation entropy in Cu, Ag, Pd and Mo, respectively. For notations, see fig 2.

Figures 2 and 3 also include available experimental data [52] obtained by a conversion of the experimental vacancy concentrations to the vacancy formation free energies. In all the cases considered here, the experimental formation energies are smaller than the corresponding theoretical results. One obvious problem with such a comparison is the fact that experimental data are available only for rather high temperatures, while the theoretical results obtained in the quasi-harmonic approximation are expected to be accurate for low temperatures. Indeed, the experimentally observed character of the temperature dependence of the vacancy formation free energy at high temperatures can most probably be attributed to anharmonic effects as discussed in detail by Glensk *et al.* [33].

Using a quadratic fit as proposed in that work [33], one can get a qualitative picture of the expected temperature dependence of the vacancy formation free energy in the real systems, G_{fit} . Such fits to the experimental data are shown in figs. 2 and 3, respectively, as the black lines. As one can see, in the case of Al and Ag, quasi-harmonic PBEsol calculations provide a very good description of the vacancy formation free energy at lower temperatures, while for Cu, the calculations considerably overestimate the low-temperature extrapolation of experimental data by about 0.2 eV. We note that Glensk *et al.* [33] have found similar result for Cu when using the local density approximation (LDA) or the AM05 [30,31] exchange-correlation functional. Since the latter produces results very close to the PBEsol functional used in this work, our large error for Cu could be attributed to the failure of PBEsol in this particular case. However, we think that the most possible source of discrepancy is the PBEsol error for

the equilibrium lattice parameter of Cu, which effectively leads to overbinding and, as a consequence, to the large values of the vacancy formation energy. In the case of Ag and Al, the PBEsol error for lattice constant is very small, and the low-temperature vacancy formation free energy is in reasonable agreement with the extrapolated experimental data.

Summary. – The quasi-harmonic approximation provides an accurate thermodynamic framework for vacancy formation calculations. We demonstrate that a single-volume approach can be applied for the calculations of thermodynamic properties of vacancies. In this case, however, the enthalpy and entropy should be calculated from the Gibbs free energy using proper thermodynamic relations. These insight can be used in order to simplify the description of thermodynamic properties of defects including vacancies. At temperatures close to the melting point, the inclusion of anharmonic effects due to vibrations of the vacancy should be considered.

Financial support by the Austrian Federal Government (in particular from Bundesministerium für Verkehr, Innovation und Technologie and Bundesministerium für Wissenschaft, Forschung und Wirtschaft) represented by österreichische Forschungsförderungsgesellschaft mbH and the Styrian and the Tyrolean Provincial Government, represented by Steirische Wirtschaftsförderungsgesellschaft mbH and Standortagentur Tirol, within the framework of the COMET Funding Programme is gratefully acknowledged. This work is partially supported by Ministry of

Education and Science of Ukraine (Grant No. 2811f). SOZ thanks the Swedish Institute (SI) for providing a scholarship for his research at the Royal Institute of Technology (KTH). AVR acknowledges the support of the Swedish Research Council (VR project 2015-05538), the European Research Council grant, the VINNEX center Hero-m, financed by the Swedish Governmental Agency for Innovation Systems (VINNOVA), Swedish industry, and the Royal Institute of Technology (KTH). Calculations have been done using NSC (Linköping) and PDC (Stockholm) resources provided by the Swedish National Infrastructure for Computing (SNIC).

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