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Mass transport properties of quasiharmonic vs. anharmonic transition-metal nitrides

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I present a development of the color-diffusion algorithm, used in non-equilibrium (accelerated) *ab initio* molecular dynamics simulations of point-defect migration in crystals [Sangiovanni et al., Phys. Rev. B 93, 094305 (2016)], to determine the temperature dependence of anion vacancy jump frequencies in rocksalt-structure (B1) TiN and VN characterized by quasiharmonic (TiN) vs. strongly anharmonic (VN) lattice dynamics. Over a temperature range [$\approx 0.6 \cdot T_m < T < \approx 0.9 \cdot T_m$] relatively close to the materials melting points T_m , the simulations reveal that anion vacancy migration in TiN and VN exhibits an Arrhenius-like behavior, described by activation energies $E_a^{\text{TiN}} = 4.2 \pm 0.3$ eV and $E_a^{\text{VN}} = 3.1 \pm 0.3$ eV, and attempt frequencies $\nu^{\text{TiN}} = 8 \cdot 10^{15 \pm 0.7} \text{ s}^{-1}$ and $\nu^{\text{VN}} = 2 \cdot 10^{17 \pm 0.8} \text{ s}^{-1}$. A comparison of activation energies E_a extracted by Arrhenius linear regression at elevated temperatures with *ab initio* $E_{a0\text{K}}$ values calculated at 0 Kelvin reveals that, while the nitrogen migration energy E_a^{TiN} varies modestly with temperature $\{\Delta E_a^{\text{TiN}} = [E_a(T_m) - E_a(0 \text{ K})]/E_a(0 \text{ K}) \approx 0.1\}$, the changes in E_a^{VN} vs. T are considerable ($\Delta E_a^{\text{VN}} \approx 1$). The temperature-induced variations in vacancy migration energies and diffusivities are discussed in relation to the TiN and VN vibrational properties determined via *ab initio* molecular dynamics at different temperatures. It is argued that *static* 0-K calculations, which account for thermal expansion effects within the framework of quasiharmonic transition-state theory, accurately reproduce the finite-temperature mass transport properties of TiN. Conversely, the use of molecular dynamics simulations, which explicitly treat lattice vibrations at any temperature of interest, is necessary to achieve reliable atomic diffusivities in B1 VN, a crystal phase dynamically stabilized by anharmonic vibrations [Mei et al., Phys. Rev. B 91, 054101 (2015)].

1. Introduction

Mass transport is a kinetic process that governs a large number of materials properties and phenomena [1] including phase stability, phase transformation, mechanical behavior, optical and electronic responses, and chemical reactivity. In crystalline solids, mass transport is primarily dictated by migration of point defects such as lattice vacancies. While vacancy diffusivity values in elemental crystals are well-established experimentally [2, 3], more scarce are the information available for compounds and alloys. This is especially the case for materials synthesized in experimental conditions far from thermodynamic equilibrium.

Transition metal nitrides and carbides are classes of technologically-important materials that combine physical properties characteristic of ceramics and metals. Due to strong metal/non-metal interatomic bonds, refractory Group IVB–VIB nitrides [4, 5] and carbides [6, 7], exhibit high hardness and thermal stability, elevated melting points (> 2000 K), and inherently low mobility of lattice vacancies [8, 9]. Available experimental data for vacancy diffusivities in transition-metal nitrides and carbides are often contradictory [5, 8-10], thus motivating the use of computational methods that can both elucidate reaction pathways and accurately determine atomic diffusivities.

Ab initio calculations of point-defect migration and formation energies in transition metal nitrides and carbides [11-18] are an excellent starting point for understanding the effective contribution to mass transport due to diffusion of vacancies, interstitials, anti-site defects, and impurities. Based on static calculations of migration energies and attempt frequencies, harmonic or quasiharmonic transition state theory (TST) [19, 20] generally provide accurate extrapolation of atomic diffusivities at finite-temperatures. Nevertheless, TST yields questionable results for systems (e.g. B1 VN) which become stabilized dynamically at finite temperatures [21] while display phonon instabilities (imaginary frequencies) at low temperatures [22]. The predictions of *ab initio* molecular dynamics (AIMD), method that solves the classical equations of motion for each particle at any temperature of interest, are free of problems related to anharmonic vibrations and dynamical instabilities. On the other hand, AIMD is highly computationally intensive. Thus,

reaction rates determined via AIMD generally have limited statistical accuracy. A remedy to this problem is the use of non-equilibrium acceleration methods, which significantly reduce AIMD computational times while preserving AIMD accuracy.

In this contribution, I use equilibrium, as well as non-equilibrium (accelerated) AIMD simulations to determine the temperature dependence of nitrogen vacancy (N_{vac}) diffusivities in B1 TiN and B1 VN, with defects at the dilute limit. TiN and VN serve as representative model systems to elucidate the effects of lattice vibrations on the mass transport properties of materials with crystal structure that retains stability (or metastability) from 0 K up to the melting point vs. material structures which become dynamically stable at finite temperatures due to anharmonic vibrations.

2. Theoretical methods and computational details

The evaluation of vacancy migration rates directly via density-functional *ab initio* molecular dynamics [23] is unfeasibly time consuming. In this work, vacancy jump frequencies are determined by exploiting the color-diffusion technique in non-equilibrium AIMD (NE-AIMD) simulations, which allows reducing simulation times by several orders of magnitude. The details of color-diffusion simulations are given in refs. [24, 25]. Briefly, in color-diffusion non-equilibrium molecular dynamics, an artificial external force field is applied to speed-up migration of a lattice atom toward the neighboring vacancy, while also requiring that the total external force and torque on the system are zero [24, 25]. An isokinetic thermostat allows rapidly draining out the extra energy introduced by the force field. The accelerated vacancy jump rates are efficiently calculated at force fields of different (high) intensities. Having determined the accelerated-rate dependence on the magnitude of the force field (see Eqs. 1, 2, and supplemental material in Ref. [24]), the equilibrium jump rate, which is the quantity of interest, is extrapolated from accelerated-rate values at the limit for vanishing force intensities.

In this work, I further develop the color-diffusion algorithm originally implemented [24, 25] in an own version of the VASP [26] code. While in previous works [24, 25], the external field

induced migration of one atom at the time, in this version of color-diffusion, all neighbor atoms are pushed at the same time toward the vacancy, as schematically illustrated in Fig. 1. The proposed variant of color diffusion allows circumventing some practical problems inherent to the previous implementation, but also presents a few shortcomings (see Appendix). As shown below, the new approach is validated by comparison with the results of equilibrium (non-accelerated) AIMD simulations at temperatures near melting, as well as with respect to the predictions of accelerated simulations based on the previous implementation [24, 25].

AIMD and NE-AIMD simulations are carried out using the VASP code implemented with the projector augmented wave method [27]. Electronic exchange and correlation energies are approximated using the Armiento-Mattsson [28] (AM05) functional. A planewave cutoff energy of 300 eV and Γ -point sampling of the Brillouin zone are used in all simulations. The equations of motion are integrated at 1 fs timesteps, using an accuracy of 10^{-5} eV/supercell for the total energy. The effect of the electronic-spin degrees of freedom on nuclei's dynamics is neglected. B1 TiN and B1 VN cubic supercells are formed of 108 metal and 107 N atoms. N_{vac} migration is probed at temperatures between 2000 – 3000 K for TiN and 1500 – 2200 K for VN. These ranges correspond to $\sim 60\% - 90\%$ of TiN and VN melting points ($T_{\text{m}}^{\text{TiN}} = 3250$ K and $T_{\text{m}}^{\text{VN}} = 2450$ K). The equilibrium nearest-neighbor distance $d_{\text{NN}}(T)$ at a temperature T is estimated using the 0-K DFT value ($d_{\text{NN}0}$) rescaled by the experimental TiN and VN thermal expansion coefficients: ~ 9 and $9.6 \cdot 10^{-6} \text{ K}^{-1}$ [4], respectively. TiN and VN supercells are equilibrated at 2000 K via NVT sampling of the configurational space, using the Nose-Hoover thermostat. Then, AIMD forces and positions are employed to produce hundreds of TiN and VN configurations equilibrated at any temperature of interest, via the temperature-dependent effective potential (TDEP) [29-31] method. These serve as starting configurations for non-equilibrium AIMD simulations. TDEP is also used to generate temperature-dependent phonon dispersion curves of defect-free B1 TiN and B1 VN by post-processing sets of atomic forces/positions calculated by AIMD for supercells formed of 512 atoms

at temperatures $T = 300, 600, 900,$ and 1200 K (NVT sampling via Nose-Hoover thermostat). Each run has duration of 10 ps using 1 fs timesteps.

Density-functional theory (DFT) nudged elastic band (NEB) [32, 33] calculations of vacancy migration energies along minimum energy paths employ $6 \times 6 \times 6$ k-point grids, 500 eV planewave cutoff energy, accuracy on forces of 0.01 eV/Å, and a minimum of 5 images between stable configurations. Charge transfer maps at room temperature are obtained by averaging over the results of DFT electron-density-differences [i.e., superposition of non-interacting atomic electron densities subtracted from the self-consistent electron density] calculated for one hundred AIMD configurations.

3. Results and discussion

3.1. N_{vac} migration in B1 TiN. DFT+NEB calculations of N vacancy (N_{vac}) migration in B1 TiN show that a N atom jump along a straight $\langle 110 \rangle$ path is the minimum energy reaction mechanism with a barrier $E_{a0K}^{N_{\text{vac}}/\text{TiN}} = 3.83$ eV [34], with a sinusoidal-like energy landscape (Fig. 2). The fact that the energy profile does not present metastable states and exhibits sinusoidal-like shape, Fig. 2, is a necessary requirement for the reliability of predictions of the color-diffusion algorithm, as implemented in Refs. [24, 25] (a constant $\langle 110 \rangle$ -oriented force pushes an individual N atom toward a neighboring anion vacancy). Equilibrium anion vacancy-jump rates k at temperatures $T = 2400, 2800,$ and 3000 K (see NE-AIMD_{one neigh} data in Fig. 3) are extrapolated from accelerated rates at the limit for vanishingly small forces (see Eqs. 1 and 2 in [24]). The vacancy jump rate obtained by NE-AIMD at 3000 K matches with the value [35] of non-accelerated AIMD simulations at the same temperature (see NE-AIMD_{one neigh} and AIMD rates in Fig. 3).

Fig. 3 also presents equilibrium jump rates k obtained at $T = 2000, 2400, 2600, 2800,$ and 3000 K by extrapolation of accelerated rates calculated by applying bias forces to all twelve vacancy-neighbors (Fig. 1). The results are in excellent agreement (within error bars) with those obtained with the original implementation of color diffusion [24, 25] as well as those of

conventional AIMD simulations (compare NE-AIMD_{all neigh} rates with AIMD and NE-AIMD_{one neigh} results in Fig. 3). The present variant of color diffusion allows solving some practical problems inherent to the previous implementation [24, 25] and provides an additional efficiency-gain for relatively low force intensities (details in Appendix). An Arrhenius linear regression of anion vacancy jump rates obtained between 2000 and 3000 K yields an activation energy $E_a^{\text{Nvac/TiN}} = 4.2 \pm 0.3$ eV and attempt frequencies $\nu^{\text{Nvac/TiN}} = 8 \cdot 10^{15 \pm 0.7} \text{ s}^{-1}$. The N-atom/N_{vac} exchange mechanism observed during AIMD – a simple N atomic jump along a $\langle 110 \rangle$ direction – is illustrated in figure 7 of Ref. [35]. The comparison between NE-AIMD and DFT+NEB results reveals that the anion vacancy migration energy *increases* ($\approx +10\%$) with T . It should be noted that, imposing a supercell volume that corresponds to the TiN equilibrium volume at 2600 K, static DFT+NEB calculations yield a N_{vac} migration energy of 4.14 eV (inset in Fig. 2), which is well within the uncertainty range of the molecular dynamics value ($E_a = 4.2 \pm 0.3$ eV) determined at temperatures between 2000 and 3000 K. As discussed below (Sec. 3.4), the excellent agreement between the two values confirms the reliability of quasiharmonic TST for determination of the TiN mass transport properties at elevated temperatures.

AIMD and NE-AIMD results are compared to those of classical molecular dynamics (CMD) simulations [35] based on the modified embedded atom method (MEAM) [36] semi-empirical potential, Fig. 3. CMD N_{vac} jump rates are consistent with *ab initio* molecular dynamics data. CMD N_{vac} migration frequencies between 1800 and 3000 K yield $E_a^{\text{Nvac/TiN}} = 3.65 \pm 0.23$ eV and $\nu^{\text{Nvac/TiN}} = 2.67 \cdot 10^{15 \pm 0.4} \text{ s}^{-1}$, that is, close to, or within, NE-AIMD uncertainty intervals. MEAM/NEB static migration energies ($E_{a0K}^{\text{Nvac/TiN}} = 3.92$ eV) calculated in this work using the LAMMPS package [37] and the MEAM parameters of Ref. [35] are also in remarkably good agreement with the DFT+NEB value ($E_{a0K}^{\text{Nvac/TiN}} = 3.83$ eV). Nevertheless, it is worth noting that *ab initio* simulations predict an *increase* in N_{vac} migration energy with T , whereas the classical results suggest a decrease in E_a vs. T , that is, a slight downward bending of the Arrhenius curve for T approaching the TiN melting point. It is important noting that also DFT+NEB calculations of Ref. [14] (see table 2 in

that work) indicated a decrease in $E_a^{\text{Nvac/TiN}}$ (from 3.75 eV to 3.32 eV) due to cell volume expansion. That finding is inconsistent with the trend determined in this work by AIMD simulations at temperatures near melting (Fig. 3) and validated by DFT+NEB 0-K calculations with the TiN cell shape fixed to the equilibrium volume at 2600 K (Fig. 2).

3.2. Comparing N_{vac} and Ti_{vac} migration in B1 TiN. The DFT+NEB energy barrier determined for N_{vac} migration ($E_{a0\text{K}}^{\text{Nvac/TiN}} = 3.83$ eV) is $\approx 10\%$ smaller than the value calculated for Ti_{vac} jumps in TiN at 0 K ($E_{a0\text{K}}^{\text{Ti vac/TiN}} = 4.26$ eV) [25]. Conversely, the N_{vac} migration activation energy calculated via NE-AIMD at temperatures $0.6T_m \leq T \leq 0.9T_m$ ($E_a^{\text{Nvac/TiN}} = 4.2 \pm 0.3$ eV) is $\approx 10\%$ larger than the value ($E_a^{\text{Ti vac/TiN}} = 3.78 \pm 0.58$ eV) obtained for Ti_{vac} migration [25] in B1 TiN within a similar temperature range (Fig. 4). Hence, the migration energies of the two species exhibit qualitatively different dependence on temperature. In the case of N vacancies, the effective migration energy *increases* with T from 3.83 eV at 0 K to ≈ 4.2 eV near the melting point. Diffusion of Ti vacancies displays the opposite trend, with a migration energy which *decreases* from 4.26 eV at 0 K to 3.78 eV at $T > 2200$ K. A decrease in $E_a^{\text{Ti vac/TiN}}$ vs. T (from 4.08 to 3.69 eV) is also supported by independent DFT+NEB 0-K calculations carried out for equilibrium and expanded supercell volumes [14]. For temperatures relatively near melting ($T > 2400$ K), the predicted N diffusivity is nearly one order of magnitude greater than that of Ti (Fig. 4). In contrast, the deviation between N and Ti vacancy jump rates becomes negligible (within error bars) for temperatures $2000 \text{ K} < T < 2200 \text{ K}$.

Based on E_a , $E_{a0\text{K}}$, and $k(T)$ results, expected trends in N and Ti jump rates from 0 K up to the melting point T_m are schematically represented in the inset of Fig. 4. In general, migration energies E_a vary as a function of temperature due to changes in lattice vibrational frequencies and/or anharmonic effects [38]. $E_a(T)$ is proportional to the slope of $\log[k(T)]$ vs. T^{-1} at a temperature T , i.e., $E_a(T) \propto \partial \log[k(T)] / \partial T^{-1}$. Thus, the slope in $\log[k(T)]$ vs. T^{-1} is larger for Ti at 0 K (right hand side of the inset of Fig. 4) because $E_{a0\text{K}}^{\text{Ti vac/TiN}} > E_{a0\text{K}}^{\text{Nvac/TiN}}$. Activation energies are expected to remain approximately constant up to $\approx 50\%$ of the melting point, around which N and Ti

vacancies may exhibit very similar jump frequencies. To summarize, it is reasonable to assume that N vacancies are more mobile than Ti vacancies both at relatively low ($T < 50\% T_m$) and relatively high ($T > 75\% T_m$) temperatures. In the intermediate temperature range, N_{vac} and Ti_{vac} are expected to exhibit similar mobility (see inset in Fig. 4).

3.3. N_{vac} migration in B1 VN. At temperatures T below 200–250 Kelvin, B1 VN is dynamically unstable: its phonon spectrum exhibits imaginary frequencies at zone boundaries [21, 22, 39]. The B1 structure is dynamically stabilized by anharmonic lattice vibrations above ≈ 250 K [21]. Consequently, the N_{vac} migration energy evaluated for B1 VN via static DFT+NEB calculations has a questionable meaning. In addition, DFT+NEB calculations of vacancy migration are practically unfeasible for B1 VN: it was not possible to reach convergence using more than one NEB image. The energy estimated for the transition state of N_{vac} migration at 0 K is $E_{a0K}^{N_{\text{vac}}/VN} \approx 1.6$ eV.

The diffusion mechanism of a N atom into a neighbor anion vacancy in B1 VN is illustrated in the insets of Fig. 5 (AIMD snapshots at 2000 K). Although the total migration event entails a net N translation along a $\langle 110 \rangle$ direction, the actual atomic motion follows a curved trajectory. The path passes near the tetrahedral eightfold-coordinated position (at the center of the elementary cubic cell), where the atom significantly decelerates (i.e. spends ~ 40 fs in this position out of a total of ~ 150 fs), which is indicative of a local free-energy minimum. This mechanism differs with the one observed for TiN, in that the N migration event is a simple neat $\langle 110 \rangle$ jump (see figure 7 in Ref. [35]). The present implementation of color diffusion (illustrated in Fig. 1), validated for N_{vac} migration in TiN (see Sec. 3.1), is employed to calculate anion vacancy migration rates in B1 VN at temperatures ranging between 1500 and 2200 K. An Arrhenius linear regression of extrapolated equilibrium N_{vac} jump rates yields $E_a^{N_{\text{vac}}/VN} = 3.1 \pm 0.3$ eV and $\nu^{N_{\text{vac}}/VN} = 2 \cdot 10^{17 \pm 0.8} \text{ s}^{-1}$. All results obtained in this work for N_{vac} migration parameters in B1 TiN and VN are summarized in Table 1.

N_{vac} jump rates in B1 VN determined via AIMD and NE-AIMD at temperatures of 2000 and 2200 K are in reasonably good agreement (Fig. 5). AIMD simulations at 2000 and 2200 K reached total durations of ≈ 2.3 and ≈ 1.3 ns, respectively. For comparison, the total simulated time required

by NE-AIMD amounted to 250 ps and 40 ps. It should be stressed that NE-AIMD results have much better statistical accuracy than AIMD rates. Evaluation of the equilibrium N_{vac} jump rate at 1500 K required total NE-AIMD simulation time of ≈ 1.7 ns. To achieve the same level of accuracy via non-accelerated AIMD simulations would require $\approx 10^{-5}$ s. Thus, at the lowest investigated temperature, NE-AIMD provides an acceleration factor of approximately $\times 10^4$.

The discrepancy between AIMD and NE-AIMD predictions at elevated temperatures is likely due to insufficient statistics of atomic jumps recorded during AIMD simulations (note large error bars in Fig. 5). On the other hand, there is no guarantee that the energy landscape at finite-temperature has sinusoidal-like shape; a necessary requirement to ensure accuracy of color diffusion predictions [24]. Nevertheless, as described below, experimental results of nitrogen diffusion coefficients in B1 VN support the NE-AIMD results presented in Fig. 5.

Comparison of theoretical anion vacancy jump rates k^{Nvac} with experimental N diffusivities D_{N} requires knowledge of the experimental anion vacancy concentration $c_{\text{Nvac}}(T)$ at a temperature T :

$$D_{\text{N}}(T) = \gamma \cdot c_{\text{Nvac}}(T) \cdot k^{\text{Nvac}}(T) \cdot [d_{\text{NN}}(T)]^2/3, \quad (1)$$

where $d_{\text{NN}}(T)$ ($= 2^{-1/2} \cdot \text{jump-length}$) is the nearest neighbor distance at a temperature T and γ (≈ 0.78) is a geometrical correlation factor for the fcc lattice that accounts for the fact that experimentally-determined diffusion coefficients originate from atomic, not vacancy, migration processes [40]. Note that Eq. (1) is valid at dilute vacancy concentrations. In their work [41], Teichmann et al. reported concentration-independent nitrogen diffusivities D'' in B1 VN. This is interpreted as experimental D'' values plotted in Ref. [41] were determined as:

$$D''(T) = D(T) \cdot [c_{\text{Nvac}}(T)]^{-1}, \quad (2)$$

for which $D(T)$ is the nitrogen self-diffusion coefficient that derives from migration of individual vacancies. Surprisingly, the experiments found that the concentration-independent nitrogen diffusivity in understoichiometric B1 $\text{VN}_{x<1}$ and hexagonal $\epsilon\text{-VN}_{0.5}$ are essentially equivalent [42]. This indicates that the intrinsic N mobility in VN is not affected by the relative concentration of defects, thus allowing direct comparison with present theoretical results by setting a constant value

$c_{\text{N}_{\text{vac}}/\text{VN}}(T) \approx 1\%$ in Eq. (1). Accordingly, in Fig. 6, the experimental $D''(T)$ values of Ref. [41] are compared to $D''(T) = D^{\text{N}_{\text{vac}}/\text{VN}}(T) \cdot [c_{\text{N}_{\text{vac}}/\text{VN}}(T)]^{-1} = \gamma \cdot k^{\text{N}_{\text{vac}}/\text{VN}}(T) \cdot [d_{\text{NN}}(T)]^2/3$. Nitrogen diffusivities determined via NE-AIMD are in good agreement with the experimental values (Fig. 6).

Fig. 7 illustrates the N_{vac} migration frequencies calculated via NE-AIMD for B1 VN vs. B1 TiN. For a meaningful comparison, the vacancy jump rates are plotted vs. the inverse temperature normalized to the corresponding melting points. The figure reveals that $\log[k(T)]$ vs. T_{m}/T determined for TiN and VN are nearly parallel, indicating a relatively similar (on the normalized temperature scale) activation energy for N_{vac} migration in the two nitrides. Nevertheless, the vacancy jump rate in VN is steadily ~ 1.5 orders of magnitude larger than that calculated for TiN. This may be due to the stronger anharmonicity of VN lattice vibrations, which assists atomic diffusion (larger attempt frequencies for vacancy jump).

Atomistic AIMD simulations are excellent tools for calculating migration frequencies. However, these do not provide a straightforward comparison with experimental results, which typically determine self-diffusion coefficients by, e.g., tracing the changes in isotope distributions with time. As discussed above, AIMD vacancy jump rates rescaled by the corresponding defect concentration (at the dilute limit) can be directly compared with experimental diffusion coefficients. However, in materials synthesized in far-from-equilibrium conditions (like transition-metal nitride films grown via physical vapor deposition), the defect concentration depends on the experimental parameters (kinetics) rather than on their formation energetics (thermodynamics). Therefore, cation and anion diffusivities in B1 TiN and B1 VN can be calculated using the data presented in Table 1, while imposing a fixed vacancy concentration (extracted by experimental results) in Eq. 1.

3.4. Effects of lattice vibrations on diffusion kinetics. *Ab initio* evaluation of point-defect diffusivities D often relies on static (0 K) calculations of activation energies, attempt frequencies, and formation energies. The values of jump frequencies $k(T)$ and equilibrium concentrations $c_{\text{vac}}(T)$ [see Eq. (1)] can be extrapolated at a temperature of interest by applying transition-state theory (TST) [19, 20] within the harmonic or quasiharmonic approximation. In the latter approach, the

effects induced by thermal expansion on phonon spectra (vibrational entropies) and migration enthalpies are estimated in a static computational framework [43]. However, intrinsic anharmonic effects at finite temperatures may induce non-negligible deviations from harmonic or quasiharmonic trends. This was proven, for example for point-defect equilibrium concentrations $c_{\text{vac}}(T)$ vs. T in pure metals [44, 45]. Conversely to static computational approaches, AIMD simulations inherently account for anharmonic vibrations and allow discovering non-intuitive reaction pathways at finite temperatures [35, 46, 47], but are also highly computationally intensive. Although NE-AIMD enables efficient evaluation of equilibrium rates at elevated temperatures, its applicability at modestly low temperatures ($< 0.5 \cdot T_m$) is yet practically limited by number and duration of simulations required to achieve sufficient statistical accuracy on extrapolated reaction rates [24, 25].

Without considering the effects of vacancy concentrations on diffusion coefficients in Eq. (1), the reliability of atomic diffusivities obtained by TST depends on the temperature variation in effective migration energies $E_a(T)$ and attempt frequencies $\nu(T)$. It is expectable that static quasiharmonic TST calculations yield accurate finite-temperature migration rates for materials in which the change in vibrational frequencies with T is merely an effect of lattice expansion. This has been demonstrated, for example, by comparison of experimental vs. DFT+TST results for Cu impurity diffusivities in B1 TiN [16]. In contrast, quasiharmonic TST is unsuited for determination of reaction rates in materials whose phonon spectrum is significantly altered by temperature.

TiN and VN reflect the two scenarios depicted above: the vibrational frequencies in B1 TiN are not significantly affected by temperature, while those of VN are strongly modified by T , as shown in phonon spectra determined via AIMD (Fig. 8). As mentioned above, static calculations are unable to determine the migration energy barrier in B1 VN due to 0-Kelvin dynamical instability of the cubic structure [22]. The N_{vac} migration energy estimated for B1 VN at 0 Kelvin (≈ 1.6 eV) is approximately half the value (3.1 ± 0.3 eV) calculated at temperatures near melting. In contrast, the nitrogen and titanium vacancy migration energies in TiN (calculated at 0 K upon

imposing expanded supercell volumes) are within the statistical error bars of $E_a \pm \sigma_E$ values determined via molecular dynamics at temperatures near melting (Table 1). A discussion dedicated to the differences in vibrational properties and lattice stability of the investigated binary nitrides is given below.

The energy of TiN acoustic modes remains essentially unchanged for temperatures increasing from 300 to 1200 K (Fig. 8). Some variations are observable for the optical modes; not surprising since Ti is three times heavier than N. For B1 VN, the modification of acoustic mode frequencies with temperature is considerable (Fig. 8). One striking feature is that, at room temperature, the acoustic modes near $\mathbf{q} = \text{X}$ zone boundaries are very soft. This is indicative of a strongly anharmonic energy landscape, as also demonstrated by electron density distributions determined via X-ray diffraction, which show pronounced shortening of V – V bonds [48]. The effect is due to the relatively high population of d-d electronic states, which strengthen the metal/metal interactions.

When cooling VN toward zero temperature, the B1 structure spontaneously transforms (dynamical instability) into tetragonal [21, 39]. The transition is caused by the fact that the high-symmetry B1 positions are unstable potential-energy landscape maxima surrounded by multifold-degenerate energy minima. Given that the entropy is reduced while decreasing temperature, the occupation of energy minima follows an ordered pattern, which induces the cubic→tetragonal lattice distortion (see figure 5 in Ref. [49]). However, since the energy difference between the tetragonal and B1 polymorph structures is relatively small (≈ 18 meV/atom) [50], the tetragonal symmetry can be easily broken by introducing thermal disorder. A room-temperature thermal energy of $k_B T \approx 26$ meV is sufficient to enable atomic motion (precession) among the minima that surround a B1 site, thus randomizing $\langle 111 \rangle$ displacements relative to the high-symmetry position: the B1 phase is stabilized dynamically [21, 39]. The schematic illustration of Fig. 9 facilitates the understanding of atomistic mechanisms that lead to dynamical instability or lead to dynamical stabilization of a crystal phase.

Fig. 10 provides further clarification regarding the differences in B1 TiN vs. B1 VN lattice dynamics. The plot in Fig. 10(a) depicts the atomic trajectories of four neighboring N and metal atoms recorded during 3 ps and projected onto a (001) plane. AIMD simulations at room temperature show that Ti and N atoms vibrate harmonically about ideal sites and that the vibrational amplitudes of N are larger than those of heavier Ti atoms. In contrast, the V mean square displacement (MSD) relative to B1 positions is greater than that of N atoms. Such anomaly has been previously noted by Kubel et al. [48], who reported room-temperature MSD $\approx 0.006 \text{ \AA}^2$ for V and MSD $\approx 0.004 \text{ \AA}^2$ for N. AIMD simulations at 300 K yield MSD $\approx 0.018 \text{ \AA}^2$ for V and MSD $\approx 0.011 \text{ \AA}^2$ for N, in qualitative agreement with experimental results [51]. In addition, the dynamics reveals that the average position occupied by a V atom during 3 ps is constantly displaced (as indicated by $\Delta \mathbf{r}$ in Fig. 10(a)) along $\langle 111 \rangle$ and $\langle 110 \rangle$ directions from the ideal position. An increased temperature (1200 K) produces broader atomic oscillations. However, while the nature of vibrations in TiN remains qualitatively the same, a temperature of 1200 K leads to *harmonization* of B1 VN, with V atoms freely vibrating across ideal B1 positions (Fig. 10). In the case of VN, the increase in vibrational entropy with temperature effectively modifies the energy landscape by stabilizing B1 lattice positions.

At 300 K, the anharmonic energy landscape of B1 VN causes significant differences in electron distribution in comparison to that of B1 TiN. For a harmonic material as TiN, the electron transfer maps determined via AIMD at 300 K is essentially equivalent to the one evaluated via DFT at 0 K (compare figure 10(a) of Ref. [52] with the upper panel of Fig. 10(b)). In contrast, *static* DFT calculations are unsuited to describe the electron distribution of B1 VN, due to the fact that this phase is stabilized dynamically at finite temperatures. In the static picture, all V and N atoms are at ideal B1 positions. Consequently, the charge transfer map of VN appears (incorrectly) qualitatively similar to that of B1 TiN (compare figure 10(a) with 10(d) in Ref. [52]). However, the electron accumulation is *not* homogeneously distributed between V atoms. An accurate description of the charge distribution in B1 VN at 300 K is obtained by superposing of the electron densities of

several AIMD configurations. As demonstrated in the lower panel of Fig. 10(b), electron accumulation (and depletion) regions are randomly arranged between V–V pairs due to stronger (weaker) V–V bonds.

4. Conclusions

Density functional theory calculations, *ab initio* molecular dynamics, and a development of color-diffusion non-equilibrium (accelerated) *ab initio* molecular dynamics simulations are used to determine the diffusivities of anion vacancies in, and phonon spectra of, B1 TiN and B1 VN as a function of temperature. The results of the simulations reveal that the activation energy E_a for N vacancy migration in B1 TiN increases with temperature from 3.83 eV (at 0 K) to 4.2 ± 0.3 eV (above 2000 K), with an attempt frequency of $8 \cdot 10^{15 \pm 0.7} \text{ s}^{-1}$. The increase in E_a vs. T is validated by DFT+NEB calculations (4.14 eV) carried out at an expanded TiN cell volume. For B1 VN, a phase which presents *dynamical* instability at 0 K, *static* DFT+NEB calculations are unsuited to provide reliable estimates of migration energies. Non-equilibrium *ab initio* molecular dynamics simulations from temperatures of 1500 K and above yield N vacancy activation energies of 3.1 ± 0.3 eV with attempt frequencies of $2 \cdot 10^{17 \pm 0.8}$. The results for N vacancy diffusion in B1 VN are validated by comparison with previous experimental findings. Based on the results presented, it is argued that

- (i) the quasiharmonic approximation within the framework of transition-state theory accurately reproduces the mass transport properties of systems (e.g. B1 TiN) which remain stable in the same structure from 0 K up to the melting point and for which the variations in phonon frequencies with temperature are merely an effect of lattice expansion.
- (ii) The explicit inclusion of vibrational effects, inherent to molecular dynamics simulations, is necessary to reliably assess the mass transport properties of material phases (e.g. B1 VN), which are stabilized dynamically at finite temperatures owing to lattice vibrations.

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Appendix

Detailed description of the color-diffusion algorithm can be found in [24]. Briefly, the maximum bias force F_{max} used in one-neighbor-accelerated color diffusion [24] does not exceed 75% of $\pi \cdot E_{a0} / (2 \cdot x_{TS0})$, where E_{a0} is the migration barrier calculated at 0 K and x_{TS0} is the distance between the diffusing atom and the transition state position at 0 K. DFT+NEB calculations yield $E_{a0} = 3.83$ eV for nitrogen migration into a neighbor anion vacancy in B1 TiN. Considering a colored N atom that lies in the same (001) plane of the neighboring vacancy, the maximum [110]-oriented bias force used [$F_{max} = F_{[100]} + F_{[010]}$] to accelerate the only colored-atom has components $F_{[100]}$ and $F_{[010]} = 2.1$ eV/Å.

For the present implementation of color diffusion, in which all neighbors are pushed toward the vacancy, F_{max} and x_{TS0} are not easily determinable. DFT+NEB calculations of N migration in B1 TiN (with other vacancy-neighbors kept fixed at positions displaced toward the vacancy) demonstrate that height and width of the sinusoidal-like energy landscape probed by an accelerated atom are strongly altered by the concomitant displacement of other atoms from their equilibrium positions. Nevertheless, the shape of the landscape remains qualitatively the same as in one-neighbor accelerated color diffusion (Fig. A.1). An increased migration energy (Fig. A.1) is due to

the repulsion experienced by several nitrogen atoms crowding near the vacancy site. Consequently, the efficiency of the present version of color diffusion is similar – or slightly superior for relatively low force-field intensities – to that of the previous implementation [24, 25], see Fig. A.2.

Given that, in the present variant of color diffusion, x_{TS0} can no longer be approximated as half jump length as in [24], see Fig. A.1, three free parameters {i.e., $\ln[k_{NE \rightarrow E}(T)]$, $x_{TS0}(T)$, and $\alpha(T)$, for which the equilibrium rate $k_{NE \rightarrow E}(T)$ ($= \lim_{F \rightarrow 0} [k_{NE}(F, T)]$) is the quantity of interest} are extracted by fitting non-equilibrium rate k_{NE} vs. force intensities F :

$$\ln[k_{NE}(F, T)] = \ln[k_{NE \rightarrow E}(T)] + \frac{x_{TS0}(T)}{k_B T} \cdot F - \alpha(T) \cdot F^2. \quad (\text{A.1})$$

The maximum force intensity F_{max} can be directly determined by non-equilibrium simulations at a given T , and then assumed to remain constant with T . In the example shown in Fig. A.3, the maximum of $\ln(k_{NE})$ vs. F is approximately at 4 eV/Å. Having three free parameters to be fitted introduces additional demand on the accuracy of each calculated k_{NE} value (note that obtaining a negative value of $\alpha(T)$ in Eq. (S1) would result in upward concavity of the parabola of Fig. A.3, which is incorrect). On the other hand, accelerating all neighbors solves the problem of undesired jumps of non-accelerated atoms, which complicates the determination of k_{NE} (and $k_{NE \rightarrow E}$) values [25]. In any case, since the shape of the energy landscape at 0 Kelvin cannot be reliably obtained for dynamically unstable systems like B1 VN [21], x_{TS0} must be treated as free parameter.

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Tables

	N_{vac}			Ti_{vac} [25]			
	$T = 0 \text{ Kelvin}$		$0.6T_m \leq T \leq 0.9T_m$	$T = 0 \text{ Kelvin}$			$0.7T_m \leq T \leq 0.9T_m$
	Equilib. Volume	Volume of $0.8T_m$		Equilib. Volume	Volume of $0.7T_m$	Volume of $0.9T_m$	
B1 TiN							
E_a (eV)	3.83	4.14	4.2 ± 0.3	4.26	3.67	3.50	3.78 ± 0.58
ν (s^{-1})	—	—	$8 \cdot 10^{15 \pm 0.7}$	—	—	—	$4.45 \cdot 10^{14 \pm 1.2}$
B1 VN							
E_a (eV)	≈ 1.6	—	3.1 ± 0.3	—	—	—	—
ν (s^{-1})	—	—	$2 \cdot 10^{17 \pm 0.8}$	—	—	—	—

Table 1. Anion vacancy migration parameters in B1 TiN and B1 VN calculated by DFT at 0 Kelvin for different volumes (relaxed vs. expanded cells that account for thermal expansion, see Fig. 2) and NE-AIMD at elevated temperatures. For comparison, the table also lists previous results obtained for Ti_{vac} migration in TiN [25]. Note that the atomic diffusivities D_N and D_{Ti} can be obtained using Eq. (1) (valid at the dilute limit of defect concentrations), by knowing the vacancy concentration c_v and the nearest neighbor distance d_{NN} . The vacancy jump rate k is obtained using Arrhenius expression $k(T) = \nu \cdot \exp[-E_a/(k_B \cdot T)]$.

Figures

Fig. 1. Schematic illustration of the present implementation of color diffusion. The filled spheres indicate atoms in ideal fcc positions (one of the sublattices in a B1 structure), whereas the empty circle indicates a lattice vacancy on a (001) crystallographic plane. The red arrows indicate forces of equal intensities which push four (of a total of twelve) neighbors, indicated by green spheres, toward the vacancy.

Fig. 2. DFT+NEB energy profile for anion vacancy jump along a straight $\langle 110 \rangle$ migration path in B1 TiN. The inset shows 0-K DFT+NEB results obtained imposing a supercell volume corresponding to the TiN equilibrium volume at 2600 K.

Fig. 3. N vacancy migration rates in TiN extrapolated from non-equilibrium AIMD (NE-AIMD) by pushing all neighbors, in comparison with NE-AIMD data obtained by pushing one neighbor (method of Refs. [24, 25]) as well as non-accelerated AIMD (result from ref. [35]). *Ab initio* rates are also compared with the rates obtained by CMD [35]. Solid lines are the results of Arrhenius linear regression of N_{vac} jump rates determined via NE-AIMD_{all neighb.} and CMD simulations [$E_a = 4.2 \pm 0.3$ eV and $\nu = 8 \cdot 10^{15 \pm 0.7} \text{ s}^{-1}$ (NE-AIMD); $E_a = 3.65 \pm 0.23$ eV and $\nu = 2.67 \cdot 10^{15 \pm 0.4} \text{ s}^{-1}$ (CMD)].

Fig. 4. Comparison of N and Ti [25] vacancy jump rates in TiN calculated via NE-AIMD simulations. The inset shows probable jump rate vs. $1/T$ trends from 0 K up to the melting point T_m accounting for migration energies calculated by DFT+NEB at 0 K and by Arrhenius linear regression of jump rates at temperatures near melting. Note, in the inset, that E_{a0K} and $E_a(T)$ are related to the slopes of $\log[k(T)]$ vs. T^{-1} near 0 K and T_m , respectively.

Fig. 5. N_{vac} jump rates in B1 VN as determined by AIMD and NE-AIMD simulations. The insets are superpositions of AIMD snapshots during N atomic jump into a neighbor vacancy at 2000 K. The orthographic views are on (001) and (011) lattice planes. The snapshots (15 in total) are taken every 10 fs (the event lasts for ~ 0.15 ps). The diffusing atom is colored in red. N and V lattice atoms are shown in black and orange, respectively.

Fig. 6. Comparison between AIMD, NE-AIMD (force field applied to all neighbors) and experimental [41] N diffusivities D'' (independent on the vacancy concentration) in B1 VN. The shaded region indicates uncertainty ranges in experimental values.

Fig. 7. Comparison in N_{vac} jump rates in TiN and VN as a function of the inverse temperature scaled by the respective melting points T_m .

Fig. 8. Phonon dispersion curves for B1 TiN and B1 VN calculated via AIMD as a function of temperature.

Fig. 9. Schematic representation of lattice dynamics in anharmonic 2-dimensional crystal system. Panel **(a)** depicts a 2-dimensional square lattice with atoms (blue circles) that reside in high symmetry positions. The (unstable) high-symmetry sites are surrounded by four energy minima (orange dots), slightly shifted along the cell diagonals. **(b)** At low temperatures, the atoms arrange in near minima creating an ordered pattern (entropy minimization) and causing a symmetry reduction, from square to rectangular. **(c, d)** A temperature increase provides enough energy for the atoms to move among energy minima via precession around the unstable high-symmetry site. This induces randomization of displacements relative to ideal positions. On macroscopic length-scales (diffraction pattern) and/or on time-average, the atoms will be seen as sitting in ideal high-symmetry positions: the square lattice **(c, d)** has stabilized dynamically. When temperature becomes sufficiently high, the atoms are also able to cross high-symmetry sites, thus effectively occupying – on time average – the square lattice sites.

Fig 10. (a) Dynamics at room temperature and 1200 K of four nearest-neighbor atoms that vibrate about ideal B1 positions in TiN and VN. The atomic trajectories, recorded during 3 ps, are projected onto a (001) plane. $\Delta \mathbf{r}$ indicates the constant displacement of V atoms from ideal positions B1 at 300 K. (b) Charge transfer maps in B1 TiN and B1 VN obtained via AIMD simulations at 300 K.

Fig. A.1. Schematic representation of energy profile probed by an individual colored atom (green circle) in the case of all vacancy-neighbors being accelerated toward the vacancy. The energy landscape (light gray) corresponding to one-neighbor acceleration is shown for comparison.

Fig. A.2. Comparison of efficiency-gain between present (all-neighbor) and previous (one-neighbor) implementation of color diffusion accelerated molecular dynamics. This example shows results obtained at 3000 K for N migration in B1 TiN. Solid diamonds indicate the non-equilibrium accelerated rates k_{NE}' that are determined in one-neighbor-color simulations. k_{NE}' values are then multiplied with the number of neighbors ($n_{\text{neighb.}} = 12$) to yield the k_{NE} rates (open diamonds) that are used to extrapolate equilibrium rates at zero-force intensity. This means that, for relatively low bias-force intensities (≈ 0.5 eV/Å in this case), the simulation time required for calculating k_{NE}' via acceleration of an individual atom is longer than the time needed in non-accelerated AIMD simulations. Applying a bias force field to all neighbors (present variant of color diffusion) provides an additional efficiency-gain (shaded region). The efficiency gain, which is $\approx \times n_{\text{neighb.}}$ for F intensities close to zero, becomes progressively smaller for F approaching F_{max} .

Fig. A.3. Extrapolation (using Eq. S1) of equilibrium rate $k_{NE \rightarrow E}(T)$ for N vacancy jump in B1 VN at 1500 K. The maximum bias-force intensity F_{max} , estimated from the maximum of the $\ln[k_{NE}(F, T)]$ vs. F curve is ≈ 4 eV/Å. Thus, fitted $k_{NE}(F, T)$ data are restricted to the range $F \leq 0.75 \cdot F_{\text{max}} \approx 3$ eV/Å.