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Finite Temperature Properties of NiTi from First Principles Simulations: Structure, Mechanics, and Thermodynamics

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Abstract

We present a procedure to determine temperature-dependent thermodynamic properties of crystalline materials from density functional theory molecular dynamics (DFT-MD). Finite temperature properties (structural, thermal, and mechanical properties) of the phases (ground state monoclinic B33, martensitic B19', and austenitic B2) of the shape memory alloy NiTi are investigated. Fluctuation formulas and numerical derivatives are used to evaluate mechanical and thermal properties. A modified version of thermodynamic upsampling is used to enable simulations with lower DFT convergence thresholds. In addition, a thermodynamic integration expression is developed to compute free energies from isobaric DFT-MD simulations that accounts for volume changes. Structural parameters, elastic constants, volume expansion, and specific heats as a function of temperature are evaluated. Phase transitions between B2 and B19' and between B19' and B33 are characterized according to their thermal energy, entropy, and free energy differences as well as their latent heats. Anharmonic effects are shown to play a large role in both stabilizing the austenite B2 phase as well as suppressing the martensitic phase transition. The quasiharmonic approximation to the free energy results in large errors in estimating the martensitic transition temperature by neglecting these large anharmonic components.

I. INTRODUCTION

First principles density functional theory (DFT) techniques have been applied to describe the thermodynamic properties (*e.g.*, free energy, heat capacity, and compressibility) of the crystalline phases of elemental metals.^{1–6} Typically, elemental metals have a well defined solid phase that is stable from zero temperature (T) up to the melting point. Procedures for a thermodynamic characterization of $T = 0$ K stable phases based fully on DFT are well-established. At low-temperatures, the quasiharmonic approximation (QHA) provides the vibrational free energy and thermal contributions to physical properties. At higher

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SUPPLEMENTARY MATERIAL

Numerical and simulation time convergence tests for the various properties investigated here may be found in the Supplementary Material.

temperatures, DFT molecular dynamics (DFT-MD) simulations utilized in conjunction with specialized thermodynamic techniques^{6,7} can go beyond QHA results by including anharmonic vibrational effects. Recently, DFT analysis of thermodynamic properties has been extended to metallic systems, often intermetallics, whose experimentally relevant phases are unstable at low temperature.^{7–10} A complication to the analysis of these systems is establishing the limits of phase stability with respect to temperature before computing thermodynamic properties.^{1,7,8,10} Furthermore, because the QHA is not applicable to unstable phases, alternative approaches for computing thermodynamic properties that account for anharmonic effects at all temperatures are required.^{8,10} These factors make DFT characterization of anharmonic phases computationally expensive and conceptually challenging.

Nitinol (NiTi) is an intermetallic shape memory alloy and is an example of a material whose observed phases are stabilized by anharmonicity and entropy. The shape memory effect in NiTi originates from a phase transition between a low-temperature phase and a high-temperature phase.^{11,12} Experimentally, the martensite phase corresponds to the monoclinic B19' structure,¹³ having an angle (γ) of 98° , while the austenite phase has the cubic B2 structure.¹⁴ The crystal structure of these phases is provided in Fig. 1. The martensitic transition between the two phases has been measured to occur at $T = 341$ K,¹⁵ although the precise transition temperature may depend on a number of factors including the quality of the material. Theoretically, a $T = 0$ K DFT energetic analysis shows that the B19' phase is unstable to shear and the B2 phase is vibrationally unstable.^{10,16–37} The only stable phase at $T = 0$ is the orthorhombic B33 structure with $\gamma = 107^\circ$;³⁷ however, the B33 phase has not been observed experimentally in this material. The disagreement between experimental observations and $T = 0$ K theoretical results may be reconciled partially by introducing finite temperature effects through DFT-MD simulations.¹⁰ Such investigations have shown that anharmonicity and entropy stabilize B19' for $T \lesssim 50$ K and B2 for $T > 300$ K, while destabilizing the B33 phase above $T = 200$ K.

The present work is an extension of our previous investigations¹⁰ on phase stability and the martensitic transition in NiTi to the temperature dependence of structural, mechanical, and thermal properties as well as free energies. Our work probes the influence of temperature on such properties through the use of DFT-MD. For each phase, DFT-MD simulations are performed for various temperatures along the $P = 0$ isobar. The isobaric simulations performed as such enable a full assessment of the structure, mechanical and thermal properties, and free energies of each phase. Mechanical properties are computed from fluctuation formulas for strain or volume derivatives of free energy, while thermal properties are computed from numerical temperature derivatives of the free energy. The value of the free energy is obtained along the isobar from internal energy data and a thermodynamic integration technique adapted to account for the low-temperature instability of the phases of NiTi. Previous DFT computations^{16–37} have provided $T = 0$ K estimates of structural and mechanical properties. Thermal effects, as will be shown, lead to nontrivial corrections to $T = 0$ K estimates of structure and mechanical properties and enable the computation of thermal properties and free energies, which cannot be obtained $T = 0$ K techniques.

Additionally, our work addresses several of the inaccuracies in thermodynamic properties that stem from low DFT convergence thresholds, which are often employed for DFT-MD simulations. In particular, the basis set must be sufficiently large and the reciprocal space sampling must be sufficiently dense to ensure accurate properties. DFT-MD simulations, which require many time steps and the use of large cells, necessitate the relaxation of some of these criteria due to computational limitations. Thermodynamic upsampling, as recently proposed by Grabowski and coworkers,^{6,38} offers a potential remedy to such errors. In this approach, DFT-MD simulations are first performed using lower convergence thresholds that accelerate phase space sampling. The results are then “upsampled” by reprocessing a limited set of configurations from the DFT-MD simulation at a higher convergence threshold for use in property evaluations. Assuming the phase space sampled by the DFT-MD simulations corresponds to that sampled by a DFT-MD simulation using the higher convergence threshold, the accuracy of the properties should be improved. We validate the thermodynamic upsampling procedure for NiTi and apply it to various physical properties of interest in the present work. Where applicable, we comment on the net impact of upsampling on the value of the property.

This paper is outlined as follows: We establish the procedures for determining thermodynamic properties along a stress free, $P=0$ isobar in Sec. II. We also perform benchmarking tests of the thermodynamic upsampling procedure on a small simulation cell in this section. In Sec. III, the methods are applied to evaluate the structure, mechanical properties, thermal properties, and free energy of the B33, B19', and B2 phases, within their respective temperature limits of stability. For further insight into the phase transitions in this system, the free energy is separated into harmonic and anharmonic contributions through a comparison to the quasiharmonic approximation.

II. METHODS

A. Temperature-Dependent Structure Optimization

The initial step in our thermodynamic analysis is to optimize the structure of the phases of NiTi as a function of temperature to obtain stress-free states. This is achieved by iteratively optimizing the lattice vectors according to the stress obtained from short DFT-MD simulations. Equivalently, this can be interpreted as minimizing the Helmholtz free energy at a given temperature with respect to the lattice vectors. If Ω is the tensor composed of the lattice vectors, the derivative of the free energy with respect to Ω may be expressed¹⁰ as

$$\frac{\partial F}{\partial \Omega} = |\det \Omega|^T \langle \sigma \rangle \Omega^{-T}, \quad (1)$$

where F is the Helmholtz free energy, $\langle \dots \rangle$ denotes the ensemble average, σ is stress, $-T$ signifies the inverse transpose, and the absolute value of the determinant of Ω^T is equivalent to volume, $V = |\det \Omega^T|$. The free energy may then be minimized according to

$$\Omega^{k+1} = \Omega^k - \alpha \partial F / \partial \Omega \Big|_{\Omega = \Omega^k}, \quad (2)$$

where α is a scaling factor. In the present work, 3 ps DFT-MD simulations are performed to estimate the stress tensor at a given Ω^k , and the value of α is set to 10^{-4} . The procedure is iterated until the absolute value of all elements of the average stress tensor is < 1 kbar.

B. Thermal Properties

1. Heat Capacity—The constant volume heat capacity (C_V) is given by

$$C_V = \frac{\partial \langle E \rangle}{\partial T} \Big|_V, \quad (3)$$

and the constant pressure heat capacity (C_P) is given by

$$C_P = \frac{\partial \langle E \rangle}{\partial T} \Big|_P, \quad (4)$$

where $\langle E \rangle$ is the average internal energy. These quantities may be evaluated either from numerical derivatives or from fluctuation formulas. As our structural optimization maintains $\langle \sigma \rangle = 0$, the value of C_V cannot be obtained from numerical derivatives of the temperature-dependent energy at constant volume. As such, we employ the fluctuation relation,³⁹

$$C_V = \frac{1}{k_B T^2} \langle E \delta E \rangle, \quad (5)$$

where k_B is the Boltzmann constant, E is the internal energy, and $\delta E = E - \langle E \rangle$. Alternatively, the value of C_P may be obtained from the numerical derivative of average internal energy as a function of T along the $\langle P \rangle = 0$ (or $\langle \sigma \rangle = 0$) isobar.

2. Coefficient of Thermal Expansion—The thermal expansion coefficient, given by

$$\alpha_V = \frac{1}{\langle V \rangle} \frac{\partial \langle V \rangle}{\partial T} \Big|_P, \quad (6)$$

can be obtained from the numerical derivative of volume as derived from the previously described T -dependent optimization. Alternatively, a fluctuation expression may be employed. Using the cyclic relationship between partial derivatives, $\frac{\partial A}{\partial B} \Big|_C \frac{\partial C}{\partial A} \Big|_B \frac{\partial B}{\partial C} \Big|_A = -1$, we may rewrite Eq. 6 in terms of values available from simulations at constant T and V . The thermal expansion coefficient may then be written as

$$\alpha_V = \frac{1}{K} \left. \frac{\partial \langle P \rangle}{\partial T} \right|_V, \quad (7)$$

where K is the bulk modulus which will be defined in the next section. Performing the manipulations to obtain fluctuation expressions at constant volume (described in Appendix A) yields

$$\left. \frac{\partial \langle P \rangle}{\partial T} \right|_V = \frac{1}{k_B T^2} \langle E \delta P \rangle, \quad (8)$$

where $\delta P = P - \langle P \rangle$ and $\langle E \delta P \rangle$ is a mixed fluctuation expression in E and P . For completeness, the full expression for thermal expansion is

$$\alpha_V = \frac{\langle E \delta P \rangle}{k_B T^2 K}. \quad (9)$$

The primary limitation to this expression is that anisotropic changes to the lattice vector with temperature are not considered (*i.e.*, the derivative of $\langle P \rangle$ with respect to T is taken under the constraint of constant lattice vectors), whereas our MD simulations fully account for changes in lattice vector with temperature. We compare this expression to the numerical derivative of volume to assess the accuracy of the fluctuation expression.

C. Mechanical Properties

1. Elastic Constants—The Helmholtz free energy of a stress free crystal may be expanded as a function of the strain tensor,

$$\frac{1}{V_0} F(\epsilon, T) = \frac{1}{V_0} F(0, T) + \frac{1}{2} \sum_{ijkl} C_{ijkl}(T) \epsilon_{ij} \epsilon_{kl} + \dots, \quad (10)$$

where ϵ_{ij} are elements of the Lagrangian strain tensor, C_{ijkl} are elements of the constant temperature elastic constant tensor, and V_0 is the volume corresponding to lattice vectors that lead to all components of the stress tensor being zero. The dependence of free energy and elastic constants on T and ϵ in Eq. 10 is explicitly indicated by parentheses. Elastic constants are determined here as a function of temperature at $\epsilon = 0$, and the convention that $C_{ijkl} = C_{ijkl}(0, T)$ is used in the remainder of this work. The Lagrangian strain tensor is defined by the lattice constants at zero-stress, Ω_0 , and the deformed lattice constants, Ω , as

$$\epsilon = \frac{1}{2} (\Omega_0^{-T} \Omega^T \Omega \Omega_0^{-1} - 1). \quad (11)$$

The volume may also be represented in terms of Ω as

$$V = |\det(\Omega^T)|. \quad (12)$$

The constant temperature elastic constants are proportional to the second derivative of free energy with respect to strain, or equivalently, the derivative of stress with respect to strain,

$$C_{ijkl} = V_0^{-1} \frac{\partial^2 F}{\partial \epsilon_{ij} \partial \epsilon_{kl}} = \frac{\partial \langle \sigma_{ij} \rangle}{\partial \epsilon_{kl}}, \quad (13)$$

where σ_{ij} are elements of the stress tensor.

The fluctuation expression for the elastic constants, as previously derived,^{40–43} is

$$C_{ijkl} = \left\langle \frac{\partial \sigma_{ij}}{\partial \epsilon_{kl}} \right\rangle - \frac{V_0}{k_B T} \langle \sigma_{ij} \delta \sigma_{kl} \rangle, \quad (14)$$

where $\delta \sigma_{ij} = \sigma_{ij} - \langle \sigma_{ij} \rangle$. The first term is the ensemble average of the instantaneous partial derivative of stress with respect to strain. The second term represents the contribution of thermally induced stress fluctuations to the elastic constants. The average partial derivative may be expanded to produce

$$\left\langle \frac{\partial \sigma_{ij}}{\partial \epsilon_{kl}} \right\rangle = \frac{2Nk_B T}{V_0} (\delta_{ik} \delta_{lj} + \delta_{il} \delta_{kj}) + \frac{1}{V_0} \left\langle \frac{\partial^2 U}{\partial \epsilon_{ij} \partial \epsilon_{kl}} \right\rangle, \quad (15)$$

where N is the number of atoms in the system and δ_{ij} is the Kronecker delta (zero when $i \neq j$ and 1 otherwise). The first and second terms in Eq. 15 represent the derivatives of the kinetic and potential contributions to stress, respectively, with respect to strain. The kinetic term is analytically defined, while the potential portion is known as the Born term. The second

derivative of energy with respect to strain, $\frac{\partial^2 U}{\partial \epsilon_{ij} \partial \epsilon_{kl}}$, for a fixed atomic configuration may be computed using previously outlined finite difference schemes.⁴⁴ The Born term is then obtained by performing this procedure on configurations extracted from the MD trajectory to provide an ensemble average of the second derivative. Throughout the majority of this work, the elastic constants and stress are given using Voigt's notation, which converts the standard rank-2 tensor representation of stress and strain into a vector with the following mapping: 11 $\rightarrow$ 1, 22 $\rightarrow$ 2, 33 $\rightarrow$ 3, 23 $\rightarrow$ 4, 13 $\rightarrow$ 5, 12 $\rightarrow$ 6. This further reduces the rank-4 tensor representation of elastic constants to a rank-2 tensor. As an important note, if the elastic constants are evaluated for states where $\epsilon \rightarrow 0$, the stress in the previous expressions must be replaced with the thermodynamic tension.⁴⁰

2. Anisotropic Bulk Modulus—The constant temperature bulk modulus (K), as well as the compressibility (K^{-1}), is defined as

$$K = V \frac{\partial^2 F}{\partial V^2} = -V \frac{\partial \langle P \rangle}{\partial V}. \quad (16)$$

The value of K may be determined from knowledge of the elastic constants. For cubic systems, like B2 NiTi, the elastic constants are related to K through the simple expression, $(C_{11} + 2C_{12})/2$. More generally, however, a system with anisotropic lattice vectors, like B19' and B33 in NiTi, will anisotropically deform in response to a hydrostatic pressure. As a result, simple analytic expressions for K in terms of elastic constants for anisotropic systems are not readily available.

A numerical procedure relating the elastic constants of an arbitrary crystal to K may, however, be defined. Such a procedure begins with the relation between macroscopic stress and strain, which, in Voigt's notation, is given by

$$\sigma_i = \sum_j C_{ij} \epsilon_j, \quad (17)$$

where the $\langle \dots \rangle$ formalism is omitted for this model, which is valid for both constant stress and constant strain ensembles. This expression may be easily inverted such that ϵ may be found parametrically as a function of σ . Values of σ are chosen in accord with the interpretation that K is proportional to the derivative of hydrostatic pressure, P , with respect to volume. To ensure our model corresponds to a mechanically stable crystal under hydrostatic pressure, we choose $\sigma_1 = \sigma_2 = \sigma_3 = -P$ and $\sigma_4 = \sigma_5 = \sigma_6 = 0$. The value of ϵ may then be parametrically determined in terms of σ and P . The lattice vector tensor at a given ϵ is obtained by rearranging Eq. 11 as

$$\Omega^T \Omega = \Omega_0^T (2\epsilon + 1) \Omega_0 \quad (18)$$

and finding Ω (modulo a rotation) through linear algebra manipulations. The volume corresponding to Ω is then given by Eq. 12. This provides values of V determined parametrically in P . The enforcement of mechanical stability through the definition of σ fully accounts for anisotropic changes in the lattice vectors as a function of V . Representative curves for P as a function of V determined using this method, which accounts for anisotropic changes in Ω , are shown in Fig. 2 for B19' and B2 at $T = 300$ K. The value of K is easily obtained through the numerical derivative of $V_0 P$ with respect to V . We refer to K obtained in this manner as the anisotropic bulk modulus.

3. Isotropic Bulk Modulus—Comparing the elastic constant method with a rigorous fluctuation expression for K is desirable. Unfortunately fluctuation expressions for K do not account for the anisotropic changes in lattice vectors that may occur upon volume expansion

and are therefore only appropriate where expansion is isotropic, as with cubic systems. For NiTi, a fluctuation expression for K could be employed accurately for the cubic B2 phase, but not the B19' and B33 phases. Nevertheless, a fluctuation formula may be constructed as

$$K = -V \left\langle \frac{\partial P}{\partial V} \right\rangle - \frac{V}{k_B T} \langle P \delta P \rangle. \quad (19)$$

The first term in Eq. 19 is the instantaneous derivative of pressure with respect to volume. The second term in Eq. 19 gives the contribution of the thermally induced fluctuation of P to K . The value of $-V \langle P / V \rangle$ may be expanded as

$$-V \left\langle \frac{\partial P}{\partial V} \right\rangle = \frac{5}{3} \frac{N k_B T}{V} + V \left\langle \frac{\partial^2 U}{\partial V^2} \right\rangle. \quad (20)$$

We include the full details of the derivation of Eqs. 19 and 20 in Appendix A. To our knowledge, a full derivation of the fluctuation expression for K in the canonical ensemble has not been provided previously. The first term in Eq. 20 is the analytical form of the derivative of the kinetic component of $\langle P \rangle$ with respect to V . The partial derivative in the second term results from the potential energy contribution to $\langle P \rangle$. This term is similar to the Born term that arises in the fluctuation expression for elastic constants and is evaluated using the same procedure *i.e.*, averaging the derivative from finite differences over the MD trajectory.

For comparative purposes, a numerical procedure relating the elastic constants to a value of K equivalent to the fluctuation formula may be defined in a fashion similar to the one previously discussed for the anisotropic bulk modulus. In this approach, ϵ corresponds to an isotropic change in the lattice vectors, which was required for the derivation of the fluctuation formula for K . For such an expansion, one defines $\epsilon_1 = \epsilon_2 = \epsilon_3 = 1/2[(V/V_0)^{2/3} - 1]$, where V_0 is the volume of the stress-free system and V is the volume at a given strain, and $\epsilon_4 = \epsilon_5 = \epsilon_6 = 0$. The value of σ can be obtained parametrically in ϵ by using Eq. 17. In general, the obtained σ tensor may not correspond to a mechanically stable configuration, *i.e.*, $\sigma_1 - \sigma_2 - \sigma_3$ and $\sigma_4 - \sigma_5 - \sigma_6 = 0$. However, the pressure may be obtained from $P = \frac{1}{3}(\sigma_1 + \sigma_2 + \sigma_3)$. As ϵ is an explicit function of V , one may compute P parametrically in V and, thereby, extract K from a numerical derivative. Representative curves for P as a function of V determined using this method, assuming isotropic changes in Ω , are shown in Fig. 2 for B19' and B2 at $T = 0$ K. We refer to K obtained by either this method or by the fluctuation formula as the isotropic bulk modulus.

D. Thermodynamic Upsampling

Ideally, DFT simulations should be performed using high convergence thresholds (*e.g.* k-points per reciprocal atom, E_∞ valence size). Often, this is easily achieved for $T = 0$ K computations, which generally employ small simulation cells and require a limited number of electronic self-consistent steps. On the other hand, DFT-MD simulations for the

computation of temperature-dependent properties that are converged with respect to phase space sampling often require large supercells and thousands of self-consistent steps. Considering present computational capabilities, this imposes a practical limitation on the thresholds tenable to DFT-MD simulations. A common approach to overcome this limitation is to reduce both the size of the plane wave basis set and degree of Brillouin zone sampling. We here characterize and outline a procedure to correct the errors in properties that result from such reduced thresholds.

We first consider the influence of convergence on the structure and mechanical properties, which are both closely related to the accuracy of stress in the simulation. Commonly, the incompleteness of the plane-wave basis set results in an error to the stress, known as the Pulay stress (governed by E_c). The volume of the cell typically shrinks to accommodate the missing contributions in the basis set.⁴⁵ This error is often an isotropic correction to the stress, or a hydrostatic pressure, and potentially can influence the derivative of stress with respect to cell displacements. There are similar issues for sparse sampling of the Brillouin zone (governed by the number of k-points per reciprocal atom) on both the magnitude and strain derivatives of stress.

We first address the sensitivity of the structure and mechanical properties at $T = 0$ K as an initial guide to understand how convergence thresholds affect DFT-MD simulations. The behavior of the structure with respect to increased E_c and number of k-points per reciprocal atom (KPPRA) is shown in Fig. S1 in the supplemental information. It is clear that there are significant inaccuracies for values of E_c below 500 eV, above which the lattice vectors of the unit cells vary by less than 0.001 Å. The mechanical properties of the phases of NiTi are shown in Fig. S2 of the supplemental information. The elastic constants are highly sensitive to KPPRA, and to a lesser extent on E_c , showing up to 25 GPa decreases upon increasing the threshold. Structure and mechanical properties of all phases show little sensitivity to the valence configuration.

To understand possible errors in properties derived from DFT-MD simulations, we compute the temperature-dependent structure and elastic constants for a small, 16 atom B2 supercell at various levels of numerical accuracy. The simulations are performed using both the thresholds employed for the majority of the DFT-MD simulations in the present work (KPPRA~3000; E_c ~300 eV) as well as with a more stringent threshold (KPPRA~10000; E_c ~500 eV), referred to simply as “MD accuracy” and “high accuracy,” respectively. The more stringent parameters were chosen on the basis of our $T = 0$ K evaluation of properties given in Figs. S1 and S2 in the supplemental information. At both levels of accuracy, the supercell is optimized to a stress free configuration over the 300-600 K temperature range, where B2 has been previously found to be stable.¹⁰ The elastic constants of the so-determined structures are then computed using the fluctuation formulas.

The structure of the supercell for the MD and high accuracy simulations is given in Fig. 3a. The simulations performed at MD accuracy underestimate the volume by roughly 1% compared high accuracy simulations. In terms of mechanical properties, we provide an analysis of the C_{11} elastic constant as a function of accuracy in Fig. 3b. Using the optimized cells, DFT-MD simulations are performed for 20 ps, and the mechanical properties are

evaluated using the fluctuation formulas in Eq. 14. The results indicate differences of up to 15 GPa, which diminish as temperature increases. Such differences are in-line with those expected from the $T = 0$ K computations in Fig. S2 of the supplemental information.

The influence of convergence thresholds on the energies and free energy differences between the phases of NiTi were discussed in a previous work.¹⁰ Changes in convergence thresholds were shown to lead to errors in the $T = 0$ K energy differences between the phases in excess of 1 meV/atom. The free energy differences between phases, however, were found to be insensitive to increases in numerical accuracy above those employed in the present DFT-MD simulations. The difference in free energies at various thresholds was in agreement within 1 meV/atom, which is within the statistical certainty of our free energy values. Anharmonic effects were shown to reduce the errors in differences at $T = 0$ K to produce similar temperature-dependent internal energy and free energy differences across various convergence thresholds.

One may attempt to correct the simulations performed at MD accuracy by using up-sampling.⁶ Upsampling asserts that if the phase space sampled by each level of accuracy is similar, then one may reprocess configurations from a lower level of accuracy with a higher level of accuracy to recompute properties. The conservation of phase space between simulations of higher accuracy is an assumption that is difficult to test. Nevertheless, we apply this principle to our simulations using MD accuracy to estimate the value of properties from simulations performed at the high accuracy. For the purposes of application here, we reprocess every 100 configurations of the simulation performed at MD accuracy with high accuracy. Only the structure and mechanical properties are corrected in this way, as the free energy has been shown to be less sensitive to threshold convergence.

For the mechanical properties, the upsampling procedure requires the re-evaluation of stress-dependent expressions given in the fluctuation formula in Eq. 14. This requires not only the re-evaluation of stress itself, but also the Born term, which is applied through finite displacements of the lattice vectors. Applying this process to the small B2 supercell, we see, as shown in Fig. 3b, that the elastic constant C_{11} produced from simulations at MD accuracy can be brought to within 2 GPa agreement with that produced from simulations at high accuracy. To correct the structure, we employ the upsampled elastic constants and the relation between stress and strain in Eq. 17. The stress tensor produced from upsampling can be converted to an effective strain. Leveraging the connection between the lattice vectors, Ω , and ϵ through Eq. 11, one may predict the lattice vectors at zero upsampled stress. An application of this procedure, given in Fig. 3a, shows that the volume obtained from MD accuracy simulation can be made to almost exactly agree with that at high accuracy. As these tests show that properties may be effectively corrected for numerical errors, all further structural values and mechanical properties reported in the present work have been upsampled from MD to high accuracy.

E. Free Energy

We compute a number of state properties for the three phases of NiTi, including internal energy ($\langle E \rangle$), enthalpy (H), Helmholtz free energy (F), Gibb's free energy (G), and entropy (S). Our approach to state properties makes use of the fact that the structures are optimized

to a stress-free state at each T . As such, various properties reduce to the same value, namely $\langle E \rangle$ to H and F to G . The value of $\langle E \rangle$ may be obtained directly from an MD simulation at fixed Ω and T . For free energy, thermodynamic integration techniques must be used, as described below. Entropy may be obtained trivially from the internal energy, free energy, and temperature as $S = (F - \langle E \rangle)/T$.

The Helmholtz free energy difference between two states can be represented using thermodynamic integration as

$$\Delta F^{0 \rightarrow \lambda'} = \int_0^{\lambda'} \frac{\partial F}{\partial \lambda} d\lambda, \quad (21)$$

where the states are defined according to a thermodynamic integration variable λ , with $\lambda = 0$ and $\lambda = \lambda'$ being the initial and final states. When comparing the thermodynamic favorability of multiple phases of a given material, the absolute free energy is required, given by

$$F|_{\lambda=\lambda'} = F|_{\lambda=0} + \int_0^{\lambda'} \frac{\partial F}{\partial \lambda} d\lambda, \quad (22)$$

where $F|_{\lambda}$ is the free energy at a given value of λ and $F|_{\lambda=0}$ is a reference free energy.

In the present work, we optimized the value of Ω as a function of T , and we computed the free energy along this path as a function of temperature. These are therefore natural variables for thermodynamic integration, and we treat both T and Ω as functions of λ . The thermodynamic integration expression under these conditions (see derivation in Appendix B) is given by

$$\left. \frac{F}{T} \right|_{\lambda=\lambda'} - \left. \frac{F}{T} \right|_{\lambda=0} = - \int_0^{\lambda'} \frac{1}{T^2} \langle E \rangle \frac{\partial T}{\partial \lambda} d\lambda + \int_0^{\lambda'} \frac{|det(\Omega^T)|}{T} (\langle \sigma \rangle \Omega^{-T}) : \frac{\partial \Omega}{\partial \lambda} d\lambda. \quad (23)$$

where “:” denotes the Frobenius inner product (*i.e.*, $\sum_{ij} \frac{\partial Z}{\partial \Omega_{ij}} \frac{\partial \Omega}{\partial \lambda_{ij}}$). The expression in Eq. 23 is similar to previous free energy expressions^{8,46} used in non-equilibrium, reversible scaling simulations. However, unlike those expressions, Eq. 23 has an additional term which fully accounts for the influence of changes in the lattice vector on the free energy as a function of temperature. In addition to non-equilibrium approaches, the quantities in the integrands of Eq. 23, like E and σ , may also be obtained from a series of equilibrium DFT-MD simulations for each λ . This is the approach we take here where we have performed simulations in steps of 50 K for times up to 50 ps.

The reference value of $F|_{\lambda=0}$ is obtained through the Einstein method^{4,6}. This gives the free energy from continuously switching the potential from one with a known reference free

energy to another more general representation, like density functional theory. In the present work, our reference system is a harmonic potential with a temperature-dependent force constant matrix, D_{ij} , as determined from the temperature dependent phonon (TDEP)^{47,48} procedure. The force constant matrix is given as $D_{ij} = \frac{1}{2} \frac{\partial^2 U}{\partial u_i \partial u_j}$, where U is potential energy and u is an atomic displacement vector. We find that a harmonic potential composed of temperature-dependent D_{ij} , given by $U^{QHA} = \frac{1}{2} \sum_{i,j} u_i D_{ij} u_j$, is an excellent reference potential. As an added benefit, this reference potential provides a stable phonon dispersion with only real eigenvalues for the high temperature B2 phase, which is unstable at 0 K. The phonon dispersion resulting from D_{ij} may be used to evaluate the free energy from the QHA. The free energy of the full DFT system at the reference temperature may then be obtained by evaluating

$$F|_{\lambda=0} = F^{QHA}|_{\lambda=0} + \int_0^1 \left\langle \frac{\partial U}{\partial \mu} \right\rangle \Big|_{\mu, \lambda=0} d\mu, \quad (24)$$

where μ is the switching variable, the potential energy is given by $U = U^{QHA} - \mu(U^{QHA} - U^{DFT})$, and all values are determined for the reference condition, $\lambda = 0$. The potential as determined from the force constants is given by $U^{QHA} = \frac{1}{2} \sum_{i,j} u_i D_{ij} u_j$, where u is atomic displacement. A series of equilibrium DFT-MD simulations is performed using this potential energy expression and a μ spacing of 0.25, which provides a smoothly varying measure of U/μ .

F. *Ab Initio* Molecular Dynamics Simulations

Simulations are performed with the Vienna *Ab Initio* Simulation Package (VASP)^{49–52} using the frozen core all electron projector augmented wave (PAW) method^{53,54} and the generalized gradient approximation of Perdew, Burke, and Ernzerhof. All DFT-MD simulations employ an energy cutoff (E_c) of 269.5 eV, an electronic energy convergence criteria of 1×10^{-7} eV, a time step of 3.0 fs, and ~3000 KPPRA. Furthermore, the electronic temperature is fixed to 0.05 eV. Spin polarization was found to have no effect on the 0 K energetics and is not included in the present simulations. For both Ni and Ti the 3d and 4s electrons are included in the valence. This configuration was found to produce free energy results within 1 meV/atom agreement with higher-accuracy simulations. Computations are performed on 144 atom supercells - $4 \times 3 \times 3$ supercell of the 4 atom unit cells. This size was found to be free of vibrational size effects and lead to a converged free energy in a previous work.¹⁰ Temperature is controlled through the use of a Langevin thermostat with a simulation-time equivalent friction factor of 100 fs.

III. RESULTS

A. Structure

The $T = 0$ K DFT structures of B33, B19' (fixed to 98°), and B2 determined from high accuracy computations, as defined previously, are provided in Table I. The B33 phase is the $T = 0$ K ground state monoclinic structure and has an angle, γ , of 107.32° and *Cmcm*

symmetry. The B19' phase is not stable at $T = 0$ K according to our simulations,¹⁰ but the structure may be estimated by constraining γ to the experimental value of 98° and removing the normal stresses by optimizing Ω , which equates to optimizing the structure under shear stress. The resulting structure, while monoclinic like B33, is of $P2_1/m$ symmetry. The length of the b lattice vector of the B19' phase is $\sim 5\%$ smaller than that of B33. The B19' phase is the martensite phase. The high symmetry, B2 phase results when $\gamma = 90^\circ$ and $b = c$ and is the high-temperature austenite phase. The symmetry of B2, $Pm\bar{3}m$, is in the same family as B19', which is requisite for the shape memory effect. The b vector of B2 is $\sim 9\%$ smaller than that of B19', while c is $\sim 5\%$ larger. Our $T = 0$ K results are in agreement with previous computational results,^{16,19} exhibiting only a fraction of a percent relative error. Our results show similar accuracy with respect to available experiments on B19',^{15,55} and B2.⁵⁶

The structural parameters of the stress-free B33, B19', and B2 phases are reported within their limits of temperature stability in Fig. 4. Concerning atomic volume, V , in Fig. 4a, the disparity in atomic volume between the different phases is small - less than one percent between the various phases at a given temperature. The volume increases with temperature are nearly linear for the monoclinic phases, while the volume of the B2 phase exhibits a greater than linear increase with temperature. The volume of B2 is the smallest of three phases over the majority of the temperatures examined. At $T = 300$ K, B2 has $\sim 1\%$ lower volume than B19'. Temperature closes this gap to yield comparable B2 and B19' volumes at $T = 600$ K.

The b/a and c/a ratios of the monoclinic B33 and B19' phases are shown in Fig. 4b as a function of temperature. Both the b/a and c/a ratios of the monoclinic phases show a minor, but systematic, increase with temperature. The average b/a ratios are 0.82 and 0.87 for B33 and B19', respectively. The c/a ratios are smaller, 0.59 and 0.62 for B33 and B19', respectively. These values imply a large difference in the value of a between the two structures, which is akin to the behavior noted at $T = 0$ K in Table I. The difference in the b/a ratio corresponds to a 5% disparity in the a lattice constant, which supports previous strain-based argument for B33 being an unsuitable B19' $\rightarrow$ B2 intermediate.¹⁶

The temperature-dependent behavior of γ is markedly different for the B33 and B19' phases, which is given in Fig. 4c. For B33, the value of γ is practically constant at 107.3° . For B19', γ is highly sensitive and exhibits large decreases with increasing temperature. At $T = 50$ K, γ is roughly 100° , and this value decreases almost linearly to 97° at $T = 600$ K. Temperature effectively drives the γ of B19' toward the B2 value of 90° .

The structural properties were all upsampled from MD to high accuracy. The net action of this process was an average volume increase of 1.1, 1.0, and 1.2 % for B33, B19', and B2, respectively. This increase is almost constant over the entire range of temperatures. In addition, the correction was found to be nearly isotropic and did not lead to changes in the shear stress. The correction, therefore, did not significantly affect the b/a ratio, c/a ratio, or γ .

B. Thermal Properties

The thermal properties, including the coefficient of volumetric expansion and heat capacity, are shown in Fig. 5. In this case, the convergence of the fluctuation formulas require many tens of picoseconds to obtain a level of reasonable accuracy, as shown in Fig. S3 of the supplemental information. Unfortunately, the temperature-dependent variations of these properties is only a few percent. The error in the resulting fluctuation expressions effectively mask the underlying temperature trends. A further error originates from possible shape changes at constant volume which are not accounted for in the fluctuation expressions for α_V . We cannot confidently apply the fluctuation formulas and expect clear temperature trends using the ~ 50 ps simulations performed here. Alternatively, as the trends in V and $\langle E \rangle$ are well-behaved with respect to temperature, we evaluate the thermal properties from the numerical derivative of polynomial fits to the raw data. The resulting values from this procedure fall within the spread of values given by the fluctuation expressions (see Fig. S6 of the supplemental information).

The coefficient of thermal expansion multiplied by volume, or V/T is shown in Fig. 5a as a function of temperature. To compute these values, we have performed the numerical derivative of volume with respect to temperature, as required by Eq. 6. The volume data provided in Fig. 4 is fitted to a third order polynomial to provide a smoothly varying function of temperature. The thermal expansion of B33 is increasing and nearly linear, varying from $3.4\text{--}3.7 \times 10^{-4}$ ($\text{\AA}^3/\text{K}$). The value of $V \times \alpha_V$ for B19' varies only slightly over the entire temperature range, with the average value being 2.5×10^{-4} ($\text{\AA}^3/\text{K}$). The $V \times \alpha_V$ of B2 varies from $3.4\text{--}6.6 \times 10^{-4}$ ($\text{\AA}^3/\text{K}$) and has the highest volume expansion coefficient of all three phases. The most notable difference between the three phases is the large increase in expansion of B2 at high temperature. This may be attributed to the greater anharmonicity of the B2 phase (the anharmonicity of B2 will be shown to be much larger than that of B33 or B19' in the following sections), which is well known to be correlated to thermal expansion. From the values of $V \times \alpha_V$ in Figure 4a and V in Figure 4, the average of α_V of the B33, B19' and B2 phase is 2.5 , 1.8 , and $3.0 \times 10^{-5} \text{ K}^{-1}$, respectively. The value of α_V is of the same order of magnitude as experimental measurements, which find $0.6\text{--}1.3 \times 10^{-5} \text{ K}^{-1}$.^{57,58} Variations between the computed and experimental values are likely a result of the polycrystalline nature of the material analyzed in experimental works.

The heat capacity is shown in Fig. 5b, where values are provided using derivatives of second order polynomial fits to the internal energy. Aside from increasing in temperature, the heat capacity of B33 and B19' are similar, though B19' is slightly lower than B33. The heat capacity of B2 is the lowest of the three phases at $\sim 0.96\text{--}0.98 \text{ meV}/(\text{atom} \times \text{K})$, and decreases with increasing temperature. This is likely a result of the strongly anharmonic nature of B2 (the anharmonicity of B2 is discussed in the following sections), which leads to thermal energy increasing by less than $3k_B T$. Temperature-dependent changes in volume and lattice vector may also impact C_P . Such changes can shift the $T = 0 \text{ K}$ energy of the crystal and influence the degree of anharmonicity. This is most likely the origin of the greater than $3k_B T$ C_P of B33 and B19' as well as the decreasing C_P of B2.

C. Mechanical Properties

The $T = 0$ K elastic constants of NiTi as determined from high accuracy thresholds are given in Table II along with the all electron, full potential (FLAP-W) computational results of Hatcher *et al.*¹⁷ and experimental measurements.^{59,60} Our elastic constants have been computed from finite displacements as described by Le Page and Saxe.⁶¹ The monoclinic phases have 13 independent elastic constants, while the B2 phase has only three independent constants. We see that the C_{ij} between the monoclinic phases are similar, varying by only a few GPa. The C_{11} of B2 takes a value similar to the C_{33} of B33 and B19' (the "3" direction in the monoclinic phases is along the lattice vectors of the cubic B2 cell). Compared to experimental results at $T = 400$ K⁵⁹ and $T = 298$ K,⁶⁰ our values for elastic constants provide an upper bound, which can be attributed to thermal effects and mixtures of phases in experiments.⁶⁰ The elastic constants of Hatcher and coworkers,¹⁷ from FLAPW computations are in good agreement; the C_{33} constants of B33 and B19' are 10-15 GPa larger, however. Our values also agree closely with previous computations performed by Hu *et al.*⁶² as well as those of Wagner and Windl.¹⁹ All phases are found to be elastically stable with respect to the criterion that the eigenvectors of the elastic constant tensor are positive.^{63,64} For stability of the B19' phase, we must consider the eigenvalues of the elastic stiffness tensor, which accounts for the non-zero shear stress on B19',⁶⁴ as opposed to the elastic constant tensor. The eigenvalues of the elastic stiffness tensor are found to be positive for B19', indicating stability under an applied shear.

We compute the $T = 0$ K bulk modulus (1) numerically from the elastic constants allowing for anisotropic lattice vector changes with respect to volume, (2) numerically from the elastic constants enforcing isotropic lattice vector changes with respect to volume, and (3) from finite differences of an explicitly determined pressure-volume curve under isotropic expansion. The application of the explicit computations with the finite displacement procedure for K provides a point of comparison to validate the isotropic value determined from elastic constants alone. These values are given in Table III along with experimental comparisons.^{59,60} We see that the isotropic value of K is larger than the anisotropic for the monoclinic cells. The largest variation between the two measures, 10 GPa, is found in the B19' phase. Both measures agree in the B2 phase, where isotropic expansion is expected from symmetry. The computed bulk moduli of the B33, B19', and B2 phases are 153, 145, and 165 GPa, respectively. The bulk modulus of NiTi has been experimentally determined to be 126 GPa at $T = 400$ K⁵⁹ and 159 GPa at $T = 298$ K.⁶⁰ Our computations fall within this range, but show better agreement with the measurements of Mercier and coworkers.⁶⁰

Evaluation of the elastic constants at temperature requires knowledge of both the fluctuation of stress as well as the Born term. An example of the convergence of these quantities is given in Fig. S4 of the supplemental information, which shows that the Born term converges rapidly, within 10 ps, and that the fluctuation term converges slowly, within ~ 50 ps. The Born term is positive and on the order of magnitude of the $T = 0$ K elastic constants, while the fluctuation term is negative and has an absolute value an order of magnitude smaller than the Born term. The relative error in the fluctuation component is larger than 10%, while the error in the Born term is on the order of 1%. Because the Born term is much larger in magnitude than the fluctuation component, the overall statistical error in the computed

elastic constants is minimal. This verifies that the fluctuation expression for the elastic constants can be readily applied using data from our ~50 ps simulations.

We provide all elastic constants as a function of temperature in Fig. 6. All phases exhibit elastic stability for the temperatures investigated. Most elastic constants exhibit a decrease with increasing temperature. This is most apparent for B19', which is stable from very low to high temperatures. The primary exception to this is the C_{44} constant of the B2 phase, which increases slightly with temperature. This could be a signature that shear deformations become less favorable at high temperatures, in line with the transition to B2 from the B19' phase. Furthermore, previous investigations¹⁷ have indicated that the small C_{44} of B2, 20-25 GPa lower than that of B33 and B19', could play a large role in the shear destabilization of B2 during the martensitic transition.

From the temperature dependent elastic constants, we have produced isotropic and anisotropic values for K , as shown in Fig. 7 along with experimental results.^{59,60} (As a brief note, the isotropic values of K derived from the elastic constants are in excellent agreement with those from the fluctuation expression, as shown in Fig. S5 of the supplemental information, which validates the use of K values derived from the elastic constants.) The value of K decreases with increasing temperature for all phases. For the isotropic measures, all phases fall along a similar temperature-dependent line. The anisotropic measures reduce the value of K for the monoclinic phases, while not significantly affecting the B2 phase. The reduction in elastic constant is similar to that noted at $T = 0$ K, with B33 being reduced by 5 GPa and B19' being reduced by ~10 GPa. Our temperature-dependent values of K show good agreement with measurements of Mercier *et al.*⁶⁰ at $T = 298$ K, despite these measurements being taken near the martensitic transition. As discussed previously, our results are an upper bound to the experimental measurement⁵⁹, though thermally-induced decreases in K lead to only a 10-20 GPa overestimation at $T = 400$ K.

As the mechanical properties were all upsampled from MD accuracy to high accuracy, we discuss the impact this procedure had on our values briefly. For elastic constants determined from the fluctuation formula, the upsampled Born term changed little from that obtained at MD accuracy; upsampling predominantly affected the value of the stress fluctuation term. For the majority of the elastic constants, the changes upon upsampling were on the order of 3 GPa or less. As with the small systems, the C_{33} elastic constant in the monoclinic phases and C_{11} constant in the B2 phase show a larger influence on the order of 5-10 GPa.

D. Latent Heat and Free Energy

The latent heat of a first order phase transition is the difference between their average internal energies, or the enthalpy differences at $\langle \sigma \rangle = 0$, at the phase transition temperature. Enthalpy differences, H , for the B33→B19' and B19'→B33 transitions (enthalpy differences for $A \rightarrow B$ is given by $\langle E \rangle^B - \langle E \rangle^A$) are shown in Fig. 8 as a function of temperature. The value of H for the B33→B19' and B19'→B2 transitions range from 0.6-1 and 20-25 meV/atom, respectively. The latent heat for the B33→B19' transition is 1.0 meV/atom, while the latent heat of the B19'→B2 transition is 22.9 meV/atom.

The free energy is determined from a combined thermodynamic integration formalism, as given in Eq. 23. This procedure fully accounts for the anharmonicity of the high temperature B2 phase, which has been outlined in previous work.¹⁰ Techniques that fully account for anharmonicity may be motivated by examining the temperature-dependent behavior of the vibrational dispersions and thermal energy as obtained from DFT-MD. We have previously applied the TDEP^{47,48} (as described in the free energy section of the Methods) technique to obtain the temperature-dependent phonons of the phases of NiTi and present these previous results in Fig. 9 (imaginary eigenvalues are given as negative numbers). At $T = 0$ K, the phonon dispersion of B2 exhibits imaginary eigenvalues that indicate vibrational instability. The imaginary frequencies of B2 become real at high temperatures, which is a direct result of anharmonic phonon scattering. The thermal energy is defined as the difference between average internal energy $\langle E \rangle_T$ and the $T = 0$ K energy (E_0). The temperature-dependent behavior of this quantity is shown in Fig. 10. The thermal energy of B33 and B19' is roughly equivalent to $3k_B T$, indicating these systems behave harmonically. The thermal energy of B2, on the other hand, is significantly lower than $3k_B T$, indicating anharmonic character.

The high accuracy application (to within 1 meV/atom) of the Einstein method portion of our free energy scheme has been previously outlined.¹⁰ To ensure a similar accuracy for the portion determined by thermodynamic integration, the internal energy must be converged with respect to phase space sampling. If we assume that the error in all obtained internal energy values is equivalent, Eq. 23 yields an upper bound of 0.2 meV/atom accuracy in internal energy to guarantee a free energy accuracy of 1 meV/atom over a $T = 50$ K to 600 K range. We explicitly tracked the convergence of internal energy, given in Fig. S7, which shows that 50 ps is sufficient to reach this accuracy for the systems investigated here.

The $T = 0$ K energy ($E(T = 0)$), the average internal energy $\langle E \rangle_T$, the product of entropy and temperature ($T \langle S \rangle$), and free energy differences for the B33 $\rightarrow$ B19' and B19' $\rightarrow$ B2 transitions are presented in Fig. 11. The value of $T \langle S \rangle$ is determined from the difference between the free energy, given by *via* Eq. 23, and $\langle E \rangle_T$. The temperature where $\langle E \rangle_T$ and $T \langle S \rangle$ have equal magnitudes corresponds to a phase transition. For the B33 $\rightarrow$ B19' transition, given in Fig. 11a, $E(T = 0)$ is about 1 meV/atom larger than $\langle E \rangle_T$, indicating that thermal contributions to the energy slightly favor B19'. The value of $T \langle S \rangle$ increases with temperature and crosses $\langle E \rangle_T$ at $T = 81$ K, indicating a transition. For the B19' $\rightarrow$ B2 transition, given in Fig. 11b, $E(T = 0)$ is 15-20 meV/atom larger than $\langle E \rangle_T$, indicating that anharmonic thermal contributions to the energy strongly favor B2. The entropic contribution to the free energy crosses the internal energy curve at $T = 481$ K in this case, indicating a transition. Other cell-deformation based approaches to compute free energy differences have yielded transition temperatures within 15 K of those reported here.¹⁰ Thus, anharmonic contributions to the B19' $\rightarrow$ B2 thermal energy is significantly larger than for B33 $\rightarrow$ B19' transition. This large anharmonic contribution plays a significant role in effectively suppressing the martensitic transition temperature by reducing the thermal energy component of the free energy.

One could alternatively neglect the anharmonic character of NiTi and determine the free energy through the QHA. The vibrational dispersion of all phases is required as a function of

temperature to determine the harmonic free energy. The total Helmholtz free energy may be given by

$$F^{QHA} = E^{QHA} - TS^{QHA}, \quad (25)$$

where E^{QHA} includes the potential at zero atomic displacement, the zero point energy, and the harmonic thermal contribution to the internal energy. One limiting factor to the application of this approach to NiTi is that the vibrations must be real and the crystal stable, meaning that the $T = 0$ K dispersion of B2 cannot be employed for this procedure. To overcome this limitation, the QHA free energy can be determined from the stable, temperature-dependent phonons, as shown in Fig. 9.

To understand the magnitude of the anharmonic contribution to the free energy of NiTi, both QHA (obtained from TDEP phonons) and fully anharmonic DFT-MD results for differences in internal energy, entropy, and free energy between B33 and B19' as well as between B19' and B2 are compared in Table IV. Concerning the B33→B19' transition, the QHA estimates of free energy are within 1 meV/atom of those from DFT-MD. This suggests the monoclinic phases are relatively harmonic and well represented by the QHA. Consequently, the QHA transition temperature is $T = 89$ K, which is close to the full anharmonic value. For the B19'→B2 transition, the QHA grossly overestimates the free energy differences between the phases. Assuming the changes in free energy are linear, the QHA transition would occur at 1074 K, an overestimate of more than 500 K. This error primarily originates from differences in internal energy, which implies a highly anharmonic B2 phase. This error in free energy can be greatly reduced by using the ensemble average of internal energy from MD within the QHA. The entropic contribution to free energy from the QHA and DFT-MD are in better agreement than internal energy, within 4 meV/atom, though this still leads to an overestimate on the order of 100 K for the B19'→B2 transition. Both procedures considered, the QHA is a poor replacement for DFT-MD for the high temperature martensitic transition.

IV. CONCLUSIONS

We have performed a full thermodynamic analysis of the B33, B19', and B2 phases of NiTi based on first principles molecular dynamics simulations. The structure and physical properties (elastic constants, bulk moduli, coefficient of thermal expansion, and heat capacity) were evaluated for each phase along a stress free isobar as a function of temperature. In addition, properties related to transformations between the phases, namely latent heats and free energy differences of the B33→B19' and B19'→B2 phase transitions were computed.

The temperature-dependent structure of the phases was obtained by applying a modified upsampling technique that corrects errors resulting from the limited density of the k-point mesh and the size of the basis set. The resulting structures were shown to be in good agreement with available experiments. As in our previous work,¹⁰ the monoclinic angle is shown to be highly sensitive to temperature. Elastic constants were obtained from

fluctuation formulas as determined through modified upsampling. The temperature-dependent elastic constants indicate that all phases are elastically stabilized through thermal effects. The bulk modulus of each phase as a function of temperature is determined from a numerical procedure, based on the elastic constants, that fully accounts for the anisotropy in the lattice vector response with respect to volume changes. Comparison of bulk moduli shows that the B19' phase is softer with respect to volume change than B33 or B2, which can be attributed to the stress accommodation through changes in the monoclinic angle. The coefficient of thermal expansion and heat capacity were determined through numerical derivatives of volume and internal energy, respectively, with temperature. Temperature-dependent trends in both properties indicate a highly anharmonic B2 phase.

The latent heat was obtained from differences in the average internal energy. The latent heat for the transition from the B33 to the B19' phase was estimated to be approximately 1 meV/atom, while that for the transition from the B19' to the B2 phase was shown to be 22.9 meV/atom. Through an analysis of temperature-dependent phonon dispersions and thermal energy, the B33 and B19' phases were shown to be harmonic in character, while the B2 phase is highly anharmonic. Therefore, the free energy was determined from a thermodynamic integration expression that fully accounts for anharmonicity, in addition to volume and cell shape changes, along the computed isobar. The free energy gives transition temperatures from B33→B19' at $T = 81$ K and from B19'→B2 $T = 481$ K. The contribution of anharmonicity to the free energy was evaluated by comparing the thermodynamic integration values with those derived from the quasiharmonic approximation, using temperature-dependent phonons. For the transition between the B33 and B19', the quasiharmonic approximation provides a good estimate for the phase transition. The quasiharmonic approximation overestimates the transition temperature of B19'→B2, however, by over 500 K. This fact emphasizes the importance of explicitly accounting for anharmonicity in the high temperature phase. The significant anharmonicity of B2 plays a major role in setting, and in fact suppressing, the martensitic transition temperature.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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A. Appendix A.: Fluctuation Formula for K

The bulk modulus (K) is represented as,

$$K = V \frac{\partial^2 F}{\partial V^2}, \quad (26)$$

where V is volume. The free energy of the system in the canonical ensemble is given by

$$F = -\beta^{-1} \ln(\mathcal{Z}), \quad (27)$$

where $\mathcal{Z}$ is the partition function and β^{-1} is equal to the product of the Boltzmann constant and temperature. The partition function is given by $\mathcal{Z} = \int \prod_i (d\mathbf{r}_i d\mathbf{p}_i) e^{-\beta E}$, where $\int \prod_i (d\mathbf{r}_i d\mathbf{p}_i)$ represents the integral over phase space and $\prod_i$ indicates the product of all i values. The energy, E , of this system is

$$E = \sum_{i=1}^N \frac{\mathbf{p}_i \cdot \mathbf{p}_i}{2m_i} + U(\{\mathbf{r}_i\}), \quad (28)$$

where $\mathbf{p}_i$ and m_i are the momentum and mass of particle i , the summation in the first term is taken over the N atoms in the system, and U is potential energy, which is determined by the set of all atomic positions $\{\mathbf{r}_i\}$.

One may expand the derivative of $\mathcal{Z}$ with respect to Ω by performing a canonical transformation on $\mathbf{r}$ and $\mathbf{p}$, such that

$$\begin{aligned} \mathbf{r}_i &= \Omega \boldsymbol{\rho}_i \\ \mathbf{p}_i &= \boldsymbol{\pi}_i \Omega^{-1}, \end{aligned} \quad (29)$$

where $\boldsymbol{\rho}_i$ are reduced coordinates, $\boldsymbol{\pi}_i$ are transformed momentum, and a superscript “ -1 ” indicates the inverse tensor. This transformation preserves the dynamics derived from the Hamiltonian and leads to the partition function being written as $\int \prod_i (d\boldsymbol{\pi}_i d\boldsymbol{\rho}_i) e^{-\beta E(\{\boldsymbol{\pi}_i\}, \{\boldsymbol{\rho}_i\})}$. The energy in this representation is given by

$$E = \sum_{i=1}^N \frac{1}{2m_i} (\boldsymbol{\pi}_i \Omega^{-1}) \cdot (\boldsymbol{\pi}_i \Omega^{-1}) + U(\{\Omega \boldsymbol{\rho}_i\}). \quad (30)$$

The value of Ω can be made an explicit function of volume as $\Omega = V^{1/3} \tilde{\Omega}$, where $\tilde{\Omega}$ is the volume independent representation of structure. As previously mentioned, the volume in this case is constrained to change isotropically. Taking the derivative of Eq. 27 leads to

$$\frac{\partial F}{\partial V} = \mathcal{Z}^{-1} \int \prod_i (d\boldsymbol{\pi}_i d\boldsymbol{\rho}_i) \frac{\partial E}{\partial V} e^{-\beta E}. \quad (31)$$

The second derivative is

$$\begin{aligned} \frac{\partial^2 F}{\partial V^2} = & \mathcal{Z}^{-1} \int \Pi_i (d\pi_i d\rho_i) \frac{\partial^2 E}{\partial V^2} e^{-\beta E} - \beta \mathcal{Z}^{-1} \int \Pi_i (d\pi_i d\rho_i) \left(\frac{\partial E}{\partial V} \right)^2 e^{-\beta E} \\ & + \beta \mathcal{Z}^{-2} \left(\int \Pi_i (d\pi_i d\rho_i) \frac{\partial E}{\partial V} e^{-\beta E} \right)^2. \end{aligned} \quad (32)$$

The derivative of E with respect to V may then be written as

$$\frac{\partial E}{\partial V} = -\frac{2}{3} V^{-5/3} \sum_{i=1}^N \frac{1}{2m_i} (\pi_i \tilde{\Omega}^{-1}) \cdot (\pi_i \tilde{\Omega}^{-1}) + \frac{\partial U}{\partial V}, \quad (33)$$

which is effectively the negative value of the instantaneous pressure, P . The second derivative follows as

$$\frac{\partial E}{\partial V} = \frac{10}{9} V^{-8/3} \sum_{i=1}^N \frac{1}{2m_i} (\pi_i \tilde{\Omega}^{-1}) \cdot (\pi_i \tilde{\Omega}^{-1}) + \frac{\partial^2 U}{\partial V^2}. \quad (34)$$

By combining these expressions, replacing E/V with $-P$, one obtains

$$\frac{\partial^2 F}{\partial V^2} = \frac{10}{9} \frac{3}{V^2} N k_B T + \left\langle \frac{\partial^2 U}{\partial V^2} \right\rangle - \beta (\langle P^2 \rangle - \langle P \rangle^2) \quad (35)$$

Inserting this into Eq. 26 leads to the fluctuation expression for K ,

$$K = \frac{5}{3} \frac{N k_B T}{V} + V \left\langle \frac{\partial^2 U}{\partial V^2} \right\rangle - \beta V \langle P \delta P \rangle. \quad (36)$$

B. Appendix B.: Thermodynamic Integration Expression for Free energy

When the changes in lattice vectors are known as a function of T along an isobar, one may write a joint free energy expression where both temperature and lattice vectors are coupled through a thermodynamic integration variable λ . Under such conditions, $T = T(\lambda)$, $E = E[\Omega(\lambda)]$, and λ values of 0 and 1 represent the initial and final states, respectively. The derivative of the free energy of the system with respect to such a λ may be written as

$$\frac{\partial F}{\partial \lambda} = -k_B \frac{\partial T}{\partial \lambda} \ln \mathcal{Z} - k_B T \mathcal{Z}^{-1} \frac{\partial \mathcal{Z}}{\partial \lambda}. \quad (37)$$

The first term on the right side of the equation is proportional to the free energy as $F/T = -k_B \ln \mathcal{Z}$. One may thereby reconfigure Eq. 37 as

$$\frac{\partial F}{\partial \lambda} = -k_B \mathcal{Z}^{-1} \frac{\partial \mathcal{Z}}{\partial \lambda}. \quad (38)$$

The derivative of the partition function can be expanded as

$$\frac{\partial \mathcal{Z}}{\partial \lambda} = \int \Pi_i (d\mathbf{r}_i d\mathbf{p}_i) e^{-\frac{E}{k_B T}} \left(-\frac{1}{k_B T} \frac{\partial E}{\partial \lambda} + \frac{E}{k_B T^2} \frac{\partial T}{\partial \lambda} \right) \quad (39)$$

Inserting Eq. 39 into Eq. 38 yields

$$\frac{\partial F}{\partial \lambda} = -\frac{1}{T^2} \frac{\partial T}{\partial \lambda} \langle E \rangle + \frac{1}{T} \left\langle \frac{\partial E}{\partial \lambda} \right\rangle. \quad (40)$$

The internal energy is only directly dependent on λ through Ω , which enables us to use the expression

$$\left\langle \frac{\partial E}{\partial \lambda} \right\rangle = \left\langle \frac{\partial E}{\partial \Omega} \right\rangle : \frac{\partial \Omega}{\partial \lambda}, \quad (41)$$

where “:” denotes the Frobenius product. The value of $\langle E / \Omega \rangle$ is equivalent to $\langle F / \Omega \rangle$, which was defined in Eq. 17. Integrating Eq. 40 leads to the previously prescribed result

$$\left. \frac{F}{T} \right|_{\lambda=\lambda'} - \left. \frac{F}{T} \right|_{\lambda=0} = - \int_0^{\lambda'} \frac{1}{T^2} \langle E \rangle \frac{\partial T}{\partial \lambda} d\lambda + \int_0^{\lambda'} \frac{|\det(\Omega^T)|}{T} \langle \langle \sigma \rangle \Omega^{-T} \rangle : \frac{\partial \Omega}{\partial \lambda} d\lambda. \quad (42)$$

References

1. Asker C, Belonoshko AB, Mikhaylushkin AS, and Abrikosov IA, Phys. Rev. B 77, 220102 (2008).
2. Vo adlo L, Wood IG, Alfé D, and Price GD, Earth Planet. Sci. Lett 268, 444 (2008).
3. Vo adlo L, Brodholt J, Alfé D, Gillan MJ, and Price GD, Earth Planet. Sci. Lett 117, 123 (2000).
4. Alfé D, Price GD, and Gillan MJ, Phys. Rev. B 64, 045123 (2001).
5. Cazorla C, Alfé D, and Gillan MJ, Phys. Rev. B 85, 064113 (2012).
6. Grabowski B, Ismer L, Hickel T, and Neugebauer J, Phys. Rev. B 79, 134106 (2009).
7. Haskins JB, Moriarty JA, and Hood RQ, Phys. Rev. B 86, 224104 (2012).
8. Moriarty JA and Haskins JB, Phys. Rev. B 90, 054113 (2014).
9. Palumbo M, Fries SG, Pasturel A, and Alfe D, J. Chem. Phys 140, 144502 (2014). [PubMed: 24735300]
10. Haskins JB, Thompson AE, and Lawson JW, Phys. Rev. B 94, 214110 (2016).
11. Shaw JA and Kyriakides S, J. Mech. Phys. Solids 43, 1243 (1995).

12. Benafan O, Padula SA, Noebe RD, Sisneros T, and Vaidyanathan R, *J. Appl. Phys* 112, 093510 (2012).
13. Michal GM and Sinclair R, *Acta Crystallogr. B* 37, 1803 (1981).
14. Brüher W, Gotthardt R, Kulik A, Mercier O, and Staub F, *J. Phys. F* 13, L77 (1983).
15. Prokishkin SD, *Acta Mater* 52, 4479 (2004).
16. Hatcher N, Kontsevoi OY, and Freeman AJ, *Phys. Rev. B* 79, 020202 (2009).
17. Hatcher N, Kontsevoi OY, and Freeman AJ, *Phys. Rev. B* 80, 144203 (2009).
18. Vishnu G and Strachan A, *Phys. Rev. B* 85, 014114 (2012).
19. Wagner MF-X and Windl W, *Acta Mater* 56, 6232 (2008).
20. Wang J and Sehitoglu H, *Appl. Phys. Lett* 101, 081907 (2012).
21. Huang X, Bungaro C, Godlevsky V, and Rabe KM, *Phys. Rev. B* 65, 014108 (2001).
22. Holec D, Friák M, Dlouhý A, and Neugebauer J, *Phys. Rev. B* 84, 224119 (2011).
23. Kibey S, Sehitoglu H, and Johnson D, *Acta Mater* 57, 1624 (2009).
24. Šesták P, erný M, and Pokluda J, *Comput. Mater. Sci* 87, 107 (2014).
25. Pasturel A, Colinet C, Manh D, Paxton A, and van Schilfgaarde M, *Phys. Rev. B* 52, 15176 (1995).
26. Wang X-Q, *Phys. Rev. B* 78, 092103 (2008).
27. Ye Y, Chan C, and Ho K, *Phys. Rev. B* 56, 3678 (1997).
28. Zeng Z-Y, Hu CE, Cai LC, Chen X-R, and Jing FQ, *J. Appl. Phys* 109, 043503 (2011).
29. Šesták P, erný M, and Pokluda J, *Intermetallics* 19, 1567 (2011).
30. Hu R, Nash P, and Chen Q, *J. Phase Equilibria* 30, 559 (2009).
31. Kubaschewski O, *Trans. Faraday Soc. Engl* 54, 814 (1958).
32. Gachon J, Notin M, and Hertz J, *Thermochim. Acta* 48, 155 (1981).
33. Guo Q and Kleppa O, *J. Alloys Compd* 269, 181 (1998).
34. Parlinski K and Parlinska-Wojtan M, *Phys. Rev. B* 66, 064307 (2002).
35. Sourvatzis P, Legut D, Eriksson O, and Katsnelson M, *Phys. Rev. B* 81, 092201 (2010).
36. Zarkevich NA and Johnson DD, *Phys. Rev. B* 90, 060102 (2014).
37. Huang X, Ackland GJ, and Rabe KM, *Nature Mater* 2, 307 (2003). [PubMed: 12704381]
38. Grabowski B, Wippermann S, Glensk A, Hickel T, and Neugebauer J, *Phys. Rev. B* 91, 201103 (2015).
39. Allen MP and Tildesley MP, *Computer Simulation of Liquids* (Oxford University Press, 1987).
40. Ray JR and Rahman A, *J. Chem. Phys* 80, 4423 (1984).
41. Ray JR, Moody MC, and Rahman A, *Phys. Rev. B* 33, 895 (1986).
42. Çan T and Ray JR, *Phys. Rev. B* 37, 699 (1988).
43. Lutsko JF, *J. Appl. Phys* 65, 2991 (1989).
44. Zhao J, Winey JM, and Gupta YM, *Phys. Rev. B* 75, 094105 (2007).
45. Vanpoucke DEP, Lejaeghere K, Van Speybroeck V, Waroquier M, and Ghysels A, *J. Phys. Chem. C* 119, 23752 (2015).
46. de Koning M, Antonelli A, and Yip S, *Phys. Rev. Lett* 83, 3973 (1999).
47. Hellman O, Abrikosov IA, and Simak SI, *Phys. Rev. B* 84, 180301 (2011).
48. Hellman O, Abrikosov IA, and Simak SI, *Phys. Rev. B* 87, 104111 (2013).
49. Kresse G and Hafner J, *Phys. Rev. B* 47, 558 (1993).
50. Kresse G and Hafner J, *Phys. Rev. B* 49, 14251 (1994).
51. Kresse G and Furthmüller J, *Comput. Mat. Sci* 6, 15 (1996).
52. Kresse G and Furthmüller J, *Phys. Rev. B* 54, 11169 (1996).
53. Blochl PE, *Phys. Rev. B* 50, 17953 (1994).
54. Kresse G and Joubert D, *Phys. Rev. B* 59, 1758 (1999).
55. Kudoh Y, Tokonami M, Myazaki S, and Otsuka K, *Acta Metall* 33, 2049 (1985).
56. Sittner P, Lukás P, Neov D, Novák V, and Toebbens DM, *J. Phys. IV* 112, 709 (2003).

57. Schuerch HU, Certain physical properties and Applications of Nitinol, Tech. Rep. NASA CR-1232 (NASA, Contractor Report, 1968).
58. Qui S, Krishna VB, Padula II SA, Noebe RD, Brown DW, Clausen B, and Vaidyanathan R, Appl. Phys. Lett 95, 141906 (2009).
59. Brill TM, Mittelbach S, Assmus W, Müllner M, and Lüthi B, J. Phys.: Condens. Matter 3, 9621 (1991).
60. Mercier O, Melton KN, Gremaud G, and Hägi J, J. Appl. Phys 51, 1833 (1980).
61. Le Page Y and Saxe P, Phys. Rev. Lett 78, 1396 (1997).
62. Hu QM, Yang R, Lu JM, Wang L, Johansson B, and Vitos L, Phys. Rev. B 76, 224201 (2007).
63. Grimvall G, Magyari-Köpe B, Ozoliš V, and Persson KA, Rev. Mod. Phys 84, 945 (2012).
64. Mouhat F and Courdert F-X, Phys. Rev. B 90, 224104 (2014).

FIG. 1.
Crystal structure for (a) B33, (b) B19' and (c) B2 crystal structures.

FIG. 2.

Representative pressure-volume curves for B2 and B19' generated from elastic constants for anisotropic (solid lines) and isotropic (dashed lines) changes in the lattice vectors.

FIG. 3.

(a) Zero-temperature convergence of the C_{11} of B2 with respect to numerical accuracy as obtained from a cubic unit cell. (b) Value of the C_{11} of B2 from DFT-MD simulations using a small 16 atom cubic cell and different levels of accuracy. DFT-MD accuracy is the default accuracy of simulations in this work. High accuracy corresponds to 8192 KPPRA and an E_c of 500 eV. Upsampling is performed on the DFT-MD trajectory with the high accuracy parameters.

FIG. 4. Temperature dependence of (a) the volume of all NiTi phases, (b) the b/a and c/a ratios of B33 and B19' and (c) the β angle of the B19'.

FIG. 5.
 (a) Coefficient of thermal expansion and (b) constant-pressure heat capacity for the B33, B19', and B2 phases of NiTi as a function of temperature.

FIG. 6. Elastic constants of the B33, B19', and B2 phases of NiTi grouped into magnitudes (a-c) 100 GPa and (d-f) < 100 GPa as a function of temperature.

FIG. 7.

Isotropic (symbols) and anisotropic (lines) bulk modulus of the B33, B19', and B2 phases of NiTi as function of temperature. Experimental measurements from Brill *et al.*⁵⁹ at $T = 400$ K and Mercier *et al.*⁶⁰ at $T = 298$ K are included.

FIG. 8. Enthalpy differences (ΔH) of the transition between the B33 and B19' phases and between the B19' and B2 phases as a function of temperature. Latent heats at the transformation temperatures are indicated.

FIG. 9. Phonon dispersions of the (a) B2, (b) B19', and (c) B33 phases of NiTi at $T = 0$ K (dashed lines) and $T = 600$ K (solid lines). Data is reproduced from a previous work.¹⁰

FIG. 10.
Thermal energy of the phases of NiTi as a function of temperature.

FIG. 11.

Differences in the $T = 0$ K energy ($\Delta E(T=0)$), with β of B19' fixed to 98° , the internal energy ($\Delta \langle E \rangle$), the entropic contribution to free energy ($T\Delta \langle S \rangle$), and free energy (F) as a function of temperature for the (a) B33 $\rightarrow$ B19' and (b) B19' $\rightarrow$ B2 phase transitions. Phase transition temperature are indicated with dotted lines and correspond to 81 K and 481 K for the B33 $\rightarrow$ B19' and the B19' $\rightarrow$ B2 phase transitions, respectively. The differences between the $\Delta E(T=0)$ and the $\Delta \langle E \rangle$ curves gives the degree of anharmonicity (Δ_{an}).

TABLE I.

Structure of the B33 ($Cmcm$), B19' ($P2_1/m$), and B2 ($Pm\bar{3}m$) phases of NiTi as obtained from $T = 0$ K DFT computations.

Phase	a	b	c	β	V
B33	4.924	4.018	2.915	107.2	13.765
B33 ^a	4.928	4.025	2.933	107.0	13.910
B19'	4.678	4.057	2.916	98.0	13.702
B19' ^a	4.677	4.077	2.917	98.0	13.771
B19' ^b	4.646	4.108	2.898	97.8	13.700
B19' ^c	4.66	4.11	2.91	98.0	13.798
B2	3.005	3.005	3.005	90.0	13.569
B2 ^a	3.019	3.019	3.019	90.0	13.758
B2 ^d	3.013	3.013	3.013	90.0	13.676

^aFLAPW computations of Hatcher *et al.*¹⁷

^bX-ray diffraction measurements of Kudoh *et al.*⁵⁵

^cX-ray diffraction measurements of Prokishkin.¹⁵

^dNeutron diffraction measurements of Sittner *et al.*⁵⁶

TABLE II.Elastic constants (in GPa) of the B33, B19', and B2 phases of NiTi from $T = 0$ K DFT and experiment.

Phase	C_{11}	C_{12}	C_{13}	C_{15}	C_{22}	C_{23}	C_{25}	C_{33}	C_{35}	C_{44}	C_{46}	C_{55}	C_{66}
B33	227	133	124	32	240	136	0	171	-14	82	-3	20	90
B33 ^a	223	129	99	27	241	125	-9	200	4	76	-4	21	77
B19'	220	129	120	31	240	131	-3	179	1	79	-5	20	78
B19' ^a	249	129	107	15	245	125	-3	212	-1	87	-4	66	86
B2	184	156								48			
B2 ^a	183	146								46			
B2 ^b	137	120								34			
B2/B19' ^c	162	129								34			

^aFLAPW computations of Hatcher *et al.*¹⁷^bMeasurements of Brill *et al.*⁵⁹ at 400 K^cMeasurements of Mercier *et al.*⁶⁰ at 298 K near martensitic transformation

TABLE III.

Bulk modulus, K , (GPa) of the B33, B19', and B2 phases at $T = 0$ K as determined from explicit isotropic computations (iso-direct) of P as a function of V , isotropic (iso) and anisotropic (aniso) changes in volume as determined from elastic constants, and from experiment.

Phase	K (iso-direct)	K (iso)	K (aniso)
B33	159	159	153
B33 ^a			156
B19'	155	155	145
B19' ^a			159
B2	166	165	165
B2 ^a			159
B2 ^b			126
B2/B19' ^c			142

^aFLAPW computations of Hatcher *et al.*¹⁷

^bMeasurements of Brill *et al.*⁵⁹ at 400 K

^cMeasurements of Mercier *et al.*⁶⁰ at 298 K

TABLE IV.

Internal energy (E), scaled entropy ($-T S$), free energy (F) changes, and phase transition temperatures (T_M) from the B33→B19' and B19'→B2 transitions as determined from both the QHA and DFT-MD simulations. Units are given in meV/atom.

Transition	T	QHA				DFT-MD			
		E	$-T S$	F	T_M	E	$-T S$	F	T_M
B33→B19'	50	0.32	-0.14	0.18		0.94	-0.58	0.36	
	200	1.04	-1.54	-0.50		0.73	-1.99	-1.26	
					89				81
B19'→B2	300	37.61	-18.69	19.32		25.57	-16.17	9.40	
	600	36.16	-29.35	11.84		20.58	-25.95	-5.37	
					1074				481