Stable atomic structure of NiTi austenite
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I. INTRODUCTION

Nitinol (NiTi), the most widely used shape-memory alloy, exhibits an austenite phase that has yet to be identified. The usually assumed austenitic structure is cubic B2, which has imaginary phonon modes, hence it is unstable. We suggest a stable austenitic structure that “on average” has B2 symmetry (observed by X-ray and neutron diffraction), but exhibits finite atomic displacements from the ideal B2 sites. The proposed structure has a phonon spectrum that agrees with that from neutron scattering, has diffraction spectra in agreement with XRD, and has an energy relative to the ground state that agrees with calorimetry data.

II. AUSTENITIC STRUCTURE

To find a stable NiTi austenite, we investigated cells of increasing size with B2 chemical order that permitted symmetry breaking by atomic displacements. We chose a 54-atom hexagonal unit cell with the c-axis along B2 (111), and two ~9 Å basal plane vectors along B2 (101) and (011). Its unit cell vectors \((\overline{a}, \overline{b}, \overline{c})\) in terms of \((x, y, z)\) for cubic B2 are \(\overline{a} = 3(z - x), \overline{b} = 3(z - y), \overline{c} = \overline{x} + \overline{y} + \overline{z}\). Using \textit{ab initio} molecular dynamics (MD) followed by relaxation at 0 K to a local energy minimum, we obtain a stable austenitic Ni27Ti27 structure (Fig. 1 c-d). This hexagonal structure (Fig. 1) has a \(c/a\) ratio of 0.3954, which is a 3% reduction compared to \(c/a\) of 0.4082 (i.e., \(1/\sqrt{6}\)) for our unit cell with ideal B2 order, where \(c = a_{B2} \sqrt{3}\) and \(a = 3a_{B2} \sqrt{2}\) in terms of \(a_{B2} = 3\) Å.

Our austenitic structure has a DFT energy \(\Delta E\) of 29 meV/atom (340 K) above BCO, in better agreement with the measured \(T_c\) for equiatomic NiTi of 313 K. Typically, \(\Delta E \approx k_B T_c\), which provides reliable estimates of phase transition temperatures, especially for magnetic transitions. From the \(\Delta E\) and estimated entropy difference of \(1/2 k_B\) per atom\(^9\) for the martensite-to-austenite transformation, we predict the latent heat to be below 15 meV/atom (1.4 kJ/mol) at \(T_c\), while the calorimetry values are 1.07 ± 0.10 (cooling) and 1.3 ± 0.2 kJ/mol (heating).\(^9\) Thus, the calculated thermodynamic quantities closely reproduce the measured values.
III. COMPUTATIONAL DETAILS

To predict this structure, we used a plane-wave pseudopotential-based DFT method using the generalized gradient approximation (GGA)\textsuperscript{21} and a projected augmented wave (PAW) basis,\textsuperscript{22} as implemented in VASP code\textsuperscript{23,24} with convergence obtained by a second Broyden’s method.\textsuperscript{25} We choose 337 eV plane-wave energy cutoff and 544.6 eV augmentation charge cutoff. We converged total energies and forces using \textit{k}-meshes with at least 50 \textit{k}-points per Å\textsuperscript{-1} (e.g., 11 \times 13 \times 17 for a 4.92 \times 4.00 \times 2.92 Å cell). The structure of the high-T phase in a 54-atom \textit{Ni}_{27}\textit{Ti}_{27} cell is investigated using \textit{ab initio} MD with 1 fs time steps in a Nosé thermostat. After 1000 fs at 800 K, temperature was quenched from 800 K to 0 K in 800 fs; next, the atoms were relaxed using the conjugate gradient algorithm. We performed an internal atomic relaxation in a large fixed unit cell, and then a full relaxation of both atoms and lattice vectors. Lastly, phonon spectra were constructed using the calculated atomic forces for 162 independent 0.04 Å displacements in a 108-atom 1\times1\times2 hexagonal supercell (only 2 independent atomic displacements in a 54-atom 3\times3\times3 cubic supercell for B2) within the small displacement method in the PHON code.\textsuperscript{26} We have checked that

FIG. 1: (Color online) Atomic structure of the \textit{Ni}_{27}\textit{Ti}_{27} austenite, compared to B2, with Ni (yellow) and Ti (blue) atoms. (a) Ideal B2. (b) Projection of \textit{Ni}_{27}\textit{Ti}_{27} atomic positions onto a B2 cell. (c) Hexagonal [0001] projection, compared to [111]B2. (d) Viewed along [100]B2.
the Phonopy code\textsuperscript{27} gives the same results.

Phonons at finite T (Fig. 2) are addressed by combining 3 codes: VASP,\textsuperscript{23,24} ThermoPhonon,\textsuperscript{28} and Phonopy.\textsuperscript{27} First, an \textit{ab initio} MD in a 54-atom, 3×3×3, (9 Å)\textsuperscript{3} cubic supercell with Nosé thermostat at a given T with 1 fs time steps is used to obtain atomic positions and forces for over 50,000 fs steps after 2000 fs equilibration. Next, force constants are calculated using our ThermoPhonon code\textsuperscript{28} in the assumption of ideal B2 average atomic positions, and used in Phonopy\textsuperscript{27} with symmetrization to construct the phonon spectrum from the \textit{ab initio} MD data. We performed MD calculations at a range of T, including 0, 300, 800, 1200, and 1586 K (melting), and found that although already at 300 K the instability is only around \(M\), and its relative weight decreases with T, this instability survives at all T up to melting.

IV. DISCUSSION

For the proposed austenitic structure, the calculated 0 K phonon spectrum is stable (Fig. 2), in contrast to ideal B2. Also, as we have confirmed up to 1586 K (experimental melting temperature), vibrational entropy does not stabilize ideal B2, see Fig. 2, where the \(M\) point remains always unstable at high temperatures. More compellingly, the calculated phonon density of states (DOS) of the predicted austenite phase (Fig. 2) agrees well with that found from neutron scattering,\textsuperscript{9} as shown directly in Fig. 3.

Interestingly, this predicted austenitic structure, with atoms displaced from the perfect B2 positions, looks like B2 on average (Fig. 1b). The simulated XRD pattern at 0 K is shown in Fig. 4. With all B2 peaks still present, this pattern does not contradict any previous experimental XRD data. The additional XRD peaks can be at various positions for different local energy minima in the austenite phase; in this case they contribute to the background after summation.

Further details of the structure offer additional insight, and potential comparison to pair distribution functions from new diffraction experiments. From the calculated pair distribution function, the nearest-neighbor (NN) distances have a distribution (Fig. 5) with <5% half-width from the 2.6 Å NN distance in B2 (2.43 to 2.88 Å). In the supplement, we provide the atomic direct lattice coordinates (Table S1) in our representation of the austenite unit cell. From this data, we plot the NN-pair distribution function (Fig. 5) and the atomic displacements relative the ideal B2 positions (Fig. 6).
In summary, there is a multiplicity of solutions to our original question: “What is the stable structure of NiTi austenite?” We have proposed a stable representative structure (one of many) for the high-T NiTi austenite phase, whose energy relative to the BCO ground state, diffraction spectra, and vibrational density of states agree, respectively, with available calorimetry, XRD, and neutron scattering data, whereas those of an ideal (unstable) B2 do not. We suggest new experiments to assess the inherent displacement in NiTi austenite, with a large Debye-Waller factor at low temperatures (not the usual thermal disordering from phonons). We are assessing the solid-solid martensitic transformation paths for NiTi.

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