

High Temperature Shape memory loss in Nitinol: A first principles study

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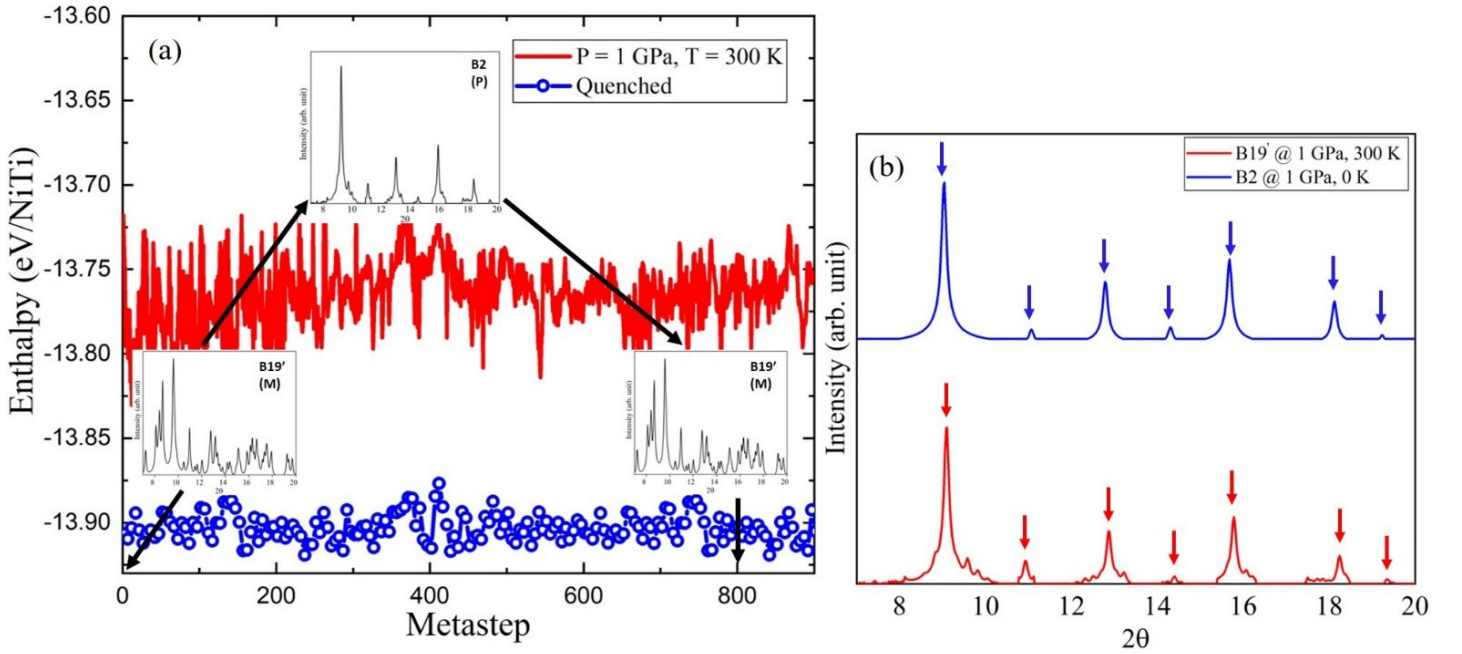
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Supplemental information

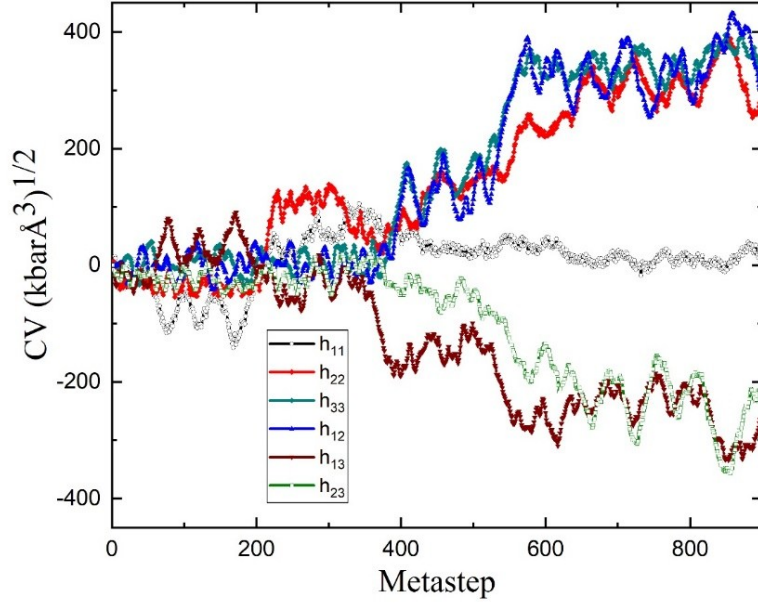
1. Metadynamics simulation of martensite \rightarrow austenite (parent) \rightarrow martensite transformation cycle

The computational method used in this work for the study of shape memory loss is first validated through the successful simulation of the experimentally observed martensitic transformation in the $B19'$. This implies that such process can be studied (with confidence) using metadynamics method. An experimental study of thermally induced transformation between martensite (M) and its parent (P) structure in NiTi was studied between 255 K and 363 K using neutron time of flight diffraction ¹. The temperature range of study covers a closed cycle of the $M \rightarrow P \rightarrow M$ transformations. The Metadynamics method used is capable of simulating phase transformation at finite pressure-temperature (PT) conditions, therefore, we approximate the ambient pressure with ~ 1 GPa pressure. A temperature point (300 K) that falls within the experimental temperature field (255 K to 363 K) was used. The x-ray diffraction (XRD) pattern of the $B19'$ (martensite) structure was calculated before the simulation starts. The simulation was allowed to proceed, and the system attain a temperature of 300 K. The XRD pattern of the configurational average of the 'warm' system was calculated at the end of the simulation time. All configurations were quenched to 0 K and the XRD patterns were also calculated as shown in SI Fig 1a. We observe that the quenched configuration has identical XRD pattern with the $B19'$ structure before the start of the simulation. However, the XRD pattern of the 'warm' configuration

is completely different from the $B19'$ s'. Interestingly, all of the distinct peaks are successfully indexed to the B2 structure at 0 K (see SI Fig 1b), which shows that the ‘warm’ $B19'$ structure transforms to the B2 structure for temperature within the martensitic transformation temperature field and back to the $B19'$ when temperature-quenched to 0 K. The evolution of the six collective variables (CV) during the metadynamics simulation of $B19' \rightarrow$ B2 transformation is shown in SI Fig. 2. The transformation occurs around 350 metadynamics step. The eigenvalues and the corresponding eigenvectors of the Hessian matrix for the $B19'$ at ~ 1 GPa is shown in SI Table I.



SI Fig. 1: (a) Evolution of the enthalpy during metadynamics simulation of martensitic transition from $B19'$ (M) to B2 (P) and back to $B19'$ (M) structure at ~ 1 GPa, 0 K to ~ 1 GPa, 300 K and ~ 1 GPa, 0 K, respectively. Inset is the calculated XRD pattern for the Martensite $B19'$ structure before the simulation, configurational average of the ‘warm’ system at the end of the simulation time and the quenched configuration (b) Comparison of the calculated XRD pattern for the B2 structure at ~ 1 GPa, 0 K and the $B19'$ at ~ 1 GPa, 300 K ($\lambda = 0.3344$ Å).



SI Fig. 2: Evolution of the six collective variables during metadynamics simulation of transition from $B19'$ to B2 structure at ~ 1 GPa, 300 K.

SI Table I: Eigenvalues (in unit of $\text{kbar } \text{\AA}$) and the corresponding eigenvectors of the Hessian matrix for the starting $2 \times 2 \times 4 B19'$ supercell calculated at ~ 1 GPa.

Eigenvalue	s_1	s_2	s_3	s_4	s_5	s_6
	1638.51	6167.38	6733.64	8247.67	10598.95	42500.10
Eigenvectors						
h_{11}	0.246	0.208	0.019	0.001	0.805	-0.498
h_{22}	-0.175	0.473	0.026	-0.001	-0.503	-0.701
h_{33}	0.055	-0.851	-0.040	0.000	-0.112	-0.509
h_{12}	0.000	-0.015	0.283	-0.960	-0.001	0.002
h_{13}	-0.952	-0.083	0.004	0.001	0.294	-0.029

h_{23}	0.006	-0.048	0.960	0.284	-0.007	0.007
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2. Electronic free energy in NiTi at ambient and elevated temperatures

If we assume that the electronic DOS is temperature independent (fixed density-of-states approximation ²), and approximate the electronic free energy using the T=0 K electronic DOS, $D(\varepsilon) = D(\varepsilon)[\rho(r, T = 0 \text{ K})]$. The electronic free energy can be written as:

$$F_{el}(V, T) = E_{el}(V, T) - TS^{el}(V, T), \quad (1)$$

where

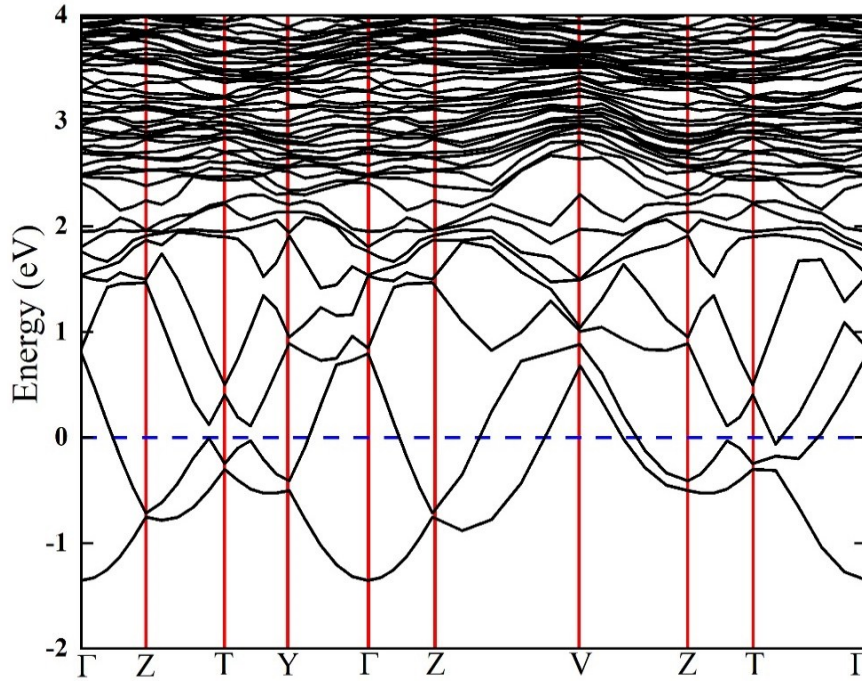
$$E_{el}(V, T) = \int_{\min. VB_{cutoff}}^{\max. CB_{cutoff}} D(\varepsilon) f(\varepsilon, T) \varepsilon d\varepsilon - \int_{\min. VB_{cutoff}}^{\varepsilon_F} D(\varepsilon) f(\varepsilon, T) \varepsilon d\varepsilon, \quad (2)$$

$$S^{el}(V, T) = \gamma k_B \int_{\min. VB_{cutoff}}^{\max. CB_{cutoff}} D(\varepsilon) S(\varepsilon, T) d\varepsilon. \quad (3)$$

$S(\varepsilon, T)$ is the temperature dependent entropic contribution to electronic free energy and is defined as:

$$S(\varepsilon, T) = - [f(\varepsilon, T) \ln f(\varepsilon, T) + (1 - f(\varepsilon, T)) \ln (1 - f(\varepsilon, T))], \quad (4)$$

and the Fermi-Dirac occupation, $f(\varepsilon, T)$ is defined as $f(\varepsilon, T) = \left[\exp\left(\frac{\varepsilon_i - \varepsilon_f}{k_B T}\right) + 1 \right]^{-1}$. In our calculations, The vibrational entropy is 5.8 meV/atom which is less than 25.7 meV, the value of $k_B T$ at 298 K. For this reason, it suffices to ignore the entropic contribution ($S^{el}(V, T)$) to free energy so that electronic contribution to free energy is approximated by the vibrational internal energy of the electron, $E_{el}(V, T)$ only. If we assume energy equipartition for the system under study in the temperature regime below the melting point, then we expect the differences of the $E_{el}(V, T)$ between the NiTi-P-1 and B19' structure to be nearly constant, hence plays no significant role in stabilizing the structures at high temperatures and as such can be ignored.



SI Fig. 3: Calculated electronic band structure of NiTi-P-1 structure at 10 GPa along the high-symmetry path. The Fermi energy level has been set to 0 eV.

SI Table II: Predicted structural parameters for the NiTi-P1 at a pressure of 10 GPa and 0 K temperature.

	a	b	c	α	β	γ	<i>Fractional atomic Coordinates</i>
Space group	(Å)	(Å)	(Å)				

							Atom	x	y	z	Site
<i>PI</i>	5.17	7.13	8.73	73.15	99.59	90.68	Ti	0.65	0.12	0.87	1a
							Ti	0.09	0.63	0.38	1a
							Ti	0.94	0.78	0.88	1a
							Ti	0.51	0.29	0.38	1a
							Ti	0.24	0.45	0.87	1a
							Ti	0.79	0.97	0.37	1a
							Ti	0.30	0.05	0.63	1a
							Ti	0.29	0.52	0.14	1a
							Ti	0.42	0.72	0.62	1a
							Ti	0.99	0.21	0.12	1a
							Ti	0.13	0.39	0.62	1a
							Ti	0.32	0.87	0.12	1a
							Ni	0.82	0.04	0.63	1a
							Ni	0.22	0.52	0.15	1a
							Ni	0.09	0.73	0.63	1a
							Ni	0.50	0.20	0.11	1a
							Ni	0.36	0.41	0.62	1a
							Ni	0.79	0.87	0.12	1a
							Ni	0.16	0.12	0.86	1a
							Ni	0.43	0.64	0.36	1a
Ni	0.56	0.77	0.89	1a							
Ni	0.03	0.28	0.39	1a							
Ni	0.29	0.46	0.88	1a							
Ni	0.71	0.96	0.37	1a							

References

1. A. A. Golestaneh, and J. M. Carpenter, *Acta metall. Mater.* 1990 **38**, 1291.
2. X. Zhang, B. Grabowski, F. Körmann, C. Freysoldt, and J. Neugebauer, *Phys. Rev. B*, 2017 **95**, 165126.