THE ELASTIC CONSTANTS OF AUSTENITIC AND MARTENSITIC PHASES OF NITI SHAPE MEMORY ALLOY

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Abstract

The elastic constants of NiTi shape memory alloy are studied using first principles calculations. All non-zero elastic constants were computed for austenitic B2 (space group Pm3m), martensitic B19' (space group $P2_1/m$) and base centered orthorhombic phase BCO (space group Cmcm) structures. The computed elastic constants were compared with available experimental data. The published results complement and extend the elastic constants dataset for selected structures of NiTi shape memory alloy. Results also confirmed, that the predicted structure with the lowest total energy has base centered orthorombic symmetry which is in correspondence with conclusion of previously published first principles calculations.

INTRODUCTION

The NiTi alloys are important materials used in many industrial (actuators) and medicine (stents, bone implants, etc.) applications due to its shape memory effect. This effect is caused by transformation from martensitic (Fig. 1a) to austenitic (Fig. 1b) phase and vice versa and can be started by an external pressure or temperature. There are several types of the transformations, depending on a particular alloy composition. An extensive overview of a current state of the art can by found in the paper by Otsuka and Ren [1].

The experimental results [1] show B19' structure of NiTi alloy as a ground state (GS) structure (structure with the lowest total energy) of martensite. However, the first principles calculations [2] determined, that the GS structure has higher (a base centered orthorhombic) symmetry, and can be also considered to be a twinned monoclinic structure with [100] twins [2]. The structural data of B19' and BCO structures are very similar, BCO structure represents a special case of monoclinic structure and can be obtained from first principles calculations by means of full relaxation of the elementary cell (i. e. including ionts and translation vectors).

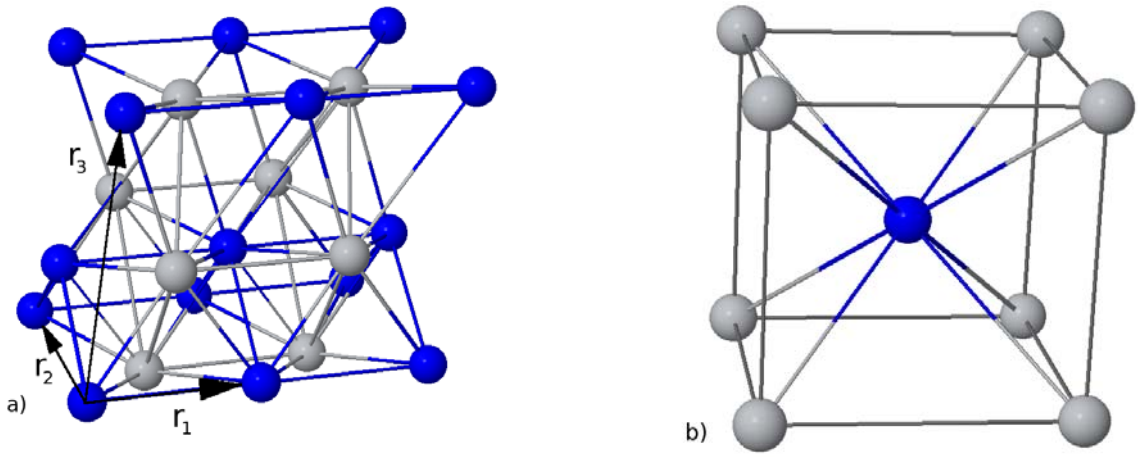

Figure 1. *a) martensite (with translation vectors* $\mathbf{r_1}$, $\mathbf{r_2}$ *and* $\mathbf{r_3}$*) and b) austenite structures of NiTi alloy*

The aim of this work is to compute all non-zero elastic constants for austenitic B2, martensitic B19' and BCO structures from first principles [3] (electronic structure or ab-initio calculations).

THE FIRST PRIMCIPLES CALCULATIONS

The total energies of the studied system have been computed by the Abinit program code [4, 5]. Abinit is a large tool for electronic structure calculations developed by the team of Prof. Xavier Gonze at the Université Catholique de Louvain, which is distributed under GNU General Public Licence. Another additional package including pseudopotentials [6] together with its generators, manuals, tutorials, examples, etc. is available at [7].

The calculations were performed using GGA norm-conserving pseudopotentials and the cutoff energy was set to 1000 eV for computations of elastic constant from response function, 900 eV for elastic constant from ground state calculations and 800 eV for other computations. The solution was considered to be self-consistent when the energy difference of three consequent iterations became smaller than 0.1 μeV for computation of elastic constant and 1.0 μeV for other computations. For the response function the convergence to residual potential was used with the value of $1x10^{-12}$.

COMPULATION OF ELASTIC CONTANTS

The elastic constants can be computed from the dependence of the total energy E_{tot} on applied deformations (ground state calculations) using the relation

$$C_{ij} = \frac{1}{V_0}\frac{d^2 E_{tot}}{d\varepsilon_i d\varepsilon_j},$$

where ε_i correspond to applied strains, and V_0 is equilibrium volume. The elastic constants C_{11}, C_{22} and C_{33} were obtained this way. Another way of their calculations is directly from the Abinit code using response function (RF) calculations. This approach enables us to obtain all elastic constants in one program run.

RESULTS

Structural parameters

The first step in our ab-initio calculations was an optimization of the elementary cell shape using changes of translation vectors with fixed ionic positions. The starting parameters for relaxations were taken from the experimental data [1]. Resulting values for B19' are listed in Table 1 along with those obtained experimentally. As a next step, we continued with full relaxation into a stress free state. Such relaxation comprises changes of translational vectors as well as ionic positions. For this purpose, we utilized an external script together with internal functions of the program code. As a result, we obtained theoretical ground-state structural data that are also included in Table 1 and Table 2 as BCO parameters. There are no structural experimental data for BCO structure. As can be seen, the difference between experimental and ab-initio data is lower than 5%. One can also see that the difference in translation vectors of martensite and BCO structure is very small.

Fig. 2 displays the total energy along a deformation path that linearly interpolates between B19' and BCO structures (describes by ab-initio data in Table 1 and 2). Deformation parameter p changes from 0 (at the B19' state) to 1 (at the BCO state). As can be seen, the structural relaxation always leads to the BCO state, because the B19' cell described by the experimentally supplied data is neither stable, nor metastable.

The ionic positions in first principles calculations must keep the same values as the experimental data for B19' structure, otherwise the relaxations of translation vectors $\boldsymbol{r_1}$, $\boldsymbol{r_2}$ and $\boldsymbol{r_3}$ (see Fig. 1a) and ionic positions always lead to BCO structure.

THE EXPERIMENTAL [1] AND AB-INITIO PRIMITIVE TRANSLATION VECTORS OF AUSTENITE, MARTENSITE AND BCO STRUCTURE

Table 1

	experimental [Å]				ab-initio [Å]				difference [%]				space group
structure	$\boldsymbol{r_1}$	$\boldsymbol{r_2}$	$\boldsymbol{r_3}$	γ[°]	$\boldsymbol{r_1}$	$\boldsymbol{r_2}$	$\boldsymbol{r_3}$	γ[°]	$\boldsymbol{r_1}$	$\boldsymbol{r_2}$	$\boldsymbol{r_3}$	γ[°]	
B2	3.02	3.02	3.02	90	3.07	3.07	3.07	90	1.7	1.7	1.7	0	Pm3m
B19'	2.89	4.12	4.62	96.8	3.04	4.08	4.84	101.1	5.1	-1.0	4.6	4.4	$P2_1/m$
BCO	-	-	-	-	3.07	4.00	4.94	107.5	-	-	-	-	$P2_1/m$

THE EXPERIMENTAL [1] AND AB-INITIO DATA FOR IONIC POSITIONS WITHIN A PRIMITIVE CELL OF NiTi ALLOY AS FRACTIONS OF THE PRIMITIVE TRANSLATION VECTORS

Table 2

	type of atom	experimental			ab-initio		
		X	Y	Z	X	Y	Z
B2	1 Ti	0	0	0	0	0	0
	2 Ni	1/2	1/2	1/2	1/2	1/2	1/2
B19'	1 Ti	0	0	0	0	0	0
	2 Ti	0.1648	1/2	0.5672	0.1648	1/2	0.5672
	3 Ni	0.6196	0	0.4588	0.6196	0	0.4588
	4 Ni	0.5452	1/2	0.1084	0.5452	1/2	0.1084
BCO	1 Ti	-	-	-	-0.0603	0	-0.0038
	2 Ti	-	-	-	0.2251	1/2	0.5709
	3 Ni	-	-	-	0.6678	0	0.4561
	4 Ni	-	-	-	0.4970	1/2	0.1110

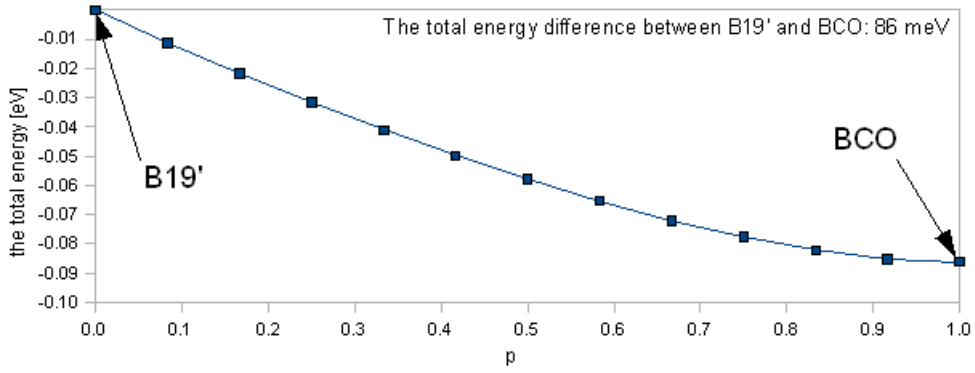

Figure 2. *The total energy during the transformation between B19' and BCO structures*

THE COMPUTED ELASTIC CONSTANTS FOR AUSTENITE B2 (THREE CONSTANTS), MARTENSITE B19' (THIRTEEN CONSTANTS) AND BCO STRUCTURE (NINE CONSTANTS) FROM RESPONSE FUNCTIONS (RF) CALCULATIONS AND GROUND STATE (GS) CALCULATIONS Table 3

El. const. [GPa]	C_{11}	C_{22}	C_{33}	C_{12}	C_{13}	C_{23}	C_{44}	C_{55}	C_{66}	C_{25}	C_{35}	C_{15}	C_{46}
B19' (RF)	188	231	245	122	89	108	77	45	90	-10	25	14	-12
BCO (RF)	166	255	268	137	75	98	81	36	108	-0.7	3.6	-1.7	-0.7
B2 (RF)	190	-	-	136	-	-	50	-	-	-	-	-	-
B19' (GS)	198	247	242	-	-	-	-	-	-	-	-	-	-
BCO (GS)	175	238	267	-	-	-	-	-	-	-	-	-	-

Elastic constants

The computed elastic constants C_{ij} are shown in Table 3 for all studied systems. The table contains results of two used approaches; GS calculations and RF calculations. The GS computation was used as a benchmark for RF calculations and as can be seen, the results from RF and GS calculations are very similar.

During the simulation, the BCO (nine non-zero elastic constants) structure was modeled as a special case of the monoclinic structure (thirteen non-zero elastic constants). In agreement with this fact, some of the elastic constants (C_{25}, C_{35}, C_{15} and C_{46}) were obtained as zero (or nearly zero).

There is no complete experimental review of elastic constants for BCO and B19' structure. Comparison between experimental and ab-initio data is available only for C_{11}, C_{12} and C_{44} elastic constants of B19' and B2 structures (Table. 4). It can be seen that while the computed C_{11} values are in a good agreement with experimental data, a less satisfactory correspondence is found for C_{12} of B19' and a significant overestimation of C_{44} for B19' is obvious. Let us note, that the experimental data were measured slightly bellow a room temperature, whereas our calculation assumed an absolute zero temperature

THE AVAILABLE EXPERIMENTAL ELASTIC CONSTANTS [8] FOR MARTENSITIC B19' AND AUSTENITIC B2 STRUCTURES Table 4

El. const. [GPa]	C_{11}	C_{12}	C_{44}
B19'	170	135	22
B2	180	150	40

CONCLUSION

Elastic constants of NiTi in martensite as well as austenitic phase were calculated from first principles. The obtained results for B2 austenitic structure are in a good agreement with available experimental data. A less satisfactory agreement was achieved for the optimized martensite B19' structure. Unlike the experimental observation the theoretical ground state structure of martensite was identified to be the base centered orthorhombic.

Acknowledgment

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References

[1] OTSUKA, K., and REN, X., *Progr. Mater Sci.*50, 511-678, 2005.
[2] Zhao, J., Meng, F., L., Zheng, W.m T.m Li, A., Jiang.,Q. *Mat. Let.* doi:10.1016/j. matlet. 2007.07.021.
[3] SOB, M., FRIAK, M., WANG, L., G., AND VITEK, V. *Key Engineering Materials* 227, 261-272, 2002
[4] Gonze, X., Beuken, J., M., Caracas, F., Detraux, R., Fuchs, M., Rignanese, G.-M., Sindic, L., Verstraete, M., Zerah, G., Jollet, F., Torrent, M., Roy, A. Mikami, M., Ghosez, Ph., Raty, J.-Y. and Allan, D.C., *Comp. Mat. Sci.* 25, 478-492, 2002.
[5] Gonze, X., Rignanese, G.-M., Verstraete, M., Beuken, J.-M., Pouillon, Y., Caracas, R., Jollet, F., Torrent, M., Zerah, G., Mikami, M., Ghosez, Ph., Veithen, M., Raty, J.-Y., Olevano, V., Bruneval, F., Reining, L., Godby, R., Onida, G., Hamann, D.,R. and Allan, D.C., *Zeit. Kristallogr* 220, 558-562, 2005.
[6] FUCHS, M., SCHEFFLER, M., *Comput. Phys. Commun.* 119, 67, 1999.
[7] Information on the web: www.abinit.org
[8] Ren, X., Miura, N., Zhang, J. Otsuka, K., Tanaka, K., Koiwa, M., Suzuki, T. Yu.,I., Chumlyakov, M., Asai,. *Mat. Sci. Eng*. A312, 196-206, 2001.