

Phase stability during martensitic transformation in ZrCu intermetallics: crystal and electronic structure aspects

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Abstract. This article is dedicated to the estimation of the relative stability for B2, B19' and Cm phase in ZrCu intermetallic compound through the ab-initio electronic structure calculations and subsequent crystal structure Rietveld refinement. The information about electronic and crystal structure of phases in ZrCu will allow selecting for this high temperature shape memory alloy such alloying elements that will significantly improve shape memory behavior through definite structural changes.

1. Introduction

It is known that ZrCu-based quasi-binary intermetallics belong to the group of high-temperature shape memory alloys (HTSMA) [1]. They, as well as the binary ZrCu, undergo the martensitic transformation (MT) from high temperature B2 austenite into two monoclinic martensites belonging to Cm and P2₁/m space groups [2]. Stress-strain behavior of HTSMA is characterized by the significant strain hardening and martensitic deformation is accompanied by the dislocation slip. As a result, shape recovery is incomplete [3]. It was suggested [1, 4] that such unacceptable shape memory behavior takes place due to the crystallographic scheme of the B2→B19' MT, which becomes closer to the Bain correspondence with the increase of MT temperature. In this regard, close-packed (easy gliding) planes of the austenite are becoming the shear planes for MT and plastic deformation by dislocation slip is inevitable. In the case of the sole B2↔Cm MT in ZrCu, which is inseparable from the simultaneous B2↔B19' MT at the moment, it is unlikely to get the Bain correspondence, as Cm martensite unit cell is bigger than unit cell of B19'. So, the aim of the present paper is to estimate the relative stability of the competing phases in ZrCu-based intermetallics undergoing MT with the help of the electronic structure calculations and crystal structure refinement in order to find the way of suppression of the B19' martensite formation.

2. Calculation details

The high precision ab-initio FLAPW method, implemented in WIEN2k software [5], was used for the electronic structure and full energy calculation of the ordered ZrCu structures. Application of this method for band structure calculations allows extracting quite precise information concerning atomic and electronic crystal structure.

The precision of the calculation for the crystal full energy depends on the following main parameters: number of K-points in the Brillouin zone, number of LM-items and Fourier-coefficients in the electron density and potential decomposition and also on the number of the flat waves in the basic wave function. All these parameters were selected in such a way that the precision of 0.001 eV for full energy of the model crystal structure was guaranteed. Radii of the Cu and Zr atomic spheres were selected as 2.2 and 2.3 a.u., correspondingly. 150 flat waves per atom were taken into account in the basic set. Wave function decomposition inside of the atomic sphere was carried out until $l_{\max}=12$. Electron density and potential were undergoing decomposition inside of the atomic spheres at basis of the crystalline harmonics up to $L_{\max}=6$. In the inter-spherical region mentioned values were decomposed into Fourier series with 850 coefficients taken into account. Calculation was carried out in 1600 K-points of the Brillouin zone.

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The Rietveld refinement [6] with the help of the Maud program [7] was carried out using our own X-ray diffraction data for ZrCu intermetallic compound [8, 9].

3. Results and discussion

The information about the crystal structure and martensitic phase transition in B2 ZrCu-based intermetallic compounds can be found in [1, 2, 4, and 8-10]. It is obvious, that at the moment there is no consensus of opinion regarding the origin of the structural instability of the ZrCu B2 phase and the martensitic transformation mechanism. In particular, it is related to difficulties with the interpretation of the structural data. In a process and at the completion of MT, ZrCu specimens contain more than one phase, elastic stresses, microstrains etc., which significantly complicates identification of phases, appearing during MT. In cases like this, it is not unreasonable to simplify the task to the limit and to find out why the symmetry decrease is energy-wise favorable. Recently, ab-initio computer modeling is used for this purpose. It allows studying interatomic interaction and the stability of different crystal phases without fitting parameters.

At the analysis of the calorimetric, dilatometric and in-situ X-ray diffraction data, the mechanism for MT in ZrCu was proposed [2]. In the frame of such mechanism, the scheme of the forward MT can be represented as $B2 \rightarrow (B19' + Cm)$. B19' martensite forms first, although, in general, the simultaneous phase formation takes place. B19' phase stops to form at further cooling, occupying about 20 % of the material volume, while Cm martensite keeps on forming and filling the remaining volume of the material at the end of the forward MT.

In order to verify the mechanism described above, the full energies for all three crystal structures modeling these phases for ZrCu intermetallic compound have been calculated. Calculations were carried out with the help of FLAPW method taking into account full structural optimization consisting of lattice parameters and atomic coordinate's optimization. Structural optimization was carried out in the frame of corresponding space groups: B2 - $\bar{N}o221$, Pm-3m; B19' - $\bar{N}o11$, P21/m; Cm - $\bar{N}o8$. Forces exerted by the electronic subsystem upon atoms were calculated. In the process of optimization, the zero balance of these forces was achieved and the minimal crystal full energy was found. The final stage of the structural optimization for three model structures is represented in Fig. 1, where full energy dependence upon the volume per atom for these structures can be seen. Calculations have shown that the Cm martensitic phase is the most energy-wise favorable. The difference in energy for this phase, comparing to B19' and B2 equals to 0.005 and 0.027 eV/atom, correspondingly. It can be seen from Fig. 1 that all three phases have very close values of volume per atom, which equals to 17.531, 17.609 and 17.547 \AA^3 , taking into account calculated lattice parameters values (Table 1), for B2, B19' and Cm phases, correspondingly. Thus, it was possible to calculate the volume change ($\Delta V/V_M$) for B2 \rightarrow B19' and B2 \rightarrow Cm martensitic transitions. It can be seen (Table 1), that in both cases the volume effect is positive and for the B2 \rightarrow B19' forward MT it is 5 times bigger in value than for B2 \rightarrow Cm. Table 2 shows unit cell atomic coordinates for three phases obtained in [9] and calculated in the present work. It should be noted that atomic coordinates for Cm phase significantly differ.

Structural optimization results for three phases allow us to obtain the changes in interatomic distances in ZrCu at B2 \rightarrow B19' \rightarrow Cm. The calculations have shown that the nearest neighborhood for Cu atoms undergoes the most significant changes. Cu-Cu and Cu-Zr interatomic distances in three calculated phases are shown in Fig. 2. The significant change of the Cu nearest neighborhood takes place at B2 \rightarrow B19' transition. In B2 structure the nearest neighbors are 8 atoms of Zr. Six copper atoms are situated in the second coordination sphere. In the B19' and Cm structures the nearest neighbors are Cu atoms, not the Zr ones. In B19' structure the number of the nearest Cu atoms equals to 2 and they are situated much nearer than Zr atoms. There are three such Cu atoms in Cm structure. Such change in the Cu atoms nearest neighborhood leads to the decrease of the structural full energy at the B2 \rightarrow B19' \rightarrow Cm transition. In this case we can speak of the increase in the Cu-Cu interatomic interaction in such a row of structural transitions. Electronic structure of three phases ought to differ significantly because their valence band is mainly determined d-electrons of copper.

Structural data obtained theoretically for the model structures were used at the calculation of their electron structure. It is interesting to clarify valence electron energy distribution in these structures. To do that, electron density of states (DOS) were calculated for Zr and Cu in the model B2, B19' and Cm structures. Fig. 4 shows partial d-electron DOS for Cu and Zr atoms in these structures. Cu d-DOS analysis shows that at transition from B2 to B19' and Cm structures d-d interaction of the copper atoms grows significantly. The width of the Cu d-band in B2 is much less than in B19' and Cm structures (Fig. 4). The increase in the interatomic Cu-Cu interaction in B2 \rightarrow B19' \rightarrow Cm structural row has to show at the valence electron density distribution. Such distributions were calculated for three model structures. Fig. 5 shows the calculation results in planes, containing copper atoms. Fig. 5a represents the electron density distribution in ordered structure modeling B2 austenite. Nearest neighborhood of the each Cu atom consists of 8 atoms of Zr. Valence electron density distribution in this phase is determined mainly by d-d interaction of the Cu and Zr electrons. It is evident from hybridization of the corresponding DOS, represented in Fig. 4. Each Cu atom contains 6 copper atoms in the second coordination

sphere. Big Cu-Cu interatomic distance (bigger than Cu-Zr) leads to energy localization of the copper atom d-states (Fig. 4). Correspondingly, electron density is localized strongly on the Cu atoms (Fig. 5a). In B19' and Cm structures the nearest neighborhood of the each copper atom consists of Cu atoms (Fig. 3). In this case, the covalent contribution into chemical bond between copper atoms appears (Fig. 5b and 5c), which leads to energy preference of these phases comparing to B2. In B19' the short range atomic order is characterized by the three nearest copper atoms and in Cm phase – by 4 (Fig. 3).

It should be fairly noted that some electronic structure calculation attempts for ZrCu have been taken place [8, 10] and once the results of work [8] can be considered as a rough approximation because of the calculation possibilities imperfection, in the work [10] the up to date ab-initio electron structure modeling apparatus was used. Authors of this work, while analyzing all the phases according to ZrCu phase diagram, tried to focus on the MT in the equiatomic compound. However, they excluded out of consideration Cm martensitic phase replacing it with the B33 structure (CrB type). This choice is quite strange because all the experimental works dedicated to the ZrCu structure [8,9,11,12] does not contain any mentioning about this phase and the use of the simple analogy with CoZr [13] and NiZr [14] can not be accepted as a correct one. It should be also noted that the first principle modeling gives information at 0 K not taking into account the morphology of the real martensitic crystals, their substructure and other structural parameters. It is obvious, that at the room temperature X-ray experiment all structural parameters ought to be different from the calculated at 0 K. Nevertheless, authors of the work [10] bring as evidence the simple coincidence of the calculated interplanar spacing's with X-ray diffraction patterns. Besides, the volume change at forward B2→B33 MT, calculated using lattice parameters form [10] ($a_{B2}=0.32706$ nm; $a_{B33}=0.32573$ nm, $b_{B33}=0.41143$ nm, $c_{B33}=1.03765$ nm), has negative sign and equals to -0.63%, which is in disagreement with dilatometric data (+0.285%) [2]. Calculated data obtained in the present work with the use of the Cm lattice parameters show that volume effect at B2→Cm MT has a positive sign (+0.446%, Table 1), which is at least in qualitative agreement with dilatometric data. However that may be, to analyze real structures much more significant X-ray data analysis is needed like Rietveld refinement [6].

In the present work such refinement was undertaken for our own X-ray data for ZrCu obtained in [9]. It was supposed that the mixture of B19' and Cm phases with starting structural parameters obtained in our ab-initio calculations is present in a material. The Rietveld refinement was carried out with the use multiple parameters, including: (i) phase scale factors and background components, (ii) 2 θ zero shift (iii) lattice parameters, (iiii) X-ray reflection profile function and anisotropy of the microstresses and microstrains [15] for both phases, (iiiiii) atomic coordinates in the unit cell and isotropic thermal displacement parameter for all atoms. Quantitative phase volume fraction analysis was performed according to Hill and Howard [16]. The results are presented in Tables 1 and 2 and in Fig. 6.

The final result for the Rietveld refinement of the X-ray diffraction pattern of ZrCu is shown in Fig. 6. The good agreement between experimental and calculated diffraction patterns is clearly seen. The reliability factors for the final cycle were equal to $R_p=5.2\%$, $R_{wp}=6.47\%$ at $R_{exp}=4.53\%$. Quantitative phase analysis has shown that at room temperature after forward MT completion there is no sign of the retained austenite and the whole material volume is occupied by 27% of B19' martensite and 73% of Cm martensite (Table 1). The Rietveld refinement has also shown that the volume effect at forward MT ($\Delta V/V_M$) obtained with the help of experimental austenite lattice parameter [8] and refined martensitic lattice parameters (Table 1) is positive for B2→B19' and B2→Cm martensitic transitions and equals to +0.286% and +0.183% correspondingly. These values are much closer to dilatometric data [2] than obtained in [9] or after our present ab-initio modeling (Table 1). In other words, the densities of the real austenite and martensitic phases obtained after Rietveld refinement are much closer to each other in value. Isotropic thermal parameter after the refinement was the same for all atoms – $B=0.89 \text{ \AA}^2$. It is necessary to emphasize that atomic coordinates in the martensite unit cells did not undergo significant changes after Rietveld refinement, comparing to the results of ab-initio modeling (Table 2). It means that real B19' and Cm martensitic structures are indeed characterized by the existence of two types of the short range order, as it is shown in Fig. 2, and are determined by Cu-Zr and Cu-Cu interatomic interaction.

4. Conclusions

1. The full energy of the ordered B2 crystal structure, modeling ZrCu austenite, decreases at the lowering of the lattice symmetry - formation of B19' and Cm martensitic phases.
2. The origin of the model ZrCu austenitic phase instability and of the B19' and Cm martensite model phase formation is in the possibility of the two types of short range order existence in ZrCu: first short range order type is determined by Cu-Zr interatomic interaction, while the second by Cu-Cu one.
3. Rietveld refinement has shown that at normal conditions in the intermetallic compound ZrCu, B19' and Cm martensite phases are present (27% and 73% of the volume fraction correspondingly). B2→B19' and B2→Cm volume change has positive sign and equals to +0.286% and 0.183%, correspondingly.

Refined atomic coordinates in the unit cells for both martensites allow us to confirm the presence of two short range order types in the real B19' and Cm martensitic crystals.

References

- [1] G.S. Firstov, J. Van Humbeeck, Yu.N. Koval, *J. Intelligent Material Systems and Structures*, **17**, No. 12, 1041 (2006).
- [2] G.S. Firstov, J. Van Humbeeck, Yu.N. Koval, *J.Physique IV*, **11**, Pr8, 481 (2001)
- [3] G.S. Firstov, J. Van Humbeeck, Yu.N. Koval, *Scr. Mater.*, **50**, No. 2, 243 (2004)
- [4] G.S. Firstov, J. Van Humbeeck, Yu.N. Koval, *Mater. Sci. Eng. A*, **378**, 1-2, 2 (2004)
- [5] P. Blaha, K. Schwarz, G.K.H. Madsen, D. Kvasnicka and J. Luitz, *WIEN2K, An Augmented Plane Wave + Local Orbital's Program for Calculating Crystal Properties* ed. Karlheinz Schwarz, Technische Universitat Wien, Austria (ISBN 3-9501031-1-2, 2001).
- [6] *The Rietveld method*, R.A. Young ed., Oxford University Press, 1995, 298 p. (ISBN 0198559127, 9780198559122).
- [7] <http://www.ing.unitn.it/~maud/>.
- [8] A.V. Zhalko-Titarenko, M.L. Yevlashina, V.N. Antonov, B.Yu Yavorskii, Yu.N. Koval, G.S. Firstov, *Physica status solidi (b)*, **184**, 121 (1994)
- [9] Schryvers D., Firstov G.S., Seo J.W., Van Humbeeck J., Koval Yu.N., *Scripta Mat.*, **36**, 1119 (1997)
- [10] S.H. Zhou, R.E. Napolitano, *Scripta Mat.*, **59**, 1143 (2008)
- [11] J.W. Seo, D. Schryvers, *Acta Mat.*, **46**, No 4, 1165 (1998)
- [12] J.W. Seo, D. Schryvers, *Acta Mat.*, **46**, No 4, 1177 (1998)
- [13] A. Francois, P. Veyssiere, *Intermetallics*, **2**, 9 (1994)
- [14] M.E. Kirkpatrick, D.M. Bailey, J.F. Smith, *Acta Crystallogr.*, **15**, 252 (1962)
- [15] N.C. Popa, D. Balzar, *J. Appl. Crystallogr.*, **35**, 338 (2002)
- [16] R.J. Hill, C.J. Howard, *J. Appl. Crystallogr.*, **20**, 467 (1987)

Table 1. Crystal structure parameters for different phases of the intermetallic compound ZrCu according to literature and calculated in present work with the help of ab-initio modeling and Rietveld refinement.

Type	Space group	at./cell		Lattice parameters				Density, kg/m ³	$\Delta V/V_M$, %	Volume fraction, %	
				a, nm	b, nm	c, nm	β , °				
B2	Pm3m (221)	2	Experiment	0.3262	-	-	90	7.404	-	100	[8]
			Calculation	0.3273	-	-	90	7.332	-	-	present work
B19'	P2 ₁ /m (11)	4	Experiment	0.3278	0.4161	0.5245	103.88	7.401	0.046	17	[9]
			Calculation	0.3237	0.4138	0.5449	105.19	7.297	0.445	-	present work
			Experiment	0.3299	0.4177	0.5212	104.22	7.383	0.286	27	
	Cm (8)	16	Experiment	0.6316	0.8562	0.5331	105.27	7.393	0.155	83	[9]
			Calculation	0.6476	0.8303	0.5433	106.04	7.323	0.094	-	present work
			Experiment	0.6356	0.8504	0.5340	105.51	7.390	0.183	73	

Table 2. Atomic coordinates in the unit cell for different phases of the intermetallic compound ZrCu according to literature and calculated in present work with the help of ab-initio modeling and Rietveld refinement.

	Zr		x	y	z	Cu	x	y	z	
Pm3m	1a		0	0	0	1b	0.5	0.5	0.5	
P2 ₁ /m	2e	Experiment	0.38273	0.25	0.20251	2e	0.11754	0.25	0.63921	[9]
		Calculation	0.35384	0.25	0.19632		0.06703	0.25	0.64036	present work
		Experiment	0.34068	0.25	0.18503		0.20242	0.25	0.63158	
Cm	2a	Experiment	0	0	0	2a	0.69309	0	0.6781	[9]
		Calculation	0	0	0		0.89793	0	0.45780	present work
		Experiment	-0.02185	0	0.042065		0.72593	0	0.56850	
	2a	Experiment	0.56362	0	0.09805	2a	0.20635	0	0.63303	[9]
		Calculation	0.49961	0	0.022717		0.31741	0	0.46764	present work
		Experiment	0.37734	0	-0.04679		0.29968	0	0.44740	
	4b	Experiment	0.45808	0.25	0.72281	4b	0.29125	0.25	0.17479	[9]
		Calculation	0.64617	0.27616	0.61656		0.28874	0.25011	0.17408	present work
		Experiment	0.51080	0.28677	0.56293		0.21039	0.24257	0.10925	

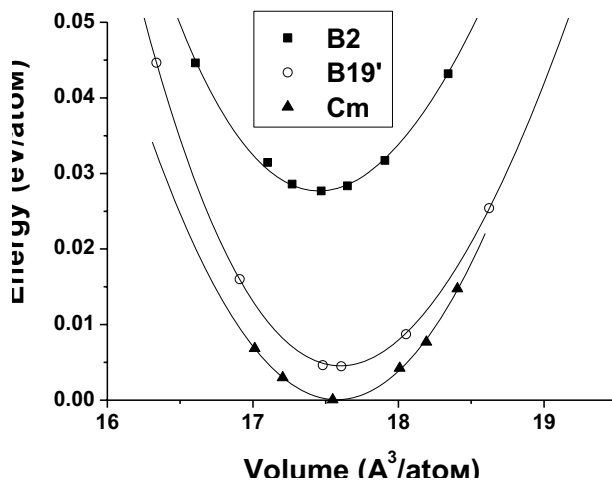


Fig. 1. Full energies of the ordered structures modeling different phases in ZrCu depending on volume per atom.

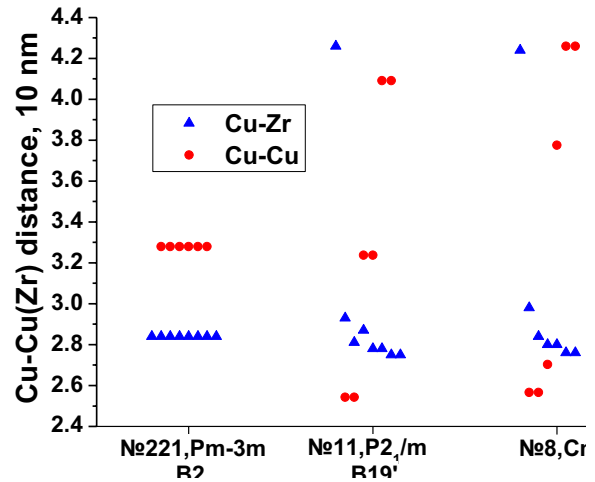


Fig. 2. Calculated nearest neighbor distances Cu-Cu and Cu-Zr, which are characterizing short range order in different phases of ZrCu.

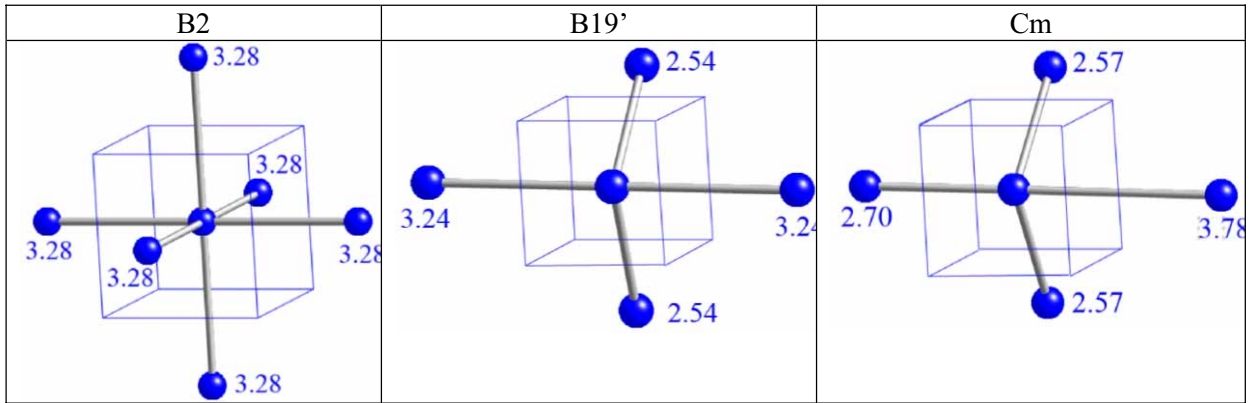


Fig. 3. Schematic representation of the nearest neighbors for the Cu atom in model B2, B19' and Cm structures of ZrCu intermetallic compound.

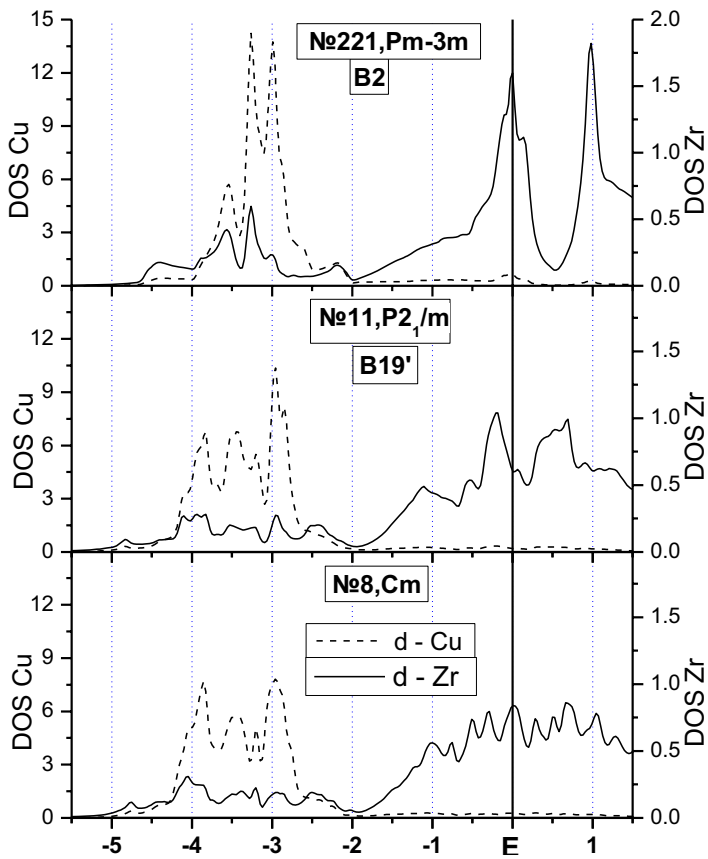


Fig. 4. Density of d-electron states of Zr (solid line) and Cu (dashed line) atoms in structures modeling different phases of ZrCu intermetallic compound.

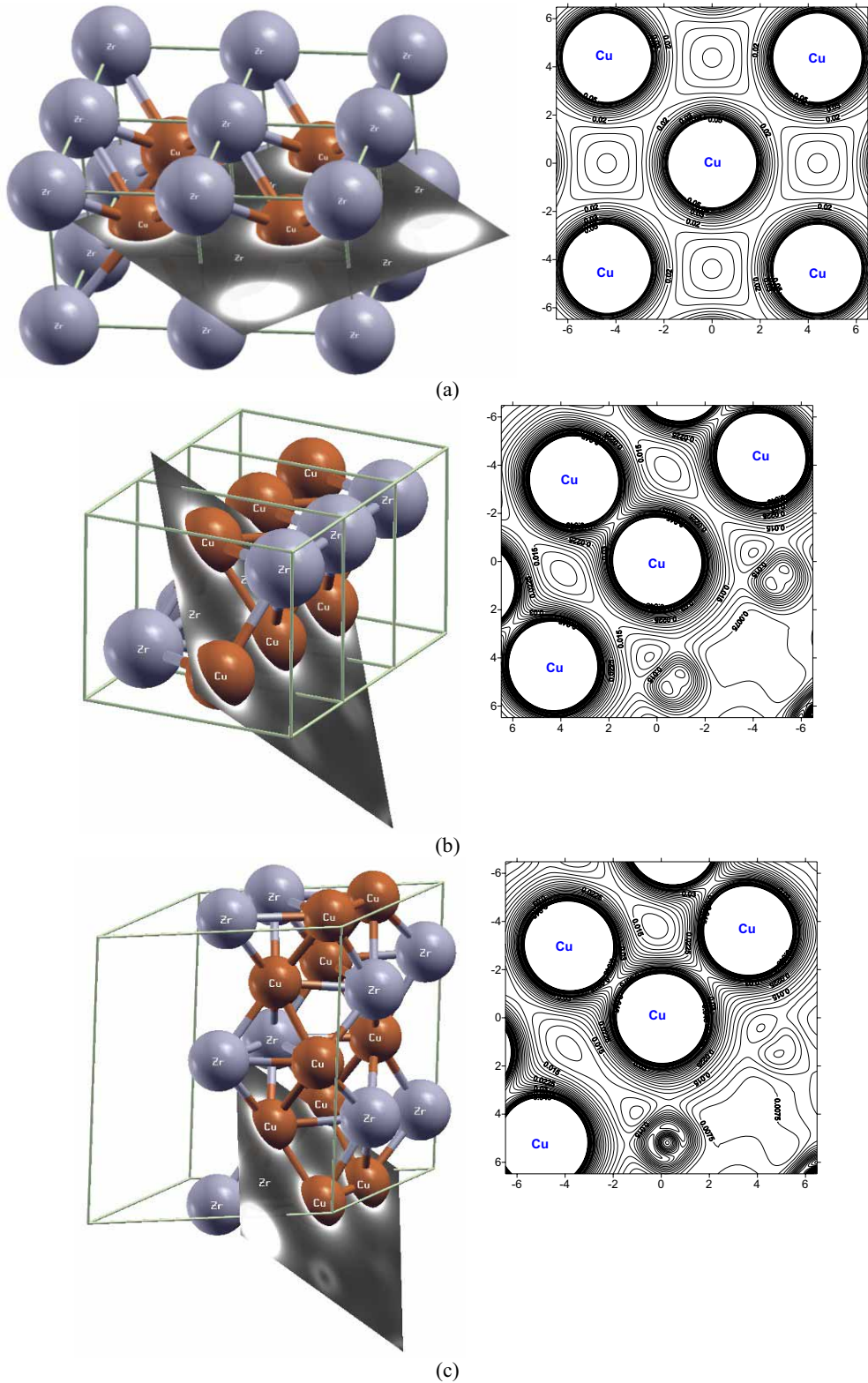


Fig. 5. Electron density distribution in a distinguished plane of the structure modeling (a) B2-austenite, (b) B19'-martensite and (c) Cm-martensite (energy interval: $-6 \div -2$ eV).

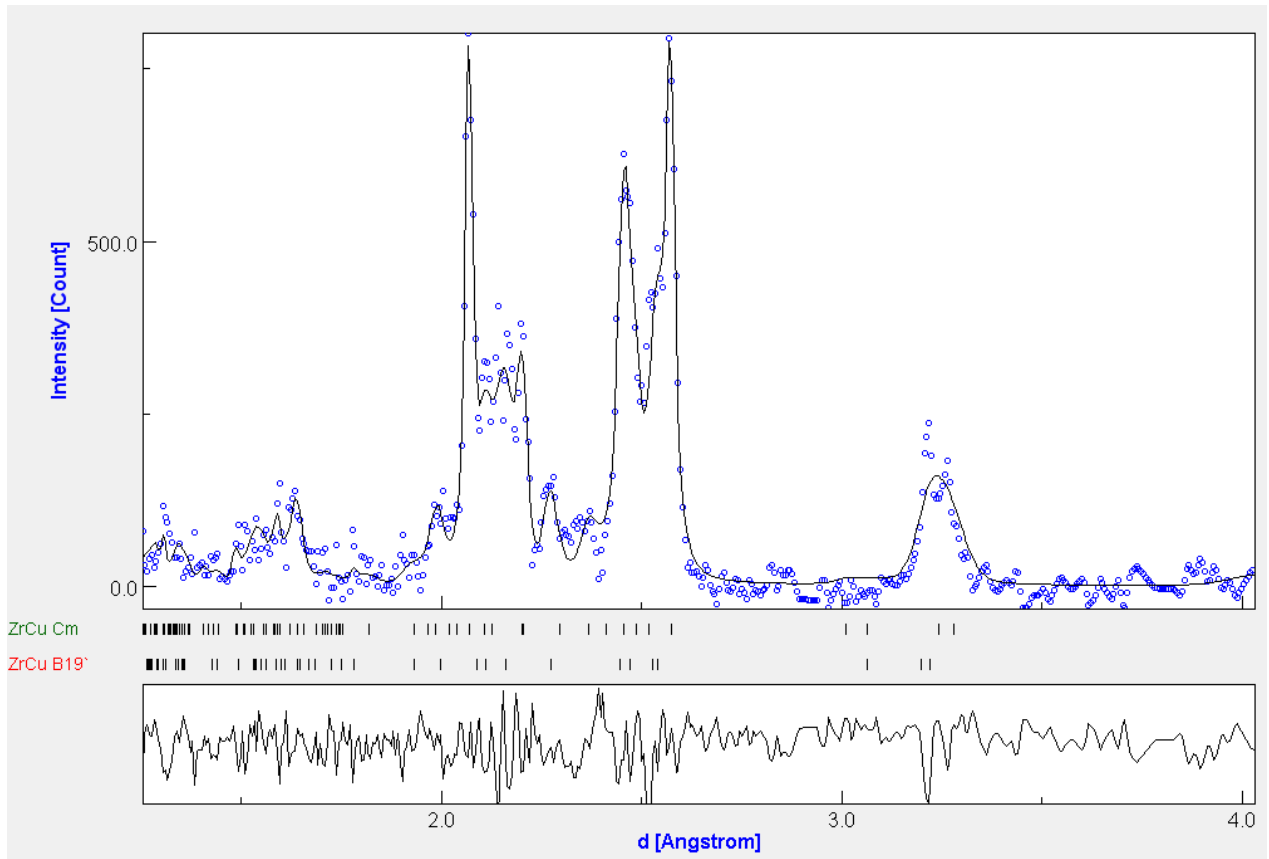


Fig. 6. X-ray diffraction pattern taken from [9] (open circles) with the result of the present Rietveld refinement (solid line). Small vertical bars below the profile represent the positions of the Bragg reflections of B19' and Cm martensitic phases. The curve at the bottom represents the difference between the measured and calculated pattern.