QUANTUM-MECHANICAL STUDY OF MAGNETIC PROPERTIES OF SUPERALLOY NANOCOMPOSITE PHASE Fe_2AlTi

SLÁVIK Anton[1,2], MIHÁLIKOVÁ Ivana[1,2], FRIÁK Martin[1,2], VŠIANSKÁ, Monika[1,3,4], ŠOB Mojmír[3,1,4]

[1]*Institute of Physics of Materials, Academy of Sciences of the Czech Republic, v.v.i., Brno, Czech Republic, EU*

[2]*Department of Condensed Matter Physics, Faculty of Science, Masaryk University, Brno, Czech Republic, EU*

[3]*Central European Institute of Technology, CEITEC MU, Masaryk University, Brno, Czech Republic, EU*

[4]*Department of Chemistry, Faculty of Science, Masaryk University, Brno, Czech Republic, EU*

Abstract

The $L2_1$-structure Fe_2AlTi intermetallic compound is one of the two phases identified in Fe-Al-Ti superalloy nanocomposites. Experimental data related to low-temperature magnetic properties of this Heusler compound indicate that magnetic moment is about 0.1 Bohr magneton per formula unit. In contrast, previous quantum-mechanical calculations predicted Fe_2AlTi to have much higher magnetic moment, 0.9 Bohr magneton per formula unit. In order to solve this discrepancy between the theory and experiment we have performed a series of quantum-mechanical fix-spin-moment calculations and compared our results with those for non-magnetic state. It turns out that the total energy of the non-magnetic state is only by 10.73 meV/atom higher than that of the magnetic state. When applying Boltzmann statistics to this very small energy difference we predict that the non-magnetic state appears at non-zero temperatures with significant probabilities (for instance, 22.36 % at T = 100 K) and reduces the overall magnetic moment. As another mechanism lowering the magnetization we studied selected shape deformations, in particular trigonal shearing. Fe_2AlTi exhibits a compression-tension asymmetry with respect to these strains and, for example, the strain $\varepsilon = -0.08$ destabilizes the spin-polarized state, leaving the non-magnetic state as the only stable one.

Keywords: Nanocomposites, Fe-Al based superalloys, ab initio calculations, fixed-spin-moment

1. INTRODUCTION

The Heusler $L2_1$-structure compounds are one of the most important classes of ternaries with magnetic order providing a wealth of not only structural but also functional properties. In particular Fe_2AlTi compound appears as one of the phases in Fe-Al-based superalloys (see, e.g., Refs. [1-4]). Interestingly, there is a long-lasting controversy between theoretical results and experimental data related to this material. For example, Shreder and co-workers [5] used Local (Spin) Density Approximation (LDA) and Linear muffin-tin orbital (LMTO) method to study magnetic state of Fe_2AlTi and predicted this compound to have the magnetic moment of 0.9 μ_B per formula unit in contrast to the experimental value of 0.1 μ_B per formula unit which they detected. Their experimental value is also very close to that reported by Buschow and van Engen [6] whose magnetic measurements resulted in the value of 0.11 μ_B per formula unit at T = 4.2 K. Theoretical calculations thus predict the low-temperature value of the magnetic moment nearly one order of magnitude higher than experiments. In order to address this discrepancy between theory and experiments, we employ fixed-spin moment (FSM) calculations to study properties of different magnetic states of Fe_2AlTi. The FSM approach [7,8] allows to keep the total magnetic moment of our computational supercell constant and equal to a pre-selected value while local magnetic moments are free to change (given the overall global constraint). A dependence of a number of properties on the total magnetic moment can be then studied (see, e.g., Refs. [9-14]).

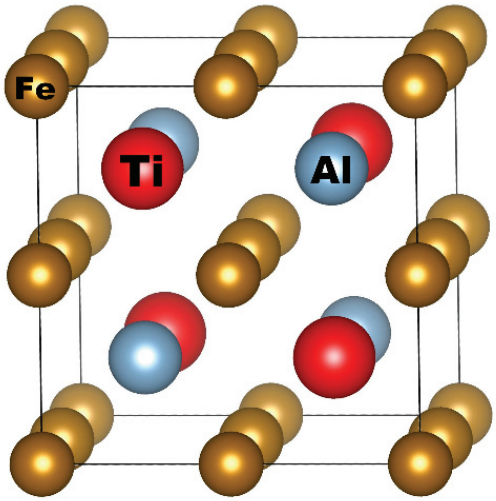

Figure 1 Schematic visualization of a cube-shape 16-atom supercell of Fe_2AlTi with four formula units used in our calculations

2. COMPUTATIONAL METHODOLOGY

Our first-principles calculations were performed within the framework of density functional theory [15,16] using the Vienna Ab initio Simulation Package (VASP) [17, 18] and projector augmented wave pseudopotentials [19,20]. The exchange and correlation energy was treated in the generalized gradient approximation as parametrized by Perdew and Wang [21] using the Vosko-Wilk-Nusair correction [22]. We used a plane-wave energy cut-off of 500 eV with a 20x20x20 Monkhorst-Pack k-point mesh in the case of a cube-shape 16-atom supercell (the product of the number of atoms in the cell and the total number of k-points being 128 000) containing 4 formula units of Fe_2AlTi (see **Figure 1**).

Our fixed-spin moment (FSM) calculations were performed with muffin-tin radii of 1.402 Å, 1.302 Å, 1.302 Å in the case of Al, Ti and Fe atoms, respectively. When fixing the total magnetic moment of the computational cell, all local magnetic moments were initially oriented in a parallel manner (a ferromagnetic state). These starting local magnetic moments of Al and Ti atoms were 0.01 μ_B while those of Fe atoms had initially the value equal to the value of the total fixed-spin moment of the computational cell divided by the number of Fe atoms in the cell.

3. RESULTS

Figure 2 summarizes energies, lattice parameters as well as local magnetic moments of Fe and Ti atoms computed for Fe2AlTi with the $L2_1$ structure as functions of the value of the fixed-spin moment (FSM) per formula unit (μ_B/f.u.). As visualized in **Figure 2a** and magnified in **Figure 2b**, the lowest energy is predicted for a state with the FSM of 0.925 μ_B/f.u. when the local magnetic moment of Fe and Ti atoms are 0.611 and -0.279 μ_B/atom, respectively (the negative sign meaning an anti-parallel orientation, i.e. a ferrimagnetic state). Our predicted values are in an excellent agreement with those of 0.95 μ_B/f.u, 0.67 μ_B/atom and -0.28 μ_B/atom) published by Fecher and co-authors [23].

Figure 2b shows how the lattice parameter of our cube-shaped 16-atom supercell monotonously increases with increasing fixed-spin moment. The lowest energy state is predicted to have the lattice parameter of 5.8178 A (for the cubic 16-atom supercell - **Figure 1**) in agreement with 5.879 A reported by Fecher and co-authors [23] as well as with the experimental values of 5.879 A reported by Buschow and van Engen [6] and of 5.858 A published in Ref. [5].

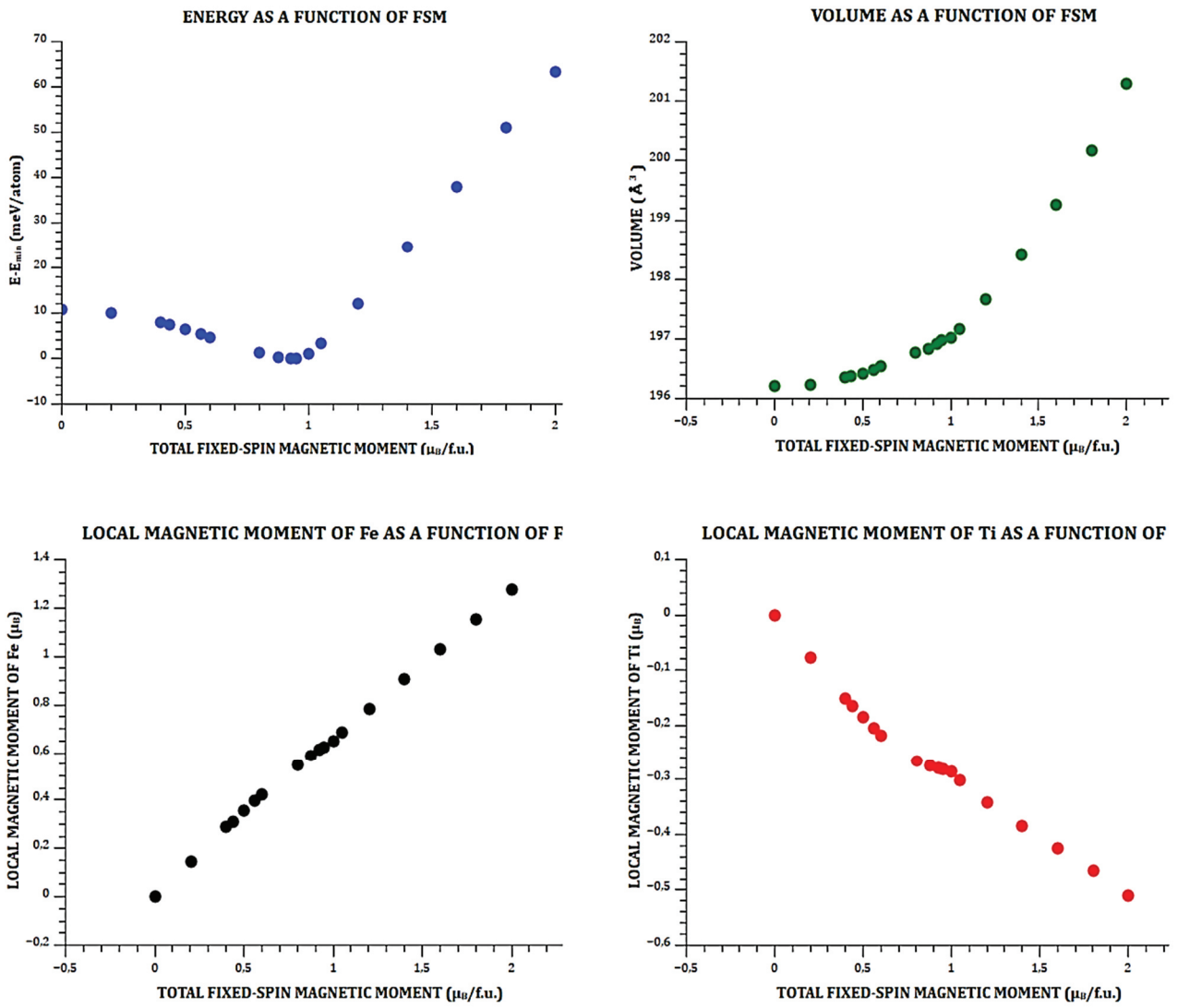

Figure 2 Computed dependences of (a) the total energy (in eV/atom with respect to the lowest obtained energy), (b) a 16-atom supercell lattice parameter (in Å) and local magnetic moments of Fe (c) and Ti atoms (d) as functions of the fixed-spin value of the total magnetic moment per formula unit (μ_B/f.u.) of Fe_2AlTi with the $L2_1$ structure

A qualitatively similar increase is exhibited also by absolute values of the local magnetic moments of Fe and Ti atoms (see parts (c) and (d) of **Figure 2**) with the latter being anti-parallel to the former and, therefore, visualized as negative values in **Figure 2d**. Aluminium atoms (not shown) are predicted to have local magnetic moments anti-parallel to those of Fe atoms but lower than 0.02 μ_B/atom within the whole range of studied FSM values, i.e. within our computational error bar, and therefore they are considered as non-magnetic.

Our calculations predict local magnetic moments of Ti atoms to exhibit an interesting feature for the states around the lowest-energy state (see **Figure 2d**). The slope of the curve of the local magnetic moments decreases prior to reaching the state with the lowest energy and starts to decrease again more sharply only for the states with the FSM higher than about 1 μ_B per formula unit. For these values of the FSM, local magnetic moments of Fe atoms show a much less pronounced deviation from a simple increasing trend (see **Figure 2c**). Therefore, the existence of the minimum of the total energy seems to be closely related to Ti atoms.

Table 1 Quantum-mechanically calculated parameters of the lowest-energy ferrimagnetic state and the non-magnetic state: the energy difference with respect to the lowest-energy ferrimagnetic state (in meV/atom), equilibrium lattice parameter of 16-atom computational supercell (in Å), the total fixed-spin magnetic moment per formula unit (f.u.) and local magnetic moments of Fe and Ti atoms. Selected results are compared with *ab initio* calculations and experimental data from Ref. [5].

Fe_2AlTi state	Energy difference ΔE (meV/atom) wrt. the lowest-energy state	16-atom cell lattice parameter [Å]	Total fixed-spin-moment [μ_B/f.u.]	Local atomic moment of Fe [μ_B/f.u.]	Local atomic moment of Ti [μ_B/f.u.]
ferrimagnetic	0	5.8179	0.925; 0.95 [5] Exp.: 0.1 [5]	0.611	-0.279
non-magnetic	10.73	5.8108	0	0	0

When analyzing our results, it is particularly striking how small is the energy difference between the ferromagnetic lowest-energy state and the non-magnetic one. Considering both as two possible states and applying Boltzmann statistics we predict that, for example, at T = 100 K, 22.36 % of the measured sample will be in a non-magnetic state, reducing thus the overall magnetization.

As another mechanism which can lower the overall magnetization we studied shape deformations. In particular we simulated a shear deformation lowering the cubic symmetry of the Fe_2AlTi to a trigonal one by changing the cell vectors from the original ones (1,0,0), (0,1,0), (0,0,1) to (1, ε, ε), (ε,1, ε), (ε,ε,1). **Figure 3** shows the computed energies as functions of the fixed-spin value of the total magnetic moment per formula unit (μ_B/f.u.) of Fe_2AlTi for ε = 0.08 (**Figure 3a**) and ε = -0.08 (**Figure 3b**). Importantly, for the latter case we do not have any energy minimum for any non-zero FSM state and the non-magnetic state is the only stable one. We thus show that Fe_2AlTi exhibits a tension-compression asymmetry with respect to trigonal deformations and the negative strain of ε = -0.08 destabilizes the ferrimagnetic state of Fe_2AlTi in favor of the non-magnetic state. Therefore, if these trigonal strains appear in the sample, the strain-induced phase transition from ferrimagnetic to non-magnetic state can reduce the overall magnetization detected in experiments.

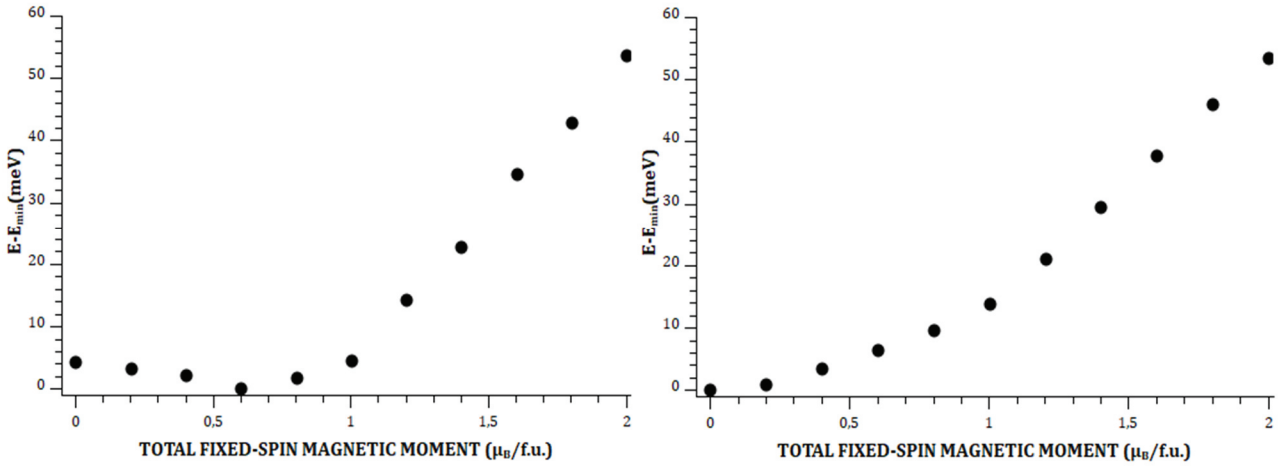

Figure 3 Computed dependences of the total energy (in eV/atom with respect to the lowest obtained energy) for trigonal deformation with the strain of ε = 0.08 (a) and ε = -0.08 (b) as functions of the fixed-spin value of the total magnetic moment per formula unit (μ_B/f.u.) of Fe_2AlTi

4. CONCLUSIONS

We have employed quantum-mechanical calculations to address a long-lasting discrepancy between computed and measured value of the magnetic moment in Heusler compound Fe_2AlTi at low temperatures. Using the fixed-spin-moment (FSM) approach we determined the total energy for a set of different states of Fe_2AlTi including the non-magnetic one. In agreement with previous *ab initio* calculations we predict the lowest energy state to be ferrimagnetic with the FSM of 0.925 μ_B per formula unit when the local magnetic moment of Fe and Ti atoms are 0.611 and -0.279 μ_B/atom, respectively (the negative sign meaning an anti-parallel orientation, i.e. a ferrimagnetic state). As the main result we identify two mechanisms which may be responsible for a lower value of magnetic moment determined in experiment, which amounts only to about 0.1 μ_B per formula unit. Namely, we demonstrate that the total energy of the non-magnetic state is only by 10.73 meV/atom higher than that of the lowest-energy spin-polarized state. When employing Boltzmann statistics, it turns out that, for instance, 22.36 % of the sample will be in a non-magnetic state at temperature of 100 K. Further, we show that Fe_2AlTi compound exhibits tension-compression asymmetry with respect to trigonal deformation. In particular, the trigonal strain of ε = -0.08 destabilizes the ferrimagnetic lowest-energy state in favor of the non-magnetic one, i.e. the non-magnetic state becomes the only stable one. Therefore, if these trigonal strains appear in experimental samples, the strain-induced phase transition from ferrimagnetic to non-magnetic state can reduce the overall magnetization detected in experiments. In future we plan to extend our study to other shape deformations (see, e.g., Refs. [24-36]) and prediction of elastic properties of samples containing both spin-polarized and non-magnetic states with their specific elastic properties (for multi-phase homogenization techniques see, for example, Ref. [37]).

ACKNOWLEDGEMENTS

The authors acknowledge the Czech Science Foundation for the financial support received under the Projects Nos. 17-22139S (M.F., A.S., I.M.) and 16-24711S (M.Š). Additional resources were provided by the Academy of Sciences of the Czech Republic through the Fellowship of J. E. Purkyně (M.F.), by the Ministry of Education, Youth and Sports of the Czech Republic under the Project CEITEC 2020 (LQ1601) and by the Research Infrastructure IPMINFRA (LM2015069). M.F., M.V. and M.Š. further acknowledge the Academy of Sciences of the Czech Republic for its institutional support (Institutional Project No. RVO:68081723). Computational resources were made available by the Ministry of Education, Youth and Sports of the Czech Republic under the Projects CESNET (Project No. LM2015042), CERIT-Scientific Cloud (Project No. LM2015085) and IT4Innovations National Supercomputer Center (Project No. LM2015070) within the program Projects of Large Research, Development and Innovations Infrastructures. The computational supercells (Fig. 1) were visualized using the VESTA package [38-40]. We also acknowledge discussions with M.Sc. Tomáš Komárek from the Masaryk University in Brno in the very early stages of the project and extensive discussions on experimental measurements with Ing. Yvonna Jirásková, Ph.D., from the Institute of Physics of Materials, Academy of Sciences of the Czech Republic in Brno, Czech Republic.

REFERENCES

[1] PALM, M., INDEN, G., THOMAS, N. *Journal of Phase Equilibria*, 1995, vol. 16, pp. 209.

[2] PALM, M., LACAZE, J. *Intermetallics*, 2016, vol. 14, pp. 1291.

[3] KREIN, R., FRIÁK, M., NEUGEBAUER, J., PALM, M., HEILMAIER, M., *Intermetallics*, 2010, vol. 18, pp. 1360.

[4] MICHALCOVÁ, A., SENČEKOVÁ, L., ROLINK, G., WEISHEIT, A., PEŠIČKA, J., STOBIK, M., PALM, M., *Materials and Design*, 2017, vol. 116, pp. 481.

[5] SHREDER, E., STRELTSOV, S., SVYAZHIN, A., LUKOYANOV, A., ANISIMOV, V. *Proceedings of the Third International Symposium on Magnetism*, 2005, vol. 220.

[6] BUSCHOW, K. H. J., VAN ENGEN, P. G. *J. Mag. Mag. Mater.*, 1981, vol. 25, pp. 90.

[7] WILLIAMS, A. R., MORUZZI, V. L., KÜBLER, J., SCHWARZ, K. *Bull. Am. Phys. Soc.*, 1984, vol. 29, pp. 278.

[8] SCHWARZ, K., MOHN, P. 1984, *J. Phys. F*, vol. 14, pp. L129.

[9] PODGÓRNY, M., THON, M., WAGNER, D. *Journal of Magnetism and Magnetic Materials*, 1992, pp. 104-107, pp. 703-704.

[10] SINGH, D. J., KLEIN, B. M. *Phys. Rev. B*, 1992, vol. 46, pp. 14969.

[11] ENTEL, P., HOFFMANN, E., MOHN, P., SCHWARZ, K., MORUZZI, V. L. *Phys. Rev. B*, 1993, vol. 47, pp. 8706.

[12] WU, S. Q., HOU, Z. F., ZHU, Z. Z. *Solid State Sciences*, 2009, vol. 11, pp. 251.

[13] FRIÁK, M., HICKEL T., KOERMANN, F., UDYANSKY, A., DICK, A., VON PEZOLD, J., MA, D., KIM, O., COUNTS, W. A., ŠOB, M., GEBHARDT, T., MUSIC, D., SCHNEIDER, J., RAABE, D., NEUGEBAUER, J. *Steel Research International*, 2011, vol. 82, pp. 86-100.

[14] HSUEH, H. C., CRAIN, J., GUO, G. Y., CHEN, H. Y., LEE, C. C., CHANG, K. P., SHIH, H. L. *Physical Review B,* 2002, vol. 66, pp. 052420

[15] HOHENBERG, P., KOHN, W. *Physical Review B*, 1964, vol. 136, pp. B864

[16] KOHN, W., SHAM, L. J. *Physical Review A*, 1965, vol. 140, pp. A1133

[17] KRESSE, G., HAFNER, J. *Physical Review B*, 1996, vol. 47, pp. 558

[18] KRESSE, G., FURTHMUELLER, J. *Physical Review B*, 1996, vol. 54, pp. 11169

[19] BLOECHL, P. E. *Physical Review B*, 1994, vol. 50, pp. 17953

[20] KRESSE, G., JOUBERT, D. *Physical Review B*, 1999, vol. 59, pp. 1758

[21] PERDEW, J. P., WANG, Y. *Physical Review B*, 1992, vol. 45, pp. 13244

[22] VOSKO, S. H., WILK, L., NUSAIR, M. *Canadian Journal of Physics*, 1980, vol. 58, pp. 1200

[23] FECHER, G. H., CHADOV, S., FELSER, C. *Theory of the half-metallic heusler compounds, Spintronics,* From Materials to Devices, eds. FELSER, C., FECHER, G. H. *Springer Dordrecht Heidelberg New York London*, 2013, pp. 115-166

[24] SOEDERLIND, P., ERIKSSON, O., WILLS, J.M., BORING, A.M., *Phys. Rev. B*, 1993, vol. 48, pp. 5844.

[25] ABRIKOSOV, I.A., JAMES, P., ERIKSSON, O., SOEDERLIND, P., RUBAN, A.V., SKRIVER, H.L., JOHANSSON, B., *Phys. Rev. B*, 1996, vol. 54, pp. 3380.

[26] LEGUT, D.; FRIÁK, M.; ŠOB, M., Phys. Rev. B 81 (2010) 214118.

[27] FRIÁK, M., HICKEL, T., KORMANN, F., UDYANSKY, A., DICK, A., VON PEZOLD, J., MA, D., KIM, O., COUNTS, WA., ŠOB, M., GEBHARDT, T., MUSIC, D., SCHNEIDER, J., RAABE, D., NEUGEBAUER, J., *Steel Research International*, 2011, vol. 82, pp. 86.

[28] CHEN, K., ZHAO, L.R., TSE, J.S., *J. Appl. Phys.*, 2003, vol. 93, pp. 2414.

[29] EKMAN, M., SADIGH, B., EINARSDOTTER, K., BLAHA, P., *Phys. Rev. B*, 1998, vol. 58, pp. 5296.

[30] ŠESTÁK, P., ČERNÝ, M., POKLUDA, J., *Mat. Sci. Eng. A*, 2008, vol. 481-482, pp. 247.

[31] JOHNSON, D.F., CARTER, E.A., *J. Chem. Phys.*, 2008, vol. 128, pp. 104703.

[32] ŠESTÁK, P., ČERNÝ, M., POKLUDA, J., *Strength Mater.*, 2008, vol. 70, pp. 12.

[33] LIU, J.B., JOHNSON, D.D., *Phys. Rev. B*, 2009, vol. 79, pp. 134113.

[34] STEINLE-NEUMANN, G., STIXRUDE, L., COHEN, R.E. *Phys. Rev. B*, 1999, vol. 60, pp. 791.

[35] ČERNÝ, M., ŠESTÁK, P., ŘEHÁK, P., *et al.*, *Mat. Sci. Eng. A*, 2016, vol. 669, pp. 218.

[36] KRASKO, G.L., RICE, B., YIP, S. *J. Comput. -Aided Mater. Des.*, 1999, vol. 6, pp. 129.

[37] FRIÁK, M., COUNTS, W.A., MA, D.C.; SANDER, B., HOLEC, D., RAABE, D., NEUGEBAUER, J. *Materials,* 2012, vol. 5, pp. 1853.

[38] MOMMA, K., IZUMI, F. Commission on Crystallographic Computing, IUCr Newsletter, 2006, vol. 7, pp. 106

[39] MOMMA, K., IZUMI, F. *Journal of Applied Crystalography*, 2008, vol. 41, pp. 653

[40] MOMMA, K., IZUMI, F. *Journal of Applied Crystalography*, 2011, vol. 44, pp. 1272