Available online at www.sciencedirect.com
SCIENCE DIRECT
Journal of Physics and Chemistry of Solids 66 (2005) 1815–1819
JOURNAL OF PHYSICS AND CHEMISTRY OF SOLIDS
www.elsevier.com/locate/jpcs

Mössbauer effect and first principle calculations of the electronic structure and hyperfine interaction parameters of Hf_2Fe

Jelena Belosevic-Cavor [a,*], Vasil Koteski [a], Giorgio Concas [b], Bozidar Cekic [a], Nikola Novakovic [a], Giorgio Spano [b]

[a] *Institute of Nuclear Sciences Vinca, P.O. Box 522, 11001 Belgrade, Serbia and Montenegro*
[b] *Dipartimento di Fisica, Universita di Cagliari and Istituto Nazionale per la Fisica della Materia-CNR, S. P. Monserrato-Sestu km 0.700, Monserrato CA I-09042, Italy*

Received 13 June 2005; accepted 12 September 2005

Abstract

A detailed theoretical study of the structure, electronic properties and the electric field gradients of the Hf_2Fe intermetallic compound is presented. Using all-electron full-potential linearized augmented plane wave (FP-LAPW) formalism the equilibrium volume, bulk modulus and electric field gradients are calculated. The obtained results are compared with EFG values inferred from measurements performed using Mössbauer spectroscopy and the earlier reported time differential perturbed angular correlation (TDPAC) measurements. The lattice relaxation and the supercell calculations are found to be essential for the correct interpretation of the experimental results.
© 2005 Elsevier Ltd. All rights reserved.

Keywords: A. Intermetallic compounds; C. Ab-initio calculations; C. Mössbauer spectroscopy; D. Electronic structure

1. Introduction

Intermetallic compound Hf_2Fe belongs to the group of binary systems formed between group IV (Ti, Zr, Hf) and other transition metals (Fe, Co, Pd, Pt). Among the other reasons, they have been investigated as systems interesting for hydrogen storage [1], able to form hydrides in hydrogen-to-metal atom ratios $H/M \geq 1$ at rather low temperatures ($T \sim 300$ °C) and pressures [2]. Recently, Hf_2Fe has become interesting as a potential cathode material in the electrolytic hydrogen production [3].

The fact that hafnium is one of the most suitable probes for perturbed angular correlation (PAC) spectroscopy has been widely used in many experimental studies on these Hf compounds [4–8]. In the PAC experiment, the electric field gradient (EFG) is measured via its interaction with the nuclear quadrupole moment Q of the probe nucleus, providing valuable experimental information about the local electronic structure around the probe nucleus. The EFG is particularly sensitive to the asymmetry of the charge density in the vicinity of the probe. However, this information is rather indirect and the interpretation of experimental results requires highly accurate electronic band structure calculations. The fact that after the radioactive decay of the ^{181}Hf nucleus, the measurement takes place on the ^{181}Ta daughter isotope suggests that supercell calculations (with Ta replacing Hf) should be used, which considerably increases the computational effort.

So far, several experimental studies devoted to PAC investigation of the hyperfine interactions in the Hf_2Fe intermetallic compound have been conducted [4–6]. The magnitudes of the principle EFG component at both non-equivalent Hf sites, the temperature dependency of the EFG, and the asymmetry parameter η reported in the earlier experiments agree within several percent, providing an excellent basis for theoretical investigations. The Mössbauer spectroscopy gives a possibility of measuring the quadrupole splitting and indirectly EFG at Fe site in this compound.

The previous theoretical study of Hf_2Fe [9], employing the linear muffin-tin orbital method (LMTO) in the atomic sphere approximation (ASA), has concentrated on (i) the electronic structure using values of the experimentally obtained lattice parameters, and (ii) the EFG at regular Hf lattice site. In this work, our main goal is to check to what extent the structure relaxation and the Ta impurity affect the calculated EFG parameters. We will show that these issues notably influence the EFG parameters, and that the attempt to explain the EFG

* Corresponding author. Tel.: +381 11 2453 681; fax: +381 11 3440 100.
E-mail address: cjeca@vin.bg.ac.yu (J. Belosevic-Cavor).

0022-3697/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jpcs.2005.09.003

measured at the Ta probe atom with the calculations on the original structure can be misleading. In addition, we have determined the equilibrium volume and bulk modulus. To the best of our knowledge, up to date, experimental data regarding the Hf_2Fe bulk modulus does not exist. Finally, we have performed the Mössbauer measurements, in order to check previously reported measurements [10] and compare the calculated result for EFG at Fe site with the measured one. The results obtained from this measurement are in excellent agreement with both earlier reported experimental data and our calculated values.

2. Computational details

The unit cell of Hf_2Fe consists of 96 atoms (space group Fd3m). We used the primitive unit cell, constructed out of 24 atoms (8 formula units of Hf_2Fe). The cell parameter a_0 was experimentally determined to be 12.0246(9) Å. Four atoms of the primitive unit cell are located at the 16c (Hf1), 12 at the 48f (Hf2) positions, while eight Fe atoms are at the 32e position. This structure posses two internal parameters, u and v, which determine the non-equivalent position of Fe (u, u, u) and Hf2 (v, 1/4, 1/4) [11].

Electronic structure and EFG calculations were performed using WIEN 97-FP LAPW code [12]. In the LAPW method, the unit cell is partitioned into muffin-tin (MT) spheres centered at the atomic positions, and an interstitial region. The generalized gradient approximation in the parameterization of Perdew–Burke–Ernzerhof [13] was employed. The MT sphere radii R_{mt} were 2.3 and 2.15 a.u. for Hf and Fe, respectively. The Hf 5p, 5s, 6s, 5d, 4f and Fe 3s, 4s, 3p, 3d states were put in the valence panel. The standard LAPW basis set is extended with local orbitals [14]. The Brillouin zone (BZ) integration was performed using a k mesh of 47 k points in the irreducible BZ wedge and the plane wave cutoff parameter R_{mt} K_{max} was set to 8.0. The core states were treated fully relativisticaly, while the valence states were treated within the scalar relativistic approximation. Spin-orbit contribution was neglected.

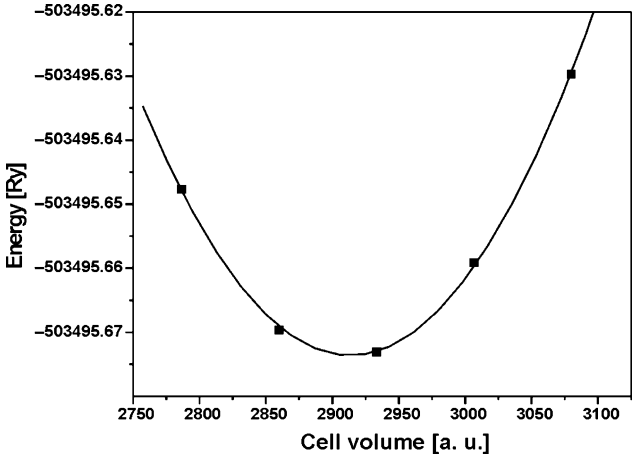

Fig. 1. Total energy vs cell volume for Hf_2Fe. The result of a Murnaghan's fit is shown as full line.

Before calculating the electronic structure, we relaxed the internal parameters of the structure, keeping the experimental lattice constant fixed. Starting from the experimental values for the structural parameters, we calculated the Hellman–Feynman forces acting on Hf2 and Fe atoms. The Hf1 atoms are fixed owing to symmetry restrictions. According to the calculated forces, the atoms were allowed to move along the symmetry directions. The relaxation was carried out until the forces were smaller than 1 mRy/a.u. Then a series of calculations was done, changing the volume within $\pm 5\%$ of the experimental volume and calculating the total energy as its function. The result of this optimization is shown in Fig. 1.

3. Computational results and discussion

The theoretically determined internal parameters u and v, bond lengths and the cell parameter a, for the fully relaxed Hf_2Fe structure, are given in Table 1. The theoretical volume underestimates the experimental one by $\sim 0.8\%$; the corresponding lattice constant differs up to $\sim 0.3\%$ from the experimental one. The bulk modulus B_0 obtained by fitting the data to the Murnaghan's equation of state [15] is 139.8 GPa.

Table 2 reveals the site projected partial charge inside the MT spheres around Hf1, Hf2 and Fe. The construction of the MT spheres is not unique, and the charge contained within by no means corresponds to the actual ionic charge. Also, the charge in the interstitial region cannot be assigned to any particular atomic species. Still, analyzing the charge confined in the MT spheres can be useful to get an overall picture about possible charge transfer between constituent atoms.

From Table 2, one can see that the s charge of Hf1, Hf2 and Fe, as well as the d charge of Hf1 and Hf2 is redistributed, filling mostly the Fe p states and the interstitial region. This

Table 1
The parameters of the Hf_2Fe structure. The distances are in Å.

	Number of bonds	Experimental	WIEN 97
u		0.21116	0.2152
v		0.8153	0.8137
16c			
Hf1–Fe	6	2.627 (5)	2.647
Hf1–Hf2	6	3.074 (2)	3.080
48f			
Hf2–Fe	2	2.80 (1)	2.732
Hf2–Fe	2	3.061 (3)	3.061
Hf2–Hf1	2	3.074 (2)	3.080
Hf2–Hf2	4	3.173 (2)	3.173
Hf2–Hf2	4	3.236 (5)	3.200
32d			
Fe–Hf1	3	2.627 (5)	2.647
Fe–Hf2	3	2.80 (1)	2.732
Fe–Fe	3	2.94 (1)	3.060
Fe–Hf2	3	3.061(3)	3.061
a_0		12.0246	11.9927

Download English Version:

https://daneshyari.com/en/article/9781576

Download Persian Version:

https://daneshyari.com/article/9781576

Daneshyari.com