# Ab initio study of electronic structure and hyperfine interaction parameters in HfV<sub>2</sub> and ZrV<sub>2</sub> Laves phases

Jana Radaković, Jelena Belošević-Čavor, Vasil Koteski, Katarina Ćirić

Institute of Nuclear Sciences Vinča, University of Belgrade, Serbia



www.advancedmaterialsgroup.edu.rs



## What was done?



- Ab initio calculations of Electric Field Gradients (EFG)
- $HfV_2$  and  $ZrV_2$  pure compounds
- <sup>181</sup>Ta and <sup>111</sup>Cd impurities supercells
- Time Differential Perturbed Angular Correlations measurements (TDPAC) with <sup>181</sup>Ta and <sup>111</sup>Cd probe atoms
- All-electrons augmented plane waves plus local orbitals formalism as implemented in Wien2k computational code

## Why did we do it?

EFG = f ( charge distribution, nearest neighbor distance and distribution )

investigation of electron density (

Experimental technique (among others): TDPAC

Problem:

- Interpretation of the TDPAC results are often inconclusive!
- Site of the probe atom (Cd/Ta) can be *unknown*!

> Ab initio calculations are used to clarify these ambiguities!

## **PAC – Basic principle**

The PAC spectroscopy is a nuclear technique by which information about the microscopic structure of solids can be obtained by hyperfine interactions.

Radioactive probe nuclei is inserted in solids, and it decays via  $\gamma$ - $\gamma$  cascade over an intermediate state.

Characterization is based upon:

interaction of nuclear quadruple moment of probe atom and electric field gradient created by the surrounding electronic and nuclear charge

Used probes: <sup>111</sup>In or <sup>181</sup>Hf

- anisotropic gamma ray cascades,
- large nuclear moments,
- relatively long lifetimes of intermediate state





## Why Laves phases?

- High melting temperature
- High strength
- Excellent oxidation resistance



High temperature materials!

Ability to absorb hydrogen (interstitial hydrides)



Hydrogen storage materials!





## **Structural information**

#### ZrV<sub>2</sub> unit cell



C15 Laves phases Space group: Fd-3m Structure type: MgCu<sub>2</sub>

Hf / Zr Wyckoff position: cubic 8aV Wyckoff position: noncubic 16d

EFG was expected only at the Vanadium atomic position, Hf or Zr do not exibit electric fields!



Supercell

Introduced impurities: <sup>111</sup>Cd and <sup>181</sup>Ta, *often used PAC probes* 

2x2x2 supercells were constructed from pure compound cell

Ta and Cd substituted both atomic positions

Impurity atom surroundings = as in the pure cell

### **Calculation details**

Muffin-tin radii:  $R_{mt}$  (Hf and Ta) = 2.3 a.u.  $R_{mt}$  (Zr and Cd) = 2.2 a.u.  $R_{mt}(V) = 2.1 a.u.$ Plane wave cutoff parameter:  $R_{mt}K_{max} = 8.5$  (*pure compound*)  $R_{mt}K_{max} = 7.0$  (supercell) Core and valence separation energy: -6.0 Ry The exchange and correlation effects generalized gradient approx. (GGA) The Brillouin zone integration: 195 k points in the irreducible wedge (*pure compound*) 10 k points in the irreducible wedge (supercell) fully relativisticaly The core states scalar relativistic approximation The valence states Charge difference between two successive iterations  $< 10^{-5}$  electrons Structure relaxation: forces < 1 mRy / a.u. Optimal structural parameters of pure cell: volume deviation  $\pm$  5%

### **Results**

Table 1. Structural parameters of pure compounds obtained fromX-ray diffraction experiments and calculations

Unit cell parameter	Experimental results	Previous calculations	Wien2k
HfV <sub>2</sub>	7.38 <sup>1</sup> 7.39 <sup>2</sup> 7.41 <sup>3</sup>	7.315 <sup>5</sup> 7.318 <sup>6</sup> 7.474 <sup>7</sup>	7.312
ZrV <sub>2</sub>	7.43 <sup>2</sup> 7.44 <sup>3</sup> 7.50 <sup>4</sup>	7.547 <sup>7</sup> 7.348 <sup>8</sup> 7.286 <sup>9</sup>	7.352

[1] V.M.Pan, I.E.Bulakh, A.L.Kasatkin, A.D.Shevchenko, Journal De Physique 39 (1978) C6-1068

[2] S. Dreßler, J. W. Taylor, B. Ouladdiaf, K. U. Neumann and K. R. A. Ziebeck, Solid State Communications 113 (2000) 649

[3] W. Daumer, H.R. Khan, K. Luders, Phys. Rev. B 38 (1988) 384427

[4] M. Jurczyk, Journal of Optoelectronics and Advanced Materials 8 (2006) 418

[5] Zhang C-W, Physica B 403 (2008) 2088

[6] Charifi Z., Reshak A. H., Baaziz H, J. Phys.: Condens. Matter 21 (2009) 025502

[7] F. Chu, T. E. Mitchell, and S. P. Chen, 1994 MRS Annual Meeting

[8] R.Z. Huang, Y.M. Wang, J.Y. Wang, Y.C. Zhou, Acta Materialia 52 (2004) 3499

[9] Anton H, Schmidt PC. Intermetallics 5 (1997) 449

# Table 2. Distance from Hf/Zr atom and V atom to its nearest neighbor in pure unit cell before and after volume optimization

Con	npound	Hf/Zr befor	– NN e	Hf/Zr after	-NN	V-NN before		V-NN after	
ŀ	HfV <sub>2</sub>	3.11		3.03		2.65		2.58	
Z	ZrV <sub>2</sub>	3.19		3.05		2.72		2.59	
Table 3. Distance from Impurity atom to its nearest neighbor in supercells									
		0		Cd/Ta – V distances (Å)					
	Compound and Impurity		Unrela structu	laxed Relaxed ture structu		ed ire			
	Hf∖	/ <sub>2</sub>	Cd (V) Cd (Hf) Ta (V) Ta (Hf)		2.58 3.03 2.58 3.03		2.27 3.03 2.71 3.03		
	Zr∖	/ <sub>2</sub>	Cd (V) Cd (Zr) Ta (V) Ta (Zr)		2.59 3.05 2.59 3.05		2.69 3.04 2.68 3.02		

Table 4. EFGs obtained on the Vanadium atom form pure compound calculations

Compound	EFG (10 <sup>21</sup> V/m <sup>2</sup> )	р-р	d-d	Others
HfV <sub>2</sub>	0.54	2.05	-1.72	-0.02
$ZrV_2$	-0.69	1.08	-1.89	-0.01

Table 5. EFGs obtained on the Impurity position form supercell compound calculations

Compound	Impurity	EFG (10 <sup>21</sup> V/m <sup>2</sup> )	EFG (10 <sup>21</sup> V/m <sup>2</sup> ) Experimental	р-р	d-d	Others
	Cd (V)	-2.66	2.48 <sup>10</sup>	-3.65	0.93	0
	Cd (Hf)	0	-			
HfV <sub>2</sub>	Ta (V)	-12.27	-	-10.42	-1.78	-0.13
	Ta (Hf)	0	0.80 <sup>11</sup>			
	Cd (V)	-4.16	-	-5.63	1.39	0
	Cd (Zr)	0	-			
$ZrV_2$	Ta (V)	-5.95	-	-2.74	-3.03	-0.19
2	Ta (Zr)	0	-			

[10] R. Heidinger, P. Peretto and S. Choulet, Solid State Comunications 47 (1983) pp. 283

[11] H. C. Jain and M. A. A. Saad, Physics Letters 96A (1983) pp. 419

## Summary

We have presented ab-initio calculations of the fully relaxed  $ZrV_2$  and  $HfV_2$  structure and provided insights into the electronic and structure properties of these intermetallic compounds.

We have shown that the values of EFGs in these two compounds are of the same order of magnitude, but main contribution to the EFG differs, in Hf major influence comes from p, while in Zr from d electrons.

The calculated EFGs at Cd and Ta impurities on V site in  $HfV_2$  has exhibited fair agreement with the existing experimental values. Unfortunately, no experimental data of EFGs of these impurities in  $ZrV_2$  exist, therefore no comparing can be made.

## Thank you for your attention!

www.advancedmaterialsgroup.edu.rs



