

Thermal Scattering Law Data for Zirconium Hydride from First-Principles

I. Švajger¹, N. C. Fleming², B. Laramée², G. Noguere³, A. I. Hawari², L. Snoj¹, A. Trkov¹

¹”Jozef Stefan” Institute

Jamova cesta 39

1000, Ljubljana, Slovenia

ingrid.svajger@ijs.si, luka.snoj@ijs.si, andrej.trkov@ijs.si

²North Carolina State University

3140 Burlington Engineering Labs, 2500 Stinson Drive

NC 27695-7909, Raleigh, USA

ncsorrel@ncsu.edu, bklarame@ncsu.edu, ayman.hawari@ncsu.edu

³CEA, DeS, DER, Experimental physic, Safety experiment and Instrumentation Section

13108 Saint Paul-lez-Durance

Cadarache, France

gilles.noguere@cea.fr

ABSTRACT

First-principles calculations are performed to obtain thermal neutron scattering law data of ZrH₂ in the ϵ phase (FCT crystal structure). The purpose of the present work is to validate our computational method and to compare calculated phonon density of states (phonon DOS) with ENDF/B-VIII.0 nuclear data evaluation. The phonon DOS is the fundamental parameter for evaluating the thermal neutron scattering law data. It is shown that analysis of phonon DOS of H in ZrH₂ is in good agreement with the experimental results.

1 INTRODUCTION

Many transition metals react with hydrogen to form stable metal hydrides. Metal hydrides are technologically attractive materials due to their ability to store high proportion of hydrogen. A considerable interest in zirconium hydrides arises in the nuclear industry, where it is essentially used as a neutron moderator in nuclear reactors. TRIGA reactors feature unique fuel composition, i.e. a homogeneous mixture of 20 % enriched uranium and zirconium hydride (ZrH ratio near 1.6). This is the primary reason for the prompt negative temperature reactivity coefficient. Since hydrogen in zirconium hydride serves as a moderator, most moderation occurs in the fuel element itself and only a small part in the water surrounding the fuel elements. Therefore, any change in power and in fuel temperature immediately reflect on the moderator in the fuel element. In this case, the fuel and the moderator promptly affect the reactivity of the core. Consequently, this emphasizes the need to understand the fundamental atomistic properties of zirconium hydrides.

ZrH_x may exist in multiple phases with varying stoichiometry, the most significant of which are the δ phase (at room temperature dominant for $1.56 < x < 1.64$) and the ϵ phase (at room temperature dominant for $x > 1.74$). Current ENDF/B-VIII.0 ZrH_x nuclear data evaluations do not distinguish between phases. In the present work, we adopt first-principles calculations to obtain thermal neutron scattering law data (TSL) of ZrH₂ in the ϵ phase with the purpose of comparison with the current ENDF/B-VIII.0 nuclear data evaluation. Using the

density functional theory (DFT) capable computer code VASP, the system is modelled and relaxed to its ground state. Atomic positions are then perturbed, and the interatomic force constants are calculated. Once the force constants are obtained, they are transferred to the Phonopy code, which perform lattice dynamics calculations in which solutions to the dynamical matrix problem are sought. The solutions constitute the dispersion relations of the system, from which the atomic vibrational density of states (DOS) are computed using a geometrical sampling procedure. [1]

2 THERMAL NEUTRON SCATTERING

In the low neutron energy range, typically below 5 eV, neutron scattering is affected by the atomic bonding of the scattering molecule in the moderator. Compared to a free nucleus, this changes the reaction cross section and, thus, the energy and angular distribution of the secondary neutrons. Neutron scattering is classified as elastic and inelastic scattering. While the former is important, the latter has a direct link to the reactor applications because neutrons need to slow down to increase the fission probability of the fissile isotopes. Both elastic and inelastic scattering can be coherent or incoherent. In coherent scattering, the interference phenomena between the waves reflected by close nuclei affect the scattering target. [2]

The importance of components differs based on the state of the scatterer (liquid, solid) and on the material properties. Incoherent elastic scattering is relevant for materials with a high hydrogen content, such as zirconium hydride, yttrium hydride, polyethylene, or water, because hydrogen has a large incoherent bound atom cross section. Coherent elastic scattering is important for crystalline materials, the most prominent examples being graphite, beryllium and uranium dioxide, because the angular distribution of scattered neutrons is affected. Inelastic scattering is important for all materials. [2]

In many materials, only inelastic scattering is considered in the calculation of thermal neutron cross sections, which are then used in nuclear data processing codes. The inelastic double differential cross section can be calculated by the well-known formula:

$$\frac{d^2\sigma}{d\Omega dE'} = \frac{1}{4\pi k_B T} \sqrt{\frac{E'}{E}} e^{-\frac{\beta}{2}} (\sigma_{coh} S(\alpha, \beta) + \sigma_{inc} S_s(\alpha, \beta)), \quad (1)$$

where E is the neutron flux energy, Ω is the direction, E' is the secondary energy, Ω' is the direction, σ_{coh} and σ_{inc} are the coherent and incoherent scattering cross sections, k_B is the Boltzmann constant, T is the temperature of the material and $S(\alpha, \beta)$ is the thermal scattering function. The thermal scattering function $S(\alpha, \beta)$ is given by the equation:

$$S(\alpha, \beta) = S_s(\alpha, \beta) + S_d(\alpha, \beta) \quad (2)$$

In the above equation $S_s(\alpha, \beta)$ represents the self-scattering function that accounts for non-interference or incoherent effects, while $S_d(\alpha, \beta)$ represents the distinct-scattering function that accounts for interference or coherent effects. The scattering law is a function of the dimensionless momentum transfer α and energy transfer β given with these two equations:

$$\alpha = \frac{E' + E - 2\sqrt{E'E}\mu}{Ak_B T}, \quad (3)$$

$$\beta = \frac{E' - E}{k_B T} = \frac{\hbar\omega}{k_B T}. \quad (4)$$

In these equations μ represents the cosine of the scattering angle in the laboratory system and A is the ratio between the mass of the scattering target M and the neutron mass m . The energy

transfer $E' - E$ is sometimes denoted as the product between the reduced Planck's constant \hbar and the excitation frequency ω . [1]

The scattering law is a fundamental quantity of the scattering system. The dynamics of the scattering law can be approximately calculated in one of two main ways: via the Van Hove space-time self-correlation function or better, its Fourier transform in time - the intermediate scattering function. However, because these cannot be calculated explicitly for systems of practical interest, the phonon expansion is used instead. The main point of the expansion is, that the thermal scattering law is written as a sum of partial thermal scattering laws S^p , where $p = 0, 1, 2, \dots$ account for scattering interaction in which the neutron interacts with p phonons. The $p=0$ term is the one in which no energy exchange takes place, so S^0 corresponds to elastic scattering, S^1 to inelastic scattering in which one phonon is exchanged etc. [2]

With the advent of advanced computer simulations, it became possible to simulate an ensemble of atoms or molecules and obtain the inter-atomic force constants from the first principles. The double differential thermal neutron scattering cross section, can be viewed as consisting of two parts: the neutron-nucleus interaction, represented by the bound atom cross section and a factor, which accounts for the dynamics of the scattering system, represented by the dynamic structure factor. More often than not, calculation of the scattering law for crystalline materials is done using the phonon expansion in the incoherent approximation, in which the distinct-scattering term of the scattering law is set to zero. The incoherent approximation (mostly) holds so well because of multi-phonon scattering where for almost any energy and/or momentum transfer, there exists a large number of combinations of multiple phonons that satisfy the energy and crystal momentum conservation relations. This approximation holds well enough for many materials of interest, but this assumption can introduce inaccuracies into the calculated cross section for materials such as graphite and beryllium. Fortunately, the missing coherent inelastic contribution can be introduced into the expression separately by various methods. Also, an ENDF format extension is being prepared to consider a coherent and incoherent contribution. For crystalline solids, the most important type of excitations, responsible for the energy exchange between the neutron and the material are phonons, and if other contributions are neglected, the calculation of differential and total cross section can be reduced to the calculation of the phonon density of states, from which all other quantities can be calculated. [2]

3 RESEARCH METHODOLOGY

With the advancement in computational power in recent years, state-of-the-art atomistic simulations based on first principles have become available for use in chemistry and physics. In these simulations, crystal lattice motion or molecular motion is simulated using algorithms from the field of computational physics, such as density functional theory (DFT) and its derivatives, for which the 1998 Nobel Prize in chemistry was awarded. Density of states can be extracted from a simulated motion of an atomic or molecular system. Thermal nuclear data (TND) calculations are possible based on the extracted density of states. In DFT the total electronic force is the sum of the Coulomb repulsion between nuclei and the quantum mechanical electron potential, which itself consists of electron-electron interactions and electron-atom interactions. A fundamental assumption of DFT is that the total energy of the electronic system can be expressed as a function of the electronic density, and that the ground state of the system can be obtained by means of minimization of the function. In principle, the success of DFT is due to the fact that there exists a bijective transformation between wavefunctions of the constituent electrons and the full molecule electron density: the many-electron problem is reduced to a one-electron problem. To accurately simulate the behaviour of an

atomic or molecular system, the interatomic (intermolecular) potential must be known so forces on constituent atoms (molecules) can be calculated. There are two main approaches:

- a) Using DFT capable computer codes, such as VASP [1] or Quantum Espresso (QE) [4], the system is modelled and relaxed to its ground state. Atomic positions are then perturbed, and the interatomic force constants are calculated. Once the force constants are obtained, they are transferred to another program, such as PHONON [5] or Phonopy [6], which performs lattice dynamics calculations in which the solutions to the dynamical matrix problem are sought. The solutions constitute the dispersion relation of the system, from which the density of states can be computed using a geometrical procedure. Once the density of states is known, the scattering law and all related quantities can be calculated.
- b) In the second approach, the interatomic force constants are arrived at by assuming an appropriate potential between constituent atoms. Once the force constants of this potential are known, the atomic trajectories are propagated using classical mechanics. The density of states can be calculated as the Fourier transform of the velocity autocorrelation function, obtained from the propagated trajectories. CASTEP [7], GROMACS [8] and LAMMPS [9] are examples of codes that utilize this approach.

Both approaches have their advantages and disadvantages. In the first approach the dynamical matrix calculation is only strictly valid at 0 K, which means the phonon density of states (DOS) obtained does not capture temperature dependent effects such as phonon softening and anharmonicity of the lattice. Also, in the first approach, materials which are non-periodic (not a crystal) cannot be treated. The second method has the disadvantage of depending on the choice of a particular potential function, which may or may not be appropriate. Also, because classical mechanics are used to propagate the atomic trajectories, the calculation is classical in nature and as such quantum mechanical effects are not reproduced. However, this approach is capable of treating amorphous materials and can, contrary to the first, capture temperature effects. A combination of both approaches has also recently been developed [10], in which DFT is used to find the force constants and at every time step the atomic trajectories are propagated in a self-consistent way, but this approach suffers from high computational costs compared with the other two.

In this paper the results of the DOS are obtained with the method described under the case a). Used computer codes are VASP and Phonopy.

4 COMPUTATIONAL METHOD

Total energy calculations are self-consistently carried out using density functional theory (DFT) as implemented in Vienna ab initio simulation package (VASP) [11], which is based on pseudopotentials and plane wave basis functions. All electron projected augmented wave (PAW) method of Blöchl [12] is applied in VASP with the frozen core approximation. The generalized gradient approximation (GGA) introduced by Perdew, Burke, and Ernzerhof (PBE) [13] is employed to evaluate the electron exchange and correlation potential. Zirconium $4s^2 4p^6 4d^2 5s^2$ and hydrogen $1s^1$ electrons are treated as valence electrons. The integration over the Brillouin Zone is performed with a grid of special k point-mesh determined according to the Monkhorst–Pack scheme [14].

Convergence test is used to test model to be fully converged. Appropriate convergence of planewave energy cutoff and k-point mesh is determined by tracking three specific outputs of the VASP calculation: unit cell volume V , energy E and pressure p . The requirements for convergence are shown below:

$$\frac{\Delta V}{V} < 0.1 \%, \quad (5)$$

$$\Delta E < 5 \frac{meV}{atom}, \quad (6)$$

$$\frac{\Delta P}{P} < 1 \%. \quad (7)$$

After convergence test, 13 x 13 x13 k point-mesh and cutoff energy of 675 eV is chosen. The self-consistent convergence of the total energy calculation is set to 10^{-8} eV.

4.1 Atomic structure

At ambient condition, the stable zirconium dihydride crystallizes in an FCT structure with space group $I4/mmm$ (No. 139). In its unit cell, there are two ZrH_2 formula units with Zr and H atoms in 2a: (0, 0, 0) and 4d: (0, $\frac{1}{2}$, $\frac{1}{4}$) sites, respectively (see Figure 1). Each Zr atom is surrounded by eight H atoms forming a tetragonal cell and each H connects with four Zr atoms to build a tetrahedron. The present optimized equilibrium lattice parameters (a and c) are 3.540 Å and 4.408 Å. These values are in accord with the experimental values (see Table 1).

Table 1: Calculated lattice constants. For comparison available experimental values.

property	present work	experiment [17]
a [Å]	3.540	3.522
c [Å]	4.408	4.451

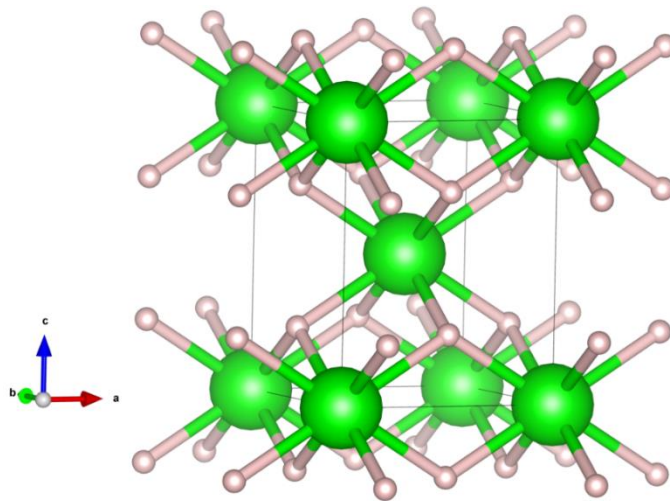


Figure 1: ZrH_2 tetragonal unit cell with larger green spheres for Zr atoms and smaller white spheres for H atoms.

4.2 Mechanical properties

In this chapter, the mechanical properties are investigated to validate our FCT ZrH_2 model, since the atomic structure and potentials affect the mechanical properties. Elastic constants can also measure the resistance and mechanical features of crystal to external stress or pressure, thus may evaluate the stability of crystals against elastic deformation. As for the FCT phase, the six independent elastic constants, i.e., C_{11} , C_{12} , C_{13} , C_{33} , C_{44} , and C_{66} , can be obtained (see Table 2).

Table 2: Calculated elastic constants for FCT ZrH₂ in units of GPa.

	C_{11}	C_{12}	C_{44}	C_{13}	C_{33}	C_{66}
present work	224.9	90.2	12.5	107.0	149.5	33.6
from [19]	165.6	140.9	30.5	106.8	145.5	60.6
from [20]	166	149	26.5	109	149	55.8
from [21]	102	20.4	35.6	11.4	108	23.7

It can be concluded that FCT ZrH₂ is mechanically stable due to the fact that its elastic constants satisfy the following mechanical stability criteria [22] of a tetragonal structure:

$$\begin{aligned}
 C_{11} > 0, C_{33} > 0, C_{44} > 0, C_{66} > 0, \\
 (C_{11} - C_{12}) > 0, (C_{11} + C_{33} - 2C_{13}) > 0, \\
 (2(C_{11} + C_{12}) + C_{33} + 4C_{13}) > 0.
 \end{aligned} \tag{8}$$

When the elastic constants for the material is known, bulk modulus K , shear modulus G and Young modulus E of the different hydrides can be calculated using standard relationship between K , G and E :

$$K = \frac{1}{9}(C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})), \tag{9}$$

$$G = \frac{1}{15}(C_{11} + C_{22} + C_{33} + 3(C_{44} + C_{55} + C_{66}) - C_{12} - C_{13} - C_{23}), \tag{10}$$

$$E = \frac{9KG}{3K + G}. \tag{11}$$

It is common practise to compare bulk modulus, shear modulus, and Young's modulus instead of comparing elastic constants, so the results for these values are given in Table 3.

Table 3: Calculated bulk modulus, shear modulus and Young modulus in GPa.

	K	G	E
present work	134.2	35.6	98.1
from [19]	130	29	80
from [20]	44.4	36.8	86.6
from [21]	44.38	36.84	86.58

4.3 Phonon density of states (phonon DOS)

Calculated phonon DOS are the fundamental parameters for evaluating the TSL, so the calculated phonon DOS are analysed. In this analysis phonon DOS of H in ZrH₂ is presented. The phonon DOS from our calculation of ZrH₂ and that from ZrH₂ in ENDF/B-VIII.0 in the region from 0.1 eV to 0.18 eV are presented in Figure 2 and they are compared to the experimental results from [23] and [24]. The phonon DOS of ZrH₂ calculated in this work shows good agreement with the experimental results. It can be seen that three peaks at experimental data (green dots) are well reproduced by calculation (red line). For the ENDF/B-VIII.0 data, peaks are also found at three energy points, but the height of the peaks deviates from the experimental results. On Figure 3 the calculated phonon DOS of ZrH₂ and phonon DOS from ENDF/B-VIII.0 data library are compared in the region from 0 eV to 0.04 eV. The phonon DOS are compared in two different regions because of different phonon DOS scale.

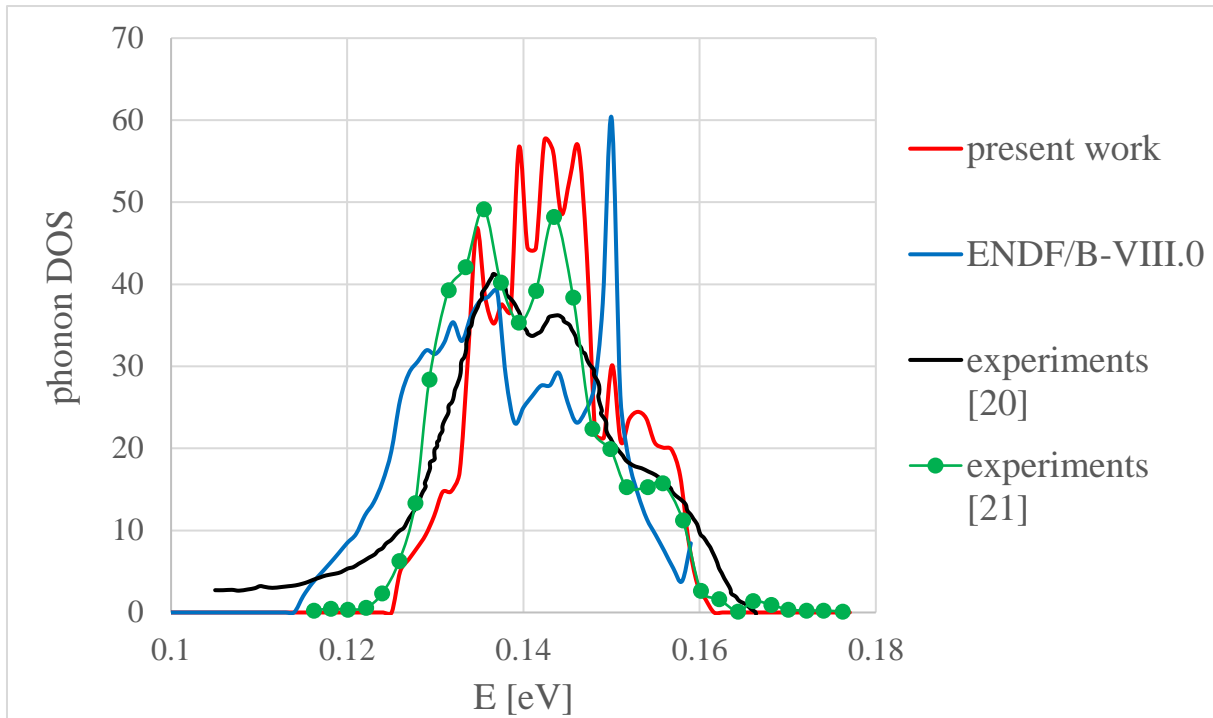


Figure 2: Comparison of the phonon DOS of H in ZrH₂ in the region from 0.1 eV to 0.18 eV.

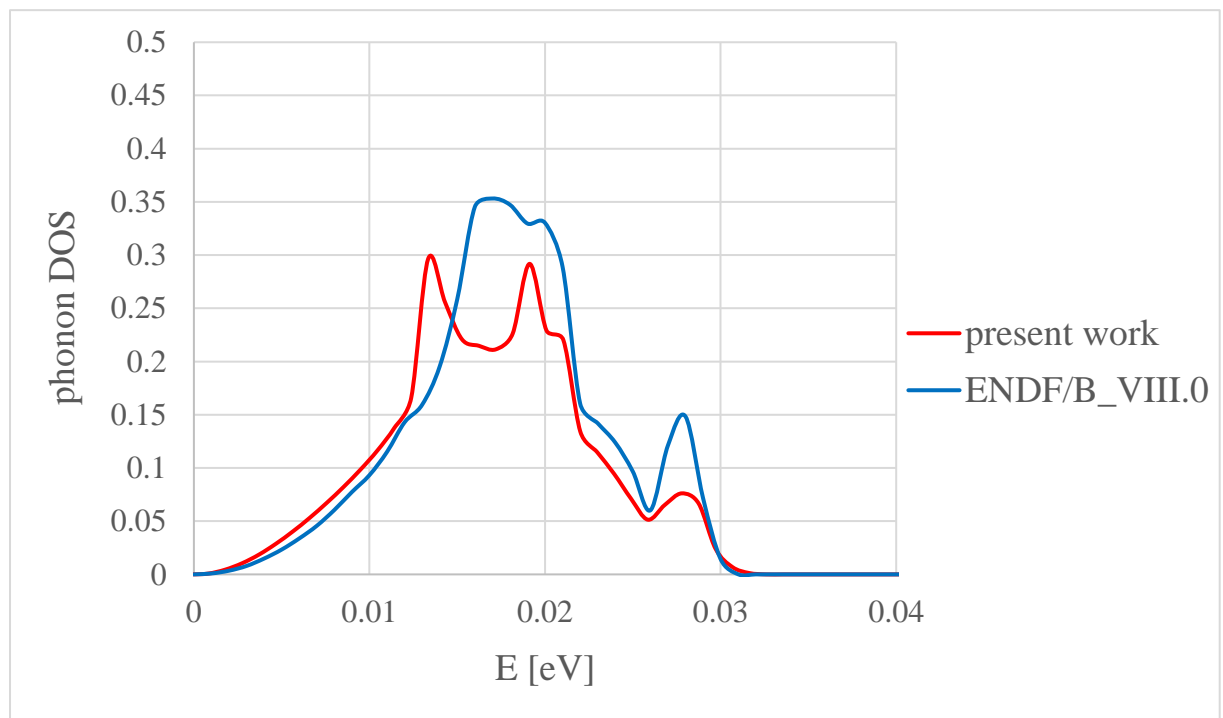


Figure 3: Comparison of the phonon DOS of H in ZrH₂ in the region from 0.0 eV to 0.04 eV.

5 CONCLUSIONS

In the present work, first-principles calculations were performed to obtain the TSL of ZrH₂ in the ϵ phase (FCT crystal structure) with the purpose of validating the computational methodology and comparison with current ENDF/B-VIII.0 nuclear data evaluation. Using the DFT capable computer code VASP, the system is modelled and relaxed to its ground state.

Atomic positions are perturbed, and the interatomic force constants are calculated. Once the force constants are obtained, they are transferred to the Phonopy code, which perform lattice dynamics calculations in which solutions to the dynamical matrix problem are sought. The solutions constitute the dispersion relations of the system, from which the phonon DOS are computed.

In order to investigate the mechanical properties, the elastic constants for FCT ZrH₂ are calculated. It is found that they are in good agreement with other values from different publications. In good agreement with different literature values are also the calculated bulk modulus, the shear modulus and the Young modulus. Because the phonon DOS is the fundamental parameters for evaluating the TSL the analysis of phonon DOS of H in ZrH₂ is made. The phonon DOS of ZrH₂ calculated in this work shows good agreement with the experimental results.

Once the density of states is known, the scattering law and all related quantities can be calculated using the program LEAPR. The scattering law is the basis for the Monte Carlo transport code from which the physical reactor parameters are derived. Our goal is the validation of neutron scattering data using experiments or measurements performed at the TRIGA Mark II research reactor by Jožef Stefan Institute.

6 LITERATURE

1. A. I. Hawari, I. I. Al-Qasir, V. H. Gillette, B. W. Wehring, T. Zhou, Ab Initio Generation of Thermal Neutron Scattering Cross Sections, Physor 2004, Chicago.
2. J. C. Holmes, Monte Carlo Calculation of Thermal Neutron Inelastic Scattering Cross Section Uncertainties by Sampling Perturbed Phonon Spectra, Raleigh, North Carolina, (2014).
3. Kresse, G., Hirsch C., <https://www.vasp.at/>, 2018.
4. Giannozzi, P., J.Phys.: Condens.Matter 29, 465901, 2017.
5. Parlinski, K., Phys. Rev. Lett. 78, 4063 (1997); K. Parlinski, Computer code phonon Cracow, 2012.
6. Togo, A., Scr. Mater., 108, 1-5, 2015.
7. Clark, S. J., Zeitschrift fuer Kristallographie 220(5-6) pp. 567-570, 2005.
8. Berendsen, et al., Comp. Phys. Comm. 91: 43-56, 1995.
9. Plimpton, S., J Comp Phys, 117, 1-19, 1995.
10. Wormald, J., Hawari, A. I. EPJ Web of Conferences, 146, 13002, 2017.
11. G. Kresse, J. Furthmüller, Phys. Rev. B 54 (1996) 11169.
12. P.E. Blöchl, Phys. Rev. B 50 (1994) 17953.
13. J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.
14. H.J. Monkhorst, J.D. Pack, Phys. Rev. B 13 (1972) 5188.
15. M. Methfessel, A.T. Paxton, Phys. Rev. B 40 (1989) 3616.
16. P.E. Blöchl, O. Jepsen, O.K. Andersen, Phys. Rev. B 49 (1994) 16223.
17. H. E. Flotow, D. W. Osborne, Heat Capacities and Thermodynamic Functions of ZrH₂ and ZrD₂ from 5 to 350°K and the Hydrogen Vibration Frequency in ZrH₂, The journal of chemical physics, October (1960).
18. J.F. Nye, Physical Properties of Crystals, Their Representation by Tensors and Matrices, Oxford Press, 1957 (Chapter VIII).
19. P. Zhang, B. T. Wang, C. H. He, P. Zhang, First-principles study of ground state properties of ZrH₂, Computational Material Science 50 (2011).
20. P. A. T. Olsson, A. R. Massih, J. Blomqvist, A. M. Alvarez Holston, C. Bjerken, Ab initio thermodynamics of zirconium hydrides and deuterides, Computational Materials Science 86 (2014).
21. W. Zhu, R. Wang, G. Shu, P. Wu, H. Xiao, J. Phys. Chem. C 114 (2010) 22361.
22. J.F. Nye, Physical Properties of Crystals, Oxford University Press, 1985.
23. Weaver J H, Peterman D J, Peterson D T and Franciosi A 198 1 *Phys. Rev. B* 23 1692.
24. Evans, A., Timms, D., Mayers, J., Bennington, S., 1996. Neutron-scattering study of the impulse approximation in ZrH₂. Phys. Rev. B - Condens. Matter Mater. Phys. 53, 3023–3031.