

Thermal Neutron Scattering Cross Sections of Thorium Hydride

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An ab initio approach is used to calculate the phonon frequency distribution of thorium hydride (ThH_2). The scattering law and the thermal neutron scattering cross sections for Th and H have been generated using this distribution. Due to the lack of experimental data, the results have been compared to zirconium hydride (ZrH_2) data that were generated using a classical lattice dynamics model. Based on this comparison, it is shown that the differences in properties of ThH_2 and ZrH_2 are entirely consistent with the physical differences between the two materials. Consequently, this work provides a set of data that is useful in nuclear reactor technology, and illustrates the utility of the ab initio approach as a unique predictive tool of the properties of materials that are of interest to nuclear reactor design.

KEYWORDS: *metal hydrides, thorium hydride, zirconium hydride, VASP, ab initio, phonon frequency distribution, thermal neutron scattering cross section*

1. Introduction

Metal hydrides represent a class of neutron moderators that is of interest in nuclear reactor design. This is mainly due to their strength and stability at elevated temperatures, while maintaining the excellent moderating properties of hydrogen [1]. An example of that is zirconium hydride, which has been widely used in TRIGA research reactors. Recently, renewed interest has emerged in power reactors fueled with uranium (or plutonium) dispersed in thorium hydride (ThH_2) [2]. To improve the accuracy of the design of such reactors, the need exists for proper data libraries that describe the interaction of thermal neutrons with the moderator constituents. Therefore, the aim of this paper is to discuss and present the generation of thermal neutron cross sections for ThH_2 using an ab initio approach.

Thermal neutron cross-sections are complicated by a sensitive dependence on the temperature and chemical state of the scattering materials. For polycrystalline materials such as thorium hydride, the details of the creation and absorption of lattice vibrations (i.e., phonons) must be taken into account. Traditionally, phonons have been calculated by proposing an analytic model for the interaction between atoms, evaluating the force constants between atoms, and constructing the dynamical matrix and diagonalizing it. The force constants used in the dynamical matrix calculation can be estimated in various ways. In some cases they are derived from thermodynamic properties such as low temperature specific heat or compressibility data. Alternatively, they could be deduced from experimental measurements of phonon dispersion relations using inelastic neutron scattering techniques. Basically, both approaches represent the fitting of theoretical models to experimental data. However, due to advances in computational power, the possibility now exists to perform detailed quantum mechanical ab initio simulations of atomic systems. These simulations are currently used in fields such as physics and materials science to predict the behavior of new and exotic materials. The use of such methods would allow direct calculations of the force constants from first principles. In the case of thermal neutron scattering, this would enable the generation of the phonon frequency distributions (i.e. density of states) and the scattering cross sections using new and more fundamental physical approaches.

2. ThH₂ crystal structure and lattice dynamics

ThH₂ has a body-centered tetragonal structure and belongs to the space group I4/mmm (Fig. 1). The unit cell is composed of 6 atoms. The Th atoms are located at (0,0,0) and (1/2,1/2,1/2), and the H atoms are located at (0,1/2,1/2), (0,1/2,3/4), (1/2,0,1/4) and (1/2,0,3/4). As optimized by VASP (Vienna ab initio Simulation Package) [3], this structure has the lattice constants $a=b= 4.04 \text{ \AA}$ and $c= 4.93 \text{ \AA}$, which agree with the experimental values $a=b= 4.10 \text{ \AA}$ and $c= 5.03 \text{ \AA}$ as determined by x-ray and neutron diffraction at room temperature [4].

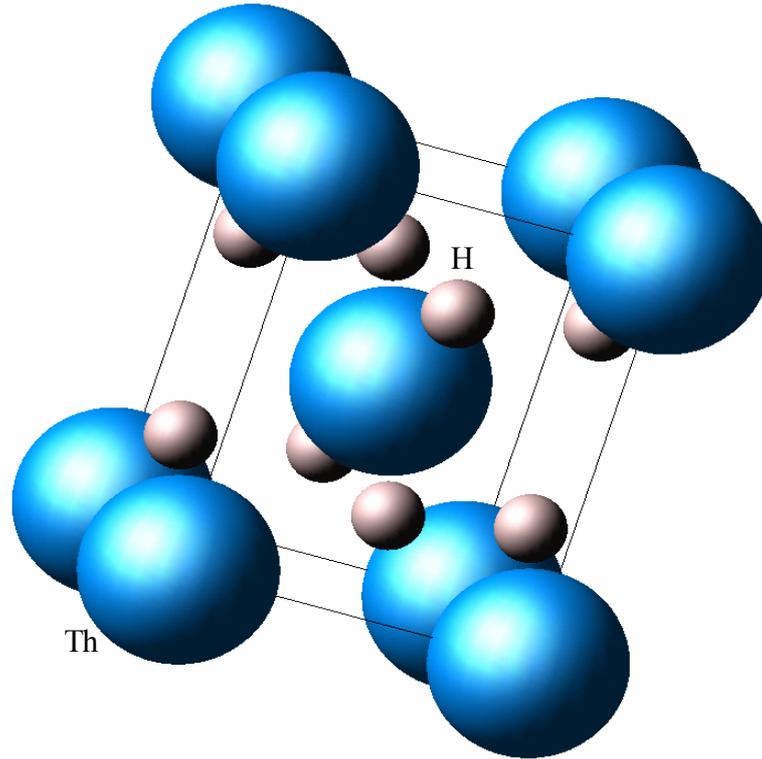


Fig. 1. The ThH₂ unit cell.

The VASP *ab initio* calculations of ThH₂ crystal are based on density functional theory, and utilize the generalized gradient approximation (GGA) with projector augmented wave (PAW) pseudopotential. VASP solves the generalized Kohn-sham equation by an iterative matrix diagonalization based on the minimization of the norm of the residual vector to each eigenstate and an optimized charge-density mixing routine. To calculate the dispersion relations a 3x3x3 supercell was used (162 atoms), and a plane-wave basis set with a 250 eV energy cutoff. The integration over the Brillouin zone was confined to 2x2x1 k-mesh points generated by the Monkhorst-Pack scheme. The phonon frequency distributions are determined from Hellmann-Feynman forces where these forces are computed from four independent displacements along x and z for the H and Th atoms using a displacement amplitude of 0.03 Å. Each displacement generates 3N force components, where N is the number of atoms in the super cell. Hence four displacements give 1944 Hellmann-Feynman forces. Finally, the partial and total phonon density of states of Th and H were obtained by sampling the dynamical matrix at randomly selected wave vectors in the reduced Brillouin zone using the PHONON code [5].

Figure 2 shows the dispersion relations along the highest symmetry points of the first reduced Brillouin zone; **Z**, **Γ**, **X**, **P**, and **N**, the lower branches are acoustical modes which are mainly due to the heavy Th atoms vibrations, while the higher modes are optical modes mainly due to the H atoms vibrations.

Unfortunately, no experimental data are available for comparison.

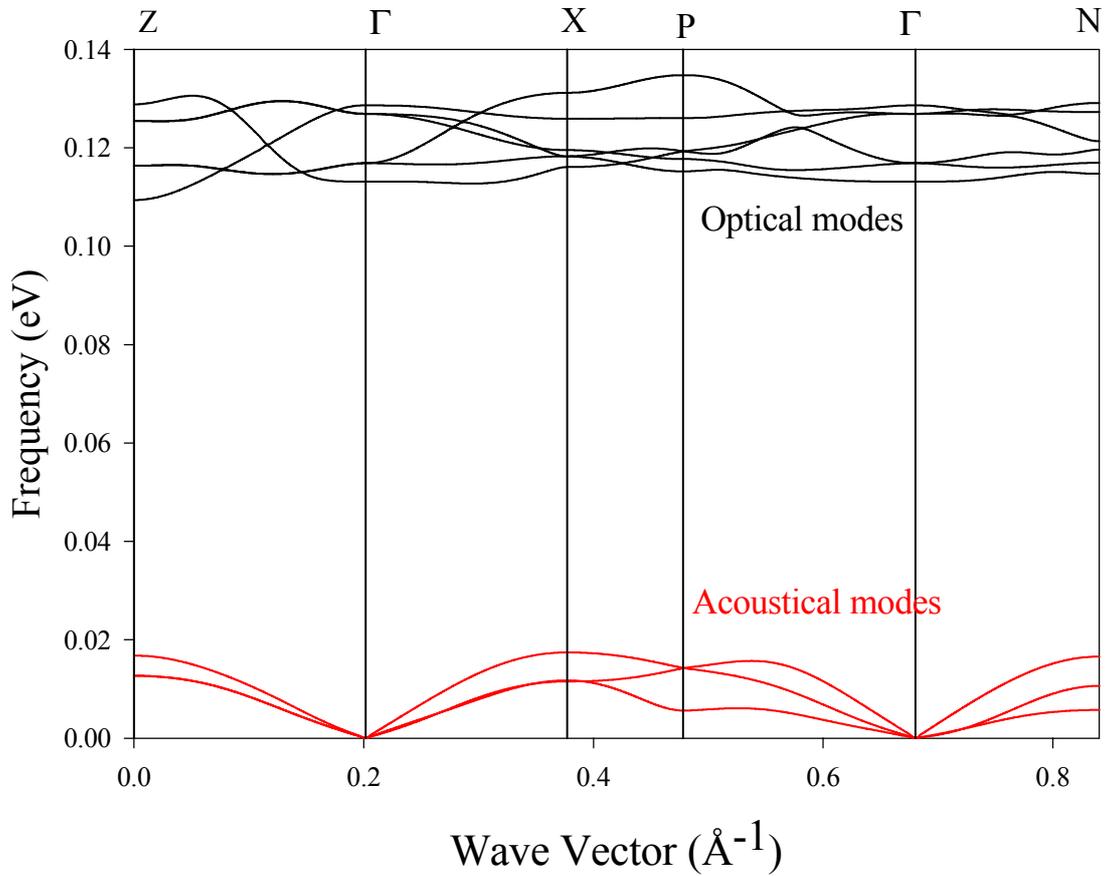


Fig. 2. Ab initio calculated ThH₂ dispersion relations (this work).

Figure 3 shows the total phonon frequency distribution for ThH₂ and ZrH₂. The total phonon density of states has two well-separated regions (due to the large mass ratio between Th and H): an acoustical region (0 - 0.017 eV), which is the preferable region for the Th atoms to vibrate, and an optical region (0.11 - 0.13 eV), which is mainly due to H atoms vibrations. The ab initio calculated total phonon density has an optical peak that is centered at 0.121 eV, which compares favorably to an estimated optical density of states that was measured by inelastic neutron scattering [6] and is centered at 0.123. The phonon frequency distribution of ZrH₂ was computed using a central-force lattice dynamics model [7] that approximated the body tetragonal structure of ZrH₂ (epsilon phase) by a face-centered cubic lattice. Four force constants were introduced to describe the interaction of a Zr atom with its nearest neighbors (8 H atoms), and next nearest neighbors (12 Zr atoms), and the interaction of a H atom with its next nearest neighbors (6 H atoms) and its third nearest neighbors (12 H atoms). The values of the force constants were obtained by fitting both specific heat and neutron scattering data [6].

Figures 4 and 5 show the partial phonon frequency distributions for H in ThH₂ and in ZrH₂, and for Th in ThH₂ and Zr in ZrH₂ in semi-log scale. Although the H acoustic modes are much less intense than the optical modes, these acoustic modes are very important for calculating the inelastic scattering cross sections, since the inelastic scattering cross section is sensitive to the phonon frequency distribution at low energy.

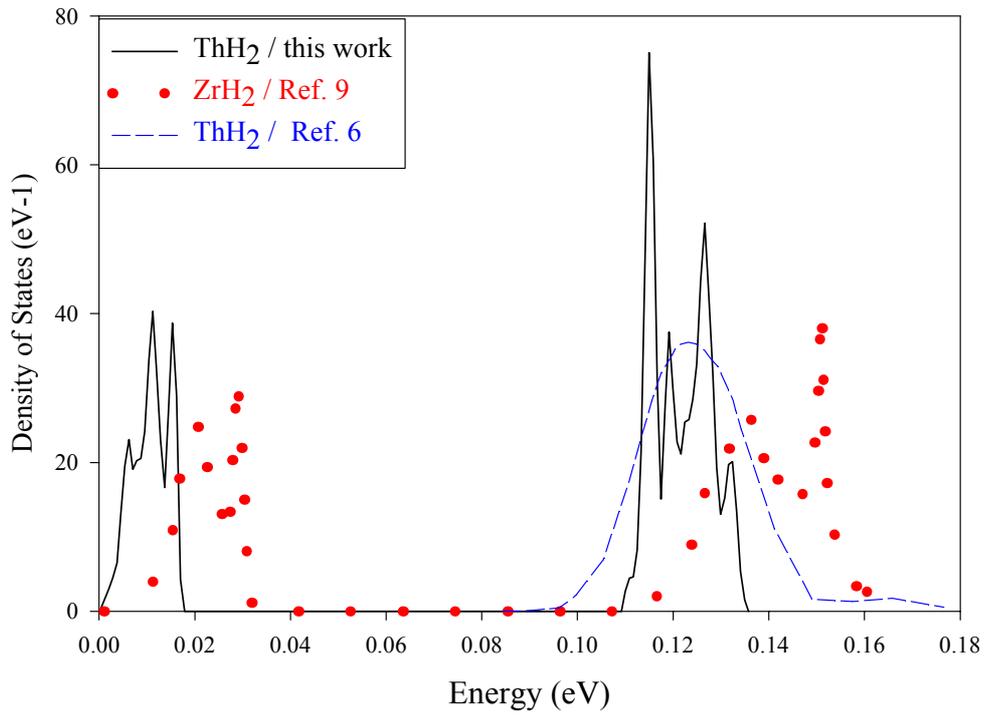


Fig. 3. The phonon frequency distribution of ThH₂ and ZrH₂.

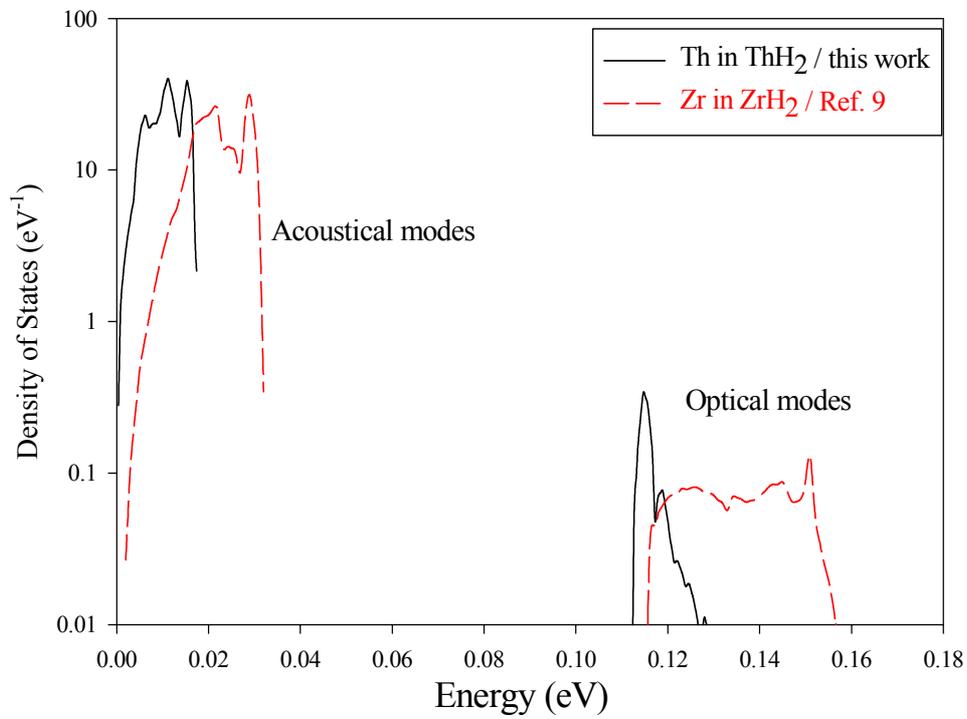


Fig. 4. Partial phonon frequency distribution of Th and Zr.

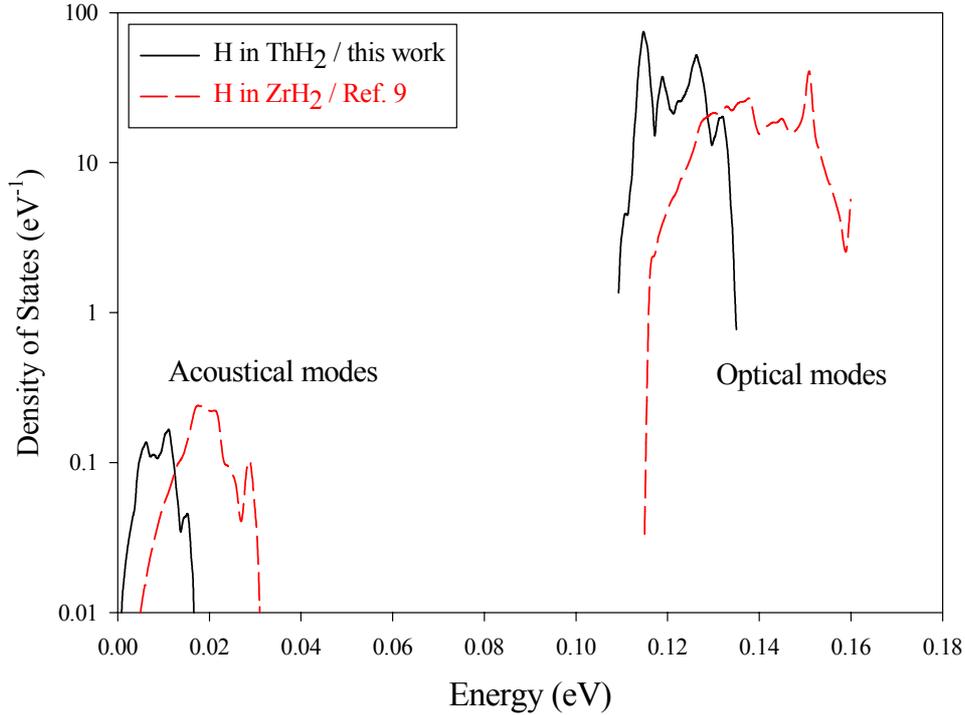


Fig. 5. Partial phonon frequency distribution of H.

3. Thermal neutron scattering cross sections

The data shown in Fig. 4 and Fig. 5 were utilized in the NJOY code system [8] to generate the thermal neutron scattering laws and cross sections at different temperatures. Figure 6 shows the cross section for H in ThH₂ (this work) and ZrH₂ [9] at 296 K and at 1200 K. At low energies, the H inelastic scattering cross section in ThH₂ and in ZrH₂ has similar features, but the H in ThH₂ has a higher cross section due to the higher values of the acoustical modes, which in both cases are small compared to the optical modes. Similar to the inelastic scattering cross section of hydrogen in ZrH₂, the inelastic scattering cross section of hydrogen in ThH₂ also shows oscillations at energies greater than 0.1 eV. Such structure is due to the details of the optical component of the hydrogen phonon frequency distribution. As the energy increases above 1 eV, the scattering cross sections are not affected by the chemical bonding of the H atoms. Figure 7 shows the thermal neutron scattering cross sections for Th in ThH₂ (this work) and ZrH₂ [9] at 296 K and at 1200 K. The inelastic scattering cross section for Th in ThH₂ has similar behavior to Zr in ZrH₂ but with higher values. This is due to the difference in the bound cross section for the two species. In addition, for low energies, the Th and Zr inelastic cross section show substantial differences in their behavior. The main reason for that is the domination of the one phonon creation and annihilation processes, which depend linearly on the frequency spectra.

4. Conclusions

In this work, we present calculations of the ThH₂ thermal neutron scattering cross sections using phonon frequency distributions generated from ab initio atomistic simulations. Based on our extensive literature searches, this work presents the first complete set of the fundamental vibrational data (i.e., phonon spectra) that are required for the generation of the thermal neutron scattering cross sections for this material. Using this approach, we were able to calculate all the vibrational modes including the

acoustical modes of H, which are not easy to determine experimentally. This data is currently available by contacting our group.

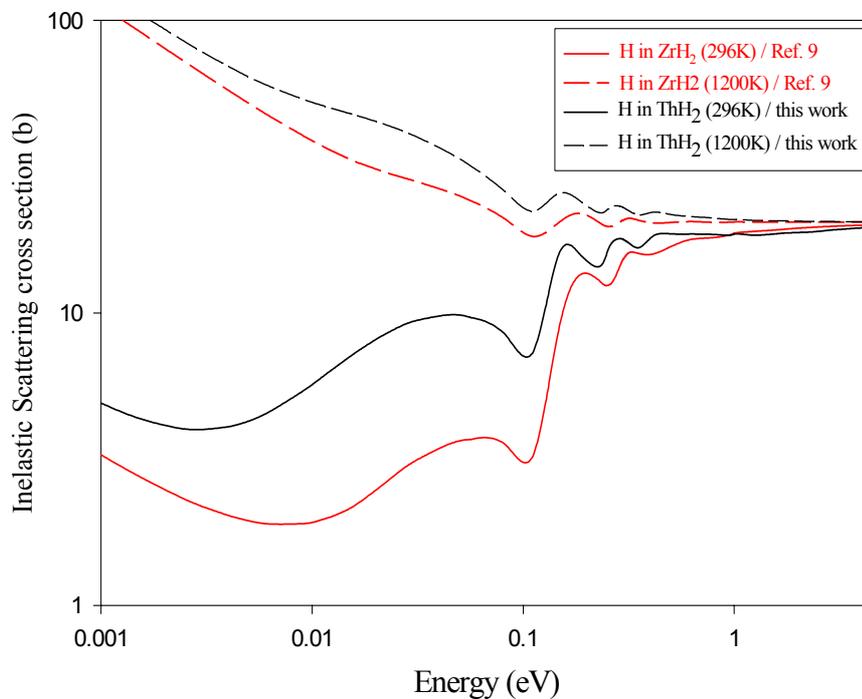


Fig. 6. Inelastic scattering cross section of H in ThH₂ and in ZrH₂.

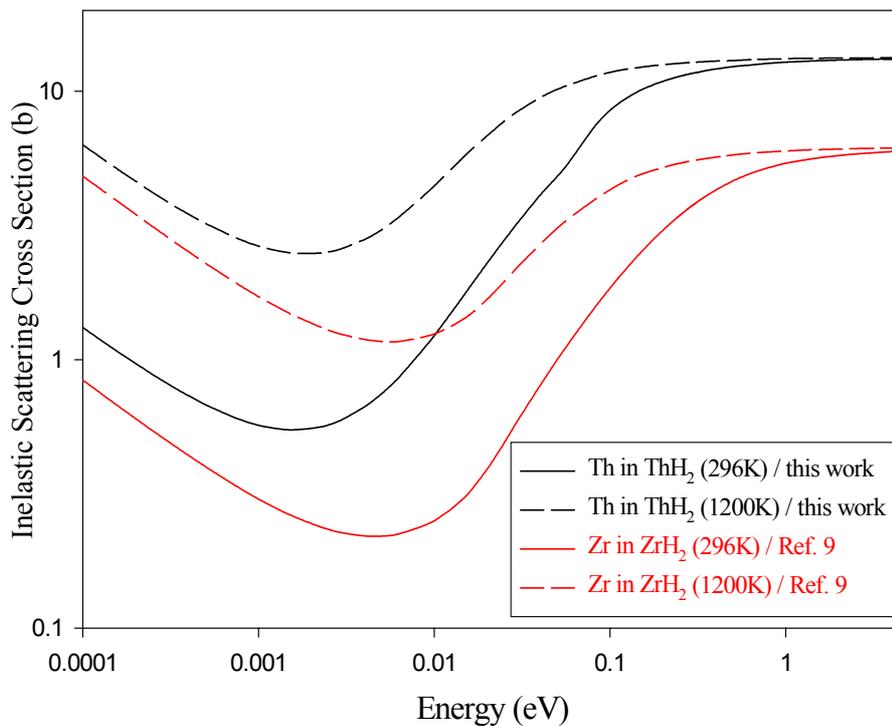


Fig. 7. Inelastic scattering cross section of Th and Zr.

Acknowledgments

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References

- 1) W. M. Muller, J. P. Blackledge, and G. G. Libowitz, "Metal Hydrides," Academic Press, New York, 22, (1968).
- 2) Ehud Greenspan, private communications, 2003. Also see <http://neri.ne.doe.gov/>.
- 3) G. Kresse, and J. Furthmuller, "Vienna Ab-Initio Simulation Package, VASP the Guide," Vienna, 2002.
- 4) R. E. Rundle, C. G. Shull and E. O. Wollan, Acta Cryst., **5**, 22 (1952).
- 5) K. Parlinski, "PHONON manual, Version 3.11," Cracow, 2002.
- 6) M. Dietrich, W. Reichardt, and H. Rietschel, Solid State Commun., **21**, 603 (1977).
- 7) E. L. Slaggie, J. Phys. Chem. Solids., **29**, 923 (1968).
- 8) R. E. MacFarlane, and D. W. Muir, "The NJOY Nuclear Data Processing System, Version 91," LA-12740M, Los Alamos National Laboratory, (1994)
- 9) R. E. MacFarlane, "New Thermal Neutron Scattering Files for ENDF/B-VI, Release2," LA-12639-MS, (1994).