Measurement of the double-differential neutron cross section of UO$_2$ from room temperature to hot full power conditions

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Abstract. Experimental phonon densities of states of UO$_2$ have been deduced from double-differential neutron scattering data measured at 300 K, 600 K and 900 K using the IN6 time-of-flight spectrometer of the Institute Laue-langewin (ILL). The comparison with ab initio phonon spectra obtained at the North Caroline South University from first-principle calculations confirms that harmonic vibrations of the atoms cannot accurately reproduce the phonon broadening related to the oxygen atoms.

1 Introduction

The slow-neutron scattering properties of uranium dioxide (UO$_2$) have been the subject of many experimental and theoretical studies since the pioneer works reported in the sixties [1, 2]. Major results about the acoustic and optical vibration modes of UO$_2$ were published in a series of symposia on neutron scattering and neutron thermalization organized by the International Atomic Energy Agency, between 1960 and 1977 [3, 4]. At room temperature, crystal dynamics properties of UO$_2$ have been well described by Dolling using dispersion curves measured at the triple-axis-crystal spectrometer at Chalk River [5]. Despite major experimental and theoretical improvements, Pang [6, 7] recently shows that first-principles phonon density of states (PDOS) simulations cannot accurately reproduce inelastic neutron scattering measurements for UO$_2$, carried out at 295 K and 1200 K using the ARCS spectrometer of the Spallation Neutron Source (SNS). Large differences between experiments and calculations are attributed to anharmonic linewidth broadening, which is observable even at room temperature. The present work aims to complement the work of Pang by providing experimental phonon densities of states for UO$_2$ from room temperature to 900 K in order to stimulate theoretical studies for improving comparison to experiment.

2 Governing equations

In the low neutron energy range, typically below 1 eV, the slowing down of neutrons in UO$_2$ is affected by the chemical bonds between the uranium and oxygen atoms. The incoherent scattering approximation allows to neglect the interference terms and to express the double differential scattering cross section of each atom separately. If $T$ is the temperature of the target and $k_B$ is the Boltzmann constant, the temperature-dependent double differential scattering cross section for $X$ =$^{238}$U (or $X$ =$^{16}$O) in UO$_2$ can be written as [8]:

$$\frac{d^2\sigma_{\alpha\beta}}{dE'd\theta} = \frac{\sigma^0_{\alpha\beta}}{2k_BT} \int \frac{E'}{E} e^{-\beta S^X_T(\alpha, \beta)},$$  \hspace{1cm} (1)

where $\sigma^0_{\alpha\beta}$ is the neutron scattering cross section at $T=0$ and $S^X_T(\alpha, \beta)$ is the symmetric form of the so-called thermal scattering law [9], which is defined as a function of the momentum transfer $q$:

$$\alpha = \frac{q^2\hbar^2}{2M_Xk_BT} = \frac{E'+E-2\mu\sqrt{E'E}}{\lambda_Xk_BT},$$  \hspace{1cm} (2)

and of the energy transfer $\varepsilon = \hbar\omega$:

$$\beta = \frac{\hbar\omega}{k_BT} = -\frac{E'-E}{k_BT},$$  \hspace{1cm} (3)

where $\mu = \cos(\theta)$ is the cosine of the scattering angle in the laboratory system and $\lambda_X$ is the ratio of the mass $M_X$ of the scattering atom X to the neutron mass. An analytical form of $S^X_T(\alpha, \beta)$ was established for a cubic symmetry by using an isotropic harmonic potential which simplifies the complex averaging over all the possible orientations of the molecules. This approximation, known as the Gaussian approximation [10], lead to the following phonon expansion:

$$S^X_T(\alpha, \beta) = e^{-s_\alpha s_\beta} \sum_{n=0}^{\infty} \frac{1}{n!} (s_\alpha s_\beta)^n T_{\alpha}(\beta),$$  \hspace{1cm} (4)

where $s_\lambda$ stands for the Debye-Waller coefficient and $T_{\alpha}(\beta)$ has the generic form:

$$T_{\alpha}(\beta) = \int_{-\infty}^{\infty} T_1(\beta') T_{\alpha-1}(\beta-\beta') d\beta'.$$  \hspace{1cm} (5)
The zero-phonon term $T_0(\beta) = \delta(\beta)$ corresponds to the elastic peak and the one-phonon term explicitly depends on the phonon density of states $\rho_X(\beta)$:

$$T_1(\beta) = \frac{\rho_X^X(\beta) e^{-\beta/2}}{2\lambda \sinh(\beta/2)}.$$  \hfill (6)

In the present work, we use ab initio phonon spectra obtained at the North Carolina South University from first-principle calculations performed with the vasp code [11].

3 Experiment

Experimental phonon densities of states of UO$_2$ were deduced from double-differential neutron scattering experiments performed at the IN6 time-of-flight spectrometer of the Intitute Laue-Langevin (ILL). Three temperatures $T$ were investigated, which correspond to “cold” zero-power (300 K), hot-zero power (600 K) and hot-full power (900 K) operating conditions in critical assemblies and pressurized water reactors. A simplified model of IN6 is shown in Fig. 1. The neutron time-of-flight technique consists of measuring the time $t$ traveled by neutrons from the sample until their detection at a given scattering angle $\theta$. The non-relativistic time-energy relation $E' = (72.298L/t)^{2}$, where $E'$ is in eV, $L$ in meter and $t$ in microseconds, is used to obtain the experimental neutron yield $Y_{th}^T(\theta, E')$ as a function of the outgoing neutron energies $E'$. In the present experiment, a rectangular monoenergetic neutron beam of $E = 3$ meV ($\lambda = 5.1$ Å) was focused to the sample, which is mounted in a high temperature furnace placed at the center of the spectrometer. The detection set-up is at a flight distance $L = 2.48(1)$ m from the sample. It forms a $^3$He detector array that covers scattering angles ranging from $10^\circ$ to $115^\circ$.

The sample is a $4.09(1)$ cm long cylinder composed of a stack of four depleted UOX pellets of $8.26(1)$ mm diameter. The total weight of the sample is $23.642(1)$ g, with a mass-fraction composition in $^{238}$U, $^{236}$U, $^{235}$U, $^{234}$U and $^{18}$O of $87.598(1)\%$, $0.005(1)\%$, $0.264(1)\%$, $0.002(1)\%$ and $12.131(1)\%$, respectively. The UO$_2$ sample was sealed in a glass tube under vacuum and encapsulated in a niobium sample-holder tube. An empty “dummy” sample was prepared to measure the background contribution.

The experiment consisted in a five days sequence of UO$_2$ and “dummy” sample measurements, including a short irradiation of a vanadium sample. As this material nearly behaves as a pure incoherent elastic scatterer, its elastic scattering peak is used as reference for calibration purpose and detector efficiency correction. The data reduction steps were handled with the ILL in-house code LAMP.

4 Thermal scattering law

The experimental quantity of interest for this work is the symmetric form of the thermal scattering law $S_{th}^T(\theta, E')$, from which the contribution of the quasielastic neutron scattering peak is removed. Working in the incoherent scattering approximation leads to:

$$S_{th}^T(\theta, E') = S_{th}^T(\theta, E') \sqrt{E E'/E'/d\theta} - S_{exp}^T(\theta, E'). \hfill (7)$$

The contribution $S_{exp}^T(\theta, E')$ was approximated by a pseudo-Voigt function.

The flight time of each neutron has been simulated with TRIPOLI4®. For convenience, we have only taken into account a central detector ring of 30 cm high, because $^3$He detectors placed below and above the central detector ring only serve to gain in statistics. The time distribution of the initial neutron burst originating from a Fermi chopper is not included in the simulation. Therefore, $S_{th}^T(\theta, E')$ is calculated from the neutron yields $Y_{th}^L$ provided by TRIPOLI4® as follows:

$$S_{th}^T(\theta, E') = \int_{L}^{\infty} R_E(\theta, t) Y_{th}^T(\theta, t) \sqrt{E E'/d\theta}dt - S_{th}^T(\theta, E'). \hfill (8)$$

The probability density functions $R_E(\theta, t)$ stand for the time-dependent experimental response function of the spectrometer. For IN6, the response function is well approximated by a Gaussian. Its full width at half maximum $\Delta t = 43(5) \mu s$ was fitted to the elastic peak of the vanadium spectra.

Figure 2 compares the experimental $S_{exp}^T$ and theoretical $S_{th}^T$ obtained at $\theta = 90^\circ$ as a function of the energy transfer $\varepsilon$. The five normal modes of vibration of UO$_2$ [5] can be distinguished around 10 meV, 20 meV, 35 meV, 55 meV and 70 meV. The two first peaks correspond to the translational and longitudinal acoustic modes of the uranium atoms, while the higher energy structures are dominated by the optical modes of the oxygen atoms. At the backward scattering angles, these structures are well reproduced by the simulation. At the forward angles, they are smooth in the experimental $S_{exp}^T$ due to the multiple scattering of neutrons which have to cross the sample before being detected.
in microseconds, is used to obtain the experimental neutron beam of a mass-fraction composition in $^{238}$U, $^{236}$U, $^{235}$U, $^{234}$U and a stack of four depleted UOX pellets of 8.26(1) mm diameter of the Intitute Laue-Langevin (ILL). Three temperature furnace placed at the center of the spectrometer. The detection set-up is at a flight distance $\theta$ meters from the sample until their detection at a given scattering angle $\theta$. The non-relativistic time-energy relation $E = \sqrt{\beta^2 + m^2 c^4}$ as a function of the outgoing neutron energy $E$. The experimental quantity of interest for this work is the contribution $S^T_{\exp}$ due to the multiple scattering of neutrons which have to cross the sample before being detected.

5 Phonon density of states

In order to reduce the contribution of the multiple scattering corrections, we decided to determine experimental phonon spectra $P^T_{\exp}(\alpha, \beta)$ for $^{238}$UO$_2$ from neutron yields corresponding to scattering angles ranging from 90° to 115°. By introducing Eq. (6) in Eq. (4) for $n = 1$ and by removing the contribution of the elastic peak ($n = 0$), the incoherent one-phonon approximation leads to:

$$P^T_{\exp}(\alpha, \beta) \approx \frac{2 \beta \sin \beta / 2}{\alpha} S^T_{\exp}(\alpha, \beta).$$  

As finite $\alpha$ boundaries are delimited by the allowed kinematic range of the IN6 spectrometer, $P^T_{\exp}(\beta)$ can be deduced as follows:

$$P^T_{\exp}(\beta) \approx \lim_{\alpha \to 0} P^T_{\exp}(\alpha, \beta).$$

In view of obtaining $P^T_{\exp}(\alpha, \beta)$ at $\alpha = 0$, we have smooth out fluctuations due to nuclei dynamics by using a log-log extrapolation of the cumulative distribution function of $P^T_{\exp}(\alpha, \beta)$. The obtained $P^T_{\exp}$ are shown in Fig. 3 as a function of the energy transfer $\varepsilon$ and are compared to results which have been linearly interpolated between PDOS measured by Pang at 295 K and 1200 K [7]. A satisfactory agreement between the two data sets is observed, at least up to $\varepsilon = 60$ meV. Above 60 meV, the sharp differences come from the increasing broadening of the phonon linewidth due to the response function of IN6, while Pang has concatenated PDOS obtained at three adequately chosen neutron wave lengths, corresponding to incident neutron energies $E$ of 30 meV, 60 meV and 120 meV.

Experimental phonon densities of states of $^{238}$UO$_2$ can only be compared with their theoretical analogues via $\text{tripoli}$ simulations that take into account multiphonon and multiple scattering contributions. Figure 4 shows the agreement achieved when the $ab$ $\text{initio}$ densities of states established at the North Carolina South University are introduced in the calculations. A closer inspection of the results indicates that the Monte-Carlo simulations are still not able to accurately describe the phonon linewidth broadening, especially around 30 meV. Similar discrepancies were already pointed out by Pang and are attributed to anharmonic vibrations of the atoms. Indeed, anharmonicity is always present in real crystal. It may cause interactions among phonons which are neglected in the present model. Despite anharmonic effects in neutron scattering by crystalline materials were the subject of numerical calculations from the early 1960s [13, 14], they still remain an issue to study the resonance line shape of $^{238}$U in $^{238}$UO$_2$ from room temperature to 1800 K [15], or to explain properties of $^{238}$UO$_2$ in extreme temperature and pressure conditions [16].

6 Conclusions

The present work reports experimental phonon density of states of $^{238}$UO$_2$ at 300 K, 600 K and 900 K. The comparison of the data with Monte-Carlo simulations confirms that the phonon broadening related to the uranium and oxygen atoms could have different origins. A more sophisticated treatment not only relying on anharmonicity is needed to account for the temperature on incoherent interactions. Following the conclusion of Ref. [21] for actinides, harmonic softening arising from a temperature-dependent harmonic potential could also play a role in the observed results.

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Figure 3. (Color online) Experimental PDOS for UO$_2$ at 300 K, 600 K and 900 K measured at ILL and SNS [7].

Figure 4. (Color online) Experimental and theoretical PDOS for UO$_2$ at 300 K, 600 K and 900 K.

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