

Thermal scattering law for ice based on neutron time-of-flight experiments carried out at the SEQUOIA spectrometer at the Oak Ridge National Laboratory

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Abstract. Precise estimation of neutron thermalization in moderators relies on high-fidelity thermal scattering cross-section data governed by the thermal scattering law (TSL). The Institut de Radioprotection et de Sûreté Nucléaire (IRSN) has been working on the development of improved TSL for light water ice. Many polymorphic phases of light water ice exist depending on the thermodynamic conditions. The most common type of ice at standard pressure and temperature below water freezing point (273.15 K) is ice-*Ih*. It is essential to have high-resolution experimental double differential data for developing and/or validating TSL for moderator materials. Existing experimental double-differential scattering data for ice-*Ih* are extremely sparse and of limited quality. New high-quality double-differential measurements for ice-*Ih* over multiple temperatures and incident neutron energies would directly support the validation and improvement of ice-*Ih* TSL models for criticality safety applications.

Series of time-of-flight (TOF) inelastic neutron scattering experiments on ice-*Ih* at temperatures starting at 271 K and down to 6 K, have been carried out at the SEQUOIA spectrometer at the Spallation Neutron Source (SNS) at the Oak Ridge National Laboratory (ORNL), United States. The experiments have been performed for incident neutron energies, $E_i = 11, 55, 160, 250$, and 600 meV, to explore different excitation energies in the vibrational phonon spectrum. This paper presents the thermodynamic conditions and the details of the TOF measurements on ice-*Ih* and the derived phonon spectrum from the experimentally measured double differential data. A study of the variation of the phonon spectrum of ice-*Ih* as a function of temperature is highlighted, and a preliminary TSL evaluation is developed based on the experimental phonon spectrum.

1 Introduction

In the low energy range (< 10 eV), there is an exchange of energy and momentum of neutrons with the interacting atom/molecule, and this phenomenon is often described by thermal scattering law (TSL), and the cross-sections are termed as thermal scattering cross-sections. The precise estimation of the thermalization of neutrons in moderators relies on high-fidelity thermal scattering cross-sections data. The Institut de Radioprotection et de Sûreté Nucléaire (IRSN) has been working on the development of improved TSL for light water ice, in particular, the most common type of ice at normal pressure and near water freezing point temperature, i.e., ice-*Ih*. It is known that the behavior of ice-*Ih* shows many anomalies [1]. These include a negative thermal expansion at $T < 65$ K, a large transition in the thermal expansion coefficient at 101 K [1, 2], a tendency to transfer to the proton-ordered ferroelectric phase ice-*XI* at $T < 72$ K, significant increase of proton mean kinetic energy around 270 K [3, 4], and others. All these anomalies are not fully understood yet and require a detailed study of the behavior of ice-*Ih* dynamics over a wide range of temperatures and energies. Not

only are the dynamics of ice-*Ih* of interest in fundamental physics and chemistry, but this information is also important in nuclear fuel cycle applications. The dynamics of ice-*Ih* can influence calculations of the criticality safety assessment for enrichment facilities, transportation casks, fresh fuel storage, and criticality safety studies. Criticality safety calculations for abnormal configurations with ice acting as a neutron moderator can be sensitive to details of the scattering of thermal neutrons. Also, active research is underway on advanced nuclear systems using ice-*Ih* as a neutron moderator (operating around 80 K) [5]. International recommendation from organizations like IAEA and UKAEA highlights the need to design packages to be transported at low temperature (as low as 233.15 K) [6, 7]. This recommendation emphasizes the need for ice neutron scattering data in the temperature range around 253-293 K.

Nowadays, to meet this need, the nuclear data used by criticality safety experts are derived from extrapolations between few existing temperatures in the TSL libraries and are based on physics models that approximate the thermal scattering effect at low temperatures. However, considering the importance of TSLs in neutronics and the impact of a reduction in the moderator temperature on the effective

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cross-sections, it is important that criticality safety calculations are carried out with validated data.

2 Need for new measurements for ice-*Ih*

TSLs for a majority of moderator materials available in the standard nuclear data libraries are based on phonon spectra either derived from time-of-flight (TOF) inelastic neutron scattering (INS) measurements or using modern computational methods like density functional theory (DFT) or molecular dynamics (MD). Although DFT and MD are powerful computational tools that have had recent success in TSL evaluations, these methods are not free of inherent biases and limitations. Following the importance and need for accurate modeling of neutron scattering distributions in energy and angle, TSLs for ice-*Ih* were recently developed for the ENDF/B-VIII.0 and JEFF-3.3 nuclear data libraries. For the ENDF/B-VIII.0 ice-*Ih* TSL [8], lattice dynamics based on forces calculated with DFT were used to generate the phonon spectrum for hydrogen and oxygen. Total cross section and INS experimental data were used to make a slight adjustment to the translational and librational region weighting of the derived phonon spectra. However, the detailed structure of the TSL was developed independent of any neutron scattering measurements. For the JEFF-3.3 ice-*Ih* TSL [9], an experimentally derived phonon spectrum based on INS experiment was applied in a physics model for hydrogen, and oxygen is treated as a free gas. While theoretically calculated total cross sections for both TSLs compare well to the limited experimental data available, with some notable deviation below about 25 meV, large differences are evident between the two TSLs.

The integral performance of the ENDF/B-VIII.0 ice-*Ih* TSL has been validated with an experimental pulsed-neutron die-away (PNDA) diffusion benchmark [10], but this does not directly validate the TSL physics model or guarantee that the TSL will perform acceptably in varying criticality safety scenarios. Except for comparing theoretically calculated total cross sections to limited experimental data [11], the performance of the JEFF-3.3 TSL has not been validated. There are no existing experimental critical benchmarks that contain and/or are sensitive to ice-*Ih*. Double differential scattering measurements constitute a powerful basis for generating or validating TSLs and can be used to identify and resolve biases or limitations in theoretical models. Also, theoretically generated TSLs based on different methodologies needs an extensive multidimensional validation, based on experimentally measured double differential and total cross section data. Existing experimental double-differential neutron scattering data for ice-*Ih* is extremely sparse and of limited quality. New high-quality double-differential measurements for ice-*Ih* over multiple temperatures and incident energies would directly support the validation and improvement of TSL models for criticality safety applications. Moreover, such measurements would provide new insight into the physics and dynamics of the ice-*Ih*.

3 TOF INS experiments for ice-*Ih*

A series of TOF INS experiments for ice-*Ih* at low temperatures (starting at 271 K and down to 6 K) have been carried out at the SEQUOIA spectrometer [12], Spallation Neutron Source, at the Oak Ridge National Laboratory. An annular aluminum container with an outer diameter of 29 mm and height 53 mm was used and, the sample thickness of 0.1 mm to minimize multiple scattering effects. The measurements were performed at $T = 6, 100, 200, 233, 243, 253, 263$, and 271 K. The energies for which the experiments have been performed are:

- **11 meV:** to resolve the first acoustic peak around 7 meV.
- **55 meV:** to resolve the translational vibration modes of ice molecules in the energy range from 0 to 40 meV.
- **160 meV:** to resolve the librational (hindered rotation) band around 50 meV to 140 meV.
- **250 meV:** to resolve the H-O-H bending mode around 200 meV.
- **600 meV:** to resolve the O-H stretching modes around 400 meV.

Different sets of measurements at different incident neutron energies will help explore all relevant features of the phonon spectrum of ice-*Ih* at different excitation energies. Phonon spectra for all the temperatures were derived from the double differential data following the standard data reduction procedure, and is presented in the next section.

4 Results

4.1 Phonon spectrum of ice-*Ih*

The derived phonon spectrum with incident neutron energies, $E_i = 11, 55, 160, 250$, and 600 meV are presented in Fig. 1-5, respectively. A thorough investigation

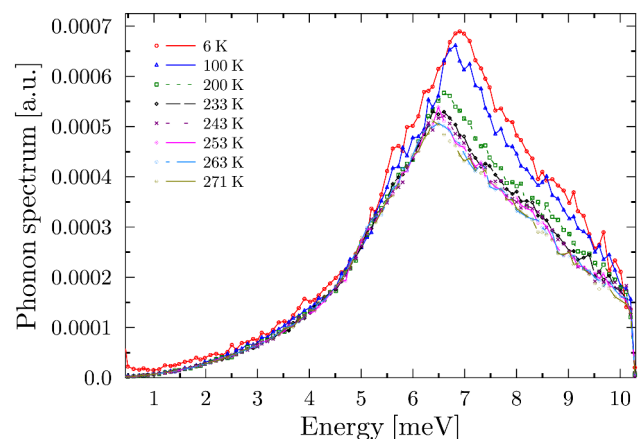


Figure 1. Variation of the first acoustic peak in the phonon spectrum of ice-*Ih* with temperature. The incident neutron energy E_i of this measurement is 11 meV.

of the changes in the dynamic structure factor and other physical properties as a function of temperature, is needed

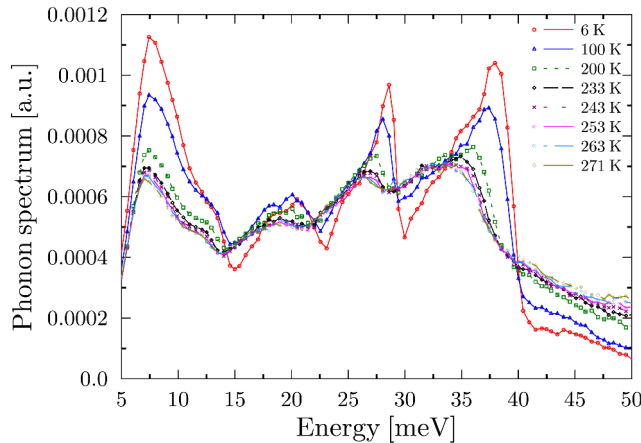


Figure 2. Variation of the translational vibration in the phonon spectrum of ice-*Ih* with temperature. The incident neutron energy E_i of this measurement is 55 meV.

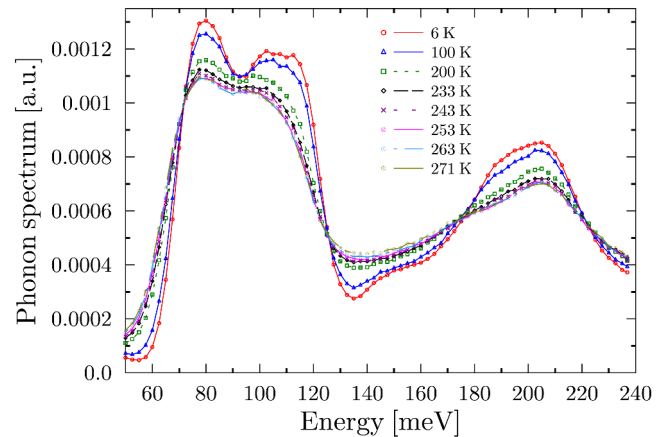


Figure 4. Variation of the H-O-H bending mode (around 200 meV) in the phonon spectrum of ice-*Ih* with temperature. The incident neutron energy E_i of this measurement is 250 meV.

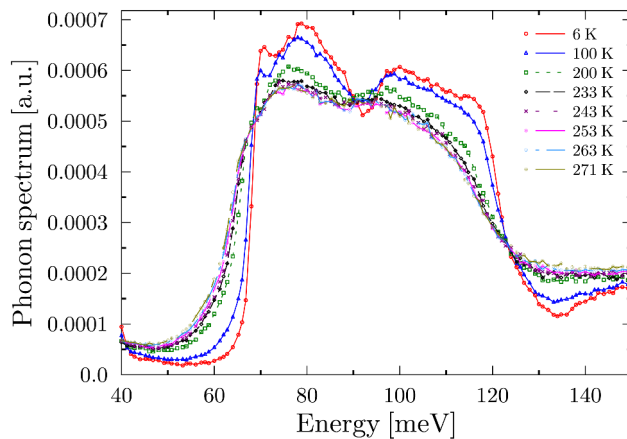


Figure 3. Variation of the libration band (between 50 and 140 meV) in the phonon spectrum of ice-*Ih* with temperature. The incident neutron energy E_i of this measurement is 160 meV.

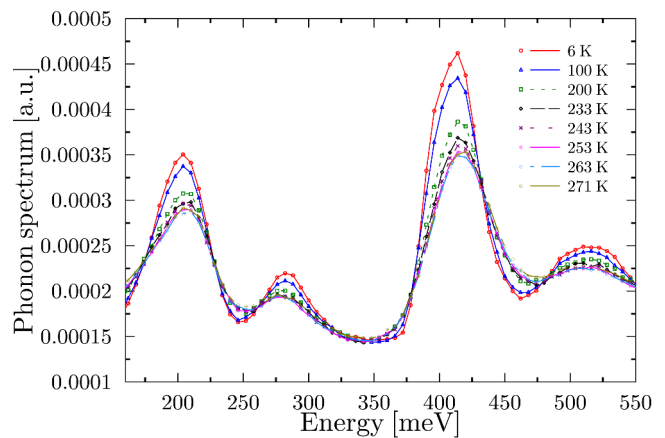


Figure 5. Variation of the O-H stretching mode (around 400 meV) in the phonon spectrum of ice-*Ih* with temperature. The incident neutron energy E_i of this measurement is 600 meV.

to be able to prepare accurate TSLs at low temperatures. One of the objectives of the present work is to investigate the impact of temperature on the dynamic structure factor of ice-*Ih*. Any significant change in the dynamic structure factor of ice-*Ih* with temperature, will be reflected in the phonon spectrum. A visual analysis of the phonon spectrum presented in Fig. 1-5, clearly indicates that the phonon spectrum of ice-*Ih* is sensitive to temperature in terms of the shape, peak energies, and their intensities. The current practice for developing TSL data for materials with negligible thermal expansion involves providing one single phonon spectrum for all the temperatures. However, from the phonon spectrum presented in this work, it is evident that this approximation will not hold true for Ice-*Ih* as the phonon spectrum changes drastically depending on the temperature of Ice-*Ih* and this change will impact the generated TSL.

4.2 Total cross section of ice-*Ih*

A preliminary TSL evaluation for ice-*Ih* at 115 K has been prepared based on the experimental phonon spectrum of 100 K. The energy resolution of the phonon spectrum changes at different incident neutron energy, and merging different data to obtain a full phonon spectrum with a significantly varying resolution is challenging. Consequently, only the data up to the rotation band (i.e., $E_i = 11, 55$, and 160 meV data) have been stitched together. The bending and stretching modes of the phonon spectrum are approximated using discrete oscillators, and oxygen is modeled as Free Gas. It should be noted that no adjustments to the phonon spectrum have been made to generate the TSL. The total cross section obtained using the newly generated TSL evaluation is presented in Fig. 6 and the results are compared with the ENDF/B-VIII.0, JEFF-3.3 ice-*Ih*, and experimental data by Torres *et al.* [11], providing promis-

ing results. The present validation is limited to the only total cross-section data for ice-Ih available in the literature [11] and a thorough verification and validation of the TSL is still a matter of future work.

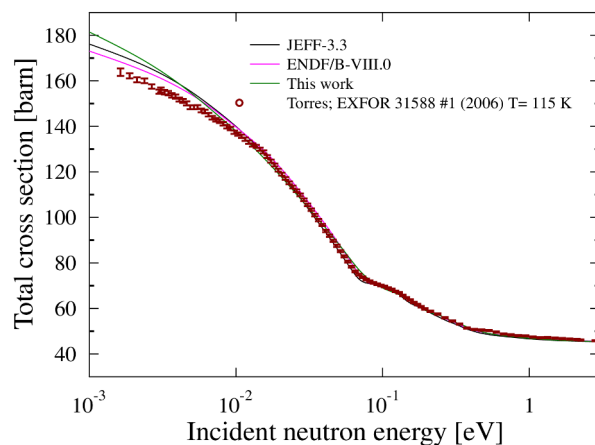


Figure 6. Comparison of total cross-section of ice-Ih at T=115 K with ENDF/B-VIII.0, JEFF-3.3, and this work.

5 Conclusions

Time-of-flight inelastic neutron scattering measurements have been carried out on ice-Ih for a series of temperatures between 6 and 271 K at the SEQUOIA spectrometer at SNS. The derived phonon spectrum for different incident neutron energies and their variation with temperature are presented. The translation, libration, bending, and stretching modes of the phonon spectrum were resolved by choosing different incident neutron energies. It was observed that the phonon spectrum is sensitive to temperatures, and care must be taken while developing TSL data for Ice-Ih for different temperatures. New TSL evaluation was developed using the measured phonon spectrum and is compared with the existing experimental total cross section data by Torres *et al.*, showing good agreement.

Further work is needed towards multiphonon correction of the experimental data and comparing the results with the experimentally measured double differential data following Monte Carlo simulations of the SEQUOIA experimental setup. It is envisioned that the robust validation basis resulting from these experiments will lead to a next-generation TSL evaluation for ice-Ih based on significantly improved material and physics models.

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References

- [1] M. K. Gupta, R. Mittal, Baltej Singh, S. K. Mishra, D. T. Adroja, A. D. Fortes, and S. L. Chaplot, "Phonons and anomalous thermal expansion behavior of H₂O and D₂O ice Ih," *PHYSICAL REVIEW B* **98**, 104301 (2018).
- [2] David T. W. Buckingham, J. J. Neumeier, Sueli H. Masunaga, Yi-Kuo Yu, "Thermal Expansion of Single-Crystal H₂O and D₂O Ice Ih," *PHYSICAL REVIEW LETTERS* **121**, 185505 (2018).
- [3] A. Pietropaolo, R. Senesi, and C. Andreani, A. Botti, M. A. Ricci, and F. Bruni, "Excess of Proton Mean Kinetic Energy in Supercooled Water," *PRL* **100**, 127802 (2008).
- [4] A. Pietropaolo et al., "Quantum Effects in Water: Proton Kinetic Energy Maxima in Stable and Supercooled Liquid," *Brazilian Journal of Physics*, vol. **39**, no. **2**, (2009).
- [5] Advanced Moderators for Intense Cold Neutron Beams in Materials Research", <https://www.iaea.org/projects/crp/f12026>.
- [6] Technical report, "IAEA Safety Standards for protecting people and the environment: Regulations for the Safe Transport of Radioactive Material," Specific Safety Requirements, No. SSR-6.
- [7] SG-3: Criticality Benchmark: A proposal for a benchmark examining the effect of temperature on the neutron multiplication factor for PWR fuel assemblies.
- [8] J. C. Holmes and M. L. Zerkle, "Production of the thermal scattering law and neutron scattering cross sections for ice from first principles," International Conference on Nuclear Criticality Safety (ICNC 2015), Charlotte, NC, USA.
- [9] F. Cantargi, J. R. Granada and J. I. Marquez Damian Nuclear Data Group - Neutron Physics Department Centro Atomico Bariloche - Argentina (CAB), JEFF-3.3 TSL evaluation for ice (2016).
- [10] J. Holmes, M. Zerkle and David Heinrichs, "Benchmarking a first-principles thermal neutron scattering law for water ice with a diffusion experiment," *EPJ Web of Conferences* **146**, 13004 (2017).
- [11] L. Torres, J. R. Granada, J. J. Blostein, "Total cross sections of benzene at 90 K and light water ice at 115 K", *Nucl. Instrum. Methods in Physics Res., Sect.B*; Vol.251, p.304 (2006).
- [12] G. E. Granroth, et al., "SEQUOIA: a newly operating chopper spectrometer at the SNS," *J. Phys.: Conf. Ser.* **251**, 12058 (2010).