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High Phonon Scattering Rates Suppress Thermal Conductivity in Hyperstoichiometric Uranium Dioxide

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Abstract
Uranium dioxide (UO₂), one of the most important nuclear fuels, can accumulate excess oxygen atoms as interstitial defects, which significantly impacts thermal properties. In this study, thermal conductivities and inelastic neutron scattering measurements on UO₂ and UO₂₋ₓ (x=0.3, 0.4, 0.8, 0.11) were performed at low temperatures (2-300 K). The thermal conductivity of UO₂₋ₓ is significantly suppressed compared to UO₂ except near the Néel temperature Tₐ= 30.8 K, where it is independent of x. Phonon measurements demonstrate that the heat capacities and phonon group velocities of UO₂ and UO₂₋ₓ are similar and that the suppressed thermal conductivity in UO₂₋ₓ results from high phonon scattering rates. These new insights advance our fundamental understanding of thermal transport properties in advanced nuclear fuels.

Keywords
Hyperstoichiometric uranium dioxide, Thermal conductivity, Inelastic neutron scattering, Phonon density of states, High phonon scattering rates

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1. Introduction
Uranium dioxide is the most widely used nuclear fuel and its thermal properties are important to reactor safety and performance[1]. UO₂ is able to accommodate a variable stoichiometry, depending on temperature and oxygen pressure[2, 3]. For example, UO₂ can be oxidized by water vapor in the rare event of a cladding breach in a reactor, which consequently raises ratio of oxygen to uranium (O/U=2+x)[2]. The excess oxygen atoms in hyperstoichiometric uranium dioxide (x > 0) were identified as interstitial defects that form partially ordered clusters[4-6]. In addition, the O/U ratio is one of the most important parameters governing fuel safety because it significantly affects the thermal properties such as the melting point[7] and thermal conductivity[8-12]. For example, Manara et al.[7] found the melting point of UO₂⁺ₓ (x = 0−0.21) decreases as the O/U ratio increases. White et al.[11] reported that UO₂⁺ₓ pellets exhibit a decrease in thermal conductivity with increasing temperature and follow 1/T dependence due to the anharmonic Umklapp phonon-phonon scattering at 363 -1673 K. The thermal conductivity of UO₂⁺ₓ also decreases as x increases, indicating the importance of phonon-defects scattering.

Although there are many studies of the thermal properties of UO₂⁺ₓ at high temperatures (300-1700 K)[7-13], there is little information on the thermal conductivity and phonon properties of UO₂⁺ₓ at low temperatures (below 300 K). The effects of excess oxygen atoms (x) on the thermal conductivity of UO₂⁺ₓ at low temperatures, especially around Néel temperature T₅= 30.8 K, are of critical importance in bench marking theoretical models. In this study, the thermal conductivity of UO₂ and UO₂⁺ₓ single crystals are reported in the temperature range of 2-300 K. We find that UO₂⁺ₓ has a much smaller thermal conductivity than UO₂ at all temperatures except near the Néel temperature, where it is unaffected. The phonon density of states (PDOS) and scattering function measured by inelastic neutron scattering (INS) demonstrate that the suppressed thermal conductivity in UO₂⁺ₓ originates with an increased phonon scattering rate with the addition of oxygen interstitial defects.

2. Method
2.1 Samples preparation and thermal conductivity measurements

Thermal conductivity measurements were performed in a DynaCool-9 Quantum Design Measurement System. The measurements were performed in the continuous heating mode of the TTO option using a pulse-power steady-state method. The crystals were measured from 2 to 300 K at 0.25 K/min. The oxygen stoichiometry of the UO₂ single crystals was set in a thermogravimetric analyzer by controlling the oxygen activity and by adjusting the partial pressure of oxygen at 1273 K. Then, the final stoichiometry of the UO₂⁺ₓ crystals was calculated from the sample weight change relative to the stoichiometric UO₂ reference data. The size of these crystals is around 1x1x3 mm³.

2.2. INS measurements

The single crystals used in the thermal conductivity measurements are too small for direct INS measurement on phonon dispersion and especially phonon linewidths. Hence, to characterize the phonon properties, instead INS measurements on powders of UO₂ and UO₂₀.₀₈ at 77 K and 295 K were performed using the wide Angular Range Chopper Spectrometer (ARCS) at the Spallation
Neutron Source (SNS) of Oak Ridge National Laboratory[14]. The setup of the spectrometer was identical to previously reported PDOS measurements for UO$_2$[15, 16]. An incident neutron energy of $E_i=120$ meV was used, which is high enough to capture the phonon cutoff around 80 meV and allows for summing over enough zones in momentum space to obtain a PDOS. Scattering introduced by the sample can and the cryostat were corrected for by subtracting the corresponding spectra from a duplicate, empty sample can measurement. The corrected scattered neutron intensities, $I(\Phi, t)$, were converted to the scattering function $S(Q,E)$, where Q is momentum transfer magnitude and E is the energy transfer. Other experimental details can be found elsewhere[15, 16] and are not repeated here. The neutron weighted PDOS $g^{NW}(E)$ was then obtained by integrating $S(Q,E)$ over Q values ranging from 4 to 10 Å$^{-1}$ for both UO$_2$ and UO$_{2.08}$, and then correcting for multiphonon scattering (using iterative procedure), the Debye-Waller factor, thermal population factor, and subtracting the elastic peak.

The measured neutron weighted PDOS can be expressed as

$$g^{NW}(E) = \frac{\sigma_u}{M_u} g_u(E) + 2 \frac{\sigma_o}{M_o} g_o(E) \quad (1)$$

where $g_i$, $M_i$ and $\sigma_i$ are the partial PDOS, the atomic mass, and the corresponding neutron scattering cross section of element i (i = U or O)[15, 17]. In order to extract the neutron unweighted PDOS, we take advantage of the fact that nearly all phonon modes below 25 meV are from uranium and nearly all phonon modes above 25 meV are from oxygen[15, 18, 19].

The specific heat at constant pressure, $C_P$, can be written

$$C_P - C_V = 9\alpha^2 B v T \quad (2)$$

where $C_V$ is the specific heat at constant volume, $\alpha$ is the linear thermal expansion, $B$ is bulk modulus, $v$ is molar volume, and $T$ is temperature[20]. The phonon contribution to the specific heat at constant volume $C_V^{ph}$ can be obtained directly from the neutron unweighted PDOS using:

$$C_V^{ph}(T) = 3k_B \int_0^{\infty} g_{T_0} \frac{E^2}{e^{E/(k_B T) - 1}} dE \quad (3)$$

where $k_B$ and $g_{T_0}(E)$ are the Boltzmann constant and neutron unweighted PDOS at temperature $T_0$, respectively[16].

3. Results and Discussion

The measured thermal conductivity of UO$_{2+x}$ single crystals as a function of temperature is shown in Fig. 1a. The thermal conductivity of UO$_{2+x}$ for all values of $x$ measured exhibits a double-peak behavior where maxima occur at ~10 and 220 K and a minimum occurs at the Néel temperature $T_N=30.8$ K, consistent with previous studies on UO$_2$[21-23]. In addition, other than in the vicinity of $T_N$, the thermal conductivity of UO$_{2+x}$ is significantly suppressed compared to UO$_2$ and decreases with increasing $x$ (see Fig. 1b). The decreasing thermal conductivity with increasing $x$ is likely driven by phonon-defects scattering and is similar to the observed high temperature behavior[8-12]. More specifically, the thermal conductivity of UO$_{2.08}$ (2.68 W/(mK)) is 67% the value for UO$_2$ at 77 K (4.46 W/(mK)). Interestingly, the thermal conductivity of UO$_{2+x}$ (~1 W/(mK)) is essentially
independent of the $x$ at $T_N = 30.8$ K, indicating negligible phonon-defects scattering likely due to strong magnetic fluctuations, see Fig. 1b.

**Fig. 1.** (a) Measured thermal conductivity of UO$_2$ and UO$_{2+x}$ single crystals as a function of temperature. Thermal conductivity of UO$_{2.08}$ is obtained by interpolation between UO$_{2.04}$ and UO$_{2.11}$ (b) Measured thermal conductivity of UO$_{2+x}$ single crystals as a function of the excess oxygen atoms $x$ at several different temperatures.

To gain deeper insights on the suppressed thermal conductivity in UO$_{2+x}$, we first checked the structure of UO$_{2.08}$ and the measured neutron diffraction pattern of UO$_{2.08}$ in Fig. S1 of Supplementary Materials (SM) shows that UO$_{2.08}$ adopts a superlattice structure which is a mix of UO$_2$ and U$_4$O$_9$, consistent with reported phase diagram at low temperatures[13, 24, 25]. We then measured their neutron weighted PDOS of UO$_2$ and UO$_{2.08}$ at 77 K and 295 K, as shown in Fig. 2a and 2b. Well-defined zone-boundary phonon peaks are observed at energies of 12, 21, 33, 56, and 72 meV for both UO$_2$ and UO$_{2.08}$ at 77 K and 295 K. With reference to the phonon dispersion of UO$_2$[15, 17], the uranium-dominated transverse acoustic (TA) and the longitudinal acoustic (LA) zone-boundary phonon energies correspond to the 12 and 21 meV peaks. These peaks show trivial difference between UO$_2$ and UO$_{2.08}$. The oxygen-dominated transverse optical (TO1 and TO2) and the longitudinal optical LO2 zone-boundary phonon energies correspond to the remaining 33, 56, and 72 meV peaks, respectively. In contrast, these peaks in UO$_{2.08}$ are less intense and slightly broader than that in UO$_2$. In addition, there are some nonnegligible intensities above phonon cutoff (78meV), which is consistent with nonlinear propagating modes (NPM) identified in a previous study[26].
Fig. 2. The neutron weighted PDOS of UO₂ (red spheres) and UO₂.08 (blue spheres) powders measured by INS at (a) 77 K (b) 295 K; The specific heat capacity ($C_P$) of UO₂ (red line) and UO₂.08 (blue line) with respect to temperature were calculated using unweighted PDOS at (c) $T_0$ = 77 K and (d) $T_0$ = 295 K. Solid and open black circles are previous experimental $C_P$ of UO₂ single crystal[16] and sintered powder[27]. A sharp spike at $T_N = 30.8$ K is a result of the Néel transition from an antiferromagnetic state to a paramagnetic state.

The calculated specific heat capacities ($C_P$) of UO₂ and UO₂.08 using the neutron unweighted 77K and 295K- PDOS based on equation (2) and (3) are shown in Fig. 2c and 2d. Our calculated $C_P$ of UO₂ shows good agreement with the experimental $C_P$[16, 27], except in the vicinity of $T_N$ where magnetic contributions are large[28-30]. Moreover, $C_P$ of UO₂ and UO₂.08 are almost same (less than 2% difference) over the entire temperature range of 2-300 K. Note that their $C_P^{ph}$ also show trivial difference as shown in Fig. S2 of SM.
Thermal conductivity \(k\) of single crystals in the phonon gas model is quantitatively defined by

\[
k = \frac{1}{3} C_V^{ph} V_g \tau^2
\]

where \(C_V^{ph}\), \(V_g\), and \(\tau\) are the phonon heat capacity, the average phonon group velocity, and the average phonon lifetimes, respectively. With the similar \(C_V^{ph}\) and \(V_g\) in UO\(_2\) and UO\(_{2.08}\), the lower thermal conductivity in UO\(_{2.08}\) must result from smaller average phonon lifetimes, i.e. higher phonon scattering rates than UO\(_2\). For example, given that the thermal conductivity of UO\(_{2.08}\) is 67% the value of UO\(_2\) at 77 K, the average phonon lifetimes in UO\(_{2.08}\) are 82% the value of UO\(_2\). To validate this, we plot the measured scattering function \(S(Q,E)\) as a function of \(E\) and \(Q\) at 77 K in Fig. 3a and 3b. \(S(Q,E)\) at 295 K can be found in Fig. S3 of SM). Interestingly, both \(S(Q,E)\) contour plots exhibit clear sinusoidal shapes at the energy range of 20-55 meV and flat shapes at 56 meV and 72 meV, corresponding to LO1, TO2 and LO2 phonon branches along [100] direction. Moreover, LO1 phonon branches in UO\(_{2.08}\) are broader than UO\(_2\), which represents larger linewidths or higher phonon scattering rates in UO\(_{2.08}\). Note that the LO1 phonon branches were found to contribute to the largest amount (>30%) of total thermal conductivity in UO\(_2\).[17] Further
energy cuts at $Q=[3.75,3.8]$ and $Q=[5.256,5.306]$ are shown in Fig. 3c and 3d. The fitted phonon energies of TO2 and LO2 modes in UO2 are very close to UO2, which reiterates the similar group velocities in them. The fitted phonon linewidths of TO2 and LO2 modes in UO2 are $3.9\pm 1.3$ meV and $2.3\pm 1.4$ meV at $Q=[3.75,3.8]$, and $2.2\pm 1.5$ meV and $2.2\pm 2.7$ meV at $Q=[5.256,5.306]$, comparable to previously measured linewidths (2-3 meV) in UO2 single crystal17. The phonon lifetimes (inverse of linewidths) of TO2 in UO2 are 0.52 ps at $Q=[3.75,3.8]$ and 0.50 ps at $Q=[5.256,5.306]$, which are 49% of 1.06 ps and 27% of 1.88 ps in UO2. In contrast, phonon lifetimes of LO2 in UO2 are 1.80 ps at $Q=[3.75,3.8]$ and 1.88 ps at $Q=[5.256,5.306]$, which are almost the same as the corresponding values in UO2 (1.38 ps at $Q=[3.75,3.8]$ and 1.88 ps at $Q=[5.256,5.306]$). In brief, with similar $C_{ph}^p$ and $V_g$ in UO2 and UO2+x, small phonon lifetimes, i.e. high phonon scattering rates, lead to much lower thermal conductivity in UO2+x.

4. Conclusion
In summary, we performed thermal conductivity and INS measurements on UO2 and UO2+x at low temperatures (2-300 K). It is found that the thermal conductivities of all UO2+x single crystals exhibit a double-peak behavior where maxima occur at 10 and 220 K and a minimum occurs at the Néel temperature $T_N=30.8$ K, consistent with previous studies on UO2. Except in the vicinity of $T_N$, the thermal conductivity of UO2+x is significantly suppressed compared to UO2 and decreases with the increasing of $x$. At $T_N = 30.8$ K, the thermal conductivity of UO2+x is essentially independent of the $x$. Further INS measurements of the PDOS and scattering function demonstrate that heat capacity and phonon group velocities of UO2 and UO2+x are similar and thus the suppressed thermal conductivity is attributed to high phonon scattering rates in UO2+x. The fundamental new knowledge gained from this study may guide the future design of safe and efficient nuclear reactors.

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The data that supports the findings of this study are available within the article and its supplementary material.

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Supplementary Materials

High Phonon Scattering Rates Suppress Thermal Conductivity in Hyperstoichiometric Uranium Dioxide

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Fig. S1. The measured neutron diffraction patterns of UO$_2$ and UO$_{2.08}$ at 295 K. U$_4$O$_9$ data is from Ref. 1.

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Fig. S2. The heat capacity \( C_v^{ph} \) of UO\(_2\) (red line) and UO\(_{2.08}\) (blue line) with respect to temperature were calculated using unweighted PDOS at (c) \( T_0 = 77 \) K and (d) \( T_0 = 295 \) K.

Fig. S3. Color contour plots of the scattering function \( S(Q, E) \) as a function of \( E \) and \( Q \) and their corresponding neutron-weighted PDOS for (a) UO\(_2\) and (b) UO\(_{2.08}\) at 295 K measured by INS.

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