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Published in:
Journal of Applied Physics

Link to article, DOI:
10.1063/1.5060976

Publication date:
2019

Document Version
Publisher's PDF, also known as Version of record

Citation (APA):

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Cite as: J. Appl. Phys. 125, 025302 (2019); https://doi.org/10.1063/1.5060976
Submitted: 21 September 2018. Accepted: 17 December 2018. Published Online: 09 January 2019

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Submitted: 21 September 2018 · Accepted: 17 December 2018 · Published Online: 9 January 2019

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ABSTRACT
Oscillating heat pipes (OHPs) provide a promising heat transfer device for a variety of applications, including the cooling of electronic devices. Recently, it has been shown that a hydrophilic, nanostructured cupric oxide (CuO) coating can significantly enhance the thermal performance of copper OHPs that use water as the working fluid. Motivated by these results, we report neutron scattering and electron microscopy (EM) measurements to investigate the interaction of water with copper-oxide surfaces on the nanoscale. Our measurements confirm earlier observations of a thin cuprous oxide (Cu2O) layer growing on a bare copper substrate followed by “grass-like” CuO nanostructures. New evidence of the nanostructure hydrophilicity is provided by EM measurements of wetting and by our high-energy-resolution elastic neutron scattering measurements, showing a continuous freezing and melting of the water in our samples over a temperature range of ∼80 K. In addition, our neutron diffraction measurements are consistent with water closest to the CuO nanostructures freezing into an amorphous solid at low levels of hydration and hexagonal ice at higher hydration. In short, our findings support a strong interaction of water with the CuO nanostructures, which could significantly affect the operation of an OHP.

I. INTRODUCTION
Invented in the 1990s, oscillating heat pipes (OHPs) offer a promising heat transfer device for a variety of applications, including the cooling of electronic devices. An OHP contains a channel meandering between a heat source (evaporator) and heat sink (condenser) that can either be made of small-diameter tubing or fabricated from a flat plate with a milled channel. The OHP is sealed, evacuated, and partially backfilled with a working fluid, which results in evaporation and condensation at opposite ends of the OHP due to heat addition and heat rejection, respectively. If the channel diameter of the OHP is sufficiently small to support capillary action, then liquid “slugs” and vapor “bubbles” will form within the channel. Pressure differences within the system drive the oscillating motion of these slugs and bubbles, enabling both sensible and latent heat transfer from the evaporator to the condenser.
Recently, it has been shown that, for a flat-plate copper OHP operating with water as the working fluid, a hydrophilic coating of CuO nanostructures on either the evaporator or condenser sections can enhance its thermal performance as measured by a reduction in the temperature difference between the heat source and sink. Despite the demonstration that such a CuO coating improves heat-transfer performance, the microscopic mechanisms responsible for this enhancement remain unknown.

The interaction of water with strongly hydrophilic, porous surfaces has received increasing attention in the last two decades with numerous review articles (see, e.g., Refs. 4–8). For the most part, these reviews have emphasized the macroscopic characterization of hydrophilic surfaces (e.g., by water contact angle measurements). The role of both surface chemistry and surface roughness in enhancing hydrophilicity, the fabrication of hydrophilic materials, and applications of these materials. However, compared to water near atomically smooth, planar surfaces, there has been less attention paid to determining the molecular-scale structure of water at the molecular level. The structure of the solid water at the molecular level. The wetting behavior and melting/freezing transitions as well as the structure of the solid water at the molecular level. The role of both surface chemistry and surface roughness in enhancing hydrophilicity, the fabrication of hydrophilic materials, and applications of these materials. Both the structure of water and its freezing/melting behavior when confined within the pores of these materials have been investigated.

In this paper, we use neutron scattering techniques to probe the structure and dynamics of water in proximity to porous and strongly hydrophilic CuO surfaces, which have a qualitatively different topography than the cylindrical pores within the silicon. We find that the water near the nanostructured CuO surfaces exhibits a continuous melting/freezing transition spanning a temperature range that extends 80 K below the bulk transition at 273 K. Also, on slow cooling of our low-hydration samples, we obtain evidence of amorphous solid water forming near a temperature of 240 K. These features differ qualitatively from that of water near ideal, planar metal-oxide surfaces for which the water structure can be described in terms of three structurally distinct layers.

As discussed in Sec. II, we use both electron microscopy and neutron scattering to probe the water structure near the CuO nanostructures. These techniques allow us to investigate the wetting behavior and melting/freezing transitions as well as the structure of the solid water at the molecular level.

II. EXPERIMENTAL

A. Electron microscopy and water contact angle measurements

To mimic the copper surfaces in a flat-plate OHP, we used thin (12.7 μm) copper foil as a substrate (All Foils, USA). CuO nanostructures were prepared on the foil using a wet chemical method. The foils were cleaned in acetone, etched in 2.0 M hydrochloric acid to remove the native oxide layer, and then immersed in a pH-14 solution consisting of NaClO₂,

NaOH, Na₃PO₄·12H₂O, and deionized water in the ratio 3.75:5:10:100 by weight. After a 10-min exposure to solution at ∼368 K, the foils were rinsed several times in deionized water and air-dried.

To characterize the copper-oxide morphology and crystallinity, we used a combination of scanning electron microscopy (SEM) and transmission electron microscopy (TEM) at the University of Missouri Electron Microscopy Core Facility. We prepared a TEM sample using a lift-out method in a focused-ion-beam SEM instrument (FEI Scios Analytical). An oxidized-copper-foil cross section was transferred to a 300 keV TEM (FEI Tecnai F30 Twin) equipped with a Gatan image filter. Electron energy-loss spectroscopy (EELS), scanning-TEM imaging, and selected-area electron diffraction (SAED) were used to characterize the chemical composition and structure of the sample. The EELS energy resolution was 1 eV based on the full-width at half-maximum of the zero-loss peak.

We determined the millimeter-scale surface wettability of untreated and CuO-coated copper foils by water contact-angle measurements (Ramé-Hart Model 200), using 1 μl droplets of purified water under ambient conditions. Results were averaged over several (3–10) droplets on different samples.

In addition, we investigated micron-scale surface wettability using an environmental-SEM instrument (FEI Quanta 600F) at a saturated water vapor pressure of 500 Pa. Foil samples of size 1 × 1 cm² were mounted at an angle of ∼15° to the primary-beam direction on custom-made oxygen-free high-conductivity (OFHC) copper stubs. We adjusted the electron beam accelerating voltage (5–20 kV), sample-detector gap distance (10–15 mm), image dwell time (0.3–30 μs), water vapor pressure (∼500 Pa), and sample temperature (268–293 K) for the best signal-to-noise ratio. Similar to the technique used by others, by lowering the sample temperature below 271 K at a pressure of 500 Pa, we could condense supercooled water on untreated-copper surfaces and the CuO nanostructures. Images were formed by electrons backscattered into a gaseous electron detector both before and after the observation of liquid water. Recording ended when the water layer thickness exceeded the escape length of backscattered electrons. Reproducibility was confirmed by repeating condensation and evaporation cycles on several samples.

B. Elastic neutron intensity measurements

Our neutron scattering samples consisted of 100 copper foil disks, each 5 cm in diameter. A large number and diameter of the foils were necessary to increase the scattered neutron intensity from the water layer on each side of the foils. The foil thickness (12.7 μm) was chosen to decrease the incoherent scattering from the copper substrates. The foils were stacked in a cylindrical aluminum can in a helium atmosphere and sealed with an iodine O-ring. Prior to sealing, samples were heated to ∼328 K in air for 48 h to remove excess water. In the sample of untreated copper, aluminum foil rings (5 cm outer diameter, ∼4.8 cm inner diameter, and ∼22.9 μm thick) were interleaved between copper foils to increase the stack density.
height in order to fill the incident neutron beam cross section (30 × 30 mm²). Sample hydration was established by a water droplet of known volume (H₂O for incoherent elastic scattering and D₂O for neutron diffraction); it was placed outside of the neutron scattering volume using a micropette before sealing (see Fig. 1).

The freezing/melting behavior of the water in our samples was observed by measuring the temperature-dependence of the intensity of neutrons scattered elastically from the sample. In our samples, the incoherent scattering from the H atoms in the water molecules dominates the elastic signal. We used the High-Flux Backscattering Spectrometer (HFBS)²⁰ at the NIST (National Institute of Standards and Technology) Center for Neutron Research, which has an energy resolution of ∼1 μeV. An increase in the elastically scattered neutron intensity on this instrument is proportional to an increase in the number of H atoms which are either immobile or moving on a time scale longer than ∼4 ns. Therefore, at low temperatures, the elastic intensity provides a measure of the amount of immobilized water in our samples.²¹ To increase the scattering signal, the elastic intensity was summed over all 16 detectors, which cover a wave vector transfer (Q) range of 0.25 Å⁻¹ < Q < 1.75 Å⁻¹, and then normalized to the incident beam monitor located in front of the sample position. Cooling and heating scans were taken at a rate of 0.08 K/min between 200 K and 280 K for three different samples: CuO-nanostructured copper foils with 60 μl of H₂O; a similar sample with 10 μl of H₂O, and, to serve as a control, untreated-copper foils with 60 μl of H₂O. These water volumes were selected based on previous proof-of-concept measurements on the HFBS as well as from our earlier work on single-supported bilayer lipid membranes.²² In practice, a volume of 10 μl yielded the smallest quasielastic intensity from water that could be analyzed.

C. Neutron diffraction

To determine the structure and composition of the copper-oxide coatings and their associated water, we conducted neutron diffraction measurements on a two-axis diffractometer equipped with five position-sensitive detectors at the University of Missouri Research Reactor (MURR).²² The incident neutron wavelength was 1.485 Å. The samples used in these diffraction measurements were identical to those used for the incoherent elastic scattering experiments except that they were hydrated with D₂O instead of H₂O (120 μl or 240 μl) to enhance the coherent scattering from the water. A third sample, which had no added D₂O, was also measured to determine background scattering. Diffraction patterns were taken in temperature steps of 5 K from ∼295 K to 200 K in search of Bragg peaks from crystalline ice.

III. RESULTS AND DISCUSSION

A. Structure of the copper-oxide coating

The physical and chemical properties of CuO nanostructures depend on the synthesis conditions under which they are grown (e.g., ion concentration, temperature, time).²³ Using the recipe by Nam and Ju,²⁴ the CuO nanostructures formed a “grass-like” morphology, uniformly coating the copper substrate. A comparison of the untreated-copper and CuO surfaces is given in the SEM images in Figs. 2(a) and 2(b), respectively, with a magnified view of the CuO grass-like morphology in Fig. 2(c). The dimensions of each triangular CuO blade are typically ∼2 μm tall, ∼0.5 μm wide at the base, and ∼20 nm thick.

To observe the layered structure of the CuO coating on copper foil, we have used high-spatial-resolution TEM. A cross-sectional view of a foil is shown in the high-angle dark-field (HAADF) image in Fig. 3(a). HAADF images are formed primarily by backscattered electrons collected at relatively large angles with respect to the incident beam. In principle, the gray-scale intensity of each pixel of an HAADF image is proportional to Z², where Z is the average atomic number.²⁵ Thus, an HAADF image can be analyzed to determine differences in chemical composition between layers in a sample. The approximate average Z² values for Cu, Cu₂O, and CuO are 841, 484, and 342, respectively. Accordingly, the gray-scale intensity of bulk copper would appear brightest, CuO the darkest, and Cu₂O in between, consistent with Fig. 3(a). The black areas in Fig. 3(a) are holes in the sample through which the incident beam passes unimpeded.

Selected-area electron diffraction (SAED) patterns were taken within the circled region at the lower interface in Fig. 3(a). The pattern in Fig. 3(b) shows Bragg spots indicative of single-crystal domains, which could be indexed to bulk copper and cuprous oxide (Cu₂O).²⁶ Moreover, the diffraction patterns reveal a complete epitaxial relationship between the Cu and Cu₂O layers: Cu[112]||Cu₂O[112]; Cu[111]||Cu₂O[111]; and Cu[220]||Cu₂O[220] as has been observed previously.²⁶ EELS scans, collected simultaneously with STEM images, were used to identify chemical composition within each layer.
labeled in Fig. 3(a). Representative scans are shown in Fig. 3(c). In these scans, the incident electron beam excites the sample's electrons into vacant states above the ionization edges of copper's core-shell electrons. The shapes of the L-transitions (2p to 3d shell) near 931 eV and 951 eV and their intensity ratio (L3-to-L2) can be used to fingerprint the oxidation state of metallic copper and its compounds. The shapes of the EELS edges agree well with those reported elsewhere and, together with HAADF images and SAED patterns, confirm the identity of the layers as labeled in Fig. 3(a).

Our neutron diffraction measurements provided additional evidence of the three layers (Cu, Cu2O, and CuO). Samples of untreated and CuO-coated copper foils were prepared as illustrated in Fig. 1. Room-temperature diffraction scans are plotted in Fig. 4. The untreated-copper contains Bragg peaks indexed to fcc copper as well as a few weak aluminum Bragg peaks contributed by the vertical spacers between copper foils. In addition to bulk copper, two copper-oxide phases were found in the treated sample: cubic Cu2O and monoclinic CuO. The weakness of the Cu2O and CuO peak intensities is consistent with the thinness of the oxide layers identified by electron microscopy in Fig. 3(a).

**B. Wetting behavior**

Micro- and nano-structuring of surfaces can enhance wetting as was found for the CuO coating used in flat-plate copper OHPs. Our water contact-angle measurements show that untreated copper is relatively hydrophobic.
with equilibrium contact angles of \( \sim 70^\circ \) [Fig. 5(a)]. In contrast, water droplets deposited on the CuO coating, similar to that in Figs. 2(b) and 2(c), immediately spread to contact angles of \( \sim 0^\circ \) [Fig. 5(b)], which is characteristic of superhydrophilic surfaces.

In addition to water contact-angle measurements, we have used environmental-SEM (ESEM) water-condensation experiments to elucidate the differences in the wetting behavior of water on untreated-copper and CuO surfaces. ESEM images were obtained by collecting backscattered electrons as the beam performs a raster scan across the surface. As in TEM-HAADF imaging [see Fig. 3(a)], the intensity of an SEM-backscattered-electron image depends on the \( Z \) of the target atoms. High-\( Z \) materials have a greater probability of elastically scattering electrons than low-\( Z \) materials and thus appear brighter, although topographic variations in these samples can modulate the image intensity. The advantages of ESEM are the ability to create a humid environment similar to that within our neutron scattering sample cell (Fig. 1) and to determine droplet shapes of micron size.

Representative ESEM images for untreated-copper [Fig. 5(c)] and CuO-nanostructured surfaces [Fig. 5(d)] were taken during the condensation process. On the untreated-copper surface, we observed hemispherically-shaped droplets that retained their shape throughout nucleation and subsequent growth. In contrast, water that condensed on the hydrophilic CuO coating nucleated near the base of the nanostructures and formed a thin film which increased in thickness as condensation proceeded. When the water reached the top of the CuO blades, it formed a hemispherical shape, like the droplets on untreated-copper surfaces, but with the droplet edges pinned to the CuO blades. We note that in addition to the grass-like blades of the CuO surfaces promoting capillary condensation, the presence of OH groups on the nanostructures may enhance their affinity for water.

**C. Freezing and melting behavior**

In addition to observations of the wetting behavior of the CuO nanostructures, the strength of their interaction with water can also be assessed by investigating their effect on the water freezing transition. Differential scanning calorimetry (DSC) is frequently used to investigate the freezing and melting behavior of water confined in porous media (see, e.g., Ref. 14). We have tried to apply the DSC technique to our system, but the specific surface area of our CuO-coated samples (\( \sim 0.6 \text{ m}^2/\text{g} \)) is so small that a DSC sample contains an amount of water that is two to three orders of magnitude less than the quantity typically used (a few mg) in measurements with commercial DSC instruments. For this reason, we have been unable to perform reliable DSC scans to investigate the continuous freezing/melting behavior of our samples.

Due to the large incoherent cross section of hydrogen and the large size of our neutron scattering samples (see Fig. 1), our elastic neutron scans provide greater sensitivity than DSC for investigating the continuous freezing/melting behavior observed in our samples. Also, we note that the elastic neutron scans are sensitive only to the motion of water molecules on a time scale slower than \( \sim 4 \text{ ns} \) whereas the DSC scans integrate molecular motion over a wider range of time scales.
Figure 6 contains our elastic neutron scans on three samples: (a) CuO-coated foils with 60 \( \mu \)l of added H\(_2\)O, (b) CuO-coated foils with 10 \( \mu \)l of H\(_2\)O, and (c) untreated copper foils with 60 \( \mu \)l of H\(_2\)O. For all three samples, each data point is the intensity measured in a counting time of five minutes during which the sample temperature changed by 0.4 K as determined by the temperature ramp rate of 0.08 K/min on cooling and on heating. The intensity of the high-hydration CuO-coated sample [Fig. 6(a)] gradually increased when slow-cooled from 280 K to 200 K. On heating at the same rate from 200 K to 280 K, hysteresis was observed, and the intensity gradually decreased. We have interpreted this behavior as representing continuous freezing and melting of water that is interacting with the CuO nanostructures. A similar trend was found in the low-hydration CuO-coated sample [Fig. 6(b)], although the hysteresis is reduced and the intensity difference between 200 K and 280 K is about half that of the high-hydration CuO-coated sample in Fig. 6(a). We note that this intensity decrease is less than the volume ratio 16 of the initial water droplets added to the two samples. Assuming that all of the initial water droplet is adsorbed onto the CuO-coated foils (see below), there are several possible reasons for this discrepancy: irreproducibility in the amount of residual water on the foils after annealing the samples and variation in their surface area and hydrophilicity.

In marked contrast, the elastic scan for the untreated-copper sample [Fig. 6(c)], conducted at the same cooling rate as the CuO-coated samples, shows an abrupt intensity increase near 266 K below which the intensity levels off. On slow heating, the intensity decreases sharply at the melting point of bulk ice, 273 K.

On closer inspection of the elastic scans of the low-hydration CuO-coated sample [Fig. 6(b)], we find that, on cooling, the elastic intensity obeys a linear dependence from 280 K down to about 237 K. Similarly, the intensity of the high-hydration sample [Fig. 6(a)] has a linear dependence initially with the same slope as the low-hydration CuO-coated sample; however, this behavior ends at about 258 K. As will be discussed further below, this initial linear term occurring in the freezing behavior of both samples, having different levels of hydration, suggests that they share a common water population confined to a similar local environment.

On cooling below 258 K, the elastic intensity of the high-hydration CuO-coated sample again increases linearly but with a larger slope than initially. This linear dependence extends down to about 237 K, the temperature at which the linear dependence of the intensity in the low-hydration sample ends. We suggest that both linear terms contribute to the intensity of the high-hydration CuO-coated sample in the temperature range 237 K < T < 258 K. The presence of a steeper linear term in the elastic intensity scan of this sample provides evidence of a second water population occupying a distinct nanoscale environment. Presumably, this second population is located further away from the copper substrate but still confined within the CuO nanostructures above which water is expected to exhibit bulk-freezing characteristics.

To quantify the hydration level in our samples, we estimate the number of immobilized water molecules from the increase in elastic intensity on cooling from 280 K to 200 K. This number is determined by calibration against a standard sample of an alkane film, containing a known number of H atoms, that freezes on a silicon substrate. A correction is applied for the larger incoherent cross section of our predominantly copper substrates relative to silicon. Assuming that the water wetting the CuO surface forms a uniform film as suggested by the ESEM image in Fig. 5(d), we find an upper bound to the water film thickness of the high- and low-
hydration samples to be ∼200 nm and ∼100 nm, respectively. Although the uncertainty in these estimates is large, we believe it is reasonable to conclude that the film thickness is less than the typical height of a CuO blade, ∼2 μm. These film thickness estimates imply water volumes of ∼80 μl and ∼40 μl adsorbed on the CuO coatings of the high- and low-hydration samples, respectively. For both samples, these volumes exceed those in the initial droplet, suggesting the presence of residual water after the samples were annealed.

The continuous freezing behavior observed for water in proximity to the CuO-nanostructured surfaces differs from that which we have found for water near other interfaces. For example, the water associated with an anionic bilayer lipid membrane also exhibited a continuous freezing behavior, but its elastic scan on cooling began with a step-like feature, somewhat broader than we have found for our untreated-copper sample in Fig. 6(c) and whose magnitude increased with the water content of the sample (see Fig. 3 in Ref. 29). This behavior suggested identifying it with the freezing of bulk-like water as was subsequently verified by measurement of its diffusivity.21 Such a step-like feature is missing in the case of water associated with the CuO-coated samples [Figs. 6(a) and 6(b)], suggesting the absence of bulk-like water.

There are reports of continuous freezing of interfacial water in other porous materials. Liu et al.15 observed elastic scans from water confined to mesoporous silica that show a gradual increase in elastic intensity from 300 K down to 150 K. Also, Mamontov et al.30 found qualitatively similar freezing behavior in elastic scans from samples of water adsorbed in ultramicroporous carbon. As in the case of our samples, they observe the intensity to increase linearly with temperature on cooling below room temperature at low relative humidity.30 However, unlike our two samples [see Figs. 6(a) and 6(b)], the slope of this initial linear term increases with water content, suggesting a greater amount of a single water type confined in the micropores. At the highest relative humidity, the temperature dependence of the elastic intensity is initially concave upward, perhaps indicating the condensation of bulk-like water within the larger pores.

D. Structure of the solid water

The elastic scans in Fig. 6 are useful for determining whether the water in a sample is liquid or solid and the nature of its freezing/melting transitions. However, the incoherent elastic intensity gives no direct information about the structure of the solid water. To determine whether the water in proximity to CuO nanostructures freezes into crystalline ice (e.g., hexagonal or cubic), we performed neutron diffraction measurements at MURR on similarly fabricated samples (see Fig. 1) except that D2O was substituted for H2O to enhance the coherent scattering from the water.

Due to the weak intensity expected for Bragg peaks from crystalline ice, we began our measurements with samples of untreated-copper and CuO-nanostructured foils containing 120 μl of D2O. As shown in Fig. 7(a), the pattern for the untreated-copper sample contains the first three peaks expected for hexagonal ice,31 which appear on cooling near 272 K or about 5 K below the freezing point of bulk D2O. However, no peaks are visible for the CuO-coated sample containing the same amount of water [Fig. 7(c)]. The pattern is virtually identical to that of the sample containing no D2O [Fig. 7(d)]. The maximum uncertainty in the temperature measurement is ∼2 K, based on a temperature gradient between the temperature sensors at the top and bottom of the sample cell.

We then dismounted the CuO-coated sample, heated it in air at ∼328 K for 24 h, and resealed it with 240 μl of D2O. A subsequent diffraction scan [Fig. 7(b)] shows the same three Bragg peaks of hexagonal ice seen for the untreated sample [Fig. 7(a)]. We interpret these results as indicating the growth of hexagonal ice at higher D2O coverage. No Bragg peaks that could be identified with cubic ice were present in repeated scans on the nanostructured samples. In this respect, our results differ from measurements on water confined to mesoporous silica where evidence of cubic as well as hexagonal and disordered ice have been found.31,32 The larger width of the peaks in Fig. 7(b) compared to those in Fig. 7(a) indicates a smaller crystallite size and/or a larger mosaic structure than for the untreated-copper sample—a feature that may be caused by the water film thickness being less than the height of the CuO nanostructures. From the observed broadening of the D2O (100) peak below 250 K, the average domain size of the ice particles is estimated to be ∼30 nm based on a Scherrer analysis.
The absence of Bragg peaks at lower D$_2$O coverages could be explained by water initially solidifying in an amorphous or glassy structure. We suggest that the most favorable candidate for amorphous solid water would be the first water population identified in the elastic scans of both the high- and low-hydration samples, whose intensity has the smaller slope on cooling [see Figs. 6(a) and 6(b)]. Because it is the first to immobilize, indicating the strongest interaction with the CuO nanostructures, this population should be the most likely to form a distorted network of hydrogen bonds that is incompatible with crystalline ice. This interpretation is consistent with our ESEM images [see Fig. 5(d)], which show water to condense first near the base of the nanostructures where the density of the CuO blades is the highest. However, it is possible that the second water population identified in the elastic scan of the high-hydration sample and believed to be further from the base of the blades might also freeze into an amorphous structure. Its higher level of hydration (60 μl of D$_2$O added) is still less than that at which the Bragg peaks of hexagonal ice appeared (240 μl). It is interesting to note that previous investigations of water freezing in mesoporous silicas have found evidence of disordered ice in a layer adjacent to the pore walls in which the local hydrogen bonding of the water molecules is believed to differ from that of bulk ice. Similar to Mamontov et al., concluded that water adsorbed in partially filled pores of their ultramicroporous carbon samples did not crystallize on cooling, which they attributed to a disruption of its hydrogen bonding network.

It is well known that metal-oxide surfaces exposed to humid air adsorb water and form hydroxyl (–OH) groups. The hydroxide reaction at the copper surface during oxidation is likely a source of –OH as well. The H atoms in these surface components will scatter neutrons incoherently, producing an isotropic background in a diffraction measurement. Consistent with this effect, we found that at all temperatures, the background intensity in the diffraction patterns of both CuO-coated samples was greater than that of the untreated-copper hydrated sample, especially at low Q (<0.5 Å$^{-1}$). This higher background of the CuO-coated samples did not depend on their hydration level (120 μl or 240 μl of added D$_2$O). A higher background due to bound water and hydroxyl groups might also explain the larger elastic intensity of the CuO-coated samples at 280 K [Figs. 6(a) and 6(b)] compared to the untreated-copper sample [Fig. 6(c)].

In Fig. 8(a), we show the temperature dependence of diffraction patterns from the CuO-coated sample hydrated with 240 μl of D$_2$O taken subsequently to the pattern in Fig. 7(b). As before, the Bragg peak positions are consistent with bulk hexagonal D$_2$O ice. In addition, we find that the intensity of the three Bragg peaks does not increase abruptly but rather grows continuously. This behavior can be seen more clearly in Fig. 8(b), where we have plotted the integrated intensity of the D$_2$O (100) peak obtained in a Gaussian fit as a function of temperature. As indicated by the dashed line, the peak intensity increases roughly linearly on cooling from 260 K to 230 K. Below 230 K, the Bragg peak intensity levels off consistent with the crystallization of all of the bulk-like water. The full-width at half-maximum of the (100) peak has a flat temperature dependence over the entire temperature range of Fig. 8(b) (not shown) from which we can conclude that ice growth on the CuO surface proceeds through nucleation of additional ice particles rather than by coalescence.

We also note that the linear dependence of the Bragg peak intensity occurs in the same temperature range as that observed for the incoherent elastic intensity of the
At this point, we can only speculate as to how the presence of the CuO coating could enhance the thermal performance of an OHP. It may be that superwetting of water to the CuO nanostructures not only facilitates heat transfer to and from the working fluid in an OHP but also changes the boundary condition for water flow at the pipe wall that could alter the amplitude and frequency of the water slug oscillations. The evidence that we have found for an amorphous solid or glassy phase of water at low temperatures suggests that water in contact with the CuO nanostructures could form a dynamic hydrogen-bond network in its fluid phase differing from that of bulk water at the same temperature. In fact, our preliminary quasielastic neutron scattering measurements indicate the presence of slower molecular diffusive motion than in bulk water. It would be interesting to investigate whether these microscopic dynamical effects correlate with changes in the amplitude and frequency of the water slug oscillations in an OHP caused by a CuO coating as has been observed by Hao et al. Thus, combining quasielastic neutron scattering on CuO-coated foils with neutron imaging on an operating OHP may lead to a better understanding of how a CuO coating enhances OHP thermal performance.

ACKNOWLEDGMENTS

This work was supported by the U.S. National Science Foundation (NSF) under Grant No. DGE-1069091. Access to the HFBS was provided by the Center for High Resolution Neutron Scattering, a partnership between NIST and the NSF under agreement No. DMR-1508249. J.T. was partially supported by a GO! Internship funded by Oak Ridge National Laboratory (ORNL). A portion of this research at ORNL’s Spallation Neutron Source was sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy (DOE). Part of the electron microscopy work was supported by the University of Missouri Electron Microscopy Core’s Excellence in Microscopy award. We thank E. Mamontov and H. B. Ma for helpful discussions.

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