Configurational Energetics in Ice I*h* Probed by Compton Scattering

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(Received 18 June 2007; published 8 November 2007)

Temperature-induced changes in the ground-state electron momentum density of polycrystalline ice I*h* are studied with high accuracy by Compton scattering utilizing synchrotron radiation. A unique feasibility of the technique to provide direct experimental information on configurational enthalpies and heat capacities is demonstrated. The configurational enthalpy, obtained with an accuracy of 1.5 meV, evolves linearly with temperature above $T = 100$ K. Consequently the configurational heat capacity is found to be constant, $c_p^{\mathrm{config}} = (0.44 \pm 0.11)\ \mathrm{J\,g^{-1}\,K^{-1}}$, in this temperature regime. Obtaining these quantities experimentally is fundamentally important for evaluating the accuracy of molecular-dynamics simulations schemes.

DOI: 10.1103/PhysRevLett.99.197401 PACS numbers: 78.70.Ck, 31.70.Ks, 65.40.−b

Despite extensive studies in the past decades, water and ice continue to attract great interest (see, e.g., Refs. [1,2]). This can partly be attributed to their unusual macroscopic properties, which are governed by the local O-H. . .O interactions (i.e., both the covalent and the hydrogen bonds). As demonstrated by the recent debate around the local coordination of water [3–5], the local O-H. . .O interactions and the ensuing configurational energies are of fundamental importance. From a macroscopic point of view, extensive sets of calorimetric data are available. However, the partitioning of the vibrational and configurational contributions is a nontrivial task. From a microscopic point of view, the information on configurational energies relies primarily on computational work [6–8], although they have also been addressed by various spectroscopies [4,9]. It should be noted, however, that the interpretation of spectroscopic data in terms of energies has hitherto relied on somewhat simplistic models. Clearly, a novel experimental approach for the direct study of configurational energies and heat capacities in water and ice is called for.

The heat capacities, being second derivatives with respect to temperature of the appropriate free energies, provide a rigorous test for the various computational water and ice I*h* models. However, their quantitative estimation directly from dynamics simulations is computationally demanding, requiring the inclusion of both nuclear quantum effects [10] and efficient heat capacity estimators [11]. Consequently, accurate computational methods based on path-integral molecular-dynamics simulations have only recently become feasible [12].

In this Letter we report the application of synchrotron-radiation-based Compton scattering to studies of polycrystalline ice I*h* at temperatures ranging from 50 to 250 K. Owing to the unprecedented experimental accuracy and consistency currently obtainable, and utilizing a formal connection between the expectation value of the electron kinetic energy and the Compton-scattering data [13], the present data can be directly interpreted in terms of configurational enthalpies and heat capacities. More specifically, the configurational enthalpy is found to be linear with respect to temperature above $T = 100$ K. Thereby a significant, constant part of the ice I*h* heat capacity can be attributed to configurational degrees of freedom. The present study thus provides a stringent test for future computational work on the ice I*h* heat capacity.

Compton scattering, which is inelastic x-ray scattering at large energy and momentum transfers, probes the electronic ground state of the target system [14,15]. The technique has previously been applied primarily to electronic-structure studies of solid-state systems [16–19], although it is currently emerging also as a novel tool for structural studies of molecular liquids [20–25]. For isotropic systems, such as water and polycrystalline ice I*h*, Compton scattering provides information on the ground-state electron momentum density $N(\mathbf{p})$ in terms of the isotropic Compton profile

$$J(q) = \frac{1}{2}\int_0^{4\pi} d\Omega \int_{|q|}^{\infty} pN(\mathbf{p})dp, \tag{1}$$

q being a scalar electron momentum variable. The local O-H. . .O interactions have been found to induce a characteristic, damped oscillating feature in the Compton profile of ice I*h* [26]. This feature has further been found to depend on the detailed local coordination [20,21]: the amplitude mainly reflects the hydrogen-bond length distribution [22], whereas the shape is governed by the interplay between the intramolecular O-H bond length and the corresponding hydrogen-bond geometry [23].

The isotropic Compton profile carries information on the electronic radial momentum distribution. As pointed out by Epstein [13] already over 30 years ago, a formal connection between the expectation value of the electron kinetic energy $\langle T_e \rangle$ and the isotropic Compton profile $J(q)$ exists, i.e.,

$$\langle T_e \rangle = 3 \int_0^\infty q^2 J(q) dq. \tag{2}$$

The connection between the total energy and the expectation value of the total kinetic energy of the system (denoted E and $\langle T \rangle$, respectively) is given by the virial theorem as $E = -\langle T \rangle$. Within the Born-Oppenheimer approximation the motion of the electrons and the nuclei is further separable, i.e., $\langle T \rangle = \langle T_e \rangle + \langle T_n \rangle$ (the kinetic energy term $\langle T_n \rangle$ including the rotational, vibrational, and translational motion of the nuclei). We note that the effect of the nuclei motion on the Compton profile is minor. Similarly the total energy of the system can be partitioned into the corresponding configurational and vibrational energies (see, e.g., Ref. [10]). Furthermore, since the present experiments were carried out in isobaric conditions, the proper measure of energy is enthalpy. Hence the configurational enthalpy can formally be connected to the expectation value of the electron kinetic energy [and the Compton profile utilizing Eq. (2)], i.e., $H^{\text{config}} \approx -\langle T_e \rangle$. It should be noted that experimental limitations have hitherto made the direct interpretation of experimental Compton-scattering data in terms of energetics impracticable [27]. Moments of the Compton profile have been utilized, however, to assess various computational approaches (see, e.g., Ref. [28]).

Compton profiles of polycrystalline ice Ih were acquired at various temperatures ranging from 50 to 250 K at beam line BL08W of SPring-8. The experimental setup was identical to that reported in Ref. [23]. The energy of the incident radiation was 115 keV and the beam size at the sample was $2(H) \times 2(V)$ mm^2. The scattered photons were collected using a ten-element Ge solid-state detector and the scattering angle was 178°. The total resolution was $\Delta q = 0.63$ atomic units (a.u.) of momentum [29] and the experimental inaccuracy of each Compton profile difference was below 0.025% of $J(0)$ at the Compton peak (i.e., at $q = 0$ a.u.) within a 0.08 a.u. momentum bin. The sample was confined in a 1.5 mm thick cell with Kapton windows and inserted in a vacuum chamber in order to minimize the background induced by scattering from air. Since the temperature-induced changes in the Compton profile are very small, the consistency of the data had to be monitored throughout the experiment. In practice, spectra were saved every 10 minutes and verified to be consistent within the statistical accuracy before summed. The raw spectra were further corrected for background, absorption, and multiple scattering, before converted to momentum scale using the relativistic cross-section correction [30]. Finally the positive and negative momentum sides of the intrinsically symmetric Compton profile differences were averaged. It should be noted that these corrections to the raw data chiefly cancel upon considering Compton profile differences.

The experimental Compton profile differences acquired from polycrystalline ice Ih at various temperatures are shown in Fig. 1, the reference profile being acquired at $T = 100$ K. The data exhibit a systematic evolution as a function of temperature. Based on previous studies [20–24], the temperature-induced changes in the Compton profile of ice Ih can predominantly be attributed to an average elongation of the hydrogen bonds. Also shown in Fig. 1 (solid line) is the difference between experimental Compton profiles acquired from water ($T = 298$ K) and polycrystalline ice Ih ($T = 223$ K) [23], the amplitude of which has been least-squares fitted to the present data. The agreement between the present data and that of Ref. [23] in terms of the shape is remarkable. This finding implies similar changes in the O-H. . .O geometry of ice Ih upon heating as observed upon melting, albeit to a lesser degree.

Next we turn to the temperature-induced changes in the configurational enthalpy as determined from the present experimental Compton-scattering data. We note that the statistical inaccuracy in the large-q regime poses a problem due to the q^2-weighting in Eq. (2) [13]. However, the problem can be effectively resolved by integrating the scaled $\Delta J(q)$ of Ref. [23] (of superior statistical accuracy) depicted in Fig. 1. This approach is justified by the ex-

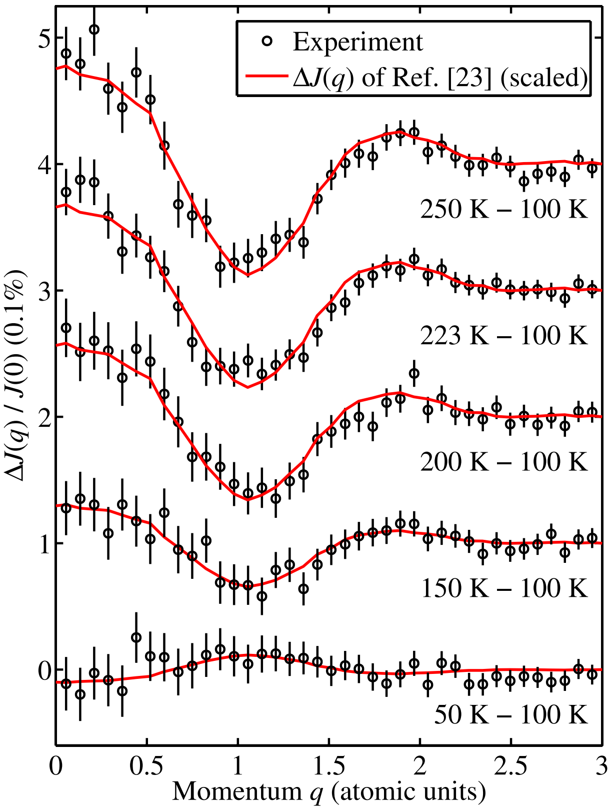

FIG. 1 (color online). Compton profile differences of polycrystalline ice Ih acquired at various temperatures, the reference profile being acquired at $T = 100$ K. The spectra are vertically offset for clarity. The solid line is the experimental data of Ref. [23], i.e., the difference between Compton profiles of water and polycrystalline ice Ih, scaled to fit to each temperature difference.

tremely close agreement between the two data sets in terms of the shape originating from the fundamentally similar elongation of the hydrogen bonds, as described in detail in the previous paragraph. Consequently the statistical error for large momentum values (i.e., the regime were the Compton profile difference is close to zero) is suppressed, improving the statistical accuracy of the kinetic energy difference as compared to integrating the experimental data directly. Another problem arising upon extracting energies from experimental Compton profiles is the choice of integration range in Eq. (2) [13,27]. However, the temperature-induced changes in the present experimental Compton profiles are limited to low momentum values, justifying the restriction of the integration range to $|q| \leq 3.0$ a.u. of momentum.

The obtained changes in the configurational enthalpy are presented in Fig. 2. Above $T = 100$ K the amplitude of the Compton profile difference, and hence the configurational enthalpy, evolves linearly with respect to temperature. The temperature-induced changes in the Compton profile have previously been partitioned into contributions arising from both thermal expansion and disorder [31,32]. However, ice I*h* exhibits practically no thermal expansion below $T = 100$ K [33]. Consequently the temperature-induced changes in the Compton profile, and thus in the configurational enthalpy, are weaker in this temperature regime. This is also the reason for using $T = 100$ K as the reference temperature. Given the present accuracy of 1.5 meV, the Compton-scattering technique can be clearly utilized as an accurate probe of (configurational) energetics.

Next we discuss the information on thermodynamic properties directly obtainable from the present Compton-scattering data, i.e., the configurational heat capacity $c_p^{\mathrm{config}} = (dH^{\mathrm{config}}/dT)_p$. The invariable shape of the Compton profile difference and the linear temperature dependence of its amplitude *de facto* implies a constant configurational heat capacity $c_p^{\mathrm{config}} = (0.44 \pm 0.11)\ \mathrm{J\,g^{-1}\,K^{-1}}$ above $T = 100$ K (i.e., the slope in Fig. 2). However, below $T = 100$ K the configurational heat capacity is smaller, due to the aforementioned very weak thermal expansion in this temperature regime [33]. The tabulated total heat capacity c_p of ice I*h* [34] (shown in Table I) exhibits a notable temperature dependence. The difference between c_p and the present finding, c_p^{config}, can be attributed to the temperature-dependent vibrational contributions [see, e.g., Refs. [35,36] for experimental studies on ice I*h* phonon density of states (DOS)]. In order to verify this latter interpretation, we have also calculated the vibrational (constant-volume) heat capacity (see Table I). This is accomplished within the harmonic approximation utilizing the phonon DOS of Ref. [35] derived from inelastic neutron scattering data. The agreement with the results of the present study is good, considering the minor deficiencies of the adopted approach (e.g., neglect of anharmonic contributions [35] and calculation of constant-volume rather than constant-pressure heat capacity).

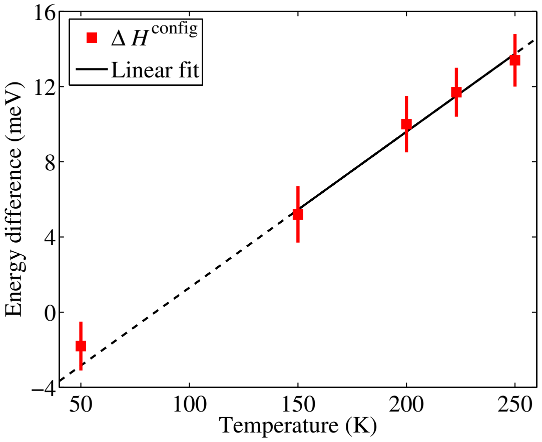

FIG. 2 (color online). Temperature-induced changes in the configurational enthalpy $\Delta H^{\mathrm{config}}$ (per molecule) of ice I*h* as determined from the present experimental data. The reference temperature is $T = 100$ K. The slope of the linear least-squares fit to the data above $T = 100$ K provides the corresponding configurational heat capacity c_p^{config}.

Finally we comment the implications of the Compton-scattering data for the energetics related to melting. By integrating the previously published experimental Compton profile difference between water and ice [23], the enthalpy value $\Delta H^{\mathrm{config}} = 48 \pm 12$ meV per molecule is obtained. This value should be compared to $\Delta H = 100$ meV derived from calorimetric data [34], i.e., from the latent heat of fusion and the corresponding total heat capacities of water and ice I*h*. The closer agreement between Compton-scattering and calorimetric data in this case can be interpreted as reflecting a large configurational character of the latent heat of fusion [1].

In conclusion, we report an experimental Compton-scattering study of polycrystalline ice I*h* at various temperatures ranging from 50 to 250 K. Utilizing a formal connection between the expectation value of the electron

TABLE I. Ice I*h* heat capacities at various temperatures T: the experimental total heat capacity c_p, the vibrational heat capacity $c_p^{\mathrm{vib}} = c_p - c_p^{\mathrm{config}}$ derived from the present data, and the calculated vibrational (constant-volume) heat capacity c_V^{vib}.

T (K)	c_p [a] ($\mathrm{J\,g^{-1}\,K^{-1}}$)	c_p^{vib} ($\mathrm{J\,g^{-1}\,K^{-1}}$)	c_V^{vib} [b] ($\mathrm{J\,g^{-1}\,K^{-1}}$)
50	0.47		0.44
150	1.21	0.77 ± 0.11	1.13
200	1.55	1.11 ± 0.11	1.39
223	1.72	1.28 ± 0.11	1.50
250	1.94	1.50 ± 0.11	1.62

[a] The values of Ref. [34] have been linearly interpolated to the temperatures of the present study.

[b] Determined for the temperatures of the present study within the harmonic approximation following Ref. [35].

kinetic energy and the Compton profile [13], the present temperature-dependent data are interpreted in terms of configurational enthalpies and heat capacities. In particular, the configurational enthalpy is found to evolve linearly with temperature above $T = 100$ K, leading to a constant configurational heat capacity $c_p^{\mathrm{config}} = (0.44 \pm 0.11)\ \mathrm{J\,g^{-1}\,K^{-1}}$ in this temperature regime. These findings provide a strict test for future computational work on the ice Ih heat capacity. Finally we note that the present experimental approach is not limited by the specific binding in the system (e.g., ionic, covalent, or hydrogen bonding). With the accuracy presently obtainable, Compton scattering should thus be applicable to various energetics studies, such as comparison of different thermodynamic states or differences between structural isomers.

The experiment was approved by JASRI, Proposal No. 2005A0438-ND3a-np. This work was supported by the Academy of Finland [through Contracts No. 201291, No. 205967, and No. 110571 as well as its Center of Excellence program (2006–2011)] and the Research Funds of the University of Helsinki.

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