Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Structures of Ions Accommodated in Salty and Sour Ice Ih Crystals

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Table S1. $r_{K\text{-}O}$ and $r_{Cl\text{-}O}$ distances in the optimized structures of Models 1–4, listed in order of increasing distance from the ion accommodated in the ice crystal lattice.

K^+	$r_{K\text{-}O}$ /Å							
Model 1	2.81	2.84	3.00	3.08	3.14	3.38	3.45	3.52
Model 2	2.89	2.90	2.94	2.96	4.42	4.43	4.46	4.49
Model 3	2.82	2.96	3.03	3.27	3.33	3.50	3.75	4.28
Model 4	2.80	2.84	2.80	3.19	3.29	3.45	3.58	4.66

Cl^-	$r_{Cl\text{-}O}$ /Å							
Model 1	3.07	3.10	3.15	3.43	3.52	3.79	3.87	3.94
Model 2	3.03	3.08	3.13	3.13	4.35	4.51	4.53	4.55
Model 3	3.04	3.37	3.38	3.62	3.78	3.81	3.99	4.22
Model 4	3.06	3.14	3.14	4.00	4.30	4.31	4.59	4.59

Table S2. XAFS parameters obtained by fitting the experimental spectra with those simulated using Models 1–4.

K^+	ΔE_0	σ /Å	*R*-factor
Model 1	0.45	0.02	0.5555
Model 2	0.39	0.03	0.1188
Model 3	0.55	0.01	0.1977
Model 4	0.44	0.01	0.4031

Cl^-	ΔE_0	σ /Å	*R*-factor
Model 1	0.21	0.01	0.2479
Model 2	0.09	0.03	0.0790
Model 3	0.48	0.01	0.1242
Model 4	0.12	0.01	0.0676

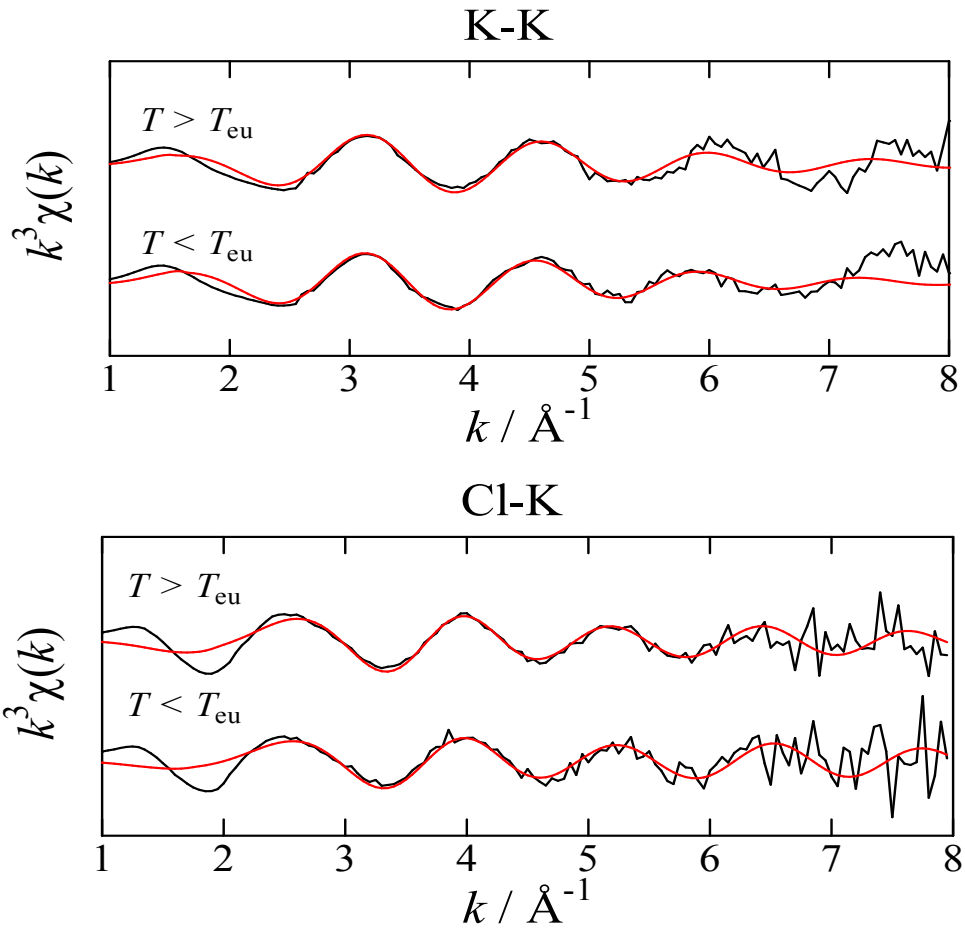

Figure S1. Averaged XAFS spectra for single-crystal ice samples at K-K edge (upper) and Cl-K edge (lower). The fitting results of those spectra are shown as red curves and the fitting parameters are summarized in Tables 1 and 2.

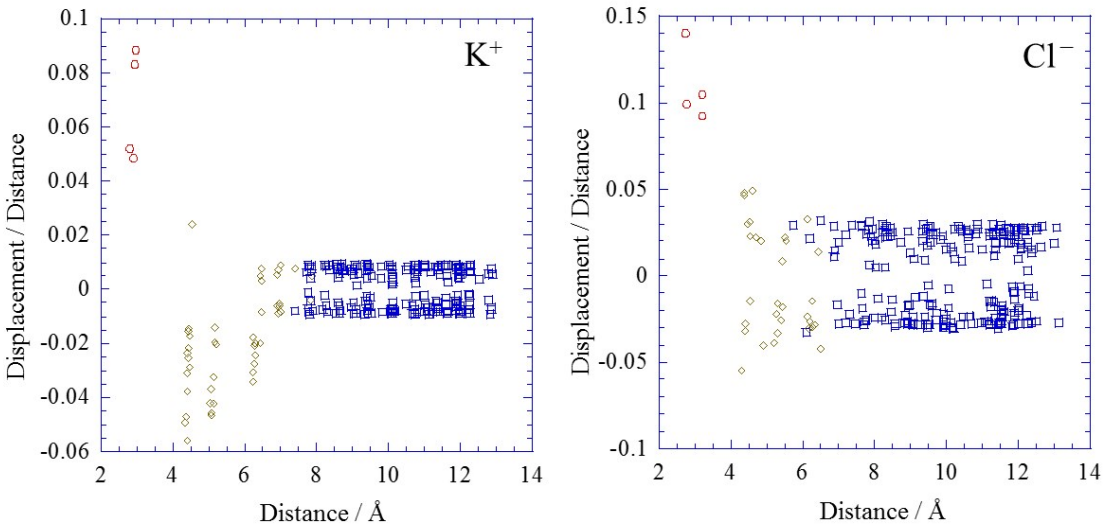

Figure S2 Relaxation of the expansion of the ice crystal lattice by replacing one water molecule by K^+ or Cl^- (Model 2). Symbols: red, oxygen atoms in the high layer; black, oxygen atoms in the medium layer; blue, oxygen atoms outside the medium layer. The distance was calculated relative to the centroid of the tetrahedral cage, in which the ion was accommodated. Because of the displacement of the central tetrahedral cage after the structural optimization, the displacement/distance values at large distances have deviations around zero.

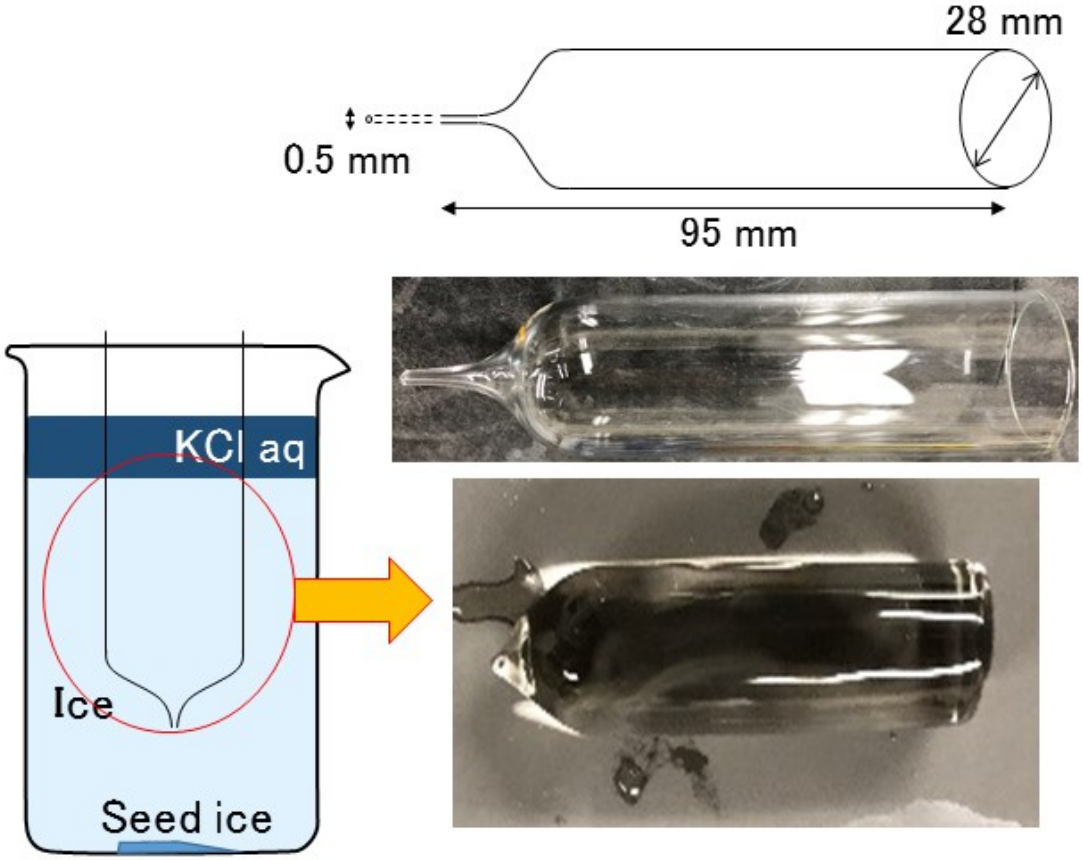

Figure S3. Schematic illustration of the preparation of the single crystal of ice.

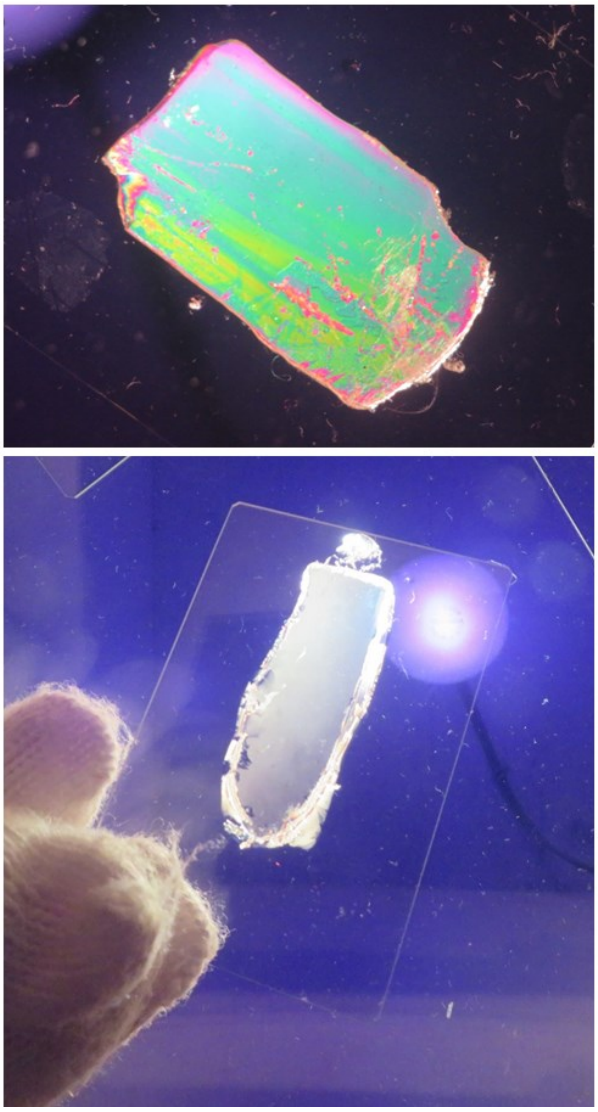

Figure S4. Photographs of sliced single ice crystals. The thickness of the sample was several tens of micrometers. Different colors denote the presence of different crystal facets, while a single color indicates that the thin ice layer originates from a single ice crystal. The red marks in the photograph shown in the top panel are due to the frozen water used for fixing the sliced ice sample on the surface of the glass plate.

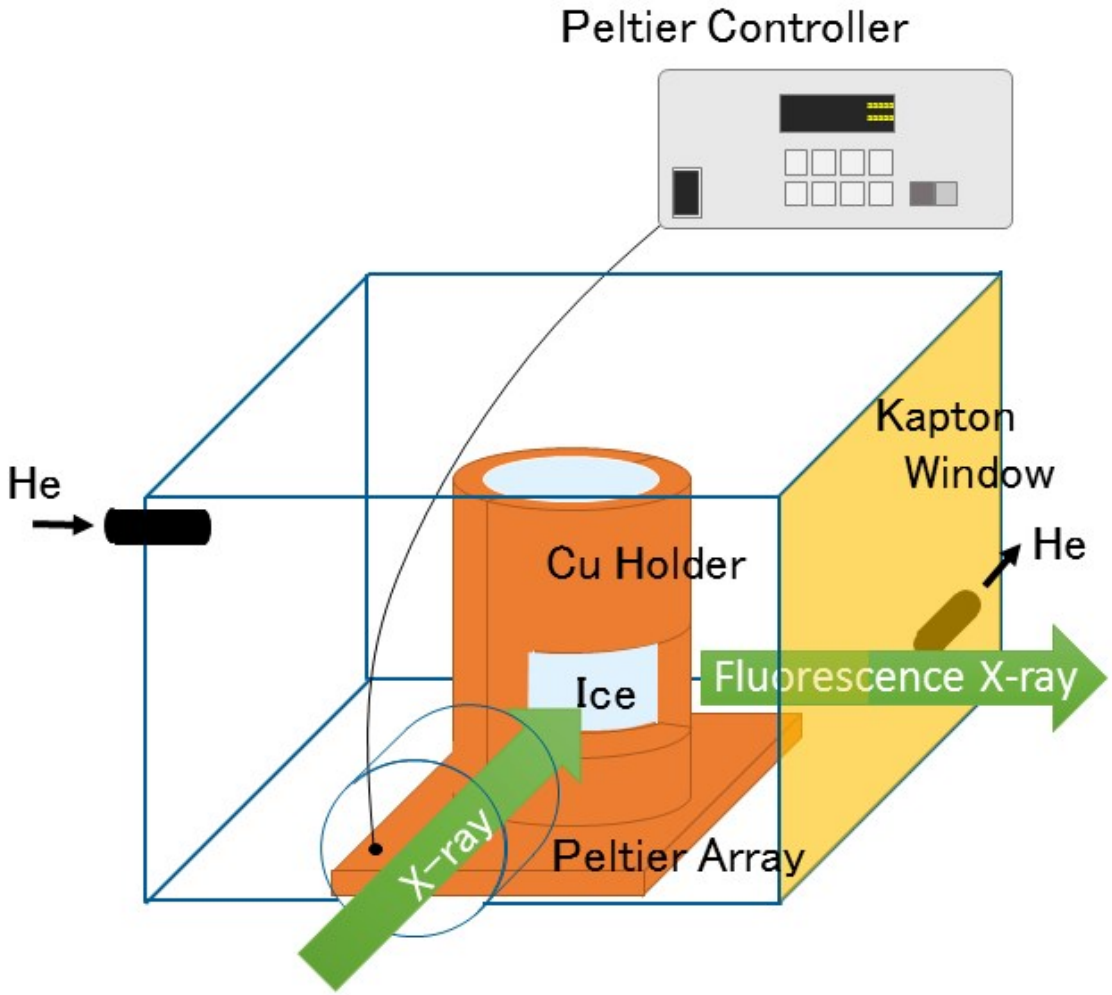

Figure S5. Schematic representation of the sample setup for XAFS measurements.