ENTHALPY RELAXATION PHENOMENON OF HEAVY ICE*

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ABSTRACT. The heat capacities of quenched and annealed heavy ice Ih were measured in the temperature range 14 to 300 K by an adiabatic calorimeter. A relaxational thermal anomaly was found at around 115 K and this phenomenon was ascribed to the onset of deuteron ordering in the crystal. The average activation enthalpy of the relaxational process was determined to be (26 ± 5) kJ mol⁻¹. Residual entropies of the crystal were recalculated on the basis of the present heat-capacity data combined with the revised values for enthalpy of vapourization, saturated vapour pressure, and spectroscopic entropy. They are (3.47 ± 0.41) J K⁻¹ mol⁻¹ for the quenched crystal and (3.44 ± 0.41) J K⁻¹ mol⁻¹ for the crystal annealed at 102–106 K for 264 h. The characteristics and the origin of the anomaly are discussed in comparison with that of ordinary ice.

RÉSUMÉ. *Phénomène de relaxation enthalpique de la glace "lourde"*. Les capacités calorifiques de glace Ih lourde trempée et recuite sont mesurées entre 14 et 300 K grâce à un calorimètre adiabatique. Une anomalie de relaxation thermique a été trouvée autour de 115 K et ce phénomène est attribué à l'apparition d'un ordre des deutériums dans le cristal. L'enthalpie d'activation du processus de relaxation est de (26 ± 5) kJ mol⁻¹. Les entropies résiduelles du cristal ont été recalculées grâce aux présents résultats de capacité calorifique combinés aux nouvelles valeurs de l'enthalpie de vaporisation, de pression, de vapeur saturante et d'entropie spectroscopique. On trouve $(3,47\pm0,41)$ J K⁻¹ mol⁻¹ pour le cristal trempé et $(3,44\pm0,41)$ J K⁻¹ mol⁻¹ pour le cristal recuit à 102–106 K pendant 264 h. Les caractéristiques et les origines de l'anomalie sont discutées en comparaison avec celle de la glace ordinaire.

ZUSAMMENFASSUNG. *Enthalpierelaxationserscheinung des schweren Eises*. Die Wärmekapazitäten von abgeschrecktem und getempertem schweren Eis Ih wurden im Temperaturbereich 14 bis 300 K mit einem adiabatischen Kalorimeter gemessen. Eine thermische Relaxationsanomalie wurde um 115 K gefunden, und diese Erscheinung wurde dem Einsetzen einer Ausordnung der Deuteronen im Kristall zugeschrieben. Die Aktivierungsenthalpie des Relaxationsprozess wurde zu (26 ± 5) kJ mol⁻¹ bestimmt. Die Restentropien des Kristalls wurden neu berechnet auf der Grundlage der gegenwärtigen Wärmekapazitätswerte in Verbindung mit den überprüften Werten für die Verdampfungsenthalpie, Dampfsättigungsdruck und spektroskopische Entropie. Sie betragen $(3,47\pm0,41)$ J K⁻¹ mol⁻¹ für die abgeschreckten Kristalle und $(3,44\pm0,41)$ J K⁻¹ mol⁻¹ für den bei 102–106 K für 264 h getemperten Kristall. Die Merkmale und der Ursprung der Anomalie werden im Vergleich zu gewöhnlichem Eis besprochen.

INTRODUCTION

The structural features of hexagonal ice as revealed by various experimental techniques and theoretical consideration are that, while the oxygen atoms form a regular hexagonal lattice, the hydrogen atoms are arranged randomly in that structure. Since such a disordered structure contradicts the Third Law of Thermodynamics, search for a possible ordering of the proton system at low temperatures has been one of the main subjects of recent investigation of hexagonal ice. Haida and others (1974) reported new facts concerning this subject. In that study, the heat capacities were measured for H_2O ice quenched and annealed at several temperatures below 100 K and at around 100 K the heat-capacity values were found to be clearly dependent upon thermal history of the crystal. The spontaneous temperature rise during the annealing experiment was followed to obtain the characteristic time for enthalpy relaxation. They interpreted these phenomena as follows: As the temperature is lowered, change in the proton configuration becomes suppressed on its way to achieving a more ordered state because of the prolonged relaxation time for realizing the process.

If this is the case, we naturally expect a similar behaviour in D_2O ice. Already, there have been some attempts to find a similar anomaly in D_2O ice corresponding to that in H_2O ice around 100 K. Many years ago, Long and Kemp (1936) measured the heat capacity of D_2O ice by use of the same calorimeter employed for H_2O ice and showed the existence of finite

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residual entropy (3.22 J K⁻¹ mol⁻¹) just as in the case of H_2O ice. Nevertheless, they were unable to detect any phenomena of slow attainment to thermal equilibrium in spite of their intention inspired by the report of Giauque and Stout (1936). On the other hand, recent investigations of elastic moduli for D_2O ice by Helmreich (1973) showed anomalous behaviour at temperatures between 100 and 150 K. Thus the present study on D_2O ice was aimed at

TABLE I. MOLAR HEAT CAPACITIES OF DEUTERIUM OXIDE
(Molecular weight = 20.028)

$\dfrac{T_{av}}{K}$	$\dfrac{C_s}{J\,K^{-1}\,mol^{-1}}$	$\dfrac{\Delta T}{K}$	$\dfrac{T_{av}}{K}$	$\dfrac{C_s}{J\,K^{-1}\,mol^{-1}}$	$\dfrac{\Delta T}{K}$	$\dfrac{T_{av}}{K}$	$\dfrac{C_s}{J\,K^{-1}\,mol^{-1}}$	$\dfrac{\Delta T}{K}$
Crystal			(Series 1)—continued			(Series 3)—continued		
13.80	0.888	0.506	101.55	17.13	2.354	151.73	25.80	2.503
14.47	0.959	0.511	103.69	17.51	1.922	154.21	26.22	2.469
15.01	1.064	0.574	105.61	17.83	1.898	156.67	26.62	2.438
15.71	1.193	0.820	107.49	18.16	1.870	159.09	27.01	2.411
16.47	1.364	0.857	109.54	18.51	2.207	161.49	27.43	2.381
17.40	1.559	0.861	111.75	18.88	2.194	163.51	27.75	3.001
18.29	1.764	0.890	114.10	19.29	2.471	166.48	28.24	2.921
19.19	1.948	0.960	115.54	19.74	2.427	169.38	28.71	2.890
20.15	2.185	0.955	118.95	20.17	2.384	172.36	29.18	3.070
21.14	2.411	0.989	121.32	20.59	2.346	175.42	29.70	2.042
22.13	2.644	0.979	123.71	21.02	2.426	176.33	29.85	3.050
23.17	2.883	1.086	126.11	21.46	2.383	179.36	30.32	3.005
24.28	3.147	1.269	128.48	21.86	2.349	182.33	30.81	2.946
25.49	3.390	1.145	130.81	22.27	2.319	185.25	31.30	2.891
26.79	3.690	1.331	133.12	22.68	2.283	188.32	31.78	3.258
28.12	3.975	1.328	135.38	23.07	2.253	191.86	32.36	3.232
29.44	4.279	1.321				195.07	32.84	3.189
30.87	4.558	1.532				198.24	33.37	3.157
32.39	4.866	1.510	(Series 2)			201.38	33.88	3.115
33.88	5.175	1.465	103.67	17.48	2.789	204.46	34.37	3.057
35.48	5.490	1.733	106.47	17.97	2.426	207.50	34.83	3.030
37.21	5.833	1.739	108.68	18.45	2.385	210.52	35.32	2.997
38.93	6.156	1.696	111.04	18.91	2.335	213.60	35.81	3.159
40.63	6.481	1.689	113.34	19.34	2.274	216.74	36.29	3.136
42.35	6.814	1.761	115.61	19.75	2.251	219.85	36.78	3.077
44.12	7.106	1.769	117.89	20.16	2.314	222.92	37.30	3.055
45.94	7.446	1.885	120.20	20.56	2.298	225.95	37.72	3.022
47.85	7.786	1.928	122.48	20.94	2.261	228.96	38.22	2.985
49.79	8.128	1.960	124.72	21.29	2.228	232.04	38.68	3.189
51.74	8.480	1.935	126.92	21.67	2.174	235.22	39.21	3.160
53.72	8.848	2.029	129.15	22.04	2.289	238.36	39.69	3.125
55.79	9.233	2.116	131.43	22.40	2.275	241.47	40.16	3.085
57.92	9.607	2.143	133.68	22.79	2.236	244.54	40.66	3.054
60.10	9.985	2.316				247.56	41.12	2.996
62.30	10.37	2.194				250.58	41.56	3.030
64.55	10.76	2.316	(Series 3)			253.58	42.06	2.967
66.88	11.16	2.342	111.18	18.86	2.120	256.65	42.55	3.181
69.21	11.57	2.328	113.19	19.25	1.912	259.82	43.04	3.161
70.21	11.74	2.552	115.09	19.58	1.889	262.96	43.57	3.113
72.72	12.18	2.465	116.97	19.92	1.863	266.07	44.06	3.100
75.14	12.60	2.368	118.86	20.29	1.926	269.27	44.61	3.315
77.48	13.02	2.317	120.77	20.63	1.900	272.42	45.31	2.984
79.84	13.41	2.041	122.71	20.95	1.977	275.12	47.18	2.402
81.86	13.75	2.000	124.68	21.26	1.955			
84.08	14.14	2.440	126.62	21.59	1.929	Liquid		
86.48	14.55	2.364	128.54	21.90	1.910	280.51	86.15	1.936
88.82	14.95	2.326	130.49	22.23	1.987	282.45	85.95	1.951
			132.46	22.58	1.962	284.49	85.71	2.128
			134.41	22.90	1.938	286.61	85.55	2.107
(Series 1)			136.65	23.29	2.429	288.73	85.38	2.134
88.53	14.90	2.202	139.07	23.69	2.402	291.03	85.24	2.471
90.70	15.29	2.133	141.45	24.09	2.367	293.52	85.06	2.492
92.81	15.64	2.062	143.80	24.49	2.336	296.01	84.91	2.495
94.90	15.99	2.062	144.49	24.60	2.046	298.50	84.78	2.495
96.95	16.35	2.040	146.73	24.99	2.422	300.63	84.74	1.786
99.17	16.73	2.403	149.21	25.37	2.538			

finding the expected anomaly analogous to that in H_2O ice and also to detect some isotope effects on the relaxational ordering process if any. A brief description of the experimental results was reported by Haida and others (1973).

EXPERIMENTAL

The heat capacities of D_2O ice were measured by the same calorimeter and auxiliary apparatus used in the investigation of H_2O ice. Briefly, it is an adiabatic calorimeter with an intermittent heating method. The performance of the adiabatic control is such that natural heat leakage to the calorimeter cell including self-heating due to thermometer current is about 8 μJ s^{-1} at around 100 K. The precision of the measurements was, in general, better than 0.1%.

Heavy water obtained from E. Merck (99.75% deuteration level) was degassed carefully by freeze–pump–thaw cycles *in vacuo*. The sample was then distilled and the middle fraction (32.381 g) was introduced into the calorimeter cell by vacuum distillation. The D_2O ice crystal made in the calorimeter cell *in situ* was annealed at 273.6 K for about 3 d and then cooled down to 77 K at a rate of about −1 K min^{-1} ("quenched" sample).

EXPERIMENTAL RESULTS

Heat-capacity measurement

The heat capacities of D_2O ice were measured in the temperature range between 14 and 300 K along the same lines as the study on H_2O ice. The first series of measurement is for a "quenched" sample, while the data for Series 2 and 3 correspond to the ones annealed at 102–106 K for 264 h and at 110 K for 166 h, respectively. The heat-capacity data are listed in Table I. For all of these series of measurements, there appeared a lag in equilibrium in the temperature region around 115 K. This observation stands in contrast to Long and Kemp's result. These thermal anomalies are illustrated in Figure 1. "Temperature drift", the ordinate of the figure, is the value $\{T\,(30\,\mathrm{min}) - T\,(10\,\mathrm{min})\}$, where $T(t)$ is the temperature at time t; the time origin is the end-point of energy input. For Series 1, an exothermic temperature drift was observed, while an endothermic one was observed for Series 2 and 3 in the temperature range between 100 and 130 K. The reversal of the temperature drift from exothermic to endothermic by annealing and also the increase of temperature drift by annealing at lower temperature for longer periods found in these measurements are characteristic of relaxation phenomena which appear in a glass-transition region of the frozen-in disordered system. Thus, some degrees of freedom in D_2O ice crystals must be frozen around 115 K.
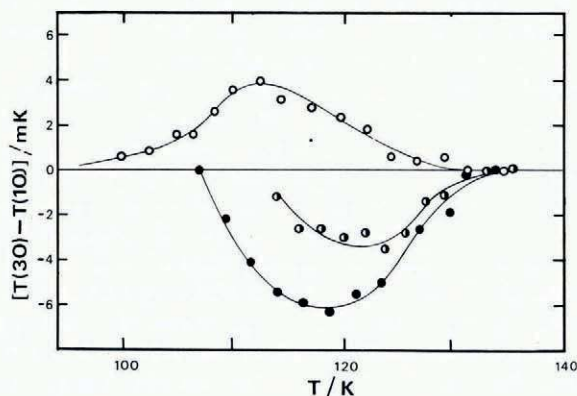

Fig. 1. Anomalous temperature drift observed in D_2O ice. ○ Series 1, ● Series 2, ◑ Series 3.

The heat-capacity data for the quenched and the annealed samples are shown in Figure 2 in the form of (C_p/T) versus T. The data for annealed samples (Series 2 and 3) exceed those for the quenched one (Series 1), the excess part being dependent on the annealing temperature. These observations confirm the existence of enthalpy relaxation around 115 K in D_2O ice. Since deuterons in D_2O ice have the disordered configuration, and since all the high-pressure polymorphs of ice reach some degree of order at low temperature, it seems natural to ascribe these anomalies to the relaxational deuteron ordering as described below.
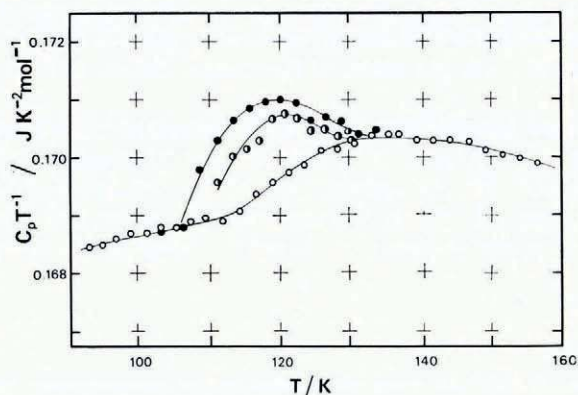
Fig. 2. C_p/T of D_2O ice plotted against temperature. ○ Series 1, ● Series 2, ◑ Series 3.

Enthalpy of fusion

The equilibrium temperatures of the fractional melting were measured and from the results, the triple point and liquid (soluble), solid (insoluble) impurities were determined to be 276.95 K and 0.000 5%, respectively. The specimen used is claimed by the manufacturer to contain 0.25% isotopic impurity. Therefore the isotopic impurity would not affect the melting behaviour. This fact was already noticed by Long and Kemp, and also observed for H_2O ice by us.

The molar enthalpy of fusion, 6 314.6 J mol^{-1}, is in reasonable agreement with that of Long and Kemp (1936) and those cited in their paper.

Residual entropy

The residual entropy calculated by Long and Kemp for D_2O ice had a discrepancy with that for H_2O ice. If the sophisticated theoretical work by Nagle (1966) describes well the actual status of the disordered proton system, this value corresponds to 6% of deuteron ordering. This seems to be too much in view of the fact that merely 2% of the residual entropy of H_2O ice was removed by annealing the crystal over a period longer than 30 d as revealed by Haida and others (1974). It seems worthwhile, therefore, to retest the value using recent more reliable data since the attainment of a more ordered state is eagerly desired for the conclusive interpretation of the anomaly at around 100 K in H_2O ice.

The calculation of the residual entropy was carried out by using our data along with the following values. The values of the molar enthalpy of vapourization, saturated vapour pressure, and the spectroscopic entropy of standard ideal gaseous state at 25°C were obtained from the works by Rossini and others (1940) and by Besley and Bottomley (1973). The residual entropies were found to be 3.47 (Series 1), 3.44 (Series 2), and 3.45 (Series 3) ±0.41 J K^{-1} mol^{-1}, respectively, as shown in Table II. These values are comparable in magnitude with those for H_2O ice. The isotope effect on the residual entropy is much less than that considered hitherto.

TABLE II. RESIDUAL ENTROPY OF HEXAGONAL HEAVY ICE

Temperature range T K	Source	Entropy change ΔS J K^{-1} mol^{-1}
0–13	Debye extrapolation	0.23_2
13–276.95	$\int (C_s/T)\,\mathrm{d}T$ (graphical) (for quenched sample)	$43.34_5 \pm 0.08$
276.95	Melting 6 314.6/276.95	$22.78_1 \pm 0.04$
276.95–298.15	$\int (C_s/T)\,\mathrm{d}T$ (graphical)	$6.30_4 \pm 0.01$
298.15	Vapourization 45.398/298.15 Compression $R \ln (20.510/760)$ Gas imperfection	$152.26_6 \pm 0.15$ $-30.03_0 \pm 0.03$ 0.009
	Total	$194.92_7 \pm 0.31$
	Spectroscopic entropy (ideal gas at 101.325 kPa, 25 °C)	$198.4 \quad \pm 0.1$
	Residual entropy: quenched sample annealed sample (series 2) annealed sample (series 3)	3.47 ± 0.41 3.44 ± 0.41 3.45 ± 0.41

The theoretical value of the residual entropy for a hypothetical completely disordered crystal based on the Bernal–Fowler–Pauling statistical model is $(3.408 \pm 0.000\,8)$ J K^{-1} mol^{-1}. The experimental value of the residual entropy for a quenched sample coincides with this value within the estimated experimental error. Therefore, the order attained can only be at most 1% even for the most annealed sample in this work (Series 2). Thus we can only investigate the very initial part of the ordering process in D_2O ice just as in H_2O ice, because the relaxation time of the ordering process increases rapidly with decreasing temperatures, at which significant deuteron ordering might proceed.

Activation enthalpy of the relaxation process

A spontaneous temperature rise due to enthalpy release in the sample during the annealing experiment was followed intermittently. Three typical examples of the temperature drift are shown in Figure 3, where the straight lines refer to the temperature drift caused by heat leakage due to incompleteness of the adiabatic control. The asymptotic approach of the temperature to the straight line was analysed by an exponential decay function with a single characteristic time τ, in the same manner as for H_2O ice. The relaxation times determined in this way are summarized in Table II along with other data. From the Arrhenius plot of the relaxation time, the average activation enthalpy of the relaxation process was determined to be (26 ± 5) kJ mol^{-1}, which is very similar to the value, (22 ± 4) kJ mol^{-1}, for H_2O ice in spite of large mass ratio of deuteron to proton. These values are within the range of 15 to 25 kJ mol^{-1} reported by Sakabe and others (1970), Helmreich (1969), and Bishop and Glen (1969) for the activation enthalpy of the anomaly in pure and doped H_2O ice at around 100 K. These values for the activation enthalpy are very similar to those ascribed to the mobility of the Bjerrum defect, e.g. Jaccard (1959), and Engelhardt and Riehl (1966) gave 22 and 17 kJ mol^{-1} for this defect, respectively. This seems to suggest, as has been pointed out by Helmreich (1969) and Bishop and Glen (1969), that the Bjerrum fault participates in the ordering process of the deuteron configuration.
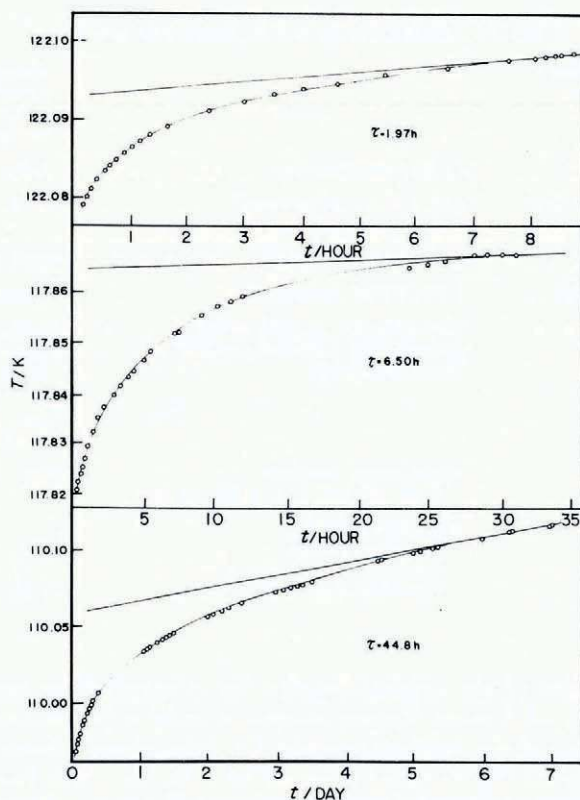
Fig. 3. Three typical examples of spontaneous temperature rise due to enthalpy relaxation of D_2O ice.

TABLE III. DATA ON ANNEALING EXPERIMENTS

Annealing temperature T_{an} K	Annealing time t_{an} h	Relaxation time τ h
110.04	166	44.8
112.89	92	12.2
113.46	68	17.2
117.85	31	6.50
120.85	28	4.63
122.09	9	1.97

DISCUSSION

If we plot the heat capacity data reported by Long and Kemp (1936) in the form of (C_p/T) versus T, we can find clearly an anomalous increase in heat capacity at around 120 K. However, they did not mention this anomalous behaviour. Their failure to observe the anomalous temperature drift seems to be due to a difference in calorimetric principles. Since their calorimeter is of the isoperibol type, a correction for heat exchange between calorimeter cell and "quasi-isothermal" shield must be applied. After this correction, their calorimeter is reported to be capable of detecting a heat evolution (or absorption) exceeding an amount of 8×10^{-4} cal mol^{-1} min^{-1} (1.9×10^{-4} J mol^{-1} min^{-1}). The corresponding temperature drift rate is approximately 4 mK/20 min. Therefore, if they had annealed the crystal for a long time, they might have observed the corresponding endothermic temperature drift.

The present calorimetric observation is of course a kinetic effect, but reflects an underlying equilibrium property of the crystal. Unless the kinetic effect were associated with equilibrium "excess" heat capacity or enthalpy, we can not observe any spontaneous temperature variation under adiabatic conditions.

Chamberlain and Fletcher (1971) and Johari and Jones (1975) have reported that the current peak due to thermally stimulated depolarization (TSD) observed at 110 K and 124 K in H_2O and D_2O ices is due to relaxation of frozen-in orientation polarization of water molecules in both crystals. The relaxation times for reorientation as determined by the TSD current and by the step-response method studied by Johari and Jones (1975) are plotted logarithmically against reciprocal temperature in Figure 4, along with the characteristic times determined by an enthalpy-relaxation experiment. The three sets of relaxation times for H_2O ice can be connected by a single smoothed curve. The calorimetric data for D_2O ice are higher by about one order of magnitude than the dielectric data and the difference is likely to be due to the different amounts of physical and chemical defects involved in the respective specimens. The deuteration level of the calorimetric specimen is 99.75%, while that of the dielectric specimen is reported to be 98.75%. In spite of some differences in their behaviour, however, this figure indicates essentially two facts. First, the degrees of freedom associated with the enthalpy relaxation are the same as in the dielectric relaxation. This explanation was also proposed by Stout and Giauque (1936) and by Johari (1976), but this figure provides convincing evidence for that. Secondly, some configurations of water molecule realized by that degree of freedom must differ energetically from others. This is the necessary condition for the relaxation to be observable calorimetrically.

Campbell and others (1967) have calculated the lattice energies of an ice crystal in terms of multipole interaction as a function of orientation of the water molecules and found significant differences between the energy of the various configurations which must affect the thermodynamic properties of the crystal at temperatures around 100 K. All of these facts lead to a picture concerning the ordering process of protons (or deuterons) in ice crystals. The water molecules are in an orientationally disordered state at high temperatures; all the
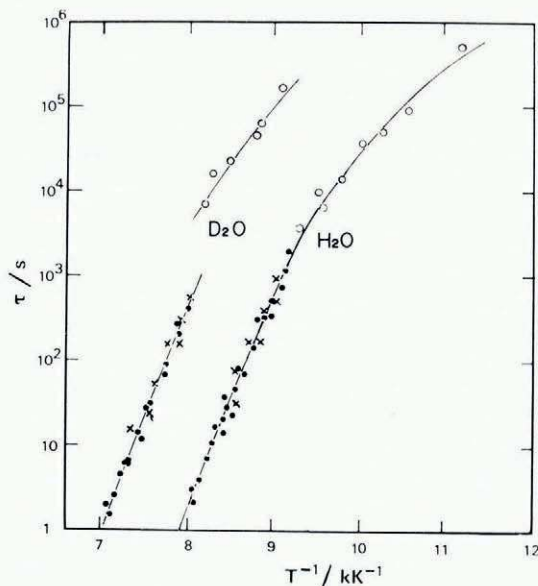

Fig. 4. Relaxation-time data of ice crystals determined by dielectric and calorimetric methods. ○ calorimetric method × TSD method, ● step-response (or bridge) method.

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six orientations of a water molecule might be realized essentially equally, as the Pauling (1935) model and the subsequent statistical model by Lieb (1967) assume ordinarily. As the crystal is cooled down, some of the proton configurations are favoured by intermolecular interactions among the water molecules, thus realizing a locally ordered state. The corresponding configurational heat capacity increases gradually as the temperature is lowered.

The configurational heat capacity would increase further and reach a maximum value at a transition point where an ordered state might be realized, if we could cool the crystal at an infinitely slow rate. The prolonged relaxation time, however, hinders the crystal from reaching the equilibrium state in an actual fast-cooling experiment and the proton configurational disorder is frozen at a certain temperature. The corresponding decrease in the configurational heat capacity occurs at 100–110 K for H_2O ice and at 120–130 K for D_2O ice, respectively. Consideration of the values of residual entropies for the quenched and the annealed samples of H_2O and D_2O ice crystals shows that we are concerned with very initial stage of the ordering process and the hypothetical transition point seems to be located much lower than 100 K. Pitzer and Polissar (1956) predicted the existence of an order–disorder transition in H_2O ice at about 60 K with a polar structure of the resulting phase.

In passing, we may mention the deviation of the calorimetric relaxation time of ice crystals from the high-temperature behaviour of the dielectric relaxation time,

$$\tau = \tau_0 \exp [B/(T - T_0)],$$

where τ_0, B, and T_0 are empirical constants. This equation was observed by Johari and Jones (1976) to hold for the dielectric relaxation time of D_2O ice in the temperature range $120 < T/K < 170$, with the values $\tau_0 = 3 \times 10^{-16}$ s, $B = 828$ K and $T_0 = 60$ K. Adachi and others (1968) observed a similar deviation of calorimetric relaxation time in the orientationally disordered crystal cyclohexanol below its "glass-transition" temperature and explained this from the viewpoint of plural relaxation mechanisms with different time constants. The multiplicity of dielectric relaxation times of D_2O ice at low temperature was pointed out by Johari and Jones (1976). Probably, the calorimetric observation corresponds to the average relaxation time at a relatively high temperature but will correspond to the fastest process when the distribution of the relaxation times becomes wider as the temperature is lowered.

The excess enthalpy released during an annealing experiment in a frozen state is regained as an increased heat capacity when the crystal is heated. If we compare curves of C_p/T versus T for H_2O and D_2O ice crystals, we notice that the excess heat capacity of D_2O ice appears about 20 K higher than that of H_2O ice. This temperature difference is likely to reflect the difference in equilibrium properties of both crystals. A Curie–Weiss representation of the dielectric constants of both crystals by Johari and Jones (1976) indicated that the extrapolated Curie point was 27 K higher for D_2O than that for H_2O ice. Therefore, the higher peak temperature of excess heat capacity for D_2O ice seems to reflect the correspondingly higher Curie temperature. An increase in the Curie point of a hydrogen-bonded crystal on deuteration is exemplified by many systems. Chan (1973) gave a possible interpretation of the increase in the Curie temperature from the viewpoint of isotopic effect on lattice vibrational frequencies and zero-point energy.

Nevertheless, the relaxation times of both crystals reach a calorimetric time scale ($\approx 10^4$ s) at 104 K and 121 K, respectively, and therefore we can observe only a high temperature part (very initial part) of the ordering process for both crystals. The amount of excess heat capacity is nearly the same for both crystals when comparing the same time-scale experiments, in spite of the difference in their respective Curie temperatures. This fact seems to indicate that the relaxation time for the reorientational degree of freedom is governed by a static property. The important role configurational entropy plays in the relaxational properties of frozen system was first proposed by Adam and Gibbs (1965). If this mechanism is operative in the

case of ice crystals, we must abandon the assumption of single relaxation time employed in the analysis of temperature–time curves from the calorimeter. Configurational order and hence the relaxation time must change as the time elapses in one experiment. The experimental verification of this mechanism requires a much better performance of the adiabatic control because of the smallness of the excess enthalpy involved and because of the ambiguity in determining the "base line" due to heat leakage. In this respect, it may be interesting to study a solid-solution system, H_2O–D_2O. The Curie point of the system may be situated between those of the parent crystals. The complexity of the system is increased by the isotopic substitution, which is expected to shorten the relaxation time of the system. Alternatively the impurity effect might cause a shortening of the relaxation time. Thus, we can hope to observe an enhanced heat-capacity anomaly.

In any event, we could detect the relaxational heat-capacity anomaly in D_2O ice in an analogous way to that in H_2O ice. This means that the rate of rearrangement of protons (deuterons) is on the calorimetric time-scale (10^3–10^6 s) at a temperature range where energy differences among the possible orientations of the disordered water molecules promote ordering even slightly. The recent observation of a heat-capacity anomaly in another orientationally disordered crystal, CO, around 18 K by Atake and others (1976) was interpreted along the same lines. The relaxational nature of the anomalies in CO and ice crystals is seemingly not independent of the existence of residual entropy in both crystals.

Up to this point, we have assumed implicitly that the observed heat-capacity anomaly was an intrinsic property of the ice crystal that was brought about by the reorienting motion of defects which lost their mobility as the temperature was lowered. There might be another possibility, that the anomaly is associated with some local order induced by lattice defects. However, we can scarcely expect to detect calorimetrically the thermal anomaly due to such defects existing in minor concentration. The amount of orientational defects in pure ice is considered to be of the order of 10^{-7} mol $\%$ even at $-10°C$, and that of ionic defects is much less. An experiment to see how the entropy of an ice crystal can be removed by doping with a particular impurity might be helpful to clarify the nature of the relaxational anomaly. If the corresponding defect were to induce some short-range local order in water molecules in the neighbourhood of the defect, we would expect an increased amount of excess heat capacity in a doping experiment, because the increase in defect concentration will increase the number of regions in which some local order is induced. The excess heat capacity will be observed at essentially the same temperature as in a pure crystal. If the defect were to shorten the reorganization rate of the whole system, we could expect an increased heat-capacity anomaly that starts from a lower temperature. Thus the doping experiment will throw some light on the "intensive" and the "extensive" roles of the lattice defects.

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