The Specific Heat of Pure and Doped Ice Near 120 °K

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The specific heat of pure and doped ice Ih single crystals was measured from 80°K to 230 °K with a differential heat-flux calorimeter. In the region near 120 °K the specific heat exhibits a positive anomaly which is explained by a partial ordering of the ice.

Introduction

Measurements of the dielectric constant[1, 2], the elastic moduli[3], the double refraction[4] and of the thermally stimulated current glow curves[5] made on ice at low temperatures exhibit an anomalous behaviour in the temperature range around 100 °K. It has been suggested by several authors that the anomalies are a result of a ferroelectric transition of the crystal from a disordered to an ordered modification near 100 °K. A sensitive and relatively simple way of studying such transitions is the measurement of the specific heat as a function of temperature. In 1936 GIAUQUE and STOUT measured the specific heat of ice Ih very precisely[6]. With the help of their measurements they calculated the "zero-point" entropy of ice to be (0.82 ± 0.05) cal/mole °K (≈ 3.44 J/mole °K). This value agrees extremely well with the value calculated by PAULING[7] and later NAGLE[8] for complete disorder, indicating that any amount of order present in ice at low temperatures must be very small. Giauque and Stout also discovered that there is a small anomaly in the specific heat between 85° and 100 °K. They associated this anomaly with the initial stages of excitation of some new degrees of freedom. The anomalous effects in several of the quoted experiments were strongly dependent upon the purity of the ice used. Ice which was either impure or doped produced larger effects than pure ice specimens. In order to disclose how the anomaly in the specific heat depends upon the amount of doping and whether this effect is an intrinsic property of pure ice, the specific heat was measured dependent upon temperature and amount of doping[9].

Calorimeter

The specific heat of the ice samples was measured by means of a heat-flux calorimeter. The construction of the calorimeter is illustrated in Fig. 1. This type of calorimeter is especially suited to the measurement of small changes in the heat capacity of samples of low thermal conductivity. The calorimeter consists of two columns of thermocouples built into borings (6 cm ∅) in a large copper cylinder. Twenty planes of six thermocouples arranged in a starlike fashion and suspending, in their center, the sample holder tube, make up one column. The thermocouples are all in series. Measurements can be made either at a constant temperature, or while slowly heating the sample. In the latter case the calorimeter block is heated as a whole. The sample itself is heated due to

a) the heat-flux through the 120 thermocouples,
b) the heat transfer by radiation and,
c) the heat-flux through the residual gas.

The thermocouples allow the exact measurement of the temperature difference between the sample and the calorimeter block. 120 thermocouples are used so as to decrease the temperature difference between the sample and the block, thereby enabling the radiation

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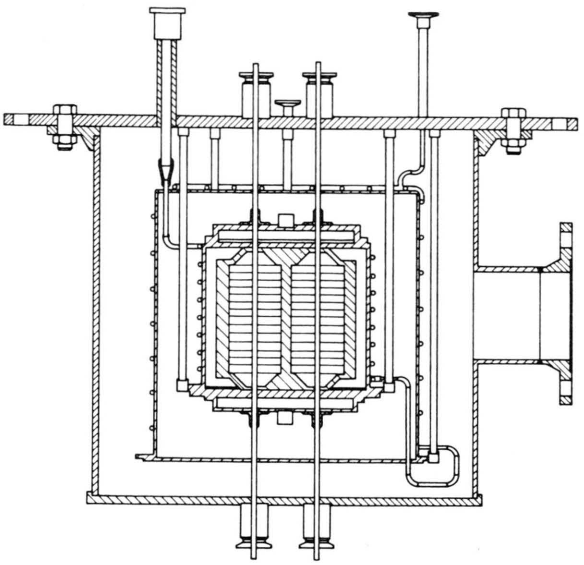

Fig. 1. The calorimeter.
1 Calorimeter tubes (the samples are inserted in these tubes). 2 Thermocouple column (120 thermocouples). 3 Radiation shields. 4 Liquid nitrogen inlet. 5 Nitrogen outlet. 6 Calorimeter block. 7 To vacuum pump. 8 Cooling coil.

to be neglected in relation to the heat flux through the thermocouples, which is a function of the measured thermoelectric voltage. A further advantage is that the many thermocouples maintain virtually the same temperature over the whole surface of the sample. In order to raise the temperature T of the sample by $\mathrm{d}T$ an amount of heat $\mathrm{d}Q$ must be supplied. $\mathrm{d}Q$ is proportional to the heat capacity $m\,c$ of the sample:

$$\mathrm{d}Q = m\,c(T)\;\mathrm{d}T$$

which is, per time interval:

$$\dot{Q}(t) = m\,c(T)\;\dot{T}(t).$$

$\dot{Q}$ is the heat flux into the surface of the sample; it is proportional to the temperature difference between the sample and the calorimeter block $(T_\mathrm{B} - T_\mathrm{S})$ and consequently to the e.m.f. across the thermocouples U of the column.

$$\begin{aligned}\dot{Q}(t) = m\,c(T)\;\dot{T}(t) &= K(T)\;\big(T_\mathrm{B}(t) - T_\mathrm{S}(t)\big)\\ &= K(T)\;U(t)\;.\end{aligned}$$

$K(T)$ is the temperature dependent heat flux constant for which the calorimeter is calibrated prior to the actual measurements.

By measuring the zero effect (without sample):

$$m_0\,c_0(T) = [K(T)\;U_0(t)]/\dot{T}_0(t) \tag{1}$$

and then the effect with the sample:

$$m_1\,c_1(T) = [K(T)\;U_1(t)]/\dot{T}_1(t) \tag{2}$$

where $\quad m_1\,c_1(T) = m_0\,c_0(T) + m_\mathrm{ice}\,c_\mathrm{ice}(T)$

and $\quad \dot{T}_1(t) = \dot{T}_0(t) = \dot{T}(t)\;.$

Subtracting (1) from (2):

$$(c_p)_\mathrm{ice} = K(T)\;\big(U_1(t) - U_0(t)\big)/m_\mathrm{ice}\,\dot{T}(t)\;.$$

This is the result for one of the columns. By using a differential heat flux calorimeter, i. e. two columns, and introducing an inert test sample into the one side the sensitivity of the instrument for changes in the heat capacity is greatly increased. A detailed theoretical description is given by RAU and WENZL [10].

$U(t)$ and $T(t)$ were registered simultaneously and continuously. Keeping the heating rate constant proved to be impractical because regulation of the applied power caused fluctuations in the heat-flux thereby reducing the accuracy of the method. A constant heating power was thus applied and a slightly temperature dependent heating rate was taken into account. Changes in the specific heat amounting to less than 0.015 J/mole °K $(2 \times 10^{-4}$ cal/g °K) could be measured.

Sample Preparation and Experimental Procedures

Samples of pure and doped poly- and single crystalline ice were prepared. The monocrystalline samples consisted of three or four cylinders of ice, each measuring approximately 3 mm in diameter and 30 mm in length. Together they amounted to about 0.5 gm. These samples were cut from a large single crystal by means of a lathe. The crystals were grown according to the method of ENGELHARDT and RIEHL [11]. The rather small dimensions were chosen in order to ensure thermal equilibrium within the specimen. The ice samples were introduced into a thin goldplated copper tube which was then inserted in the calorimeter. The calorimeter tube was filled with helium exchange gas to provide for a good thermal contact between the sample and the tube. The polycrystalline samples were made by simply freezing the highly distilled, and if required, HF-doped water; the concentration ranged from 1.6×10^{-6} mole HF/mole H_2O to 5.4×10^{-5} mole HF/mole H_2O.

All experiments were performed under the same experimental conditions:

1. The sample was installed and cooled immediately at a rate of 1 °K/min. The monocrystalline samples were introduced into the calorimeter only after it had been cooled to −10 °C.

2. The temperature was kept constant for two hours slightly above the boiling point of nitrogen in order to bring the whole calorimeter into thermal equilibrium.

3. A constant power source was switched on, causing an initial heating rate of about 1 °K/min at 90 °K and decreasing steadily to about 0.7 °K/min at 230 °K. The same procedure was repeated several times for each sample.

Consecutive measurements were made with and without the ice and subtracted from one another.

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Results

Figures 2 and 3 show two examples of the complete curves. In these curves anomalies can be seen at temperatures around 120 °K which can be interpreted as being related to a phase transition. Fig. 4 shows the results for Δc of several of the measured specimens. Definition of Δc: Δc is the enhancement of the specific heat over "baseline" values corresponding to a smooth curve interpolated from the behaviour of c outside the region of anomaly. a) and b) are both pure single crystals. c) is a sample of polycrystalline ice made of ion-exchanged water. d) is a single crystal doped with 1.8×10^{-5} mole HF/mole H_2O. e) is a single crystal doped with 3.6×10^{-5} mole HF/mole H_2O. f) shows the results of VAN DEN BEUKEL[12].

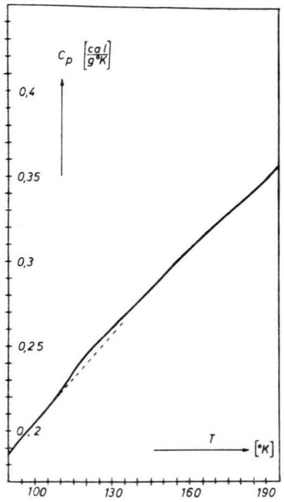

Fig. 2. Specific heat of a pure ice.

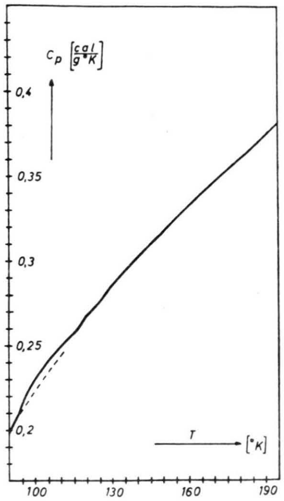

Fig. 3. Specific heat of doped ice.

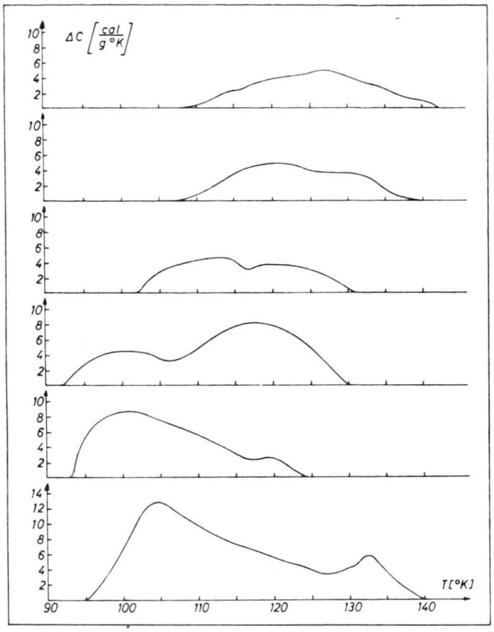

Fig. 4. Excess specific heat of various ice samples.

Values for the heat of the presumed transition and for the corresponding transition entropy can be calculated from the specific heat curves. The problem of exactly where to draw the baseline $\Delta c = 0$ introduces an uncertainty factor into the determined values. The heat of transition ΔQ ranges from (5.9 ± 0.8) J/mole for the purest crystals to (17 ± 4) J/mole for the strongly doped crystals i. e. 5.4×10^{-5} mole HF/mole H_2O. The corresponding values for the transition entropy ΔS range from (0.06 ± 0.01) J/mole °K to (0.15 ± 0.04) J/mole °K. The heat of transition and the transition entropy obtained by Van den Beukel for his heavily doped ice amount to (18 ± 3.3) J/mole and to 0.17 J/mole °K respectively. These values compare favourably with those obtained for the heavily doped crystals studied here.

The trend which is apparent in Fig. 4 was followed by all the samples studied: the anomaly decreases in size and moves toward higher temperatures as the purity of the sample is increased. Samples doped less than about 8×10^{-6} mole HF/mole H_2O all showed almost identical effects, a), b) and c). As the doping increased the shape of the anomaly became increasingly irreproducible, particularly the two peaks which are clearly visible in the results of Van den Beukel were sometimes clear and sometimes barely visible. This could be the result of an inhomogeneous distribution of HF within the crystal. The value for the transition entropy, however, followed the trend, increasing with the amount of doping. Several of the experiments were repeated with a cooling rate of about $^1/_2$ °K/min. No appreciable difference in the result was found for the same

Discussion

At normal pressure ice can exist in three different modifications; a hexagonal (Ih), cubic (Ic) and an amorphous form. The cubic phase can only be obtained by a transformation from a high-pressure or

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amorphous phase. The vitreous or amorphous phase is formed by slowly condensing the vapour at liquid nitrogen temperature. Ice grown at 0 °C and normal pressure is hexagonal and so far no indications of a transition to other modifications at low temperatures have been observed by crystallographic studies. SUGISAKI, SUGA and SEKI [13] have shown that the transition amorphous to cubic takes place near 130 °K and is strongly exothermic. The transformation of the cubic crystal to the hexagonal modification occurs in the temperature region from 160° to 210° and is also slightly exothermic, the heat of transition amounting to 160 J/mol. These phases appear, therefore, to always be metastable relative to ice Ih. If, however, parts of the sample do transform to the amorphous or cubic modifications, these parts would, on heating, again convert to the hexagonal phase, resulting in an apparent decrease in the specific heat in the temperature regions mentioned, contrary to the observed increase.

Giauque and Stout suggested that the anomaly is due to degrees of freedom with sharp excitation energy levels associated with the dipole orientation mechanism. Such an excitation should be visible in the phonon spectrum of ice as measured by inelastic neutron scattering. No anomaly can be detected there [14, 15]. Moreover, even a sharp peak of density of states inserted into the phonon spectrum at the frequency corresponding to an excitation at 100 °K does not change the specific heat in the manner observed but increases the specific heat over a very broad temperature region [16].

Another explanation for the anomaly would be that it indicates the onset of an order-disorder phase transition. Several authors have tried to calculate a critical temperature below which the disordered proton configuration would become ordered [17, 18]. PITZER and POLLISAR predicted a Curie temperature of 60 °K, HIPOLITO and LOBO of 100 °K [19].

In the perfect crystal this transition can only occur under violation of the BERNAL and FOWLER [20] rules. The real crystal, however, contains all kinds of imperfections which provide a number of mechanisms for the proton rearrangement. Since the anomaly is strongly dependent on the impurity concentration one must draw the following conclusion: mobile defects are generated at the impurity sites and the crystal reorients itself preferentially at these disturbed lattice sites. The time constant for the rate of ordering will be inversely proportional to the concentration times mobility of the various defects. As the temperature is lowered, the number and usually also the mobility of the defects will decrease. The time constant thus increases to values which hinder the ice in attaining an ordered structure. Another factor which acts to increase the required time is the fact that the effectivity of each defect in reorienting the ice will decrease as the amount of order increases. Below the ordering temperature the defects will tend to reorient the passed molecules into favorable orientations thereby rarefying the number of misoriented molecules. This, in turn, leads to an increase in the average number of diffusional jumps the defects must undertake in order to further orient the ice.

The experiments show that only a small fraction of the crystal becomes ordered as the temperature is lowered. The observed entropy change amounts to $1-5\%$ of the zero-point entropy corresponding to a completely disordered state. This agrees with the results of measurements of the dielectric constant [1] and electrical polarization [24]. BISHOP and GLEN [24], who found a large peak in the electrical polarization of heavily doped ice (HF) at 107 °K mention that the actual polarization observed is only about 6% of that for complete polarization of the sample. The observed size of the anomaly in the specific heat does not perceptibly change if the ice is cooled more

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slowly or even stored at 95 °K for 8 or 16 hours[12]. The ordering of this small part of the ice seems to be an almost spontaneous occurrence as the temperature is lowered to about 120 °K. A lowering of the activation energy for the movement of the defects in the neighbourhood of the dopant molecule could be the cause. It would mean that the area around a foreign molecule is quickly reorientated as the temperature reaches the transition temperature but that the mechanism then changes to a much slower procedure of reorienting the ice by the migration of the defects in the undisturbed crystal. It seems that in all the experiments so far the time required to reach more than only a few percent of order in the ice is far longer than the time normally available for these physical experiments.

Conclusion

Ice seems to possess a transition temperature near 120 °K at which it would become ordered during cooling if one would wait long enough. Doping the crystal catalyses the transition by lowering the activation energy for the mobility of the various defects in the neighbourhood of the dopant molecule.

Electroluminescence in Mylar Films

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Dedicated to Professor Dr. N. Riehl on his 70th birthday

Non-destructive electric breakdown through mylar films is associated with emission of an intense light flash. Within an active volume of about 4×10^{-8} cm³, $L \geqq 10^9$ photons are generated during a current pulse. L is proportional to the number of transported charge carriers (electrons) and independent from sample thickness. The emission spectrum is a superposition of ordinary mylar fluorescence centered at 370 nm and impurity bands at longer wavelengths. Interpretation is given in terms of acceleration of injected electrons within the positive cathodic spacecharge zone giving rise to both impact excitation and ionization, predominantly involving guest molecules.

Introduction

Since the discovery of electroluminescence in inorganic semiconductors and insulators[1] many papers have appeared reporting on the observation of the effect also with organic materials. Bernanose et al.[2] among others[3] have shown that organic scintillators, when embedded in a thin polymer matrix, can be excited in the same way by a periodic electric field as inorganic phosphors. Later on, however, Short and Hercules[4] were able to demonstrate that in most cases the observed emission bands can be identified with the second positive series of nitrogen, which is the spectrum obtained from the positive column of discharge tubes containing air or N_2 at low pressure. Thus the effect of organic electroluminescence could be traced back to spurious glow discharge taking place within microcavities of the matrix which contain small amounts of N_2 encapsulated during sample preparation.

In general the absence of electroluminescence – the term should not be confused with recombination radiation emitted as a result of annihilation of a thermalized electron-hole pair – in organic materials is a re-

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