

Thermoelectric Power of Ice Containing HF or NH₃

By G. W. BRYANT and N. H. FLETCHER

Department of Physics, University of New England,
Armidale, N.S.W., Australia

[Received 6 October 1964, and in revised form 9 February 1965]

ABSTRACT

Measurements have been made of the homogeneous thermoelectric power of ice containing differing amounts of HF or NH₃ impurity. The thermoelectric power is of the order of a few millivolts per degree and depends markedly in both sign and magnitude upon the type and concentration of impurity present. The experimental results are qualitatively in accord with the theory developed by Jaccard but there is considerable numerical disagreement. This is probably due in part to segregation effects in the polycrystalline specimens used. The experiment allows determination of several quantities relating to the effective charge and mobility ratio of current carriers in ice.

§ 1. INTRODUCTION

THE electrical properties of ice have been studied intensively during recent years and, as a result of the work of Workman *et al.* (1954), Eigen and De Maeyer (1956), Granicher (1958), Jaccard (1959) and others, there now exists a reasonably complete and consistent picture of conduction processes in ice.

The thermoelectric effect in pure ice has been studied by Latham and Mason (1961) who put forward a simple theory based on the fact that the mobility of protons in ice is 10 to 100 times greater than that of negative OH⁻ ions. They proposed that in the presence of a temperature gradient the more mobile protons migrate preferentially to the cooler end of the crystal, leaving the warmer end negatively charged. Experimental work on pure ice confirmed the existence of the effect and both theory and experiment agreed that, for a temperature difference ΔT across the crystal, a potential difference of $0.002\Delta T$ volts was developed. The effect of impurities in the ice was not investigated in detail by Latham and Mason, though they observed that addition of small amounts of HF or CO₂ tended to increase the charge separation.

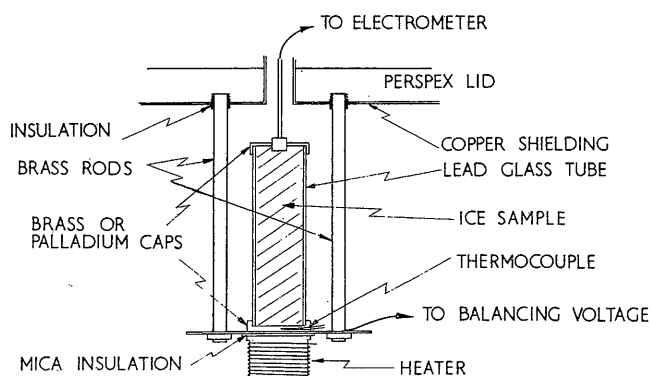
More recently Jaccard (1963) has put forward a fairly complete theory of the thermoelectric effect in pure ice and in ice containing HF impurity based on the four-carrier model previously developed (Jaccard 1959). This theory has not hitherto been tested experimentally except at the single point given by Latham and Mason, where the available parameters allow satisfactory agreement to be produced.

It is the purpose of the present paper to present the results of a study of the thermoelectric power of ice over a range of acidic and alkaline solid solutions with HF and NH_4OH respectively and to discuss these results in the light of our present understanding of transport processes in ice.

§ 2. EXPERIMENTAL

The experiments were carried out in a small cylindrical cold box whose temperature was held at -35°C . The perspex lid of the cold box was lined with copper which was connected to the copper walls and base and earthed. Ice samples were grown in the cold box in a lead-glass tube, 1.4 cm in diameter and 10 cm long, closed at each end with a brass cap and held vertical at its base on a thin copper plate as in fig. 1. The base of the tube was fixed in thermal contact with a small copper block on which was wound a heater, but was electrically insulated from it by a thin sheet of mica. The temperature of the tube base could thus be changed by variation of the heater current and was measured by a thermocouple inserted in the brass cap.

Fig. 1



Arrangement of the ice sample for the experiment. The assembly is placed in a cold-box which is maintained at -35°C . The copper shield lines the whole interior of the cold-box and is earthed to provide electrostatic screening.

The ice specimen was formed by putting water a little at a time into the tube through a small hole in the upper brass cap so that freezing took place from the tube base. In this way segregation of the acid or alkaline component was minimized and the ice specimen produced should have had a fairly uniform, though perhaps slightly striated, impurity distribution. When the tube was filled with polycrystalline ice, the hole in

the upper cap was closed by the insertion of a short brass rod which was frozen into place. The two brass caps were then used as electrodes, the upper cap being connected to an electrometer with an input resistance of 10^{14} ohms while the lower cap was earthed through an accurately calibrated 1000 ohm potentiometer. The resistance of the ice sample was about 10^9 ohms.

To check on possible electrode effects, as noted later, some measurements were made with palladium instead of brass as the electrode material.

The experimental procedure was to vary the base temperature from about -25°C to -1°C and to measure the potential difference across the ends of the ice by applying a balancing potential with the potentiometer and using the electrometer as a null detector. Potentials of 1 to 1000 mv could be applied and potentials were measured to the nearest 0.5 mv. Base temperatures could be held constant to within 0.1°C while measurements were being made. Increase in the base temperature gave rise to a small increase in the temperature at the top electrode. This was measured in a separate experiment and a correction made.

The experiment was performed with samples grown from water whose pH was varied from 2 to 10 by the addition of very dilute HF or NH_4OH . In each case the pH of the water to which the ice melted at the end of the experiment was also measured, taking care to avoid pH changes due to dissolved atmospheric CO_2 . It is this final pH value which is used later in interpreting the experimental results. For very high impurity concentrations, instead of measuring a pH value it was found more convenient to make up aqueous solutions of known strengths using standardized materials.

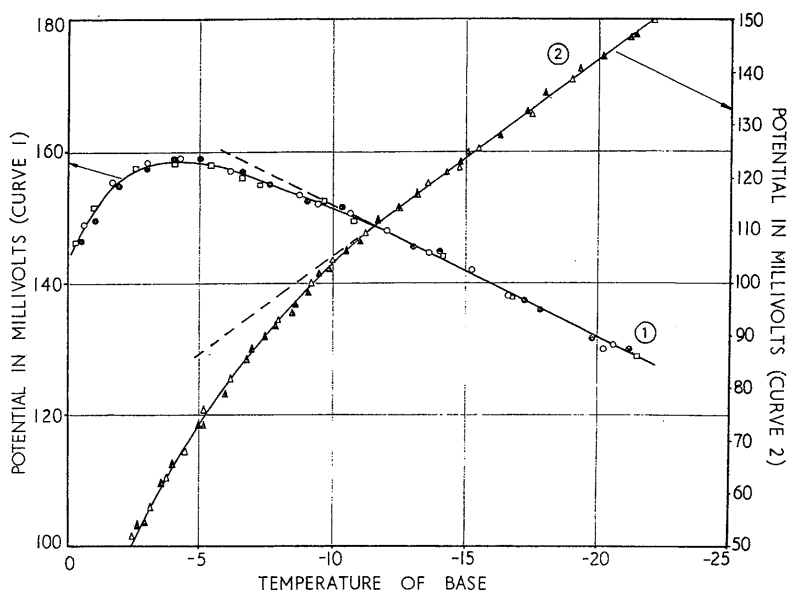
The potential difference measured in the experiment has several components of which the most important are the true thermoelectric potential across the ice sample, thermoelectric effects in the metallic parts of the electrical circuit and the potentials generated at the two ice-metal electrodes. The thermal e.m.f.'s in the metallic circuit can be neglected since they are only of the order to tens of microvolts per degree. The electrode potentials, however, cannot be eliminated or neglected in the experimental configuration used.

The isothermal standing potential difference measured across the ice specimen was of the order of tens of millivolts and varied apparently randomly from sample to sample or in a single sample if it was allowed to melt near one electrode. In the experiment the temperature of the top electrode was held constant and the potential across the sample plotted as a function of the temperature of the base electrode. Despite variations in the standing potential with different samples of the same impurity content and from brass to palladium electrodes, the slopes of these curves were consistent to within a few per cent. It seems valid to conclude that the temperature derivatives of the electrode potentials and other extraneous effects are small in comparison with the thermoelectric power of ice and that the measurements give a true indication of this quantity.

For specimens grown from water with pH less than 4 or greater than 9 the brass electrodes gave erratic results, presumably because of chemical reaction with the HF or NH_4OH . In these regions, therefore, only palladium electrodes were used.

The curves shown in fig. 2 have the same general form as those reported by Latham and Mason. Below about -10°C the potential varies nearly linearly with temperature, but deviates increasingly from linearity at higher temperatures. Restricting attention to temperatures below -10°C , the slope of the curve gives the thermoelectric power.

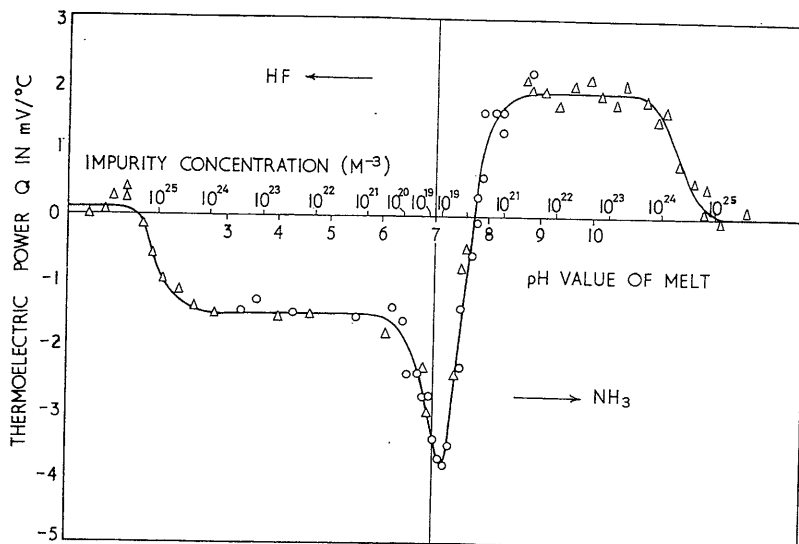
Fig. 2



Typical plots of thermoelectric potential across the ice specimen as a function of the temperature of the base. Curve 1 is for ice which melts to water of pH value of 8.7, curve 2 for a pH value of 7.1. The different sets of symbols on each curve represent data taken on successive runs with the same sample. The temperature of the top of the sample is -35°C in each case.

In fig. 3 the thermoelectric power, determined in this way, is plotted against the pH value of the water to which the ice melted. This pH value, of course, has no direct significance for the ice sample itself but from it the concentration of HF or NH_4OH in the ice can be deduced. This quantity is also indicated in fig. 3. For very high concentrations of either doping agent the pH ceases to be a useful quantity because of incomplete ionization in aqueous solution. In these ranges, only the directly determined impurity content is indicated.

Fig. 3



The thermoelectric power of ice as a function of the content of HF or NH₃ (given as impurity molecules per m³) or the pH value of the water to which the ice melts.

○: data taken with brass electrodes.

△: data taken with palladium electrodes.

§ 3. THEORETICAL

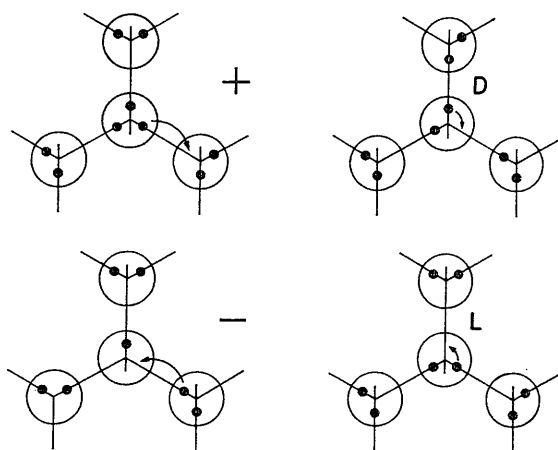
The theory of the electrical properties of ice is complicated by the structural complexity of the solid itself and it is only recently that a reasonably complete and consistent theory has been put forward (Jaccard 1959). It is found that four different charge carriers are required to account for the observed electrical properties—the ion states H₃O⁺ and OH⁻, and the Bjerrum or valence defects which consists respectively of doubly occupied bonds (D) and empty bonds (L). These defects and their mode of motion are illustrated schematically in fig. 4. Because the energy barrier to proton transfer along a bond is small, the proton jumps in the motion of ion states are thought to occur by a quantum tunnelling mechanism with effectively zero activation energy. The Bjerrum defects on the other hand, move in a classical, thermally activated manner.

Though there is now fairly general agreement on the existence of these four defects, the energies of formation and diffusion and the exact structure of Bjerrum defects are still the subject of theoretical speculation (Dunitz 1963, Eisenberg and Coulson 1963). Jaccard's theory of the electrical properties of ice of necessity therefore uses an idealized model for these defects and for the ion states.

The electrical conductivity of ice at zero frequency is a consequence of the interactions between the two types of charge carrier. If only ion

states were present, they would migrate in opposite directions under the influence of a static electric field and the resulting change in proton configuration on the bonds would polarize the crystal and prevent further charge transport. The motion of D and L defects, which behave as positive and negative carriers respectively, also polarizes the crystal but in the opposite sense. The combined motion of both types of defects can thus lead to a non-zero static conductivity. The ion states and Bjerrum defects provide conduction mechanisms which are effectively in series, however, rather than in parallel as is usually the case. The static conductivity is therefore determined by the less efficient process, which happens to be that of the ionic states which are much fewer in number.

Fig. 4



Ion states and Bjerrum defects and their motion in a simplified ice structure.

The high frequency conductivity and dielectric properties of ice, on the other hand,⁵ depend additively upon the contributions of all the defects. This is basically because the defects move over only very small distances and their interactions are not important.

By the analysis of static and high frequency conductivity data and their dependence upon temperature, combined with results obtained by other studies, it has been found possible to derive several important quantities relating to the charge carriers in ice. These are listed in table I.

When hydrofluoric acid is added to ice it is thought to be incorporated substitutionally in the lattice. Each HF molecule, because of its proton deficiency relative to H_2O , therefore contributes a single empty bond or L defect to the crystal. This defect is apparently very weakly bound to the impurity and is essentially free at $-10^\circ C$. This is verified by a study of the high frequency conductivity which increases linearly with HF concentration. The substitutional HF molecule can also be ionized and

Table 1. Properties of carriers in ice at -10°C

	Bjerrum defects	Ion states
Reaction equation	$2N \rightleftharpoons D + L$	$2H_2O \rightleftharpoons H_3O^+ + OH^-$
Energy of formation (ev)	$E^{DL} = 0.68 \pm 0.04$ (4)	$E^\pm = 1.2 \pm 0.1$ (4)
Concentration in pure ice (m ⁻³)	$n^D_0 = n^L_0 = 7 \times 10^{21}$ (4)	$E^\pm = 0.96 \pm 0.13$ (4)
Activation energy for diffusion (ev)	$E^L = 0.23$ (4)	$n^+_0 = n^-_0 = 1.8 \times 10^{16}$ to 9×10^{16} (1)
Mobility (cm ² /v sec)	$E^D \approx 0.23$ (?) (3)	$E^+ = E^- \sim 0$ (2)
Mobility ratio	$\mu^L = 2 \times 10^{-4}$ (4)	$\mu^+ = 0.1$ to 0.5 (1)
Effective transported charge	$\phi^{DL} = \mu^L / \mu^D \geq 1$ (4)	$\phi^\pm = \mu^- / \mu^+ = 0.01$ to 0.1 (1)
	$\phi^{DL} \sim 10$ (3)	$e^\pm = 0.55e$ (5)
	$e^{DL} = 0.44e$ (5)	

(1) Eigen and De Maeyer (1958).

(2) Jaccard (1959).

(3) Levi and Lubart (1961).

(4) Granicher (1963).

(5) Jaccard (1963).

in this way contribute a positive ion state to the crystal. The concentration of such free ion states, as found from the static conductivity, varies as the square root of the HF concentration, indicating that a very small proportion of the HF molecules are ionized at -10°C. This ionization is characterized by an activation energy E_F and equilibrium constant k_F which are given in table 2 from the results of Steinmann (1957) and Jaccard (1959).

An analogous though opposite situation occurs with solid solutions of NH₃ in ice. Again, the impurity is thought to be included substitutionally and, because of its proton excess, gives an easily freed D defect. Ionization gives an immobile NH₄⁺ ion together with a free negative ion

Table 2. Properties of impurities in ice

Dissociation constant for ionization of HF, $k_F = 6 \times 10^{16} \text{ m}^{-3}$	(2)
Activation energy for ionization of HF, $E_F = 0.64 \text{ ev}$	(1, 2)
Dissociation constant for ionization of NH ₄ OH, $k_N = 3 \times 10^{14} \text{ m}^{-3}$	(3)
Activation energy for ionization of NH ₄ OH, $E_N = 0.74 \text{ ev}$	(3)
Activation energy for L defect liberation from HF ~ 0	(2)
Dissociation constant for D defect liberation from NH ₄ OH $\sim 10^{22} \text{ m}^{-3}$	(3)
Activation energy for D defect liberation from NH ₄ OH $\sim 0.3 \text{ ev}$ (?)	(3)
Segregation coefficient of HF in ice/water $\sim 10^{-2}$	(2)
Segregation coefficient of NH ₄ OH in ice/water $\sim 10^{-3}$	(3)

(1) Steinmann (1957).

(2) Jaccard (1959).

(3) Levi and Lubart (1961).

state. The electrical conductivity of ice doped with ammonia has been investigated experimentally by Levi and Lubart (1961). The results for low concentration of the impurity are similar to those for the case of HF and from them can be deduced the ionization energy E_N and equilibrium constant k_N , which are also given in table 2. There is some evidence that there is an activation energy associated with the liberation of a D defect from NH_3 but the value of this energy is uncertain.

A theory of the thermoelectric power of pure and doped ice has recently been put forward by Jaccard (1963). The theory is conceptually simple but algebraically rather complicated because of the complexity of the ice structure and of the interactions between defects.

Under the combined influence of an electric potential gradient dV/dx and a thermal gradient dT/dx the flux of positive ion states can be written:

$$j^+ = -\mu^+ n^+ \frac{dV}{dx} - \frac{d}{dx} (D^+ n^+) - \Omega^+ n^+ S_0, \quad \dots \quad (1)$$

where n^+ is the density of positive ion states and μ^+ and D^+ are their electrical mobility and diffusion coefficient respectively. In a chemically homogeneous crystal the second term on the right can be converted to a temperature derivative. The diffusion coefficient is also differentiated because it will, in general, be temperature dependent. The final term takes into account the interaction of the various carrier fluxes through the polarization of the crystal. Ω^+ is a geometrical factor having the dimensions of a diffusion coefficient and S_0 is the crystal polarization, defined by

$$S_0 = \int (j^+ - j^- - j^D + j^L) dt. \quad \dots \quad (2)$$

A more detailed derivation of this flux equation, through not of the form of the interaction term, is given in a recent review by Howard and Lidiard (1964).

The four carrier currents in the ice sample are thus described by four equations of the form (1). The conditions of the experiment supply two additional constraints. In the first place the potential gradient in the specimen is measured under open circuit conditions so that

$$e^\pm (j^+ - j^-) + e^{DL} (j^D - j^L) = 0, \quad \dots \quad (3)$$

where e^\pm and e^{DL} are the effective charges transported by ion states and valence defects respectively. Secondly, the sample is in a steady state so that the polarization S_0 does not change with time, implying

$$j^+ - j^- - j^D + j^L = 0. \quad \dots \quad (4)$$

Equations (3) and (4) together require

$$j^+ - j^- = 0 = j^D - j^L. \quad \dots \quad (5)$$

This set of equations can be simply solved to yield an expression for the thermoelectric power. We introduce the ratios:

$$\phi^\pm \equiv D^-/D^+ \text{ and } \phi^{DL} \equiv D^L/D^D, \quad \dots \quad (6)$$

and let H and E , with appropriate superscripts, represent the activation energies for formation and diffusion of defects so that

$$\frac{d}{dT} \log(Dn) = (E + H)/kT^2. \quad \dots \quad (7)$$

The homogeneous thermoelectric power Q is then found by Jaccard to be:

$$Q \equiv \frac{dV}{dT} = - \frac{G}{eT} \{ 27[n^+(E^+ + H^+) - \phi^\pm n^-(E^- + H^-)] / (n^+ + \phi^\pm n^-) + 32[n^D(E^D + H^D) - \phi^{DL}n^L(E^L + H^L)] / (n^D + \phi^{DL}n^L) \}. \quad (8)$$

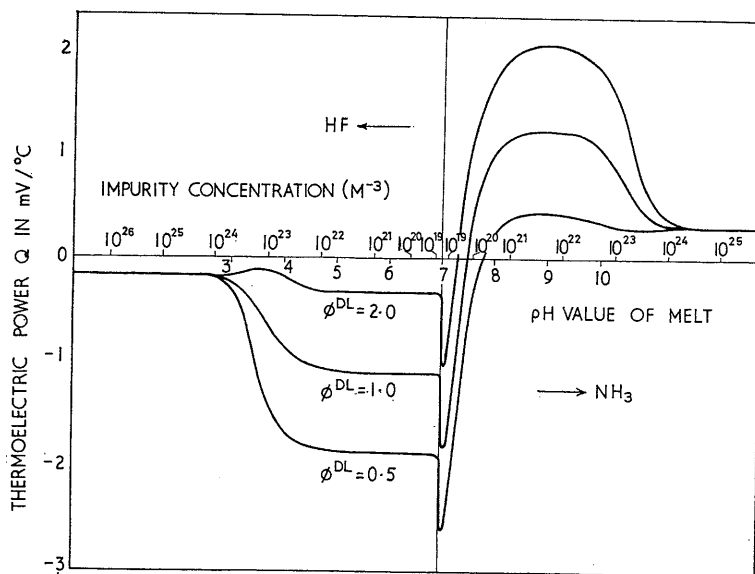
(It should be noted that sometimes in the literature Q is defined with a sign opposite to this.) The quantity G is defined by:

$$1/G = 27(e^\pm/e) + 32(e^{DL}/e). \quad \dots \quad (9)$$

The factors 27 and 32 arise from geometrical considerations in calculating jump probabilities in the ice structure. The activation energies for carrier formation, H , are not constants but depend upon the concentration of impurity in the ice. Explicit expressions for this dependence are given by Jaccard (1963).

The result (8) shows a very interesting behaviour which is a consequence of the form of the interaction between carriers. Instead of each carrier

Fig. 5



Calculated behaviour of thermoelectric power as a function of impurity content assuming $E^D = E^L$ and neglecting any activation energy for liberation of D defects from NH₃. Other parameters as in tables 1 and 2.

type contributing to Q in proportion to its concentration, the effects of the ions and valence defects are separated and depend only upon the ratios n^+/n^- and n^D/n^L respectively. Since the equilibrium number of ion states is perhaps five orders of magnitude smaller than that of the Bjerrum defects, small concentrations of impurity essentially affect only the ratio n^+/n^- . Conversely, large additions of impurity affect Q only through their effect on n^D/n^L , since n^+/n^- is effectively either zero or infinite. This feature of the form of Q allows quantities related to ion states and valence defects to be separately determined.

The form of the dependence of Q on impurity concentration is shown in fig. 5. For ease of comparison with the experimental results the same scales have been adopted as in fig. 3. The central minimum is due to variation in the ratio n^+/n^- and the changes in Q on the wings of the curve are caused by changes in n^D/n^L .

§ 4. DISCUSSION

Comparison of the theoretical curves of fig. 5 with the experimental results plotted in fig. 3 shows reasonable qualitative agreement, provided $\phi^{DL} \sim 1$. The quantitative agreement, however, is not good. The principal discrepancies are:

- (i) The central minimum predicted by the theory for small impurity concentrations is very much narrower than that found experimentally.
- (ii) The further change in Q at high impurity concentrations is predicted by the theory to occur at concentrations about 100 times smaller than those found experimentally.
- (iii) Experimental values of Q at corresponding regions of the curve are about 1.5 times as large as the theoretical values.

Discrepancies (i) and (ii) can be most easily resolved by assuming that impurity segregation effects in the polycrystalline sample lead to effective impurity concentrations which are about 100 times smaller than the average impurity concentration. This is quite possibly the case, though it is difficult to estimate the effects of increased impurity concentrations at the crystallite boundaries. Alternatively these discrepancies can be resolved by assuming values for the defect concentrations in pure ice, the mobility ratio ϕ^\pm or the dissociation constants k_F and k_N which differ considerably from those given in tables 1 and 2. It is of course possible that a combination of these two explanations might apply. There may also be some uncertainty in measurements between pH values of 6 and 7 due to traces of atmospheric CO_2 . The matter can only be resolved by an experiment using single crystal specimens.

The third discrepancy leads to more useful conclusions. The value of Q in a plateau region of the curve is determined by the various formation and transport activation energies, by the factor G which involves the

effective charges e^{\pm} and e^{DL} , and by the mobility ratio ϕ^{DL} . The activation energies are fairly reliably known, except for some ambiguity in E^{D} which is connected with the existence of an activation energy for the liberation of D defects from NH₃ centres. These energies have been used in drawing fig. 5 from which it can be seen that ϕ^{DL} must be quite close to unity to give a curve of the shape found experimentally. Allowing for the uncertainty in E^{D} , we conclude that $1 < \phi^{\text{DL}} < 2$. This agrees with Granicher's conclusion $\phi^{\text{DL}} > 1$ but is smaller than the value of 10 suggested by Levi and Lubart.

When the value of ϕ^{DL} is thus fixed, the relative heights of the various parts of the theoretical curve are similar to those found experimentally, except for an overall scale error of about a factor 1.5. This strongly suggests that the value of G should be about 0.05 rather than Jaccard's value of 0.035. This correction, implying as it does a decrease in the effective charges e^{DL} and e^{\pm} , may not be unreasonable in view of the simplified defect model used in the theory.

One further feature of the experimental results merits comment: that is the deviation of the curves in fig. 2 from a simple linear relationship above about -10°C . The same effect was observed by Latham and Mason (1961) in their measurements of the thermoelectric effect in nearly pure ice and by Bradley (1957) and others in measurements of the electrical conductivity for steady currents. The two effects are undoubtedly related but their origin is not yet clear. Latham (1963) found the effect to depend on the surface to volume ratio of the ice specimen and it is tempting to interpret it in terms of the existence of a quasi liquid layer at the electrodes or at the free surface (Fletcher 1962). We shall defer further discussion of this temperature region to a later publication.

§ 5. CONCLUSIONS

Measurement of the homogeneous thermoelectric power of ice containing controlled amounts of impurity gives information on several important physical parameters not easily accessible by other means. The theory of Jaccard seems well able to interpret the experimental results, though there are several points which require further elucidation. Future experiments should be performed with single crystal specimens to reduce possible sources of uncertainty.

ACKNOWLEDGMENT

This work is part of a programme of fundamental studies of the physics of ice and related materials made possible by a grant from the C.S.I.R.O., Division of Radiophysics.

REFERENCES

- BRADLEY, R. S., 1957, *Trans. Faraday Soc.*, **53**, 687.
DUNITZ, J. D., 1963, *Nature, Lond.*, **197**, 860.
EIGEN, M., and DE MAEYER, L., 1956, *Z. Elektrochem.*, **60**, 1037; 1958, *Proc. roy. Soc. A*, **247**, 505.
EISENBERG, D., and COULSON, C. A., 1963, *Nature, Lond.*, **199**, 368.
FLETCHER, N. H., 1962, *Phil. Mag.*, **7**, 255; 1963, *Ibid.*, **8**, 1425.
GRANICHER, H., 1958, *Proc. roy. Soc. A*, **247**, 453; 1963, *Phys. kondens. Materie*, **1**, 1.
HOWARD, R. E., and LIDIARD, A. B., 1964, *Rep. Progr. Phys.*, **27**, 161 (especially § 5.4.1).
JACCARD, C., 1959, *Helv. phys. acta*, **32**, 89; 1963, *Phys. kondens. Materie*, **2**, 143.
LATHAM, J., 1963, *Nature, Lond.*, **200**, 1087.
LATHAM, J., and MASON, B. J., 1961, *Proc. roy. Soc. A*, **260**, 523.
LEVI, L., and LUBART, L., 1961, *J. Chim. phys.*, **58**, 836.
STEINMANN, A., 1957, *Helv. phys. acta*, **30**, 553 and 581.
WORKMAN, E. J., TRUBY, F. K., and DROST-HANSEN, W., 1954, *Phys. Rev.*, **94**, 1073.