

	Square lattice	Triangular lattice
L	$-\frac{B\varphi_0}{(4\pi\lambda)^2} \times 0.14911$	$+\frac{B\varphi_0}{(4\pi\lambda)^2} \times 1.5683$

For the square lattice $L < 0$, which implies an instability. It has been shown³⁾ that L is smaller than K by a factor $(d/\lambda)^2$. This weakness of the shear modulus can be very important for the technical behaviour of materials of the second kind.

We can now give explicit form of the dispersion relation of the collective modes propagating perpendicularly to the applied field (a qualitative form of this relation for a polycrystal has been given in ref. 3). We find

$$\omega = 1.26 \frac{e^2 B}{m^* c} \lambda dk^2.$$

We want to thank Dr. P. G. De Gennes and Dr. C. Caroli for many helpful discussions on this work.

References

- 1) A.A. Abrikosov, J. Exptl. Theoret. Phys. (USSR) 32 (1957) 1442; translation Soviet Phys. JETP 5 (1957) 1174.
- 2) W.H. Kleiner, L. M. Roth and S.H. Autler, to be published in Phys. Rev.
- 3) P.G. De Gennes and J. Matricon, to be published in Revs. Modern. Phys.

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FERROELECTRIC BEHAVIOUR OF ICE

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In substances which contain hydrogen-bonds between two O-atoms (e.g., Rochelle salt) the ferroelectric behaviour is due to the proton jumping from one possible position between the O-atoms to the other one. Therefore ice was expected to be ferroelectric in suitable temperature regions because it contains hydrogen-bonds¹⁻³⁾. However no experimental evidence for ferroelectric behaviour of ice has been found as yet.

Experiments which show ferroelectric behaviour of ice are described below. The ferroelectricity appears at very low temperatures of about 100°K with a relaxation time of the order of hours. This should be the reason that ferroelectricity of ice could not be found before.

Experiments: The ice sample was placed into a cryostat cooled with liquid nitrogen. By additional heating every desirable temperature between 77°K and 170°K could be maintained. Electrodes

(polished brass plates or aluminium foils) were fixed to the sample. The capacitive charging current was measured by using an electrometer which allowed the detection of currents down to 10^{-14} A. Two independent series of experiments were made with this arrangement: (a) current measurements at constant heating and cooling rates, (b) measurements of the charging or discharging current as a function of time at a fixed temperature so that the dielectric constant was given by the time integral of this current.

In the first series of experiments at a constant heating rate the current increased strongly at first and after passing through a maximum at a distinct temperature a very steep decrease set in yielding a change in direction, so that the current flowed against the applied voltage (see fig. 1). On further heating, the negative current diminished and became zero, and at still higher temperatures the ordinary positive current due

to protonic conductivity was observed.

This behaviour of ice can be understood as a consequence of ferroelectricity with Curiepoint at about 100°K. The current measured at temperatures higher than 150°K is due to the ordinary protonic conductivity, as mentioned above. This current rises at first more steeply than would be expected from the well known exponential temperature dependence of conductivity of ice. It may be possible that an additional Curiepoint at about 135°K causes this sharp increase in current. On cooling the ice crystal down we observed the same effects with reversed signs.

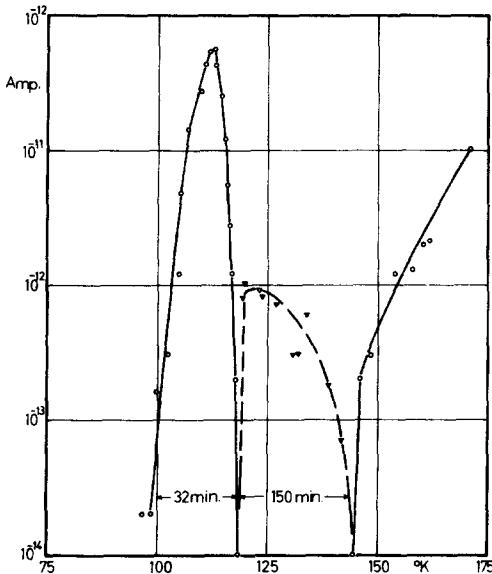


Fig. 1. Current observed in a slowly heated ice sample. (Applied field 400 V/cm). Full line - current in field direction, dashed line - current against field direction.

To test whether the effect described above is due to ferroelectric behaviour, a second series of experiments was performed. A voltage of about 400 V was applied instantaneously to the sample and the capacitive current due to the ice crystal, which decreased down to zero with time, was measured. From the time-integral of this current the value of ϵ was calculated. Such meas-

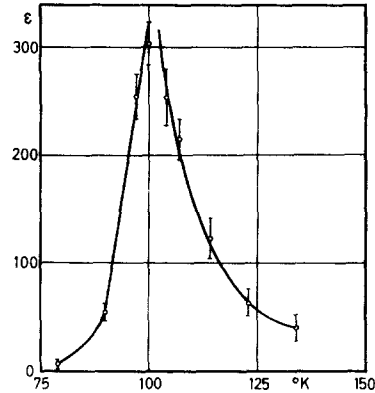


Fig. 2. Dielectric constant ϵ of ice as a function of temperature. Sample: 2.0 cm, distance between electrodes 1.0 cm, applied electric field 400 V/cm.

urements were made for different temperatures. The results are shown in fig. 2. The curve shows that the dielectric constant ϵ passes through a maximum at about 100°K. This temperature dependence of ϵ is characteristic for ferroelectrics.

The relaxation time of the ferroelectric, yielding oriented regions, was estimated roughly from the time dependence of the capacitive current. The $\log I$ vs t -curves do not show a pure exponential shape, probably because the elementary processes are not independent of each other.

The ferroelectric behaviour of ice described above could be observed only if the water used for the crystal growth was not extremely pure. This indicates that foreign atoms promote the appearance of ferroelectricity in a certain way. It cannot be decided whether this influence is due only to a shortening of the relaxation time of the ferroelectric polarization or whether the foreign atoms themselves contribute to the charge displacement.

References

- 1) L. Onsager and M. Dupuis, Rendiconti S. I. F. Corso X, (Bologna, 1960), p. 294.
- 2) A. Deubner, R. Heise and K. Wenzel, Naturwissenschaften 47 (1960) 600.
- 3) A. Kahane, Coll. Physics of ice crystals (Zürich, 1962).

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