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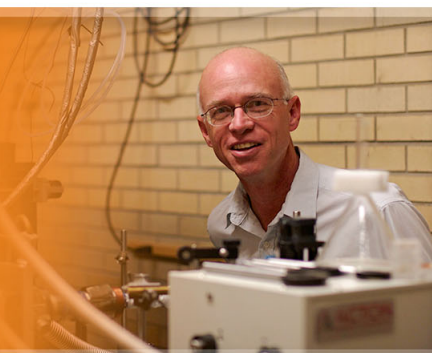
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The dielectric properties of H₂O and D₂O ice Ih at MHz frequencies

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The permittivity and loss of ice Ih have been measured between 0.5–100 MHz in the temperature range 243–273°K. An analysis of the temperature dependence of the limiting high-frequency permittivity ϵ_∞ shows that the known decrease in frequency of lattice vibrations with increasing temperature predicts values of ϵ_∞ much higher than those measured. It is suggested that the absorptivity at the infrared frequencies should decrease with increasing temperature. Deuteration of ice decreases its ϵ_∞ by ~3%. This is interpreted to indicate less absorption of infrared frequencies in D₂O than in H₂O ice. Ice shows a secondary relaxation centered in the MHz frequency range with an amplitude of 0.08 at 268°K. The ϵ_∞ of single crystal ice, measured perpendicular to the *c* axis, is indistinguishable from that of polycrystalline ice, thus indicating little anisotropy of the high-frequency polarization.

I. INTRODUCTION

As a result of investigations reported during the course of nearly 60 years, the spectrum of ice Ih is accurately known from 1 mHz to 1 MHz and from 150 MHz to 2000 THz. The main features of the spectrum suggest that absorption of an electromagnetic radiation in ice is due mainly to (i) the orientation polarization of water molecules in the frequency range 1 mHz to 100 kHz, characterized by the sum of several first-order relaxation processes, (ii) the vibrational polarization in the frequency range 150 MHz–5.4 THz contributed by several inter- and intramolecular vibrational modes and (iii) the electronic polarization at frequencies >200 THz. Evidently, there is a frequency region from 1–100 MHz in which the spectrum of ice is not known. The dielectric properties of ice in this frequency range are useful for an understanding of the electrical properties associated with both the molecular reorientation and inter- and intramolecular vibrations, as well as being of considerable practical interest in connection with the absorption of radiowaves from ice particles in the atmosphere, and in the study of the thickness and temperature of naturally occurring ice masses.¹ It is desirable, therefore, to measure the dispersion and absorption in ice in the frequency range 1–100 MHz.

Isotopic substitution affects, in addition to those properties of matter which are determined by the nuclear spin and nuclear size, the properties which are mainly determined by the inter and intramolecular vibrations. Since nearly 45% of the limiting high frequency permittivity, ϵ_∞ , of ice is due to molecular vibrations,² the isotope effect on ϵ_∞ can be significant. A further objective of this study was, therefore, to investigate the effect of deuteration on the contribution to permittivity arising from vibrational polarization in ice at temperatures close to the melting point.

This paper reports both the dielectric properties of ice Ih in the megahertz frequency range and the isotope effect on its ϵ_∞ .

II. EXPERIMENTAL

The dielectric cell was a two-terminal coaxial type with an outer cylinder made of stainless steel acting as

the low electrode at the ground potential. The high electrode was a coaxial rod made of stainless steel. The cylinder was filled with ice, which acted as its own pressure transmitting medium, and was pressurized to about 50 bar by a mushroom-shaped piston which was held in place by a gland nut.

Double distilled deionized water was pumped on for 2 h or more in order to remove the dissolved air and was then poured into the dielectric cell. The polycrystalline ice was obtained by cooling the cell to –5 °C. The single crystal of ice was prepared by a zone-refining method from deionized water contained in a polyethylene tube. A cylindrical piece of ice cut from a single crystal was fitted into the dielectric cell. 98.75% D₂O was obtained from Atomic Energy of Canada, Ltd., Chalk River. This was used as received.

All measurements on single crystal ice were made with the *c* axis oriented at an angle of 90° ± 2° to the electric field. Because of the radial direction of the electric field lines in the dielectric cell, orientation of (only) the *c* axis parallel to the field is not possible.

The electrical measurements at frequencies from 0.5 to 100 MHz were carried out by means of an RX-Meter type 250-A (manufactured by Boonton Radio Corporation, Boonton, New Jersey). The instrument is completely self-contained and consists of a refined Schering bridge, together with its associated oscillator, an amplifier, a null detector and a power supply. The values of permittivity and conductivity were obtained by the method of substitution. These values are accurate to within ±0.3%, and ±2%, respectively, and, by virtue of the method used, are free from systematic errors. The temperature was measured by means of a calibrated thermocouple and is accurate to within ±0.2°. Details of the experimental arrangement have been described earlier, as has the *modus operandi*.³

Measurements of the permittivity and dissipation factor, tanδ, at 1 MHz were also made using a Hewlett-Packard model 4271 A LCR meter. The dielectric cell used in this case was a three-terminal concentric electrode type as described elsewhere.⁴ The capacitance and tanδ readings were corrected for the effect due to cables and connectors by using various capacitance

standards. The ϵ' and $\tan\delta$ at 1 MHz measured using the LCR meter agreed with those measured with the RX meter to within $\pm 0.3\%$ and 2% , respectively.

III. RESULTS

The permittivity ϵ' for single crystal H_2O ice is plotted against frequency in Fig. 1, and the data at $268.1 \pm 0.2^\circ\text{K}$ are given in Table I. The ϵ' decreases from 3.330 at 0.5 MHz to 3.186 at 100 MHz, most probably due to a relaxation of orientation polarization. The decrease is anticipated to be less at lower temperatures, and indeed at 248°K , ϵ' is nearly constant between 5 and 100 MHz as seen in Fig. 1.

The ac conductivity σ and the dielectric loss ϵ'' of single crystal H_2O ice at $268.1 \pm 0.2^\circ\text{K}$ are given in Table I. The σ increases from 19 to $43.4 \text{ M}\Omega^{-1} \cdot \text{m}^{-1}$ in the range 0.5–100 MHz. The plot of σ against the logarithm of frequency, shown in Fig. 2, is of a sigmoidal shape, indicating the presence of a relaxation region in the megahertz frequency range. The ϵ'' of 0.683 at 0.5 MHz at 268.1°K is fairly high and decreases to 0.0078 at 100 MHz. No literature data on σ or ϵ'' are available for comparison.

The attenuation α at MHz frequencies is of practical interest in connection with the propagation of radio-waves through ice and snow. The α in nepers m^{-1} was calculated from the equation

$$\alpha = \frac{\omega}{c} \left[\frac{\epsilon'}{2} (\sqrt{1 + \tan^2\delta} - 1) \right]^{1/2},$$

where c is the speed of light, $\tan\delta = (\epsilon''/\epsilon')$, ω is the circular frequency, and ϵ' the permittivity. The values are given in Table I.

The real and imaginary parts of the complex refractive index, n' and n'' , respectively, can be calculated and can be used to calculate the reflectivity R from a vacuum-ice interface at normal incidence using the following relations,

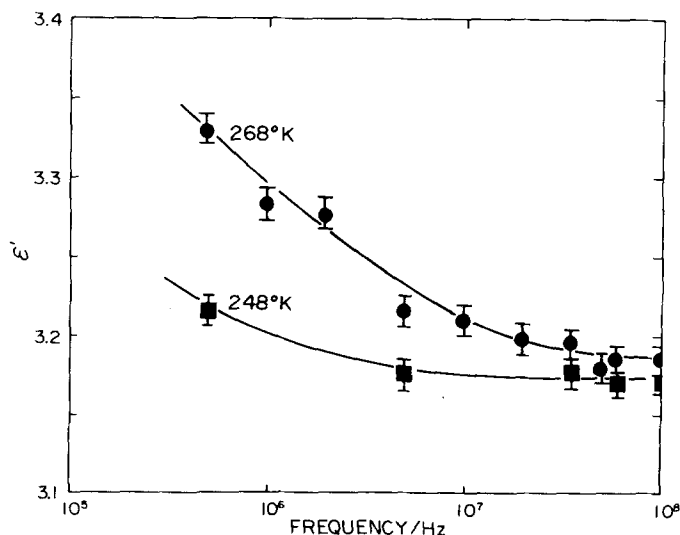


FIG. 1. The frequency dependence of permittivity of single crystal ice Ih at two temperatures.

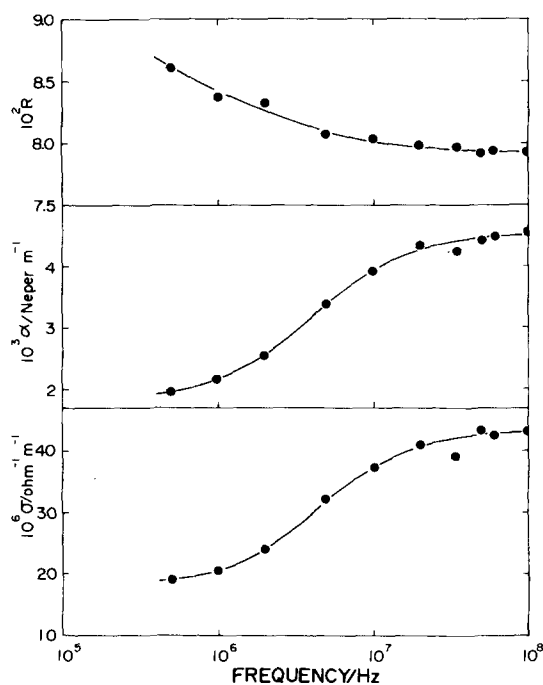


FIG. 2. The frequency dependence of ac conductivity, attenuation and reflectivity of single crystal ice Ih at $268.1 \pm 0.2^\circ\text{K}$.

$$\epsilon'' = 2n'n''; \quad \epsilon' = n'^2 - n''^2,$$

and

$$R = [(1 - n')^2 + n''^2] / [(1 + n')^2 + n''^2].$$

Values of n' , n'' , and R , calculated from our data at 268.1°K , are given in Table I. The reflectivity of ice decreases by 7.8% in the range 0.5–100 MHz. The attenuation and reflectivity are plotted against the logarithm of frequency in Fig. 2. These plots may be useful in studies involving absorption and reflection of radio waves in ice.

Since little anisotropy of ϵ_∞ and α is known in ice,³ the results in Table I would be valid also for polycrystalline ice.

The ϵ' at 100 MHz, approximated as being equal to ϵ_∞ , is plotted against temperature in Fig. 3. Results on five samples of polycrystalline and four samples of single crystal H_2O ice oriented with the c axis perpen-

TABLE I. The dielectric properties of H_2O ice Ih at $268.1 \pm 0.2^\circ\text{K}$.

f MHz	σ $10^6 \Omega^{-1} \cdot \text{m}^{-1}$	ϵ'	ϵ''	$10^3 \alpha$ Np m^{-1}	n'	n''	$10^2 R$
0.5	19.00	3.330	0.683	1.95	1.861	0.184	8.61
1	20.58	3.284	0.370	2.14	1.824	0.101	8.37
2	24.37	3.277	0.219	2.53	1.814	0.0604	8.32
5	32.27	3.216	0.116	3.39	1.794	0.0323	8.07
10	37.27	3.209	0.067	3.92	1.792	0.0187	8.04
20	41.17	3.198	0.0371	4.34	1.788	0.01037	7.99
35 ^a	39.14	3.195	0.0201	4.13	1.787	0.00562	7.98
50	43.39	3.180	0.0151	4.41	1.783	0.00423	7.92
60 ^a	42.49	3.186	0.0127	4.49	1.785	0.00356	7.94
100	43.39	3.186	0.0078	4.58	1.785	0.00219	7.94

^aData from Ref. 3.

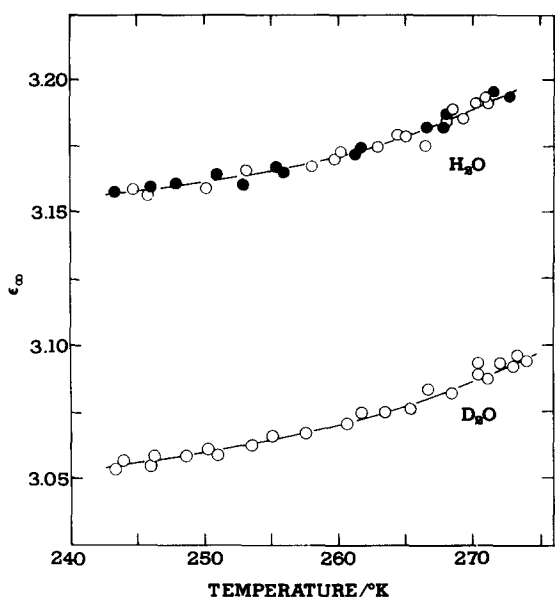


FIG. 3. The limiting high-frequency permittivity of ice Ih approximated as that at 100 MHz for H₂O and D₂O plotted against temperature. ●, single crystal ice oriented with the electric field perpendicular to the *c* axis; ○, polycrystalline ice.

dicular to the electric field, and four samples of polycrystalline 98.75% D₂O ice are given in this figure. The scatter of the data, which appears somewhat less than that at 35 MHz,³ indicates the reproducibility of measured values.

The ϵ' at a few frequencies may be compared with values for laboratory-grown ice given in the literature. Our ϵ' at -5°C of 3.31 at 1 MHz agrees with Lamb's⁵ value of ϵ' . The ϵ' values at GHz frequencies obtained by Lamb and Turney⁶ and Cumming⁷ seem insignificantly different from those at 100 MHz obtained in this study.

The ϵ_∞ , which is the limiting term in the Debye equation,⁸ is defined as

$$\epsilon' = \epsilon_\infty + \sum_{n=1}^{n=N} \frac{\Delta\epsilon_n}{1 + \omega^2\tau_n^2},$$

where N is the number of Debye processes, $\Delta\epsilon_n$ and τ_n are the contribution to the permittivity and relaxation time of each process, respectively, and ω is the circular frequency. It is obvious that an unequivocal evaluation of ϵ_∞ requires that the frequency of measurement should be high enough such that the dielectric loss ϵ'' due to dipolar reorientation given by,

$$\epsilon'' = \sum_{n=1}^{n=N} \frac{\Delta\epsilon_n}{1 + \omega^2\tau_n^2} \omega\tau_n, \quad (1)$$

should decrease to zero. Experimentally, it is not possible to obtain the absolute value of ϵ_∞ , for the resonance absorption begins to contribute to ϵ'' at frequencies at which the dielectric loss due to relaxation is still well above zero. It becomes necessary, therefore, to make measurements of the dispersion in ϵ' due to the orientational polarization to sufficiently high frequencies. Since the frequency of 100 MHz is about 10^4

times higher than the relaxation rate⁹ ($<10^4\text{s}^{-1}$) of the predominant orientation polarization, the absolute value of ϵ_∞ is not likely to be more than 0.1% lower than the ϵ' at 100 MHz; and for our discussion $\epsilon' (100\text{ MHz}) = \epsilon_\infty$.

Our values of ϵ_∞ agree with most of the literature values of ϵ_∞ ⁹⁻¹³, considering the uncertainty involved in their extrapolation, but are somewhat higher than those of Le Petit and LaFargue.¹⁴ Our values are lower than those of Taubenberger,¹⁵ who found that ϵ_∞ at 258°K increased from 3.23 to 3.54 on aging for 1850 h. Aging of ice in our studies for 1290 h at $263 \pm 5^\circ\text{K}$ caused no detectable change in ϵ' or ϵ'' at 100 MHz. The ϵ_∞ for D₂O ice at 271.5°K agrees reasonably well with Auty's and Cole's⁹ value of 3.06 at 271.5°K .

IV. DISCUSSION

A. The temperature dependence of ϵ_∞

In Fig. 3, the ϵ_∞ of both the H₂O and D₂O ice increases with temperature. Furthermore, the rate of increase, $(d\epsilon_\infty/dT)$, increases from 6.0×10^{-4} to $2.3 \times 10^{-3}^\circ\text{K}^{-1}$ between 245 and 273°K for H₂O ice and from 7.0×10^{-4} to $2.1 \times 10^{-3}^\circ\text{K}^{-1}$ in the same temperature range for D₂O ice. The increase in ϵ_∞ with temperature is well known for ionic crystals^{15,16} in which strong lattice vibrations occur at low frequencies, in H₂O ice Ih,^{10,12} II,¹⁷ VI,¹⁸ VIII,¹⁹ and IX,¹⁷ and in clathrate hydrates where the effect is largely due to hydrogen-bond vibrations.²⁰ According to Clausius-Mossotti's equation, a decrease in the density of ice with increasing temperature is anticipated to decrease ϵ_∞ if the lattice vibrations in a crystal, both mechanical and electrical, are harmonic and consequently the absorptivity and frequency of each mode of lattice vibrations are independent of temperature. In this sense an increase in ϵ_∞ with temperature is related to the anharmonicity of lattice vibrations,¹⁰ although the exact contribution due to anharmonicity in ice has not been considered in detail.

A discussion of the increase in ϵ_∞ with temperature is conveniently done by examining Fig. 4, where ϵ_∞ of H₂O ice is plotted against temperature from 2 to 273°K . The plot from 2– 240°K has been constructed using Gough's data,¹⁰ which were found to be 0.3% higher than our results in the temperature range 77 – 250°K , and the data from 248 – 273°K obtained in this study. The ϵ_∞ (CM) was calculated from the Clausius-Mossotti equation, $(\epsilon_\infty - 1)v/(\epsilon_\infty + 2) = P$, where v is the molar volume and P is the molar polarizability assumed to remain constant with temperature. v was calculated from the density and expansivity data of Brill and Tuppe²¹ and LaPlaca and Post²² for single crystal ice converted to that of polycrystalline ice using the equation, $\alpha = \frac{1}{3}\alpha_{\parallel} + \frac{2}{3}\alpha_{\perp}$, where α is the expansivity and the subscripts \parallel and \perp denote the direction parallel and perpendicular to the *c* axis, respectively. At 10°K , $\epsilon_\infty = 3.093$ ¹⁰, $v = 19.27\text{ cm}^3\text{ mole}^{-1}$, and $P = 7.919\text{ cm}^3$. The ϵ_∞ (CM) plotted against temperature in Fig. 4 is the ϵ_∞ anticipated if the lattice vibrations in ice were entirely harmonic. This is a behavior typical of most dipolar solids.

The refractive index for Na-D line, n_D , was calcu-

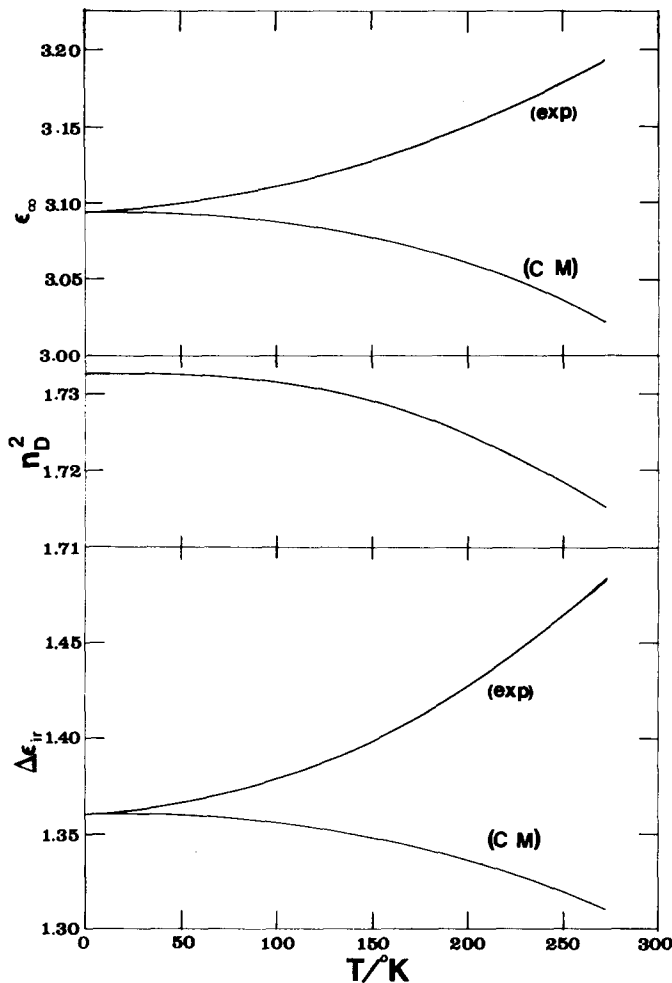


FIG. 4. The limiting high frequency permittivity of ice Ih plotted against temperature from 2 to 273 °K. Values from 2 to 200 °K were calculated from the equation given by Gough,¹⁰ from 77 to 273 °K, this work. The ϵ_∞ is resolved into the infrared and optical contributions. See text for details.

lated from the Lorentz-Lorenz equation, assuming that the electronic polarizability is independent of temperature and using Ehrlinghaus²³ refractive index values for single crystal ice converted to polycrystalline ice. The densities were calculated as given in the preceding paragraph. At 270 °K, $n_D = 1.3097$, $\nu = 19.64 \text{ cm}^3 \text{ mole}^{-1}$, and the electronic polarizability = 1.4993 \AA^3 . The calculated value of optical permittivity, n_D^2 , is also plotted against temperature in Fig. 4. The contribution to permittivity due to infrared polarization $\Delta\epsilon_{ir} = (\epsilon_\infty - n_D^2)$. This value is plotted against temperature in Fig. 4. The plot labelled CM is the anticipated $\Delta\epsilon_{ir}$, if lattice vibrations in ice were electrically and mechanically harmonic and the ice obeyed the Clausius-Mossotti equation, and that labeled exp is the actual $\Delta\epsilon_{ir}$ obtained from the measured ϵ_∞ . The experimental $\Delta\epsilon_{ir}$ increases from 1.36 to 1.48 between 0 and 273 °K, although it is anticipated to decrease from 1.36 to 1.31 according to the Clausius-Mossotti equation.

The $\Delta\epsilon_{ir}$ is given by the relation

$$\Delta\epsilon_{ir} = \Delta n^2 + 2n_D \Delta n, \quad (2)$$

where Δn is the sum of contributions made by the in-

frared absorption bands to the low-frequency refractive index and n_D is as defined earlier. According to the Kramers-Krönig relation, Δn is related to the negative second moment of the absorptivity, κ , over the bands by

$$\Delta n = \sum_1^n 0.5\pi^{-2} \int_{band} \kappa(\nu)\nu^{-2}d\nu,$$

where ν is the wavenumber of the radiation and κ is defined by the relation

$$\kappa = x^{-1} \log_e(I/I_0),$$

I and I_0 being the intensity of radiation after and before travelling the distance x in the sample. The $\Delta\epsilon_{ir}$ is given by

$$\Delta\epsilon_{ir} = \sum_1^n 0.5\pi^{-2} \int_{band} \kappa\nu^{-2}d\nu \left(2n_D + \sum_1^n 0.5\pi^{-2} \int_{band} \kappa\nu^{-2}d\nu \right). \quad (3)$$

The anharmonicity of lattice vibrations in ice causes the frequency, integrated intensity and half-width of a particular normal vibration to depend upon temperature and these changes with temperature alter the $\Delta\epsilon_{ir}$ as given by Eq. (3). The changes in the absorptivity and frequency with temperature are known and this information can be useful in resolving whether the increase in $\Delta\epsilon_{ir}$ is due entirely to a decrease in ν and/or increase in κ .

The frequency of the absorption bands in the range $360-17 \text{ cm}^{-1}$ decreases by about $3 \pm 1\%$ between 100 and 168 °K and the absorptivity at 40 cm^{-1} increases by 60% between 100 and 200 °K.²⁴ From the 100 °K results of Bertie *et al.*²⁵ nearly 71% contribution to $\Delta\epsilon_{ir}$ comes from translational vibrations whose absorption bands are centered in the region $320-17 \text{ cm}^{-1}$. A linear extrapolation of the temperature dependence of these bands indicates that the increase in $\Delta\epsilon_{ir}$ due to the decrease in the frequency of translational vibrations alone would be about 20% between 0 and 273 °K. The actual increase in $\Delta\epsilon_{ir}$ between 0 and 273 °K in Fig. 4 is ~9%. It may be argued that a linear extrapolation of the temperature dependence of the bands to low temperatures is not an accurate one, for near 0 °K the lattice vibrations in ice are likely to be mainly harmonic and therefore little temperature dependence of the frequency of absorption bands would be found at very low temperatures. However, the decrease in frequency from 229.2 cm^{-1} to 222 cm^{-1} of the major translational band in the temperature range $100-168 \text{ °K}$ ²⁶ gives an increase in $\Delta\epsilon_{ir}$ of 0.084, which is three times higher than the experimentally found increase of 0.028 in Fig. 4. It seems, therefore, that the experimentally observed decrease in the frequency of lattice vibrations with increasing temperature must be accompanied by a decrease in the absorptivity in order to account for the temperature dependence of ϵ_∞ . Unfortunately, the temperature dependence of absorptivity above 40 cm^{-1} is not accurately known, but the absorptivity below 40 cm^{-1} has been found to increase with temperature.²⁴

It is, in principle, possible to obtain some information regarding the electrical anharmonicity of vibrations in ice from an analysis of the temperature dependence

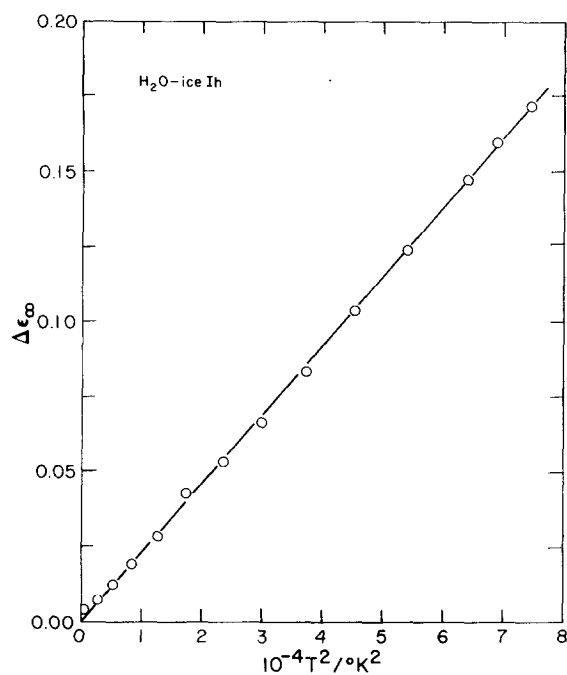


FIG. 5. The difference between the experimental value of the limiting high frequency permittivity and that calculated from the Clausius-Mossotti equation plotted against the square of temperature.

of ϵ_{∞} and the infrared absorption bands. Leadbetter²⁷ has analyzed the contribution to heat capacity of ice from the anharmonicity of lattice vibrations using a quasiharmonic theory. A similar analysis of ϵ_{∞} is somewhat complicated for both the absorptivity and frequency of the absorption bands are temperature dependent and further, as indicated earlier, the measured temperature dependence of the absorption frequencies predicts an ϵ_{∞} higher than the experimental value. However, an approximate but useful qualitative analysis of the contribution to ϵ_{∞} from anharmonicity can be made as follows: at temperatures near 0 °K, both the electrical and mechanical vibrations in ice are essentially harmonic and consequently the absorptivity and frequency of each vibrational mode would be approximately independent of temperature, except for a small effect due to a possible negative thermal expansion caused by excitation of the intermolecular bending vibrations, and $\epsilon_{\infty}(\text{exp}) = \epsilon_{\infty}(\text{CM}) = 3.094$ at near 0 °K would be equal to the sum of n_D^2 and the contribution to permittivity from harmonic lattice vibrations. The difference between the experimental ϵ_{∞} and that calculated from Clausius-Mossotti's equation, $\Delta\epsilon_{\infty} = \epsilon_{\infty}(\text{exp}) - \epsilon_{\infty}(\text{CM})$, at a given temperature may then be a measure of the contribution to permittivity from the anharmonicity of lattice vibrations. The $\Delta\epsilon_{\infty}$ is plotted against the square of temperature in Fig. 5. As evident, the plot is linear in the entire temperature range, with slope $= 2.3 \times 10^{-6} \text{°K}^{-2}$. This shows that the leading anharmonic term in a theoretical equation for $\Delta\epsilon_{\text{lr}}(\text{exp})$ is likely to be of second order in temperature. This conclusion may be of potential use in the development of a theory of anharmonicity of lattice vibrations, although it is an approximate one, for the volume term in the Clausius-Mossotti equation itself takes account of a partial contribution

from the anharmonicity.

It is interesting to note in this connection that while the anharmonicity of lattice vibrations is a feature common to the majority of molecular crystals, only CH_3OH ,²⁸ the polymorphs of ice and clathrate hydrates are known to show a positive temperature coefficient of ϵ_{∞} . Most solids, including those in the amorphous state in which the contribution due to the anharmonicity of vibrations is likely to be much higher than in ice, show a negative temperature coefficient of ϵ_{∞} qualitatively similar to that predicted by the Clausius-Mossotti equation.

The Clausius-Mossotti equation is based on the assumption that (i) the internal field in the material is isotropic and is given by $\frac{1}{3}(\epsilon_{\infty} + 2)$, (ii) the molecules in the material are isotropically polarizable, and (iii) the arrangement of the molecules in the matter is isotropic. Strictly, neither of the three conditions are fulfilled by ice Ih. Hollins²⁹ has suggested that the internal field in ice Ih should be given by $\frac{1}{3}(n_D^2 + 2)$ instead of $\frac{1}{3}(\epsilon_{\infty} + 2)$ for, by symmetry, the reaction field of a molecule in ice cannot cause it to rotate and therefore the distortion introduced within the molecule is mainly electronic. The Clausius-Mossotti relation modified to include Hollins' equation for the internal field gives $(\epsilon_{\infty} - 1)v/(n_D^2 + 2) = P$, and ϵ_{∞} at 273 °K calculated from this is 3.047, a value 0.8% higher than that calculated from Clausius-Mossotti's equation in Fig. 4 but 5% lower than the experimental value. The polarizability of the water molecule is known to be anisotropic. Minton³⁰ has proposed that the intermolecular interaction in ice can cause a small anisotropy of molecular polarization and the low value of the integrated intensity of the rotation bands observed in the Raman spectrum of ice Ih by Wong and Whalley³¹ implies that the anisotropy of molecular polarizability is finite, although small. Lastly, the ice is structurally anisotropic. We conclude, therefore, that the increase in ϵ_{∞} with temperature is probably connected with the internal field and anisotropy of polarization in addition to the anharmonicity of lattice vibrations. It should be worthwhile to investigate the temperature dependence of the infrared polarization of molecularly and structurally isotropic crystals to help resolve, by comparison, the extent to which ϵ_{∞} is increased by the anharmonicity of lattice vibrations.

B. The isotope effect on ϵ_{∞}

As seen in Fig. 3, the ϵ_{∞} of D_2O ice is lower than that of H_2O ice at all temperatures. The decrease in ϵ_{∞} on deuteration, which is 0.101 at 268 °K, may be due partly to a decrease in the optical permittivity, n_D^2 , and partly to that in the contribution to permittivity from the vibrational polarization, $\Delta\epsilon_{\text{lr}}$. The relative contribution to the decrease in ϵ_{∞} from the two processes is of some interest here.

The electronic polarizability of a D_2O molecule between 278.16–318.16 °K, calculated from the density data of Steckel and Szapiro³² and the n_D values from Luten³³ converted to absolute values using Tilton's data³⁴ for the refractive index of air, ranges between 1.4591–1.4630 Å³. From the Lorentz-Lorenz equation and the

density of D₂O ice at 268 °K of 1.0177 g cm⁻³ obtained from an interpolation of Lonsdale's values,³⁵ which were calculated from the crystal structure data of Megaw,³⁶ $n_D^2 = 1.689$. From Sec. IV. A, n_D^2 for polycrystalline H₂O ice at 268 °K is 1.716 and therefore the decrease in the optical permittivity on deuteration is by only 0.02. The remaining difference between the ϵ_∞ of H₂O and D₂O ice is almost certainly due to a decrease in $\Delta\epsilon_{1r}$.

According to Eq. (3), both the absorptivity due to, and the frequency of, the various lattice vibrations contribute to $\Delta\epsilon_{1r}$ of the material. The spectrum of the H₂O and D₂O ice has not been studied near 268 °K but it is known that at 100 °K, the frequency of the absorption band due to translational vibrations, which contribute nearly 71% to $\Delta\epsilon_{1r}$, decreases from 229.2 cm⁻¹ to 221 cm⁻¹ on 99.8% deuteration of ice Ih. If the decrease in frequency is in the same proportion at 268 °K as at 100 °K, then according to Eq. (3) the $\Delta\epsilon_{1r}$ should increase by about 16% on deuteration. The $\Delta\epsilon_{1r}$ actually decreases and this indicates that the absorptivity in D₂O ice should be lower than that in H₂O ice. Unfortunately, this conclusion cannot be confirmed because the absorptivity of D₂O ice is not known.

Some useful information regarding the decrease in $\Delta\epsilon_{1r}$ on deuteration can, however, be obtained as follows. If all molecular oscillations in ice are harmonic, the $K(\nu)$ for a given band can be calculated from the relation²⁴

$$K(\nu) = \frac{2\pi^2}{3VC} \frac{(n^2 + 2)^2}{9n} R\nu^2 g(\omega),$$

where C is the speed of light, n the refractive index at a frequency ν , $g(\omega)$ represents the density of vibrational states, and R is a factor determined by the electrical properties of vibrations, namely, the force constants for the displacement of the internal coordinate and the corresponding dipole moment. The molar volumes of H₂O and D₂O ice are nearly the same and $(n^2 + 2)^2/9n$ is not significantly affected on deuteration. It follows then that the decrease in $\Delta\epsilon_{1r}$ arises from the effect of deuteron substitution on the density of vibrational states and/or the electrical properties associated with vibrations as determined by R .

It has been reported that on deuteration the H bond in ice is elongated by 0.002 Å,³⁵ the intermolecular forces become stronger²⁷ and the molecular force constants for both the change of O–O bond length and the change of O–O–O bond angle increases. Because the zero point vibrations are anharmonic, the mean internuclear distance between H and O in H₂O is slightly greater than that between D and O in D₂O. Consequently, the electron distributions in H₂O and D₂O are slightly different. The various contributions to the intermolecular potential, such as from the dipolar forces,³⁷ quadrupoles, and higher moments, dispersion forces caused by the polarizability, the repulsive forces,³⁸ and the delocalization forces, will differ because of this. A combination of these effects on the density of vibrational states and on the electrical properties associated with each mode of vibration is likely to be the cause of a decrease

in ϵ_∞ on deuteration.

C. The high-frequency relaxation region

The Debye equation (Eq. (1) for condition $N=1$) suggests that at frequencies many times higher than the relaxation rate, a logarithmic plot of ϵ'' against frequency should be a straight line with slope = -1 and intercept = $\log(\Delta\epsilon/2\pi\tau)$. The logarithmic plot of ϵ'' of single crystal ice at 268.1 °K against frequency is shown in Fig. 6. The plot, which is concave to the axis, indicates an additional relaxation region centered in the megahertz frequency range. An attempt was therefore made to resolve the ϵ'' and frequency data into two relaxation regions as follows.

After the measurements at frequencies from 0.5 to 100 MHz on the single crystal ice having the c axis oriented perpendicular to the electric field were complete, the ϵ' and ϵ'' of the sample were measured *in situ* in the frequency range 50–2 × 10⁵ Hz. The measured values of ϵ' and ϵ'' when plotted in a complex plane showed that the low-frequency end of the plot approached the axis at an angle of ~90°, although the absolute values of ϵ' and ϵ'' could not be obtained in these measurements because of an unknown (small) amount of stray capacitance in the unguarded two-terminal cell. The approach of the low-frequency end of the complex plane plot to the axis at ~90° indicates little contribution to ϵ' and ϵ'' from space charge and/or Maxwell–Wagner polarization at 50 Hz. Ice cut from the same single crystal was then measured at 268.1 °K in a parallel plate three-terminal dielectric cell with the c axis oriented perpendicular to the electric field in the frequency range 10–100 Hz by means of a bridge designed after Berberian and Cole,³⁹ and in the range 50 Hz–200 kHz by means of a GR 1615 A Bridge. The ϵ' and ϵ'' of this sample fitted to a Debye-type single relaxation process with $\Delta\epsilon = 92.4$ and $\tau = 4.1 \times 10^{-5}$ sec. These values agree reasonably well with the corresponding values in literature.^{9,40–42} The ϵ'' in the frequency range 0.5 MHz–2 GHz calculated from Eq. (1), using the above $\Delta\epsilon$ and τ values, are shown by a continuous straight line in Fig. 6.

The measured ϵ'' at megahertz frequencies was fitted to Eq. (1) for two Debye-type relaxation processes. At 268.1 °K, $\Delta\epsilon_1 = 92.4$, $\tau_1 = 41 \mu\text{sec}$, $\Delta\epsilon_2 = 0.08 \pm 0.01$ and $\tau_2 = 30 \pm 10 \text{ nsec}$. The calculated values of ϵ'' from Eq. (1) for $N=2$ at MHz frequencies is shown by the dashed curve in Fig. 6, where Westphal's⁴³ and our earlier³ and present ϵ'' data are included. Although the results of the analysis into several relaxation regions are somewhat ambiguous, a point already reasoned by Gough *et al.*,⁴⁴ they do show the presence of a high frequency relaxation region in ice. The resolved relaxation regions are also shown in Fig. 7, where a logarithmic plot of ϵ'' against frequency shows the position of the two absorption peaks, corresponding to the analysis shown in Fig. 6. We conclude that the dielectric absorption in ice is due at least to two relaxation processes whose amplitudes differ by nearly three orders of magnitude at 268 °K.

The presence of a second relaxation process in ice

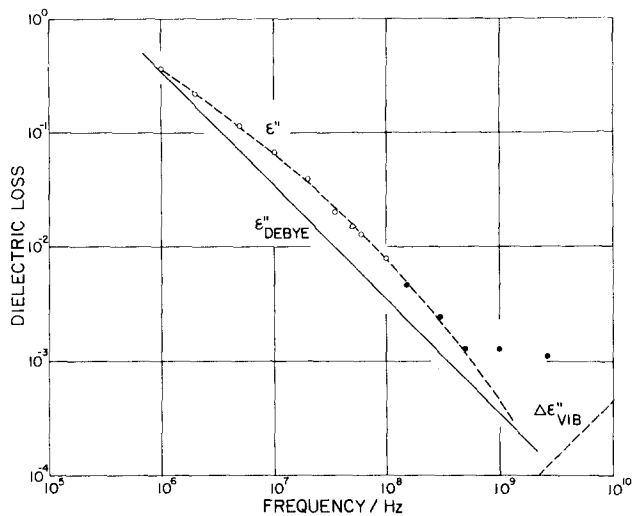


FIG. 6. The dielectric loss of ice Ih at radio and microwave frequencies at 268.1 °K; ○, this work; ●, Westphal's measurement.⁴³ The continuous straight line is for the Debye process with a single relaxation time with $\Delta\epsilon = 92.4$, and $\tau = 41 \mu\text{sec}$; the dashed curve represents the calculated values of ϵ'' for two Debye-type relaxation processes, $\Delta\epsilon_1 = 92.4$, $\Delta\epsilon_2 = 0.08 \pm 0.01$, $\tau_1 = 41 \mu\text{sec}$, and $\tau_2 = 30 \text{nsec}$. The broken straight line labeled $\Delta\epsilon''_{\text{VIB}}$ is after Whalley and Labbé²⁴ and represents the anticipated contribution from molecular vibrations.

has also been detected by Gough and Davidson,⁴¹ Gough,¹⁰ von Hippel *et al.*,¹¹ Ruepp,¹² and Johari and Whalley⁴⁵ but at kilohertz frequencies and at low temperatures. Von Hippel *et al.*,¹¹ resolved this relaxation process at temperatures below 235 °K in single crystal ice and found that at 194 °K, the amplitude of the dispersion due to this process varies between 0.044 and 0.48 for various samples and the relaxation time is of the order of 10^{-5} sec. This process is probably due to the orientation of water molecules at the grain boundaries or at the imperfection sites which requires less energy for reorientation and which is shifted to megahertz frequencies at 268.1 °K as seen in this study

At frequencies >1 GHz, the ϵ'' is higher than anticipated from the sum of the two Debye-processes. Whalley and Labbé²⁴ have suggested that the microwave absorption at frequencies >0.5 GHz is caused by transitions involving two-phonon energy difference. The dielectric loss, $\Delta\epsilon''_{\text{vib}}$, was calculated from their values of absorptivity measured in the range 0.48–1 THz from the equation,

$$\Delta\epsilon''_{\text{vib}} = \sqrt{\epsilon'} K / c\omega,$$

where all terms are defined as earlier. The values were extrapolated using the relation $K \propto \omega^2$ to lower frequencies, and these values are plotted logarithmically against frequency in Fig. 6. Walford⁴⁶ has also extrapolated Cartright and Errera's⁴⁷ measurements of absorptivity using the relation $K \propto \omega^2$ based on a single damped harmonic oscillator. The ϵ'' calculated by Walford⁴⁶ is in reasonable agreement with that calculated by Whalley and Labbé.²⁴ Neither of the models, however, account for the high value of measured ϵ'' at GHz frequencies unless it is assumed that an increase

in temperature from 100 to 268 °K increases the absorptivity by an order of magnitude.

It may be mentioned that the relaxation in a very small amount of water, if present in ice, can also account for the high losses at frequencies >1 GHz. A calculation on the basis of heterogeneous dielectric mixture shows that if 10^{-4} mole fraction of ice were dispersed as liquid spheres, it would contribute an amount of the order of 10^{-4} to ϵ'' at 3 GHz at 268 °K, but a much lower amount at MHz frequencies. It is important to recall in this context that ϵ'' data at frequency >0.15 GHz in Fig. 6 are for glacier ice,⁴³ which contains air bubbles and a certain amount of dissolved impurities. The latter can be present in sufficient concentrations at the grain boundaries in polycrystalline ice to depress the freezing point by 5–10 °K. The presence of a small amount of water in glacier ice would not be unlikely at temperatures close to 273 °K. No dielectric data on laboratory-grown ice are available in this frequency range or at low temperatures.

D. The anisotropy of ϵ_{∞}

In Fig. 1, the ϵ_{∞} of single-crystal H_2O ice measured perpendicular to the c axis is the same as that of polycrystalline ice. This, however, does not show that the limiting high frequency polarizability is absolutely isotropic, for, within the experimental error of $\pm 0.3\%$, a difference of 1% between the ϵ_{∞} , measured parallel and perpendicular to the c axis, can remain undetected in our measurements. The results contrast with those of Taubenberger,¹⁵ where a difference of 6% between the ϵ_{∞} measured parallel and perpendicular to the c axis was found at 258 °K.

The anisotropy of ϵ_{∞} represents the sum of the anisotropy in the optical permittivity, n_D^2 , and that in the

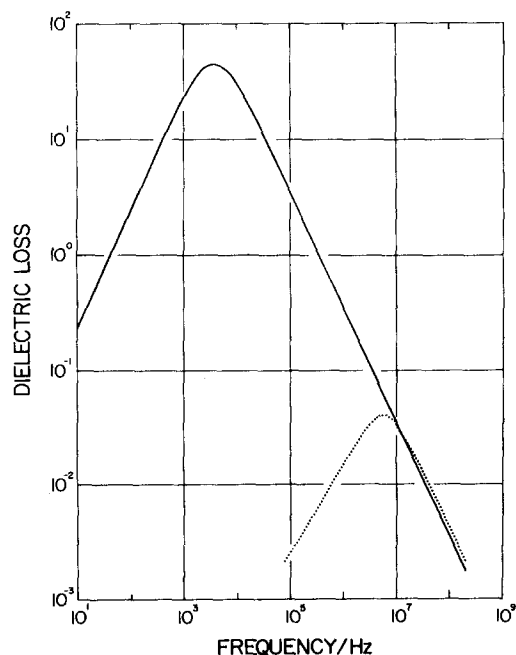


FIG. 7. Analysis of the dielectric loss of single crystal ice Ih at 268.1 °K into two dispersion regions.

contribution to permittivity due to infrared polarization, $\Delta\epsilon_{ir}$. Ehrlinghaus²³ reported that n_D for the extraordinary wave travelling parallel to the c axis in ice at 272 °K is 1.3105 and that for the ordinary wave (travelling perpendicular to the c axis) is 1.3091. Thus, there is an anisotropy of 0.0037 in the optical permittivity of ice at 272 °K, which has been attributed to the anisotropy of the local electric field in the ice lattice.^{30,48}

The $\Delta\epsilon_{ir}$, which is given by Eqs. (2) and (3), is not known to have been measured in single-crystal ice. However, since the transition moments associated with the molecular vibrations have a directional dependence, and since the O–O–O bond angles differ along the various planes in the ice lattice, a finite value of anisotropy of $\Delta\epsilon_{ir}$ is anticipated. Our data indicate that this anisotropy is likely to be not more than 1%.

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