

# Thermal conductivity of ice

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The thermal conductivity of ice, the low-pressure *Ih* phase of  $H_2O$ , is reviewed and good agreement is found with the theoretical calculations of its absolute value and temperature dependence. Measurements under pressure show an anomalous decrease in conductivity with decreasing molar volume. This is explained by the negative Grüneisen parameter for the transverse acoustic modes which dominate the heat transport. The conductivity behaves predominantly like that of a wurtzite lattice of rigid mass points with an atomic mass of 18. Some traces of the interaction of the lattice phonons with the higher-lying librational modes can be seen. The volume dependence of the conductivity of the higher-pressure phases of ice and of  $NH_4F$  is related to that of *Ih* ice.

## INTRODUCTION

The thermal conductivity of ice has been studied by many different authors.<sup>1-12</sup> The early work has been well summarized by Powell.<sup>1</sup> Most of the work has been done on the *Ih* phase of ice, which is stable at atmospheric pressure from 0 to 273.2 K. Other ice phases exist at higher pressure, and some recent studies<sup>9-12</sup> have been concerned with these. The present study concerns mainly the *Ih* phase and is an analysis of previously published results based on recent measurements and calculations of the phonon-dispersion curves,<sup>13-17</sup> elastic constants,<sup>18-23</sup> thermal-expansion coefficients,<sup>24-27</sup> and specific-heat capacity.<sup>28-30</sup>

## STRUCTURE

The crystal structure<sup>31</sup> of ice *Ih* is, if the hydrogen atoms are ignored, a wurtzite type where the oxygen atoms have replaced both the zinc and the sulfur. If it is assumed that the two hydrogen atoms are tightly bound to their parent oxygen (i.e., about 1 Å away), then, as the phonon-dispersion curves show, the low-frequency propagating phonons can be thought of as the cooperative vibrations of a crystal with an atomic mass of 18. The oxygen-hydrogen vibrations and rotations are at phonon energies from 300 to 3000  $cm^{-1}$ , have very small group velocities, are generally uncoupled from the translational vibrations,<sup>31</sup> and are thus assumed here not to take part in the heat transport up to melting point.

The hexagonal crystal structure<sup>32</sup> has a  $c_0/a_0$  ratio of 1.629, which is very close to the ideal ratio of 1.6330. Thus the oxygen-oxygen distances of the four different bonds are all nearly equal in length. This means that the anisotropy in the thermal conductivity should be small. Measurements<sup>33</sup> of the thermal conductivity of single

crystals near 270 K have shown that the anisotropy is of the order of 5% or less. Data on the elastic constants<sup>18,19,22</sup> and the thermal-expansion coefficient<sup>25-27</sup> also show a small anisotropy. Thus thermal-conductivity measurements on polycrystalline and on single-crystal ice should yield similar thermal-conductivity results as long as the crystallites are large enough to avoid the effects of grain-boundary scattering. The calculations of Klinger and Neumaier<sup>7</sup> indicate that grain sizes of  $<10^{-3}$  cm would be needed to affect the thermal conductivity above 80 K. Thus experimental data on coarsely polycrystalline, unoriented ice above 80 K will be treated as if they represented single-crystal ice.

## THERMAL-CONDUCTIVITY RESULTS

A composite curve of thermal conductivity  $\kappa$  versus temperature  $T$  is shown in Fig. 1. The data of Klinger *et al.*<sup>7,8</sup> are for single crystals

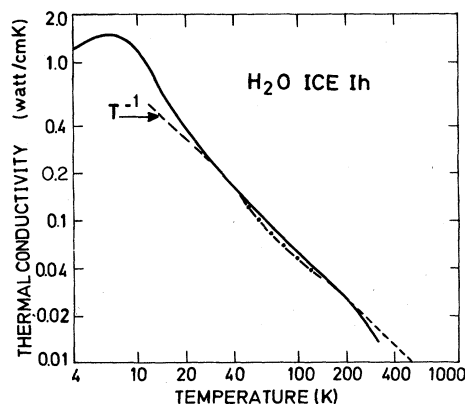


FIG. 1. The thermal conductivity of ice as a function of temperature at atmospheric pressure. The dot-dash curve between 50 and 175 K is suggested by the data of Anderson *et al.* (Ref. 12). The dashed line is a  $T^{-1}$  behavior.

with the heat flow along the  $c$  axis. The other data of Ratcliff,<sup>2</sup> Dillard and Timmerhaus,<sup>4,5</sup> and Andersson *et al.*<sup>12</sup> are for polycrystalline ice. Most of the data in Fig. 1 have been taken at atmospheric pressure. The data of Andersson *et al.*<sup>12</sup> were measured at a pressure of 0.07 GPa ( $\sim 700$  atm) and have been corrected to a pressure of one atmosphere using the measured<sup>10</sup> pressure coefficient of thermal conductivity at 248 K. The solid line in Fig. 1 is the best estimate of the proper thermal conductivity  $\kappa$  versus temperature  $T$  curve for  $H_2O$  ice Ih. The dot-dash curve in Fig. 1 is the approximate behavior found by Andersson *et al.*<sup>12</sup> from 175 to 120 K using a transient hot-wire method. The difference between the solid and dashed curve is, perhaps, caused by Bjerrum defects.<sup>34,35</sup> Such defects produce anomalies in the specific-heat capacity,<sup>28,30</sup> and in the elastic constants.<sup>21,23</sup> These defects are the result of disorder in the hydrogen atom positions, not in the oxygen positions. The  $\kappa$  versus  $T$  curve for  $D_2O$  exhibits a similar behavior,<sup>11</sup> and Bjerrum defects also occur<sup>23</sup> in  $D_2O$ . Since their concentration is time dependent in the temperature range between 80 and 140 K, they may influence the transient hot-wire method of measuring  $\kappa$ . This method has a characteristic time of the order of 1 sec. They do not appear to influence the value of  $\kappa$  measured by a steady-state heat-flow technique,<sup>5</sup> although the scatter in the data<sup>5</sup> may mask such a small effect. The maximum effect on  $\kappa$  appears from Fig. 1 to be about 10% at 80 K. Further work is needed to clear up this question.

In Fig. 2 the results of various<sup>2,4,5,12</sup> authors have been plotted as  $\kappa T$  vs  $T$  on a log-log scale. Some of the points by Andersson *et al.*<sup>12</sup> have been

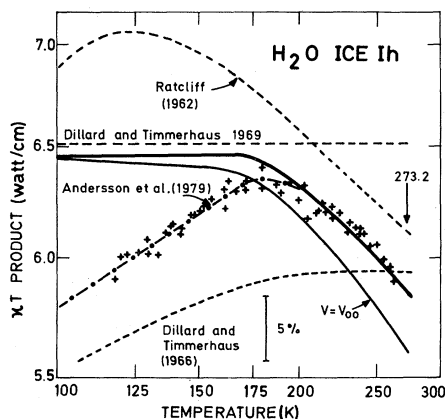


FIG. 2. The  $\kappa T$  product versus  $T$  for ice at high temperatures. The heavy solid curve is the best estimate of the behavior at atmospheric pressure. The light solid curve is this best estimate corrected to a constant volume of  $V_{00}$ .

plotted. However since there are 411 data points, many have been omitted. The average deviation from the smooth curve is about  $\pm 1\%$ . The 1969 results of Dillard and Timmerhaus are the more accurate and their 1966 results should be disregarded. The best estimate of the behavior of  $\kappa$  vs  $T$  for ice at atmospheric pressure under nearly equilibrium conditions is the heavy solid curve in Fig. 2. The best estimate of the value of  $\kappa$  at representative temperatures is given in Table I.

Since the thermal-expansion coefficient of water is fairly large, the  $\kappa$  at constant pressure is substantially different from that at constant volume. An estimate of the correction is shown in Fig. 2. The  $g$  value, where  $g$  is defined<sup>36</sup> as

$$g = - \left( \frac{\partial \ln \kappa}{\partial \ln V} \right)_T, \quad (1)$$

is negative<sup>10-12</sup> for Ih ice. Thus if  $\kappa$  is corrected to the molar volume of ice at 0 K and zero pressure, i.e., to  $V_{00}$ , the corrected  $\kappa$  will be less than that measured at constant pressure. At 248 K the value<sup>12</sup> of  $g$  is  $-2.5$ . The molar volume at 273.2 K and zero pressure (or one-atmosphere pressure) is<sup>32</sup>  $19.643 \text{ cm}^3/\text{mole}$ . Using this value and the thermal-expansion values of Dantl<sup>26</sup> one obtains  $V_{00} = 19.290 \text{ cm}^3/\text{mole}$  ( $1.0707 \text{ cm}^3/\text{g}$ ). This is also the molar volume at 100 K.

At 273.2 K the calculated  $\kappa$  at  $V_{00}$  is  $20.5 \times 10^{-3} \text{ W/cm K}$  (under pressure). At one atmosphere it is  $21.4 \times 10^{-3} \text{ W/cm K}$ . The corresponding one-atmosphere values from Ratcliff<sup>2</sup> are 22.5, while Dillard and Timmerhaus<sup>5</sup> (1969) give 23.8. The agreement is to within 11%. In view of an anisotropy in  $\kappa$  of 5%, not much better agreement can be expected for polycrystalline samples. The best agreement that might be expected is about  $\pm 1\%$  because the molar volume of ice is a function of its history, and volume fluctuations of 0.3% are known.<sup>37</sup> This volume fluctuation multiplied

TABLE I. Best estimate values of  $\kappa$  of Ih  $H_2O$  ice at atmospheric pressure (to  $\pm 10\%$ ).

$\kappa$ (W/cm K)	$T$ (K)
1.2	10
0.60	15
0.38	20
0.161	40
0.081	80
0.065	100
0.054	120
0.043	150
0.032	200
0.024	250
0.0214	273.2

by  $|g|$  gives a predicted uncertainty in  $\kappa$  of  $\Delta\kappa/\kappa = 0.8\%$  even for oriented single crystals.

#### ABSOLUTE VALUE OF $\kappa$

From the known<sup>13-17</sup> phonon-dispersion curves for Ih ice one can tabulate the phonon energies at the Brillouin-zone boundary for the acoustic phonon branches in the A, K, and M directions (see Table II). The average zone-boundary values for the transverse and longitudinal phonon branches are  $\bar{\nu}_T = 53 \text{ cm}^{-1}$  and  $\bar{\nu}_L = 125 \text{ cm}^{-1}$ , respectively. If it is assumed that  $g(\nu)$  varies as  $\nu^2$ , then from Eqs. (8.1) and (8.2) of Ref. 36, one obtains, in K,

$$\bar{\Theta}_T = 75, \quad (2a)$$

$$\bar{\Theta}_L = 180.$$

The average for both polarizations is then, again in K,

$$\bar{\Theta}_\infty = 120. \quad (2b)$$

From heat-capacity measurements on ice at low temperatures<sup>29</sup> one obtains  $\Theta_0 = 226 \text{ K}$ . Since there are  $n = 4$  molecules in a primitive unit cell of Ih ice, the equivalent acoustic phonon value of  $\bar{\Theta}_0$  is

$$\bar{\Theta}_0 = \Theta_0/n^{1/3} = 145 \text{ K}$$

[see Eq. (3.4) of Ref. 36]. This gives a ratio of  $\bar{\Theta}_0/\bar{\Theta}_\infty = 1.21$ . Such a ratio is generally observed for many adamantane-structure crystals (see Table II of Ref. 36). From  $\bar{\Theta}_\infty$  and  $\bar{\gamma}_\infty$  and Eq. (3.3) of Ref. 36 it is possible to calculate an expected value of the thermal conductivity,  $\kappa'(\bar{\Theta}_\infty)$ , at  $T = \bar{\Theta}_\infty$ . The equation is

$$\kappa'(\bar{\Theta}_\infty) = Bn^{1/3}\bar{M}\delta^3(\bar{\Theta}_\infty)^2(\bar{\gamma}_\infty)^{-2}, \quad (3)$$

where  $\kappa'$  is in units of W/cm K,  $B = 3.04 \times 10^{-8}$ ,  $\bar{M}$  is the average molecular mass in g,  $\delta^3$  is the average volume per molecule in  $\text{\AA}^3$ ,  $\bar{\Theta}_\infty$  is in K, and  $n$  is the number of molecules per primitive unit cell. The evaluation of  $\bar{\gamma}_\infty$  is somewhat involved.

The thermal-expansion-coefficient data<sup>24-26</sup> on bulk samples show that the expansion is negative

TABLE II. Phonon energies (in  $\text{cm}^{-1}$ ) at Brillouin-zone boundary in  $\text{H}_2\text{O}$  Ih ice ( $\pm 5 \text{ cm}^{-1}$ ).

Mode	Zone Boundary Point		
	A	K	M
TA	35	70	55
LA	85	155	135

for temperatures below about 60 K. This gives<sup>38-40</sup> negative values of the average  $\gamma$  at low temperatures. The x-ray results of Brill and Tippe<sup>27</sup> do not agree but are disregarded in the present discussion. The ultrasonic-velocity measurements of Brockamp and Rüter<sup>20</sup> show that the  $\gamma$  value for the lowest-frequency transverse phonons is negative. Thus one expects the value of  $\gamma$  from thermal-expansion data  $\gamma^{\text{th}}$  to be negative at  $T = 0 \text{ K}$ . The adamantane-structure crystals ZnS (Ref. 41), CdTe (Ref. 41), and CuCl (Ref. 42) also have negative values of  $\gamma_0^{\text{th}}$ , whereas Ge and Si do not.<sup>41,43,44</sup> Whalley<sup>40</sup> has estimated values for the transverse and longitudinal acoustic phonons. The present estimates, explained later, are

$$\gamma_T = -0.85, \quad (4)$$

$$\gamma_L = +1.05.$$

The average value for calculating  $\kappa'$  is found from

$$\langle \gamma^2 \rangle = (2\gamma_T^2 + \gamma_L^2)/3 = 0.85 \quad (5)$$

and

$$\langle \gamma^2 \rangle^{1/2} = 0.92.$$

Thus in Eq. 3 we shall use  $\langle \gamma^2 \rangle = 0.85$ . The result expressed in W/cm K is

$$\kappa'(120 \text{ K}) = 47 \times 10^{-3}. \quad (6)$$

The measured value of  $\kappa$  at 120 K from Table I expressed in the same units as (6) is

$$\kappa(120 \text{ K}) = 53 \times 10^{-3}. \quad (7)$$

The agreement between  $\kappa'$  and  $\kappa$  is quite good in view of the many approximations involved. The conclusion is that the  $\kappa$  of Ih ice behaves similarly to that of other adamantane-structure crystals and is governed by the phonons of a simple lattice with vibrating mass points of  $\bar{M} = 18 \text{ g}$ . The O-H rotations and vibrations do not influence  $\kappa$  very much, although Bjerrum defects may produce some small reduction in  $\kappa$  in a limited temperature range. This point will be discussed further in the next section.

#### TEMPERATURE DEPENDENCE OF $\kappa$

If acoustic phonons are the carriers of thermal energy, as we have concluded, then their interactions with other phonons in three-phonon processes should yield  $\kappa$  proportional to  $T^{-1}$ . This is the behavior in Fig. 1 for  $35 \text{ K} \leq T \leq 175 \text{ K}$ . Let us define<sup>38</sup>

$$m = -(\partial \ln \kappa / \partial \ln T)_v. \quad (8)$$

For  $T < 35 \text{ K}$  the  $\kappa$  vs  $T$  curve in Fig. 1 starts to rise more rapidly than  $T^{-1}$  and  $m > 1$ . This behavior is typical of umklapp processes with a

characteristic temperature of about twice 35 K or 70 K. From Eq. (2a) we see that  $\bar{\Theta}_T = 75$  K. It is these transverse phonons that dominate the thermal transport below 35 K and determine the  $m$  vs  $T$  behavior in this region. A plot of  $m$  versus  $T$  from Figs. 1 and 2 is given in Fig. 3 for a constant volume of  $V_{00}$ . From 40 to 175 K  $m$  has its "normal" value of 1.0. Above 175 K  $m$  again rises. This rise may be caused by the scattering of acoustic phonons by optic phonons.<sup>12,36</sup> The rise in  $m$  above 1 for  $T > 175$  K has been seen by Ratcliff<sup>2</sup> and by Andersson *et al.*<sup>10-12</sup> but was not seen by Dillard and Timmerhaus.<sup>5</sup> An increase in the measured  $\kappa$  at 273.2 K of 10% while holding the value at 175 K constant would eliminate the upturn in  $m$  of Fig. 3. The random errors of Andersson *et al.* are about  $\pm 1\%$ . If the unknown systematic errors are also of this magnitude, then the upturn in  $m$  is a real effect. In the following analysis it is assumed that the upturn for  $T > 175$  K in Fig. 3 is real.

#### OPTIC-PHONON SCATTERING

Crystals of Ih ice possess rotational or librational modes of the  $H_2O$  molecule and there is a peak<sup>45</sup> in the infrared absorption for these modes at  $\bar{\nu} = 800$   $cm^{-1}$ . There are also many optic-phonon branches of the translational vibrations<sup>13-17</sup> in the range 50 to 290  $cm^{-1}$  wave numbers. The sharp rise in  $m$  for  $T > 175$  K in Fig. 3 cannot be explained by these optic phonons below 290  $cm^{-1}$  because they are too low in energy. The 800- $cm^{-1}$  phonons have the correct energy. The modes in ice<sup>45</sup> from 1000 to 3600  $cm^{-1}$  are too high in energy to explain  $m$  vs  $T$ . Using Eq. (12.4) of Ref. 36 the dot-dash curve in Fig. 3 was calculated with  $\bar{\nu}_{op} = 800$   $cm^{-1}$  and  $S_{op} = 1.9$ . The agreement is reasonably good and indicates that there may

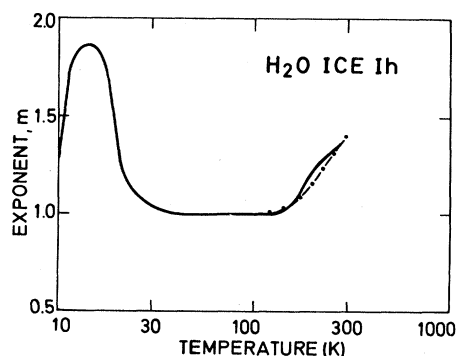


FIG. 3. The exponential factor  $m$  vs  $T$ . The dot-dash line is the calculated behavior for coupling of the acoustic phonons to the librational modes.

be some interaction between the translational acoustic modes and the rotational modes. Note that there are 12 rotational modes and three acoustic modes in the Brillouin zone. Hence the coupling coefficient per acoustic mode to each optic mode is, on the average,  $S_{op}/4 = 0.5$ . In several adamantane crystals<sup>36</sup> this mode-to-mode coupling coefficient for translational-to-translational modes is 1.2. The translational-to-rotational coupling is apparently somewhat weaker than this. Andersson *et al.*<sup>12</sup> found  $S_{op} = 3.8$  using a slightly different analysis of the  $\kappa$ -versus- $T$  results. They assumed that at 273.2 K in the absence of optic-mode scattering  $\kappa$  would be  $24.3 \times 10^{-3}$  W/cm K, whereas the present assumption is  $22.6 \times 10^{-3}$  W/cm K. This small difference changes the calculated value of  $S_{op}$  but not  $\bar{\nu}_{op}$ .

#### VOLUME DEPENDENCE OF $\kappa$

The change in the  $\kappa$  with pressure of  $H_2O$  and  $D_2O$  ice has been measured.<sup>9-12</sup> The quantity  $R = (\partial \ln \kappa / \partial P)_T$  is negative for phases Ih and Ic of  $H_2O$  and for the Ih phase of  $D_2O$ . Its value for the Ic phase of  $D_2O$  is unknown but is probably also negative. For the other higher-pressure phases<sup>9-12</sup> the quantity is positive. Table III gives some of the measured values<sup>9-12</sup> for Ih ice and for ice VII and VIII for comparison.<sup>9-12</sup> Phase I of  $NH_4F$  is also known<sup>46</sup> to have a negative pressure coefficient and is included in Table III. Phase III of  $NH_4F$  has a structure similar to phase VIII of ice and a similar  $R$  value. Negative  $R$  values are unusual, so an attempt is made here to explain why they occur. The volume coefficient of  $\kappa$  is defined in Eq. (1). This is related to the pressure coefficient by

$$g = B_T R, \quad (9)$$

where  $B_T$  is the isothermal bulk modulus

$$B_T = - \left( \frac{\partial P}{\partial \ln V} \right)_T. \quad (10)$$

The values of  $B_T$  in Table III are taken from the

TABLE III. Pressure and volume dependences of  $\kappa$ .

Crystal	Temp. K	$P$ (GPa)	$B_T$ (GPa)	$R$ (GPa <sup>-1</sup> )	$g$
Ih $H_2O$	248	0.1	9.00	-0.28	-2.5
Ih $H_2O$	120	0.1	10.6	-0.37	-3.9
VII $H_2O$	286	2.4	24	+0.2	+4.8
VIII $H_2O$	246	2.4	24	+0.2	+4.8
I $NH_4F$	298	0.2	23.9	-0.26	-6.2
II $NH_4F$	379	0.9	30	+0.25	+7.5
III $NH_4F$	386	2.0	71	+0.26	+18

recent literature for water<sup>19,47,48</sup> and ammonium fluoride.<sup>49,50</sup> The adiabatic bulk modulus  $B_S$  measured ultrasonically has been converted to  $B_T$  using values<sup>35</sup> of the thermal Grüneisen constant  $\gamma^{\text{th}}$ , and the linear thermal-expansion coefficient<sup>26</sup>  $\alpha$  by

$$B_S = B_T(1 + 3\alpha\gamma T). \quad (11)$$

Since  $B_T$  varies with pressure<sup>47</sup> as

$$B_T = B_{T0} + B'_{T0}P, \quad (12)$$

the values in Table III are those for the average pressure used during the measurement, shown in column 3. The  $B'_{T0}$  value<sup>20</sup> for ice Ih is 4.4 and for<sup>47</sup> ice VII it is 5.3.

The calculation<sup>36</sup> of  $g$  depends on the values of  $\gamma$  and  $q$ . The  $\gamma$  values for the very-low-frequency transverse and longitudinal phonons in ice can be obtained from the pressure dependence of the average sound velocities of Brockamp and Rüter<sup>20</sup> using the theory developed by Sheard.<sup>51</sup> Thus

$$\gamma_i = \frac{1}{3} + B_T \left( \frac{\partial \ln S_i}{\partial P} \right)_T, \quad (13)$$

where the subscript  $i$  refers to the particular mode and  $S_i$  is the average velocity of sound for that mode. Whalley<sup>40</sup> has omitted the  $\frac{1}{3}$  term in Eq. (13) in his calculation of  $\gamma$ . The average values<sup>20</sup> of  $(\partial \ln S_i / \partial P)$  for transverse and longitudinal phonons averaged over all directions at 253 K, expressed in units of  $\text{GPa}^{-1}$  are

$$\left( \frac{\partial \ln S_T}{\partial P} \right) = -0.132, \quad \left( \frac{\partial \ln S_L}{\partial P} \right) = +0.081. \quad (14)$$

The result is [see Eq. (4)]

$$\gamma_T = -0.85, \quad \gamma_L = +1.05.$$

If we weigh these two values according to their contributions to the Debye heat capacity at low temperature<sup>51</sup> using Eq. (2a), we obtain a limiting value at absolute zero for the thermal expansion Grüneisen parameter of

$$\gamma_0^{\text{th}} = -0.78. \quad (15)$$

The value of  $\gamma^{\text{th}}(T)$  for the acoustic modes is given by

$$\gamma^{\text{th}}(T) = \frac{2\gamma_T D(\Theta_T/T) + \gamma_L D(\Theta_L/T)}{2D(\Theta_T/T) + D(\Theta_L/T)}, \quad (16)$$

where  $D$  is the Debye heat-capacity function. A plot of Eq. (16) combined with Eqs. (2a) and (4) is given in Fig. 4 as the lower dashed curve for the three acoustic modes. The experimental solid curve in Fig. 4 is taken from Leadbetter.<sup>38,39</sup> If it is assumed that the nine optic modes can be represented by a characteristic temperature  $\Theta_{\text{op}} = 350$  K, and that they all have  $\gamma_{\text{op}} = 1.00$ , then

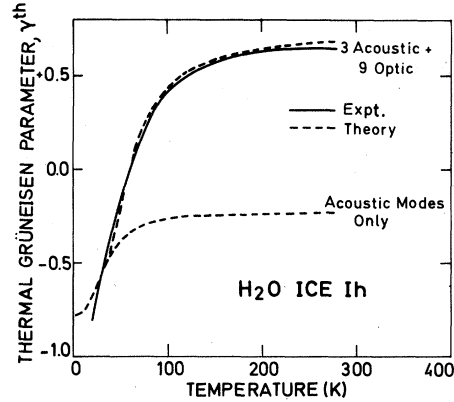


FIG. 4. The thermal-expansion Grüneisen parameter versus temperature, solid curve. The dashed curves are the calculated contributions from the various lattice vibrational modes.

$$\gamma^{\text{th}}(T) = \frac{2\gamma_T D(\Theta_T/T) + \gamma_L D(\Theta_L/T) + 9\gamma_{\text{op}} E(\Theta_{\text{op}}/T)}{2D(\Theta_T/T) + D(\Theta_L/T) + 9E(\Theta_{\text{op}}/T)}, \quad (17)$$

where  $E$  is the Einstein specific-heat function. This equation gives the upper dashed curve in Fig. 4; the agreement with the experimental data is quite good. The conclusion is that the  $\gamma$  values in Eq. (4) are in good accord with the measured thermal expansion.

The next step in deriving the volume dependence of  $\kappa$  is to assume that  $\kappa_{\text{tot}}$  is composed of separate contributions from the transverse and longitudinal modes. Thus

$$\kappa_{\text{tot}} = \kappa_T + \kappa_L. \quad (18)$$

If we use Eq. (1) to define  $g_{\text{tot}}$ , then

$$g_{\text{tot}} = g_T \left( \frac{\kappa_T}{\kappa_{\text{tot}}} \right) + g_L \left( \frac{\kappa_L}{\kappa_{\text{tot}}} \right); \quad (19)$$

with this model the only way to obtain a negative  $g_{\text{tot}}$  is for  $g_T$  to be negative. The longitudinal phonons always have positive values of  $\gamma$ ,  $g$ , and  $q$ . From Ref. 36 the value of  $g$  is given by

$$g = 3\gamma + 2q - \frac{1}{3},$$

where  $q$  is defined as

$$q = \left( \frac{\partial \ln \gamma}{\partial \ln V} \right)_T. \quad (20)$$

The calculation of  $q$  can be a complex process.<sup>52</sup> For the high-temperature region  $T \geq \Theta_L$  some simplification<sup>53</sup> is possible. From Eq. (4) of Ref. 53,

$$q = \gamma(1 + 3\delta_s \alpha T),$$

where  $\delta_s$  is the Anderson-Grüneisen constant, and

$\alpha$  is the linear thermal-expansion coefficient. The value of  $\delta_s = 3.4$  is based on Eq. (3) of Ref. 53 and the data of Brockamp and Rüter.<sup>20</sup> For ice at all temperatures  $1 \gg 3\delta_s\alpha T$ , hence

$$q = \gamma. \quad (21)$$

It is assumed that Eq. (21) is valid for both the transverse and longitudinal modes. Then from Eq. (9.4) of Ref. 36

$$g = 5\gamma - \frac{1}{3}. \quad (22)$$

The result is

$$g_T = -4.58, \quad g_L = +4.92. \quad (23)$$

Note that  $g_T$  is negative as required.

From Table III at 248 K one finds  $g_{\text{tot}} = -2.5$ . Using this value and Eqs. (19) and (23) the result is

$$(\kappa_T/\kappa_{\text{tot}}) = \begin{cases} 0.78 & \text{at 248 K,} \\ 0.93 & \text{at 120 K.} \end{cases} \quad (24a)$$

$$(24b)$$

This is the first experiment that has been able to separate the  $\kappa_T$  and  $\kappa_L$  contributions to  $\kappa_{\text{tot}}$ .

These values of the fraction of the heat transported by the transverse waves should not be taken too seriously. However the numbers are plausible<sup>54</sup>; the theoretically expected fraction is uncertain. The results also show that as the temperature is lowered the heat transport becomes dominated by the phonons (transverse) with the lower Debye temperature [see Eq. (2a)]. This is the reason that  $g$  for *Ih* ice becomes increasingly negative as the temperature is lowered (see Table III). The transverse phonons also dominate the thermal expansion at low temperatures and are responsible for the negative  $\gamma^{\text{th}}$  values in Fig. 4 below 60 K.

It would be instructive to measure  $g$  as a function of temperature to temperatures even lower than 120 K in order to determine the  $g$  value when the transverse waves truly dominate the behavior. Temperatures of 20 K should be sufficiently low to see this effect.

#### OTHER MATERIALS

In Table III the  $g$  values for several phases of  $\text{NH}_4\text{F}$  are also given. Phase I shows a  $g < 0$ , and it is considerably lower than for *Ih* ice. No thermal-expansion or Grüneisen-constant data for  $\text{NH}_4\text{F}$  are known. Hence no calculations can be made. However, the rather open tetrahedral lattice structure of phase I of  $\text{NH}_4\text{F}$  is similar

to that of ice *Ih*, and negative  $\gamma$  and  $g$  values for the transverse modes should be expected. The  $g$  values become increasingly positive as the phases of  $\text{NH}_4\text{F}$  become more dense, as shown in Table III. Phase III of  $\text{NH}_4\text{F}$  has a structure similar to that of ice VII and VIII, in which a "double lattice" of the adamantine lattice of phase I is present. The vacant positions<sup>55</sup> in the lattice are now filled, the transverse atomic displacement will not have such weak restoring forces, and no negative  $\gamma$  values or negative  $g$  values are expected. Indeed the  $g$  values for  $\text{H}_2\text{O}$  and  $\text{NH}_4\text{F}$  are now positive. If  $\gamma_T = \gamma_L = 1$  for phases VII and VIII of  $\text{H}_2\text{O}$ , then we expect  $g = 5\gamma - \frac{1}{3} = 4.67$ . This is close to the observed value of 4.8. An estimate for ice VII gives<sup>56</sup> an approximate value of  $\gamma = +0.5$  at room temperature. The estimated  $\gamma$  for  $\text{NH}_4\text{F}$  phase III is  $\gamma = +3.6$  based on  $g = +18$  from Table III.

If a negative thermal expansion at low temperatures is characteristic of materials with negative  $g$  values, then ZnS (Ref. 41), CdTe (Ref. 41), CuCl (Ref. 42), and maybe other materials should have  $g < 0$ . Further experiments are needed to test this prediction.

The thermal conductivity of *Ih* ice at the melting point is abnormally high<sup>57</sup> compared to that of liquid water at the same temperature. The effective mean free path  $l$  of the phonons in the solid can be calculated from

$$\kappa = l\bar{v}\bar{C}/3, \quad (25)$$

where  $\bar{v}$  is the average sound velocity, and  $\bar{C}$  is the heat capacity per unit volume for only the acoustic modes. Using  $\kappa = 2.14 \times 10^{-2}$  W/cm K, a value<sup>20</sup> of  $\bar{v} = 2.13 \times 10^5$  cm/sec, and  $\bar{C} = 3R/4 = 0.317$  J/cm<sup>3</sup>deg, the result is

$$l(273.2 \text{ K}) = 95 \text{ \AA}.$$

Since  $\delta = 3.19 \text{ \AA}$ , then  $l/\delta = 30$ . This means that the phonons in *Ih* ice at the melting point travel about 30 lattice constants before being scattered. So ice *Ih* melts long before the  $\kappa$  reaches its minimum value.<sup>57</sup> The high  $\kappa$  of *Ih* ice relative to water<sup>36</sup> and the nearby ice phases<sup>10</sup> is produced by its much simpler crystal structure. Note that in calculating  $l$  we have used  $\bar{C}$  instead of the total measured specific-heat capacity.

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