

## Thermal conductivity of the *Ih* and XI phases of ice

O. Andersson and H. Suga\*

*Department of Experimental Physics, University of Umeå, S-901 87, Umeå, Sweden*

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The thermal conductivity  $\lambda$  of KOH-doped ice was measured using the transient hot-wire method at temperatures in the range 55–250 K and at pressures up to 0.15 GPa. With an isobaric increase of temperature at 0.08 GPa,  $\lambda$  decreased 17% at about 74 K. This decrease is associated with the known transition from ordered phase XI to phase *Ih* which exhibits orientational disorder of H<sub>2</sub>O. A model for  $\lambda$  indicates that the decrease of  $\lambda$  at the transition is due to an increase of the lattice anharmonicity which might be caused by the disorder in phase *Ih*. It was inferred from the temperature dependence of  $\lambda$  that phonon scattering in both phases *Ih* and XI is dominated by three phonon unklapp processes. At 58 K,  $\lambda$  of supercooled phase *Ih* decreased slightly with increasing pressure whereas  $\lambda$  of phase XI was independent of pressure.

### I. INTRODUCTION

Ice is a typical hydrogen-bonded crystal which has been described in detail elsewhere.<sup>1</sup> An oxygen atom in ice *Ih* is hydrogen bonded to four neighboring oxygen atoms in a tetrahedral arrangement. The oxygen-oxygen distances of the four hydrogen bonds are all nearly equal in length, about 276 pm. Between two adjacent hydrogen-bonded oxygen atoms are two potential wells symmetrically placed with respect to the center of the bond. The location of the protons in the potential wells is governed by the ice rules proposed by Bernal and Fowler.<sup>2</sup> These rules state that each of the four hydrogen bonds to an oxygen must be occupied by one proton. That is, only one of the two wells in a bond is occupied by a proton. In addition, two of the four protons in the bonds must be in potential wells close to the oxygen.

In spite of the simplicity of the ice *Ih* crystal structure, it is accepted as a crystal that does not obey the third law of thermodynamics. The residual entropy at 0 K, determined by Giauque and Stout,<sup>3</sup> is explained fairly well by the half-hydrogen statistical model proposed by Pauling.<sup>4</sup> Pauling calculated the entropy associated with the number of equienergetical states the protons can adopt, based on the ice rules, and found good agreement with the residual entropy.

It is clear that the constraints imposed by the ice rules imply that an ordering transition is difficult to achieve. Every displacement of a proton must, in general, be followed by a number of proton movements among the nearest neighbors. As a result, there is a strong correlation of the proton movements or, equivalently, of the reorientational motion of the H<sub>2</sub>O molecules. The probability of such thermally activated processes occurring decreases, of course, with decreasing temperature. Apparently this motion essentially ceases at a temperature that is higher than the hypothetical transition temperature to an ordered proton state. It follows that the disorder associated with the protons becomes frozen in, which results in the observed residual entropy.

Onsager<sup>5</sup> proposed using an impure ice specimen in or-

der to relax the severe constraints imposed by the ice rules and thereby obtain an ordered ice phase. In fact, an ice specimen doped with a small amount of KOH has been shown to exhibit a first-order phase transition at 72 K.<sup>6</sup> Consequently, KOH incorporated into the lattice enhances dramatically the mobility of the H<sub>2</sub>O molecules making the transition possible to realize within the time of an experiment. A neutron-diffraction experiment<sup>7</sup> on KOD-doped heavy ice revealed that the low-temperature phase has the space group of *Cmc*2<sub>1</sub> (orthorhombic) with the H<sub>2</sub>O molecules in an ordered state. The ordered phase has a polar structure along the *c* axis of the original hexagonal lattice and was designated ice XI.<sup>8</sup>

The purpose of the present work is to investigate the relative importance of proton disorder on the thermal conductivity  $\lambda$  of ice. As described above, there is good evidence that proton disorder is present in ordinary ice *Ih*. Furthermore, this disorder is, to a large extent, removed at the transition *Ih* → XI, which occurs in KOH-doped ice. Therefore, the change in  $\lambda$  at the transition should reflect the extent to which proton disorder scatters phonons or otherwise influences  $\lambda$ .

There are a substantial number of investigations of  $\lambda$  of ice. In a review of work done before 1980, Slack<sup>9</sup> found a difference of  $\pm 10\%$  between the reported values for  $\lambda$  at 100 K after excluding some of the work he considered to be less accurate. No investigation of  $\lambda$  of phase XI has previously been made.

### II. EXPERIMENTAL

We used the transient hot-wire method<sup>10</sup> to measure the thermal conductivity  $\lambda$ . The hot-wire probe used was a Ni wire (0.1 mm diam) placed horizontally in a ring of constant radius within a Teflon cell. The probe, surrounded by the medium under investigation, was heated by a (1-s) pulse of about constant power and the wire resistance was measured versus time. This enabled the temperature rise of the wire to be determined. A theoretical expression for the temperature rise was fitted to the data points, thereby yielding  $\lambda$ . For temperatures above

100 K, the inaccuracy was estimated as  $\pm 2\%$ .<sup>10</sup> Owing to the decreased sensitivity of the hot-wire, the inaccuracy in  $\lambda$  increases with decreasing temperature and was  $\pm 4\%$  at 40 K. The standard deviation was an order of magnitude smaller than the inaccuracy. The hot-wire method also yields values for the heat capacity per unit volume, but these are subjected to a large uncertainty, especially at low temperatures, and are therefore not presented here.

The Teflon cell was mounted in a piston-cylinder type of pressure vessel of 45-mm internal diameter, and the load was applied using a 5-MN hydraulic press. Temperature was varied by cooling or warming the whole pressure vessel and was measured using an internal chromel versus alumel thermocouple, which had been calibrated against a commercially available silicon-diode thermometer. Pressure was determined from load/area with an empirical correction for friction, which had been established using the pressure dependence of the resistance of a manganin wire. The vessel was cooled with a refrigerator using a closed helium gas cycle. The apparatus has been described in detail elsewhere.<sup>11</sup>

A standard 0.1-M KOH aqueous solution was purchased from Wako Pure Chemical and used without further purification. The concentration corresponds to a  $1.8 \times 10^{-3}$  mole fraction of KOH to  $H_2O$ . In an investigation of the heat capacity of phase XI,<sup>6</sup> this concentration was found to be the most effective in producing the low-temperature phase XI. In order to obtain this phase, the sample was cooled at a low pressure ( $\approx 0.005$  GPa) down to about 65 K and was annealed for three days at temperatures in the range 65–70 K following the procedure reported by Tajima, Matsuo, and Suga.<sup>6</sup>

For large values of thermal diffusivity (below about 100 K for ice), reflection of the heat wave against the wall of the sample cell causes additional heating of the hot wire. In order to compensate for this, a small temperature drift (linear with time) was subtracted from the measured values for the temperature rise of the hot wire. This procedure decreased the standard deviation of the fits by about three times. The values for  $\lambda$ , which were compensated in this way differed in the worst case by 3% to the uncompensated data.

### III. RESULTS

Figures 1 and 2 show the temperature dependence of  $\lambda$  at pressures of 0.08 GPa and 0.16 GPa, respectively. The transition between the proton-ordered phase XI and the proton-disordered *Ih* can be detected as a decrease of  $\lambda$  by about 17%. As discussed in more detail later, the temperature dependence of  $\lambda$  for both phases *Ih* and XI is typical for crystals for which  $\lambda$  is limited mainly by three phonon umklapp scattering ( $\lambda \propto T^{-1}$  at  $T \gtrsim$  Debye temperature).

Figure 1 includes data for  $\lambda$  of phase *Ih* pertaining to the supercooled state below the transition temperature of about 74 K. As explained in the experimental section, it is necessary to anneal below the transition temperature for several days in order to obtain a substantial amount  $\approx 70\%$  of phase XI (to obtain a 100% transformation

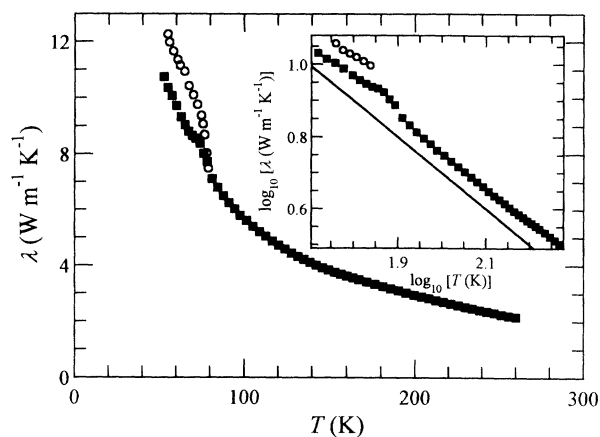


FIG. 1. Thermal conductivity  $\lambda$  of ice plotted against temperature  $T$  at a pressure of 0.08 GPa: (■) phase *Ih* and (○) phase XI. The inset shows  $\log_{10}\lambda$  plotted against  $\log_{10}T$ . The line corresponds to  $\lambda \propto T^{-1}$ .

would take a prohibitively long time).<sup>6</sup> The small anomaly in the data for  $\lambda$  of the supercooled phase *Ih*, near the transition temperature, is probably due to some degree of transformation to the ordered phase XI.

The magnitude of the data for  $\lambda$  of the doped phase *Ih* at 80 K is 8% lower than the “best value” of pure phase *Ih* at 80 K.<sup>9</sup> Our data for  $\lambda$  are, in general, lower than that of previous work.<sup>9</sup> However, the data agree well with those for a single crystal reported by Klinger.<sup>12</sup>

In order to estimate if the dopant has any influence on  $\lambda$ , a comparison between the phonon mean free path  $l$  and the average distance between two KOH provides an indication. If we assume that the dopant is homogeneously distributed in the ice lattice then the average distance between two KOH is roughly 25 Å. The phonon mean free path calculated at 270 K from the equation  $\lambda = \frac{1}{3}\rho c_v l$  (where  $\rho$  is the density,  $c_v$  is the isochoric heat capacity, and  $v$  is the phonon velocity) gives  $l \approx 20$  Å. Since  $l$  is of the same magnitude as the average distance between the KOH we can expect that  $\lambda$  will be less for

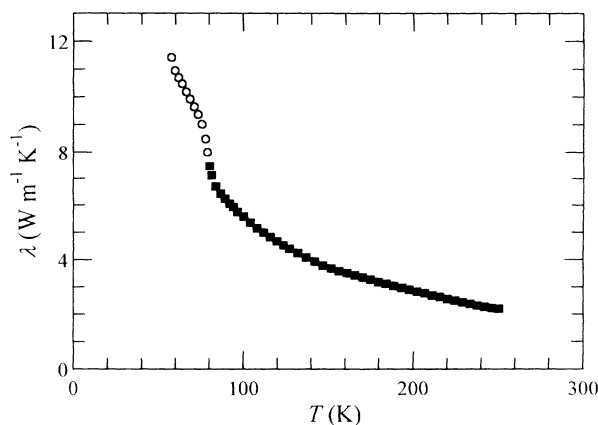


FIG. 2. Thermal conductivity of ice plotted against temperature at a pressure of 0.16 GPa: (■) phase *Ih* and (○) phase XI.

the doped specimen than that of an undoped specimen. In fact, a measurement of  $\lambda$  of pure ice resulted in larger values than those of the doped ice. The data of the pure ice were in good agreement with those of Ross, Andersson, and Bäckström.<sup>13</sup> However, since the dopant will affect  $\lambda$  of both phases *Ih* and XI to approximately the same degree, the difference of  $\lambda$  between the phases should still reflect the effect of the proton disorder in phase *Ih*.

The isothermal pressure dependence of both the phases *Ih* and XI was measured at 58 K (Fig. 3). In general, crystalline phases exhibit a significant increase of  $\lambda$  with increasing pressure,<sup>14</sup> but both phases *Ih* and XI differ from that general pattern. In particular, phase *Ih* shows a slightly negative pressure dependence of similar magnitude as that found previously at 248 K.<sup>13</sup> This behavior of  $\lambda$  has been explained by a negative mode Grüneisen parameter for the transverse acoustic modes.<sup>9</sup> In the case of phase XI, it can be seen from Fig. 3 that  $(\partial\lambda/\partial P)_T$  is very small in magnitude. A near-zero value of this partial derivative is unusual but has been found previously for clathrate hydrates.<sup>14</sup>

From data for isothermal  $\lambda(P)$  it is possible to determine the density dependence of  $\lambda$ , described by the Bridgman parameter  $g$ , where  $g = (\partial \ln \lambda / \partial \ln \rho)_T$ . Using data for adiabatic compressibility of phase *Ih* (Ref. 15) ( $\approx$  isothermal compressibility at these low temperatures) together with the data for  $\lambda(P)$  (Fig. 3), it is straightforward to calculate the  $g$  value. Assuming the same compressibility for phase XI, we found  $g = -2.8$  and  $g = 0.2$  for phases *Ih* and XI, respectively. It is difficult to estimate the inaccuracy in these data but  $g$  for phase *Ih* is certainly negative. The experimental value for  $g$  of phase XI is 0.2 but a negative value is probably within the inaccuracy limits. However,  $g$  for phase XI is certainly larger than that for phase *Ih*. The  $g$  value of *Ih* is in good agreement with  $g = -2.6$  determined at 248 K.<sup>13,16</sup> In general, crystalline phases exhibit  $g$  values larger than 6.<sup>14</sup> Consequently, both phases *Ih* and XI are exceptional concerning their pressure and density dependencies for  $\lambda$ .

Since the transition temperature at two different pres-

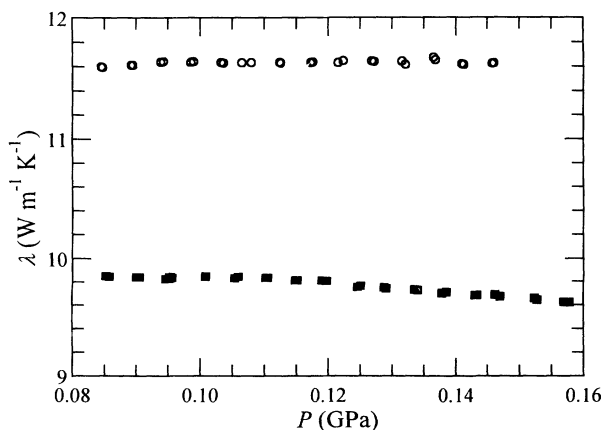


FIG. 3. Thermal conductivity of ice plotted against pressure at a temperature of 58 K: (■) phase *Ih* and (○) phase XI.

ures was determined, it is possible to calculate roughly the slope of the transition line  $\Delta P/\Delta T = 0.1$  GPa/K. This value is in rough agreement with  $\Delta P/\Delta T = 0.067$  GPa/K determined in a high-pressure investigation of the heat capacity of ice.<sup>17</sup>

#### IV. DISCUSSION

We shall devote the main part of the discussion to the decrease of  $\lambda$  at the XI  $\rightarrow$  *Ih* transition. As mentioned in the Introduction, it appears fairly well established that the main structural difference between the phases is that the protons are disordered in phase *Ih*, whereas they are ordered in phase XI. If this picture is correct, then we can use the change in  $\lambda$  at the transition to determine the significance of proton disorder in phonon-scattering processes.

Ahmad and Phillips<sup>18</sup> have investigated the effect of proton disorder in ice *Ih* and also in 1,3-dioxolane (DO) clathrate hydrate using low-temperature data for  $\lambda$ . In their model, tunneling states associated with proton disorder caused phonon scattering. A theoretical expression for the relaxation time  $\tau$  of tunneling-state scattering together with that for point, boundary, and umklapp scattering was used to interpret the data for  $\lambda$ . In their results, Ahmad and Phillips<sup>18</sup> did not explicitly express the relative importance of phonon scattering associated with proton disorder. However, our interpretation of their results is that phonon scattering arising from proton disorder was insignificant at 50 K in the case of ice *Ih*, whereas it was the major source of phonon scattering in (rapidly cooled) DO clathrate hydrate. In our view, their model indicates that proton disorder in ice *Ih* is important to thermal resistivity only at low temperatures, whereas in the case of DO clathrate hydrate it is of great significance in a wide temperature range. Another interpretation in which proton disorder is not present to the same extent in ice *Ih* as it is in DO clathrate hydrate is also possible.

In another investigation of  $\lambda$  of ice, Klinger<sup>12</sup> found that the data were well described by a model that included phonon scattering from point defects, boundaries and dislocations as well as phonon-phonon scattering. That is, proton disorder was not attributed to a specific  $\tau$ , but its significance may perhaps be described approximately by that for point defects or dislocations. As a result, in the model of Klinger,<sup>12</sup> a part of the scattering provided by these terms may perhaps be due to scattering from proton disorder. Phonon interactions involving both normal and umklapp processes were also considered in his model. However, it was found that normal processes were insignificant with regard to the thermal resistivity.

The theoretical basis for the discussion of our results is provided by the Debye formula for  $\lambda(T)$  given by<sup>19,20</sup>

$$\lambda = \frac{k_B^4 T^3}{2v\pi^2 \hbar^3} \int_0^{\Theta_D/T} \tau(x) \frac{x^4 e^x}{(e^x - 1)^2} dx, \quad (1)$$

where  $\Theta_D$  is the Debye temperature,  $v$  is the phonon velocity,  $\tau(x)$  is the relaxation time,  $x = \hbar\omega/k_B T$ , where  $\omega$  is the phonon angular frequency, and the other symbols have their usual meaning. Many simplifications have

been made in order to obtain this formula for  $\lambda$ .<sup>19,20</sup> Despite this, it has been shown to be successful in describing  $\lambda$  for completely different systems such as electrical insulators as well as semiconductors, metals and high- $T_c$  superconductors when the influence of free electrons is properly taken into account.

There are, at least, two ways to account for the proton disorder in a theoretical model based on Eq. (1). Phonon scattering can be divided into two major parts: phonon-phonon scattering (three-phonon umklapp scattering) and phonon-structural scattering. In the two models for  $\lambda$  of ice which we shall describe, the proton disorder affects mainly: (i) the phonon-phonon scattering, (ii) the phonon-structural scattering. In model (i), the effect of the proton disorder on the phonon scattering is of a secondary type. The strength of the interaction in three-phonon umklapp processes depends on the anharmonicity of the lattice. As is well known, phonons are not scattered in phonon-phonon interactions in a perfectly harmonic lattice. Consequently, if the proton disorder can increase the anharmonicity of the ice lattice, then this would enhance the phonon scattering in phonon-phonon interactions. In model (ii), the proton disorder is accounted for in a similar way as for point defects, dislocations and other forms of structural disorder. That is, a specific  $\tau$  is attributed to the interaction between the phonons and the proton disorder. This approach is the same as the one described by Ahmad and Phillips.<sup>18</sup> However, we could not obtain a good agreement with the experimental results using their expression for  $\tau$ , which they attributed to scattering from tunneling states associated with the proton disorder. As mentioned, their model indicates insignificant scattering of this kind at temperatures where the transition occurs. As a result, the decrease of  $\lambda$  at the XI  $\rightarrow$  Ih transition cannot be accounted for solely by the disappearance of this scattering process.

In summary, the models include phonon scattering from the following.

(i) *Three phonon umklapp processes and point defects.* The scattering strength of the umklapp processes can be different in the two phases as the proton disorder present in phase Ih can increase the lattice anharmonicity. Considered as phonon scattering centers other than proton disorder, the point defects are assumed to be present to the same extent in both phases Ih and XI.

(ii) *Three phonon umklapp processes, proton disorder and point defects.* The scattering strength of the three phonon umklapp processes is assumed to be the same in phases Ih and XI. Moreover, the scattering from proton disorder is assumed to be described by the same type of  $\tau$  as that from point defects. Hence, a part or all of this scattering should disappear at the Ih  $\rightarrow$  XI transition when the protons become ordered.

We have no theoretical argument for using the same  $\tau$  for scattering from proton disorder as that from point defects. However, if this type of description for the proton disorder [i.e., model (ii)] were to account for the change in  $\lambda$  at the transition then the phonon scattering from the proton disorder must depend strongly on the phonon frequency (as it does from point defects). Otherwise, the temperature dependence of  $\lambda$  of phase Ih would be

significantly less than  $\lambda \propto T^{-1}$ , which is approximately obtained in an analysis of the data for  $\lambda(T)$  (see inset in Fig. 1). According to Klemens,<sup>21</sup> phonon scattering dominated by that from point defects yields  $\lambda \propto T^{-1}$  in a broad temperature range above the maximum in  $\lambda$  (the maximum is below the temperature range investigated here). Consequently, it would be a possibility that point-defect scattering, associated with proton disorder, exists in phase Ih to a sufficient extent that its disappearance account for the increase in  $\lambda$  at the Ih  $\rightarrow$  XI transition, and still  $\lambda \propto T^{-1}$  would be obtained for phase Ih.

The relaxation time for three-phonon umklapp processes at temperatures of order of the Debye temperature and below is of the form<sup>19-21</sup>

$$\tau_u^{-1}(x) = Ax^2T^3e^{-(\Theta_D/\beta T)}, \quad (2)$$

where  $A$  is the scattering strength and  $\beta$  is a constant, which depends on the details of the Brillouin zone and the dispersion of the lattice waves near the zone boundaries.<sup>21</sup>

The relaxation time for scattering from point defects is given by<sup>19-21</sup>

$$\tau_p^{-1}(x) = Bx^4T^4, \quad (3)$$

where  $B$  depends on the number of point defects. We will refer to  $B$  as the scattering constant in point scattering as well as in proton scattering [the latter in model (ii)].

The total relaxation times in the two models are then given by the same expression:

$$\tau^{-1}(x) = Ax^2T^3e^{-(\Theta_D/\beta T)} + Bx^4T^4. \quad (4)$$

In model (i),  $B$  was assumed to be the same in the phases Ih and XI, whereas in model (ii)  $A$  was assumed to be the same in both phases.

The Debye formula does not take into account changes in  $\lambda$  due to thermal expansion. It follows that in order to make the best comparison with theory, the measured isobaric data for  $\lambda$  should be transformed to isochoric conditions. The change in  $\lambda$  due to expansion alone is given by

$$\left[ \frac{\partial \ln \lambda}{\partial T} \right]_\rho - \left[ \frac{\partial \ln \lambda}{\partial T} \right]_p = -g\alpha, \quad (5)$$

where  $g = (\partial \ln \lambda / \partial \ln \rho)_T$  is the Bridgman parameter and  $\alpha$  is the thermal expansivity. Using the calculated data for  $g$  together with data for  $\alpha$ ,<sup>15</sup> the isobaric data for  $\lambda$  were transformed to isochoric conditions. The transformation introduced a change in  $\lambda$  by an amount less than 4%.

In order to minimize the number of fitted parameters, data for  $\Theta_D$  and  $\beta$  were taken from Klinger<sup>12</sup> and for the phonon velocity  $v$ , we used the average value for the sound velocity in the temperature range 55–250 K (Ref. 18) ( $\Theta_D = 226$  K,  $\beta = 6.5$ ,  $v = 2400$  m/s). Consequently, Eq. (1) with  $\tau$  given by Eq. (4) was fitted to the data for  $\lambda$  of phase Ih with  $A$  and  $B$  as the only adjustable parameters. The result of the fit is shown as a solid line in Fig. 4. A detailed examination of the relative importance of the Eqs. (2) and (3) in the calculation shows that the term de-

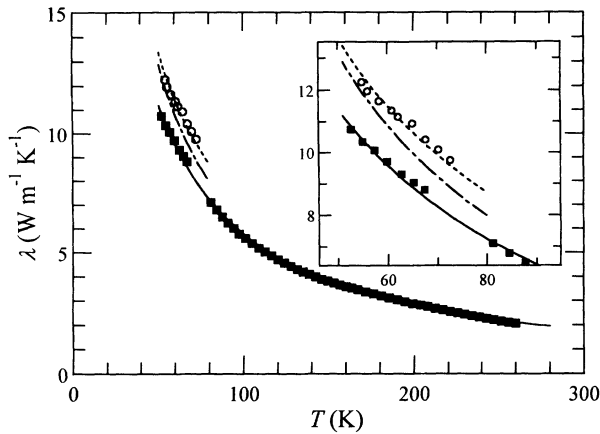


FIG. 4. Thermal conductivity of ice plotted against temperature after transformation to isochoric conditions pertaining to the volume at 0.08 GPa and 55 K: (■) phase Ih and (○) phase XI. The lines are theoretical fits of Eq. (1): (—) models (i) and (ii) for  $\lambda$  of phase Ih, (---) model (i) for  $\lambda$  of phase XI, and (-·-·-) model (ii) for  $\lambda$  of phase XI.

scribed by Eq. (2) is by far the dominant term. That is, phonon scattering in ice is determined mainly by three-phonon umklapp processes. In order to explain the increase of  $\lambda$  at the Ih  $\rightarrow$  XI transition, we now turn to the difference between the two models (i) and (ii) and the fitting to the data for phase XI.

In model (i), the scattering constant in point scattering  $B$  was the same in phase XI as in phase Ih. That is, Eq. (1) with  $\tau$  given by Eq. (4) was fitted to the data for  $\lambda$  of phase XI with  $A$  as the only adjustable parameter. The result is shown as a dashed curve in Fig. 4 (---).

In model (ii), the scattering strength of the three-phonon umklapp processes  $A$  was the same in phase XI as in phase Ih. That is, Eq. (1) with  $\tau$  given by Eq. (4) was fitted to the data for  $\lambda$  of phase XI with  $B$  as the only adjustable parameter. As mentioned, in model (ii) we attribute  $B$  to the scattering constant arising from both point defects and proton disorder. The result is shown by the chain curve in Fig. 4 (-·-·-). Since the fit yielded a negative value for  $B$ , the smallest possible value for  $B$  which makes physical sense ( $B = 0$ ) was used to generate this curve.

The parameters obtained in the fitting procedure are summarized in Table I, which shows that the scattering strength for umklapp processes in phase Ih agrees very well with that used by Klinger.<sup>12</sup> As can be seen in Fig. 4, model (i) gave a better fit than model (ii), which could not account for the change in  $\lambda$  at the transition and, in addition, yielded a somewhat more pronounced tempera-

ture dependence of  $\lambda$  than that of the measured data for phase XI.

Roufousse and Klemens<sup>22</sup> have derived a theoretical expression for the scattering strength  $A$  of three-phonon umklapp processes in a simple cubic lattice, given by

$$A = \frac{4\pi a \gamma^2 k_B^3}{\sqrt{2} v^3 M \hbar^2}, \quad (6)$$

where  $a$  is the lattice parameter,  $\gamma$  is the Grüneisen parameter, and  $M$  is the mass of a unit cell. [The form for Eq. (6) given here is the original form<sup>22</sup> multiplied by the factor  $k_B^2/\hbar^2$  to account for the fact that  $\tau$  was given as a function of the phonon angular frequency  $\tau(\omega)$ .] It follows from Eq. (6) that the scattering strength is proportional to  $\gamma^2$ . In other words, three-phonon umklapp scattering depends strongly on the anharmonicity of the lattice, which is conveniently described by the absolute magnitude of  $\gamma$  (an increase of the anharmonicity corresponds to an increase of  $|\gamma|$ ).

Equation (6) can be used to calculate  $A$  for comparison with the fitted value for phase Ih. In order to do this we associated  $a^3$  with the volume per molecule ( $\cong 32 \text{ \AA}^3$ ) and  $M$  with the molecular mass ( $3 \times 10^{-26} \text{ kg}$ ). An estimate for  $\gamma$  ( $= -0.5$ ) was taken from the calculations by Leadbetter<sup>15</sup> and the phonon velocity was the same as used in the fitting process ( $v = 2400 \text{ m/s}$ ). The calculated value of  $A = 4 \times 10^5 \text{ K}^{-3} \text{ s}^{-1}$ , although perhaps an overestimate, is in fair agreement with the fitted value, indicating the reasonableness of the model. An overestimate of the scattering strength calculated in this way was also noticed by Roufousse and Klemens.<sup>23</sup>

A comparison of the data represented by the chain curve in Fig. 4 with those reported by others is interesting, since these data correspond to  $\lambda$  in absence of any point-defect scattering. After accounting for the difference of pressure, we find good agreement (within 1%) with the best value for  $\lambda$  at 80 K.<sup>9</sup> This makes it plausible that the effect of KOH on  $\lambda$  is accounted for by the term described by Eq. (3), which, consequently, is not connected with the proton disorder.

In our discussion, we have simply claimed that the change of the scattering strength  $A$  is due to an increase of the lattice anharmonicity. However, if we examine the parameters which determine  $A$  [Eq. (6)] this assumption appears to be the most reasonable one. As described above, we have used the same phonon velocity and Debye temperature in the calculations of  $\lambda$  in the two phases. It can be shown using data for heat capacity in the temperature range 16–25 K of the phases Ih (Ref. 3) and XI (Ref. 24) that the Debye temperature is the same to within 1%. It probably follows that the sound velocity is the same (same elastic constants) in the two phases and, hence,

TABLE I. Parameters obtained by the fitting of Eq. (1) using  $\tau$  given by Eq. (4) and with the parameters:  $v = 2400 \text{ m/s}$ ,  $\Theta_D = 226 \text{ K}$ , and  $\beta = 6.5$ .

Parameters	Models (i) and (ii) phase Ih	Model (i) phase XI	Model (ii) phase XI	Klinger (Ref. 12) phase Ih	Equation (6) phase Ih
$A \text{ (K}^{-3} \text{ s}^{-1}\text{)}$	$2.93 \times 10^5$	$2.39 \times 10^5$	$2.93 \times 10^5$	$3.0 \times 10^5$	$4.0 \times 10^5$
$B \text{ (K}^{-4} \text{ s}^{-1}\text{)}$	120	120	0	0.1	

that the assumption of the same phonon velocity in the two phases can be a good approximation. Consequently, a change in the lattice anharmonicity is the most probable reason for a substantial change in  $A$ . The fitting procedure yielded the result of 23% increase of  $A$  at the transition XI $\rightarrow$ Ih (Table I). This would correspond to an increase of the lattice anharmonicity, defined by  $|\gamma|$ , of 11.5%. In obtaining this result, we assumed that the scattering constant for point defect scattering is independent of the anharmonicity. However, this is not always the case. A wrong atom in the lattice will, in general, displace neighboring atoms and therefore introduce a strain field in the lattice. This leads to point-defect scattering for which the scattering constant varies as  $\gamma^2$ .<sup>19</sup> In such case ( $B \propto \gamma^2$ ), a detailed analysis showed that  $|\gamma|$  increased 10% at the transition.

As described above, our theory for  $\lambda(T)$  yields about 10% larger  $|\gamma|$  in phase Ih than that in phase XI. Using this result together with a theoretical expression for  $g$  [Eq. (7)] give an indication how the value for  $g$  can change at the transition. In a crystal of monatomic lattice, where the phonons are scattered only in three-phonon umklapp processes,  $g$  is given by<sup>25</sup>

$$g = 3\gamma + 2q - \frac{1}{3}, \quad (7)$$

where  $q = -(\partial \ln \gamma / \partial \ln \rho)_T$  and  $q = \gamma$  can be used as an

approximation, at least at high temperatures.<sup>9</sup> The value for  $\gamma$  of phase XI ( $= -0.45$ ) is obtained from that of phase Ih ( $= -0.5$ ) using our result of a 10% change of  $\gamma$  at the transition. Assuming Eq. (7) is valid for the ice lattice yields  $\Delta g = 0.2$  at the phase Ih $\rightarrow$ phase XI transition. The value for  $\Delta g$  calculated from the experimentally determined  $g$  values is 3. These calculations show that the theory we have described for  $\lambda(T)$  is consistent with a somewhat larger  $g$  value for phase XI than that of phase Ih, but the increase is an order of magnitude smaller than that experimentally observed.

In summary, the theoretical calculations indicate that phonon scattering in both phases XI and Ih is due mainly to three-phonon umklapp processes and, in addition, that the decrease of  $\lambda$  at the XI $\rightarrow$ Ih transition might be due to an increase of the lattice anharmonicity caused by the orientational disorder of the H<sub>2</sub>O molecules (proton disorder).

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\*Permanent address: The Research Institute for Science and Technology, Kinki University, Kowakae, Higashi-Osaka 577, Japan.

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