Thermal conductivities of a clathrate with and without guest molecules

Marek Zakrzewski* and Mary Anne White†
Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3
(Received 25 June 1991; revised manuscript received 5 September 1991)

The thermal conductivities of Dianin's compound [4-(*p*-hydroxyphenyl)-2,2,4-trimethylchroman] and its ethanol adduct in the temperature range from 20 to 250 K are reported. This clathrate has the same stable structure both with and without guest molecules in its hourglass-shaped cages, thereby allowing the first direct experimental investigation of the effect of a clathrate's guest species on the thermal conductivity. Both with *and without* the guest molecules, the thermal conductivity is similar to that of a glass, and the presence of the guest molecule enhances the resistance to heat flow. The thermal conductivity is described in terms of umklapp-, boundary-, and resonant-scattering resistance contributions. The latter is ascribed to the interaction of localized modes with the acoustic modes of the host lattice. It is proposed that the localized modes are associated with the motion of the methyl groups of the Dianin molecule for the unsolved host lattice, and the motions of host methyl groups and the motions of the ethanol guest molecules within the cages for the ethanol adduct of Dianin's compound.

INTRODUCTION

We report measurements of the thermal conductivity of a clathrate (binary inclusion compound with guest molecules residing in the cavities of a host lattice) both with and without included guest molecules; to the best of our knowledge this is the first such direct experimental investigation.

Thermal conductivity is one of the most fundamental properties of a solid. The thermal conductivity (κ) of many simple insulating solids can be described with the phonon gas model: the phonon mean free path decreases with increasing temperature at high temperatures and becomes limited by the defect separation (or sample dimensions for a very pure sample) at low temperatures. For this simple model the thermal conductivity is given by[1]

$$\kappa=\frac{Cvl}{3}\ , \tag{1}$$

where C is the specific heat per unit volume, v is the phonon group velocity, and l is the phonon mean free path. Therefore, starting from very low temperatures (where the l is constant and C dominates the temperature dependence of κ), κ first increases and then decreases with increasing temperature.

However, this does not describe all simple solids. Amorphous materials, for example, are known to have very low thermal conductivities, with a positive derivative of κ with respect to temperature at all temperatures.[2–9] Ferroelectrics,[10] spin glasses[11] including KCN-KCl mixed crystals,[12] monomers and polymers with optic-acoustic coupling,[13] systems with dynamical Jahn-Teller distortion,[14] and the N_2-Ar quadrupolar glass[15] all exhibit thermal conductivities that are similar to structural glasses in their temperature dependences. Each of these types of solids appears to have a highly efficient thermal-resistance mechanism, which lowers the thermal conductivity and dominates the (somewhat more usual) negative $(\delta\kappa/\delta T)$ at higher temperatures that arises when phonon-phonon interactions are controlled by the probability of umklapp processes.

The thermal conductivity κ of a clathrate hydrate, i.e., a clathrate with a host lattice composed of water molecules, has previously been reported.[16,17] At relatively high temperatures, κ was found to increase with increasing temperature. This was surprising in light of the usual negative temperature coefficient of κ in this temperature range for its closest analog, ice-Ih.[18] Furthermore, κ for the clathrate hydrate was considerably less than that of ice-Ih.

On the basis of low-temperature measurements of the thermal conductivity of a clathrate hydrate,[19] it has been proposed[19,20] that the source of the additional thermal resistance in the clathrate hydrates is the interaction between optical mode(s) associated with the motion of the guest molecule species in the cavities and the acoustical modes of the host lattice. The optic modes are thought to fall in the same energy range as the heat-carrying acoustic modes, attenuating the ability of the latter to carry heat and resulting in a reduction in κ. This additional thermal resistance mechanism has similarities to the phonon scattering due to two-level systems in ferroelectrics,[10] resonant scattering due to librating impurity ions in ionic solids,[11,12] resonances due to dynamical Jahn-Teller effects,[14] optical-acoustical coupling in some molecular solids,[13] and localized oscillators in amorphous materials.[21]

Although consistent with experiments to date, and supported by the finding[22] that the thermal conductivity for the urea-hexadecane channel complex is intermediate between that of clathrate hydrates and "normal" crystalline solids, the concept of guest-host coupling has not been tested experimentally for the clathrate hydrates for one simple reason: their host lattice cannot be prepared without the guest species. Pure ice forms its own closer-packed structure.

Therefore, in order to experimentally explore the role of the guest molecules in the thermal conductivity of a clathrate, we have initiated investigations of Dianin's compound [4-(*p*-hydroxyphenyl)-2,2,4-trimethylchroman], a clathrate that has the same stable structure both with and without guest molecules in the cages.[23] The

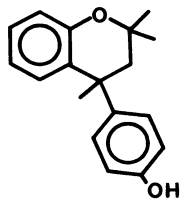

FIG. 1. The molecular structure of Dianin's compound.

molecular and crystallographic structures of Dianin's compound are shown in Figs. 1 and 2, respectively. The unusual stability of this structure arises from the (relatively) strong intermolecular hydrogen bonding of the phenolic groups, which gives symmetric egg-cup shaped hexamers (with monomer Dianin molecules alternately pointing up and down) that stack on top of each other through van der Waals interactions. The result is hourglass-shaped cavities (11 Å long and 6.3 Å at the broadest[24]) with or without included guest molecules. Heat-capacity[25] and nuclear quadrupole resonance (NQR) results[26] show that CCl_4 guest molecules can move relatively freely in the cages. In the case of the ethanol adduct, on which part of the present measurements were based, it is known that two ethanol guest molecules reside in each cage,[24] and the guest molecules are thought to be dimerized through hydrogen bonding.[27]

In this paper we report the results of the thermal conductivity measurements of single crystals of Dianin's compound, both with and without guest molecules.

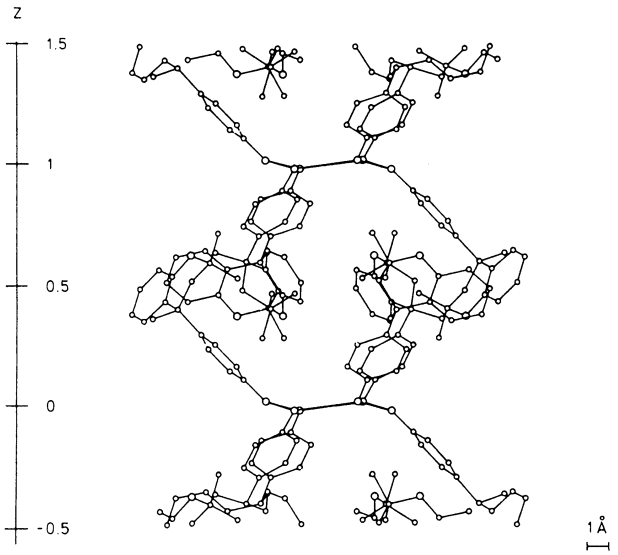

FIG. 2. The crystal structure of Dianin's compound, adapted from the structure of the ethanol adduct.[24] For clarity, neither the ethanol molecules (which would reside at about $z = 0.3$ and 0.7) nor the phenolic protons are shown. The z axis shown is in the direction of the crystallographic c axis in the hexagonal unit cell.

EXPERIMENTAL METHODS

The ethanol adduct of Dianin's compound and the unsolvated Dianin host lattice were synthesized according to a published procedure.[23] The samples were characterized[25,28,29] by their melting points, chemical analysis, thermogravimetric analysis, and ir and Raman spectroscopy. Good-quality large single crystals of the ethanol adduct of Dianin's compound were grown relatively easily from ethanol, and similar quality (but smaller) crystals of the unsolvated host lattice were obtained from decanol solutions. The crystals used for thermal conductivity measurements were both colorless and transparent, with no cloudiness or internal cracks. The uniformity of extinction of polarized light, as seen on an optical microscope for all crystal orientations of both crystals, showed that the crystals were single with respect to twinning and grain boundaries. The crystals used for the thermal conductivity measurements were smaller but of better optical quality than those used successfully for Brillouin-scattering measurements.[29] (In the Brillouin-scattering experiments, seven different crystals of the ethanol adduct of Dianin's compound, oriented from their habit, gave consistent Brillouin-scattering spectra in 23 different directions.[29]) The crystal structure of the ethanol adduct of Dianin's compound is known[24] and that of unsolvated Dianin's compound has been successfully solved[30] (weighted residuals of 0.047 at a temperature of 293 K and 0.059 at 213 K), showing the long-range order in these materials. Because of the importance of other defects to the interpretation of thermal conductivity results, we assessed the vacancy (ethanol adduct) and interstitial (unsolvated) concentrations from density determinations. The bulk density of the ethanol adduct fell slightly short of the density calculated from x-ray-diffraction data[24] for two guest molecules per cage; we calculate its guest occupancy to be 1.94 ± 0.01 ethanol guest molecules per hexamer of host lattice, and this is consistent with thermogravimetric analysis. For unsolvated Dianin's compound the bulk density was slightly greater than that calculated from x-ray-diffraction data,[30] consistent with a mole fraction of interstitial Dianin molecules of 0.005 ± 0.001, or a mole fraction of interstitial decanol (solvent) molecules of 0.008 ± 0.002. In addition, since it is known that ^{13}C NMR linewidths are sensitive to short-range disorder especially in these solids,[31] we measured cross-polarized magic angle spinning NMR spectra of crystallites of these adducts, and found the linewidths to be comparable to those observed for low-defect Xe clathrates of Dianin's compound.[31]

Thermal conductivity measurements of free-standing single crystals (12.5 and 9.5 mm long, with cross-sectional areas 18.6 and 9.0 mm^2 for the ethanol adduct and the unsolvated host lattice, respectively) were carried out in the temperature range from about 20 to 250 K by the steady-state method. The apparatus is described in detail elsewhere;[20] an adiabatic shield was added for these measurements to reduce radiative heat losses at higher temperatures. The power to the sample heater during the measurements was chosen to give a temperature difference of 1–1.5 K between the thermocouple junc-

tions, optimizing the opposing constraints of accuracy of the measurement and time required to achieve steady-state conditions. Including both systematic (e.g., measurement of the thermocouple separation) and random (e.g., noise in the thermocouple emf's) errors, we estimate the uncertainty in the measurements to be less than 20%. The thermal conductivities were measured along the crystallographic c axis for both samples.

EXPERIMENTAL FINDINGS

The measured thermal conductivities of the ethanol adduct of Dianin's compound, and the unsolvated host lattice, are presented in Tables I and II, respectively, and shown in Fig. 3. The relaxation times required to achieve steady-state conditions were about 40–50 min for unsolvated Dianin's compound and about 40–60 min for its ethanol adduct. In both cases the relaxation time increased with increasing temperature.

κ for the ethanol adduct of Dianin's compound is of the same order of magnitude and has a temperature dependence similar to that of the clathrate hydrates.[17,20] At first look the most surprising and, on further consideration, the most exploitable information (*vide infra*) is that the host lattice shows a similar temperature dependence *even in the absence of guest molecules.*

TABLE I. The thermal conductivity κ of unsolvated Dianin's compound as a function of temperature.

T/K	κ/W m^{-1} K^{-1}	T/K	κ/W m^{-1} K^{-1}	T/K	κ/W m^{-1} K^{-1}
23.73	0.31	108.05	0.73	238.30	0.89
25.87	0.31	108.51	0.71	240.46	0.92
28.77	0.32	112.29	0.73		
31.19	0.36	115.45	0.70		
33.93	0.37	117.03	0.74		
37.05	0.41	117.72	0.73		
39.23	0.41	121.21	0.76		
40.39	0.42	121.78	0.81		
40.90	0.43	123.67	0.84		
42.53	0.46	126.31	0.79		
43.41	0.45	126.57	0.83		
45.96	0.50	128.80	0.80		
48.39	0.46	133.41	0.78		
49.38	0.52	137.33	0.72		
50.92	0.51	141.06	0.72		
51.40	0.53	144.75	0.78		
55.48	0.53	148.42	0.75		
55.53	0.54	152.06	0.72		
56.97	0.60	159.33	0.80		
59.35	0.60	162.91	0.79		
59.92	0.64	166.32	0.89		
64.77	0.65	172.92	0.89		
64.95	0.63	174.26	0.86		
64.95	0.63	176.11	0.89		
67.08	0.64	177.80	0.94		
70.92	0.63	181.27	0.91		
71.96	0.71	183.98	0.93		
76.76	0.62	188.08	0.92		
76.98	0.65	189.26	0.89		
78.30	0.67	190.02	0.97		
79.68	0.71	192.40	1.01		
83.19	0.61	193.26	0.98		
83.90	0.70	196.29	1.03		
87.27	0.64	198.65	0.94		
87.47	0.69	199.89	1.00		
90.16	0.72	201.84	0.94		
91.30	0.67	205.44	0.94		
94.72	0.67	209.24	1.01		
94.97	0.71	212.47	0.96		
99.17	0.68	217.55	1.00		
99.62	0.69	220.87	0.90		
102.18	0.73	223.67	0.91		
104.12	0.71	233.83	0.98		
104.92	0.71	233.83	0.98		

EFFECT OF THE GUEST MOLECULES

A perfect crystalline solid held together with perfectly harmonic interactions has infinite thermal conductivity, as there is no mechanism for thermal resistance. Of course, real (anharmonic) lattices have finite thermal conductivities, and, in general terms, the thermal conductivity is related to the anharmonicity of a lattice. Other experimental manifestations of anharmonicity in real lattices include the deviations of the lattice thermal expansion and Grüneisen parameters from zero.

The thermal conductivities measured here show that the presence of the guest molecules lowers the thermal conductivity of this solid, and hence makes the lattice more anharmonic. This is consistent with our observations of increased thermal expansion,[28] and increased deviation of the Grüneisen parameter from its harmonic-lattice value[32] when guest molecules are present in the Dianin cage. Furthermore, the present observation of increased thermal resistance with the guest molecule present is consistent with the guest-host thermal resistance mechanism proposed for the clathrate hydrates.[20]

TABLE II. The thermal conductivity κ of the ethanol adduct of Dianin's compound as a function of temperature.

T/K	κ/W m^{-1} K^{-1}	T/K	κW m^{-1} K^{-1}	T/K	κ/W m^{-1} K^{-1}
16.94	0.13	84.08	0.28	160.11	0.35
19.96	0.15	84.44	0.25	162.49	0.40
20.39	0.14	84.65	0.26	164.15	0.38
22.69	0.15	85.10	0.30	168.68	0.38
22.85	0.16	86.30	0.27	173.23	0.38
25.19	0.17	87.22	0.33	177.74	0.40
25.67	0.17	87.87	0.33	182.26	0.41
26.90	0.19	91.05	0.28	186.75	0.42
28.44	0.18	92.22	0.36	188.41	0.43
29.55	0.18	96.53	0.37	192.79	0.44
30.75	0.19	99.58	0.31	193.83	0.39
31.44	0.20	100.74	0.36	194.83	0.45
33.43	0.20	101.40	0.36	195.86	0.43
33.90	0.19	104.74	0.33	197.22	0.44
36.17	0.20	105.74	0.36	199.19	0.43
36.80	0.19	109.99	0.38	201.53	0.44
36.84	0.21	113.01	0.35	202.64	0.44
40.94	0.20	114.20	0.37	203.57	0.48
43.31	0.21	116.48	0.36	205.69	0.45
43.97	0.23	118.33	0.38	207.94	0.47
44.97	0.23	121.10	0.33	212.16	0.47
47.64	0.22	121.14	0.34	216.57	0.45
48.82	0.22	122.18	0.33	220.54	0.47
49.18	0.22	122.31	0.40	220.90	0.49
51.29	0.22	122.85	0.33	222.38	0.45
51.78	0.23	123.37	0.39	257.10	0.47
53.76	0.24	123.47	0.34	262.92	0.46
57.51	0.24	127.23	0.34	268.55	0.51
58.06	0.24	127.60	0.36	274.16	0.50
61.20	0.25	129.56	0.38		
63.32	0.25	131.45	0.35		
65.45	0.28	135.33	0.32		
67.18	0.28	138.01	0.38		
70.07	0.24	140.62	0.40		
72.30	0.26	141.74	0.33		
72.33	0.29	142.26	0.35		
76.82	0.28	145.41	0.39		
76.93	0.28	146.54	0.36		
79.17	0.29	148.87	0.41		
80.58	0.29	151.04	0.38		
82.11	0.31	151.16	0.41		
82.77	0.29	154.97	0.40		
82.83	0.27	156.41	0.34		

SIMILARITY TO GLASSES

From the results of Fig. 3, the unsolvated host lattice itself resists thermal conduction in a way that seems phenomenologically like the proposed attenuation due to guest-host interactions. That this is also similar to the thermal conductivity of glasses can be seen from the universal form of the thermal conductivity:[5]

$$\frac{\kappa(T)}{C'}=\left[\frac{T}{\Theta_D}\right]^3\int_0^{\omega_D}(k_B\Theta_D)(\tau_{\text{total}}/h)\left[\frac{\hbar\omega^4}{k_BT^2}\right]\left[\frac{e^{\hbar\omega/k_BT}}{(e^{\hbar\omega/k_BT}-1)^2}\right]d\omega\ , \tag{2}$$

where $C'=4\pi k_B^3\Theta_D^2/h^2v$, Θ_D is the Debye temperature (170 K for both the unsolvated and the ethanol adduct of Dianin's compound[32]) corresponding to a Debye cutoff frequency of ω_D, k_B is the Boltzmann constant, $\hbar$ is Planck's constant divided by 2π, and the group velocity v is the weighted geometric average of the longitudinal and transverse sound velocities ($v=2.21\times10^3$ and 2.25×10^3 m/s for the unsolvated and ethanol adducts, respectively[32]). The scaled ("universal") thermal conductivities of both solids examined here are presented as functions of reduced temperature (T/Θ_D) in Fig. 4, along with results for several glassy materials. The results show the general similarity of the thermal conductivities of Dianin's compound (with and without guest molecules) and glassy materials.

LOCALIZED OSCILLATORS AND THE MINIMUM THERMAL CONDUCTIVITY

What is this factor that appears to attenuate heat flow in these crystalline molecular materials, with or without guest molecules in the cage, in much the same way as in a glass? The lattice vibrations responsible for thermal conductivity in glasses can best be described at temperatures above ~30 K as localized Einstein oscillators, with the heat being carried through the lattice by a random walk,[21] and the physical picture may be similar here.

Disorder-induced localization of excitations has been known for some time to affect electronic properties of solids,[33,34] and analogous localization has been used recently to describe light in dielectric microstructures.[35] For phonons, *true* localization due to disorder occurs only for the high-frequency modes because there may be interactions with the extended acoustic modes at low frequency[36] and, therefore, the disorder-induced "localized" states are more correctly termed "quasilocalized".[37] These modes are still localized with respect to their scattering properties but are hybridized (resonant) with the low-frequency acoustic modes,[37] and they may well be the common link between glasses and clathrates.

Molecular dynamics simulations of clathrate hydrates have shown distinct dynamical localized mode behavior for the guest molecules trapped in their cages.[38–41] In the present case, a simple analysis of the mean free path in the lattice [using Eq. (1) and the present experimental data] yields mean free paths in the ranges from 30 to 10 Å for unsolvated Dianin's compound and 10 to 5 Å for its ethanol adduct. (The mean free path decreases with increasing temperature for both solids.) These short mean free paths imply that localized oscillations are responsible for the similarities between this clathrate and glasses. It has been suggested that the oscillations are so heavily damped in glasses because the neighboring atomic structure differs significantly from the average glass environment;[37] the strong interaction here may be the result of resonance with the lattice acoustic modes (*vide infra*).

At high temperatures, the theoretical minimum

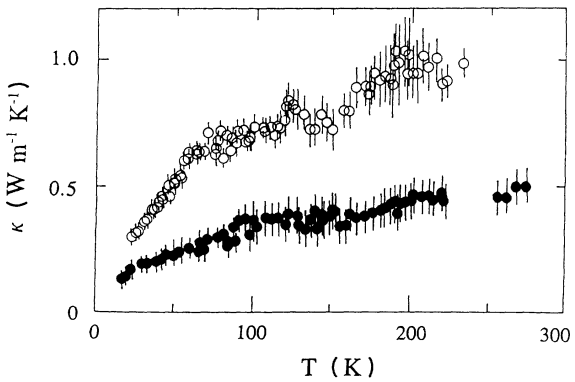

FIG. 3. The thermal conductivity of Dianin's compound: ○, unsolvated; ●, ethanol adduct. The vertical lines represent the error bars for each measured point.

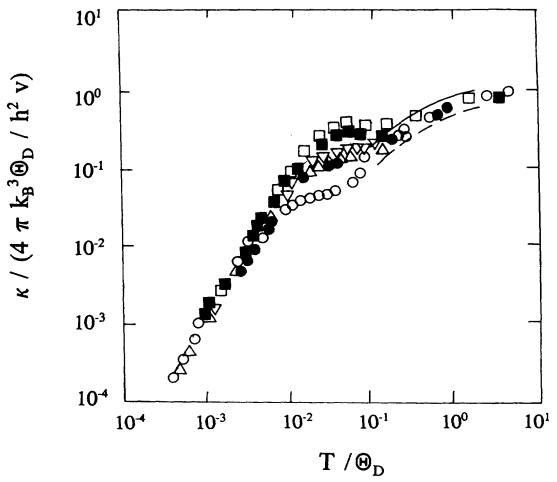

FIG. 4. Scaled ("universal") thermal conductivities of six amorphous solids[5] [○, SiO_2; △, B_2O_3; □, polybutadiene; ▽, poly(ethyleneterephthalate); ●, polystyrene; ■, poly(methylmethacrylate)], in comparison with unsolvated Dianin's compound (——) and its ethanol adduct (— — —).

thermal conductivity (calculated from the highest efficiency of thermal resistance mechanisms) is approached for glasses, and we consider now how closely it is approached in the materials under consideration here. Since the optic phonons generally do not have sufficient dispersion to give them a group velocity that contributes to the conduction of heat, they can be neglected for the purposes of this part of the discussion, although their role is important in the overall picture (see later).

Slack[42] developed a model of minimum thermal conductivity for a lattice based on the minimum mean free path of a phonon being of the order of one phonon wavelength. One can calculate the thermal conductivity for this model by assuming that all phonons in the lattice are so frequently scattered that their mean free path is this minimum value. The high-temperature limiting value of the thermal conductivity in this model, $\kappa_{\mathrm{SMINA}\,\infty}$, is given by

$$\kappa_{\mathrm{SMINA}\,\infty}=\frac{3k_B v^2}{2n\delta^3\nu_A}\ , \tag{3}$$

where ν_A is the highest acoustic phonon frequency and, for a monatomic species, n is the number of atoms per primitive unit cell, and δ^3 is the average volume per atom.

Calculation of $\kappa_{\mathrm{SMINA}\,\infty}$ for a monatomic is straightforward. For a polyatomic molecular species, as here, where the entire molecule is not a rigid group but there are rigid subgroups, n and δ can be treated according to the number of rigid subgroups. From a Debye-like analysis of our heat-capacity results, we have found that each molecule of Dianin's compound can be treated as six rigid subgroups.[32] Then, for n subgroups per primitive cell[42]

$$\nu_A=\frac{k_B\Theta_D}{hn^{1/3}} \tag{4}$$

and applying Eq. (3) for unsolvated Dianin's compound, with six rigid groups per molecule and six molecules per primitive unit cell, gives $\kappa_{\mathrm{SMINA}\,\infty}$ of 0.041 $\mathrm{W\,m^{-1}\,K^{-1}}$.

The temperature dependence of the Slack minimum thermal conductivity is given by[42]

$$\frac{\kappa_{\mathrm{SMINA}}}{\kappa_{\mathrm{SMINA}\,\infty}}=\frac{2}{x_A^2}\int_0^{x_A}\frac{x^3e^x}{(e^x-1)^2}dx\ , \tag{5}$$

where $x=h\nu/k_BT$ and $x_A=h\nu_A/k_BT$. The observed thermal conductivity of unsolvated Dianin's compound is less than κ_{SMINA}, by a factor of about 30 throughout the measured temperature range, showing that the phonon-phonon scattering is at less than the maximum effectiveness of the Slack model.

Cahill and Pohl[21] recently extended the Slack minimum thermal conductivity model to the case where the heat-carrying waves are represented by a random walk between Einstein oscillators of varying sizes. In this model, the minimum thermal conductivity, κ_{CPMIN}, is given by

$$\kappa_{\mathrm{CPMIN}}=\frac{1}{1.24}k_Bd^{2/3}v\left[\frac{T}{\Theta_C}\right]^2\int_0^{\Theta_C/T}\frac{x^3e^x}{(e^x-1)^2}dx\ , \tag{6}$$

where d is the number density of subgroups and Θ_C is the cutoff frequency (expressed in kelvin) defined by

$$\Theta_C=\frac{h}{2\pi k_B}v(6\pi^2d)^{1/3}\ . \tag{7}$$

The Cahill and Pohl model, with a slightly less efficient thermal resistance mechanism than in the Slack model, gives a minimum thermal conductivity only slightly larger than the Slack model.

The observed thermal conductivity of unsolvated Dianin's compound is considerably larger than either of these minima, assuming the heat is carried totally by the acoustic phonons (the group velocity of the optic phonons is expected to be negligible): The phonon-phonon scattering in Dianin's compound is at less than maximum possible effectiveness.

RESONANT SCATTERING

Unsolvated Dianin's compound

Nevertheless, the thermal conductivities of both unsolvated Dianin's compound and its ethanol adduct are lower than for most crystalline solids, and have the temperature dependence associated with an extra thermal resistance mechanism, as for the several systems described in the Introduction. If the extra resistance is the interaction of the acoustic modes with low-frequency optic modes, as proposed for the clathrate hydrates[20] (where the important optic modes are those due to motion of the guest molecule in the cage[20,43]), the question now is what mechanism could provide the extra thermal resistance in the *unsolvated* Dianin's compound?

The answer may come from investigations of both monomeric and polymeric molecular solids, where low-energy optic phonons associated with the hydrocarbon side chains are thought to scatter acoustic phonons.[13] In the case of Dianin's compound, these modes may well arise from internal degrees of freedom within the host molecule. Candidates are three methyl groups on each molecule (which maintain their motion even in the solid state[44]), the motions of the phenolic hydrogens,[45] and the flexibility of the carbon skeleton itself to move into and out of the cage [especially two methyl carbons, as seen by ^{13}C NMR (Refs. 44 and 31)]. On the basis of frequency, the first of these is the most likely candidate, with a frequency of $\sim10^{11}$ $\mathrm{s^{-1}}$ estimated from ^{13}C NMR data.[44] This is the only known motion in the frequency range (3×10^{11}–4×10^{12} $\mathrm{s^{-1}}$) of phonons that would be responsible for heat transfer.[21]

For unsolvated Dianin's compound the experimental thermal conductivity data was least-squares fit to a Debye model,[46]

$$\kappa(T)=\frac{1}{2\pi^2v}\int_0^{\omega_D}\tau_{\mathrm{total}}\frac{\hbar\omega^4}{k_BT^2}\frac{e^{\hbar\omega/k_BT}}{(e^{\hbar\omega/k_BT}-1)^2}d\omega\ , \tag{8}$$

treating the overall relaxation time τ_{total} as from three separable contributions,[46,47]

$$\tau_{\mathrm{total}}^{-1}=\tau_U^{-1}+\tau_B^{-1}+\tau_S^{-1}\ , \tag{9}$$

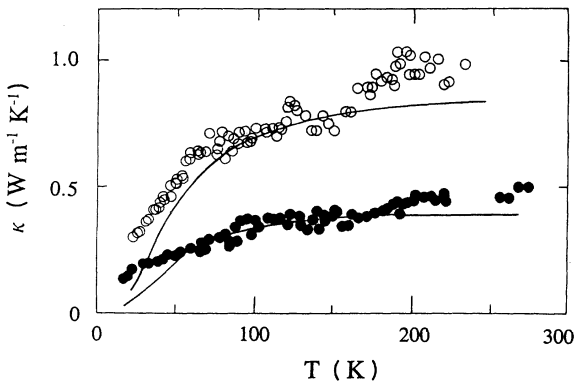

FIG. 5. The thermal conductivities of unsolvated Dianin's compound (○) and its ethanol adduct (●), and the least-squares fits to the resonance model (solid lines), as described in the text.

with the relaxation time due to the umklapp processes, τ_U, given[48] by

$$\tau_U^{-1}=B_U\omega^2 T e^{-\Theta_D/\alpha t}, \tag{10}$$

where B_U and α are empirical parameters. The relaxation time due to boundary scattering, τ_B, is given[49,50] by

$$\tau_B^{-1}=\frac{v}{2.36r}, \tag{11}$$

where r is the radius of the sample. The relaxation time due to resonant scattering, τ_S, is given[47,51–54] by

$$\tau_S^{-1}=GD\frac{\omega_0^2\omega^2}{(\omega_0^2-\omega^2)^2}, \tag{12}$$

where G is the concentration of the resonant scatterer (7.84×10^{27} m^{-3} for the methyl groups here), D is related to the strength of the optic-acoustic coupling, and ω_0 is the optical vibrational frequency involved in the resonant scattering.

The resulting fit to the thermal conductivity of unsolvated Dianin's compound is shown in Fig. 5. The values of ω_0, D, B_U, and α extracted from the fit were 7.4×10^{11} s^{-1}, 1.4×10^{-13} m^3 s^{-1}, 1.4×10^{-19} s K^{-1}, and 1.57, respectively.

Ethanol adduct of Dianin's compound

If the model of resonant scattering of acoustic (heat-carrying) phonons in clathrates by optic modes due to the motion of their guest molecules is correct, the ethanol adduct of Dianin's compound should have a thermal conductivity described by the above parameters for the unsolvated compound, with the addition of a guest-host resonant-scattering contribution. Allowing the guest-host parameters and all of the parameters described above to be freely optimized, the thermal conductivity data for the ethanol adduct of Dianin's compound was fitted within this model. The result is shown in Fig. 5.

The values of ω_0 and D extracted from the fit were 8.4×10^{11} s^{-1} and 1.6×10^{-13} m^3 s^{-1} (for the methyl groups) and 1.7×10^{12} s^{-1} and 1.6×10^{-13} m^3 s^{-1} (for the ethanol molecules). B_U and α were 1.9×10^{-19} s K^{-1} and 1.50, respectively. ω_0 for the ethanol molecule represents the frequency of the optic (guest) mode that is involved in the resonant scattering. From the heat-capacity measurements of Dianin's compound with and without the ethanol guest molecules, we know that the molar heat-capacity contribution of the ethanol guest molecule is about R (R is the gas constant) greater than that of pure (bulk) ethanol at about 40 K, and nearly $3R$ greater at 100 K.[25] This is consistent with a mode in the clathrate due to the ethanol for the ethanol molecules vibrational rattling in the cages, at a frequency close to the value of ω_0 for the ethanol molecules derived from the fit.

The most important feature of this work arises from the availability of the thermal conductivity data for a clathrate with and without its guest molecules. Since it is known that the structure of Dianin's compound is substantially unchanged by the presence of guest molecules,[24,30] the resonant-scattering model can be tested directly. The close agreement of the optimized parameters for the host lattice methyl group contribution from both the unsolvated compound and the ethanol adduct (ω_0 of 7.4×10^{11} and 8.4×10^{11} s^{-1}, and D of 1.4×10^{-13} and 1.6×10^{-13} m^3 s^{-1}, respectively) shows the consistency of the resonant-scattering model.

Comparison with other systems

Several other systems have thermal conductivities that have been described in terms of this resonant-scattering model, and it is useful to compare values of relevant parameters. The D coupling parameters obtained here are of the order 10^{-13} m^3 s^{-1}, compared with 3.8×10^{-15} m^3 s^{-1} for tetrahydrofuran (THF) clathrate hydrate,[20] and 1.6×10^{-16} m^3 s^{-1} for CN^--doped KCl.[52] Although the larger value of the "free volume" of the methyl group or the included guest molecule, compared with the THF molecule in THF clathrate hydrate and CN^- in CN^-:KCl may also be a factor, the larger D values for Dianin's compound and its ethanol adduct also may reflect better matching of the optic and acoustic modes in Dianin's compound due to the complexity of the molecular structure and the resulting virtual continuum of optic modes between 40 cm^{-1} (or lower) and 3000 cm^{-1}.[55,56] From molecular dynamics calculations[38–40] it is found that the rattling motions of the guest molecules in clathrate hydrates occur in the range 6×10^{11}–3.6×10^{12} s^{-1}, which overlaps with the frequency range (3×10^{11}–4×10^{12} s^{-1}) of phonons that are responsible for heat transfer.[21] Similarly, the frequencies of the vibrational rattling mode for the ethanol molecules in the cages and of the motion of the Dianin host lattice itself, 1.7×10^{12} and 8×10^{11} s^{-1} from the fits to the thermal conductivity data, are found to be in this same range.

CONCLUDING REMARKS

The optic-acoustic resonance model is able to reproduce the thermal conductivity of this clathrate both with and without guest molecules, and the thermal conductivi-

ty appears to obey the "universality" of glassy materials. Heat conduction in glasses can be described in terms of localized Einstein oscillators that are heavily damped. We find that the heat conduction in this clathrate system is strongly influenced by localized modes (with mean free paths of the order of the lattice constant) that interact with, and damp the transmission of, heat through the acoustic modes. The existence of localized modes in this system is independent of the presence of the guest molecule in the cage, although enhanced by it. We propose that the source of the localized modes is dynamical disorder of the host lattice for unsolvated Dianin's compound, and dynamical disorder in both the host lattice and the guest molecules for the ethanol clathrate, and their resonant interaction with the heat-carrying acoustic modes is enhanced by the good energy match between the optic and acoustic modes due to the broad range over which the former exist in this system. If so, this "glasslike" thermal conduction should prevail in many complex molecular solids, and have wide-ranging implications in materials science.

ACKNOWLEDGMENTS

The authors thank Dr. J. Tse, Dr. Y. P. Handa, Dr. J. Ripmeester, and Professor M. Jericho for useful discussions, and Professor T. S. Cameron, Professor C. H. Warren, and Professor R. E. Wasylishen for assistance. This work was supported by the Natural Sciences and Engineering Research Council of Canada.

*Present address: Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6.

†Author to whom correspondence should be addressed.

[1]P. Debye, *Vortraege ueber die Kinetische Theorie der Materie und der Elektrizitaet* (Tuebner, Berlin, 1914), p. 17.

[2]A. Euken, Ann. Phys. **34**, 185 (1911).

[3]A. C. Anderson, in *Amorphous Solids Low-Temperature Properties,* edited by W. A. Phillips (Springer-Verlag, Berlin, 1981), p. 6.

[4]R. O. Pohl, Phase Trans. **5**, 239 (1985).

[5]J. J. Freeman and A. C. Anderson, Phys. Rev. B **34**, 5684 (1986).

[6]D. G. Cahill and R. O. Pohl, Phys. Rev. B **35**, 4067 (1987).

[7]A. Jagannathan, R. Orbach, and O. Entin-Wohlman, Phys. Rev. B **39**, 13 465 (1989).

[8]S. Alexander, O. Entin-Wohlman, and R. Orbach, in *Phonon Scattering V, Proceedings of the Fifth International Conference, Urbana, 1986,* edited by A. C. Anderson and J. P. Wolfe (Springer-Verlag, Berlin, 1987), p. 15.

[9]D. G. Cahill and R. O. Pohl, Solid State Commun. **70**, 927 (1989).

[10]W. N. Lawless, Phys. Rev. B **30**, 6555 (1984).

[11]P. W. Anderson, B. I. Halperin, and C. M. Varma, Philos. Mag. **25**, 1 (1972).

[12]J. J. Yoreo, M. Meissner, R. O. Pohl, J. M. Rowe, J. J. Rush, and S. Susman, Phys. Rev. Lett. **51**, 1050 (1983).

[13]M. N. Wybourne, B. J. Kiff, and D. N. Batchelder, Phys. Rev. Lett. **53**, 580 (1984).

[14]J. Maier and E. Signmund, J. Phys. (Paris) Colloq. **42**, C6-233 (1981).

[15]L. N. Yadon, C. I. Nicholls, and D. G. Haase, Phys. Rev. B **40**, 5215 (1989).

[16]R. D. Stoll and G. M. Bryan, J. Geophys. Res. **84**, 1629 (1979).

[17]R. G. Ross, P. Andersson, and G. Bäckström, Nature (London) **290**, 322 (1981).

[18]G. A. Slack, Phys. Rev. B **22**, 3065 (1980).

[19]M. A. White, J. Phys. (Paris) Colloq. **48**, C1-565 (1987).

[20]J. S. Tse and M. A. White, J. Phys. Chem. **92**, 5006 (1988).

[21]D. G. Cahill and R. O. Pohl, Annu. Rev. Phys. Chem. **39**, 93 (1988).

[22]R. G. Ross, J. Incl. Phenom. Molec. Recog. Chem. **8**, 227 (1990).

[23]W. Baker, A. J. Floyd, J. F. W. McOmie, G. Pope, A. S. Weaving, and J. H. Wilde, J. Chem. Soc. **1956**, 2010 (1956).

[24]J. L. Flippen, J. Karle, and I. L. Flippen, J. Am. Chem. Soc. **92**, 3749 (1970).

[25]M. A. White and M. Zakrzewski, J. Incl. Phenom. Molec. Recog. Chem. **8**, 215 (1990).

[26]L. Pang and E. A. C. Lucken, J. Incl. Phenom. **5**, 245 (1987).

[27]J. E. D. Davies, J. Incl. Phenom. **3**, 269 (1985).

[28]M. Zakrzewski, M. A. White, and W. Abriel, J. Phys. Chem. **94**, 2203 (1990).

[29]M. Zakrzewski, B. Mróz, H. Kiefte, M. A. White, and M. J. Clouter, J. Phys. Chem. **95**, 1783 (1991).

[30]T. S. Cameron, A. Linden, W. Abriel, M. Zakrzewski, and M. A. White (unpublished).

[31]F. Lee, E. Gabe, J. S. Tse, and J. A. Ripmeester, J. Am. Chem. Soc. **110**, 6014 (1988).

[32]M. Zakrzewski and M. A. White, J. Phys.: Condens. Matter **3**, 6703 (1991).

[33]P. W. Anderson, Phys. Rev. **109**, 1492 (1958).

[34]D. J. Thouless, in *Ill-Condensed Matter,* edited by R. Balian, R. Maynard, and G. Toulouse (North-Holland, Amsterdam, 1979).

[35]S. John, Phys. Today **44**(5), 32 (1991).

[36]S. John, H. Sompolinski, and M. J. Stephen, Phys. Rev. B **27**, 5592 (1983).

[37]B. B. Laird and H. R. Schober, Phys. Rev. Lett. **66**, 636 (1991).

[38]J. S. Tse, M. L. Klein, and I. R. McDonald, J. Phys. Chem. **87**, 4198 (1983).

[39]J. S. Tse, M. L. Klein, and I. R. McDonald, J. Chem. Phys. **78**, 2096 (1983).

[40]J. S. Tse, M. L. Klein, and I. R. McDonald, J. Chem. Phys. **81**, 6146 (1984).

[41]J. S. Tse (unpublished).

[42]G. A. Slack, in *Solid State Physics: Advances in Research and Applications,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1979), Vol. 34, p. 1.

[43]J. S. Tse, C. I. Ratcliffe, B. M. Powell, V. F. Sears, and Y. P. Handa (unpublished).

[44]J. A. Ripmeester, J. Incl. Phenom. **1**, 87 (1983).

[45]T. Bernhard, H. Zimmerman, and U. Haeberlen, J. Chem. Phys. **92**, 2178 (1990).

[46]J. Callaway, Phys. Rev. **113**, 1046 (1959).

[47]V. Narayanamurti and R. O. Pohl, Rev. Mod. Phys. **42**, 201 (1970).

[48]P. G. Klemens, in *Solid State Physics: Advances in Research and Applications,* edited by F. Seitz and D. Turnbull (Academic, New York, 1958), Vol. 7, p. 1.
[49]P. Carruthers, Rev. Mod. Phys. **33**, 92 (1961).
[50]H. B. G. Casmir, Physica **5**, 495 (1938).
[51]R. O. Pohl, Phys. Rev. Lett. **8**, 481 (1962).
[52]W. D. Seward and V. Narayanamurti, Phys. Rev. **148**, 463 (1966).
[53]C. T. Walker and R. O. Pohl, Phys. Rev. **131**, 1433 (1963).
[54]M. Wagner, Phys. Rev. **131**, 1443 (1963).
[55]D. F. R. Gilson, Ph.D. thesis, University of British Columbia, 1962.
[56]M. Brooker (private communication).