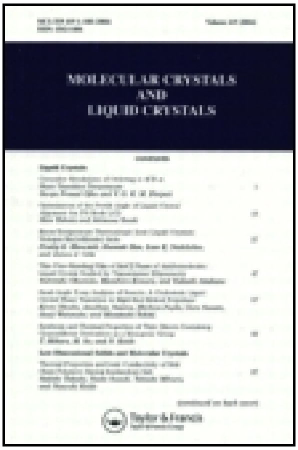

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Thermal Conductivity and Heat Capacity of Adamantane and Hexamethylenetetramine Under Pressure

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We have used the transient hot-wire technique to measure simultaneously the thermal conductivity and the heat capacity per unit volume of solid adamantane and hexamethylenetetramine. Data were obtained over the temperature range 115 K to 445 K, and at pressures up to 2.5 GPa. The thermal conductivity of plastic crystalline adamantane is much less temperature dependent than those of normal crystalline adamantane and hexamethylenetetramine. The volume dependence of the thermal conductivity of plastic crystalline adamantane is considerably smaller than those of the normal crystalline phases, and thus more similar to that of a liquid. The molar heat capacities for the different phases and substances were found to change very little with pressure. We discuss the temperature and volume dependences of the thermal properties in relation to available theoretical models.

INTRODUCTION

In previous reports[1–3] from our laboratory we have presented experimental results for the thermal conductivity, λ, and the heat capacity per unit volume, ρc_p, for several molecular substances showing plastic crystalline phases. In such phases the molecules are orientationally disordered. In fact, the term Orientational Disorder in Crystals (ODIC) is gradually replacing the older and somewhat confusing term plastic crystals. These phases are characterized by a low entropy of melting and a high degree of plasticity. On cooling the disordered phase (in some substances there are more than one such phase) transforms to a normal crystal phase. The thermal conductivity of a disordered phase shows[2] a behaviour similar to that of the corresponding liquid, i.e. a relatively low λ-value with a small temperature coefficient $(\partial \ln \lambda/\partial T)_p$. For the normal crystalline phase the λ-values are considerably higher than those for the disordered phase and the temperature coefficient is much higher, and corresponding to an approximate T^{-1} dependence in λ. The pressure dependence of λ for a disordered phase is similar to that of the compressed liquid.

The purpose of this paper is to compare thermal conductivity and heat capacity for plastic and normal crystal phases and as a suitable substance we have chosen adamantane, $C_{10}H_{16}$, which is somewhat of a key example of a plastic molecular crystal. For comparison we also present experimental thermal conductivity and heat capacity results for hexamethylenetetramine (HMT), $C_6H_{12}N_4$. The two substances have same molecular symmetry, and roughly the same melting temperatures (~540 K). However intermolecular hydrogen bondings in HMT causes the crystal structures to be different. At low temperatures adamantane is tetragonal[4] with $a = 0.660$ nm and $c = 0.881$ nm and two molecules per unit cell. The space group is $P\bar{4}2_1c$.

On heating it undergoes a first order transition to a highly plastic phase in which the molecules are dynamically, orientationally disordered. The transition,[5] which at zero pressure occurs at 208.6 K, is accompanied with a high entropy change and a change of mass density from 1.15 g cm^{-3} to 1.12 g cm^{-3}. The disordered phase is face centered cubic[4] with $a = 0.945$ nm and four molecules per unit cell. The space group is Fm3m.

HMT is body-centered cubic[6] with $a = 0.702$ nm and two molecules per unit cell. The space group is $I\bar{4}3m$. No orientationally disordered phase is observed.

The high-pressure phase diagrams for the two substances are known.[7,8]

EXPERIMENTAL

The transient hot-wire technique was used to measure simultaneously both the thermal conductivity, λ, and the heat capacity per unit volume, ρc_p, where ρ is the mass density. As the details are given elsewhere[9,10] we only describe the method briefly: a nickel wire, immersed or enclosed in the specimen, is heated by a constant power. During the heat pulse (duration ~1 s) the temperature-time response of the wire is measured by making use of the wire as a resistance thermometer. From these data the conductivity and heat capacity of the surrounding medium are determined using an automatic analysis procedure. For measuring the temperature of the sample just before the heat pulse a chromel-alumel thermocouple is used. The experiments were carried out in a piston-cylinder apparatus. The vessel could be heated by means of an electrical heater or cooled by liquid nitrogen.

Details of the high pressure arrangements are described elsewhere.[11] The specimen was mounted in the cell in the form of plates placed above and below the plane containing the hot wire probe and the thermocouple junction. These plates were made by compacting powder at a pressure of 0.3 GPa. The purity of the admantane was 99 % (supplied by Ega-Chemie, Steinheim/Albuch, West Germany) and of the HMT 99.5 % (supplied by Merck, Darmstadt, West Germany). Before an actual run the pressure was increased to 0.3 GPa at 300 K to ensure good thermal contact.

The accuracy of our measurements is 2 % in λ and about 10 % in ρc_p.

RESULTS

Phase diagrams

The phase diagrams of adamantane and HMT are shown in Figure 1. The I → II transition in admantane was easily detected both on cooling and heating at constant load, and on pressure increase or decrease at constant temperature by a discontinuity in λ (Figures 2 and 3). Thermocouple response due to latent heat was also observed. The transition was determined to occur

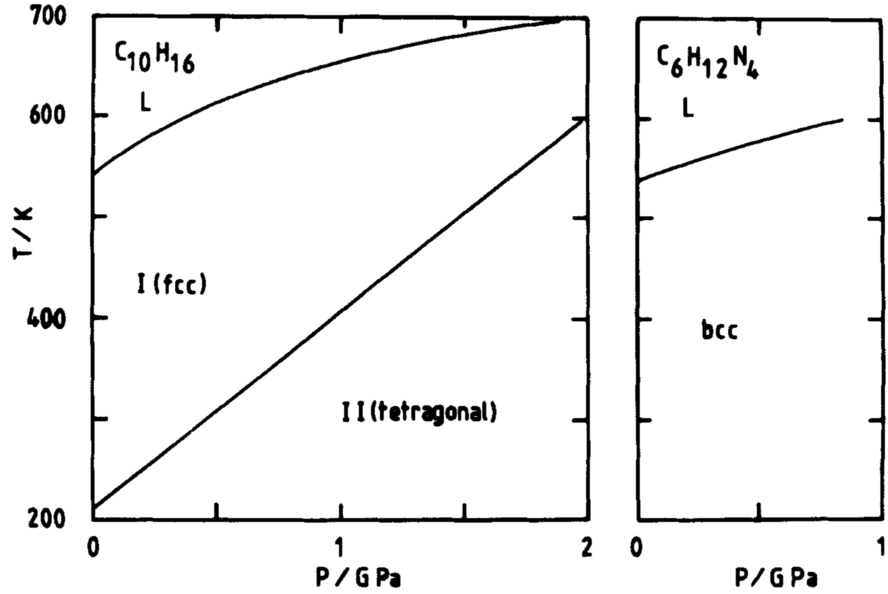

FIGURE 1 Phase diagrams[7,8] of adamantane, $C_{10}H_{16}$, and hexamethylenetetramine, $C_6H_{12}N_4$.

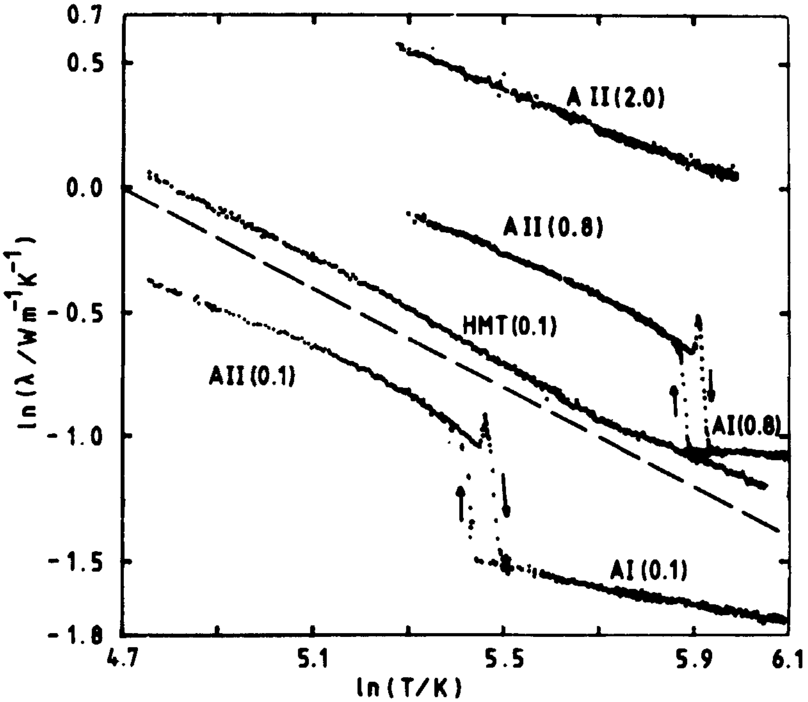

FIGURE 2 Thermal conductivity, λ, versus temperature for adamantane (A) and hexamethylenetetramine (HMT). The pressure in GPa is given in parentheses. The broken line represents $\lambda \propto T^{-1}$.

at the following P-T-coordinates: 0.11 GPa and 228 K, 0.78 GPa and 358 K, obtained from cooling; 0.43 GPa and 291 K, 1.07 GPa and 401 K, obtained from pressurization. These results are in reasonable agreement with previous work.[8,12]

Thermal conductivity

The thermal conductivity of adamantane and HMT along isobars is shown in Figure 2. The results were obtained for both cooling and heating. There is a pronounced hysteresis at the I → II transition in adamantane, which is characteristic of a first-order transition. Our measurements are performed at constant press load, and care must be taken to avoid change of pressure, especially at the transition. When the specimen is cooled through the transition the volume decreases by about 3 %, but friction between the piston and the cylinder might prevent the piston from moving along. Thus, there will be

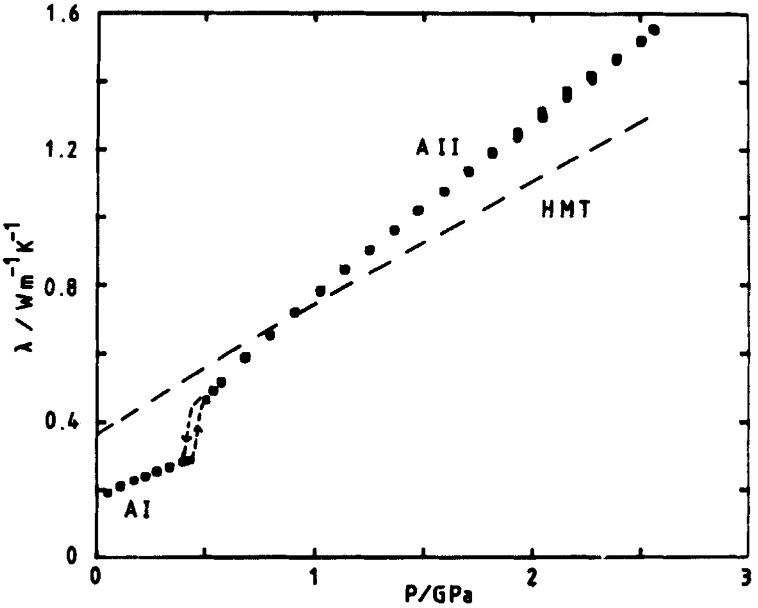

FIGURE 3 Thermal conductivity, λ, versus pressure at 298 K for adamantane (A) and hexamethylenetetramine (HMT). For clarity the data points for HMT are represented by their least squares fit.

a slight decrease in pressure, and this will result in low λ-values in phase II on cooling. Similarly, on heating there will be a pressure increase at the transition, and this will result in slightly high λ-values in phase I. By cycling the press load around the actual value and thereby releasing the piston, these shifts in the λ-values can be made negligible. When the temperature was cycled within a given phase, as in the cases of adamantane at 2.0 GPa and HMT at 0.1 GPa, no hysteresis was observed. This indicates that the change in pressure due to thermal expansion of the specimen is small.

The peak in λ, clearly observed at the transition on heating, is because the sample starts to transform around the wire in the course of the heat-pulse ($\sim$5 K). The resulting reduction in temperature increase gives an apparent increase in conductivity. The "false" peak in λ also results through the iteration procedure in a dip in ρc_p (Figure 4). Similarly, the peak in ρc_p obtained on cooling can be explained in terms of the two-system character of the medium at temperatures near the transition. True values of λ and ρc_p are not observed in this region.

The thermal conductivities versus pressure are shown in Figure 3. The conductivity data have been fitted to equations and the results are given in

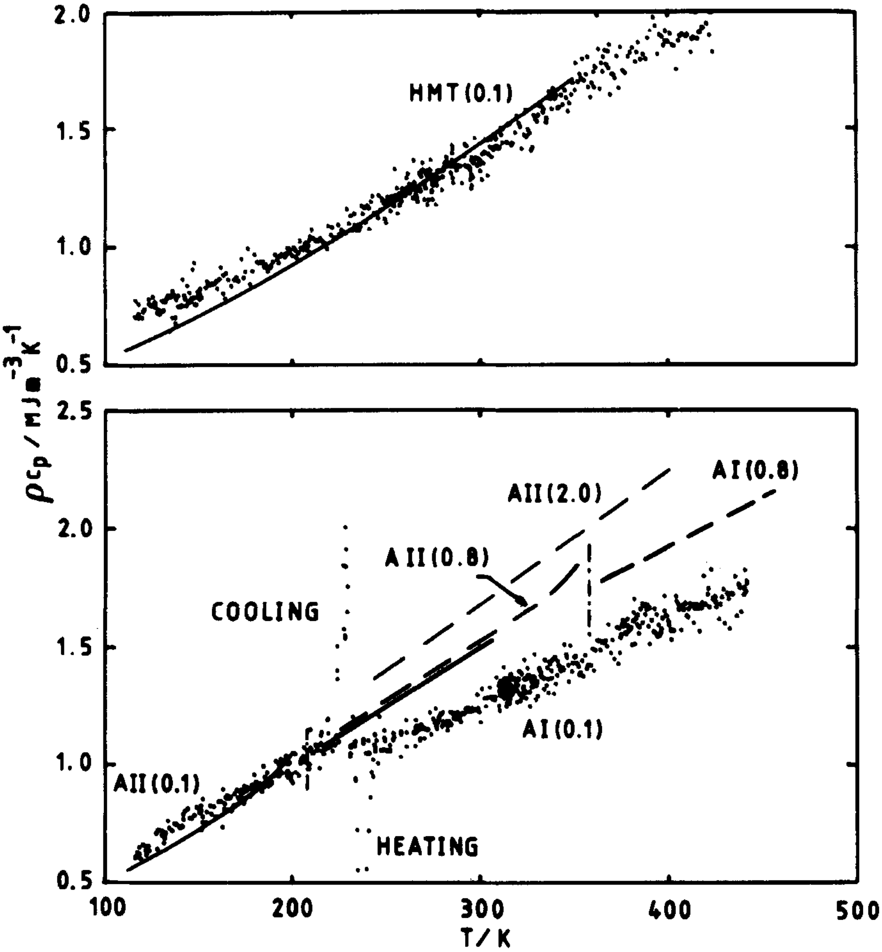

FIGURE 4 Heat capacity per unit volume, ρc_p, versus temperature for adamantane (A) and hexamethylenetetramine (HMT). The pressure in GPa is given in parentheses. For clarity, only the data points obtained at 0.1 GPa are shown. The solid lines refer to values calculated from previous measurements[5,13] at zero pressure. The broken lines are least squares fits to the data points obtained at 0.8 GPa and 2.0 GPa.

TABLE I

Isobaric temperature dependence of thermal conductivity λ fitted to equations of form $\ln(\lambda/W\,m^{-1}\,K^{-1}) = A + B\ln(T/K) + C(\ln(T/K))^2$

Substance and phase	A	B	C	P/GPa	T/K
Adamantane I	0.56	-0.378	—	0.1	240-445
	-0.59	-0.080	—	0.8	365-445
Adamantane II	-12.95	5.774	-0.6592	0.1	115-230
	-2.75	1.826	-0.2497	0.8	200-355
	4.51	-0.746	—	2.0	195-400
Hexamethylenetetramine	7.83	-2.121	0.1037	0.1	125-425

TABLE II

Isothermal pressure dependence of thermal conductivity λ fitted to equations of form $(\lambda/W\,m^{-1}\,K^{-1}) = A + B(P/\mathrm{GPa}) + C(P/\mathrm{GPa})^2$

Substances and phases	A	B	C	T/K	P/GPa
Adamantane I	0.181	0.253	—	298	0 -0.42
	0.160	0.225	—	400	0 -1.0
Adamantane II	0.167	0.642	-0.040	298	0.48-2.5
	-0.090	0.718	-0.079	400	1.1 -2.1
Hexamethylenetetramine	0.358	0.390	-0.007	298	0 -2.5

Tables I and II. As far as we know, there is no previous work to compare with.

Heat capacity

Our results for ρc_p along isobars are shown in Figure 4. We can compare our results with previous work by using heat capacity measurements[5] of adamantane and HMT at zero pressure. We use smoothed value for the thermal expansitivities[13] and assume densities[14] of 1.08 g cm^{-3} and 1.34 g cm^{-3} at 293 K for adamantane and HMT, respectively. Values of ρc_p, which are calculated in this way, are shown by the solid lines in Figure 4. Ignoring the difference between zero pressure and 0.1 GPa, which is justifiable in view of the small pressure dependence of ρc_p, agreement is reasonably good, except for adamantane I, where our ρc_p-values are about 15% lower than the calculated ones.

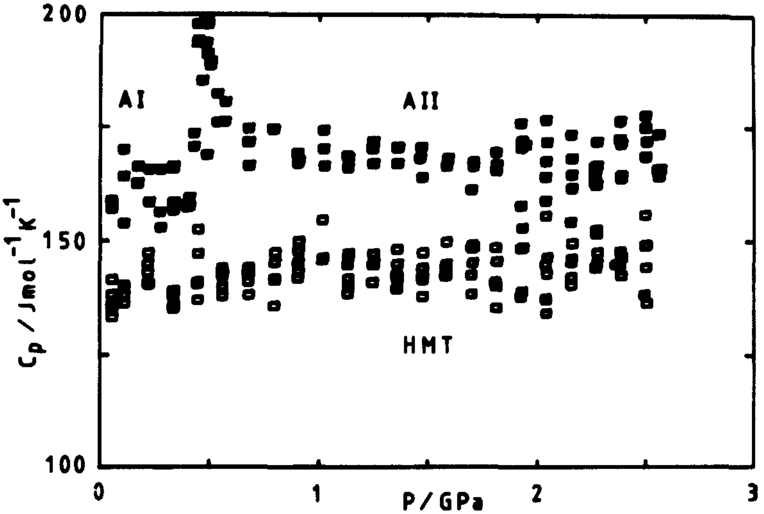

FIGURE 5 Molar heat capacity, C_p, versus pressure at 298 K for adamantane (A) and hexamethylenetetramine (HMT). True values of C_p are not observed at the I → II transition region.

The pressure dependence of the molar heat capacity, C_p, at 298 K was calculated from our measured values of ρc_p, by making use of known compressibility data[8,12,15] (Figure 5).

DISCUSSION

Heat capacity

It can be seen from Figure 5 that C_p of phase I of adamantane is about 10% lower than that of phase II, and that the variation of the molar heat capacities over the pressure range used is within 5% for both adamantane II and HMT.

In principle, we can predict the initial slope of $C_p(P)$ from the identity

$$\left(\frac{\partial C_p}{\partial P}\right)_T = -TV\left(\alpha^2 + \left(\frac{\partial \alpha}{\partial T}\right)_P\right)$$

where V is the molar volume and α is the thermal expansitivity. However, available data for α differ considerably. Mirskaya[13] gives $\alpha = 4.4 \cdot 10^{-4}$ K^{-1} for adamantane I, $\alpha = 0.7 \cdot 10^{-5}$ for adamantane II and $\alpha = 1.8 \cdot 10^{-4}$ K^{-1} for HMT above 170 K. Breitling *et al.*[16] report $\alpha = 4.7 \cdot 10^{-4}$ K^{-1} for adamantane at about room-temperature. Becka and Cruickshank[6] give $\alpha = 0.66 \cdot 10^{-4}$ K^{-1} for HMT at $100 < T < 298$. Furthermore, data for $(\partial\alpha/\partial T)_p$ are not available with any reasonable accuracy. The only judgement one can make is that $(\partial\alpha/\partial T)_p > 0$, so one can conclude $(\partial C_p/\partial P)_T < 0$.

Temperature dependence of thermal conductivity

For a perfect crystal at constant volume the theoretical prediction is $\lambda \propto T^{-n}$, where n equals 1, due to three-phonon interactions. A good approximation to this behaviour is found for HMT below 300 K (Figure 2 and Table I). For the normal crystal phase of adamantane a slightly smaller temperature dependence is found, with the exponent $n \simeq 0.8$. The disordered phase of adamantane, however, shows a much smaller value of λ than the normal crystal phase and also a considerably smaller temperature dependence, with $n \simeq 0.1$–0.4. This is in agreement with previous work[1–3] on plastic crystals, and might be understood qualitatively on the basis of the Debye formula

$$\lambda = \tfrac{1}{3}cul \tag{1}$$

where c is the heat capacity per unit volume, u is the average phonon velocity and l is the phonon mean free path. None of the quantities on the right-hand side of Eq. (1) should depend strongly on T. The mean free path should be limited to a small value due to scattering of phonons by structural disorder. The elastic constants have been measured for both adamantane I[17] and HMT.[18] Using the formula $u = (1/\kappa\rho)^{1/2}$, where κ is the adiabatic compressibility, averaged sound velocities can be calculated. At 298 K we find $u = 1{,}940$ m/s and $u = 2{,}500$ m/s for adamantane I and HMT, respectively. A low value of the sound velocity seems to be characteristic[19] for plastic crystals. Using these values and measured values of ρc_p and λ a rough estimate of the phonon mean free path can be made from Eq. (1). The results are $l \simeq 0.19$ nm and $l \simeq 0.29$ nm for adamantane I and HMT, respectively, These values can be compared with the cube root of the volume per molecule, which for both substances is about 0.6 nm.

The temperature dependence of λ can also be discussed by considering the thermal resistivity, λ^{-1}, which is shown in Figure 6. Suppose we write

$$\lambda^{-1} = A + BT$$

where A and B are constants. We associate the term A with disorder scattering, and the coefficient B with three-phonon interactions. For adamantane II and HMT, λ^{-1} is approximately proportional to T, and three-phonon scattering is thus the dominant resistivity process. For adamantane I, however, the term A is of considerable size. This corresponds to increased disorder scattering in the plastic crystal phase.

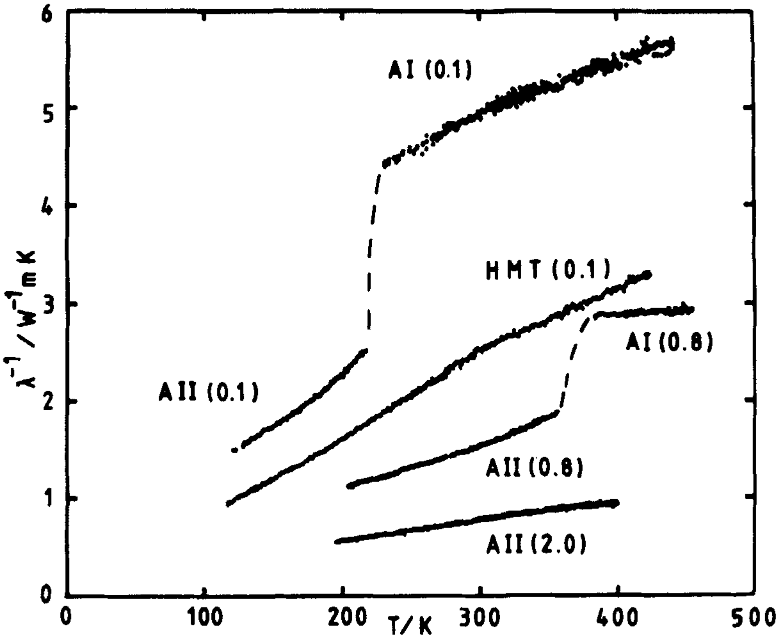

FIGURE 6 Thermal resistivity, λ^{-1}, versus temperature for adamantane (A) and hexamethylenetetramine (HMT). The pressure in GPa is given in parentheses.

Effects of density and crystal structure on the thermal conductivity

Figure 3 shows that λ increases with pressure in a given phase region, and at the I → II transition in adamantane. This reflects the general feature that λ increases with decreasing volume, although there are exceptions.[20,21]

Adamantane II shows a stronger pressure dependence than HMT. This reflects mainly the fact that adamantane II is more compressible than HMT. With the use of compressibility data we can plot ln λ as a function of ln V. Straight lines can be fitted to the obtained data points with reasonable accuracy, and we find the relative volume coefficient, $-(\partial \ln \lambda / \partial \ln V)_T$, equal to 6.4, 9.8 and 8.9 for adamantane I, adamantane II and HMT, respectively. Those values should be compared with those for liquids, which typically are[22] between 3 and 4. We can thus conclude that the value of the volume dependence for the disordered phase lies between that of the normal crystalline phase and that of a liquid.

A comparison between the absolute values of λ for the two substances can be made in several ways. One way is to compare the λ-values under isothermal-isobaric conditions. For $T = 298$ K and $P = 1$ atm we find λ (adamantane I) $= 0.18\ W\text{m}^{-1}\ \text{K}^{-1}$ and λ (HMT) $= 0.36 W\text{m}^{-1}\ \text{K}^{-1}$. This difference is, at least, partly due to difference in densities and the fact that adamantane I, is plastic crystalline, and HMT is not. For $T = 298$ K and $P = 2.5$ GPa we get λ (adamantane II) = $1.52 W\mathrm{m}^{-1}\,\mathrm{K}^{-1}$ and λ (HMT) = $1.29 W\mathrm{m}^{-1}\,\mathrm{K}^{-1}$, while the densities are $1.34\,\mathrm{g\,cm}^{-3}$ and $1.55\,\mathrm{g\,cm}^{-3}$, respectively. This must be understood in terms of the different crystal structures for the two substances.

Another way is to compare the λ-values under isothermal-isochoric conditions, say at a common density of $1.34\,\mathrm{g\,cm}^{-3}$ at 298 K. The results for λ in $W\mathrm{m}^{-1}\,\mathrm{K}^{-1}$ are 1.52 (at 2.5 GPa) and 0.36 (at 1 atm) for adamantane II and HMT, respectively. This confirms that the difference in crystal (and molecular) structure strongly affects the λ-values.

Acknowledgement

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