

## **Phase Behavior and Thermal Conductivity of Urea at Pressures up to 1 GPa and at Temperatures in the Range 50–370 K**

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*Received December 14, 1993*

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The thermal conductivity of the solid phases I and III of urea was measured at temperatures in the range 50–370 K for pressures up to 1 GPa. Phase III, previously detected only at pressures above 0.5 GPa, was observed here at low pressures ( $<0.07$  GPa) below about 230 K. Extrapolation of the I–III phase line indicates that phase III might be obtained at 218 K at atmospheric pressure and, consequently, that urea might exhibit two solid phases at atmospheric pressure. The temperature dependence of the thermal conductivity of both phase I and phase III could be described by the Debye model for thermal conductivity assuming phonon scattering by three phonon umklapp processes only. Despite a volume decrease at the I  $\rightarrow$  III transition, the thermal conductivity decreased by about 20%. Normally, thermal conductivity increases at a phase transition at which volume decreases. This rather unusual behavior of urea might be due to an increase in the nearest-neighbor distance at the I  $\rightarrow$  III transition.

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**KEY WORDS:** high pressure; phase behavior; thermal conductivity; urea.

### **1. INTRODUCTION**

As emphasized in an earlier investigation [1], urea  $(\text{NH}_2)_2\text{CO}$  is an important substance since it is used as a model for more complicated compounds and, in addition, it exhibits nonlinear optical properties. The physical properties of urea, at atmospheric pressure, have been studied extensively. The investigations have concerned, for example, the lattice structure [2, 3]; dynamics of molecules [4, 5], and thermal properties [1, 6]. Urea crystallizes in a tetragonal lattice,  $P\bar{4}2_1m$ , with two molecules per unit cell [2].

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In one of the investigations at atmospheric pressure, a phase transition was reported [3]. Lebioda et al. [3] performed X-ray diffraction measurements down to about 100 K and, at about 190 K, observed an anomaly in their data for the *c*-axis lattice parameter. They interpreted this anomaly as being due to a phase transition. However, Yoshihara and Bernstein [5] found no evidence for a transition using Brillouin and Rayleigh scattering techniques, and this is generally true for other investigations of urea at atmospheric pressure [1, 2, 4–6]. The question of a further solid phase of urea at atmospheric pressure is specifically addressed in the present work.

Very few investigations of urea have concerned the properties at high pressures. Bridgman [7, 8] used measurements of volume to determine the pressure–temperature phase diagram above 273 K. He found three solid phases at pressures below 1 GPa (Fig. 1). Extrapolation of the phase line between phase I and phase III shows that it would intersect atmospheric pressure at about 90 K. It follows that phase III might be stable also at atmospheric pressure. The only other investigation of urea at high pressure appears to be that of Hamann and Linton [9]. They recorded infrared spectra at room temperature and verified the existence of phase III.

The main aim of the present paper was to extend the phase diagram of urea down to low temperatures and, in particular, to study the phase

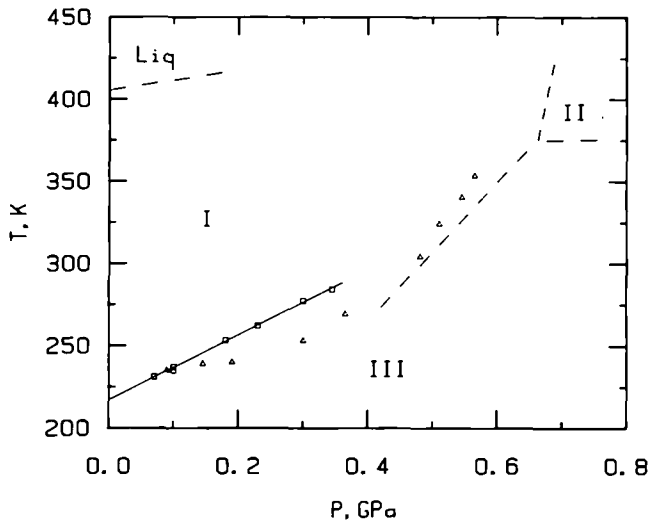


Fig. 1. Phase diagram of urea: (□) carefully purified sample; (△) commercially pure sample; (---) according to Bridgman [7]; (—) linear least-squares fit to the transition coordinates of the carefully purified sample.

line between phase I and phase III. This was done by means of thermal conductivity measurements. The thermal conductivity is, in general, very sensitive to changes in crystal structure and molecular motions [10]. Consequently, phase transitions are easily detected in data for thermal conductivity. In addition to the phase diagram, we can of course study the heat transport properties of urea. No data for the thermal conductivity of urea exist in the literature.

## 2. EXPERIMENTS

We used the transient hot-wire method to measure simultaneously both the thermal conductivity  $\lambda$  and the heat capacity per unit volume  $\rho c_p$ , where  $c_p$  is the isobaric specific heat capacity and  $\rho$  is the mass density. The hot-wire method we used has been described previously [11]. An outline of the method is that the hot-wire probe was a Ni wire (0.1-mm diameter) placed horizontally in a ring of constant radius within a Teflon cell. The hot-wire probe, surrounded by the medium under investigation (polycrystalline urea), was heated by a (1-s) pulse of almost-constant power and the wire resistance was measured versus time, which 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  $\lambda$  and  $\rho c_p$ . For temperatures above 100 K, the inaccuracy was estimated as  $\pm 2\%$  in  $\lambda$  and  $\pm 5\%$  in  $\rho c_p$  [11]. Due to the decreased sensitivity of the hot-wire (smaller derivative of resistance with respect to temperature), the inaccuracy in  $\lambda$  increased with decreasing temperature and was  $\pm 4\%$  at 40 K. (We have not estimated the inaccuracy in  $\rho c_p$  for temperatures below 100 K.) The standard deviation in the measurements was an order of magnitude smaller than the inaccuracy.

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 measured using an internal Chromel-versus-Alumel thermocouple which had been calibrated against a commercially available silicon diode. This calibration was performed inside a helium dewar with a Chromel-versus-Alumel thermocouple and the diode mounted together in a copper block. The copper block was heated at rate of about 3 K/h as the liquid helium was slowly boiling off. Using the thermocouple calibrated by this procedure, the estimated inaccuracy in temperature was less than 0.5 K. 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 inaccuracy in pressure was estimated as  $\pm 40$  MPa at 1 GPa. For measurements below room tem-

perature, the vessel was cooled with a refrigerator using a closed helium gas cycle. The apparatus has been described in detail elsewhere [12].

Two samples of urea with different degrees of purity were studied. One sample was taken from the same batch as that used in a previous investigation of the heat capacity of urea [1]. The starting material, Fluka BioChemika Microselect, >99.5%, was recrystallized four times from acetate (Fluka; >99.5%; H<sub>2</sub>O, <0.005%). The purity was better than 99.92% as determined by differential scanning calorimetry (Perkin-Elmer, DSC-II). Another sample, supplied by Merck AG ( $\geq 99.5\%$ ), was used without further purification.

### 3. RESULTS AND DISCUSSION

#### 3.1. Phase Diagram and Phase Behavior

Figure 1 shows the phase diagram of urea. During pressurization at room temperature, the I  $\rightarrow$  III transition was detected as a decrease in the data for thermal conductivity  $\lambda$ , shown in Fig. 2. Moreover, these data for  $\lambda$  (Fig. 2) exhibit weak evidence for another transition, at about 0.15 GPa, shown as a discontinuity in the pressure derivative of  $\lambda$ . A transition at 0.15 GPa was not reported by either Bridgman [7, 8] or Hamann and Linton [9]. Since the evidence for a transition at this pressure is weak

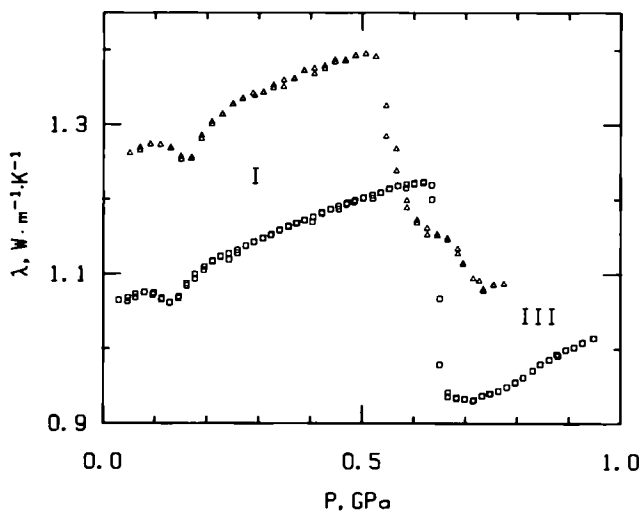


Fig. 2. Thermal conductivity as a function of pressure: (□) at 295 K; (△) at 252 K.

(Fig. 2), further investigations are necessary to establish a possible new solid phase of urea. Measurements of the equation of state of urea in our laboratory [13] do not, however, corroborate the existence of such a phase transition.

It is common experience that solid phases can be superpressed and/or supercooled. To avoid such effects, we determined the phase lines here by heating at constant pressure. Since superheating of phases is rather uncommon, this can be a better way to establish phase diagrams than using isothermal pressurisation. The I  $\rightarrow$  III transition proved to be fairly sluggish, especially when the temperature was reduced. As shown in Fig. 2, the transition occurred over a substantial pressure range at 255 K. Furthermore, the difference between the transition coordinates at increasing and those at decreasing pressure (isothermal runs) was larger at lower temperatures than that at room temperature (not shown). Our procedure to determine the I-III phase line was first to form phase III by pressurization at room temperature. The sample was thereafter cooled to low temperatures,  $\sim 150$  K, at which temperature the pressure was decreased. Subsequently, the sample was heated ( $\sim 0.3$  K  $\text{min}^{-1}$ ) to room temperature (Fig. 3). The coordinates for the III  $\rightarrow$  I transition obtained by this procedure are shown in Fig. 1. Isothermal runs at decreasing pressure produced the III  $\rightarrow$  I transition at coordinates which are in good agreement with those obtained in the isobaric heating runs. The discrepancy between the coor-

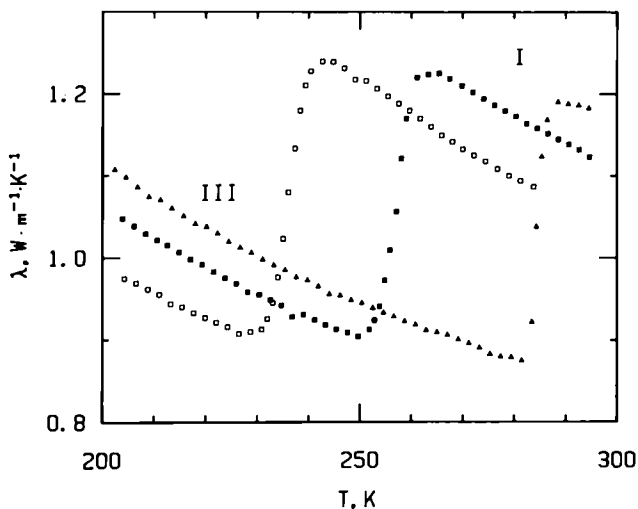


Fig. 3. Thermal conductivity as a function of temperature: (□) at 0.07 GPa; (■) at 0.18 GPa; (▲) at 0.35 GPa.

dinates for the I–III phase line of Bridgman (Fig. 1, [7]) and those of the present investigation may be due to different ways in determining the line or to different degrees of purity of the samples. As just described, we used isobaric heating runs, whereas Bridgman [7] probably used isothermal pressurisation.

Several attempts were made to obtain the I → III transition at decreasing temperatures (isobaric runs). However, phase III could be formed only by way of isothermal pressurisation. This was tested in the temperature range 250–350 K and the I → III transition occurred between 0.5 and 0.65 GPa in the whole temperature range (Fig. 2). These results (Fig. 2) show that phase III must, at least, be stable above 0.6 GPa at room temperature. However, an isobaric run (300–370 K) at 0.6 GPa did not produce the I → III transition (on cooling).

It is perhaps not unreasonable to expect some difference between superpressing and supercooling in connection with phase transition kinetics. Assume the coordinates for phase equilibrium to be  $P_0$  and  $T_0$  and consider the situation where a difference in Gibbs free energy  $\Delta G$  exists between metastable and stable phases. This difference  $\Delta G$  provides the driving force for the transition and can arise from either superpressing or supercooling. In the former case, suppose that the coordinates (where the difference  $\Delta G$  exists) are  $P = P' (> P_0, \text{i.e., superpressing})$  and  $T = T_0$ , and in the latter case  $P = P_0$  and  $T = T' (< T_0, \text{i.e., supercooling})$ . If the phase transition is regarded as a thermally activated process, then it is clear that there is less thermal energy, and therefore probably slower kinetics, in the supercooled compared with the superpressed condition.

On the other hand, nonthermodynamic considerations could also have an important effect. For example, a small amount of shear deformation might be of importance in helping to induce the transition. Under the conditions of our experiment, such deformation is more likely to arise during change of pressure than during change of temperature.

Figure 1 shows our results for the I–III transition obtained using both “pure” (99.92%) and “impure” (99.5%) specimens. There is evidently some difference between these two sets of results. It can be seen from Fig. 1 that the transition temperature, at a given pressure, can differ by as much as 20 K between pure and impure specimens. We find it surprising that an impurity content of only about 0.5% should have such a large effect on transition temperature. Our previous experience [14] indicates that such an impurity content can cause a change in transition temperature of not more than a few kelvins. It can also be seen from Fig. 1 that when we refer to data for the impure specimen, we find  $d^2T/d^2P > 0$  along the phase line. Inspection of any compilation of  $P$ – $T$  phase diagrams will show that phase boundaries are most often represented well by straight lines, and if there is

curvature, then it is usually with  $d^2T/d^2P < 0$ . Here, we find a straight-line phase boundary for the pure specimen and an unusual curvature for the impure specimen. On the basis of all these observations, we must draw the general conclusion that the I-III phase boundary in urea is unusually sensitive to impurity content, although the details are obscure. Our best estimate for the equilibrium phase boundary must therefore be based entirely on our data for the pure specimen. (Unfortunately, the sample cell with the carefully purified urea broke before the I-III phase line above 0.5 GPa had been established.)

Quite a few phases have remained undiscovered for many years due to sluggish transition kinetics. In particular, not until recently was it shown that ordinary ice (Ih) exhibits a transition at about 72 K at atmospheric pressure [15]. In the case of ice, as well as for other substances, the introduction of a dopand has increased transition rates by several orders of magnitude, leading to the discovery of many new phases [16]. It is quite possible that doping of urea with a suitable substance might serve the same purpose and, consequently, reveal a I  $\rightarrow$  III transition at about 218 K at atmospheric pressure. In fact, we have observed in the present work that impurities present in commercially purified urea affected the phase behavior in an unusual way, indicating that the transition behavior may be influenced by impurities.

### 3.2. Thermal Conductivity

As shown in Fig. 2,  $\lambda$  decreases at the I  $\rightarrow$  III transition. Using thermodynamics, it can be shown that the volume must decrease during isothermal transitions at increasing pressures. This has also been shown experimentally for the I  $\rightarrow$  III transition [7, 13]. The decrease in  $\lambda$  at the transition is therefore unusual since  $\lambda$  normally increases when the volume decreases. However, such behavior has been found previously in alkali and silver halides and ammonium fluoride, as well as in ice [17] but, as far as we know, not in an organic crystal. Using a theoretical model, Roufosse and Jeanloz [18] have shown that the transition from NaCl (B1) to CsCl (B2) structure in alkali halides, which occurs at increasing pressure, can result in a decrease in  $\lambda$ . Their model shows that the decrease in  $\lambda$  in the alkali halides was closely connected to an increase in the nearest-neighbor distances. Consequently, if the nearest-neighbor distances increase at the I  $\rightarrow$  III transition of urea, then their model can probably also account for the observed decrease in  $\lambda$  at this transition in urea.

The type of transition that leads to the unusual decrease in  $\lambda$  has, in some cases, turned out to be very sluggish. For example, the I  $\rightarrow$  II transition in KBr was found to be very sluggish [17]. Analogously, the

corresponding transition in urea might also be expected to be sluggish, especially since urea has a rather large molecule. As discussed above, the amount of thermal energy and/or shear stresses may be critical for the molecules to rearrange. Consequently, high temperatures and/or shear stresses may enhance the transition.

The data for  $\lambda(T)$  of phases I and III are shown in Fig. 4. The data can be compared with those expected for  $\lambda$  from theory. The commonly employed Debye formula for  $\lambda(T)$  is given by [19]

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

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. This model is derived for a monatomic substance, but if the molecules of urea can be regarded as rigid, it should be able to describe  $\lambda(T)$ . That is, the model should work in the case when intramolecular vibrations do not influence the heat transport properties to a great extent.

The relaxation time involves, in general, many different terms to account for structural scattering such as that from point defects, grain boundaries, and dislocations. However, in the present instance, only

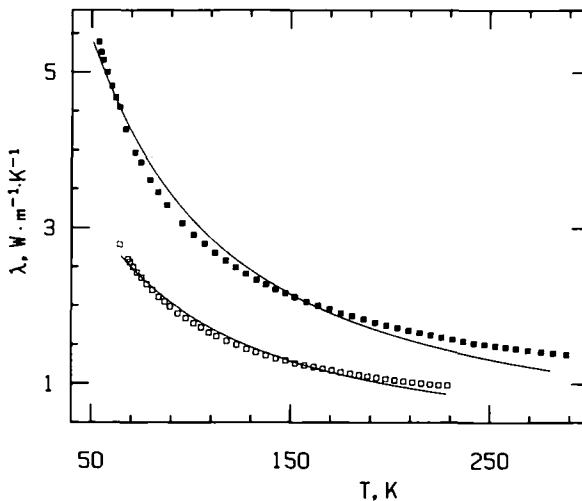


Fig. 4. Thermal conductivity as a function of temperature under isochoric conditions: (■) supercooled phase I at a pressure of 0.28 GPa; (□) phase III at a pressure of 0.07 GPa. The solid lines are theoretical fits of Eq. (1).



scattering from three-phonon processes was considered in the model. The relaxation time for three-phonon umklapp processes at temperatures of the order of the Debye temperature and above is [20, 21]

$$\tau(\omega) = (A\omega^2 T)^{-1} \quad (2)$$

where  $A$  is the scattering strength.

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

$$\left(\frac{\partial \ln \lambda}{\partial T}\right)_p - \left(\frac{\partial \ln \lambda}{\partial T}\right)_\rho = -g \times \alpha \quad (3)$$

where  $g = (\partial \ln \lambda / \partial \ln \rho)_T$  is the Bridgman parameter and  $\alpha$  is the volumetric thermal expansivity. Using data for  $\lambda(P)$  (Fig. 2) together with the bulk modulus at room temperature [13], we determined  $g$  to be 4.2 for phase I and 3.2 for phase III. These values of  $g$  were assumed to be independent of temperature. To calculate the thermal expansivity, a polynomial function was fitted to data for the volume of the unit cell [2]. Using the fitted function,  $\alpha = 1.3 \times 10^{-4} \text{ K}^{-1}$  for phase I was calculated at 150 K and the same value was used for phase III. The isochoric data for  $\lambda$ , calculated from the measured isobaric data using Eq. (3), are shown in Fig. 4. The differences between the measured isobaric data and the calculated isochoric data are less than 15 and 7% for phases I and III, respectively.

The solid lines in Fig. 4 show the best fits of Eq. (1) using the relaxation time given by Eq. (2). In the fitting procedure, the Debye temperature and the scattering strength were used as adjustable parameters. We used an approximate value for the phonon velocity  $v$  for phase I of  $2400 \text{ m s}^{-1}$  [1], which was calculated using data for the elastic constants [22] and assumed independent of temperature. The same value of  $v$  was assumed for phase III. A typical fit of Eq. (1) to the isochoric  $\lambda(T)$  of phase I yielded  $\theta_D = 139 \text{ K}$ . This value agrees well with  $\theta_D = 135 \text{ K}$ , which was calculated using data for heat capacity [1]. (However, the agreement of values for  $\theta_D$  depends on the temperature range selected for the fit.) The fairly good description by the fitted curves (Fig. 4) as well as the reasonable value for  $\theta_D$  supports the model for  $\lambda(T)$  of urea which has been described. It probably follows that the phonons are scattered mainly in three-phonon umklapp processes and that other scattering processes are insignificant for the thermal resistivity of urea. Therefore, we do not need to consider other types of scattering processes in the model. However, in some other substances which are similar to urea it has been found that additional scattering

processes arising from structural disorder have been required to fit the Debye model [14].

The value for  $A$  of phase I obtained in the fitting procedure can be compared to one calculated using an equation derived for a simple cubic lattice by Roufosse and Klemens [21],

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

where  $a$  is the lattice parameter,  $\gamma$  is the Gruneisen parameter, and  $M$  is the mass of a unit cell. In this case, we have associated  $a^3$  with the volume per molecule ( $\cong 73.5 \text{ \AA}^3$  [2]) and  $M$  with the molecular mass ( $9.97 \times 10^{-26} \text{ kg}$ ). To calculate  $A$  from Eq. (4), we used the thermodynamic Gruneisen parameter  $\gamma_{\text{th}} = \alpha B / (c_p \rho)$  to approximate  $\gamma$  and assumed  $\gamma_{\text{th}}$  independent of temperature ( $B$  is the bulk modulus). Using data for phase I at room temperature of  $\alpha = 2.7 \times 10^{-4} \text{ K}^{-1}$  [2] (from the fitted polynomial function; see above),  $B = 10.8 \text{ GPa}$  [13],  $c_p = 1540 \text{ J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$  [1], and  $\rho = 1300 \text{ kg m}^{-3}$ , we obtained  $\gamma_{\text{th}} = 1.4$ . The corresponding calculated value of  $A$  by Eq. (4) was, in the worst case, four times larger than the fitted one, probably due partly to the uncertainty in the Gruneisen parameter and the sound velocity. A similar overestimate by a factor of

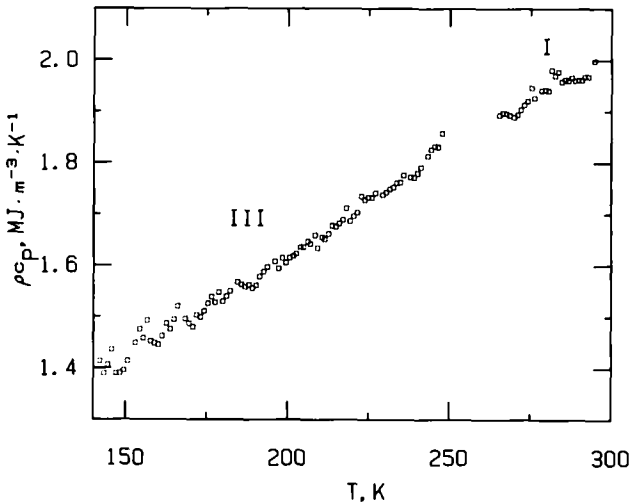


Fig. 5. Heat capacity per unit volume as a function of temperature at a pressure of 0.18 GPa. Data at the transition have been removed since the hot-wire method yields erroneous results at the transition.

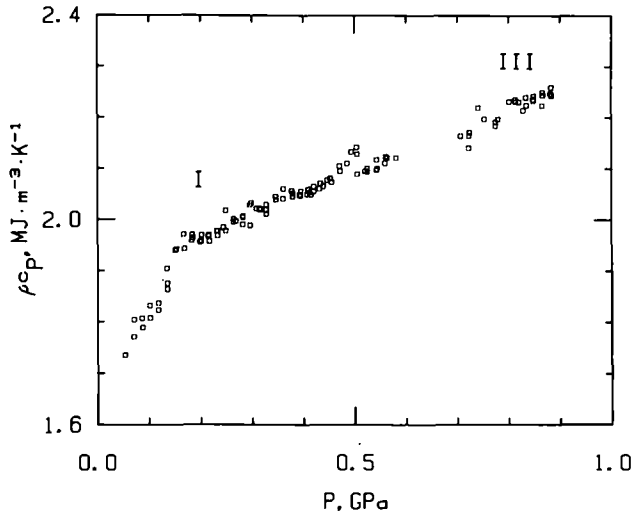


Fig. 6. Heat capacity per unit volume as a function of pressure at a temperature of 295 K. Data at the transition have been removed since the hot-wire method yields erroneous results at the transition.

two has been noted previously by Roufosse and Klemens [23]. Since the theoretical scattering strength is of the same order as the fitted one, this supports the model we have described.

### 3.3. Heat Capacity per Unit Volume

Although data for heat capacity per unit volume  $\rho c_p$  were not of special concern in this investigation, the hot-wire method inevitably yields these as well as data for  $\lambda$ . The data for  $\rho c_p(T)$  are shown in Fig. 5 and those for  $\rho c_p(P)$  are shown in Fig. 6. At transitions, the hot-wire method yields anomalous values for  $\rho c_p$  (and  $\lambda$ ). These data have been removed to avoid confusion. Using the data for the equation of state [13] together with the data for  $\rho c_p$  yields  $c_p(\text{phase III}) \approx 0.93c_p(\text{phase I})$  at the transition at room temperature.

## 4. CONCLUDING REMARKS

This investigation has shown that phase III of urea can be preserved down to at least 0.07 GPa below about 230 K (Fig. 3). An extrapolation of the I-III phase line intersects atmospheric pressure at about 218 K. It probably follows that urea exhibits two solid phases at atmospheric pressure and that the low-temperature phase III is stable below about

218 K. However, to obtain phase III at atmospheric pressure it may be necessary to enhance the transition kinetics by some method such as doping the specimen.

The transition between the phase I and phase III could be obtained by isothermal pressurization but not at isobaric cooling. We find two possible explanations for this difference in phase transition kinetics. One is that the driving force (thermal energy) should be larger for isothermal pressurization. The other is that shear stresses, which might enhance the transition, are more likely to appear during isothermal pressurization than during isobaric cooling.

Since urea exhibits an unusual change in thermal conductivity at the I  $\rightarrow$  III transition, it would be of great interest to study the change of the lattice structure at this transition.

## ACKNOWLEDGMENT

We are grateful to Professor P. Ferloni for supplying the purified sample of urea.

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