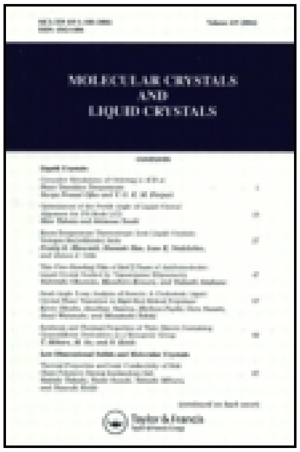

Molecular Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl15

Compressibility and Melting Curve of Adamentane to 20 Kbar

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Version of record first published: 21 Mar 2007.

To cite this article: Carl W. F. T. Pistorius & H. A. Resing (1969): Compressibility and Melting Curve of Adamentane to 20 Kbar, Molecular Crystals, 5:4, 353-361

To link to this article: http://dx.doi.org/10.1080/15421406908082943

Molecular Crystals and Liquid Crystals. 1969. Vol. 5, pp. 353–361

Compressibility and Melting Curve of Adamantane to 20 Kbar

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Received November 25, 1968

Abstract—The compressibility of adamantane was measured to 20 kbar at 20 °C. The solid-solid transition occurs at this temperature at 4.1 kbar with a volume change of 1.8 cm^3/mole. The melting curve of adamantane rises with pressure with an initial slope of 26.6 °C/kbar, but shows considerable curvature at higher pressures. The triple point tetragonal/fcc/liquid can be expected near 460 °C, 27 kbar. The volume of activation for self-diffusion in adamantane is estimated at 75 cm^3/mole by using Nachtrieb's T/T_m law.

Introduction

Adamantane (tricyclo-(3 : 3 : 1 : 3) 3 : 6-decane) is a key example of a plastic molecular crystal. It crystallizes with a disordered f.c.c. structure at room temperature,[1,2] but undergoes a solid-solid phase transition at 208.6 °K to a brittle phase which is tetragonal,[3] space group $P\bar{4}2_1c$. Reorientational disorder is removed in this phase.

A knowledge of the compressibility and of the P–T phase diagram of adamantane is necessary in order to estimate the effect of pressure on diffusion in adamantane.[4] The compressibility has not been determined before. The phase diagram of adamantane was studied by Pistorius and Snyman,[5] using a piston-cylinder press. While there is no reason to doubt the accuracy of their piston-displacement values of the transition pressures at various temperatures, the technique of properly correcting for friction when using internal heating was somewhat primitive at that time, and the accuracy of their melting curve is doubtful. The procedure actually used[6] consistently yielded bad agreement with hydrostatic work[7–9] as well as with internally-calibrated high-pressure X-ray studies.[10] More sophisticated ways of evaluating the symmetrical frictional component are now in use,[11,12] and in addition it has proved to be usually necessary to make further corrections for the non-symmetrical component of friction.[13] A redetermination of the melting curve of adamantane is therefore necessary.

Experimental

Adamantane was prepared by Dr J. P. de Villiers of the National Chemical Research Laboratory, Pretoria, using a method described elsewhere.[14] The zero-pressure melting point was 267.5 °C in good agreement with the highest literature value,[15] viz. 269 °C.

Pressures up to 30 kbar were generated in a piston-cylinder device.[16] The compressibility was determined at 20 °C by comparing the compression of a precompressed slug of adamantane to that of a similar slug of NaBr of exactly the same volume. The compressibility of NaBr had been measured to 49 kbar by Bridgman,[17] and proper manipulation of the results enables one therefore to correct for the distortion of the pressure vessel. The compression values obtained for adamantane must be considered upper limits, since bulk compressions are almost invariably higher than true compressions determined by means of high-pressure X-ray diffraction techniques. However, the error is usually less than 5–10%. The melting curve was determined by means of differential thermal analysis (DTA) using Chromel-Alumel thermocouples, corrected for the effect of pressure.[18] The furnace assembly was similar to that used by Cohen *et al.*[12] The samples were contained in stainless-steel capsules which incorporated thermocouple wells.[19] The axial thermal gradient along the sample capsule was reduced by sandwiching the capsule between two insulated metal plugs.[20] A typical DTA signal obtained on melting is shown in Fig. 1. No reaction of the adamantane with the stainless steel was observed. The heating rate was in the range 0.5–1.5 °C/sec. Sliding friction was determined by comparing results obtained on increasing and on decreasing pressure. The pressures obtained in this way were

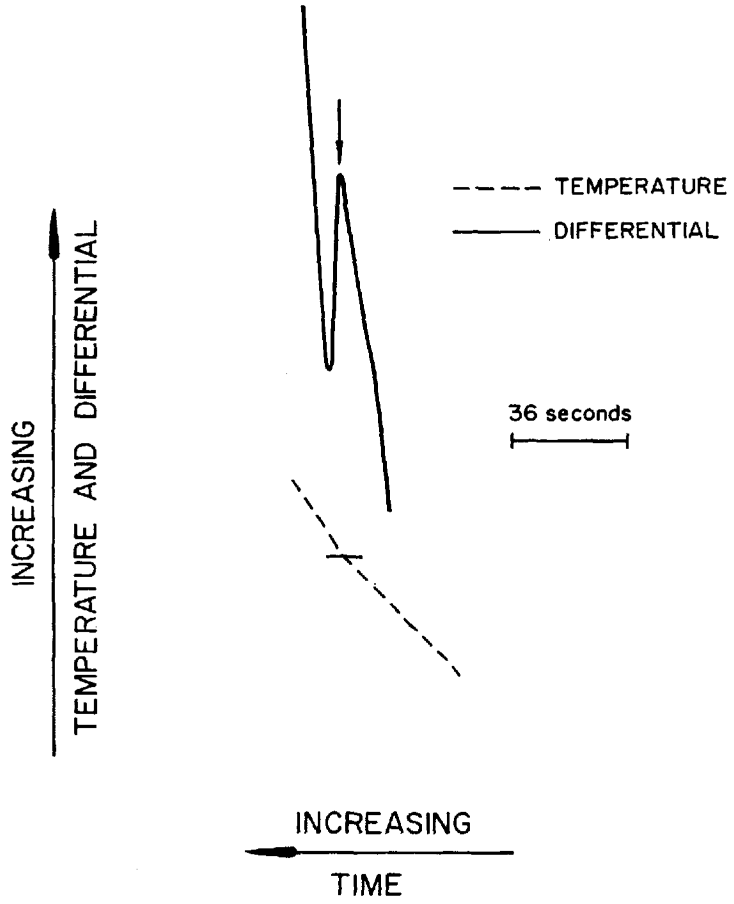

Figure 1. Typical DTA signal obtained upon melting adamantane at 13.1 kbar, 398.5 °C.

further corrected for the effect of non-symmetrical pressure losses.[13] The corrected pressures are believed accurate to ± 0.5 kbar. The points plotted represent the melting signals.

Results

Compressibility

The compression of adamantane at 20 °C is shown in Fig. 2. The I/II phase transition is clearly visible at 4.1 ± 0.5 kbar, in excellent agreement with the earlier results.[5] The volume change

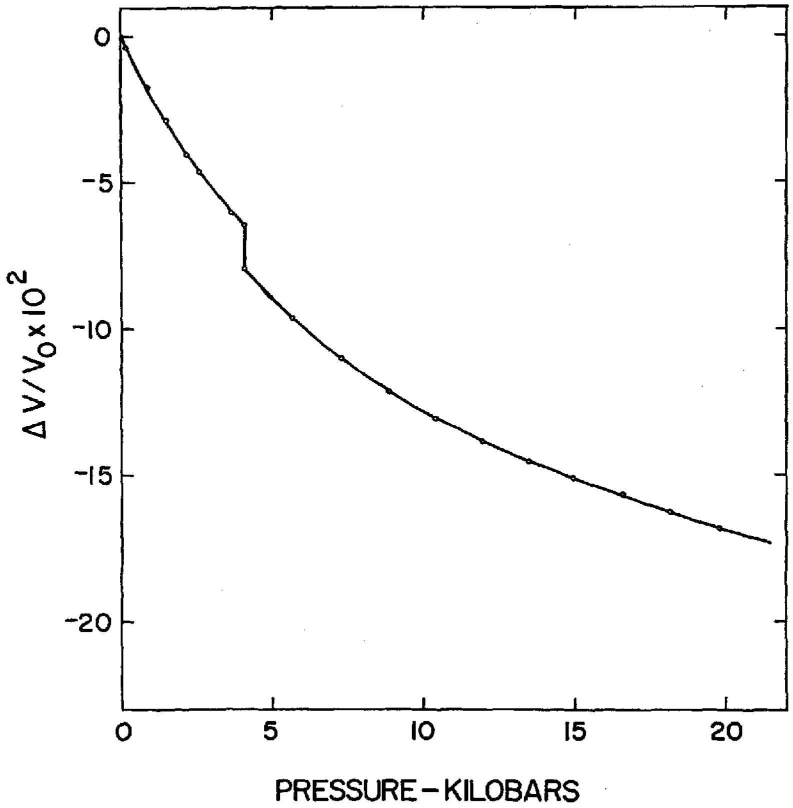

Figure 2. Compression of adamantane at 20 °C.

at the transition at 20 °C is 1.4%, i.e. 1.8 cm³/mole. The volume change at − 64.6 °C is 2.8 cm³/mole by extrapolation of the low-temperature lattice constants.[3] It is clear that the volume change decreases considerably with increasing pressure and temperature. The transition temperature can be expressed[5] as

$$t(^\circ\mathrm{C}) = -64.6 + 21.1P - 0.0734P^2$$

where P is the pressure in kbar. The slope dt/dP therefore only decreases from 21.1 °C/kbar at − 64.6 °C to 19.3 °C/kbar at 183 °C. Application of the Clapeyron equation now shows that the entropy of transition decreases considerably with temperature. Using the observed[21] latent heat of transition at zero pressure, viz. 807 cal/mole, the volume change at − 64.6 °C predicted by the Clapeyron equation using the observed initial slope of the transition line is 3.41 cm³/mole. The present value is probably preferable to the X-ray value[3] in view of the considerable extrapolation required in that case, and suggests that the previously observed average thermal expansion coefficient of the high-temperature phase, viz. 4.4×10^{-4} cm³/cm³-deg, may be slightly too high.

The compression of adamantane I at 20 °C can be expressed as

$$-\Delta V/V_0 = 2.057 \times 10^{-2}P - 1.163 \times 10^{-3}P^2$$

with a standard deviation of 0.00075. The compression of adamantane II at 20 °C can similarly be expressed as

$$-\Delta V/V_0 = 7.846 \times 10^{-2} + 1.144 \times 10^{-2}(P-4.1) - 6.15 \times 10^{-4}(P-4.1)^2 + 1.58 \times 10^{-5}(P-4.1)^3$$

with a standard deviation of 0.00011.

Melting Curve

The high-temperature portion of the phase diagram of adamantane is shown in Fig. 3. The observed melting points were fitted to the Simon equation[22]

$$P = A[(T/To)^c - 1]$$

where T° and T_0 °K are the melting points at P kbar and zero pressure, respectively, and A and c are adjustable constants.

A and c were determined by means of Babb's method.[23] The best fit was obtained for

$$P = 2.392[(T/541)^{8.493} - 1]$$

with a standard deviation of 4.7 °C. The initial slope of the melting curve is given by

$$(dT/dP)_{P=0} = T_0/Ac = 26.6 \pm 4.0\,°\mathrm{C/kbar}$$

by differentiation of the Simon equation. The newly determined value[24] of the heat of fusion is 3062 ± 9 cal/mole, which gives a volume change upon melting of 6.2 cm^3/mole.

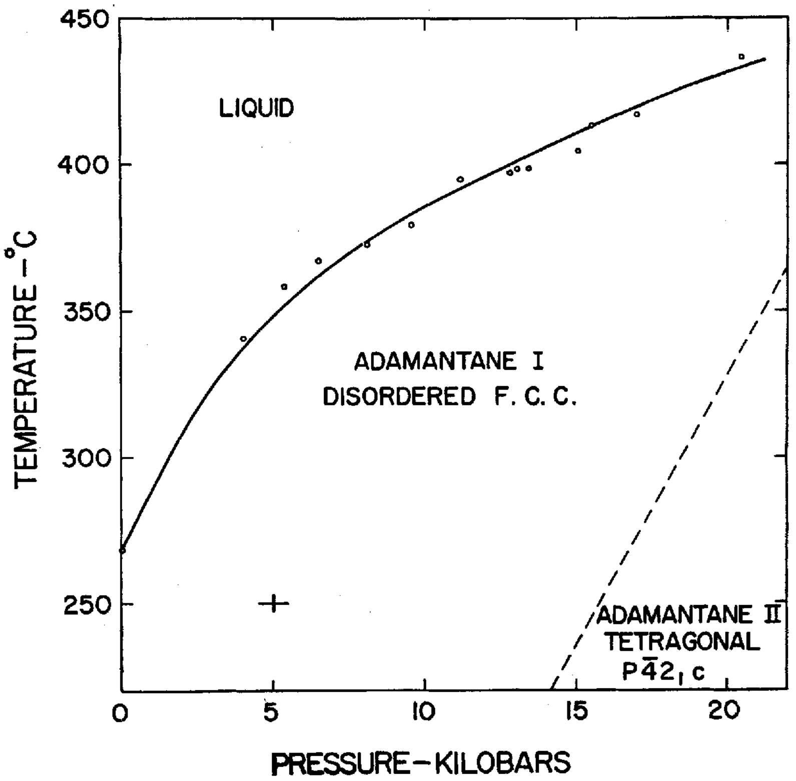

Figure 3. High-temperature region of the phase diagram of adamantane to 22 kbar.

The present melting curve is in fair agreement with the earlier work[5] at high pressures, but deviates considerably at lower pressures due to inadequate friction corrections in the earlier work.

Adamantane graphitizes at ~ 480 °C at 10–45 kbar,[5] and it was not possible to follow the melting curve much beyond 20 kbar. However, the triple point II/I/liquid can be expected near 460 °C, 27 kbar.

Discussion

Resing[4] has attempted to estimate the volume of activation V_{act} for self-diffusion in adamantane I. If V_{act} were an appreciable fraction of the molar volume of 128 cm^3, the effect of pressure on diffusion and hence on relaxation would be large. He found a considerable discrepancy between values of V_{act} estimated by means of various semi-empirical relationships and by means of Nachtrieb's T/T_m law,[25] and suggested that the effect of pressure on adamantane diffusion may be a crucial test of the T/T_m law. However, Resing[4] had to use an estimated value for the compressibility β, and it is now clear that the earlier initial slope[5] of the melting curve of adamantane was incorrect.

The enthalpy of activation H_{act} equals 36.7 kcal/mole.[4] A correlation found by Keyes[26] suggests that

$$V_{\mathrm{act}} = 4\,\beta\,H_{\mathrm{act}} = 126 \text{ cm}^3/\text{mole},$$

using the present initial compressibility of adamantane I, viz. 2.06×10^{-2} cm^3/cm^3-kbar. According to Lawson's thermodynamical analysis[27]

$$V_{\mathrm{act}} = (\beta/\alpha)S_{\mathrm{act}} = 80 \text{ cm}^3/\text{mole}.$$

Nachtrieb's T/T_m law[25] yields

$$V_{\mathrm{act}} = H_{\mathrm{act}}\frac{1}{T_m}\frac{dT_m}{dP} = 75 \text{ cm}^3/\text{mole}$$

if one uses the present initial slope of the melting curve. This result is in excellent agreement with Lawson's estimate, but in bad agreement with the estimate of Keyes or with Burton and Jura,[28] who suggested that $V_{\mathrm{act}} = 1.2\ V_{\mathrm{mol}}$ for argon. However, the glaring discrepancy previously reported[4,5] is removed.

Acknowledgments

The least-squares calculations were carried out on the IBM system 360/40 of the National Research Institute for Mathematical Sciences. The authors would like to thank Mrs Martha C. Pistorius for writing the computer programs and Mr J. B. Clark for assistance with some of the experimental work. Mr J. Erasmus and his staff and Mr G. O'Grady and his staff kept the equipment in good repair and were responsible for the manufacture of the furnace parts.

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