Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 14 Oct 2011.

To cite this article: Russell G. Ross & Per Andersson (1981): Thermal Conductivity, Heat Capacity and Phase Diagram of Tetrahydrofuran Under Pressure, Molecular Crystals and Liquid Crystals, 78:1, 35-40

To link to this article: http://dx.doi.org/10.1080/00268948108082145

Mol. Cryst. Liq. Cryst., 1981, Vol. 78, pp. 35–40
0026-8941/81/7804–0035 $06.50/0

Printed in the United States of America

Thermal Conductivity, Heat Capacity and Phase Diagram of Tetrahydrofuran Under Pressure

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(*Received August 10 1981*)

The thermal conductivity, λ, and the heat capacity per unit volume, ρc_P, have been measured for tetrahydrofuran (THF) using the transient hot-wire method in the temperature range 130–300 K and at pressures up to 2 GPa. Most of the data relate to the single solid phase which was found to exist over these ranges of the variables. The liquidus curve was determined roughly up to the maximum pressure, and we estimated the density of the solid phase at the normal melting point using the Clausius-Clapeyron relation. We inferred from the measurements that solid THF was a normal crystal phase in which three-phonon umklapp processes provided the only significant source of thermal resistivity. There was evidence for the effect of thermal expansion on λ, and this effect decreased under pressure.

1 INTRODUCTION

In the course of a recent investigation of the tetrahydrofuran-water (THF-H_2O) system, which will be published elsewhere, we made a few measurements for pure THF which are reported here. Our main interest was in the thermal conductivity and heat capacity under pressure. We also made a very limited investigation of the phase diagram, in particular the liquidus, since no data are available in the literature.

2 EXPERIMENTAL DETAILS

The thermal conductivity, λ, and the heat capacity per unit volume, ρc_P, were measured simultaneously using the transient hot-wire method. c_P is the spe-

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cific heat capacity at constant pressure, and ρ is the mass density. Details of the method have been given elsewhere.[1] Measurements were made in the temperature range T = 130–300 K and for pressures P = 0.1–2.0 GPa. For reasons given elsewhere,[2] it will sometimes be convenient for us to present and discuss our results in terms of the thermal resistivity, r (=1/λ).

We obtained data for both solid and liquid phases, although we were mainly interested in the solid state. For reasons discussed elsewhere,[2] our results for liquids are less accurate than for solids.

The liquid-solid transition was detected both by a discontinuity in λ and by response from a thermocouple located inside the Teflon cell of our piston-cylinder type of pressure vessel.

We used spectroscopic grade THF.

For measurements in the solid state, the accuracy was ±3% in λ and ±10% in ρc_P. Liquid-solid transition temperatures could be determined with an accuracy of about 1 K.

3 EXPERIMENTAL RESULTS

3.1 Phase diagram

The few results we obtained for the liquidus are shown in Figure 1. The point shown at zero pressure is the highly precise value of 164.76 K for the normal freezing point of THF obtained by Lebedev *et al.*[3]

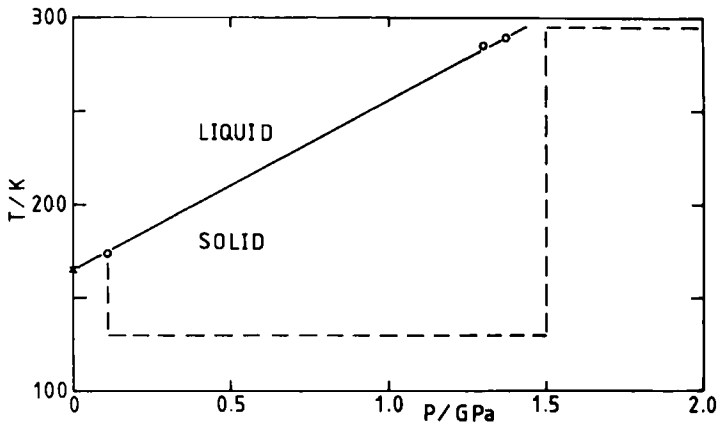

FIGURE 1 Phase diagram of THF. Liquidus: O-present work, x-Lebedev *et al.*[3] The broken line shows the trajectory in P-T space over which only a single solid phase was detected in our experiments.

Only one solid modification was detected over the trajectory in P-T space shown by the broken line in Figure 1. Lebedev *et al*[3] found only a single solid phase at temperatures down to 8 K at normal pressure.

3.2 Thermal conductivity

Our results for $\lambda(P)$ are shown in Figure 2(a), with equivalent numerical data in Table I.

Our results for $r(T)$ are shown in Figure 3(a), with equivalent numerical data in Table II.

For P = 0.11 GPa, we found $\lambda(\text{solid})/\lambda(\text{liquid}) = 2.06$ at the equilibrium temperature of 173 K.

There are no previous data with which our results can be compared.

3.3 Heat capacity per unit volume

Our results for ρc_P are shown in Figures 2(b) and 3(b). For $\rho c_P(T)$, a comparison may be made with previous work at normal pressure. We used the heat capacity results of Lebedev *et al.*[3] The two available measurements for $\rho(T)$, Carvajal *et al*[4] and Metz and Glines,[5] disagree by about 3% at 200 K. We were unable to choose between them, so we took the average. We ignored the effect of the pressure difference between 0 and 0.11 GPa. We used a constant value

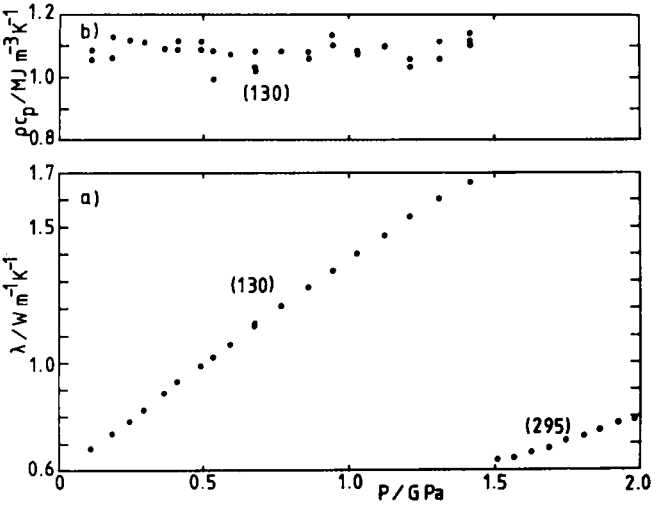

FIGURE 2 Isothermal pressure dependence of (a) thermal conductivity λ and (b) heat capacity per unit volume ρc_P for solid THF. Temperature in K is given in parentheses.

TABLE I

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

A	B	C	T/K	P/GPa
0.578	0.879	−0.077	130	0.11–1.5
0.160	0.316	—	295	1.5–2.0

for the density of the solid phase which was calculated as described below. The result of combining these data is given in Figure 3(b), and shows agreement within experimental error.

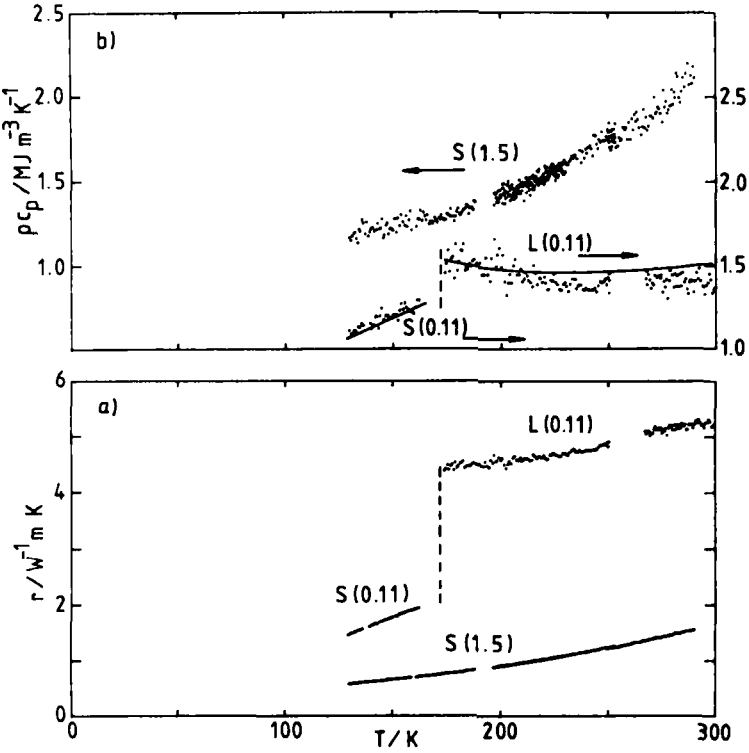

FIGURE 3 Isobaric temperature dependence of (a) thermal resistivity r and (b) heat capacity per unit volume ρc_P for solid (S) and liquid (L) phases of THF. Pressure in GPa is given in parentheses. The solid lines shown in (b) are from previous work[3-5] at zero pressure.

TABLE II

Isobaric temperature dependence of thermal resistivity r fitted to equations of form $r/(W^{-1} m K) = D + E(T/K) + F(T/K)^2$

Phase	D	E	F	P/GPa	T/K
Liquid	3.13	$0.71 \cdot 10^{-2}$	—	0.11	174–300
Solid	−0.475	$0.150 \cdot 10^{-1}$	—	0.11	129–162
Solid	0.434	$-0.61 \cdot 10^{-3}$	$0.153 \cdot 10^{-4}$	1.5	130–290

4 DISCUSSION

With the aid of our results, we estimated the density of solid THF, a quantity which is not available elsewhere. We took the change of entropy on fusion as 0.8153 J K^{-1} g^{-1} from Lebedev *et al.*[3] and found the slope of the liquidus $dT/dP = 90.7$ K GPa^{-1} in present work. The Clausius-Clapeyron equation then yields a value for the change of specific volume on melting of 0.0739 cm^3 g^{-1}. We took the specific volume of the liquid at the normal melting point to be 0.9605 cm^3 g^{-1} from an extrapolation of the average of previous work.[4,5] The result was a density of 1.128 g cm^{-3} for the solid phase at the normal melting point.

Figure 3a includes $r(T)$ for the solid at 1.5 GPa. It can be seen that $r \propto T$ is a good approximation to the results for $T \lesssim 180$ K. This is the behavior expected for a normal crystal phase in which three-phonon umklapp interactions amongst acoustic phonons are the only significant source of thermal resistivity.[6] We infer that solid THF should be regarded as a normal crystal phase in this sense, which is also indicated by the relatively large increase of λ on freezing.[7] The prediction $r \propto T$ strictly relates to constant volume conditions, and the deviation from proportionality evident for $T > 180$ K at 1.5 GPa was probably due to thermal expansion.[7] In order to test this, we need data for thermal expansivity and compressibility, which are not available.

At 0.11 GPa, r increased more rapidly than proportional to T over our range of measurement. This was probably mainly due to thermal expansion, as we have proposed in connection with the data at 1.5 GPa and higher temperatures. If so, a qualitative inference is that thermal expansivity decreases with increasing pressure, as would be expected intuitively.

Acknowledgment

This work was supported financially by the Swedish Natural Science Research Council.

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