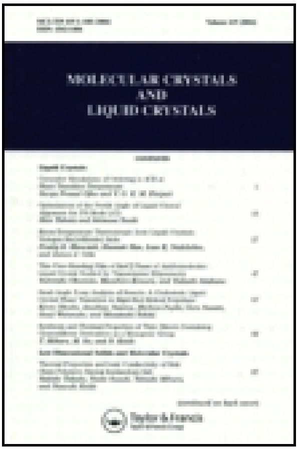

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Thermal Conductivity, Heat Capacity and Phase Diagrams of the Trichloroethanes Under Pressure

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Thermal Conductivity, Heat Capacity and Phase Diagrams of the Trichloroethanes Under Pressure

II. 1,1,2-trichloroethane

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The thermal conductivity, λ, the heat capacity per unit volume, ρc_p, and the phase diagram of 1,1,2-trichloroethane have been investigated in the temperature range 115 to 300 K and at pressures up to 2.5 GPa. The transient hot-wire method was used for the simultaneous measurement of λ and ρc_p. Only solid phases I and II were detected, in agreement with the known phase diagram. A phase I–II transition was detected at about 200 K and 0.1 GPa, which are conditions under which it had not previously been observed. It was doubtful whether phase I could be retained metastably to low temperatures at low pressures with the most rapid cooling rate we were able to employ. The thermal resistivity of phase I was proportioned to temperature, which is consistent with regarding it as a normal phase. The form of equation required to describe our results for the thermal resistivity of phase II contained an additional constant term, which we inferred to be a residual contribution associated with static structural imperfection in this phase.

1 INTRODUCTION

We have investigated the thermal conductivity, heat capacity per unit volume and phase diagram of 1,1,2-trichloroethane in the temperature range 115 to 300 K and at pressures up to 2.5 GPa. The results of a similar investigation of 1,1,1-trichloroethane were presented in the immediately preceding paper, hereafter referred to as (I). In (I), we included general comments on various physical and technical aspects of our investigations, and these comments are also relevant to the work presented here.

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A phase diagram of 1,1,2-trichloroethane in the temperature range 230 to 365 K and at pressures up to 1.0 GPa has been given previously by Babb and Christian,[1] and their results are reproduced here in Figure 1. They found two solid phases, and, as they described, it has been inferred from spectroscopic evidence[2,3] that phase I corresponds to C_1 molecular symmetry and phase II to C_s molecular symmetry. No crystal structure data are available for either phase, but there is no evidence for plastic crystal type of behaviour for this substance. As described in (I), the situation is different in the case of 1,1,1-trichloroethane, where there is a stable plastic crystal phase.

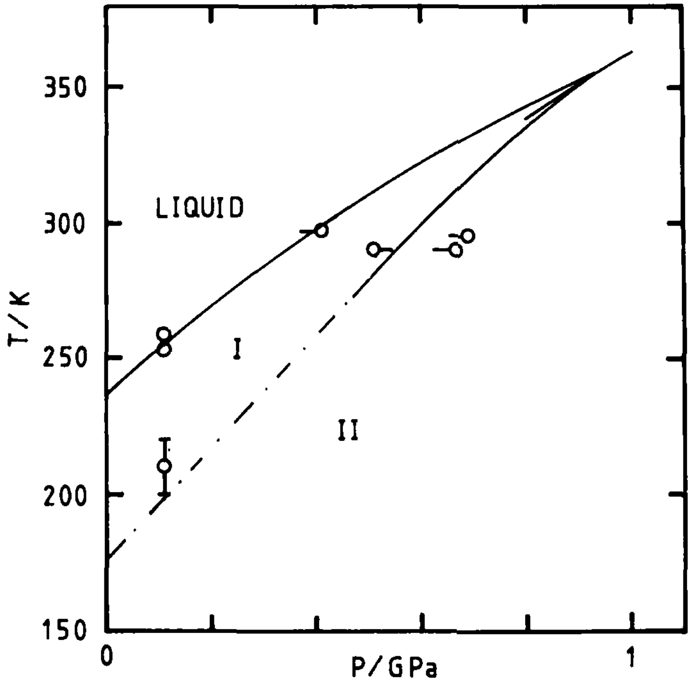

FIGURE 1 Phase diagram of 1,1,2-trichloroethane, after Babb and Christian.[1] Extrapolation of their I–II phase boundary shown as (·—·—·). O-phase transitions above 250 K in present work; tail on symbol indicates direction from which change of variable took place. Error bars shown at 0.11 GPa indicate range of temperature over which II → I transition occurred on warming.

2 EXPERIMENTAL DETAILS

Our experimental procedures in investigating 1,1,2-trichloroethane were in general the same as described in (I), which should be consulted for details. We simply repeat here the symbols we have used for the quantities which were measured; namely, the thermal conductivity, λ, or equivalently its reciprocal the thermal resistivity, r, and the heat capacity per unit volume, ρc_p, where ρ is the mass density.

The 1,1,2-trichloroethane which we used was of >99% purity from Fluka AG, W. Germany.

3 RESULTS AND COMPARISON WITH PREVIOUS WORK

3.1 Phase diagram

Our observations in connection with the phase diagram of 1,1,2-trichloroethane were in agreement with the results of Babb and Christian,[1] although in some circumstances interpretation was complicated by metastability or sluggish transition kinetics. The pressure-temperature (P-T) co-ordinates at which we found transitions to occur are shown in Figure 1. We detected only phases I and II over our ranges of measurement.

We found that phase I could be pressurized metastably to 2 GPa at 250 K, or cooled metastably to 150 K at a pressure of 0.39 GPa. The corresponding measurements of $\lambda(P)$ and $r(T)$ are shown in Figures 2 and 3 respectively, and varied smoothly. Phase II formed readily when the phase boundary was crossed at room temperature.

At low pressures, we found that phase I–phase II equilibrium was complex, and that metastable retention of phase I to low temperatures was difficult and uncertain. Our first procedure, which attempted to maximize the possibility of retention of phase I, was to form the phase at 235 K and atmospheric pressure, and to cool it to 115 K at the maximum practicable rate of 2.5 K min^{-1}. We then increased the pressure to 0.11 GPa at this temperature, and made measurements on warming. As shown in Figure 3, the measured $r(T)$ was proportional to T above about 170 K, but approached a constant value for lower temperatures. The latter behaviour was probably due to extraneous effects. Our second procedure was to form phase II at room temperature, cool it to 115 K at a pressure of 0.78 GPa, and reduce the pressure to 0.11 GPa at this temperature. We then made measurements on warming this specimen of phase II. As shown in Figure 3, the measured $r(T)$ was substantially less at the lowest temperatures than was found for the first procedure, but $r(T)$ increased rapidly in the region of 210 K to values in good agreement with data for phase I obtained in other runs. $\rho c_p(T)$ showed a similar rapid increase, as may be seen from Figure 5. We associated rapid increase of $r(T)$ and $\rho c_p(T)$ with transition from phase II to phase I, on warming. The corresponding P-T co-ordinate is shown in Figure 1, and is in reasonable agreement with an extrapolation of the phase boundary which was determined by Babb and Christian.[1] A specimen which was cooled relatively slowly at an average rate of about 0.8 K min^{-1} yielded results for $r(T)$ which

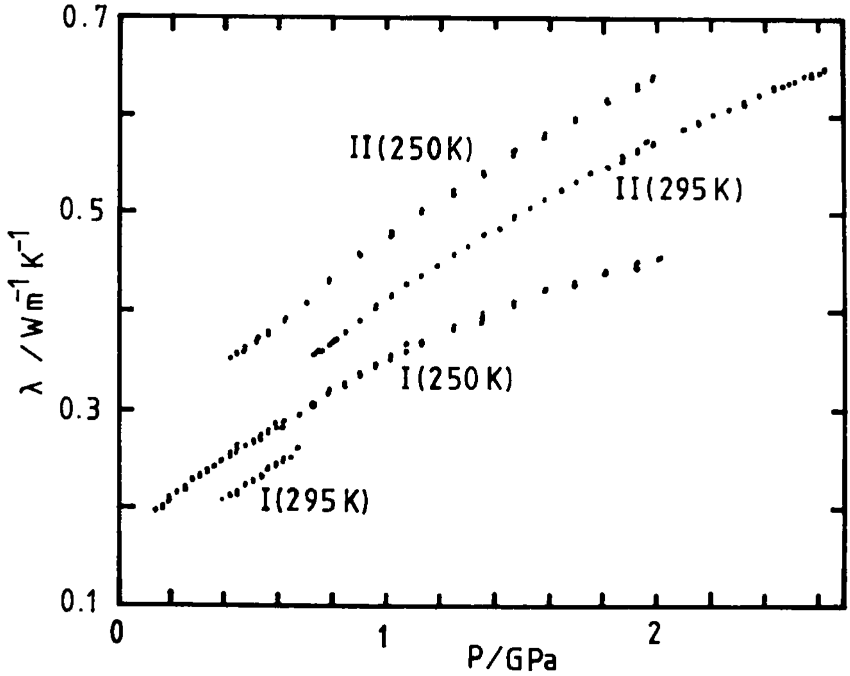

FIGURE 2 Isothermal variation with pressure of thermal conductivity, λ, for solid phases of 1,1,2-trichloroethane. Temperature is given in parentheses after each phase symbol. At 250 K, phase I was metastable with respect to phase II for $P \gtrsim 0.4$ GPa.

reproduced well on cooling and warming. Below about 200 K, these results were intermediate between those resulting from the first two procedures, as may be seen from Figure 3.

We conclude from our observations that there is an asymmetry in temperature of the kinetics of the phase I–phase II transition at low pressures. The transition from phase I to phase II on cooling was sluggish but difficult to suppress completely, except, perhaps, by very rapid cooling. The transition from phase II to phase I on warming occurred fairly readily. This difference in transition rate is reasonable on general grounds; increasing temperature should accelerate the transition rate, and conversely.

3.2 Thermal conductivity

Our results for $\lambda(P)$ are shown in Figure 2, and the parameters in the equations which were used to represent the data given in Table I. Figure 3 and Table II provide the corresponding information for $r(T)$. There are no other published data for the thermal conductivity of the solid phases with which our results could be compared.

TABLE I

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

Phase	A	B	C	T/K	P/GPa
I	0.132	0.189	—	295	0.40–0.67
I	0.166	0.212	−0.034	250	0.14–2.0
II	0.182	0.258	−0.031	295	0.73–2.6
II	0.241	0.267	−0.034	250	0.42–2.0

We also determined the ratio $\lambda_l/\lambda_{\text{liquid}}$ by crossing the liquidus under pressure, and obtained values for this quantity of 1.25 at $T = 297$ K and $P = 0.41$ GPa and 1.35 at $T = 255$ K and $P = 0.11$ GPa. Section 2 of (I) included a description of the relevant technical considerations in our measurements of λ_{liquid} under pressure. The important point to note is that

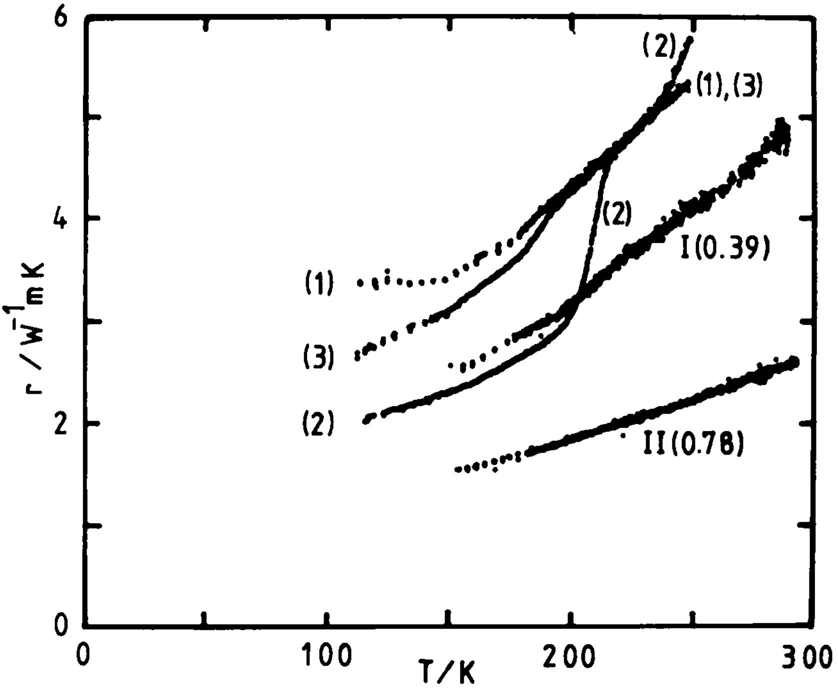

FIGURE 3 Isobaric variation with temperature of thermal resistivity, r, for solid phases of 1,1,2-trichloroethane. Pressure is given in GPa after each phase symbol except for the sets of data points labelled as (1), (2), (3), all of which refer to 0.11 GPa. The points shown in these three numbered sets were measured: (1) on warming a rapidly-cooled specimen of phase I, (2) on warming a specimen of phase II from 115 K showing transition to phase I, (3) on cooling or warming a slowly-cooled specimen of phase I. At 0.39 GPa, phase I was metastable with respect to phase II for $T \lesssim 250$ K.

TABLE II

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

Phase	D	E	F	P/GPa	T/K
I	0.07	$2.12 \cdot 10^{-2}$	—	0.11	174–248
I	0.41	$1.09 \cdot 10^{-2}$	$1.51 \cdot 10^{-5}$	0.39	150–290
II	2.46	$-1.16 \cdot 10^{-2}$	$7.07 \cdot 10^{-5}$	0.11	115–195
II	0.82	$2.97 \cdot 10^{-3}$	$1.07 \cdot 10^{-5}$	0.78	153–293

this ratio was much larger in the present work than the value $\lambda_{\mathrm{Ib}}/\lambda_{\mathrm{liquid}} \approx 1.05$ for 1,1,1-trichloroethane, as given in (I).

As described in Section 3.1, we found that there were technical difficulties in obtaining a well-characterized specimen of metastable phase I below about 200 K at low pressures. As described there and shown in Figure 3, measurements of $r(T)$ made on warming a rapidly-cooled specimen at 0.11 GPa yielded $r \propto T$, as expected for a normal crystal phase, from about 170 K to close to melting. For temperatures below about 170 K, $r(T)$ approached a constant value. From experience, we doubt that the latter behaviour reflected the properties of phase I, and it was probably due to extraneous effects. Examples of such effects would be uncertainty in pressure arising from excessive friction in the piston-cylinder pressure vessel at such low temperatures, and/or lack of internal equilibrium in the specimen due to the relatively rapid cooling. Figure 3 also shows that $r(T)$ for a slowly-cooled specimen of phase I was close, on the average, to the prediction $r \propto T$, but we consider that this probably arose accidentally from some mixture of phases I and II.

As described in Section 3.1, and shown in Figure 3, we found that when phase II was warmed from 115 K at 0.11 GPa, the measured $r(T)$ showed a rapid increase at about 210 K to values found for phase I in other runs. Such an increase was plausibly associated with a transition from phase II to phase I. It can also be seen from Figure 3 that the measured $r(T)$, during the same warming run, increased detectably above the prediction $r \propto T$ for a short range of temperature close to melting. We have not attempted to investigate further the latter rather minor feature of our measurements, since we suspected it was due to some extraneous effect.

3.3 Heat capacity

Our results for ρc_p are shown in Figures 4 and 5.

We may compare our results at 0.11 GPa with previous measurements at atmospheric pressure. The heat capacity has been measured by Crowe and

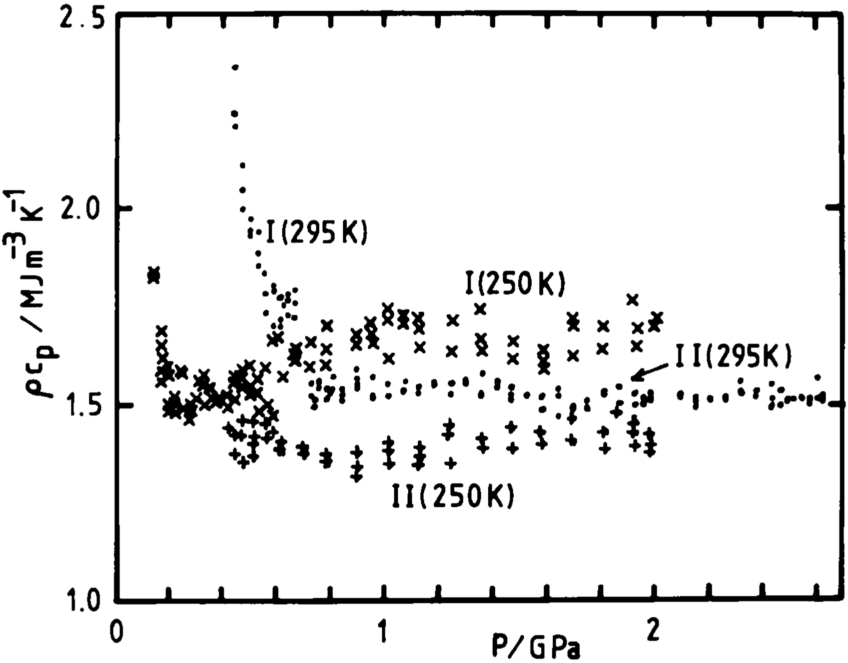

FIGURE 4 Isothermal variation with pressure of heat capacity per unit volume, ρc_p, for solid phases of 1,1,2-trichloroethane. Temperature is given in parentheses after each phase symbol. At 250 K, phase I was metastable with respect to phase II for $P \gtrsim 0.4$ GPa.

Smyth.[4] We obtained an estimate of 1.60 Mg m^{-3} for the density of phase I by combining the literature value for liquid density[5] with the change of density on solidification given by Babb and Christian.[1] As shown in Figure 5, agreement is within about 10%, which is our stated limit of error, but with the important distinction that previous work did not exhibit the rapid increase which we found on warming through a temperature of about 200 K. As has been described, we found that such an increase could in one case be reliably associated with a transition from phase II to phase I. In cases where the specimen was prepared by cooling phase I the increase was still present, and might have been due to the presence of at least some phase II in the specimen at low temperatures.

Crowe and Smyth[4] found a rapid increase of C_p for phase I near melting. As can be seen from Figures 4 and 5, we found similar behaviour for ρc_p. Crowe and Smyth[4] also made measurements on 1,1,1-trichloroethane, and found analogous behaviour. As discussed in (I), rapid increase of C_p in their measurements for 1,1,1-trichloroethane was probably due to the effect of trace impurities. It seems likely that a similar situation pertains for 1,1,2-trichloroethane, in both present work and in that of Crowe and Smyth.[4]

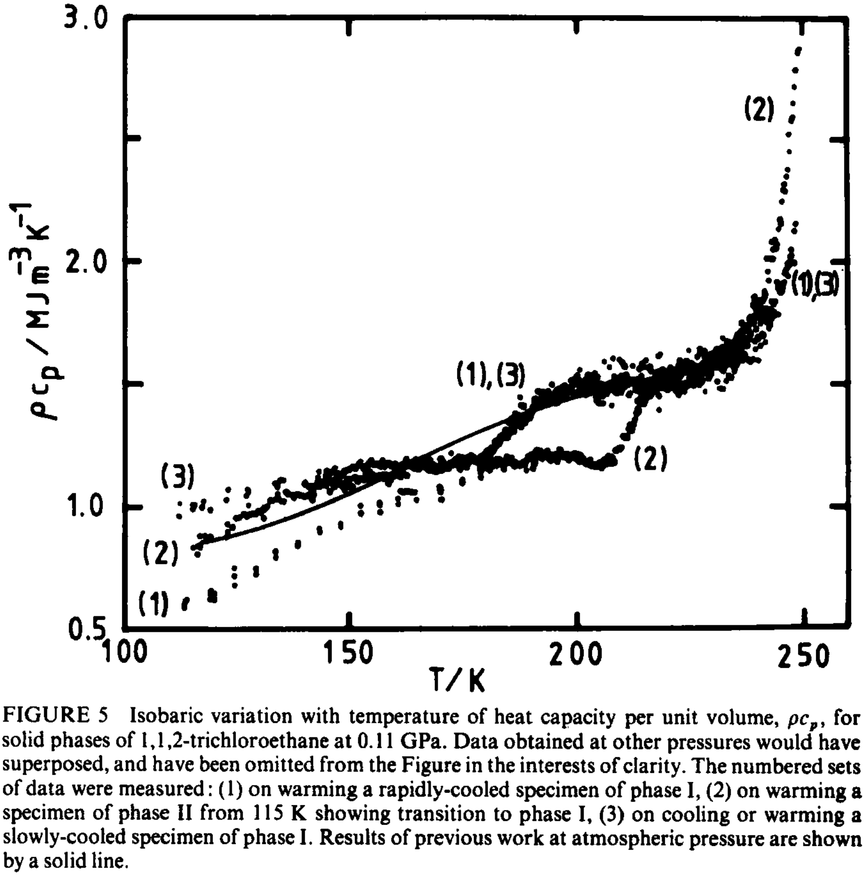

FIGURE 5 Isobaric variation with temperature of heat capacity per unit volume, ρc_p, for solid phases of 1,1,2-trichloroethane at 0.11 GPa. Data obtained at other pressures would have superposed, and have been omitted from the Figure in the interests of clarity. The numbered sets of data were measured: (1) on warming a rapidly-cooled specimen of phase I, (2) on warming a specimen of phase II from 115 K showing transition to phase I, (3) on cooling or warming a slowly-cooled specimen of phase I. Results of previous work at atmospheric pressure are shown by a solid line.

4 DISCUSSION

Included in (I) was a description of the structural and thermal properties of plastic crystal, normal crystal and disordered normal crystal phases. We now examine on the basis of this classification the behaviour of $r(T)$ for phases I and II of 1,1,2-trichloroethane.

It can be seen from Figure 3 that $r \propto T$ is a good approximation to the measured values of $r(T)$ for phase I, if we exclude situations where we suspected extraneous effects, such as a mixture of phase I and phase II, or a lack of internal equilibrium. Moreover, as noted above, r increased by about 30% on transition from phase I to the liquid phase. From these observations, we infer that phase I should be regarded as a normal crystal phase.

On the other hand, data for $r(T)$ for phase II, shown in Figure 3, can be fitted most satisfactorily to Eq. (1) of (I) by taking $D > 0$. According to the analysis given in (I), this would imply a residual contribution to the total thermal resistivity, which for phase II can be estimated from Figure 3 to be in the region of 10–20 % at 300 K. Such a magnitude of residual contribution to the total r is substantially less than that which has typically been found for a plastic crystal phase. For example, as described in (I), under similar P-T conditions, the residual contribution was found to be about 80 % of the total thermal resistivity for plastic crystal phase Ib of 1,1,1-trichloroethane. We conclude that according to our classification phase II of 1,1,2-trichloroethane should be regarded as a disordered normal crystal phase.

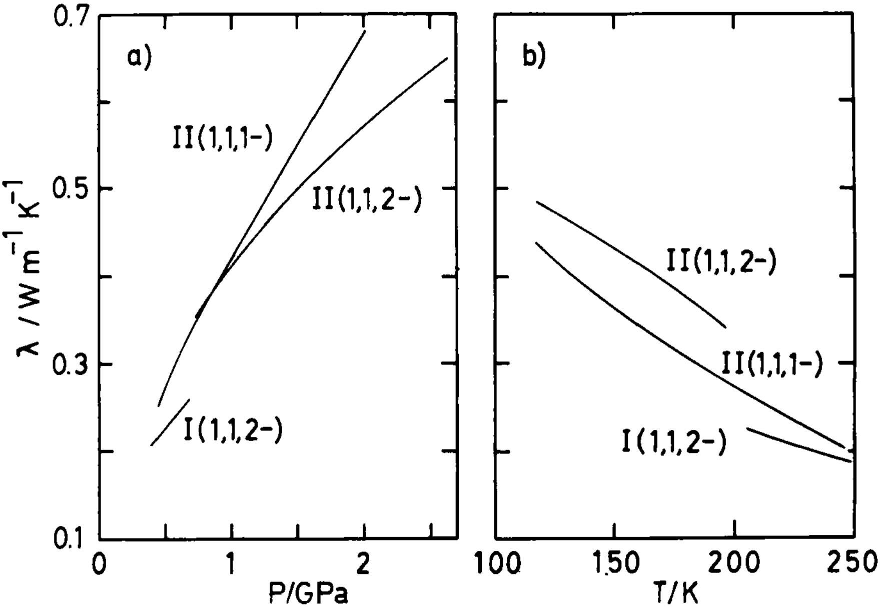

FIGURE 6 Selected results for thermal conductivity, λ, showing comparison between phase II of 1,1,1-trichloroethane and phases I and II of 1,1,2-trichloroethane. Part (a) of the Figure shows isothermal variation with pressure at 295 K and part (b) shows isobaric variation with temperature at 0.11 GPa.

Regarding phase I as a normal crystal phase and phase II as a disordered normal crystal phase is consistent with other work in the sense there has been no suggestion that either should be regarded as a plastic crystal phase.

Analysis of the relative thermal properties of the normal and disordered normal crystal phases of 1,1,1- and 1,1,2-trichloroethane is difficult in the absence of other data. Figure 2 shows that $\lambda_{II} > \lambda_{I}$ for 1,1,2-trichloroethane, at the same P-T conditions, despite the residual contribution to r for phase II which we deduced above. λ_{II} is greater than λ_I by about 35%, although the difference in density[1] is only about 1%. Figure 6 shows that phase II of 1,1,1-trichloroethane has the highest thermal conductivity of any of these phases for $P \gtrsim 1$ GPa, but not at lower pressures. Since there are no compressibility data available for any of these phases, and no crystal structure data for the phases of 1,1,2-trichloroethane, we are unable to proceed further at present to test features such as the relation between λ and the molecular and crystallographic structure.

5 CONCLUSIONS

Phases I and II of 1,1,2-trichloroethane were detected under conditions in agreement with the known phase diagram. Our results for the thermal resistivity are consistent with regarding phase I as a normal crystal phase, and phase II as a disordered normal crystal phase. Neither phase shows behaviour expected for a plastic crystal phase, which is in agreement with other work.

Acknowledgment

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