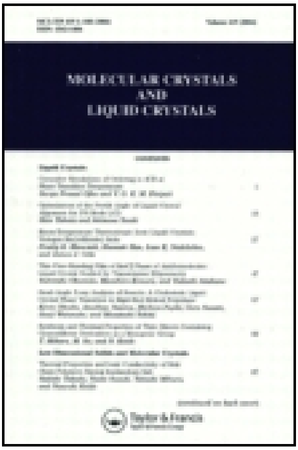

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Thermal Conductivity, Heat Capacity and Phase Diagrams of the Trichloroethanes Under Pressure

I. 1,1,1-trichloroethane

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The thermal conductivity λ, the heat capacity per unit volume ρc_p, and the phase diagram of 1,1,1-trichloroethane have been investigated in the temperature range 115 to 350 K and at pressures up to 2 GPa. The transient hot-wire method was used for the simultaneous measurement of λ and ρc_p. Of the stable phases only Ib and II were detected, and not phases III and IV which had been reported in our range of measurement by some previous investigators. Furthermore, metastable phase Ia was not detected. The measured thermal resistivity of phase Ib was almost independent of temperature and close to the value for the liquid phase. The thermal resistivity of phase II was roughly proportional to temperature. Such behaviour is consistent with regarding phase Ib as a plastic crystal phase and phase II as a normal crystal phase, which is in agreement with other work.

1 INTRODUCTION

The trichloroethanes are of special interest in studying the thermal properties of organic substances. As is well-known, the ethane molecule ($H_3C\text{-}CH_3$) can be triply-chlorinated in two ways. If the substitutions of chlorine for hydrogen atoms all occur at the same end of the C-C single bond the result is 1,1,1-trichloroethane. Alternatively, if two chlorine atoms are substituted at one end, and one at the other, the result is 1,1,2-trichloroethane. These alternative substitutional procedures yield molecules of identical mass and slightly differing structure.

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The differing molecular structure must be the underlying cause of property differences in the condensed state. For example, the phase diagram of 1,1,1-trichloroethane[1] contains at least one stable plastic crystal phase[2] whereas the phase diagram of 1,1,2-trichloroethane[3] does not. This behaviour is presumably connected with the higher molecular symmetry of 1,1,1-trichloroethane compared with 1,1,2-trichloroethane. As we shall show in this and the following paper, such a difference in phase type is reflected in the thermal properties.

The thermal properties we have measured are 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. Most of our data for these properties relate to the solid phases, with only restricted results for the liquid for technical reasons which we shall describe. We have also extended the previously-determined phase diagrams[1,3] of both substances in pressure (P) and temperature (T) variables, and, in the case of 1,1,1-trichloroethane, find fewer stable phases than had previously been suggested.[1] Our results for 1,1,1-trichloroethane are given in the present paper, and for 1,1,2-trichloroethane in the paper immediately following.

In presenting our results for the transport of heat, we shall make use of either λ or r as is most appropriate, on grounds which we now outline. The ability of a phase to transport heat, by lattice conduction in the case of a nonmetallic solid phase, is naturally expressed in terms of λ. It is also a general empirical result that $\lambda(P)$ is roughly linear, so λ is a convenient quantity to consider in relation to pressure dependence.

On the other hand, in relation to temperature dependence, the most appropriate quantity for us to employ is the thermal resistivity, r, essentially because our results have been obtained in the so-called high-temperature regime of thermal conduction. We propose that there are two basic types of solid phase to consider in this regime, specifically for molecular solids. According to our classification, the first basic type in fact spans a spectrum of specific examples for which a limiting case is what we refer to as a normal crystal phase. We define a normal crystal phase as one which exhibits no significant static or quasi-static structural disorder. The thermal resistivity then arises almost entirely from three-phonon interactions, and the resultant theoretical prediction[4] is $r \propto T$. This prediction strictly relates to a perfect crystal of monatomic basis under isochoric conditions, ignoring higher order phonon-phonon interactions. As is well-known, the predicted behaviour is found approximately for the solid phases of many real substances under isobaric conditions, even though they may be of more complex structure as is the case, for example, for molecular solids.

The first basic type is extended by adding to a normal crystal phase some degree of static structural imperfection. There are various ways in which such static imperfection could be supposed to arise in a solid phase. One way would be the misorientation of otherwise identical molecules, which would include the case of misorientation due to a rotation about the C-C bond for molecules of C_1 symmetry in 1,1,2-trichloroethane. Another possible source of static imperfection could be a mixture of molecular conformations, such as molecules of C_1 and C_s symmetry in this same substance. Finally, it is possible in principle for a molecule to be displaced to other than a correct lattice site in a crystal. Static imperfection, of whatever origin, would be expected to scatter phonons, and to result in an additive and probably temperature-independent "residual" contribution to the total thermal resistivity. A normal crystal phase to which some static structural disorder has been added we refer to as a disordered normal crystal phase. Such a phase would be expected to have a temperature dependence of the thermal resistivity of the form

$$r(T) = D + ET \tag{1}$$

with D and E positive constants. The special case, for Eq. (1), of $D = 0$ corresponds to a normal crystal phase, and it seems clear that in principle a disordered normal crystal phase could be transformed continuously into the limiting case of a normal crystal phase as the static structural disorder was reduced to zero. Normal and disordered normal crystal phases together thus constitute one basic type of solid phase in the high-temperature regime, according to our classification.

The other basic type is a plastic crystal phase. Plastic crystal phases are characterized[5,6] by facility of molecular reorientation amongst a number of energetically-equivalent orientations, whilst long-range translational periodicity of molecular centres is retained. A plastic crystal phase thus exhibits significant quasi-static structural disorder. The thermal resistivities of a number of plastic crystal phases have been measured to date.[7] The features of $r(T)$ which have invariably been found are: a major residual contribution to the total thermal resistivity (term D of Eq. (1)), a small temperature dependence, and an absolute value of r only a few percent less than that of the corresponding liquid phase at co-existence.

There is an important and probably essential distinction to be made between a plastic crystal and a disordered normal crystal phase. We have argued that a disordered normal crystal phase could in principle be transformed continuously into a normal crystal phase, as the static structural disorder was reduced to zero. There is, however, no known example of a continuous transition between a plastic crystal phase and a normal crystal phase. The latter transitions have always been found to be first-order. This first-order character may be rationalized by recognizing that in a plastic crystal phase the lattice has higher point symmetry at a molecular centre than does the isolated molecule. This well-known fact is, of course, the underlying reason for there being a number of energetically-equivalent molecular orientations, which is characteristic for a plastic crystal phase.

It is clear that such a situation can be eliminated, to yield a normal crystal phase, by change of lattice symmetry, which implies a first-order transition.

As we shall see, $r(T)$ for the trichloroethanes will exemplify plastic crystal, normal crystal and disordered normal crystal phase behaviour.

2 EXPERIMENTAL DETAILS

The thermal conductivity and the heat capacity per unit volume were measured simultaneously using the transient hot-wire method. Details of the method, and of our general experimental arrangements, have been given elsewhere.[8] Measurements were made in the temperature range 115 to 350 K and at pressures up to 2 GPa.

The 1,1,1-trichloroethane which we used was of nominal >99% purity from Fluka AG, W. Germany, and analysis by gas chromatography showed a purity >99.5%. In one run, the sample was distilled immediately before use, as has been recommended by some investigators,[9] but this made no difference to the results. The sample was charged into the measurement cell at room temperature and pressure, and in high pressure experiments was frozen either by pressurization or by cooling at a pressure of 0.1 GPa.

There are general technical considerations which need to be taken into account in our application of the transient hot-wire method to solid and liquid phases and under pressure. One important technical consideration is whether the hot-wire is arranged horizontally or vertically within a specimen cell. A horizontal arrangement of the hot-wire is suitable for solid phases, and has the practical advantage in high pressure experiments of minimizing the axial dimension required in our piston-cylinder type of pressure vessel. Furthermore, it is our experience in measurements on solid phases that some minimum pressure is essential in order to ensure good thermal contact between hot-wire and specimen. The minimum pressure required in a particular experiment will depend on the hardness of the specimen, but it is typically about 0.1 GPa. On the other hand, pressure is not necessary when the specimen is in the liquid state, since good thermal contact is achieved even at atmospheric pressure. However, measurements on the liquid state are susceptible to the extraneous effects of convection, especially when using a horizontal arrangement of the hot-wire. It is therefore preferable to use a vertical arrangement of the hot-wire for liquids, since in our experience this reduces the effects of convection. Unfortunately, with our present equipment, a vertical arrangement of the hot-wire can be used only at atmospheric pressure.

Because of such technical difficulties, we attempted only to *compare* values of λ in the liquid and solid phases. Such a comparison was of interest, since the difference in λ for liquid and plastic crystal phases of 1,1,1-trichloroethane was expected to be small, as discussed in Section 1. We used two basically different procedures in making such a comparison. One procedure was to cross the liquidus, at high pressure, by following either an isothermal or an isobaric trajectory. The measurements in such cases necessarily involved use of a horizontal arrangement of the hot-wire, with the associated uncertainty as to the effects of convection on data for the liquid phase. The other procedure was to attempt to minimize the effects of convection by using a vertical arrangement of the hot-wire for measurements on the liquid phase at atmospheric pressure, together with a short extrapolation of high-pressure plastic crystal data in order to make a comparison near the normal melting point.

As in previous work,[8] and in relation to the solid phases, the error in λ was $\pm 3\%$, although changes in λ as small as 1% would have been detectable across a phase transition. The error in ρc_p was about $\pm 10\%$.

We observed the $P - T$ co-ordinates at which phase transitions occurred primarily by noting thermocouple response due to enthalpy change on transition. Corresponding results for the change of thermal properties agreed within 1 K when extraneous effects due to the temperature excursion of the hot-wire during a measurement were taken into account.

3 RESULTS AND COMPARISON WITH PREVIOUS WORK

3.1 Phase diagram (see note added in proof)

A phase diagram for 1,1,1-trichloroethane up to 0.6 GPa and in the range 200 to 310 K has previously been given by Figuière *et al.*[1] These workers obtained evidence for the existence of phases I, II, III and IV, and the phase boundaries they determined are shown in Figure 1. It has also been proposed[2,10,11] that phase I has in fact two different crystalline modifications, designated Ia and Ib, both of which are considered to be plastic crystal phases.[2] These modifications are distinguishable on the basis of their liquid → solid transition temperatures. Such evidence identifies the solid formed directly from liquid as phase Ib both in present work and in that of Figuière *et al.*[1] Phase Ia is probably[11] metastable with respect to phase Ib, since it has been reported[2] that phase Ia cannot be formed by warming phase II, but only by cooling the liquid.

In the present work, we detected only phases Ib and II, and the points at which we observed phase transitions are shown in Figure 1. We were unable to find any evidence for the existence of phase IV either from the measured thermal properties or from enthalpy change on transition. We explored carefully through the proposed field of stability of phase IV both by changing

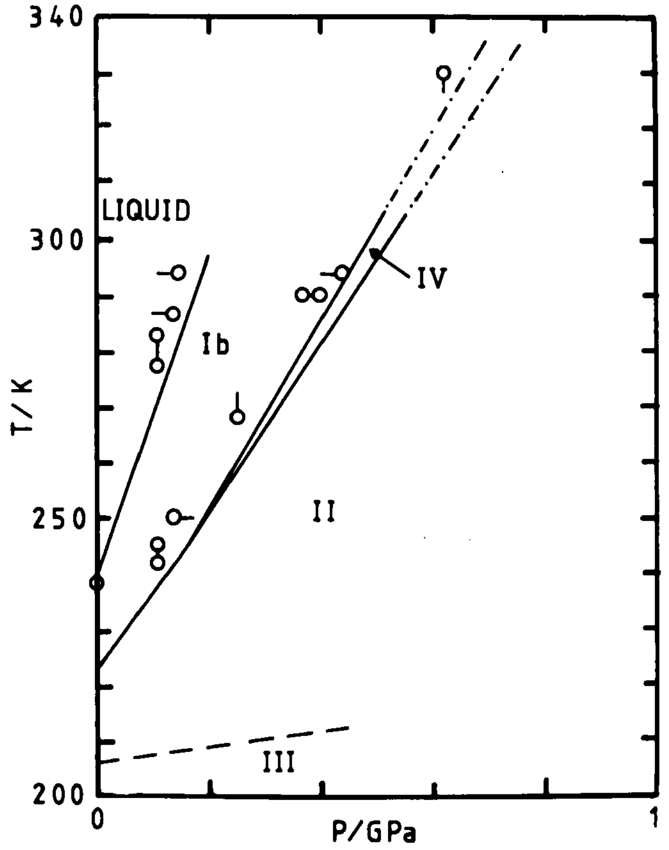

FIGURE 1 Phase diagram of 1,1,1-trichloroethane. Phase boundaries shown after Figuière *et al.*[1], and given as (----) where tentative or (·-·-·-·) where extrapolated. Ơ-transitions from present work; tail on symbol indicates direction from which change of variable took place.

pressure at room temperature, and by heating at a pressure of 0.62 GPa. Data for $r(T)$, measured at 0.62 GPa, are presented in Figure 3, and all the data points which are shown can be identified with either phase Ib or phase II. It should be noted from this figure that there is a temperature interval of about 7 K indicated at this pressure within which no data points are shown. This interval corresponded to a region of measurement where we considered that the trajectory in temperature of the hot-wire, during its excursion in our transient method, had intersected a phase boundary. It has been our consistent experience, and would be expected on general grounds, that reliable measurements of thermal properties using the transient hot-wire method are impracticable under such conditions. Since phase IV has been proposed[1] to exist in this region of the phase diagram, it follows from our results that the corresponding temperature range of stability of phase IV, if it exists, cannot be greater than 7 K. The measurements of Figuière *et al.*[1] imply a temperature range of stability of about 9 K for phase IV at this pressure.

No transition from phase II was observed down to 115 K at low pressure, or up to 2 GPa at room temperature. The measured thermal properties varied smoothly over these ranges, as is evident from Figures 2–5. In particular, our data for both $r(T)$ (Figure 3) and $\rho c_p(T)$ (Figure 5) for phase II varied smoothly. From the latter observations, we infer that there was no phase equilibrium II–III as had been proposed to occur[1,12,13] at a temperature of about 210 K at low pressures. Our results are thus consistent with recent structural investigations,[14] heat capacity measurements on very pure material,[16] and phase transition studies.[11]

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 are given in Table I. Figure 3

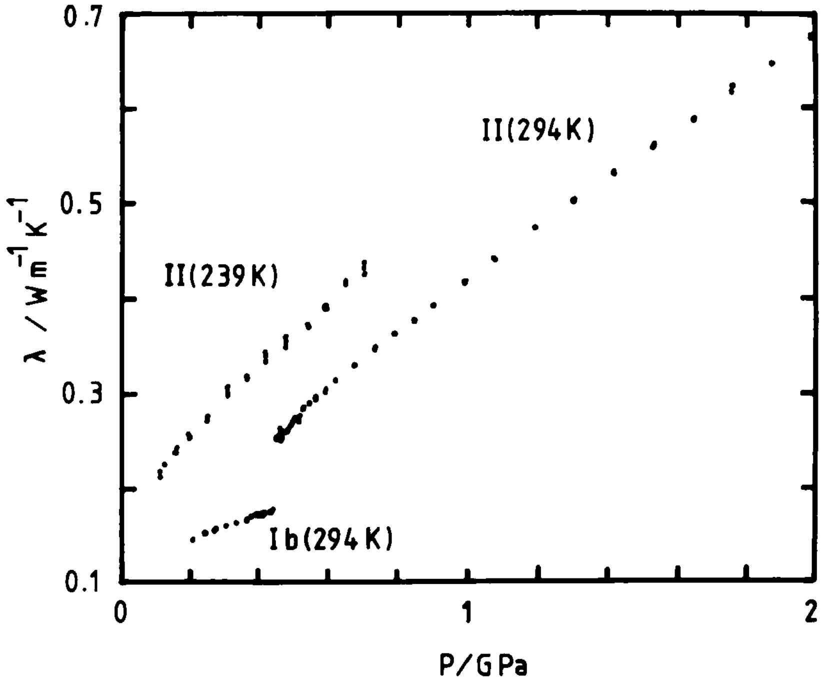

FIGURE 2 Isothermal variation with pressure of thermal conductivity, λ, for solid phases of 1,1,1-trichloroethane. Temperature is given in parentheses after each phase symbol.

TABLE I

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

Phase	*A*	*B*	*C*	*T*/K	*P*/GPa
Ib	0.122	0.125	—	294	0.21–0.44
II	0.104	0.349	−0.031	294	0.45–2.0
II	0.171	0.433	−0.091	239	0.11–0.70

and Table II provide the corresponding information for *r*(*T*). Our reasons for employing the quantity *r* in relation to temperature dependence were given in Section 1. There are no other published data for thermal conductivity of the solid phases with which our results could be compared.

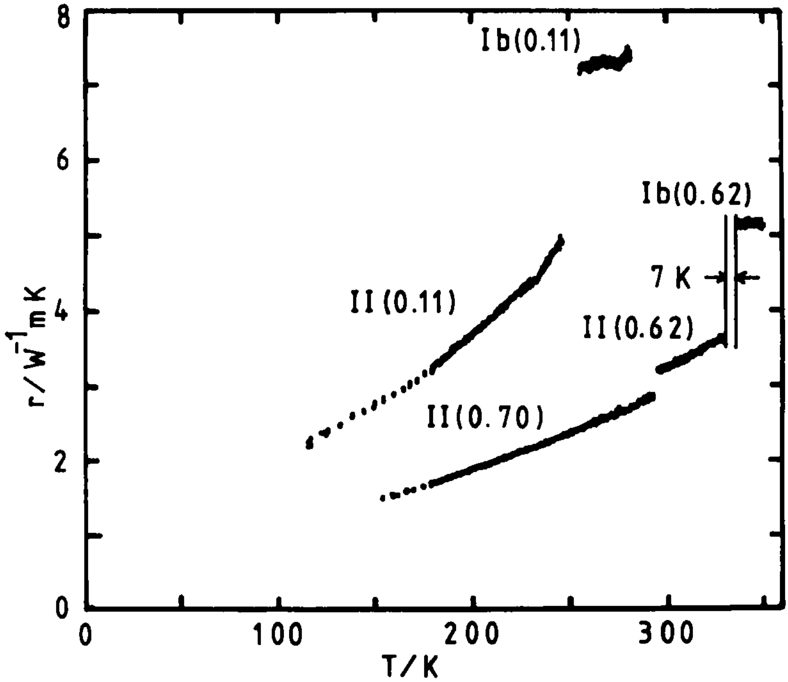

FIGURE 3 Isobaric variation with temperature of thermal resistivity, *r*, for solid phases of 1,1,1-trichloroethane. Pressure in GPa is given in parentheses after each phase symbol.

TABLE II

Isobaric temperature dependence of thermal resistivity r for solid phases of 1,1,1-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
Ib	5.97	$4.95 \cdot 10^{-3}$	—	0.11	255-282
Ib	5.15	—	—	0.62	337-350
II	1.74	$-2.70 \cdot 10^{-3}$	$6.19 \cdot 10^{-5}$	0.11	115-244
II	−0.67	$1.30 \cdot 10^{-2}$	—	0.62	295-330
II	0.72	$2.65 \cdot 10^{-3}$	$1.58 \cdot 10^{-5}$	0.70	154-292

As described in Section 2, we used various procedures and changes of variable in comparing the thermal conductivities of liquid and plastic crystal phase Ib. The results for $\lambda_{\mathrm{Ib}}/\lambda_{\mathrm{liquid}}$ are:

1.06, (T = 294 K, P = 0.15 GPa), (isothermal compression),
1.04, (T = 280 K, P = 0.11 GPa), (isobaric heating and cooling),
1.07, (T = 238 K, P = 0.10 MPa), (extrapolation).

From these results we infer that λ_{Ib} is only about 5% greater than $\lambda_{\mathrm{liquid}}$ at co-existence.

3.3 Heat capacity

Our results for the heat capacity per unit volume are shown in Figures 4 and 5. As described in Section 2, λ and ρc_p were measured simultaneously. As a result, the data points shown in Figures 2 and 4, and in Figures 3 and 5, in general correspond to identical sets of observations with two exceptions. One exception occurs for our results for $\rho c_p(T)$ of phase II at 0.70 GPa, which have been omitted from Figure 5. The reason for this omission is that we find ρc_p of phase II to be essentially independent of pressure, as is evidently the case for the results shown in Figure 4. The data for ρc_p of phase II at 0.11 and 0.70 GPa would have virtually superposed over a substantial range of temperature had both been included in Figure 5, which might have been a source of confusion. Similarly, data for ρc_p for phase II at 239 K have been omitted from Figure 4 because they would have superposed with the data for phase Ib at 294 K.

We may compare our results with previous work by combining x-ray density data[14,15] with heat capacity measurements at atmospheric pressure.[16] The comparison is given in Figure 5, and shows agreement to 10% over most of the temperature range.

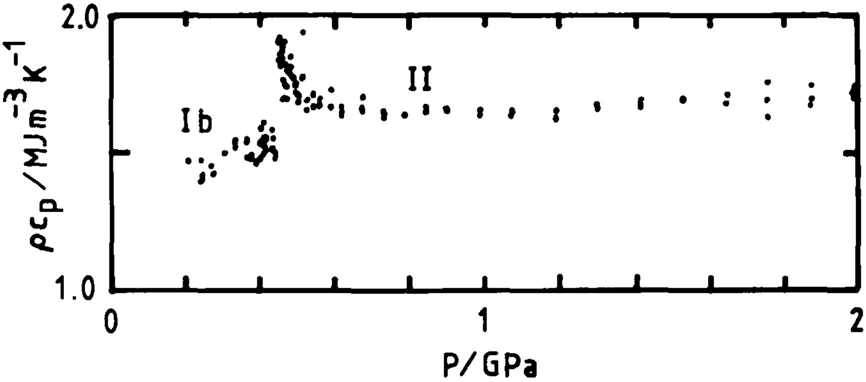

FIGURE 4 Isothermal variation with pressure of heat capacity per unit volume, ρc_p, for solid phases of 1,1,1-trichloroethane at 294 K.

It will be noted from Figures 4 and 5 that our results for ρc_p sometimes indicate exceptionally high values near phase transitions. The simultaneously-measured values of λ (or r) do not show such exceptional behaviour, as can be seen from Figures 2 and 3 respectively. It is likely on the basis of previous work[11–13,16] that this behaviour for ρc_p can be at least partially accounted

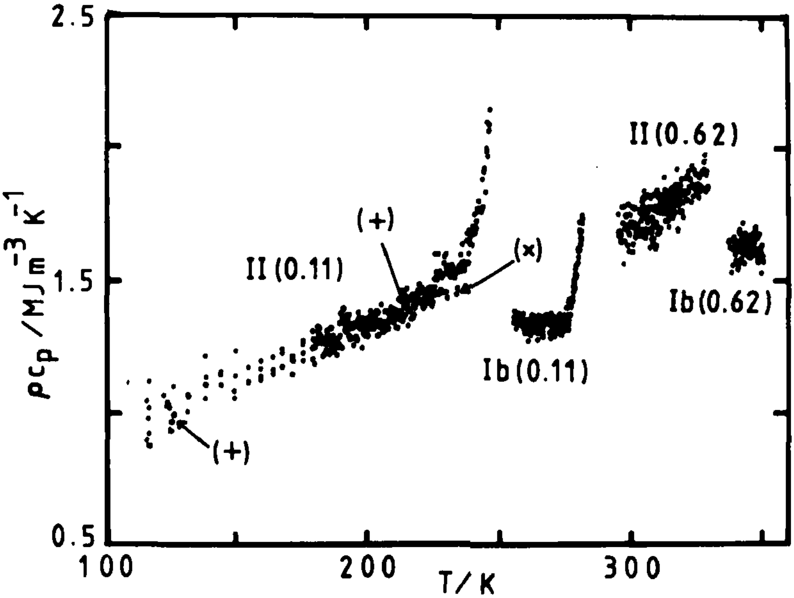

FIGURE 5 Isobaric variation with temperature of heat capacity per unit volume, ρc_p, for solid phases of 1,1,1-trichloroethane. Pressure in GPa is given in parentheses after each phase symbol. ρc_p from previous work at atmospheric pressure for phase Ib[15,16] (×), and phase II[14,16] (+).

for by the sensitivity of c_p to trace impurities. Alternatively, or additionally, exceptional behaviour for ρ may be involved, but there are insufficient data available to enable us to separate variations of ρ and c_p. If trace impurities are indeed responsible for the observed behaviour of ρc_p near phase transition, our results show that λ is not sensitive to the same extent.

4 DISCUSSION

The salient features of $r(T)$ for plastic crystal, normal and disordered normal crystal phases, were described in Section 1. We now examine how well the solid phases of 1,1,1-trichloroethane conform to our scheme of classification.

Phase Ib is known to be a plastic crystal phase, on the basis of other work.[2] Our results for $r(T)$ for phase Ib show the same behaviour as found for plastic crystal phases of other substances.[7] It can be deduced from Figure 3 and Table II that there is a major residual contribution to the total thermal resistivity; term D of Eq. (1) contributes about 80–85% of the total measured r at $T = 270$ K and $P = 0.11$ GPa. It can be similarly seen that $r(T)$ for this phase has a small temperature dependence, and, as noted in Section 3.2, the increase of r on transition to the liquid state is only about 5%.

Previous structural investigations[14] indicate that phase II is a normal crystal phase. It can be seen from Figure 3 that $r \propto T$ is a good approximation for this phase under most conditions. The more rapid increase of r with T evident from the Figure at 0.11 GPa and the highest temperatures may be plausibly attributed mainly or entirely to the effects of thermal expansion, since r increases with increase of volume, as may be deduced from Figure 2. It would be of interest to determine whether similar but less pronounced behaviour would still be found if data were adjusted to correspond to isochoric conditions.[17] Unfortunately, such an adjustment cannot be undertaken at present, since only limited thermal expansivity[14] and no compressibility data are available.

We may conclude that the measured behaviour of $r(T)$ is consistent with regarding phase Ib as a plastic crystal and phase II as a normal crystal phase, in agreement with other work.

It was noted that r increased by only about 5% on transition from phase Ib to the liquid phase. On the other hand, it may be deduced from Figure 3 that r increased by about 40–50% on transition from phase II to phase Ib. Although no theoretical model is yet available for the thermal conductivity of a plastic crystal phase, we may infer from our observations that the loss of long-range orientational periodicity on transition from a normal to a plastic crystal phase is evidently of much greater importance in connection with the conduction of heat than the additional loss of long-range translational periodicity of molecular centres on transition from a plastic crystal to a liquid phase.

5 CONCLUSIONS

Only phases Ib and II of 1,1,1-trichloroethane were detected at temperatures in the range 115 to 350 K and at pressures up to 2 GPa at room temperature. Our results for the thermal resistivity are consistent with regarding phase Ib as a plastic crystal phase and phase II as a normal crystal phase, in agreement with other work.

NOTE ADDED IN PROOF

Only stable phases Ib and II, and metastable phase Ia, were detected in a recent investigation by H. Saint-Guirons and P. Xans, *J. Phys. C: Solid State Phys.*, **13**, L535 (1980).

Acknowledgment

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