

Calculation of thermodynamic quantities for carbon tetrachloride (CCl_4) close to the III-IV phase transition

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Abstract—We calculate the thermal expansion α_p , isothermal compressibility κ_T and the specific heat, C_p-C_v , as a function of pressure using the observed V-P data at room temperature close to the III-IV phase transition in CCl_4 . Calculated κ_T , α_p and C_p-C_v decrease as the pressure increases from phase III to phase IV in this molecular crystal system, as expected. On the basis of our calculations of the κ_T , α_p and C_p-C_v , the Pippard relations are established close to the III-IV phase transition in CCl_4 , which can be verified experimentally.

Key words: Pippard Relations, Phase Transition, CCl_4

INTRODUCTION

CCl_4 exhibits four phases under temperature and pressure conditions [1-4]. At zero pressure and 230.5 K, carbon tetrachloride is a disordered plastic crystal. As the temperature decreases, this solid phase transforms into the phase I with a disordered rhombohedral crystal structure. At 225.5 K, below the melting point, phase I is transformed into phase II with a monoclinic structure. Under the compression of 0.13 GPa, at room temperature (300 K), the liquid phase solidifies to the phase I, which is transformed into the phase II at 0.4 GPa and into the phase III at 0.7 GPa with a monoclinic structure. At a higher pressure of above 2 GPa at 520 K, III-IV phase transition occurs [3], as also observed by Raman spectroscopy [5,6].

Among those phases, phase I occurs by cooling at atmospheric pressure, the liquid freezes as the I_a or I_b phase [1,7] with crystal structures of face-centered cubic and rhombohedral, respectively. I_a as a metastable phase melts at 245 K and I_b melts at 250 K [8-11] as a stable phase, which transforms into the orientationally ordered phase II below 225 K, as stated above. Thus, there exist dual melting curves for I_a/L and for I_b/L , which diverge as the temperature and pressure increase [12]. Both I_a and I_b crystals are plastic crystals with positionally ordered and orientationally disordered molecules, as pointed out previously [12], whereas the low temperature phase II has the fully ordered structure. The solid phase III is stable under pressure, which is a highly birefringent phase, whereas a nonbirefringent phase IV has a highly symmetric structure [3]. It has been reported that the crystal structure of phase IV has not been determined yet [6]. The solid phases of I, II and III, and the liquid phase (L) have been obtained experimentally in the T-P phase diagram [2], as also given in Fig. 1. Dual melting curves for the I_a -liquid and I_b -liquid, and also curve for the II- I_b transition have been determined in the experimental T-P phase diagram [13]. An experimental V-P phase diagram showing the solid phases III and IV in CCl_4 has been given in a previous study [6].

Phase transitions among the various phases in carbon tetrachlo-

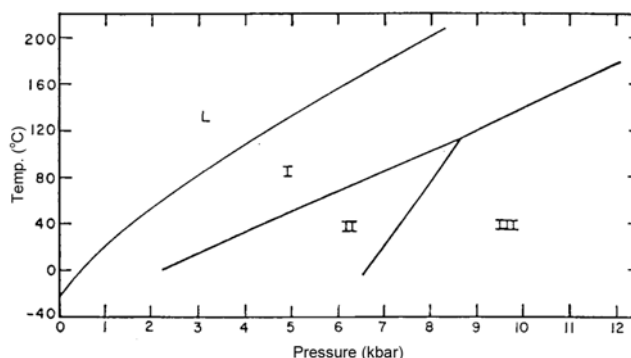


Fig. 1. Experimental T-P phase diagram of CCl_4 [2].

ride have been studied using different experimental techniques. Differential thermal analysis (DTA) [7,11,14], calorimetry [8-10,15], X-ray diffraction [1-3], birefringence [16], Raman [6,17] and Brillouin scattering [18,19] have been used to investigate experimentally the phase transition in CCl_4 .

It has been observed that CCl_4 like some other molecular crystals exhibits a second-order phase transformation prior to melting [20]. It has also been pointed out that the thermodynamic quantities such as the thermal expansion α_p , isothermal compressibility κ_T and the specific heat C_p diverge as approaching the melting point in these molecular crystals [20]. The critical behavior of those thermodynamic quantities can be described by a power-law formula near the melting point and they can be correlated with each other linearly. By analyzing the experimental data for the thermal expansion at various pressures in CCl_4 [20], we have related α_p to κ_T and also the specific heat C_p to α_p (Pippard relations) near the melting point for the solid phase [21] and for the liquid phase [22] in this molecular crystal. We have also calculated the temperature and pressure dependence of the molar volume of CCl_4 close to the melting point in our recent study [23].

In this study, we analyze the observed data for the pressure dependence of the volume for the III-IV phase transition in CCl_4 and we construct the linear relations among the thermal expansion α_p ,

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isothermal compressibility κ_T and the specific heat C_p in this molecular system.

Below, we give our calculations for the pressure dependence of α_p , κ_T and C_p in section 2. We discuss our results in section 3. Conclusions are given in section 4.

CALCULATIONS AND RESULTS

We analyzed here the observed volume data [6] at various pressures close to the III-IV transition in CCl₄ according to

$$V=a+bP+cP^2 \quad (1)$$

Values of the coefficients a , b and c from our fit, are given in Table 1. Fig. 2 gives the experimental volume values [6] at various pressures close to the III-IV transition in CCl₄.

The pressure dependence of the isothermal compressibility $\kappa_T \equiv -(1/V)(\partial V/\partial P)_T$ can be obtained from Eq. (1) close to the III-IV transition in CCl₄, which we plotted for the III and IV phases of CCl₄, as given in Fig. 3. A straight line gives the slope and the intercept according to

$$\kappa_T=a_0+a_1P \quad (2)$$

in both phases III and IV of CCl₄, which we tabulate in Table 2.

Table 1. Values of the coefficients a , b and c according to Eq. (1) which was fitted to the observed volume data [6] for the phases III and IV in CCl₄

Phase	a (\AA^3)	$-b$ ($\text{\AA}^3/\text{GPa}$)	c ($\text{\AA}^3/\text{GPa}^2$)
III	132.76	19.86	3.61
IV	117.73	6.63	0.48

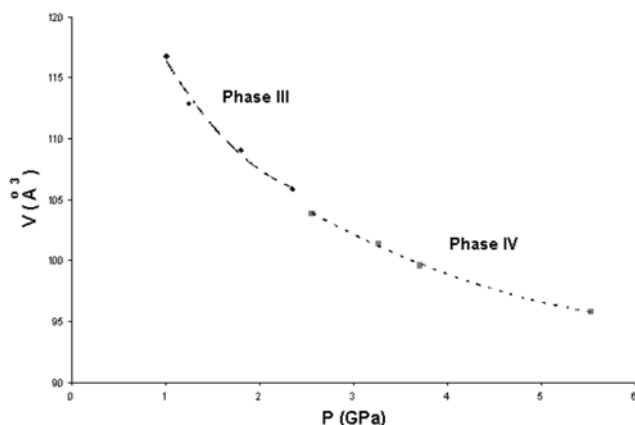


Fig. 2. Pressure dependence of volume of a molecule for the phases III and phase IV. Dotted curves give fits to the experimental data [6] according to Eq. (1).

Table 2. Values of the coefficients for the isothermal compressibility κ_T , the thermal expansion α_p and the difference in the specific heat $C_p - C_v$, according to Eqs. (2), (4), (5), respectively, close to III-IV phase transition in CCl₄

Phase	κ_T (GPa^{-1})		α_p (K^{-1})		$C_p - C_v$	
	a_0 (GPa^{-1})	a_1 (GPa^{-2})	b_0 (K^{-1})	$-b_1$ (K^{-1}/GPa)	c_0 ($\text{J}/(\text{mol} \cdot \text{K})$)	$-c_1$ ($\text{J}/(\text{mol} \cdot \text{K} \cdot \text{GPa})$)
III	0.17	0.06	17.02	6.03	0.60	0.22
IV	0.06	0.01	6.35	0.90	0.20	0.03

The thermal expansion α_p can also be calculated using the thermodynamic relation

$$\alpha_p/\kappa_T = dP/dT \quad (3)$$

where $\alpha_p \equiv (1/V)(\partial V/\partial T)_P$ and dP/dT denotes the slope in a P-T phase diagram. Using the experimental value of $dP/dT = 10 \text{ MPa/K}$ for CCl₄ [20], the pressure dependence of the thermal expansion α_p was calculated according to Eq. (3). The thermal expansion α_p was plotted as shown in Fig. 4 at various pressures as straight lines in both phases III and IV separately according to

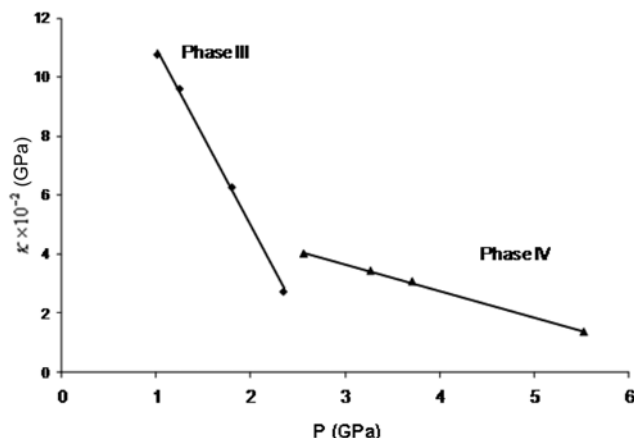


Fig. 3. The isothermal compressibility κ_T calculated as a function of pressure from Eq. (1) for the phases III and IV in CCl₄. Straight lines are drawn according to Eq. (2) with the coefficients a_0 and a_1 , as given in Table 2.

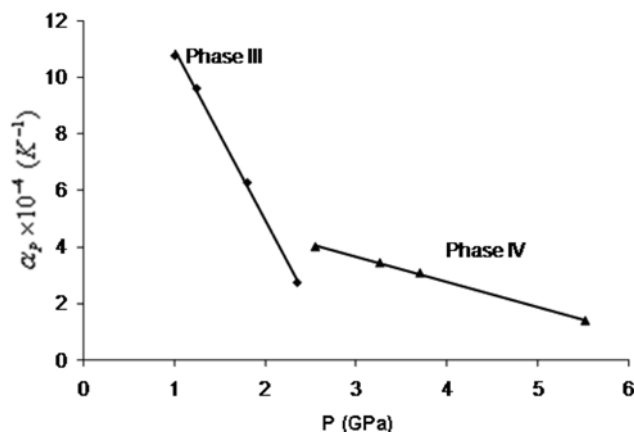


Fig. 4. The thermal expansivity α_p calculated as a function of pressure from Eq. (3) for the phases III and IV in CCl₄. Straight lines are drawn according to Eq. (4) with the coefficients b_0 and b_1 , as given in Table 2.

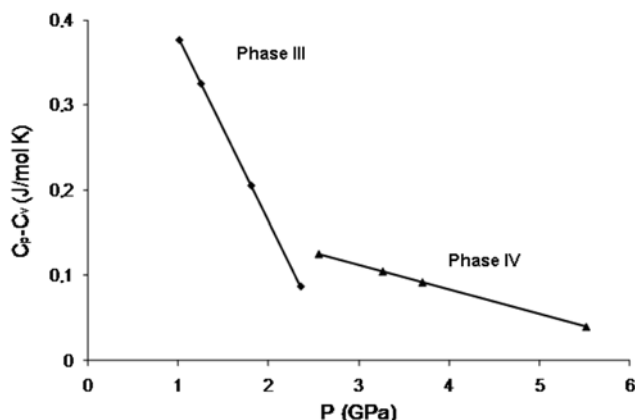


Fig. 5. The specific heat difference $C_p - C_v$, calculated as a function of pressure from Eq. (5) for the phases III and IV in CCl_4 . Straight lines are drawn according to Eq. (6) with the coefficients c_0 and c_1 , as given in Table 2.

$$\alpha_p = b_0 + b_1 P \quad (4)$$

with the coefficients b_0 and b_1 for both phases in CCl_4 , which we give in Table 2.

Finally, we calculated the pressure dependence of the specific heat using the thermodynamic equation

$$C_p - C_v = T V \alpha_p^2 / \kappa_T \quad (5)$$

for the phases III and IV in CCl_4 . Using the observed volume data [6], and our calculated α_p and κ_T values, the difference in the specific heat $C_p - C_v$ was calculated for the phases III and IV as a function of pressure at room temperature ($T=300$ K). This was plotted according to a linear relation

$$C_p - C_v = c_0 + c_1 P \quad (6)$$

with the coefficients c_0 and c_1 , as given in Table 2. Our plot is shown in Fig. 5.

Since we calculated the thermal expansivity α_p , isothermal compressibility κ_T and the specific heat ($C_p - C_v$) as a function of pressure for the phases III and IV in CCl_4 , the Pippard relations can be examined for this crystalline system. Thus, we can write the Pippard relations as

$$C_p = T V (dP/dT) \alpha_p + T (dS/dT)_t \quad (7)$$

and

$$\alpha_p = (dP/dT) \kappa_T + 1/V (dV/dT)_t \quad (8)$$

close to the III-IV phase transition in CCl_4 . In Eqs. (7) and (8), $(dS/dT)_t$ and $(dV/dT)_t$ represent the variation of the entropy and volume with the temperature at the transition point t , respectively. Thus, a linear plot of the specific heat C_p against the thermal expansivity α_p gives the values of the slope and the intercept according to Eq. (7). Using the thermodynamic relations (Eqs. (3) and (5)), the specific heat at constant volume C_v through the first Pippard relation (Eq. (7)) corresponds to

$$C_v = T (dS/dT)_t \quad (9)$$

at the transition temperature for the III-IV phase transition of CCl_4 .

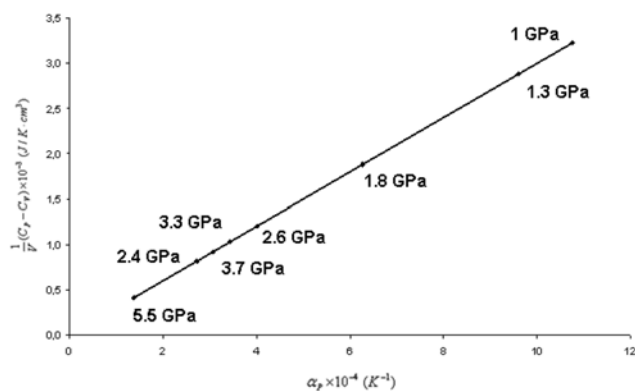


Fig. 6. Variation of the $(C_p - C_v)/V$ with the α_p according to the first Pippard relation (Eq. (7)) close to the III-IV phase transition in CCl_4 .

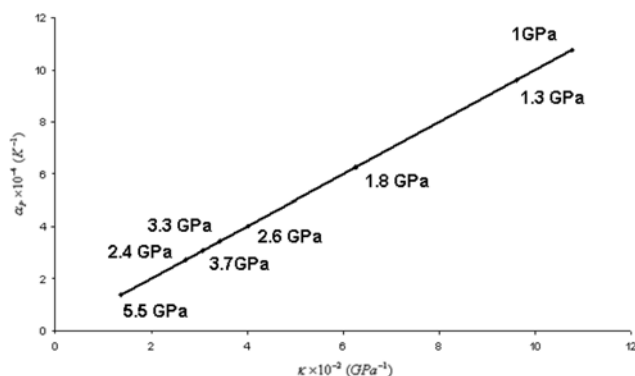


Fig. 7. Variation of the thermal expansivity α_p with the isothermal compressibility κ_T according to the second Pippard relation (Eq. (8)) close to the III-IV phase transition in CCl_4 .

Similarly, a linear plot of the thermal expansivity α_p against the isothermal compressibility κ_T can be constructed according to Eq. (8). Figs. 6 and 7 give our linear plots of $(C_p - C_v)/V$ vs. α_p and α_p vs. κ_T , respectively, close to the III-IV phase transition in CCl_4 . From both linear plots (Eqs. (7) and (8)), we obtained the slope value of $dP/dT = 10$ MPa/K for CCl_4 .

DISCUSSION

We analyzed here the pressure dependence of the observed volume [6] for the III-IV phase transition in CCl_4 , which exhibited an abrupt change, as also observed in optical properties in polarized light [3]. The highly birefringent phase III is transformed into a non-birefringent phase IV rapidly at temperatures above 250°C and 20 kbar, as pointed out previously [3]. On the contrary, Ebisuzaki has indicated that the Raman spectra do not give a clear evidence of the III-IV transition in CCl_4 under isothermal compression of 300 K [24].

We calculated in this study the pressure dependence of the isothermal compressibility κ_T , thermal expansion α_p and the specific heat ($\Delta C = C_p - C_v$) near the III-IV phase transition in CCl_4 . For this calculation, we used the V-P data [6] at various high pressures ($T = 300$ K). The pressure dependence of κ_T , α_p and $C_p - C_v$ was obtained

as linear plots (Figs. 3-5) according to Eqs. (2), (4) and (6), respectively (Table 2). For our calculations of α_p and $C_p - C_v$, we used the experimental value of $dP/dT = 10$ MPa/K [20]. We then established the Pippard relations (Eqs. (7) and (8)) close to the III-IV phase transition in CCl₄, as plotted in Figs. 6 and 7. As expected, we obtained the same slope value for dP/dT from our linear plots (Figs. 6 and 7). This shows that the Pippard relations can be applied to the III-IV phase transition which occurs at high pressures in CCl₄. Variation of the specific heat with the α_p (Eq. (7)) and also the variation of the thermal expansion α_p with the isothermal compressibility κ_T (Eq. (8)) linearly, indicates that those thermodynamic quantities (C_p , α_p and κ_T) exhibit similar critical behavior close to the III-IV phase transition in CCl₄.

The pressure dependence of our calculated κ_T , α_p and $C_p - C_v$, using the V-P data [6], which were plotted in Figs. 3-5 and α_p vs. κ_T (Fig. 4) can be tested by the experimental measurements in phases III and IV of CCl₄. From the experimental measurements, one would also examine the applicability of the Pippard relations (Eqs. (7) and (8)) to CCl₄ experimentally, as we calculated in this study (Figs. 6 and 7).

CONCLUSIONS

The transition between the solid phases III and IV was studied in CCl₄ using the experimental volume data. The thermodynamic quantities, namely, the thermal expansion, isothermal compressibility and the specific heat, were calculated as a function of pressure at room temperature close to the III-IV phase transition in this molecular crystal. From linear plots of those thermodynamic quantities, the Pippard relations were constructed for the III-IV phase transition in CCl₄. These relations can be verified experimentally.

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