

A HIGH PRESSURE N.M.R. INVESTIGATION OF THE SOLID METHANES.  
- THE LOW TEMPERATURE PHASE TRANSITION OF  $\text{CH}_4$  -

A.J. Nijman and N.J. Trappeniers

Van der Waals-laboratory, University of Amsterdam, Valckenierstraat 67, Amsterdam.

**Abstract.** The proton spin-lattice relaxation time  $T_1$  of  $\text{CH}_4$  is measured as a function of pressure and temperature. The low temperature phase transition ( $\beta$ - $\gamma$ ) is detected by a discontinuity in  $T_1$ . The P.vs.T plot of this phase transition is strongly curved and the transition pressure shows a minimum as a function of temperature.

1. **Introduction.** All deuterated methanes exhibit two phase transitions at zero pressure.  $\text{CH}_4$  at zero pressure has a phase transition ( $\alpha$ - $\beta$ ) at  $20.4^\circ\text{K}$ . There is disagreement about a second phase transition at around  $8^\circ\text{K}$  (M. Bloom and J.A. Morrison). Golwell et al. found a thermal inertia in the temperature region below  $10^\circ\text{K}$ . They describe this phenomenon as a phase transition ( $\beta$ - $\gamma$ ) analogous to the low temperature phase transitions in the deuterated methanes. Another explanation was that this anomaly is caused by interconversion between the three spinisomers of  $\text{CH}_4$ . The first explanation was favoured for three main reasons. Firstly, high pressure studies showed two phase transitions at considerable pressure. When the phase line of the low temperature transition is extrapolated to zero pressure one gets a transition temperature of about  $10^\circ\text{K}$ . Secondly, it was known that mixtures of  $\text{CH}_4$  and  $\text{CD}_4$  exhibit two phase transitions (E. Bartholomé et al.). The dependence of the transition temperatures upon composition suggested a phase transition in pure  $\text{CH}_4$  below  $10^\circ\text{K}$ . In the third place the entropy of the thermal inertia was estimated to be  $0.58 \text{ cal mol}^{-1} \text{ deg}^{-1}$ . This value is very much less than  $R \ln 16$  which corresponds to complete interconversion between the spinisomers. The authors decided to start high pressure measurements of  $T_1$  to elucidate the methane phase diagram and to get information about the molecular dynamics in the  $\beta$  and  $\gamma$  phase.

2. **Experimental and Results.** The proton spin-lattice relaxation time  $T_1$  in  $\text{CH}_4$  is measured with an n.m.r. pulse spectrometer at a working frequency of 28.8 Mhz using a  $10 \times 90^\circ - \tau - 90^\circ$  pulse sequence. A C.D.C. 1700 computer generates the pulse sequences and calculates  $T_1$ . The measurements on solid methane are performed on a very pure polycrystalline sample contained in a high pressure vessel of beryllium copper. The variable temperature cryostat in which the pressure vessel is contained ensures a temperature constant to within  $0.01^\circ\text{K}$ . The temperature is measured with a calibrated platinum resistance thermometer. Corrections for the magnetic field are carried out. The estimated accuracy of the temperature is within  $0.05^\circ\text{K}$ . Special provisions are made to minimize temperature gradients along the pressure vessel. The pressure, generated by a combination of a hydraulic oil compressor and a mercury piston gas compressor, is measured with a calibrated manometer with an accuracy of the order of  $5\%$ . Hydrostatic pressure is applied to the  $\text{CH}_4$  sample by using fluid helium as a pressurizing medium. The measurements of  $T_1$  are carried out at constant temperature. The phase transformation is detected by a discontinuity of  $T_1$  as a function of pressure. Measurements of  $T_1$  at a given constant pressure and temperature require several hours, because the  $\beta$ - $\gamma$  transition takes a very long time to complete, especially at low temperatures (about two days at  $8^\circ\text{K}$ ). The authors assume that the phase is stable when  $T_1$  is constant within 1% during two hours.  $T_1$  is measured during another period of two hours if there occurred a change exceeding 1%. This procedure is repeated till there is a total change of at least 10%. Fig. 1 shows a typical example of  $T_1$  as a function of pressure. In fig. 2 the resulting phase diagram together with the He melting curve is displayed.

The  $\beta$ - $\gamma$  transition has several very unusual and remarkable properties. First of all the P.vs.T plot of the transition line as measured with decreasing pressure is strongly curved and the transition pressure shows a minimum as a function of temperature. Secondly the hysteresis of

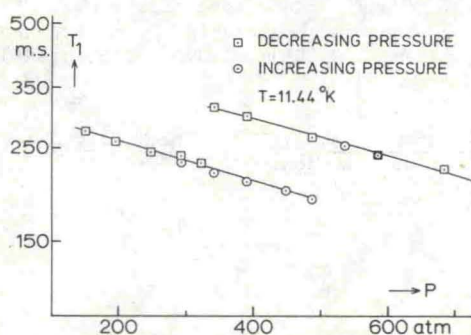


Fig. 1  $T_1$  as a function of pressure

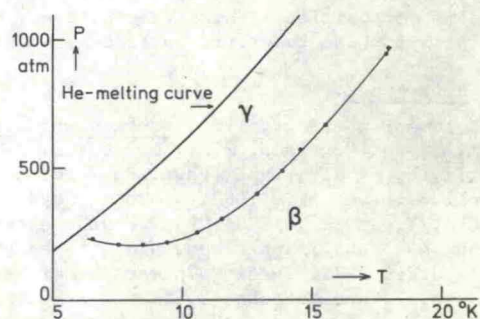


Fig. 2 Phase diagram of  $\text{CH}_4$  (decreasing pressure).

the transition pressure at low temperatures is much larger than at high temperatures. In the third place there is also a discontinuity in the proton magnetic susceptibility  $\chi_0$  at the phase transition. This discontinuity disappears at high temperature.

3. Discussion. The  $\beta$ - $\gamma$  transition shows a very unusual behaviour, which can only be understood by considering  $\text{CH}_4$  as a quantum mechanical alloy of ortho, para and meta methane. If the composition of the alloy would remain constant it could be expected that the  $\beta$ - $\gamma$  phase line is a nearly straight line. The alloy at high temperatures has a constant composition as given by the classical equilibrium conditions (in the ratio 5:9:2) and is called normal alloy. Thus a nearly straight phase line has to be expected at high temperatures. The lowest energy levels of the  $\text{CH}_4$  librator, the only populated levels at low temperature, depend strongly on the crystal structure. Thus the composition of the alloy depends on the phase in the low temperature region. This explains the discontinuity of  $\chi_0$  at the phase transition. The foregoing argument explains also the fact that the discontinuity of  $\chi_0$  disappears at high temperatures. On the other hand the concentration of the meta spin species grows with decreasing temperature because the ground state of the  $\text{CH}_4$  librator belongs to the meta spinisomer. It is also known that meta methane is more difficult to orient (T. Yamamoto and Y. Kataoka) in a crystalline field than ortho or para methane. Thus an alloy, which is rich in the meta spin species, needs a stronger crystalline field to reach the  $\gamma$  phase because this phase has a higher degree of order than the  $\beta$  phase. Applying more pressure is the only way in this case to achieve a stronger crystalline field. This effect causes the curvature of the P.-vs.-T plot of the  $\beta$ - $\gamma$  phase transition. The curvature is so strong that it causes a minimum pressure of the phase transition as illustrated in fig. 2.

An important conclusion can be drawn: all zero pressure measurements on solid  $\text{CH}_4$  below  $20^\circ\text{K}$  are carried out in  $\beta$  phase methane. For example the susceptibility measurements of Piott are explained very well by using the  $\beta$  phase structure (one out of four molecules is a nearly free rotator; the other molecules are oriented) and the level scheme of Glättli et al. for the oriented molecules. The level scheme is interpreted here according to Y. Kataoka et al. It is possible to explain the hysteresis of the  $\beta$ - $\gamma$  phase transformation by a coupling between the concentrations of the spinisomers and the phase transition. An alloy that minimizes the Gibbs potential of the  $\beta(\gamma)$  phase is called a  $\beta(\gamma)$  alloy. The  $\gamma$  phase of the  $\gamma$  alloy is the thermodynamic stable situation at elevated pressures as is illustrated in fig. 3. The  $\beta$  phase of the  $\beta$  alloy is the thermodynamic stable condition for  $\text{CH}_4$  if the pressure falls below  $P_L$ . However, there is no way to reach the  $\beta$  phase at pressures between  $P_L$  and  $P_M$  (fig. 3) because now the Gibbs potential at a given pressure and temperature has a relative minimum for the  $\gamma$  phase of the  $\gamma$  alloy. This can be seen in the following way: the Gibbs potential increases if the  $\gamma$  phase converts into  $\beta$  phase while the alloy remains  $\gamma$  alloy ( $4 \rightarrow 1$  in fig. 3). The Gibbs potential grows also if only the  $\gamma$  alloy converts into  $\beta$  alloy ( $4 \rightarrow 3$  in fig. 3). Thus the  $\gamma$  alloy together with  $\gamma$  phase is metastable between  $P_L$  and  $P_M$ . The  $\gamma$ - $\beta$  phase transition becomes possible at pressures below  $P_L$ , because at a transition from  $\gamma$  phase to  $\beta$  phase G decreases. ( $4 \rightarrow 1 \rightarrow 2$  in fig. 3). The same line of argument applies at increasing pressure. The  $\beta$ - $\gamma$  phase transition takes place at  $P_H$  in that case (fig. 3). This mechanism should give a large hysteresis at low temperatures because the compositions of the two alloys are quite different there. The hysteresis should vanish at high temperatures because both alloys have the same composition at high temperatures. More information about the hysteresis, T<sub>1</sub> measurements and the  $\alpha$ - $\beta$  phase transition will be given in a following paper (A.J. Nijman, N.J. Trappeniers).

#### 4. References.

- Bartholomé E., et al., 1938, Surface and defect properties of solids, Z. Phys. Chem. B39, 371.  
 Bloom, M. and Morrison, J.A., 1973, Vol. 2, The chemical society, London.  
 Glättli, H. et al., 1972, Phys. Rev. Letters 28, 871.  
 Golwell, J.H. et al., 1963, J. Chem. Phys. 39, 635.  
 Kataoka, Y. et al., 1973, Chem. Phys. Letters 19, 365.  
 Nijman, A.J. and Trappeniers, N.J., to be published.  
 Piott, J.E., 1971, Thesis, University of Washington.  
 Yamamoto, T. and Kataoka, Y., 1968, J. Chem. Phys. 48, 3198.

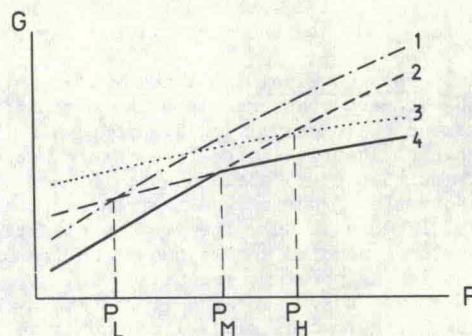


Fig. 3 The Gibbs potential at constant temperature

- 1:  $\beta$  phase and  $\gamma$  alloy
- 2:  $\beta$  phase and  $\beta$  alloy
- 3:  $\gamma$  phase and  $\beta$  alloy
- 4:  $\gamma$  phase and  $\gamma$  alloy