# EXPERIMENTAL OBSERVATION OF SECOND PHASE TRANSITION IN SOLID $CH_4$

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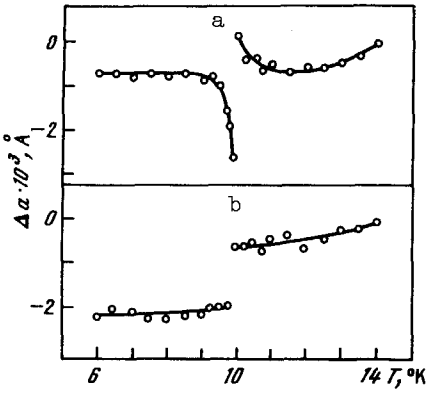
Precision x-ray investigations of the temperature dependence of the lattice parameter of methane were performed in the interval 6 - 14°K. A volume jump of approximately 0.15% was observed at T = 9.9 ± 0.2°K.

The problem of the second phase transition in solid $CH_4$ was raised following the first studies of the specific heat of methanes [1 - 5], when it was observed that at T > 10°K ordinary methane, unlike partly and fully deuterated methane ($CH_nD_{n-4}$, n = 0, 1, 2, 3), have only one polymorphic transition with $T_c$ = 20.4°K. Subsequent calorimetric measurements [6, 7] have revealed the presence of a second phase transition in $CH_4$ at pressures higher than 200 atm, with $T_c$ increasing linearly with increasing pressure. A phase transition in methane at 8°K and at equilibrium vapor pressure, reported in [8], was doubted in [9], in which it sas shown that the thermal anomaly observed in the region of 8°K could be due to conversion between three spin modifications of methane (ortho, para, and meta; see also [10, 11]). Although observation of birefringence again suggested the presence of a second transition in solid methane, the question of its real existence still remains open at present. Under the present situation, only direct structure investigations can answer this question unequivocally. We have therefore performed precision x-ray measurements of the temperature dependence of the lattice parameter of polycrystalline $CH_4$ samples in the interval 6 - 14°K. The measurements were made with a URS-50 IM diffractometer. Samples 0.1 - 0.2 mm thick were condensed from the gas phase on a copper substrate cooled to 6°K and were annealed for an hour at T = 30°K. A high measurement accuracy was obtained because the diffraction patterns contained, besides the $CH_4$ lines, also reflections from the copper substrate, and this made it possible to trace the temperature variation of the lattice parameter of the $CH_4$ relative to the parameter of copper, which hardly varied with temperature. Since the photographs and diffraction patterns for $CH_4$ revealed at all temperatures, just as in [14, 13], only FCC lattice reflections, we confined the investigation to the behavior of the relative angular position of two sufficiently close lines, (311)$CH_4$ and 200 Cu. The measurement results for a sample containing 0.01 - 0.02% $O_2$[1)] are shown in Fig. a. It is seen clearly that an approximate volume jump of 0.15% takes place at 9.9 ± 0.2°K. The temperature of the observed phase transition coincides, within the limits of errors, with the value 10°K obtained by extrapolating the $T_c$ dependence of [6] from the high-pressure region. Practically identical curves were obtained in several experiments in which the samples were either heated or cooled. The fact that the parameter remained unchanged after keeping the samples at several points on the curve for three hours indicates that an equilibrium spin-modification composition exists for each temperature. According to our observations, this time was sufficient to establish an equilibrium concentration of the modifications in the initial point 6°K. In analogy with $CD_4$ [15, 16] and the data of [12], it can be assumed that the phase transition in methane is connected with complete orientational ordering of the molecules, and this should lead to a small, experimentally unobservable tetragonality of the lattice. This state, however, exists in a narrow temperature range and apparently goes over into the intial state, or into a com-




[1)] According to the data of [10, 11], the rate of conversion in methane is quite sensitive to the presence of the $O_2$ impurity.

pletely disordered state as a result of the rapid growth of the meta-modification concentration (S = 2) with decreasing temperature. The possibility of the latter transition was discussed earlier in [17, 18]. The increase of the lattice parameter as a result of the increased meta-modification concentration [19] was observed in our experiments starting approximately with 12°K, which agrees with data on neutron scattering [20], which show that this value of T corresponds to a minimum content of the meta-modification. The influence of the conversion on the behavior of the lattice parameter in the temperature interval investigated by us becomes quite clearly pronounced when the obtained curve is compared with the plot for samples containing several thousandths of a per cent of $O_2$ (Fig. b). At the low conversion rates typical of these oxygen concentrations, the $\Delta a(T)$ plot does not show the sections with negative expansion coefficient, which are typical of equilibrium samples.

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[1] K. Clusius, Z. Phys. Chem. B3, 41 (1929).
[2] E. Bartholome, G. Drikos, and A. Euken, Z. Phys. Chem. B39, 371 (1938).
[3] K. Clusius, L. Popp, and A. Frank, Physica 4, 1105 (1937).
[4] A. Frank, K. Clusius, Z. Phys. Chem. B36, 291 (1937).
[5] K. Clusius and L. Popp, Z. Phys. Chem. B46, 63 (1940).
[6] O. N. Trapeznikova and G. A. Miljutin, Nature 144, 632 (1939).
[7] J. S. Roesenshein and W. M. Whitney, IEEE Proc. LT-9, 1114 (1965).
[8] J. H. Colwell, E. K. Gill, and J. A. Morrison, J. Chem. Phys. 36, 2223 (1962); 39,635(1963).
[9] H. P. Hopkins, P. L. Donoho, and K. S. Pitzer, J. Chem. Phys. 47, 864 (1967).
[10] K. P. Wong, I. D. Noble, M. Blook, and S. Alexander, J. Mag. Reson. 1, 55 (1969).
[11] P. Van Hecke, P. Grobet, and L. van Gerven, J. Mag. Reson. 7, 117 (1972).
[12] E. A. Ballik, D. J. Gannon, and J. A. Morrison, J. Chem. Phys. 57, 1793 (1972).
[13] S. C. Greer and L. Meyer, Z. angew. Phys. 27, 198 (1969).
[14] J. Herczeg and R. E. Stoner, J. Chem. Phys. 54, 2284 (1971).
[15] H. M. James and T. A. Keenan, J. Chem. Phys. 31, 12 (1959)
[16] D. N. Bol'shutkin, V. M. Gasan, A. I. Prokhvatilov, and A. I. Erenburg, Zhur. Strukt. Khim. 12, 336 (1971).
[17] Y. Kataoka and T. Yamamoto, Progr. Theor. Phys. Suppl., Extra Number, 436 (1968).
[18] S. Alexander and M. Lerner, Can. J. Phys. 50, 1568 (1972).
[19] T. Yamamoto and Y. Kataoka, Prog. Theor. Phys. Suppl. 46, 383 (1970).
[20] N. T. Johnston and M. F. Collins, J. Chem. Phys. 57, 5007 (1972).

## ELECTRON EMISSION IN THE TRANSITION TO THE SUPERPLASTICITY STATE

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Electron emission was observed when the superplastic state set in and developed in metastable eutectics.

The nature of superplasticity (SP), an extremal state of a metal, is still not clear, in spite of the extensive use of the SP effect in practice. Information on the changes of the physical properties in superplasticity is therefore of interest.

We report here observation of electron emission at the instant of the transition of the alloy Pb + 43.5%Bi into the SP state. The tension was produced at a rate $1.85\times10^{-3}$ $sec^{-1}$ at room temperature in a vacuum of $10^{-5}$ Torr. To detect the electrons, we used a VEU-1A secondary-electron multiplier. The electron emission and the tension force were registered simultaneously for samples pre-deformed by compression ($\varepsilon$ = 90%. The working part of the sample measured 20 ×3×3 mm.

The figure shows a plot of the electron emission intensity (I) on the degree of deformation ($\varepsilon$) and the elongation diagram. During the initial stage of the deformation (up to 15%), when strengthening of the sample takes place and the tension force P increases, no electron emission is observed. With further deformation, the load on the sample decreases (without formation of a neck in the sample, corresponding to the SP state) and reaches a steady-state value at an elongation 85 - 90%.

An emission current is registered at the instant when the SP sets in. Simultaneously with