X-Ray Investigation of the Structure Transition of Methane at the λPoint
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X-ray investigation of the structure transition of methane at the λ point

By Adolf Schallamach

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[Plates 11, 12]

1. Introduction

A great deal of work has been done on the crystal structure of long-chain hydrocarbons and their behaviour near transition points. These transitions are as a rule quite normal, in so far as the transition is marked by the liberation or binding of a definite heat of transformation and change in structure.

The simplest of the hydrocarbons, methane, shows a change from the ordinary behaviour. At 20·4° K a so-called transition of the second kind (Clusius and Perlick 1933) takes place, of which an abnormal rise of the specific heat is typical. This begins at low temperatures where the specific heat rises at first slowly to reach a very sharp maximum at 20·4° and then falls abruptly to somewhat normal values. No latent heat appears. The effect bears a strong resemblance to the λ point of helium and other substances.

The crystal structure of methane has been directly determined by two authors (McLennan and Plummer 1929; Mooy 1931) of whom only Mooy paid special attention to any possible change of structure at the transition point. He observed no change in the critical range. The structure is cubic face-centred according to both authors, but we would like to point out that Mooy's table contains two lines which do not belong to reflexions from that lattice and which he labelled "parasitic lines".

In view of the scarcity of data I felt justified in repeating the experiments. These were carried out in a small hydrogen liquefier as described by Ruhemann (1937) especially adapted for X-ray work. The liquefier works with an outside film. The primary and the reflected beam having each to pass only two low-absorption windows, a satisfactory photograph can be taken in 15 min. with the gas-focus tube generally used in this laboratory. This time of exposure is short compared with that recorded by previous observers. This advantage is due to the sharp focus and the correspondingly high intrinsic X-ray intensity of the gas tube which

cannot be obtained with the normal commercial tubes usually employed in this kind of work.

As a consequence of this reduced time a large number of observations can be made within a short time limit, and this proved to be important in the course of the present work. At the beginning of the investigation the new phenomenon to be described did not always show and might have remained unobserved if only a small number of photographs had been taken.

2. The liquefier

A cross-section through the complete liquefying apparatus is given in fig. 1 which is drawn to scale apart from thickness of wall. The actual liquefier is enclosed in the vacuum space 1 and consists of the heat exchanger 2, the expansion nozzle 3 and the liquid hydrogen container 4. The annular vessel 5 forms the bulb of a gas thermometer.

Liquefiers built on conventional lines are usually immersed in liquid air. It is rather cumbersome to clear a passage for X-rays through a Dewar vessel. For this reason the following arrangement is made. Vacuum enclosure 1 is surrounded by the liquid-air container 6, liquid air or nitrogen is filled in through tube 8. The bottom of 1 is closed by the corrugated cellophane diaphragm 7. A small tail of the liquid hydrogen container 4 protrudes through the cellophane diaphragm and carries the specimen holder which will be referred to later on. A hemispherical screen 9 in contact with

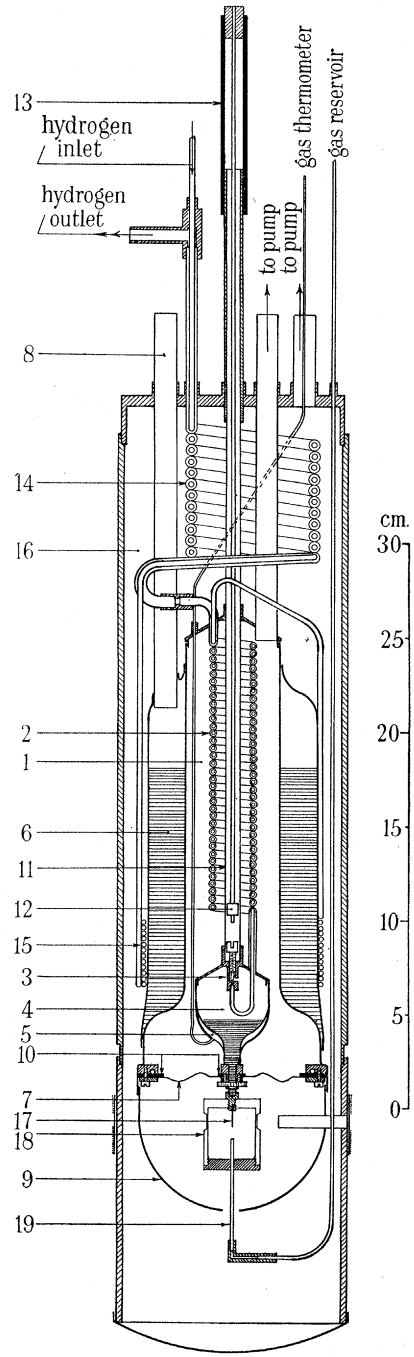


Fig. 1. Apparatus

1 shields the specimen holder from heat radiation from parts at room temperature. A slot is cut in it through which the X-rays pass.

The cellophane diaphragm 7 is a vital part of the apparatus. It bridges the temperature difference between liquid or solid hydrogen and liquid nitrogen and for this reason has to be a poor heat conductor; hence the use of cellophane. The necessary vacuum-tight joints between metal and cellophane on either side are made with india-rubber washers 10. The corrugation is necessary as plain disks break through contraction due to drying and cooling.

The nozzle 3 is worked with a key which is not in constant contact with it, and so losses through heat conduction are eliminated. This is done by enclosing the nozzle in a thin-walled german silver tube 11 which reaches right outside the apparatus. The nozzle screw has a slotted head in which a screwdriver-shaped key 12 engages. The key is normally about $\frac{1}{2}$ in. above the nozzle and is kept in this position by the rubber tube 13 which at the same time makes a tight joint with tube 11. To adjust the nozzle, the key is pressed down until it engages with the slot and the nozzle turned to the required opening. Then the key is released and goes back to its old position. The elasticity of the rubber tube is ample to allow these movements. An additional advantage of this scheme is that glands and packing systems are avoided.

The second heat exchanger 14 and coil 15 which is wound and soldered around the liquid nitrogen container 6 form the pre-cooling stage of the hydrogen. The introduction of the heat exchanger 14 materially reduces the quantity of liquid nitrogen used for liquefaction.

All parts so far described are housed in the evacuated brass tube 16 and are suspended from its lid by the various leads. There is a joint in tube 16 so that the lower part can be removed if a change of the specimen holder is necessary. A passage for the X-rays is cleared by cutting a slot in this lower part corresponding to the one in the radiation screen 9. The slot is covered with cellophane made tight with a cellulose varnish and anchored with two coils of string.

There are two vacuum systems, in 1 and in 16. The latter is always kept at the best possible vacuum. It is, however, necessary to admit a small amount of gas (helium or hydrogen at a few mm. Hg) at the beginning of an experiment in order to lower the temperature of the Linde heat exchanger to well below the inversion point. This so-called "exchange gas" is led in through a branch line which connects 1 with the exchange gas reservoir.

The vacuum leads, after passing through the lid of 16, are connected

with the vacuum system through copper-glass joints. The glass apparatus consists in each case of discharge tube, mercury trap and wide-bore tap. Both branches join in a T-piece which leads to the mercury pump. A third branch serves the auxiliary apparatus, i.e. exchange gas reservoir and gas thermometer. In this way one pump is sufficient for the whole liquefier.

Hydrogen is taken from a cylinder at 120 atm. and is available for liquefaction down to 60 atm. The hydrogen passes a charcoal cleaner immersed in liquid nitrogen and a dust trap, and then enters the liquefier. The expanded hydrogen goes through a flowmeter and then escapes into the atmosphere, or it is pumped off by a rotary pump in order to lower the temperature.

The substance under investigation is deposited on the short copper wire 17. This is attached to a small cup which fits the tail of the liquid hydrogen container 4. Gases, such as methane, have to be condensed from the gas phase. For this reason the specimen holder is enclosed in a cylindrical screen of Perspex 18 which is transparent and so allows inspection of the deposit. It is turned down to about $\frac{1}{10}$ mm. where the X-rays pass. The X-ray absorption is very small. A thin german silver tube 19 leads through the bottom of 18 and communicates with the gas store outside. The purpose of the screen is to prevent the gas from spreading. It need not be vacuum tight as the gas condenses in any case without deteriorating the vacuum.

3. X-ray technique

A gas-focus tube with a copper target is used for all experiments. The tube can easily be moved and clamped in front of the liquefier and carries an adjustable collimator. The beam is made to strike the copper wire almost tangentially. The copper lines reflected from the wire serve as additional calibration. The film carrier is a wide brass tube concentrically fixed around the liquefier and has a diameter of 147 mm. The times of exposure are considerably shortened by using an intensifying back screen (Fluorazure, Ilford). All photographs were taken in 15 min. The power consumed by the X-ray tube is estimated as 400 W.

4. Procedure at methane investigation

The methane used in the present experiments is taken from a high-pressure cylinder supplied by the Cymmer Collieries in South Wales. The gas passes through caustic potash, concentrated sulphuric acid and over phosphorus pentoxide into an evacuated glass container immersed in liquid

nitrogen, where it liquefies. After the collection of a few cm.^{3} the pressure is quickly lowered by an oil pump when the methane solidifies giving off the absorbed gas shortly before freezing. This procedure is repeated several times until no further emission of absorbed gas is noticeable. Methane purified in this way has been tested previously by Dr Childs who used a sensitive density test.

The connexion between the methane container and tube 19 which leads to the specimen holder is then opened and the methane sublimates over under its own vapour pressure. The deposit grows on the copper needle reaching a diameter of 1·5 mm. in about 7 min.

Hysteresis plays an important part even at higher temperatures. In order to avoid any effects originating from this source care is taken to deposit each specimen at that temperature at which it is examined. Some effects of hysteresis will be pointed out in the discussion of the results.

5. Results

For classification purposes the temperature range is best divided into three parts, the first one well below the transition temperature, i.e. from 13·9 to 17°, the second one from 17 to 22° which we will call the transition range, and lastly the third one covering temperatures higher than 22°.

The reflexions obtained in the first and third range are all compatible with a cubic face-centred lattice and thus agree with the findings of Mooy. Things are more complicated in the transition range. Here it is found in 80 % of our experiments that in addition to the lines of the face-centred cube a set of new lines appears which have no relation with that structure and which are frequently quite strong. The conditions for the appearance of these new lines are not yet ascertained. It happened that in two consecutive experiments first the ordinary and then the complicated results were found.

Reproductions of six representative films (nos. 1–6, fig. 2 and fig. 3), will illustrate the point. Table I gives the particulars of films 1, 2 and 3. Of these, films 1 and 2 are taken immediately after each other at 20·35° under the same circumstances to the best of our knowledge. Film 3 is taken with the same specimen as film 2 after raising the temperature to 50°. Film 4 is obtained with methane at 35°.

All lines on film 1 can be deduced from a cubic face-centred lattice. It will be seen, however, that film 2 contains five lines unaccounted for. Now it is of interest to note that spacings calculated from Mooy's "parasitic lines" are 4·28 and 3·58 which closely correspond to two of our additional

TABLE I

No. of line	Angle of reflexion	Spacing	Copper and accidental* reflexions	Methane reflexions
	Film 1. Methane deposited and taken at 20·35° K			
1	11·885	—	—	β line of (111) CH_4
2	13·210	3·362	—	(111) CH_4
3	15·305	2·912	—	(200) CH_4
4	21·73	2·075	(111) Cu	—
5	22·145	2·04	—	(220) CH_4
6	25·31	1·798	(200) Cu	—
7	26·08	1·748	—	(311) CH_4
8	27·44	1·668	—	(222) CH_4
9	36·475	1·293	—	(420) CH_4
10	37·19	1·271	(220) Cu	—
	Film 2. Methane deposited and taken at 20·35° K			
1	10·325	4·29	—	New
2	11·03	4·02	—	New
3	11·765	—	—	β line of (111) CH_4
4	12·31	3·605	—	New
5	13·11	3·390	—	(111) CH_4
6	13·99	3·184	—	New
7	15·165	2·938	—	(200) CH_4
8	18·29	—	Acc.	—
9	19·465	—	β line of (111) Cu	—
10	20·99	—	Acc.	—
11	21·73	2·075	(111) Cu	(220) CH_4
12	22·715	—	Acc.	—
13	23·855	1·900	—	New
14	25·31	1·798	(200) Cu	—
15	25·745	1·769	—	(311) CH_4
16	27·085	1·688	—	(222) CH_4
17	35·96	1·309	—	(420) CH_4
18	37·19	1·271	(220) Cu	—
	Film 3. Methane of film 2 taken at 50° K			
1	10·28	4·31	—	New
2	10·91	4·04	—	New
3	11·64	—	—	β line of (111) CH_4
4	12·965	3·425	—	(111) CH_4
5	15·09	2·952	—	(200) CH_4
6	18·29	—	Acc.	—
7	19·465	—	β line of (111) Cu	—
8	21·025	—	Acc.	—
9	21·58	2·09	—	(220) CH_4
10	21·73	2·075	(111) Cu	—
11	25·31	1·798	(200) Cu	—
12	25·69	1·773	—	(311) CH_4
13	26·855	1·702	—	(222) CH_4
14	34·555	1·356	—	(331) CH_4
15	35·575	1·322	—	(420) CH_4
16	37·19	1·271	(220) Cu	—

* Lines, called "accidental", are found on blank photographs as well and are due to reflexions at the radiation shield.

lines, namely nos. 1 and 4 on film 2. These, however, are not the most conspicuous lines. The spacing 3·184 (no. 6) is far the strongest but on the other hand it vanishes completely on warming up, whereas some of the others even then persist. This is demonstrated by film 3 which still shows two of the new lines surviving from the earlier modification. In contradiction to this film 4, taken at 35°, shows no trace of any lines which do not belong to the regular structure.

No stress is laid on absolute values of the lattice constant as this work does not aim at precision determination of that quantity but is primarily concerned with collection of experimental material. We have, nevertheless, established the fact that the lattice constant is in the transition range without exception larger when the new lines appear than when they do not appear. The actual values as taken from films 2 and 1 are 5·865 and 5·780 respectively.

TABLE II

Temperature ° K	Lattice constant A	
13·9	5·84	
14·25	5·82	
14·3	5·82	
15·0	5·76	
17·0	5·76	
18·5	*N*	5·845
20·35	*N*	5·855
20·35	5·78	
22·0	*N*	5·85
27·5	5·845	
35·0	5·89	

Table II gives the value of the lattice constant at various temperatures. Experiments in which the new lines appear are marked "*N*". Another fact emerges from Table II. It will be seen that the lattice constant rises again at temperatures below about 17°. As our temperature range is limited at present we could not ascertain whether this rise leads to a maximum. But we might mention another phenomenon which we occasionally found at the lowest temperature at our disposal, i.e. 13·9°. Methane deposited at this temperature sometimes does not form a well-defined lattice but gives a reflexion characteristic of a ring. Film 5 (fig. 3) indicates this result. Film 6 is taken with the same specimen as film 5 after raising the temperature to 41°. At this temperature the substance seems to have "crystallized", all lines apart from nos. 3 and 4 belonging to a cubic lattice. The latter lines look like remainders of the original ring. Particulars of these two experiments are given in Table III.

TABLE III

No. of line	Angle of reflexion	Spacing	Copper and accidental reflexions	Methane reflexions
	Film 5. Methane deposited and taken at 13·9° K			
1	About 13·80	3·22	—	"ring"
2	21·73	2·075	(111) Cu	—
3	25·31	1·798	(200) Cu	—
4	37·19	1·271	(220) Cu	—
	Film 6. Methane of film 6 taken at 41° K			
1	11·825	—	—	β line of (111) CH_4
2	13·205	3·364	—	(111) CH_4
3	13·68	3·251	—	New
4	14·565	3·057	—	New
5	15·30	2·913	—	(200) CH_4
6	21·73	2·075	(111) Cu	(220) CH_4
7	25·31	1·798	(200) Cu	—
8	25·755	1·769	—	(311) CH_4
9	27·04	1·692	—	(222) CH_4
10	37·19	1·271	(220) Cu	—

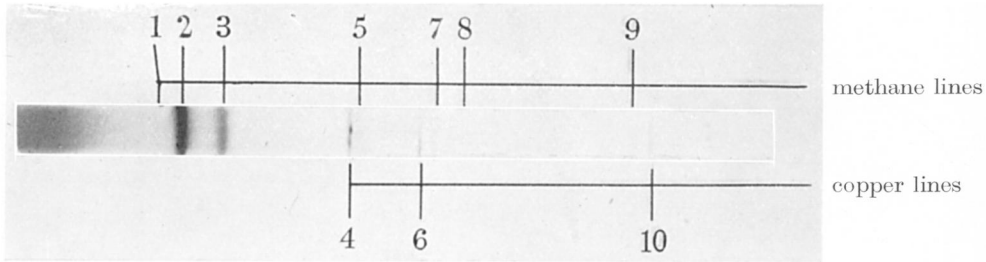
6. DISCUSSION

The results of the present investigation may be summarized as follows. Below and above the λ point there is a region in which the methane crystallizes in a face-centred cubic lattice. This is in agreement with the results of previous observers.

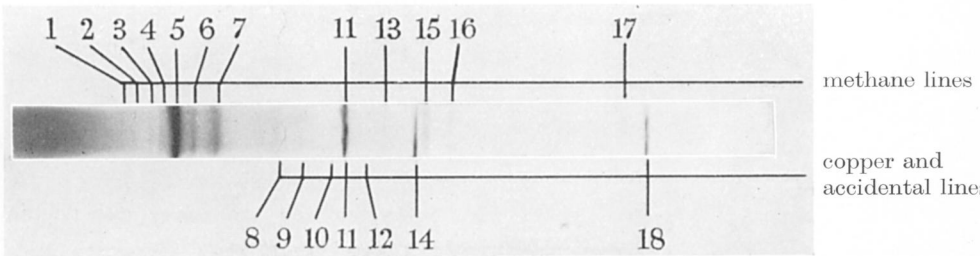
In the neighbourhood of the λ point the X-ray pictures show additional spacings besides those belonging to the face-centred cube. Mooy (1931) has already mentioned two of these, calling them "parasitic lines". He is inclined to treat them as purely accidental. From the present more extensive material it is concluded that they are essentially associated with the transition phenomenon at the λ point.

The intensities of the additional lines vary sometimes considerably with the experimental conditions and so they may easily be overlooked if only a few observations are made. Another possible reason for their absence is due to hysteresis. It is found that if the methane is condensed at a certain temperature and then raised to a higher temperature, the resulting X-ray photograph may differ from one obtained with the substance deposited at this higher temperature.

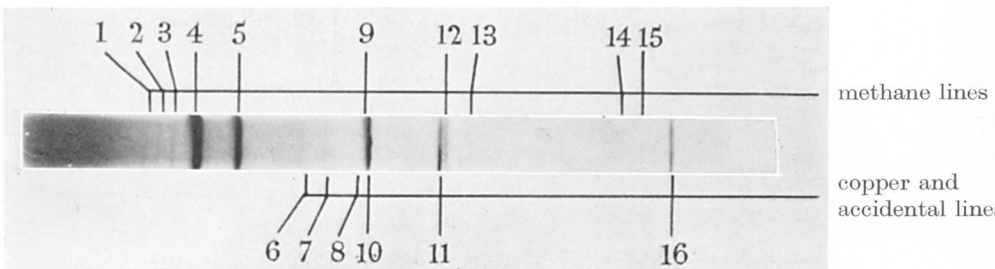
It must be borne in mind that it is difficult to ensure uniformity of temperature over the whole specimen since it may take a long time before equilibrium is established. Consequently it is impossible to say whether



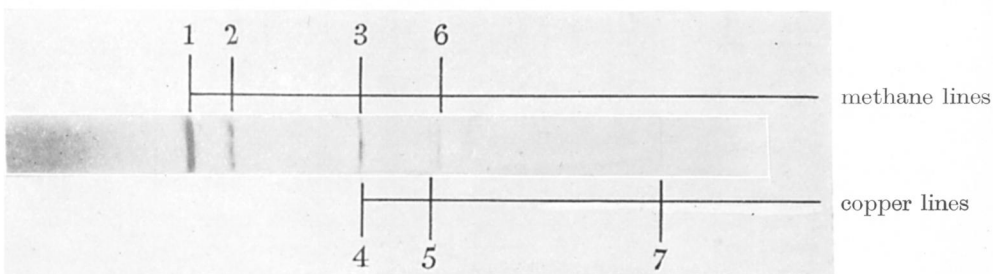
Film 1, methane deposited and taken at 20·35° K.



Film 2, methane deposited and taken at 20·35° K.



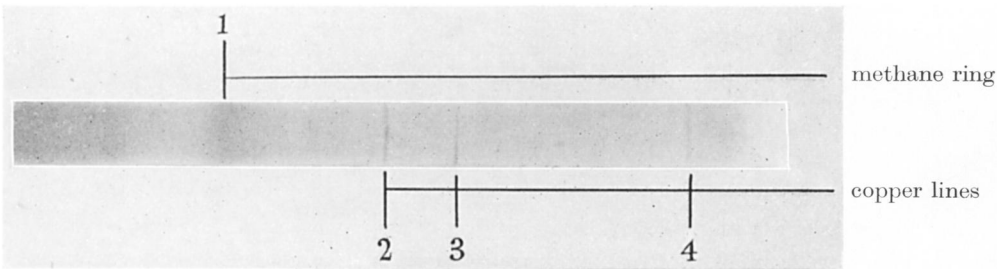
Film 3, methane of film 2, taken at 50° K.



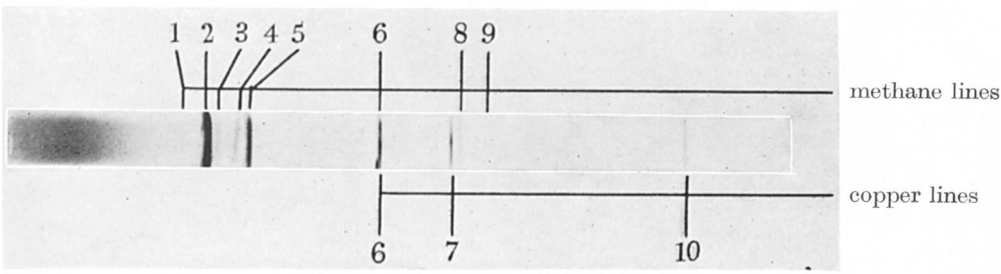
Film 4, methane deposited and taken at 35° K.

FIG. 2. Reproductions of typical photographs.

(*Facing p.* 576)



Film 5, methane deposited and taken at 13·9° K.



Film 6, methane of film 5 at 41° K.

FIG. 3. Reproductions of typical photographs.

or not any individual X-ray picture is characteristic for the particular temperature reading at which it is made. This uncertainty holds essentially only for the comparatively narrow transformation region. The fact remains that, whatever the thermal conditions are, the additional spacings persist during a period of time long enough for them to be photographed repeatedly. It is further important to note that these new spacings always retain the same numerical value. This leads to the conclusion that they must belong to certain definite structures which exist only in the vicinity of the λ point. As for the rise of the lattice constant at lower temperatures, we hope to clarify this point by an extension of our temperature range.

A word may be said in conclusion about the commonly accepted explanation of the λ phenomenon in methane. It is assumed that the anomalous rise in the specific heat is due to a rapid increase of rotation of the molecules in the crystal lattice. The lattice itself is assumed to retain its face-centred cubic structure. There is no direct evidence of this rotation. There may be some truth in this hypothesis, but the present work shows that the actual transition is a much more complicated phenomenon. Any theory which claims to predict the shape of the λ curve would necessarily have to take into account the existence of those intermediate structures. The transition from one structure into another is bound to be associated with a change of free energy, and these changes must show in the specific heat. The argument put forward probably applies not only here, since the λ phenomenon in methane is not an isolated case, but also for other substances where λ points are observed. No X-ray evidence of the same nature as that given in the present work has been obtained for any other substance, but judging from analogy it would not be surprising if similar intermediate structures were found in other λ transformations.

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