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STUDY OF THE EDGE EMISSION OF CADMIUM SULPHIDE BOMBARDED BY ELECTRONS.

Final Technical Report

First of October 1962 - 30 September 1963

Contract n° N 62558-35'

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STUDY OF THE EDGE EMISSION OF CADMIUM SULPHIDE BOMBARDED BY ELECTRONS

During the year 1962-1963 the activity of the group was devoted to preliminary research on the luminosity emitted when cadmium sulphide, cooled to liquid helium temperature, is bombarded with electrons.

These first results formed the subject of the third cycle thesis by M. de Gaalon, the text of which has been forwarded to you. The results are discussed again in this report. The material necessary to build an apparatus for liquid helium temperature work has been assembled, and the mounting of the units is going forward; new and very simple liquid hydrogen and liquid helium cryostat devices have been developed.

An apparatus which may be considered as definitive for the study of these crystal bombardments has been perfected, and several models built; we are now able to pursue our researchs on three separate instruments simultaneously.

Studies on the bombardment of silicon have been started; they show the existence of a bombardment-induced radiation, the characteristics of which indicate the need to modify to some extent the theoretical interpretations we proposed to explain the phenomena observed previously.

1 - General theory

In our final technical report for the year 1960/1961 we summarized a certain number of observations by various authors who had discussed recombination possibilities, and concluded that this occurs not directly from band to band, but through an exciton level.

These ideas are no doubt interesting enough, but one may wonder if they really touch the root of the problem.

In effect, when an electron and a hole recombine, this merely proves the existence of an electron and a hole which happen to interact. Recombination is, apparently, the result of a particularly strong interaction. Now, to say that an electron and a hole interact is to say that an electron can be shown to be present in the potential field of a particular atom, and not only in the periodic field of the crystal lattice as a whole.

It is well known that the band theory, in which the interaction between an electron and a periodic field of force is considered, is only a first mathematical approximation to simplify the calculations, and that an attempt to improve this first approximation leads to the introduction of the exciton idea.

The question which arises in the interpretation of the bands is therefore, not whether a band originating in a recombination through an exciton level can in fact be produced, but whether this band is in fact visible under the condition of the experiment. This would mean, in a first analysis, looking for the lifetime of the electron on the exciton level. It will show up if the lifetime is long, a thin, intense ray being produced, whereas otherwise the ray will be broad and barely visible, or even invisible.

On the other hand it seems much more interesting to find out whether the transitions observed are "vertical" transitions, i. e. with emission or absorption of a phonon.

We showed in our communication at the Luminescence Conference at New-York, in October 1961, that the vertical transition occurring at the centre of the Brillouin zone was possible under our experimental conditions. This does not mean that it occurs in fact, nor even less that it becomes preponderant.

Unlike what has just been said on the subject of direct recombination - band to band - or indirect recombination - via an exciton level -, the difference between a "vertical" and an "oblique" recombination is perfectly clear-cut and refers to two quite distinct phenomena. We must distinguish in effect between a recombination with creation of a phonon, in other words the formation of an acoustic wave circulating in the crystal, and a recombination occurring without phonon emission. Either of these two means of recombination can be produced by way of an exciton level.

The experiments being carried out at present aim to produce information leading to the solution of this problem.

1,1 - Study with variable current and voltage. In principle it should be possible to distinguish between a "central" and an "oblique" transition directly, simply by measuring the wavelength of the radiation emitted. The "central" transition, which does not leave from the lowest point of the conduction band, should produce a radiation of shorter wavelength than the "oblique" transition (fig. 1)

In practice this direct distinction is difficult in the case of cadmium sulphide, since the vertical energy level difference between the conduction band

minimum and the central point of the Brillouin zone in the energy diagram is both small and little known. In fact the authors who have attempted to measure it disagree amongst themselves. It is estimated to be about 0.01 ev. A variation of this order of magnitude, with respect to the height of the forbidden band, i. e. 2,5 volts in the case of cadmium sulphide, leads to a variation of about 20 \AA in the wavelength emitted. Such a displacement is of course detectable in the spectrum, but it is difficult to show it up sufficiently clearly, under our experimental conditions, for a study to be made without ambiguity in the separation of the two bands.

However, useful information can be obtained from a study with variable current and voltage.

If we refer to the points discussed in our New York communication, it can be concluded that if the recombination is chiefly "central", the number of electrons reaching the level of the centre of the Brillouin zone should increase as the bombardment current increases. Inversely, the number of electrons from the region around the conduction band minimum should remain approximately constant, since all the places liable to be occupied in this band are so in fact. In practice this is conveyed by a relative increase in the intensity of the shortest wavelengths, i. e. those which correspond to the greatest energy leap. Under these conditions a very low intensity of the short-wave band would be observed for very low bombardment currents, with an appreciable intensity of the higher wavelength. As the current becomes stronger, an increase in intensity of two bands should be observed at first, then that of the shorter wavelength should progressively overtake the other.

On the other hand the recombination may be mainly "oblique". This means that the probability of occurrence of transitions forbidden by the selection rules increases, in proportion to the perturbation produced in the lattice by the electron impact, as the strength of the electron beam increases. A relatively greater increase of long-wave radiations, as compared with those of shorter wavelength, should then be observed. The latter would still be detectable however, because of the small difference in energy level between the minimum and the centre of the Brillouin zone.

1,2 - Study on silicon. This difference in energy level is large in the case of silicon, of the order of 1,4 volts. To bring the electrons to the centre of the band it would be necessary to bombard with enormous intensities in the cathode beam, impossible to obtain in practice, or extremely high voltages which would damage the crystal lattice.

The radiation emitted by silicon must therefore be attributed exclusively to an "oblique" recombination, causing an emission in the infra-red. The intensity of the "central" recombination emission is then negligible. When a phenomenon with these characteristics is observed, it means that the second of the two mechanisms considered plays the preponderant part.

1,3 - Time constant measurements. If the phenomenon observed is the result of an "oblique" recombination, forbidden by the selection rules, the time constant characterising it must be high, of the order of 10^{-6} second at least, decreasing progressively as the current strength in the bombarding electron beam increases. If the phenomenon is due, partially at least, to an allowed transition, a very rapidly appearing and disappearing ray can be expected to be produced suddenly when this transition occurs. The time constant characteristic of this ray should be of the order of 10^{-8} to 10^{-9} second, and possibly less.

2 - Experimental equipment.

2,1 - Valves and cryostats. The various apparatuses used in the past were either too complex and fragile, or difficult to evacuate because of the excessive length of the piping.

The new set-up avoids these disadvantages; it consists essentially of a demountable glass cryostat made up of a vertical outer tube of 50 mm external diameter, with the electron gun tube and a ground glass input for the high tension fitted at the side. (fig. 2)

The top of the vertical tube ends with a ground male joint which fits into a female joint on the liquid nitrogen container. A copper sample holder is welded to the base of this latter through a Kovar ring.

The electron gun has already been described in detail in the final report for 1961/1962, as well as in the French patent which covers it. The text of this patent has been sent to you.

The vertical tube is mounted directly, by means of an O - ring, onto a metal bell-jar made from a duralumin rod. This bell-jar rests on an evaporation plate. The apparatus is thus very easily and quickly mounted.

The cryostat device for cooling to liquid helium temperature uses a double Dewar flash system; the inner tube is reserved for the helium and the outer flash can contain nitrogen, which will serve to limit losses by radiation. (fig. 3)

2,2. Installation of the helium circuit. This circuit feeds liquid helium to the Dewar and recuperates it, this material being very scarce and costly. The diagram of the circuit is given in fig. 4.

2,3 - Measurement of the helium level. The apparatus consists essentially of a small resistor of 10Ω . The principle is as follows: when the resistor is immersed in liquid helium it is cooled suddenly, the resistance varying sharply as the liquid level is crossed. The position at which this variation occurs can be easily observed, and determines the liquid helium level.

2,4 - Time constant measurements. The phenomenon under observation can be exceedingly rapid if an allowed transition is involved. The difficulty of measuring the evolution of such brief phenomena is well known, and for this reason we decided to use a "sampling" method, the principle of which follows. It should be noted that it is applicable here because the phenomenon to be observed can be repeated at the rhythm desired.

The method is very simple; a regular series of signals is emitted under the influence of an excitant, in this case an electron flux, acting over a very short period. The result is obtained here by means of a pulse generator sending square signals of very short duration, of the order of 10^{-9} second, onto the Wehnelt of the electron gun.

Under these conditions the electron gun sends a constant flux of electrons, at regular intervals over a very short period, onto the crystal under observation.

The illumination of the crystal lasts a relatively long time. The crystal is examined at regular intervals, slightly longer than the intervals of illumination. This result is obtained by means of an adjustable delay circuit forming part of a so-called "sampling" apparatus. This is sold as an accessory for certain cathode oscillographs.

The pulses occur at times $0, t, 2t, 3t$ etc..., and observations are made at times $0, t + \Delta t, 2t + 2\Delta t, 3t + 3\Delta t$ etc... The phenomenon is thus observed $\Delta t, 2\Delta t, 3\Delta t$ etc... after its occurrence. If t is small and the events observed during a very short time inscribed, the oscillograph screen will show the curve giving the emission of the screen as a function of time, the duration of this emission being several times Δt . The apparatus is in the course of construction.

3 - Experimentals results.

3,1 - Tests at 4°K. If the crystal is taken to liquid helium temperature it is no longer necessary to increase the strength of the electron current, since the luminance of the blue emission increases greatly as the temperature decreases. At 4°K we can thus improve the resolution of the measurement (by reducing the input slit of the spectrograph) without spoiling the crystal. In addition tests at 4°K are necessary, since it is at this temperature that the absorption and emission

spectra (under UV irradiation) of CdS, and thus the optical transitions possible are best known.

Tests have been carried out at 4°K on many samples of various thicknesses and with different excitation intensities. Having obtained a stronger luminous emission, we have also been able to carry out studies on polarization (the transmission of the polarizers used being only about 30 % in favourable cases).

We then observed that the blue emission observed at 77°K was displaced towards the short wavelengths and had become almost as strong as the green emission. On the other hand no appreciable displacement was observed for this latter.

We also found that the strongest ray which had been observed around 4.880 Å at 77°K decomposed at 4°K into a series of very narrow rays, the most intense of which lies around 4.870 Å. By then arranging an analyser in front of the input slit of the spectrograph, we observed that the spectrum previously obtained decomposed into two spectra, similar but with different intensities, and that certain rays were slightly displaced (from 8 to 10 Å).

The position of the various rays obtained at 4°K is summarized in the following table. (see next page)

The CdS sample on which the above results were obtained was very thin, the temperature difference between the two faces therefore being small.

On figure 5, showing the spectra obtained for the two kinds of polarization, the E/C polarized emission seems to be the stronger; this is due to an increase in excitation between the two recordings.

In reality the E⊥C polarized emission is the more intense, as shown by the results recorded in figure 6, obtained with a thicker sample. Because of the greater thickness of this sample, the temperature difference between the two faces is higher, which leads to a displacement of the emission towards the long wave: the E//C polarized emission, recorded first, is displaced by about 5 Å, as compared with about 7 Å for the E⊥C polarized one (reheating of the crystal between the two readings).

The liquid helium, transferred to the central flask of the cryostat just before the experiment, evaporates as it proceeds; since the liquid helium is not replenished to compensate for this evaporation, the crystal begins to warm up slightly after about an hour. The blue emission is then seen to move towards the long wavelengths, eventually merging with that observed at 77°K.

3,2 - Displacement of the blue emission between 4°K and 77°K. Now that our liquid helium tests have taught us more about the structure of the blue emission, we have tried again to improve our equipment in an attempt to find this

NOT POLARIZED			POLARIZATION $\vec{E} \perp \vec{C}$			POLARIZATION $\vec{E} \parallel \vec{C}$		
POSITION λ	WIDTH	INTENSITY	POSITION λ	WIDTH	INTENSITY	POSITION λ	WIDTH	INTENSITY
4828		2	4828		1	4828		2
4845			4850	A	4	4845	A	
4862	A	4	4870		5	4862	A	4
4870	L	5	4919	L	3	4918	L	3
4918	L	3	5005		2	5005		2
5005		2						

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Gif-sur-Yvette

emission at 77°K and thus determine its displacement as a function of temperature. We have in fact observed a structure similar to that obtained at 4°K, but displaced by about ten Å towards the long wave region (fig. 7)

The following table shows the displacement of the different rays between these two temperatures (the results given here were obtained with a very thin sample).

POLARIZATION $\vec{E} \parallel \vec{C}$		POLARIZATION $\vec{E} \perp \vec{C}$			
4°K		77°K	4°K		77°K
4.828 Å	$\underline{8 \text{ \AA}}$	4.836 Å	4.828 Å	$\underline{8 \text{ \AA}}$	4.836 Å
A 4.856 Å	$\underline{10 \text{ \AA}}$	4.866 Å	4.854 Å	$\underline{11 \text{ \AA}}$	4.856 Å B
A 4.870 Å	$\underline{13 \text{ \AA}}$	4.883 Å	4.862 Å	$\underline{8 \text{ \AA}}$	4.870 Å B
4.919 Å	$\underline{8 \text{ \AA}}$	4.927 Å	4.918 Å	$\underline{7 \text{ \AA}}$	4.925 Å

A - Completely polarized rays $E \parallel C$.

This table also shows that for a given temperature there are two similar groups (A and B) of rays, polarized $\parallel C$ and $\perp C$ respectively, and about ten Å apart (fig. 5, 6, 7).

3,3 - Measurements as a function of intensity and voltage at liquid air temperature. We proposed to study the variations in intensity of the 4880 Å and 4920 Å bands as a function of the acceleration voltage of the electron beam, and of the current in the bombarding stream of electrons. To this end the power dissipated in the filament or the Wehnelt voltage is adjusted. With each measurement the concentration is so fixed that the diameter of the spot remains constant, this being checked by sighting with a microscope.

The luminosity strengths were measured by means of a Beckman spectrograph equipped with an IP 21 photomultiplier.

It can be observed visually that the luminous intensity increases with excitation; when the current becomes very strong it remains constant, while at the same time a displacement of the spectrum towards the yellow appears. This phenomenon, already described in our earlier reports, is due to heating of the system.

A study of the spectrum shows that the two rays behave differently. The excitation conditions remaining constant (acceleration voltage 20 KV, Wehnelt polarization 30 V) the band centred on the wavelength 4880 Å increases progressively and linearly over a very wide field corresponding to electron currents between 0

and 20 μA . When this current is exceeded, the intensity first remains constant and then decreases. (fig.8)

Under the same conditions the band centred on the wavelength 4920 $\overset{\circ}{\text{A}}$ varies slowly at first; when the electron current of the incident beam reaches 14 μA the luminous intensity rises sharply and then increases linearly. The current at which the maximum intensity of this band is observed is greater than that corresponding to the preceding band.

As may be seen on the curves, the intensity of the 4920 $\overset{\circ}{\text{A}}$ band, while at first weaker than that of the 4880 $\overset{\circ}{\text{A}}$ band, increases more rapidly and then overtakes it, to reach a maximum then descend again. (fig. 9)

The current for which these phenomena appear remains very roughly constant if different points of the same crystal are examined, but the value varies markedly from one crystal to another.

3,4 - Measurements on silicon. Measurements were carried out on samples of pure, intrinsic non-compensated silicon, of resistivity 1000 Ω/cm cut perpendicular to the axis (111) and unetched.

These samples are cut in the form of platelets about 0,1 mm thick.

The anode voltage was 23 KV and the bombardement current varied between 0 and 600 μA .

The radiation emitted by the silicon was received by a Philips 61 SV lead sulphide cell, connected to the selective amplifier built in collaboration with the TELEC Company and described in our earlier reports.

The first results were as follows :

3,41 - For weak currents, up to about 300 μA , no effect is observed.

3,42 - When the current reaches this value a small, not very bright bluish spot appears on the crystal; as we shall see, this spot appears not to have any direct bearing on the phenomenon in which we are interested, but proves useful for adjusting the instrument.

3,43 - When the current increases and reaches 500 μA , a strong emission is suddenly observed (the dial reading changes sharply); this radiation lies in the near infra-red, since our glass optics and lead sulphide cell system is only sensitive in this region.

The silicon used was checked and found to be transparent in the near infra-red, and to possess the optical characteristics of pure silicon (transparency from 1,1 μ).

It can be concluded from this that the radiation is concentrated in the region of 1μ , and it may be ascertained that by comparison with the radiation emitted by an incandescent lamp filament, this emission is appreciably superior, in this region, to that of a black body at a temperature of 700°K . However, for the moment the intensity emitted is still insufficient for a precise spectrographic study to be undertaken.

To this end a high tension unit for work at higher power is at present under construction.

4 - Discussion

4,1 - Cadmium sulphide. The first part of this report shows that the experiments carried out on cadmium sulphide tend to emphasize the importance, increasing with current, of the oblique transition.

The "central" transition, not very strong for weak currents, increases with the current although more slowly than does the oblique transition. This means that for cadmium sulphide, the number of electrons reaching the centre of the Brillouin zone increases less rapidly than the probability of oblique transition due to increasing perturbations in the lattice.

4,2 - Silicon. The conclusions, although of a provisional nature, are of the same order. Vertical transitions, according to the results found in the literature, should cause a green rather than a blue luminescence in the neighbourhood of 5200 \AA . This can probably be attributed to a very thin layer of silica SiO_2 which forms on the surface of the silicon.

Only the oblique transition which should occur around $1,1 \mu$ would therefore be observed.

5 - General conclusions

From these considerations we can form a fairly coherent picture of the phenomena.

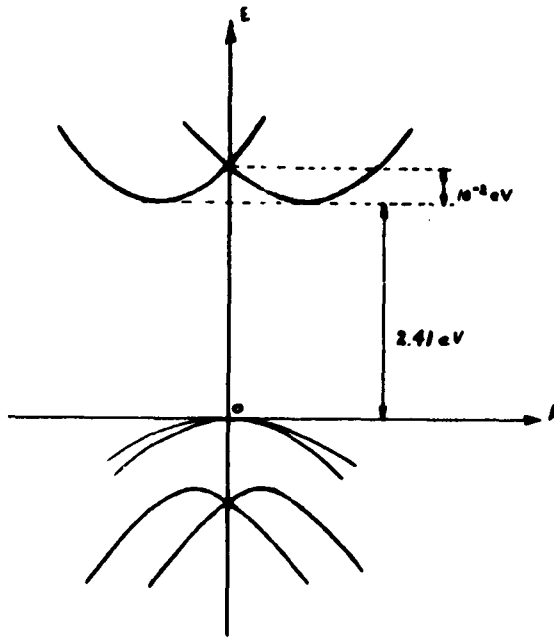
If the minimum is situated in the middle of the Brillouin zone only the "central" transition is observed.

If the energy level at the centre of the zone rises little above the minimum, central and oblique transitions appear simultaneously, the ratio between the intensities of the corresponding radiations decreasing when the energy level difference increases. For large differences the central transition becomes negligible. The increase in probability of the oblique transition under the influence of the inciting factor will certainly depend on the nature of the irradiating agent (electrons, photons, nuclear particles etc...), but the phenomenon remains the

same in essence, only the conditions of its manifestation varying. It would seem that a study of these effects in the different cases would enable the true nature of the impacts between the irradiating agent and the lattice to be clarified.

These results, compared with those to be found in the literature, tend to disprove a too widespread opinion that cathodoluminescence, like electroluminescence, radioluminescence etc... are specific phenomena.

In any case the structure of the crystal lattice and the nature of the substance of which it consists are brought to light; the electron jumps from one level to another are linked up with the absorption or emission of the radiation, which means that the levels and their position can be shown. These characterise the substance and its state of aggregation. The intensities of the various rays or bands emitted probably vary with experimental conditions, but here again we are always essentially dealing with one and the same phenomenon.



Band Structure in CdS, near the centre of the Brillouin Zone in the direction $k_{(xz)}$ (or $k_{(yz)}$)

fig.7

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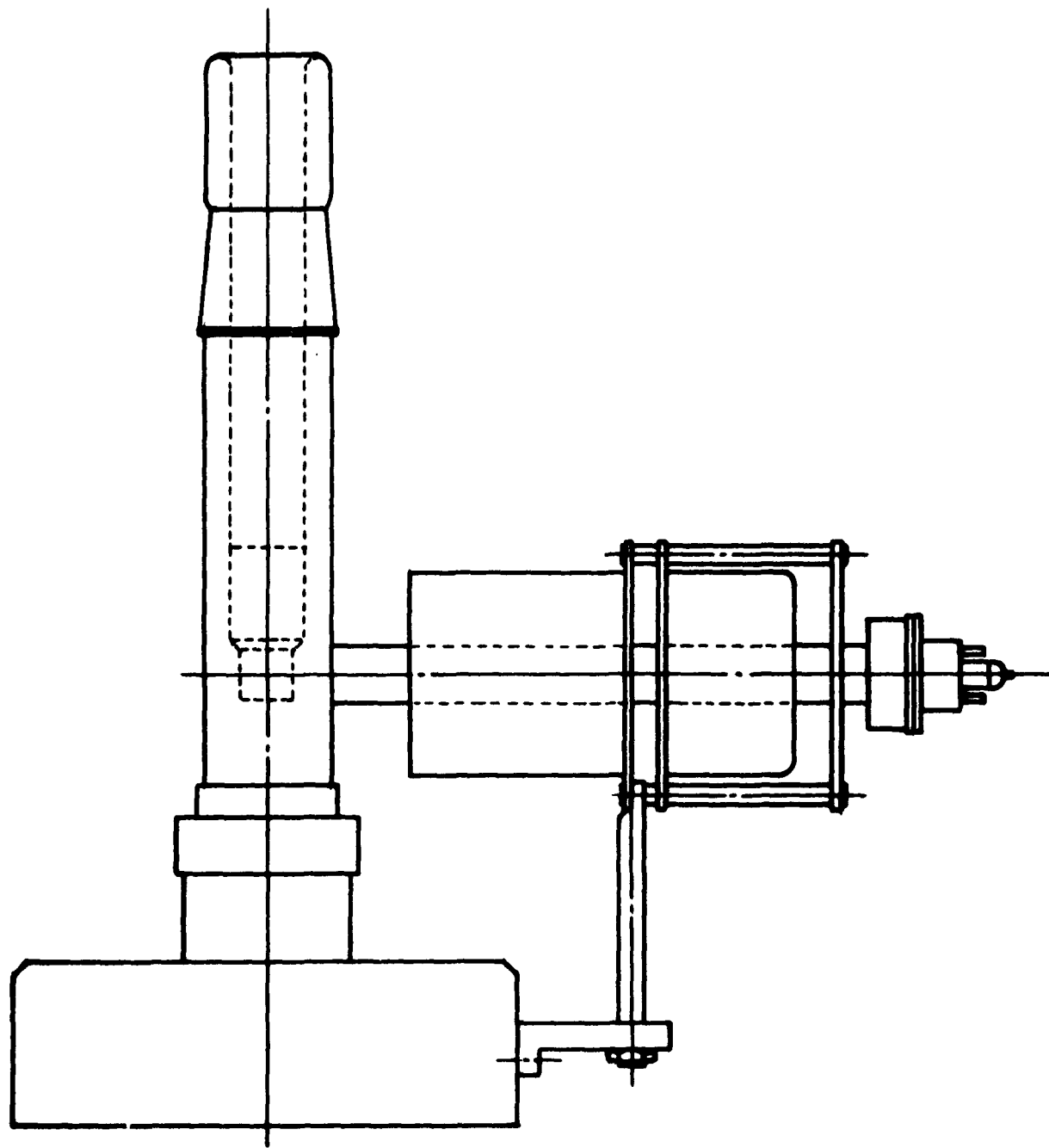


Fig. 2

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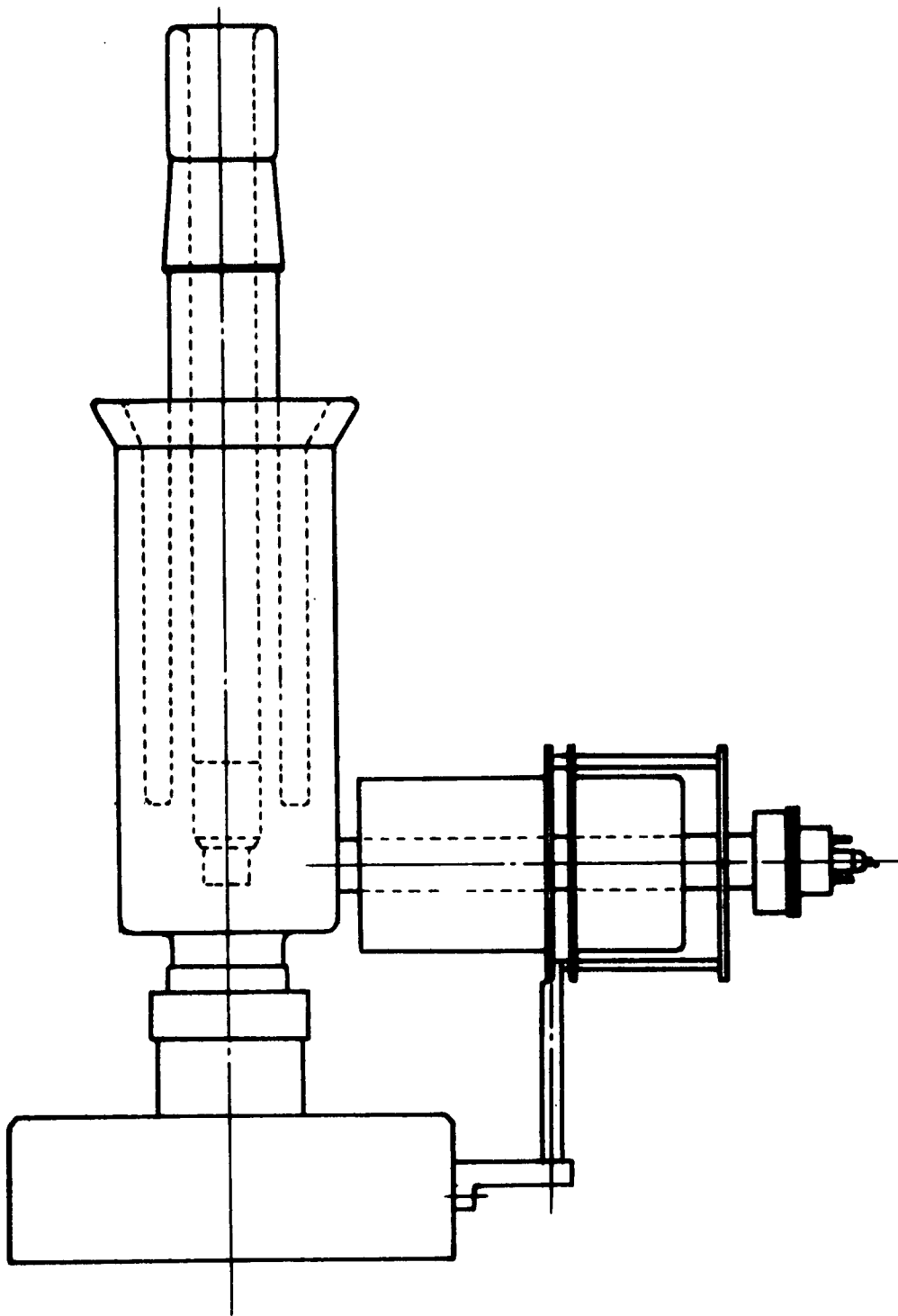


Fig. 3

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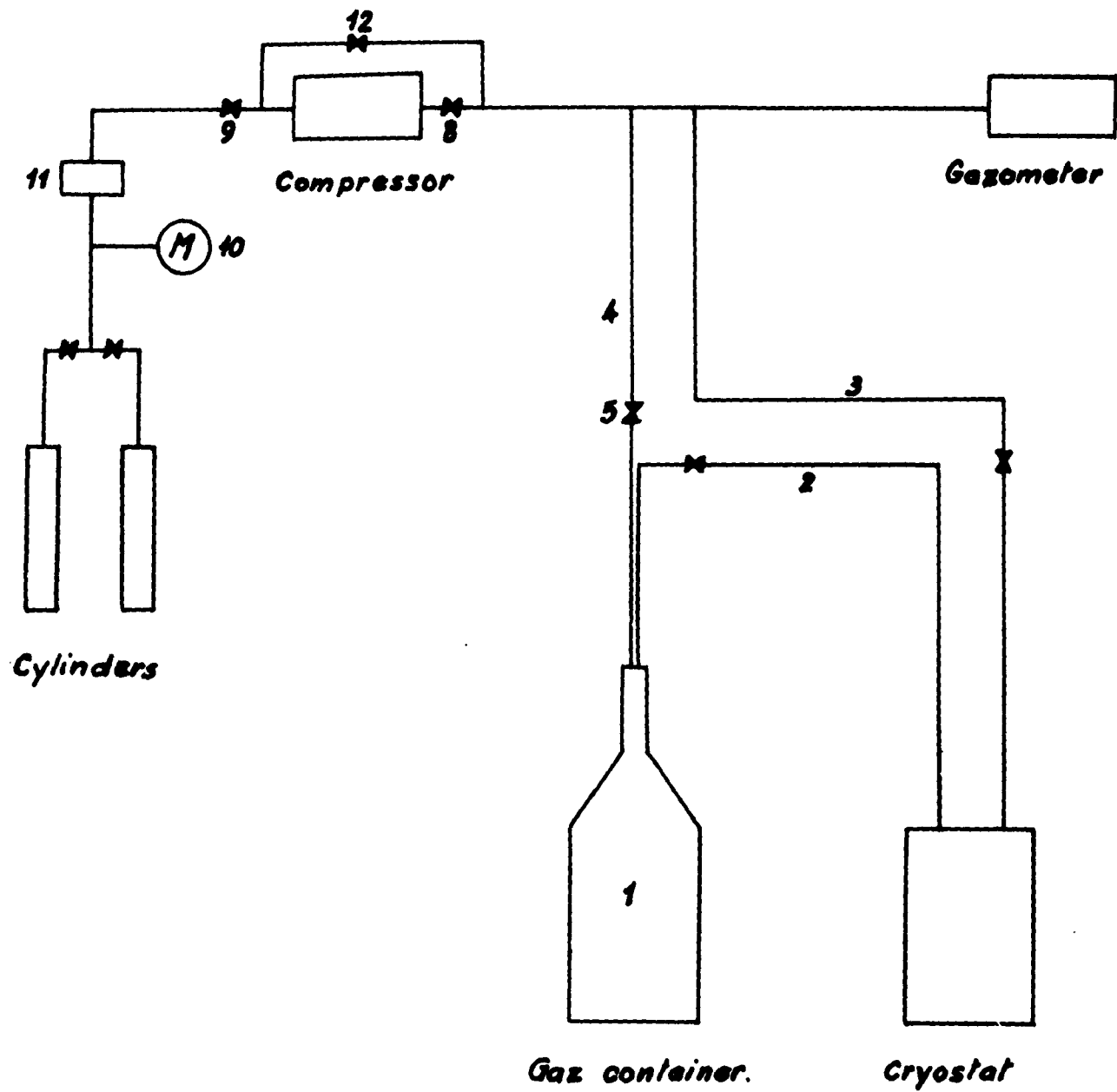
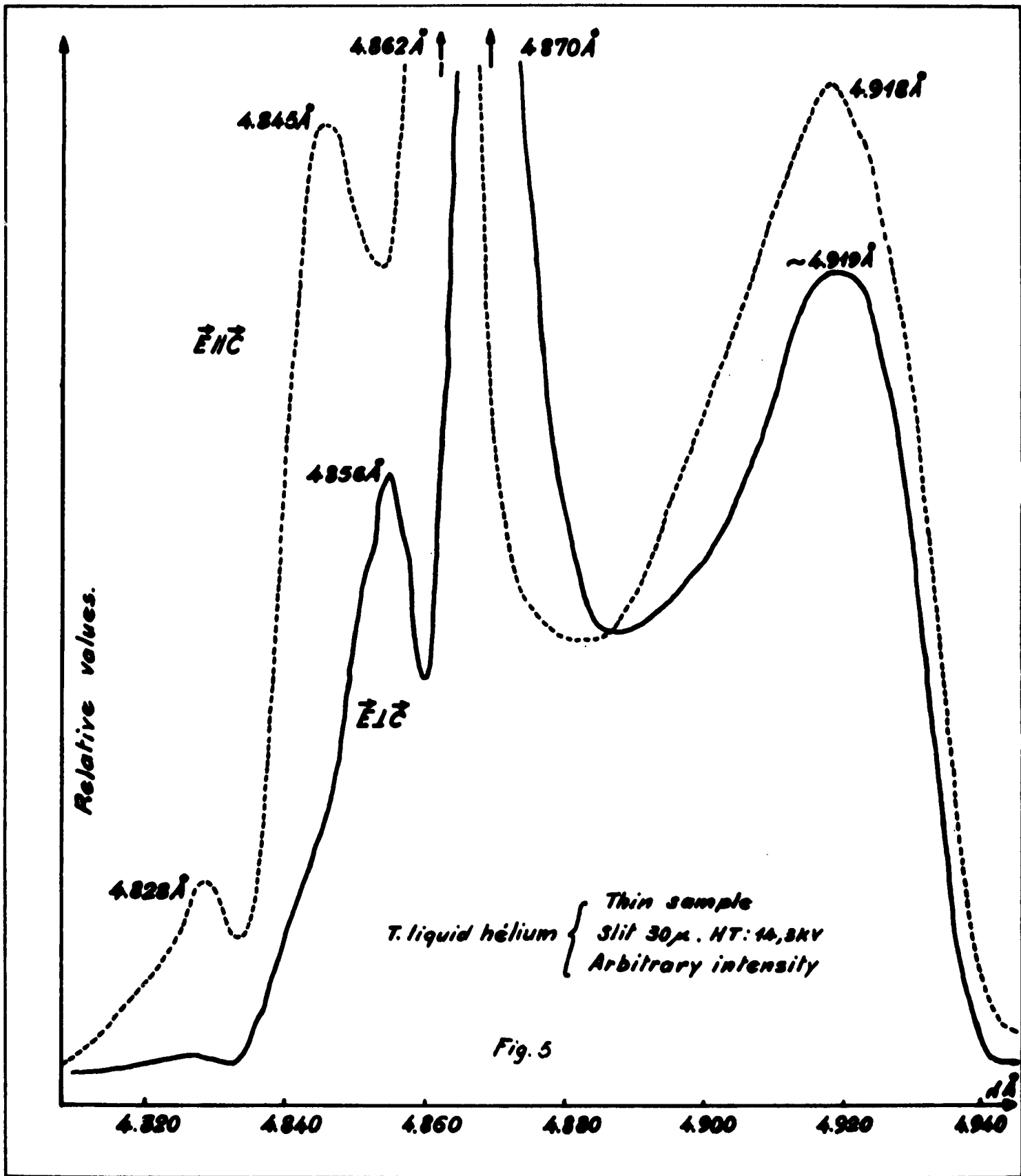


Fig.4

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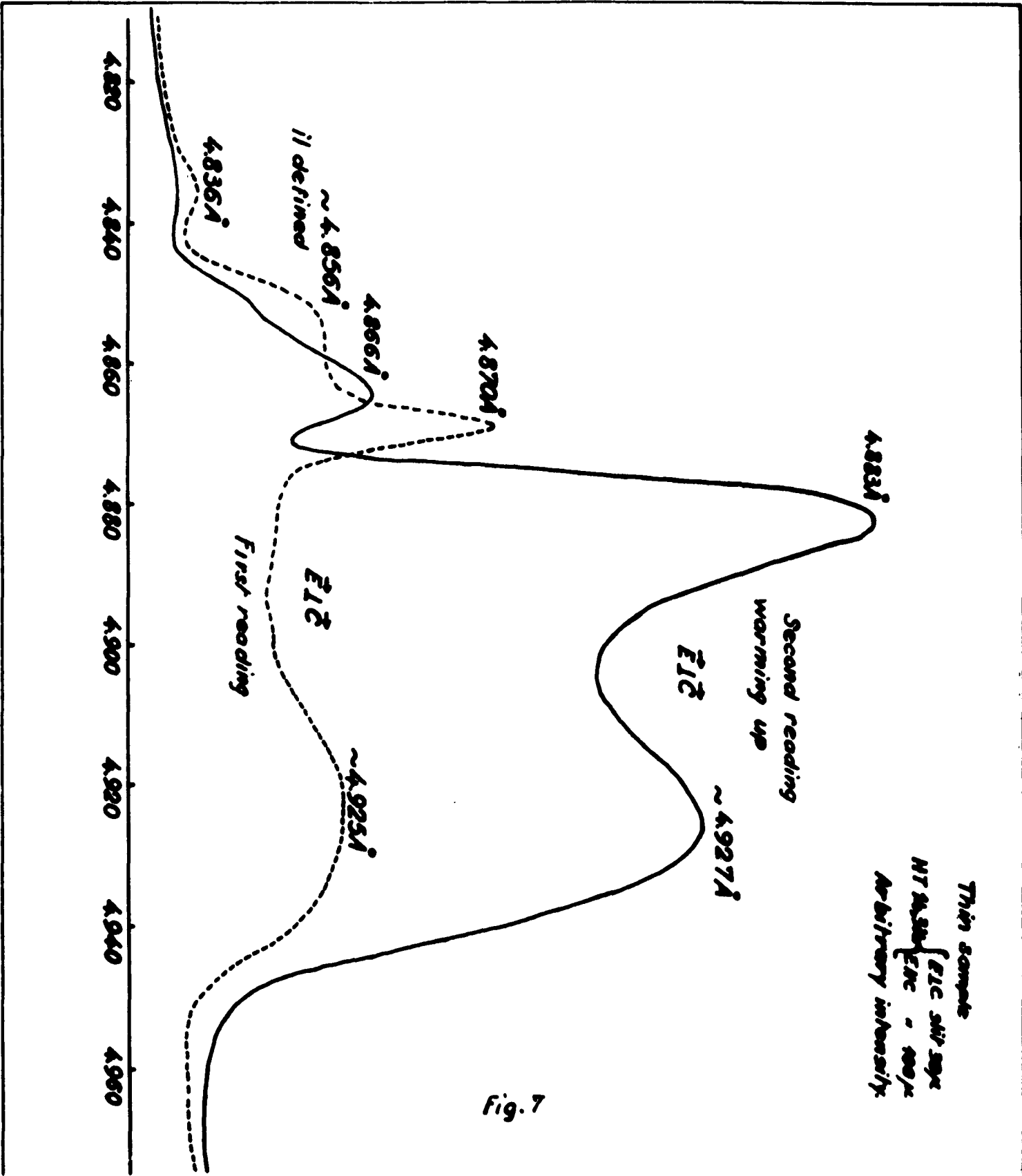


Fig. 7

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T. LIQUID NITROGEN					

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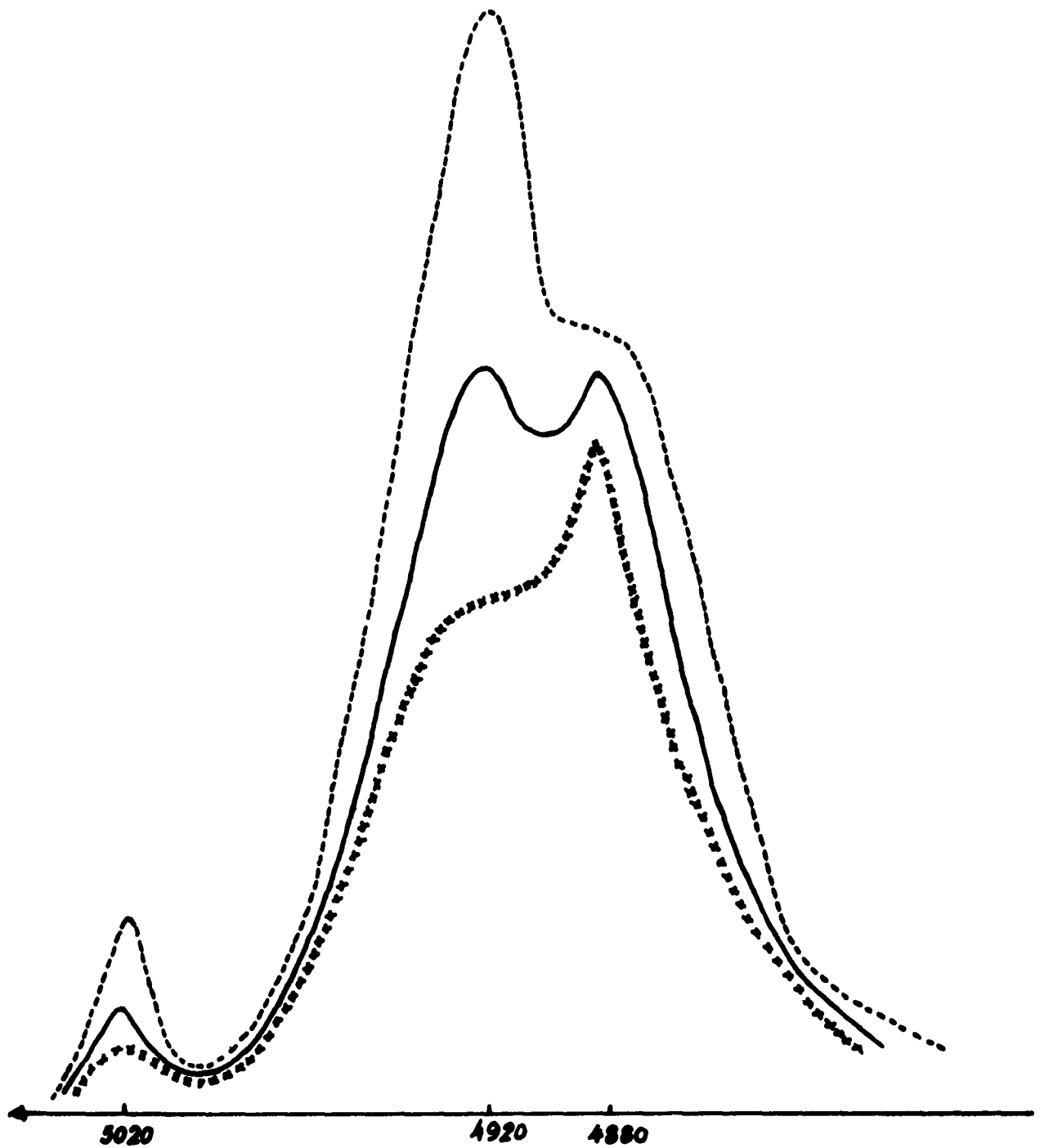


Fig. 8

— 20kA
 - - - 30kA
 40kA

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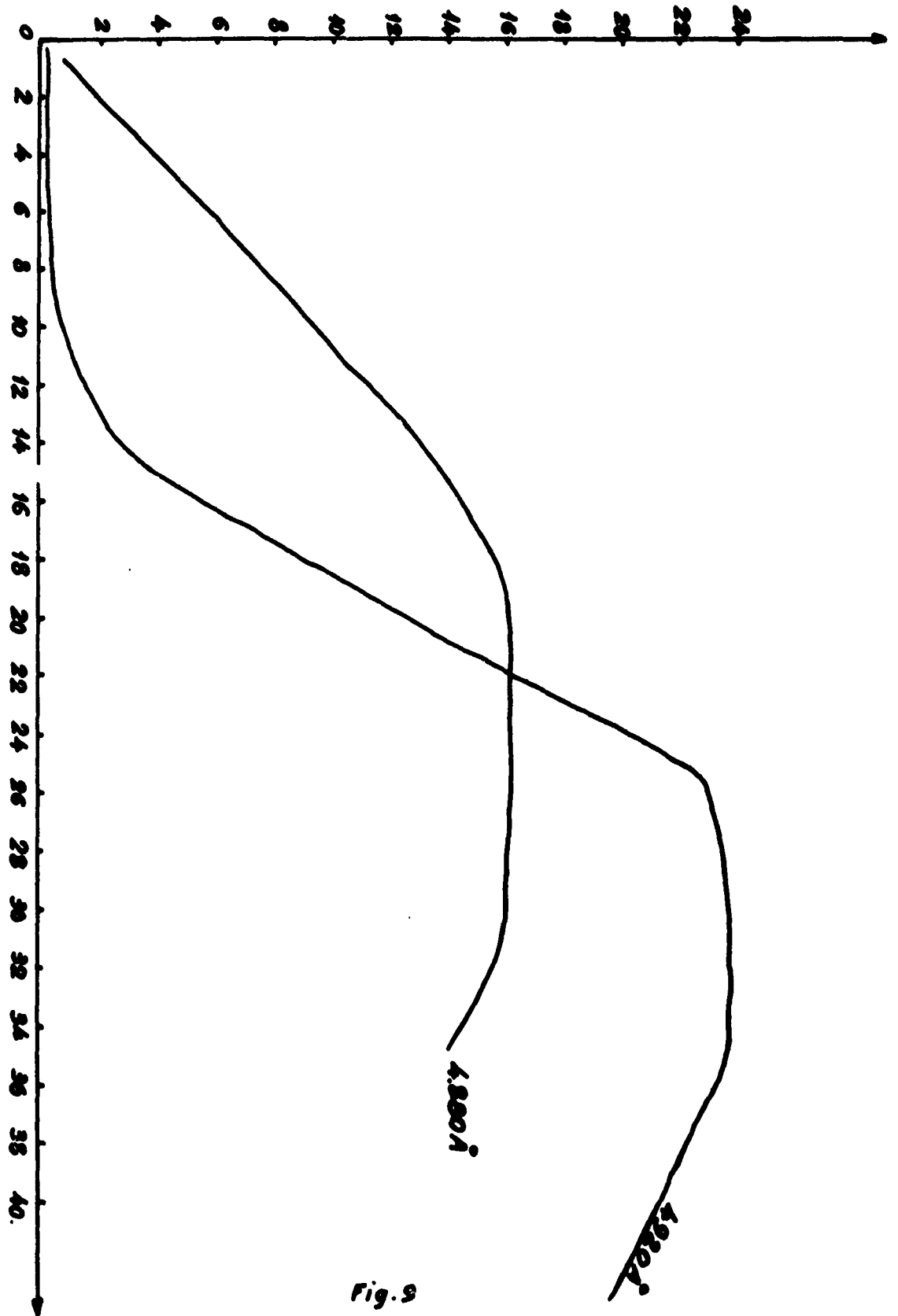


Fig. 9

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