CHAPTER III

Electrical switching and SCL Currents in Copper Ferrites

3.1 THEORETICAL DEVELOPMENT

Most of the ferrites have variety of applications in microwave fields[1]. Some ferrites are suitable as filter inductors for band pass filters in carrier telephone circuits. Due to high resistivity they may be used to make pole pieces for concentration of flux in h-f induction heaters. Miniature components like inductors and transformers can be prepared from ferrites. Their future use in construction of microwave integrated circuits is highly expected[2]. Non-reciprocal microwave devices like isolators, circulators, phase shifters and modulators utilize the phenomenon of Faraday rotation and ferromagnetic resonance. Mg-Mn ferrites are mostly used in these devices as they have low resonance loss[3].

Now-a-days the immense use of ferrites is made in memory and switching circuits in digital computers[4]. The degree of rectangularity, the uniformity and stability of characteristics has directly used in memory devices for storage capacity. Cores of Mg-Mn ferrites have been produced with a good degree of rectangularity and the uniformity is expected to be achieved through control of composition and processing[5].

Many oxides and semi-conductors have exhibited the switching and memory phenomena. The preparation technique, incubation time before switching, the field inside the material, presence of regenerative negative resistance region etc. are the undesirable features which limit the switching behaviour. The semiconductors exhibiting the similar conduction phenomenon at high fields get trapped the flow of charge due to existence of space charge and also the recombination process plays a major role. The high field transport properties are most complicated and hence are poorly understood. Therefore, the study of conduction mechanism must include the structural changes incubation period, the field inside the material and its distribution; temperature, electron emission, photo response and electroluminance effects.

Switching phenomenon is already reported in copper ferrite by T.Yamashiro[6]. Ferrites like Mg-Mn, Li-doped YIG and single crystal of Yb Fe O_3, Li-ferrite exhibit the same phenomenon[7]. Hisatake et al.[8] have reported the similar behaviour in Cu-ferrite and Li-ferrite. Patil S.A. et al.[9] have also reported the switching and memory effects in stoichiometric copper ferrite. These studies seem to be inadequate and attracts one's mind to study in detail the non-stoichiometric systems.

A short outlook of the relevant subject is reviewed and the results of our studies on non-stoichiometric Cu-ferrites regarding the switching behaviour is presented in this chapter.

3.2 I-V CHARACTERISTICS MEASUREMENTS

A schematic circuit diagram for I-V characteristics measurements is shown in fig.(3.1a). A polished and silver pasted pellet was sandwitched in a special pellet holder. The block diagram of the pellet holder is also shown in fig. (3.1b).

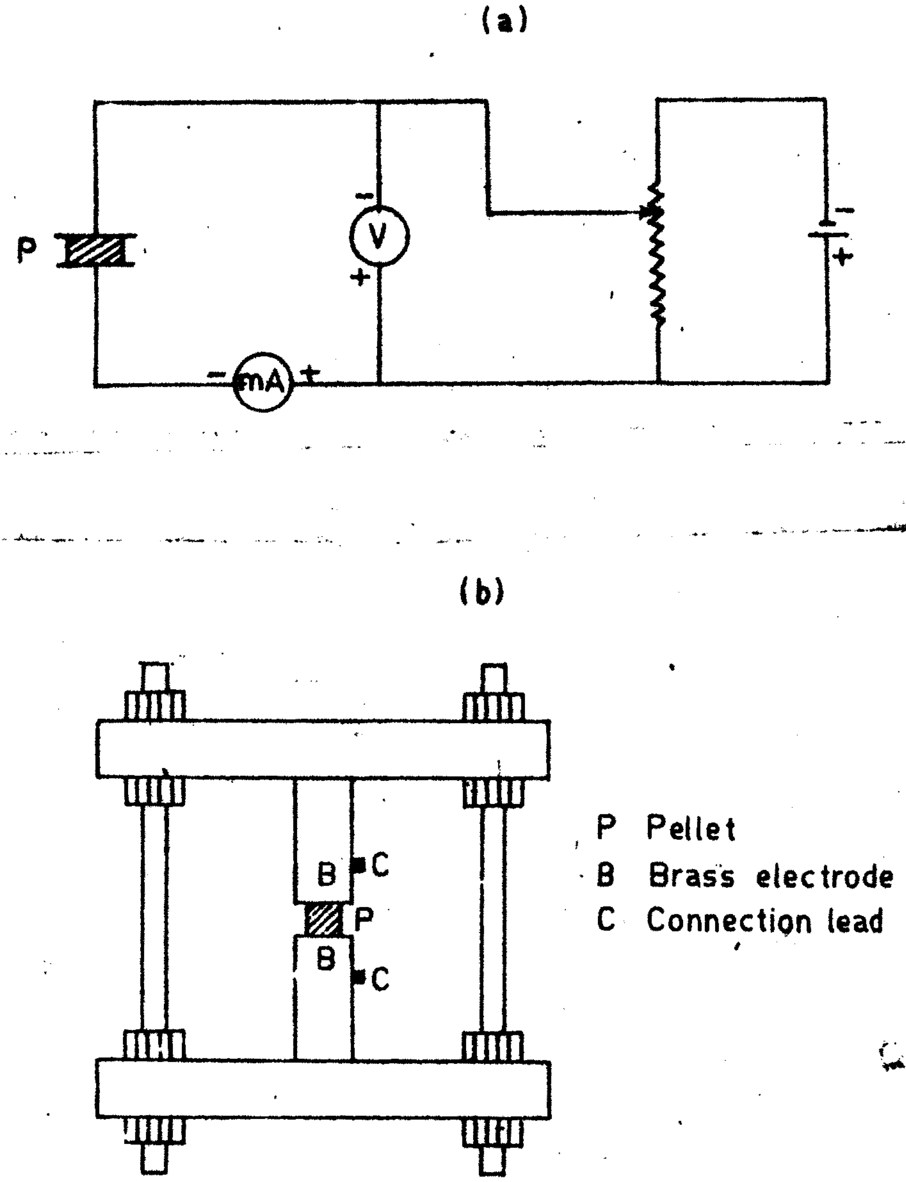


Fig. 3·1 (a) A schematic circuit diagram for I-V characteristic measurements.

(b) Block diagram of pellet holder.

The two brass electrodes with platinum foils act as sample contact plates. These plates are further connected to conducting wires with the help of a screw which is very close to the sample. The side screws, insulated from brass plates, provide the tightening of the sample for firm contacts.

The current controlled oven was used to maintain successively the constant temperatures 25°C (RT), 50°C, 100°C, 150°C, 200°C, 250°C and 300°C. The constant temperature varies through 5°C. The mercury thermometer having range 0°C to 350°C was provided to measure the temperature. The I-V characteristics at constant temperatures ranging from 25°C (RT) to 300°C were determined for the single pellet by applying varying d.c. voltage across the sample.

Aplab regulated power supply unit was used. The voltage and current limits were selected upto 300 volts and 300 mA respectively. Philips PM type electronic meter was used for the measurements of sample currents. The I-V measurements for pellets of each composition and different quenching temperatures were made for different constant temperatures.

3.3 THEORIES OF SWITCHING BEHAVIOUR

The measurements of the current (I) as a function of applied voltage (V) in semiconductors exhibit the ohmic relation at low electric fields. The deviation of I-V characteristics from ohmic relation becomes more prominent as the voltage across the sample increases. The increase of the voltage rises the current rapidly exhibiting power relation, or an exponential dependence on the voltage, which follows ultimately either electronic or thermal breakdown of the material. A high resistivity materials sandwitched between metal electrodes in the form of thin films, on the application of d.c. voltage, produce largely the I-V characteristics before the final irreversible breakdown occurs. The unstable conduction regions are generally of three types as shown in fig.(3.2) where conductivity switches from one value to another through unstable region. The three models of switching behaviour have described below as i) VCNR ii) CCNR and iii) bistable or memory switching.

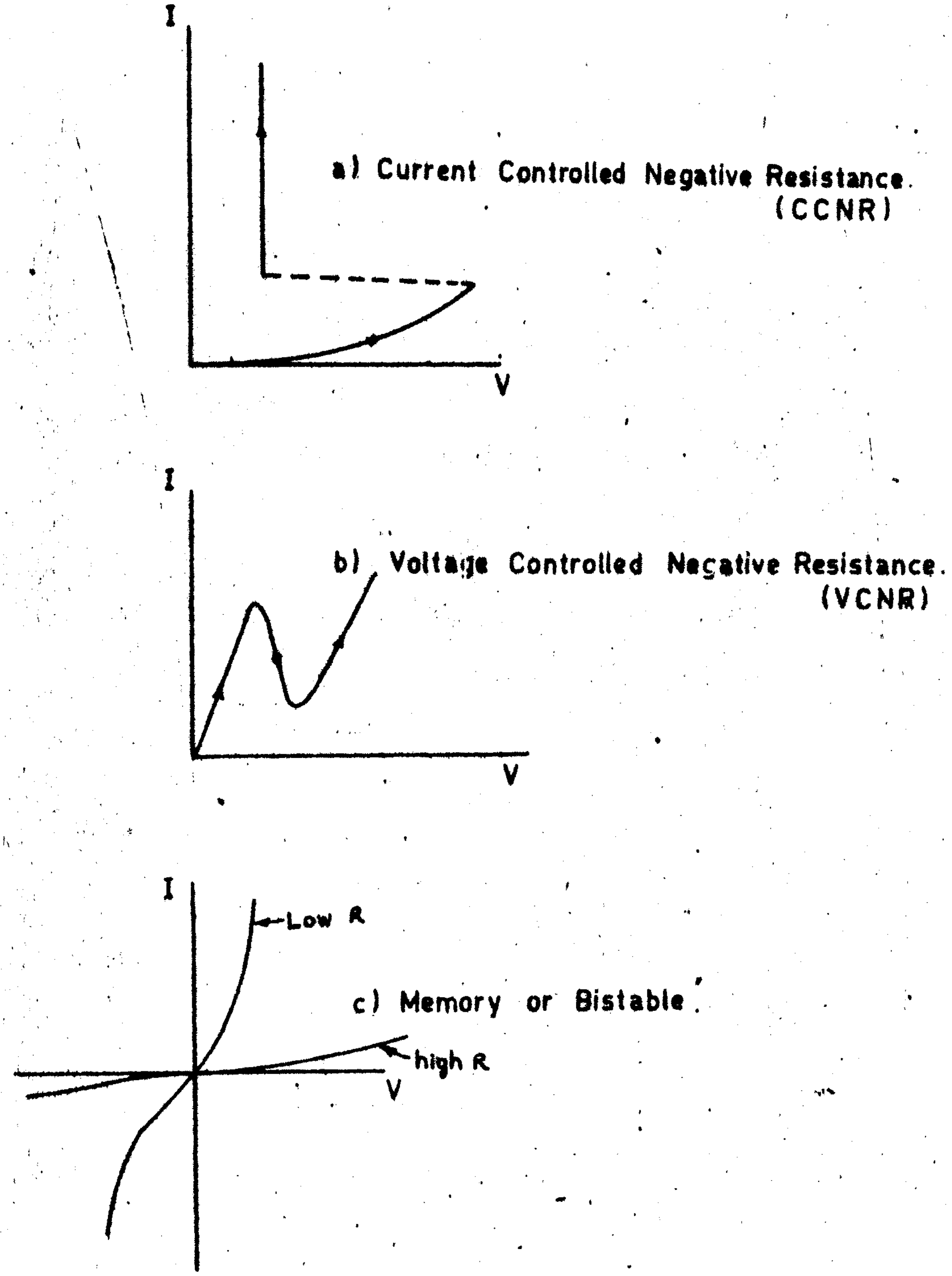
3.3a. Voltage Controlled Negative Resistance (VCNR) or N-Type :

The general observations show that the applied voltage appears across the thin region of an insulator film. It is proposed that the field of ionisation of impurities from an impurity band located somewhere between the valence and conduction bands of the insulator, increase the conductivity. Further increase in the field may set a competitive recombination process which lowers the conductivity. It is possible that the ionic movement and the accompanying space charge play a significant role in VCNR.

3.3b. Current Controlled Negative Resistance (CCNR)or S-Type :

The general conclusions from the observations regarding CCNR or S-type are briefed and put as below :

This phenomenon is a bulk limited effect. The behaviour of semiconducting material is least dependent on the electrode materials. At high fields, the current transport through



a) Current Controlled Negative Resistance. (CCNR)

b) Voltage Controlled Negative Resistance. (VCNR)

c) Memory or Bistable.

Fig. 3·2: Schematic diagrams of three types of high field instability.

disordered semiconducting material is observed, in general, with a high density of traps. The threshold voltage depends on the preparation treatment, geometry, history and surrounding temperature of the material. The sustaining voltage, V_s is nearly independent of the above variables. As the field is a significant physical quantity, the constant value of V_s must be due to some apparent effect. Thermal and filamentary processes are present in some cases. There is no evidence about these processes to be dominated in all the cases. The relaxation time of oscillations in CCNR region being typically 10^{-8} secs., the switching process must be clearly electronic in nature.

3.3c. Bistable Switching or Memory :

Bistable switching or memory exhibited in glasses[10] is explained by proposing a mechanism of freezing or defreezing at high and low conductivity states. Bistable switching is attributed to filamentary conduction and structural changes. Mott and Davis[11] suggested that the multicomponent semiconducting glass film cooled from the certain temperature may result in a state where all the electrons get distributed in low conductivity state. While the cooling of the sample from a different temperature may allow a redistribution of position of atoms in which some of the conducting constituents get isolated forming a high conducting states. A mechanism based on the temperature dependent structural changes is as below -

The temperature rises to such a value to cause the material to melt and the rapid cooling follows the amorphous state frozened. Sometimes the temperature rise in the reset pulse may be sufficient to cause only amorphous crystalline transformation without melting.

A suitable mechanism to explain CCNR must contain a field dependent process for enhancing either the life time of one type of carriers or the density of carriers by generation, injection or by multiplication. This process should result in redistribution of the field and thus may be sustained at lower applied voltage appearing across a narrower region of specimen.

3.4 RESULTS AND DISCUSSION

The general nature of switching behaviour observed in stoichiometric and non-stoichiometric copper ferrite samples, both slow cooled and quenched from different temperatures is shown in fig. (3.3). In this figure, the two successive cycles of d.c. I-V characteristics are given. With the increase of voltage across the sample the deviation from Ohm's law becomes more prominent following the power relation $I = a V^n$. When the voltage reaches just over the value represented by A for the first cycle; the breakdown suddenly occurs known as first breakdown which results in the sudden fall of voltage to the value indicated by point D and abrupt rise of current following the path ABC. The I-V characteristic for the subsequent decrease in voltage is indicated by the curve CDO.

The breakdown process of the same sample and at the same temperature for the second and succeeding cycles are indicated

TABLE NO. 3.1

MEASUREMENTS OF FIRST SWITCHING TEMPERATURES

Sample	Slow cooled (°C)	Quenched at 400°C (°C)	Quenched at 600°C (°C)	Quenched at 800°C (°C)
$Cu\ Fe_2O_4$	50°C	100°C	25°C (R.T.)	25°C(R.T.)
$Cu_{0.8}Fe_{2.8}O_4$	150°C	100°C	50°C	25°C(R.T.)
$Cu_{0.6}Fe_{2.4}O_4$	250°C	100°C	50°C	50°C
$Cu_{0.4}Fe_{2.6}O_4$	250°C	150°C	150°C	100°C
$Cu_{0.2}Fe_{2.8}O_4$	-	300°C	330°C	300°C

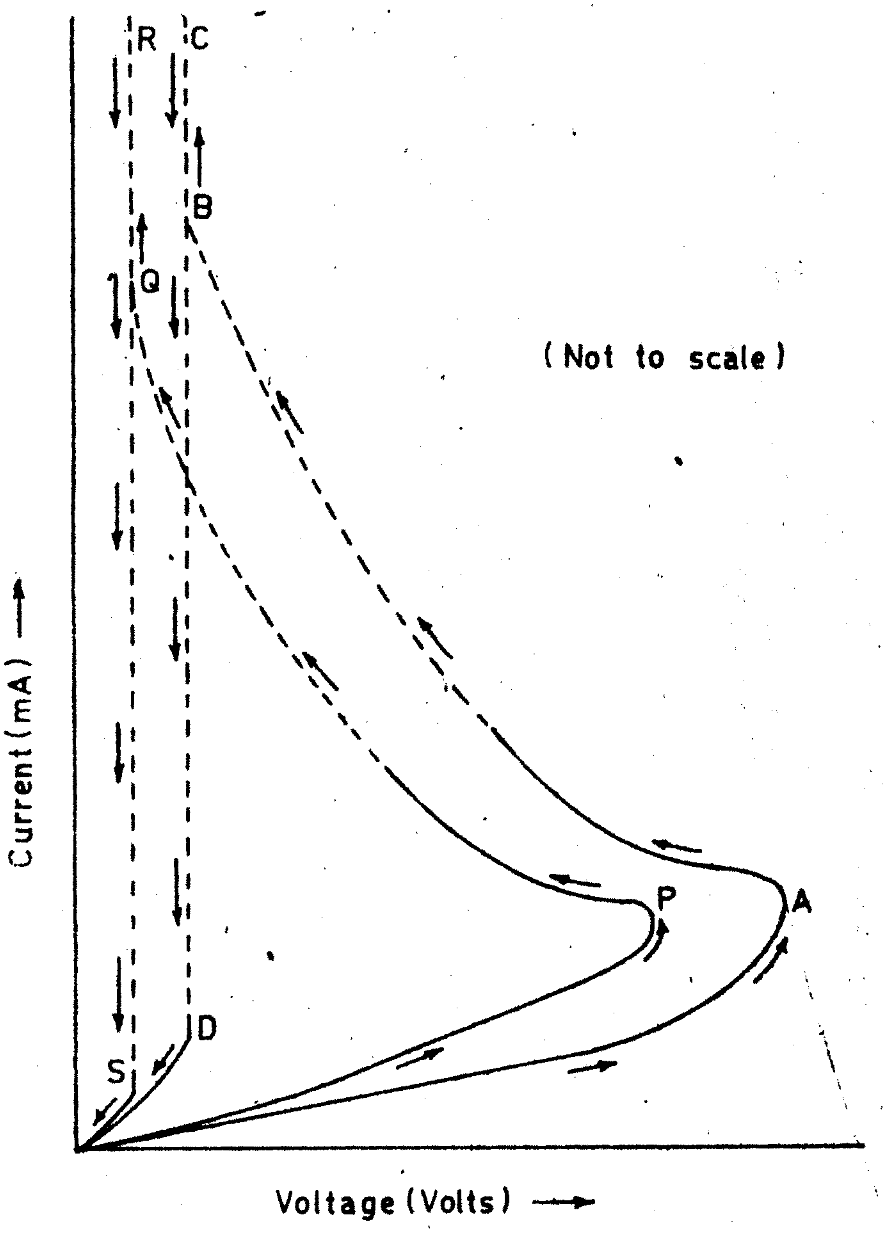


Fig. 3·3 : General nature of Switching behaviour.

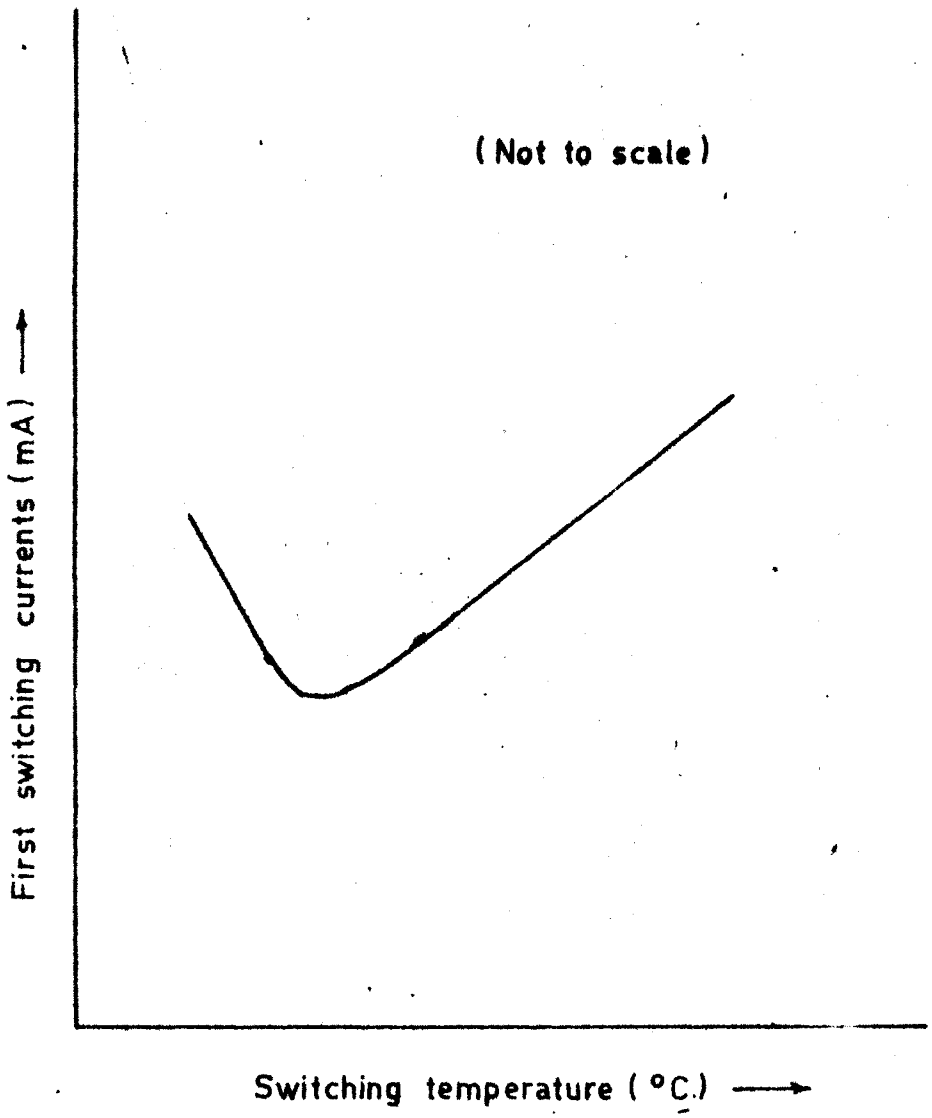


Fig. 3:4 First switching currents vs switching temperature.

by the curve OPQ during increase of voltage and RSO during the decrease of voltage. The second and following cycles of I-V characteristics for the same sample at the same temperature may be repeated as OABCDO or may remain distinct as indicated by the curves OABCDO and OPQRSO. Sometimes the rising curves are different from each other while the decreasing curves are the same.

In Figs. (3.5 to 3.31) are given the d.c. I-V characteristics experimentally obtained for stoichiometric and non-stoichiometric copper ferrite samples either slow cooled or quenched from different temperatures. The pellets prepared for I-V measurements were not necessarily of the same thickness; so the first switching currents of the same sample either slow cooled or quenched from different higher temperatures do not exhibit nearly the same value as reported by T.Yamashiro.

3.4a Switching in Copper Ferrites ($CuFe_2O_4$)

The switching behaviour in a slow cooled $CuFe_2O_4$ sample cooled from 950°C, at different temperatures in the range 25°C to 300°C is given in fig (3.5). Electrical switching was observed in a slow cooled copper ferrite above room temperature at 50°C registering the first switching current 14.5 mA. The second cycle for the same sample at 50°C is found not to repeat which is as indicated in fig (3.3) and the switching current at 100 V falls to 2.8 mA. The next and succeeding cycles at 50°C are all repeatative, exhibiting current and relations just the

TABLE No.3.2

MEASUREMENTS OF SWITCHING CURRENTS AT DIFFERENT TEMPERATURES

SAMPLE : $CuFe_2O_4$

Temperature (°C)	Slow cooled (mA)			Quenched at								
				400°C (mA)			600°C (mA)			800°C (mA)		
	a	b	c	a	b	c	a	b	c	a	b	c
25°C (R.T.)	-	-	-	-	-	-	11.5	2.3	3.9	-	30	20
50°C	-	14.5	2.8	-	-	-	4.5	6.8	6.8	9.5	17.5	20
100°C	3.8	4.2	-	18	6.2	4.6	6.7	6.8	14.5	24	40	40
150°C	6	7.5	-	7.5	8	9.4	20	27	32	40	50	70
200°C	14	18	-	16	17	20	28	40	42	60	75	90
250°C	30	32	-	24	27	36	42	55	100	90	120	130
300°C	42	70	-	50	70	70	100	110	160	100	120	130

a : Switching currents at the first cycle

b : Switching currents at the second cycle

c : Switching currents at the third cycle

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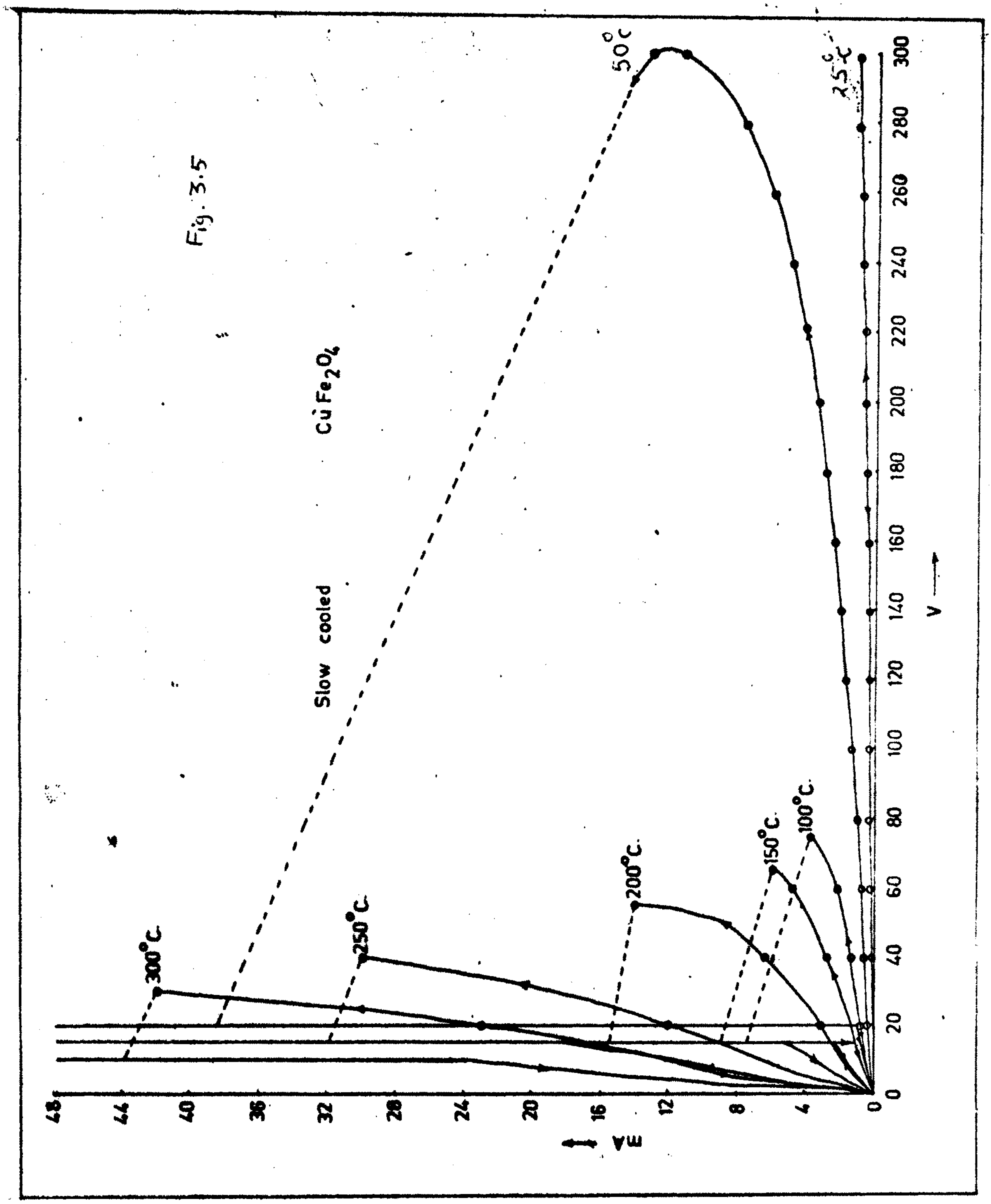


Fig. 3.5

CuFe$_2$O$_4$
Slow cooled
300°C
250°C
200°C
150°C
100°C
50°C
25°C
V →
ΔE →
0
4
8
12
16
20
24
28
32
36
40
44
48
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300

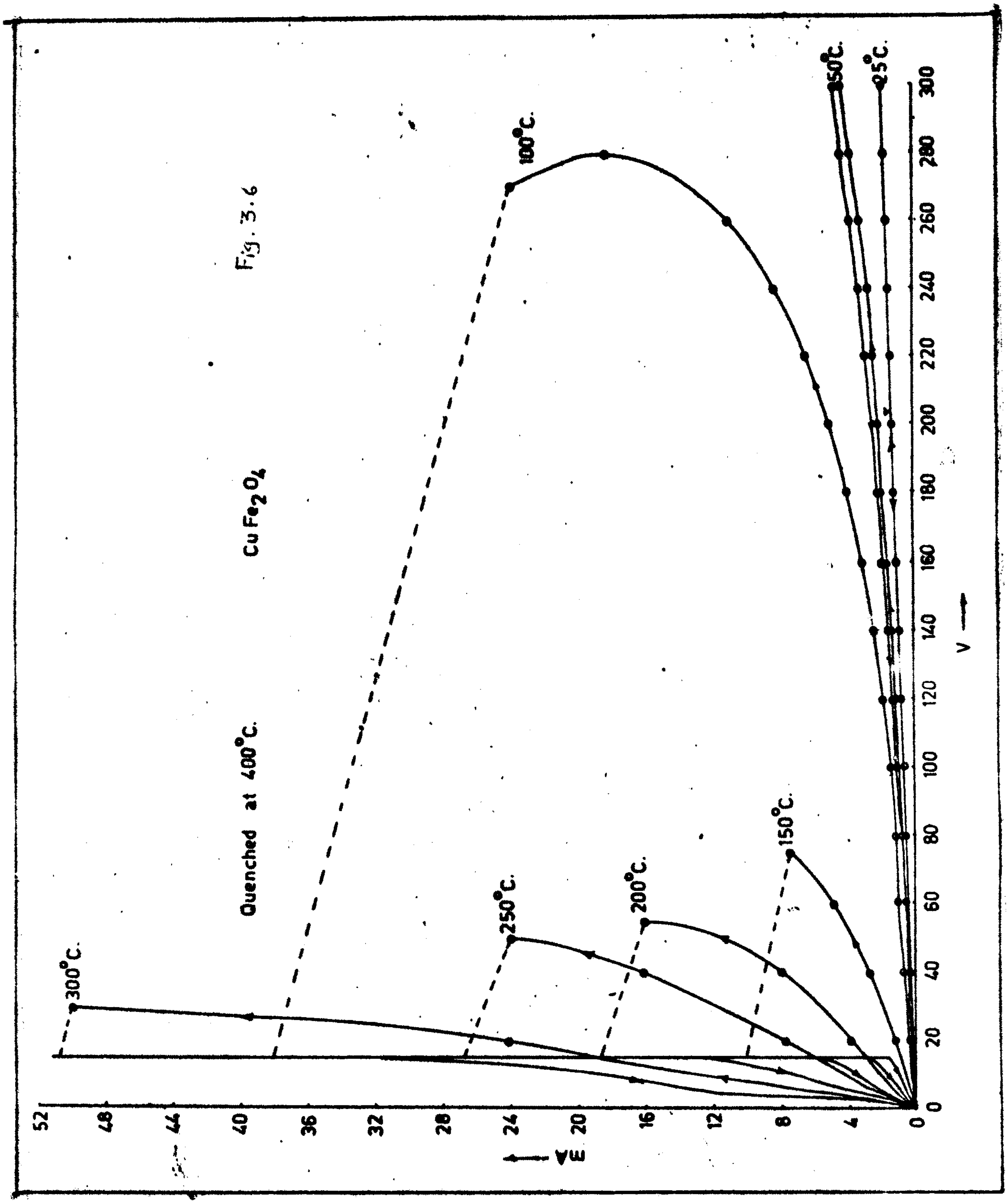
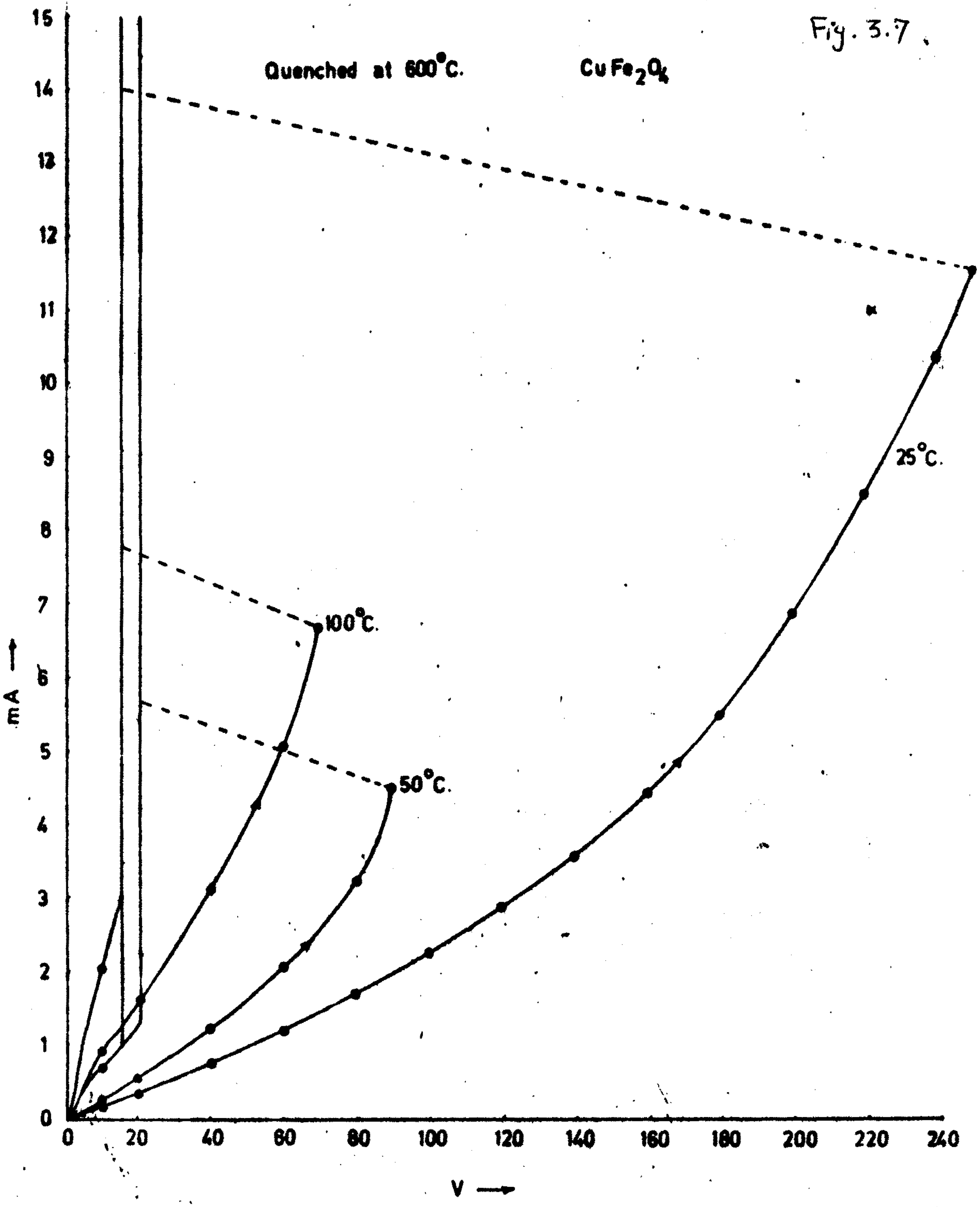


Fig. 3.6

CuFe$_2$O$_4$
Quenched at 400°C.
300°C.
250°C.
200°C.
150°C.
100°C.
50°C.
25°C.
ΔE →
V →
0
4
8
12
16
20
24
28
32
36
40
44
48
52
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300

Fig. 3.7.


Quenched at 600°C.
CuFe$_2$O$_4$
mA
V
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
0
20
40
60
80
100
120
140
160
180
200
220
240
100°C.
50°C.
25°C.

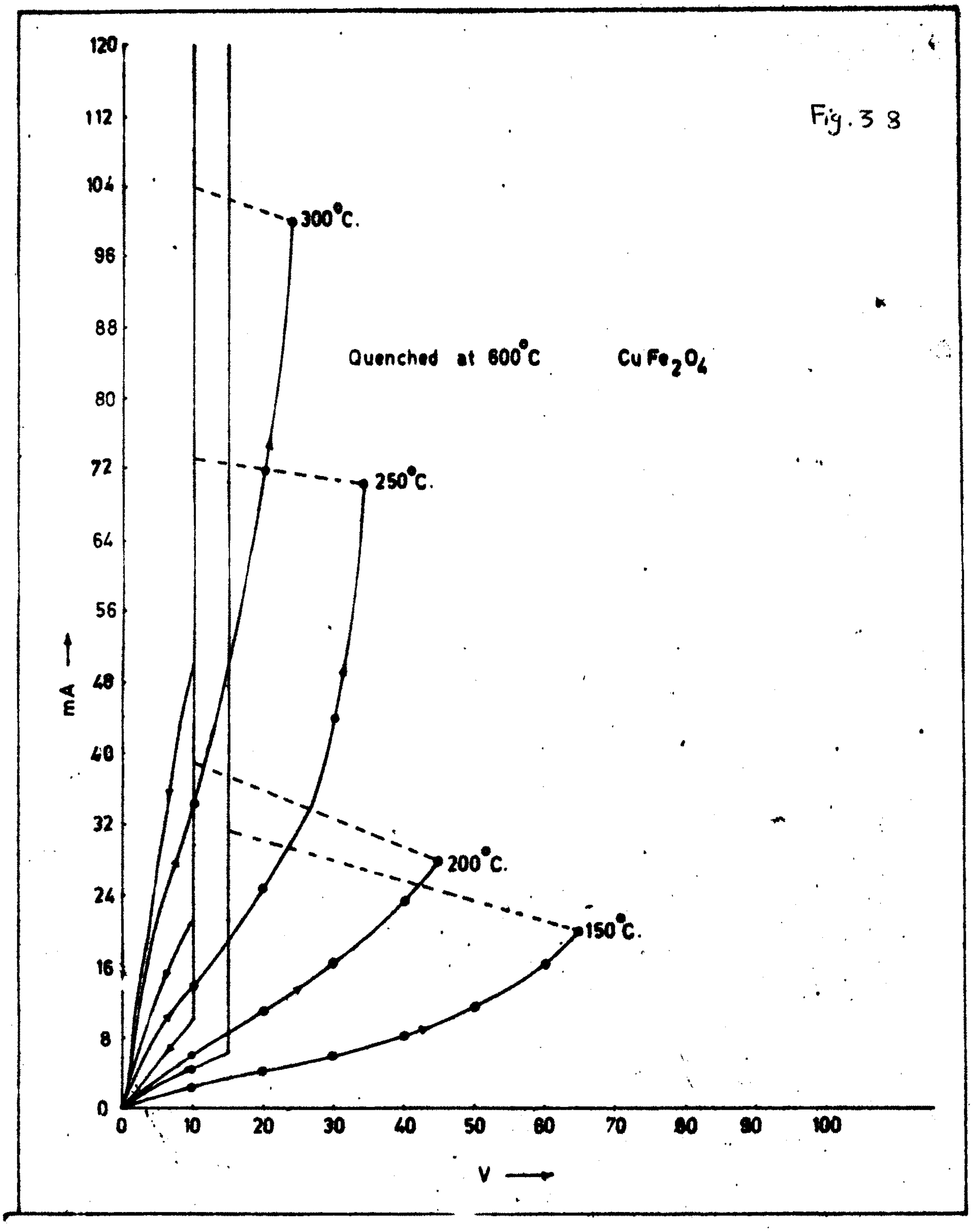


Fig. 3 8
Quenched at 600°C
Cu Fe2O4
300°C.
250°C.
200°C.
150°C.
mA
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
0
10
20
30
40
50
60
70
80
90
100
V

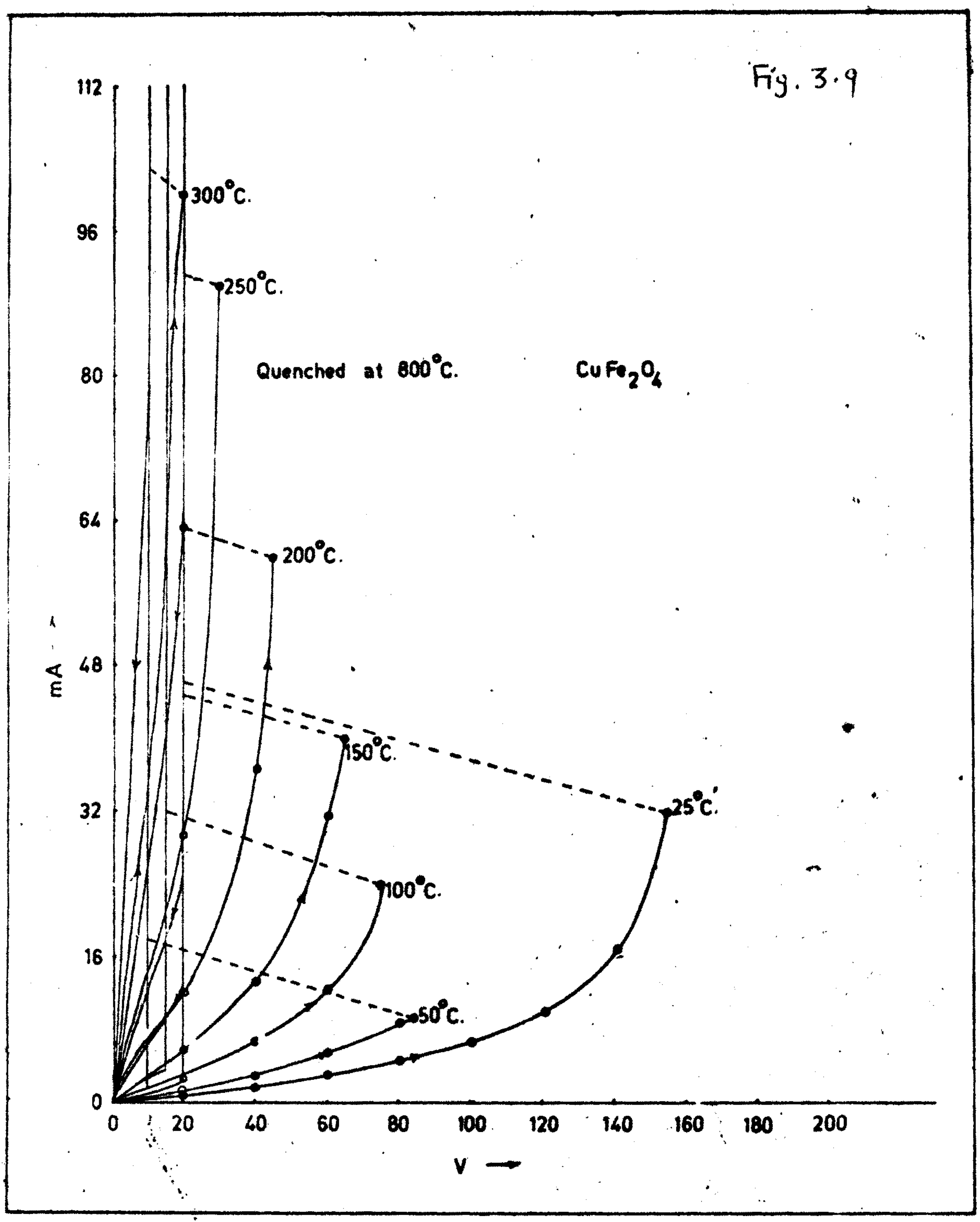


Fig. 3·9
Quenched at 800°C.
$CuFe_2O_4$
mA
V
112
96
80
64
48
32
16
0
0
20
40
60
80
100
120
140
160
180
200
300°C.
250°C.
200°C.
150°C.
100°C.
50°C.
25°C.

same as for second cycle. The slow cooled copper ferrite exhibits no switching below 50°C, which can be noted from the exhibited I-V characteristics.

The slow cooled copper ferrite, after completion of reaction, has tetragonal crystal structure. This was identified as was discussed in Chapter 2. The slow cooled copper ferrite when undergoes further heat treatment is reported to show different features. A peculiar result by Miyadai et al.[12] is that the slow cooled copper ferrite which is in tetragonal phase transforms to cubic phase at about 340°C when heated.

Electrical switching in furnace cooled Cu-ferrite was first reported by T. Yamashiro[6]. However, different points of view have been put forth for an explanation. On the one hand it is said to occur due to Jahn Teller distortion due to Cu^{+2} at B site of spinel structure and on the other hand it is explained on the basis of Joule self heating effect[8]. The Cu^{+2} ions are well known for exhibiting Jahn Teller distortion. However in the present investigation the switching observed may be attributed to the Joule self heating. From Figs.(3.5) it can be noted that the switching is not exhibited by slow cooled copper ferrite at room temperature and upto 50°C but it occurs at higher temperatures. During the experimentation of noting down the I-V characteristics the temperature of the pellet inside may be raised to the level which may bring in the breakdown in the sample peculiar result is reported by Miyadai[12] that the slow cooled copper ferrite which exists in tetrgonal phase transforms to cubic phase at about 350°C when reheated. Patil S.A. et al.[9]

has shown that the change of crystal structure from tetragonal to cubic brings in the effect of the switching phenomenon in copper ferrite. Thus our results could be explained by taking into consideration the above two arguments. Owing to Joule self-heating during experimentation the temperature of the pellet may be raised to bring in the structural transformation from tetragonal to cubic which may result in the electric switching in slow cooled copper ferrite at 50°C and above. Moreover the slow cooled copper ferrite is reported to exhibit a mixed crystal structure that is having the planes of both cubic and tetragonal phases. We have also observed the similar results which is discussed in Chapter 2.

Copper ferrite is basically a semiconductor and is expected to exhibit the similar properties. This is observed and can be seen from the fig. (3.4) that at higher temperatures the first switching current goes on increasing. The first switching currents at different temperatures initially decrease and then increase through a minimum. The increase of current at higher temperature by the same applied voltage is expected due to the availability of number of carriers and therefore, the initial decrease in first switching currents needs some explanation.

N.Nanba and S.Kobayashi [13] have reported by studying the temperature dependence of Seebeck coefficient and resistivity of $Cu_x Fe_{3-x}O_4$ that the conduction in slow cooled sample may be caused predominantly by electron-hopping between Fe^{+2}- Fe^{+3} on B sites. In the temperature range higher than 360°C Fe^{+2} ion on B site gets populated by electron transfer and the temperature dependence of cation migration. Below this temperature the cation migration is not possible but electron transfer is possible. Thus the rising of first switching currents with temperature could be explained on the basis of carrier mobility and seebeck ccefficient together.

N.Nanba and S.Kobayashi have further reported in quenched copper ferrite sample that the value of resistivity has a substantial rise at particular temperature called as characteristic temperature which may have been caused due to enhance migration and conversion from P to N type conductivity. Thus the decrease in first switching current upto a minimum observed by us in copper ferrite may be attributed to P-N type conductivity.

In Figs.3.6 to 3.9 are given the I-V characteristics for stoichiometric copper ferrite samples quenched from 400°C, 600°C and 800°C to room temperature. The samples quenched from 400°C, 600°C and 800°C experience the first breakdown at first switching temperatures 100°C and room temperature respectively. Table 3.1 indicates that the switching temperatures decrease as the quenching temperature of the samples increase. The first switching cycle is found not to repeat during the second cycle while the second and the successive cycles are repeatative.

Thus though the copper ferrite, slow cooled and quenched at 400°C do not exhibit switching behaviour at room temperature, it clearly exhibits this phenomenon at room temperature and above when quenched at 600°C and 800°C. This may be because with increasing quenching temperatures, the c/a ratio goes on decreasing[14,15] and it reaches unity above 900°C. In other words as the tetragonal phase changes over to cubic phase which looks to be a continuous process, the switching seems to occur. Thus once again though the Joule self-heating may be the cause of switching; the structural transformation from tetragonal to cubic in the copper ferrite may be also the reason for electrical switching.

In case of quenched $Cu_x Fe_{3-x}O_4$ samples, N.Nanba and S.Kobayashi have reported that the resistivity of ferrite has a sudden rise and seebeck coefficient gets concaved at a characteristic temperature; at which the constituent cations initiate migration[15]. It is further said that a substantial rise in resistivity with the change in sign of seebeck coefficient might have enhanced the P-N conversion in quenched samples. As the positive seebeck coefficient supports the conduction neither by electron-hopping between Fe^{+2}- Fe^{+3} on B site nor between Cu^{+1}- Cu^{+2} on A site, the P-type conduction is suggestive due to Cu^{+2} ion on A site. Thus the decrease in first switching current initially and then increase through a minimum observed by us in quenched stoichiometric samples may be attributed to P-type conductivity associated with P-N conversion.

3.4b. Switching in Non-Stoichiometric $Cu_{0.8}Fe_{2.2}O_4$ and $Cu_{0.6}Fe_{2.4}O_4$ Ferrites

The switching behaviour in $Cu_{0.8}Fe_{2.2}O_4$ and $Cu_{0.6}Fe_{2.4}O_4$ samples at different temperatures ranging from 25°C to 300°C is presented in figs.3.10 to 3.18. In the same figures the switching characteristics in quenched samples of the same

TABLE NO. 3.3

MEASUREMENTS OF SWITCHING CURRENTS AT DIFFERENT TEMPERATURES

SAMPLE : $Cu_{0.8}Fe_{2.2}O_4$

Temperature (°C)	Slow cooled (mA)			Quenched at								
				400°C (mA)			600°C (mA)			800°C (mA)		
	a	b	c	a	b	c	a	b	c	a	b	c
25°C (R.T.)	-	-	-	-	-	-	-	-	-	28	16	16.5
50°C	-	-	-	-	-	-	-	24	14	7.3	13	19
100°C	-	-	-	-	-	25	14	15	15	9	24	30
150°C	-	26	10	14	16	16	22	26	30	40	40	40
200°C	10	10.5	11.5	22	24	30	28	30	31	40	70	70
250°C	13.5	18	18	22	24	30	28	30	36	70	100	130
300°C	14	19	24	30	31	32	39	44	60	100	120	210

a : Switching currents at the first cycle
b : Switching currents at the second cycle
c : Switching currents at the third cycle

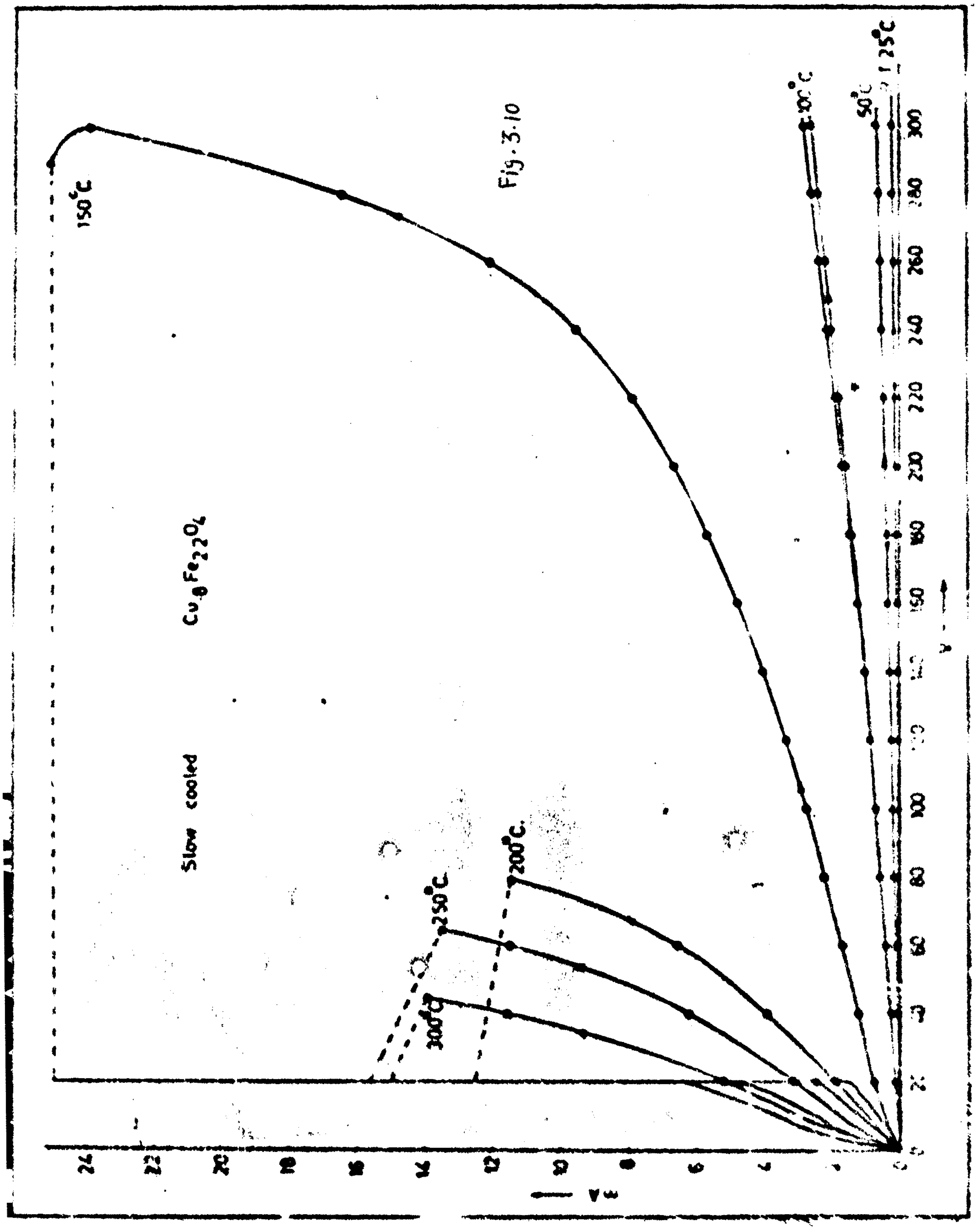


Fig. 3.10

$Cu_{.8}Fe_{2.2}O_4$
Slow cooled
150°C
100°C
50°C
25°C
200°C
250°C
300°C
mA
0
2
4
6
8
10
12
14
16
18
20
22
24
V
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300

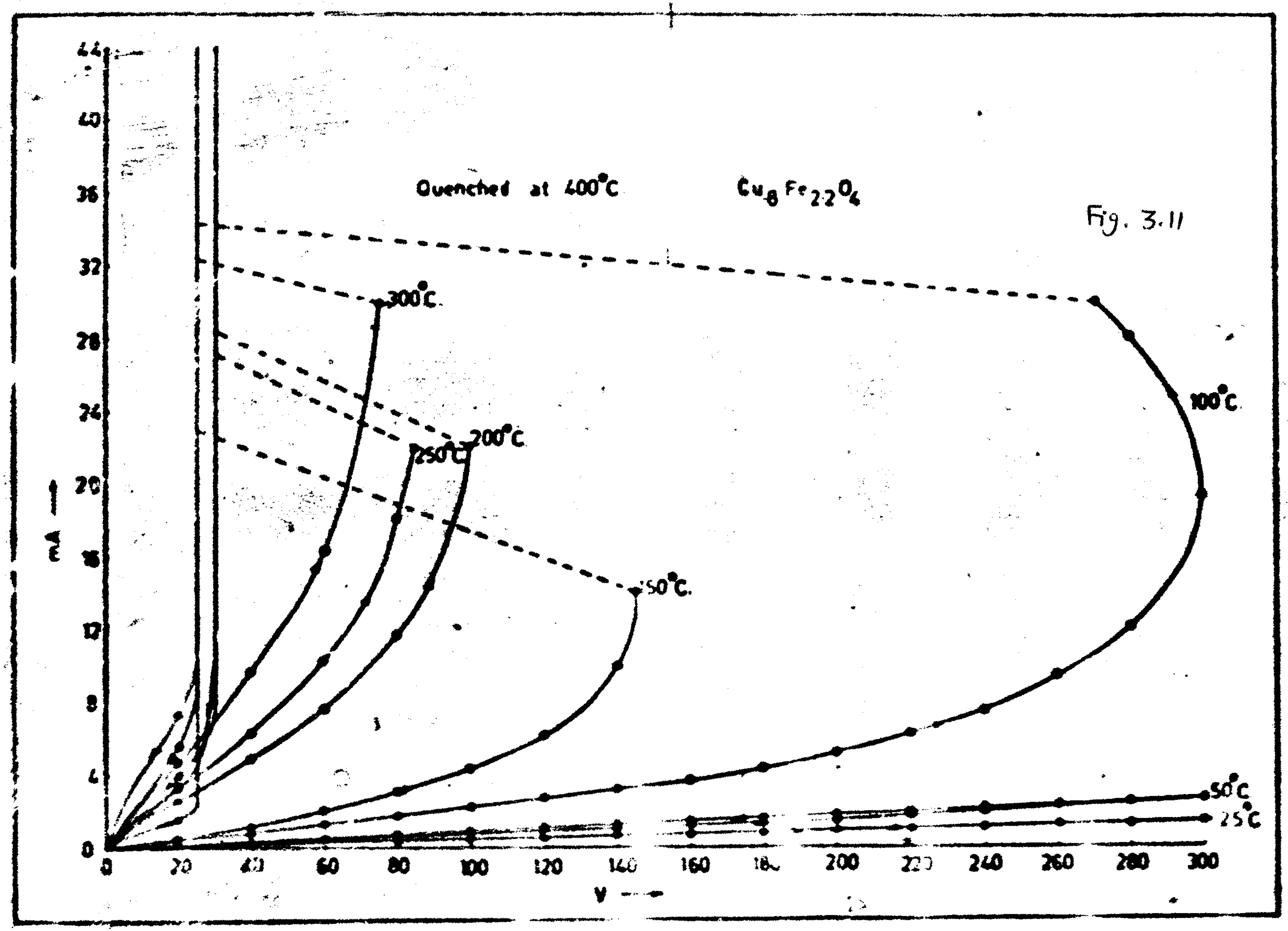


Fig. 3.11

Quenched at 400°C
$Cu_{.8}Fe_{2.2}O_4$
300°C
250°C
200°C
150°C
100°C
50°C
25°C
mA →
0
4
8
12
16
20
24
28
32
36
40
44
V →
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300

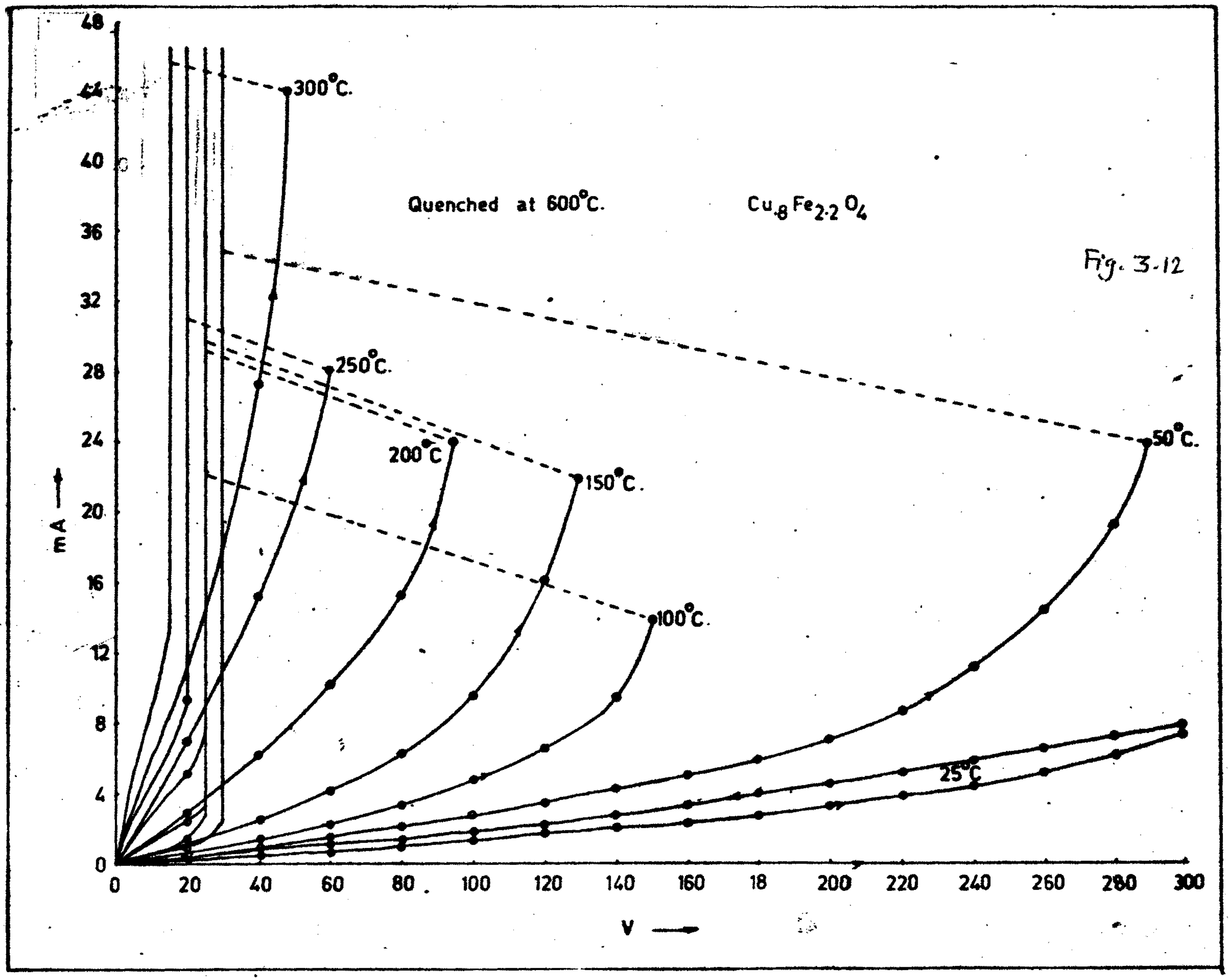

Quenched at 600°C.
$Cu_{.8}Fe_{2.2}O_4$
300°C.
250°C.
200°C
150°C.
100°C.
50°C.
25°C
mA
0
4
8
12
16
20
24
28
32
36
40
44
48
V
0
20
40
60
80
100
120
140
160
18
200
220
240
260
280
300

Fig. 3-12

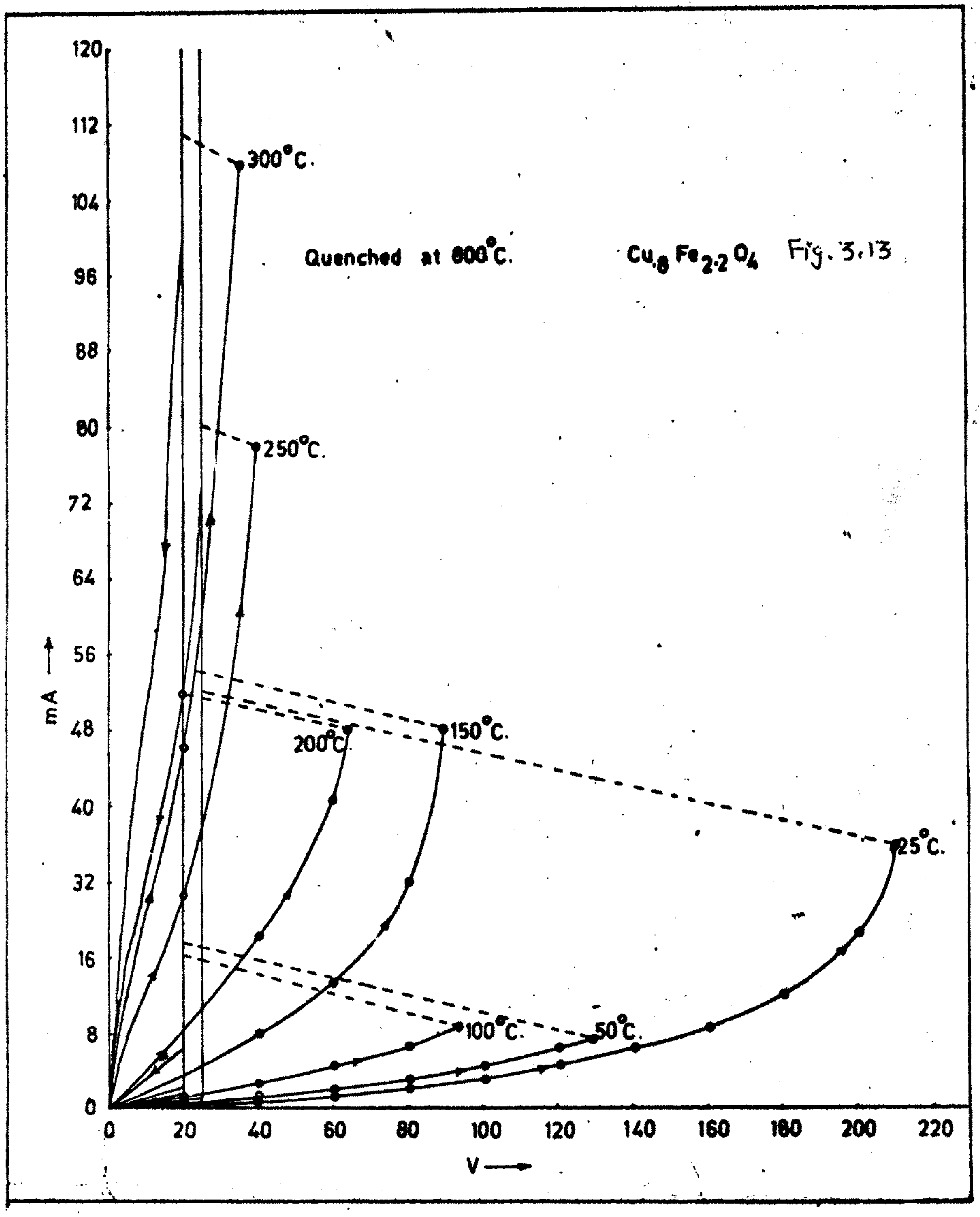

Quenched at 800°C.
$Cu_{.8}Fe_{2.2}O_4$
300°C.
250°C.
200°C.
150°C.
100°C.
50°C.
25°C.
mA ⟶
120
112
104
96
88
80
72
64
56
48
40
32
16
8
0
V ⟶
0
20
40
60
80
100
120
140
160
180
200
220

Fig. 3.13

TABLE NO. 3.4

MEASUREMENTS OF SWITCHING CURRENTS AT DIFFERENT TEMPERATURES

SAMPLE : $Cu_{0.6}Fe_{2.4}O_4$

Temperature (°C)	Slow cooled (mA)			Quenched at								
				400°C (mA)			600°C (mA)			800°C (mA)		
	a	b	c	a	b	c	a	b	c	a	b	c
25°C (R.T.)	-	-	-	-	-	-	-	-	-	-	-	-
50°C	-	-	-	-	-	-	-	-	22.5	18	5	3.8
100°C	-	-	-	-	-	26	12	3.9	4.3	5.1	5.1	5.3
150°C	-	-	-	8.2	6.2	8	5.9	9.7	9.5	8.2	13	13.
200°C	-	-	-	9.5	14	14	9.5	15.5	18	23.5	24	33
250°C	7.5	11.5	6.5	15	40	50	22	20	19	30	42	60
300°C	3.8	4.15	5	26	30	60	28	42	65	85	100	110

a : Switching currents at the first cycle
b : Switching currents at the second cycle
c : Switching currents at the third cycle

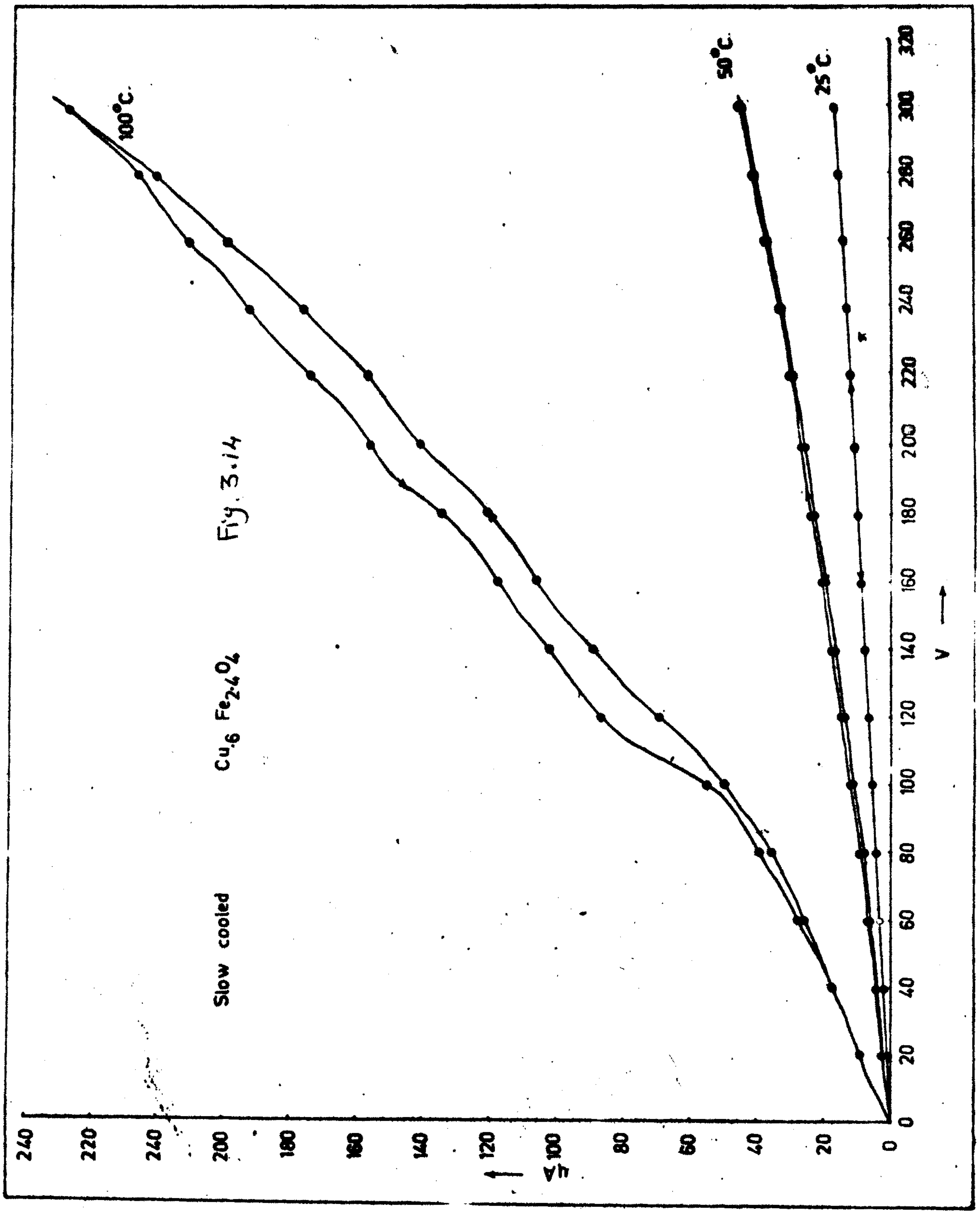


Fig. 3.14

Slow cooled
$Cu_{.6}Fe_{2.4}O_4$
100°C
50°C
25°C
V →
μA ←
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
0
20
40
60
80
100
120
140
160
180
200
240
220
240

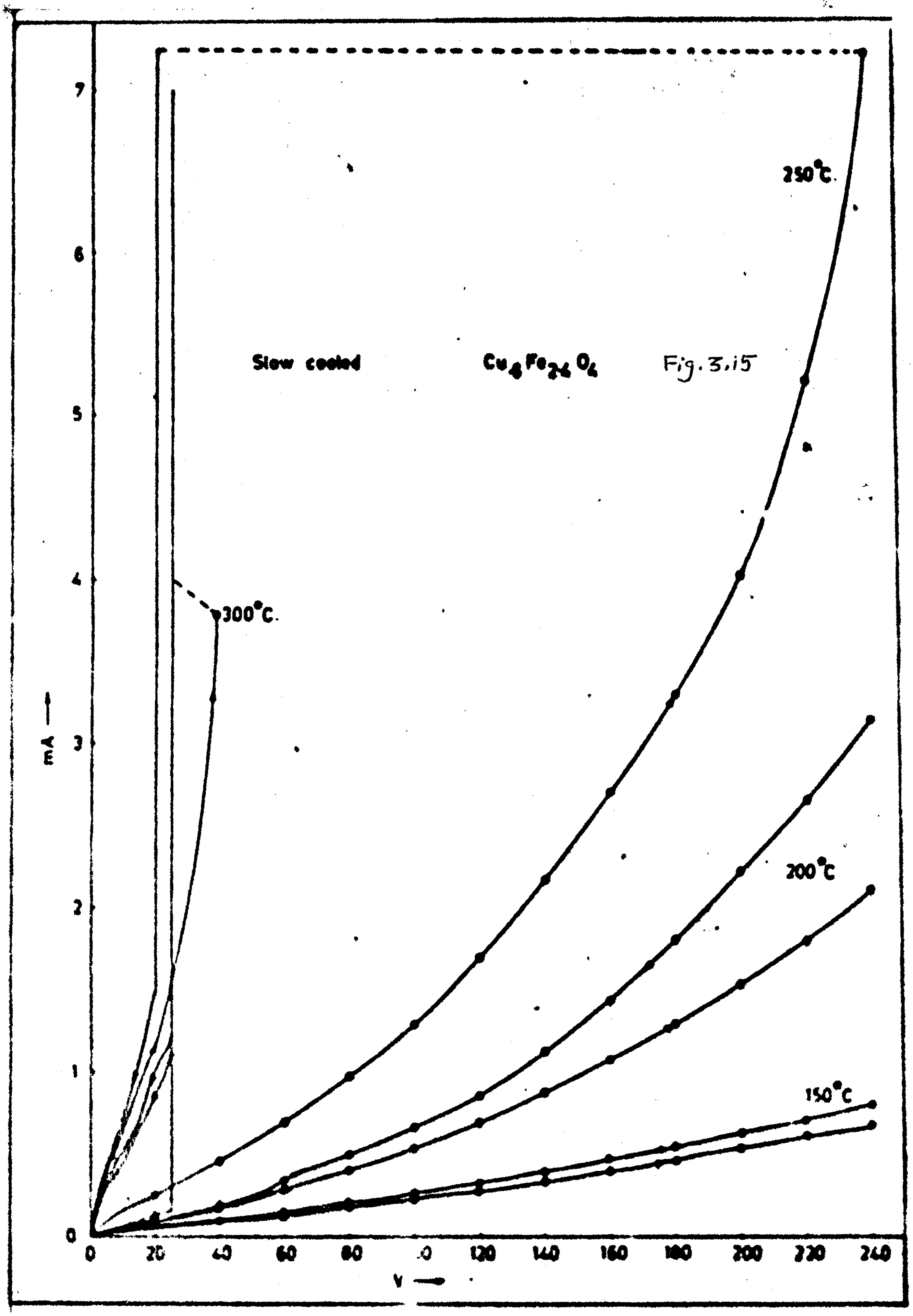

Slow cooled
$Cu_4Fe_{2.6}O_4$
250°C
300°C
200°C
150°C
mA
0
1
2
3
4
5
6
7
V
0
20
40
60
80
.0
120
140
160
180
200
220
240

Fig. 3.15

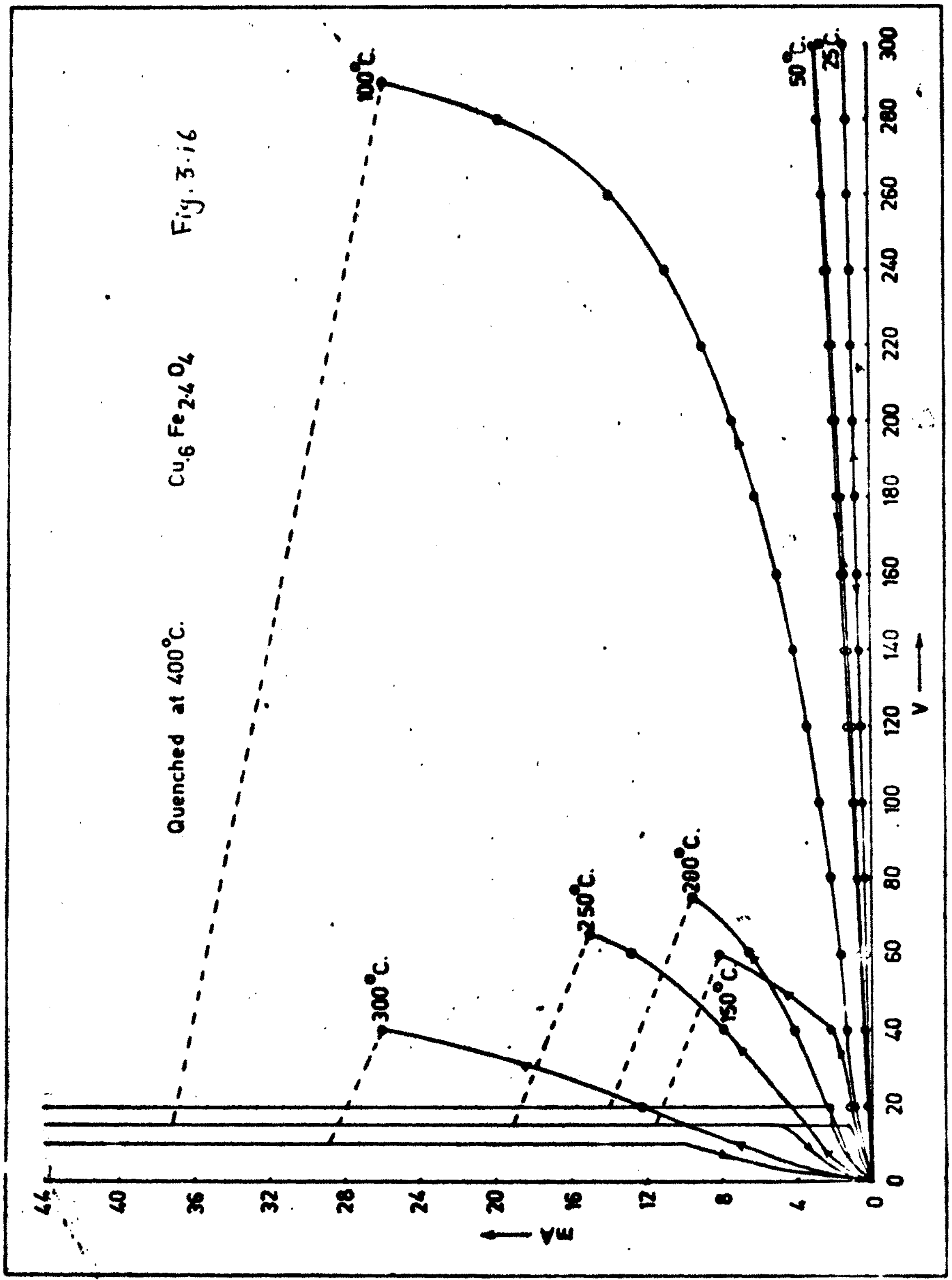


Fig. 3·16
$Cu_{.6}Fe_{2.4}O_4$
Quenched at 400°C.
100°C.
50°C.
25°C.
300°C.
250°C.
200°C.
150°C.
mA ⟵
0
4
8
12
16
20
24
28
32
36
40
44
V ⟶
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300

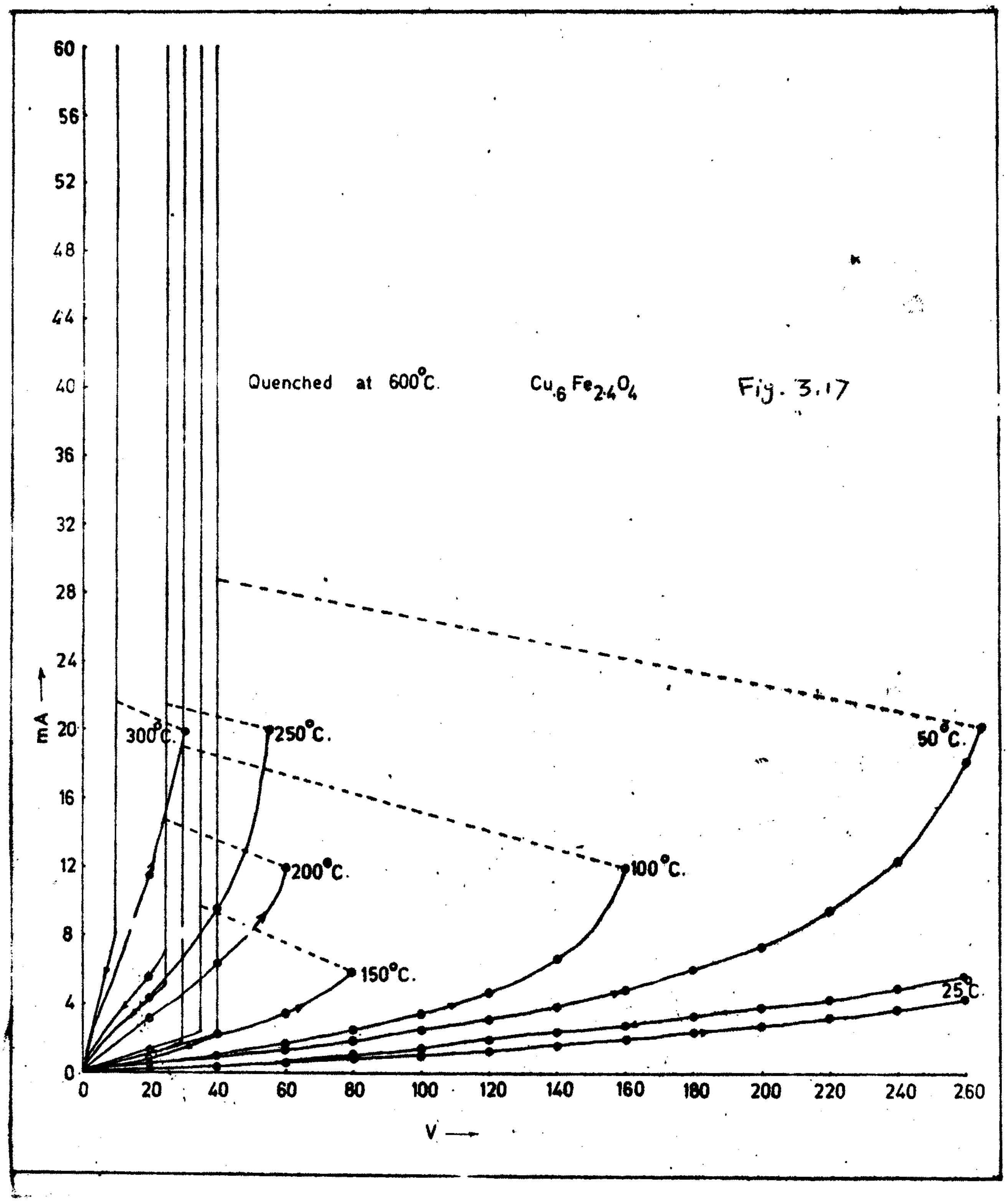


Fig. 3.17

Quenched at 600°C.
$Cu_{.6}Fe_{2.4}O_4$
mA →
V →
0
4
8
12
16
20
24
28
32
36
40
44
48
52
56
60
0
20
40
60
80
100
120
140
160
180
200
220
240
260
300°C.
250°C.
200°C.
150°C.
100°C.
50°C.
25°C.

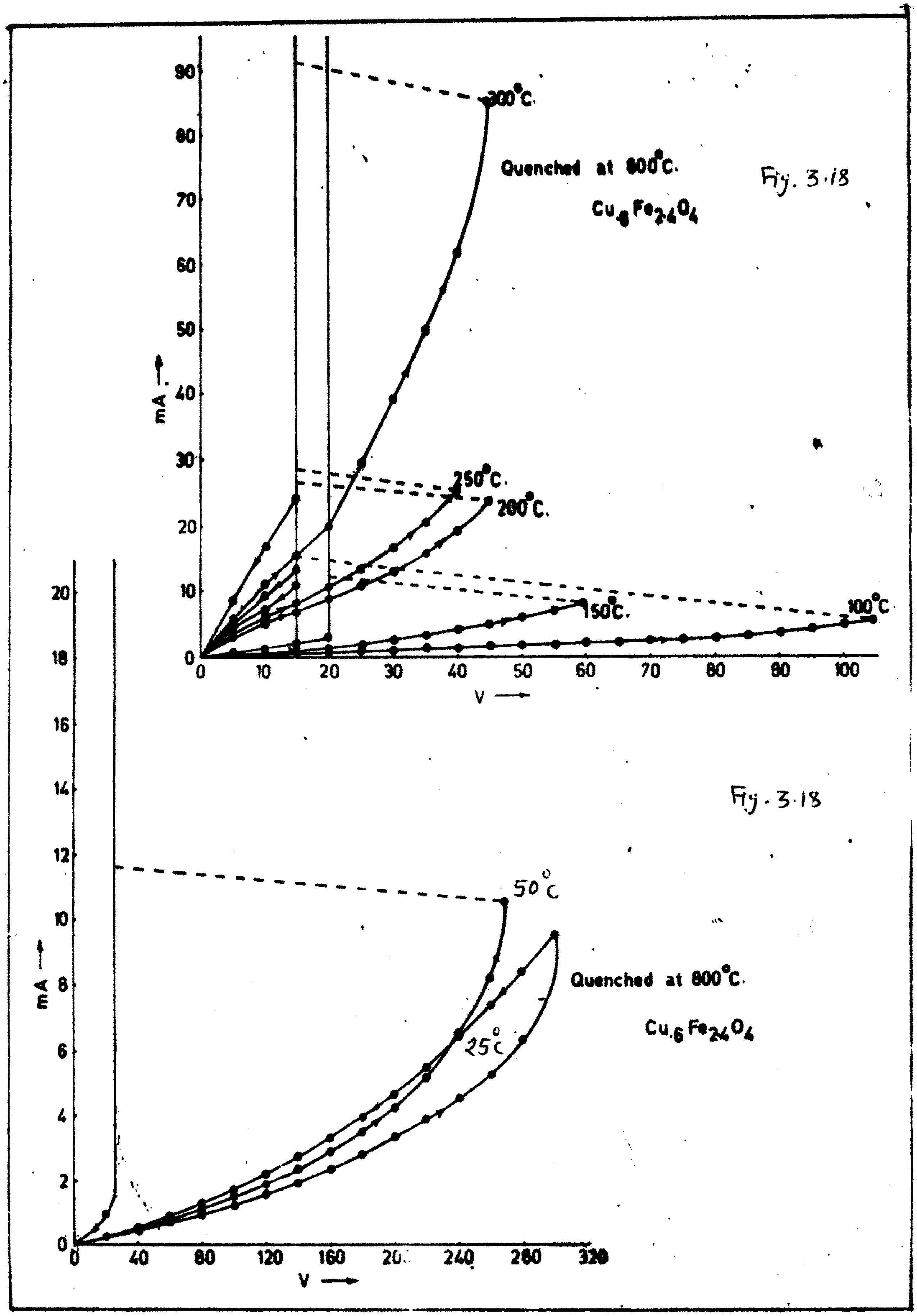


Fig. 3.18

Fig. 3.18

composition, quenched from 400°C, 600°C and 800°C are also shown. Tables 3.3 and 3.4 indicate the switching current values at different temperatures. The first electrical switching was observed at 150°C in slow cooled $Cu_{0.8}Fe_{2.2}O_4$ and at 250°C in slow cooled $Cu_{0.6}Fe_{2.4}O_4$ samples. The slow cooled $Cu_{0.8}Fe_{2.2}O_4$ and $Cu_{0.6}Fe_{2.4}O_4$ show tetragonal crystal structure which is discussed in Chapter 2. $Cu_{0.8}Fe_{2.2}O_4$ registers first switching current of 26 mA at 150° which is non-repeatative, while the second cycle is observed repeatative registering the lower switching current of 10 mA. This is very similar to the result obtained from the stoichiometric slow cooled copper ferrite, $Cu\,Fe_2O_4$, where the first switching cycle is different than the second cycle; while second and successive cycles are repeatative. The effective temperature of the pellet might have been raised above the switching temperature which is 150°C. Thus for slow cooled non-stoichiometric copper ferrite, referring to the discussion for stoichiometric compounds, the switching behaviour may be attributed to the structural transformation from tetragonal to cubic phase together with the Joule self-heating.

From Table 3.3 and Fig.3.4 it can be observed that the first switching currents decrease initially and then increase through a minimum. Thus this characteristic exhibits the semiconductive behaviour where Cu^{+2} ions on A site might act as P-type leading to electron-hopping conduction associated with P-N conversion. From table (3.4) and Figs.3.14 and 3.15, it can be observed that the structural transformation and semiconductive property is speculative at higher temperatures and needs further detailed investigation in case of slow cooled non-stoichiometric $Cu_{0,6}Fe_{2.4}O_4$ compound.

In Figs.3.11 to 3.13 and 3.16 to 2.18 are given the I-V characteristics for the quenched nonstoichiometric compound having compositions $Cu_{0.8}Fe_{2.2}O_4$ and $Cu_{0.6}Fe_{2.4}O_4$. The values of first switching currents at different switching temperature are noted in tables 3.3 and 3.4. It can be noted by following the discussion made above that these quenched samples also exhibit the semiconductive properties. It can be further noted that the switching temperature goes on decreasing with increasing quenching temperature of the samples. The quenched copper ferrite samples are studied by N.Nanba and S.Koyabashi[13] and they have predicted, for the case of stoichiometric compound, the P-N conversion which may be due to the migration of cations. We have seen in above discussion that the case of non-stoichiometric quenched compounds of composition $Cu_{0.8}Fe_{2.2}O_4$ and $Cu_{0.6}Fe_{2.4}O_4$ exhibit similar characteristics and the same argument can be put forth that the conduction may be due to electron-hopping mechanism between Fe^{+2} - Fe^{+3} ions on B sites.

3.4c. Switching in Non-stoichiometric Ferrites of Composition $Cu_{0.4}Fe_{2.6}O_4$ and $Cu_{0.2}Fe_{2.8}O_4$:

The slow cooled $Cu_{0.4}Fe_{2.6}O_4$ and $Cu_{0.2}Fe_{2.8}O_4$ samples exhibit cubic structure which was identified as discussed in chapter 2, by diffractrometric records obtained. It can be seen from table 3.5 and the I-V characteristics given in figs. 3.19 to 3.23 that both the slow cooled and quenched samples of $Cu_{0.4}Fe_{2.6}O_4$ exhibit switching at higher temperature i.e. above 250°C and 100°C respectively. No switching was observed in this composition at room temperature. Further there is no change in

TABLE NO. 3.5

MEASUREMENTS OF SWITCHING CURRENTS AT DIFFERENT TEMPERATURES

SAMPLE : $Cu_{0.4}Fe_{2.6}O_4$

Temperature	Slow cooled (mA)			Quenched at								
				400°C (mA)			600°C (mA)			800°C (mA)		
	a	b	c	a	b	c	a	b	c	a	b	c
25°C (R.T.)	-	-	-	-	-	-	-	-	-	-	-	-
50°C	-	-	-	-	-	-	-	-	-	-	-	-
100°C	-	-	-	-	-	-	-	-	-	30	3.5	8.5
150°C	-	-	-	-	-	38	-	36	20	18	20	24
200°C	-	-	-	22	9	12	20	22	28	34	38	40
250°C	8.1	7	5.5	12	14	18	28	32	36	70	60	65
300°C	6	6	6	12	18	26	38	44	46	150	200	150

a : Switching currents at the first cycle
b : Switching currents at the second cycle
c : Switching currents at the third cycle

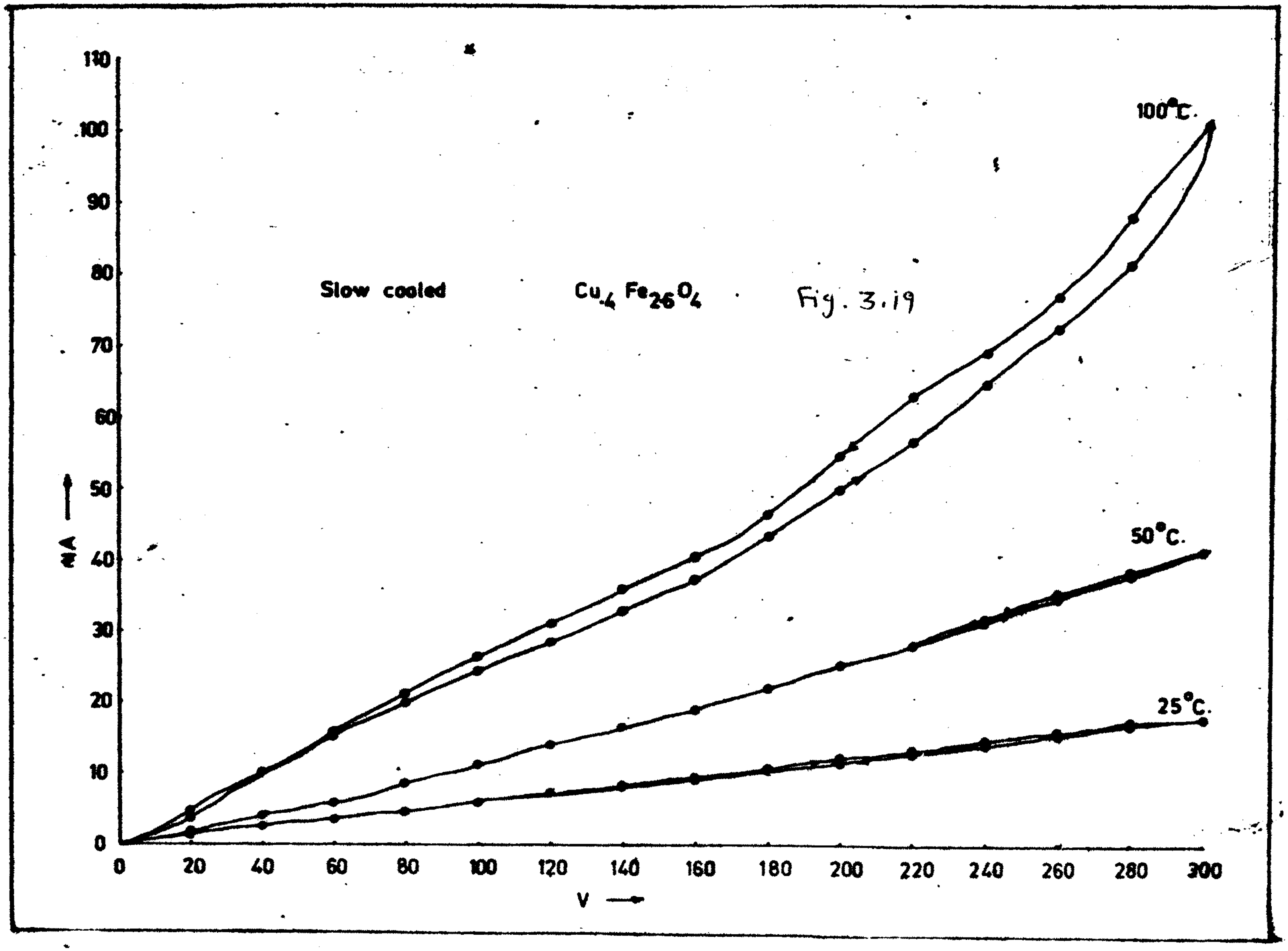

Slow cooled
$Cu_{.4}Fe_{2.6}O_4$
100°C.
50°C.
25°C.
mA
110
100
90
80
70
60
50
40
30
20
10
0
V
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300

Fig. 3.19

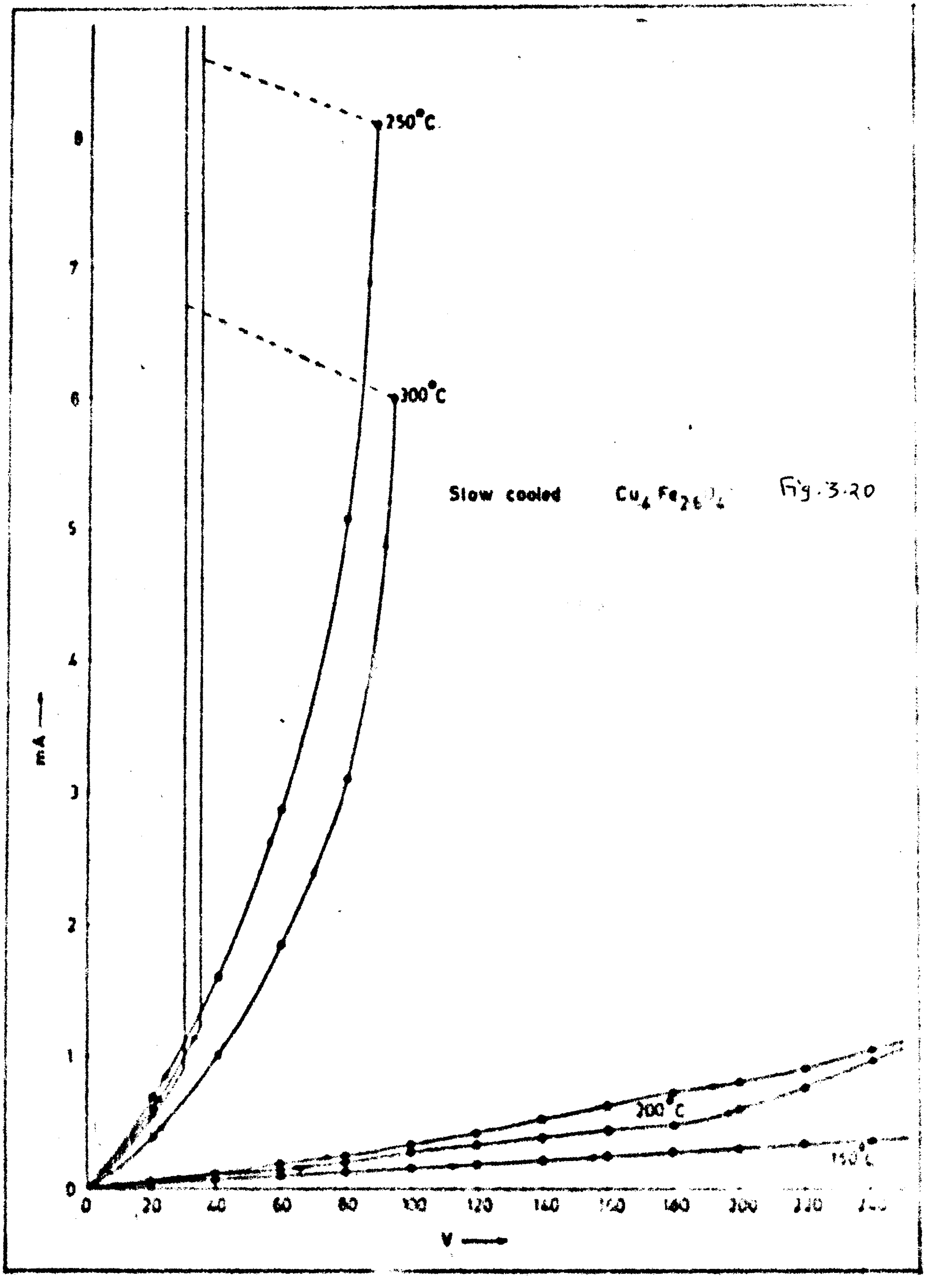

Slow cooled
$Cu_4Fe_{26}O_4$
250°C
300°C
200°C
150°C
mA
V
0
1
2
3
4
5
6
7
8
0
20
40
60
80
100
120
140
160
180
200
220
240

Fig. 3.20

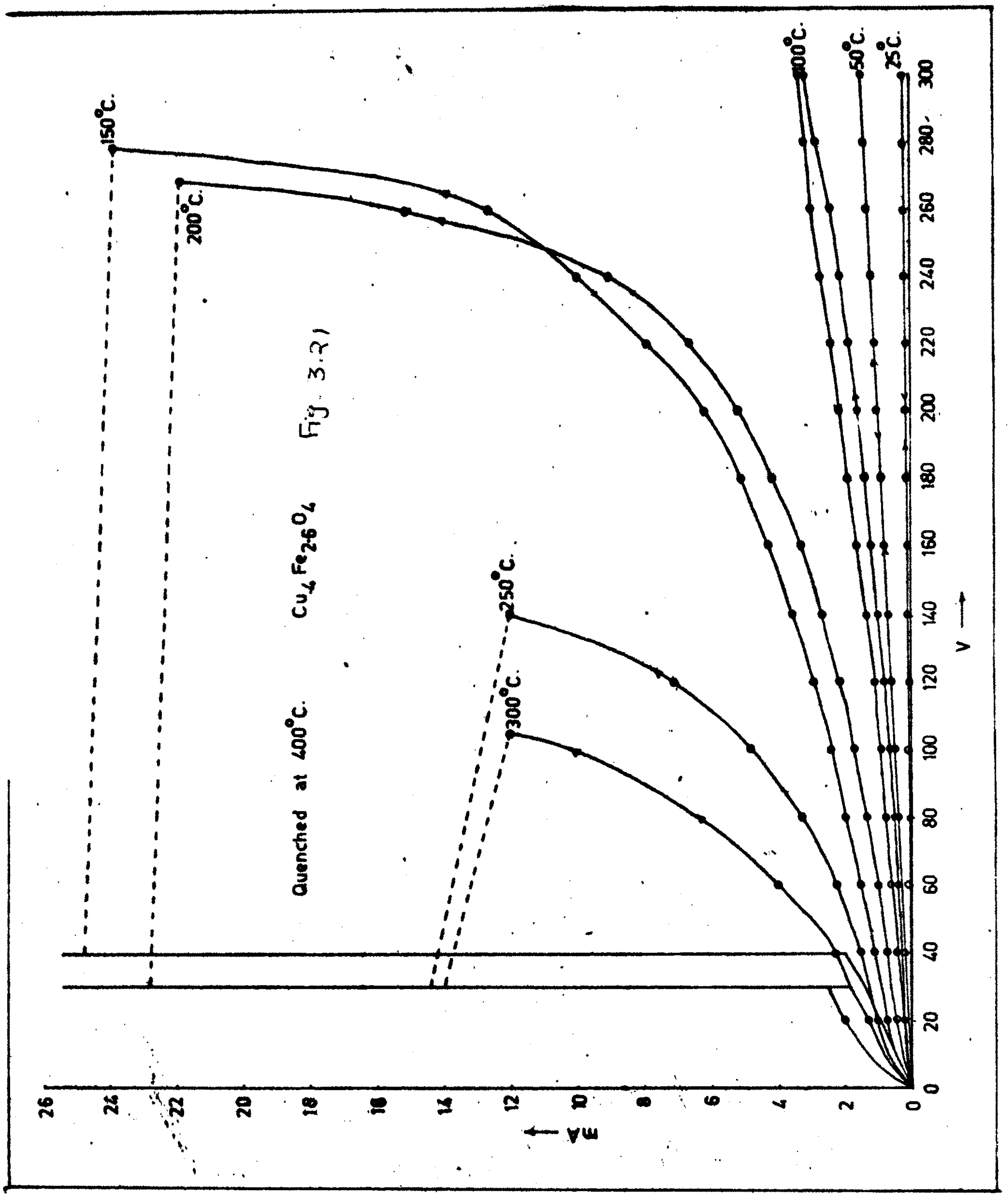


Fig 3.21
Quenched at 400°C.
$Cu_4 Fe_{2.6} O_4$
150°C.
200°C.
250°C.
300°C.
100°C.
50°C.
25°C.
ΔE →
0
2
4
6
8
10
12
14
16
18
20
22
24
26
V →
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300

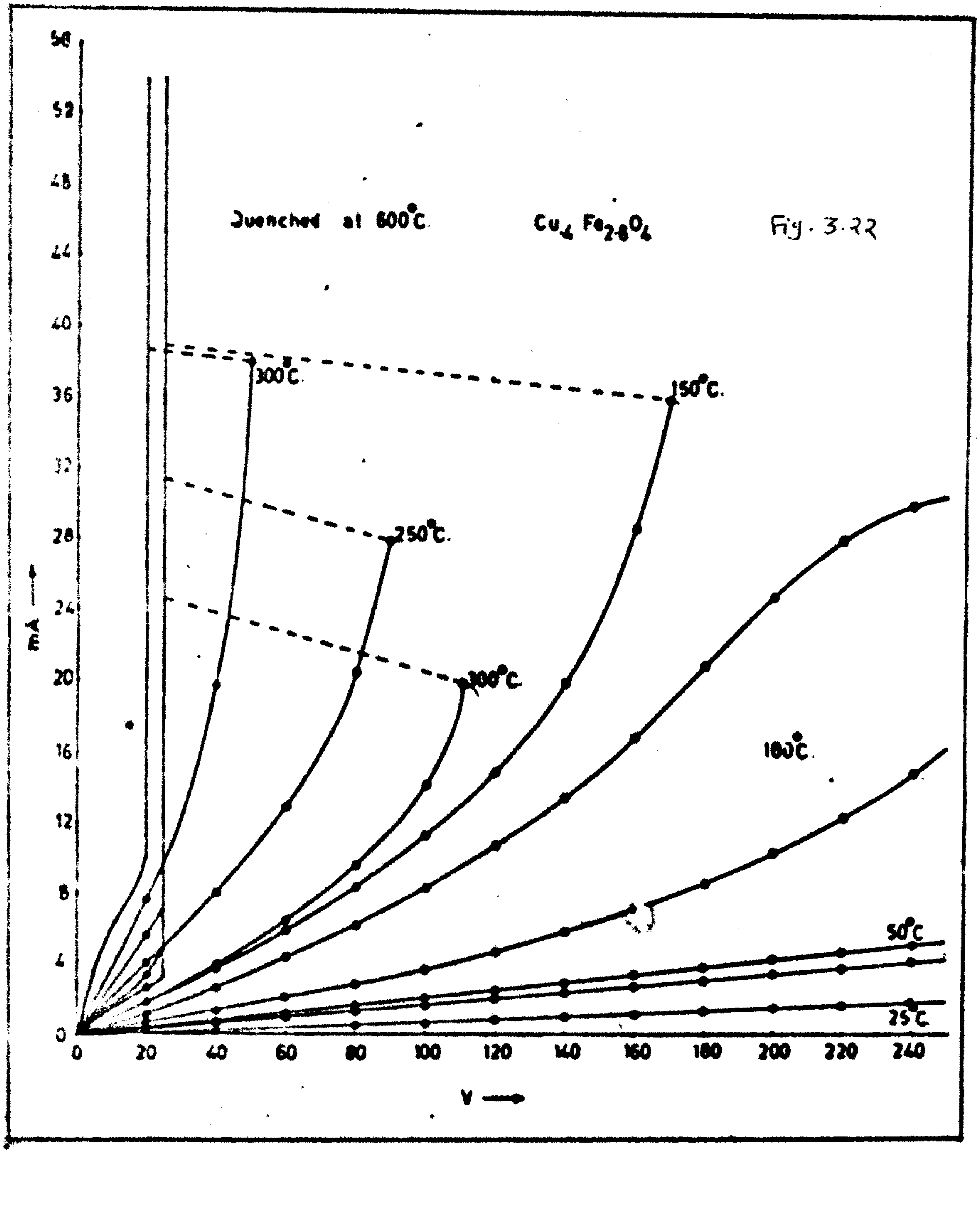

Quenched at 600°C.
Cu.4 Fe2.6 O4
Fig. 3.22
300°C.
250°C.
200°C.
150°C.
100°C.
50°C
25°C
mA
V
0
4
8
12
16
20
24
28
32
36
40
44
48
52
56
0
20
40
60
80
100
120
140
160
180
200
220
240

Fig. 3.23

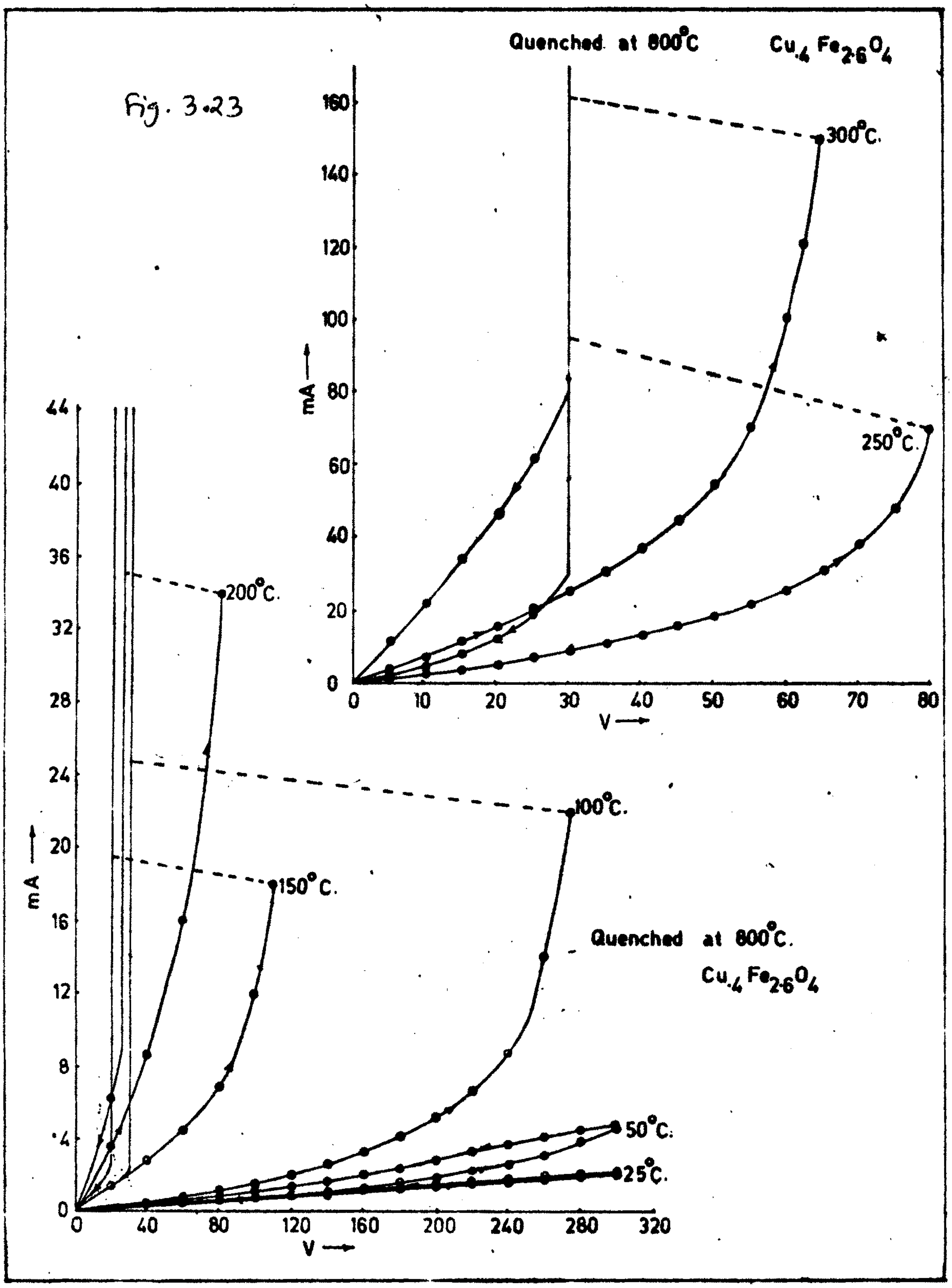

Quenched at 800°C
$Cu_{.4}Fe_{2.6}O_4$
mA
160
140
120
100
80
60
40
20
0
0
10
20
30
40
50
60
70
80
V
300°C.
250°C.
44
40
36
32
28
24
20
16
12
8
·4
0
0
40
80
120
160
200
240
280
320
V
mA
200°C.
100°C.
150°C.
50°C.
25°C.
Quenched at 800°C.
$Cu_{.4}Fe_{2.6}O_4$

TABLE NO. 3.6

MEASUREMENTS OF SWITCHING CURRENTS AT DIFFERENT TEMPERATURES

SAMPLE : $Cu_{0.2}Fe_{2.8}O_4$

Temperature	Slow cooled (mA)			Quenched at								
				400°C (mA)			600°C (mA)			800°C (mA)		
	a	b	c	a	b	c	a	b	c	a	b	c
25°C (R.T.)	-	-	-	-	-	-	-	-	-	-	-	-
50°C	-	-	-	-	-	-	-	-	-	-	-	-
100°C	-	-	-	-	-	-	-	-	-	-	-	-
150°C	-	-	-	-	-	-	-	-	-	-	-	-
200°C	-	-	-	-	-	-	-	-	-	-	-	-
250°C	-	-	-	-	-	-	-	-	-	-	-	-
300°C	-	-	-	-	-	25	-	-	-	-	22	10
330°C	-	-	-	-	-	-	24	-	-	-	-	-

a : Switching currents at the first cycle
b : Switching currents at the second cycle
c : Switching currents at the third cycle

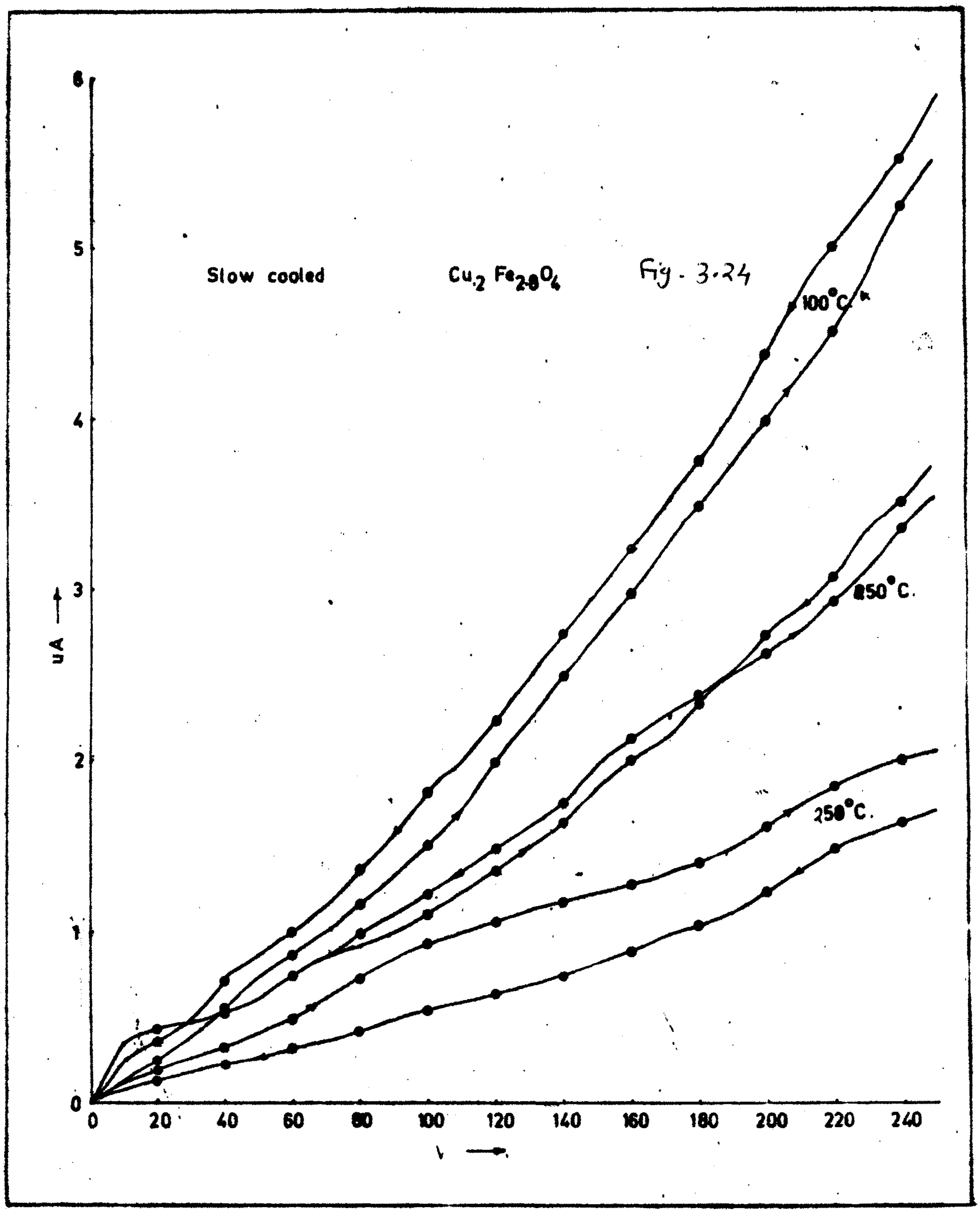

Slow cooled
$Cu_{.2}Fe_{2.8}O_4$
100°C
150°C
250°C
uA →
V →
0
1
2
3
4
5
6
0
20
40
60
80
100
120
140
160
180
200
220
240

Fig. 3.24

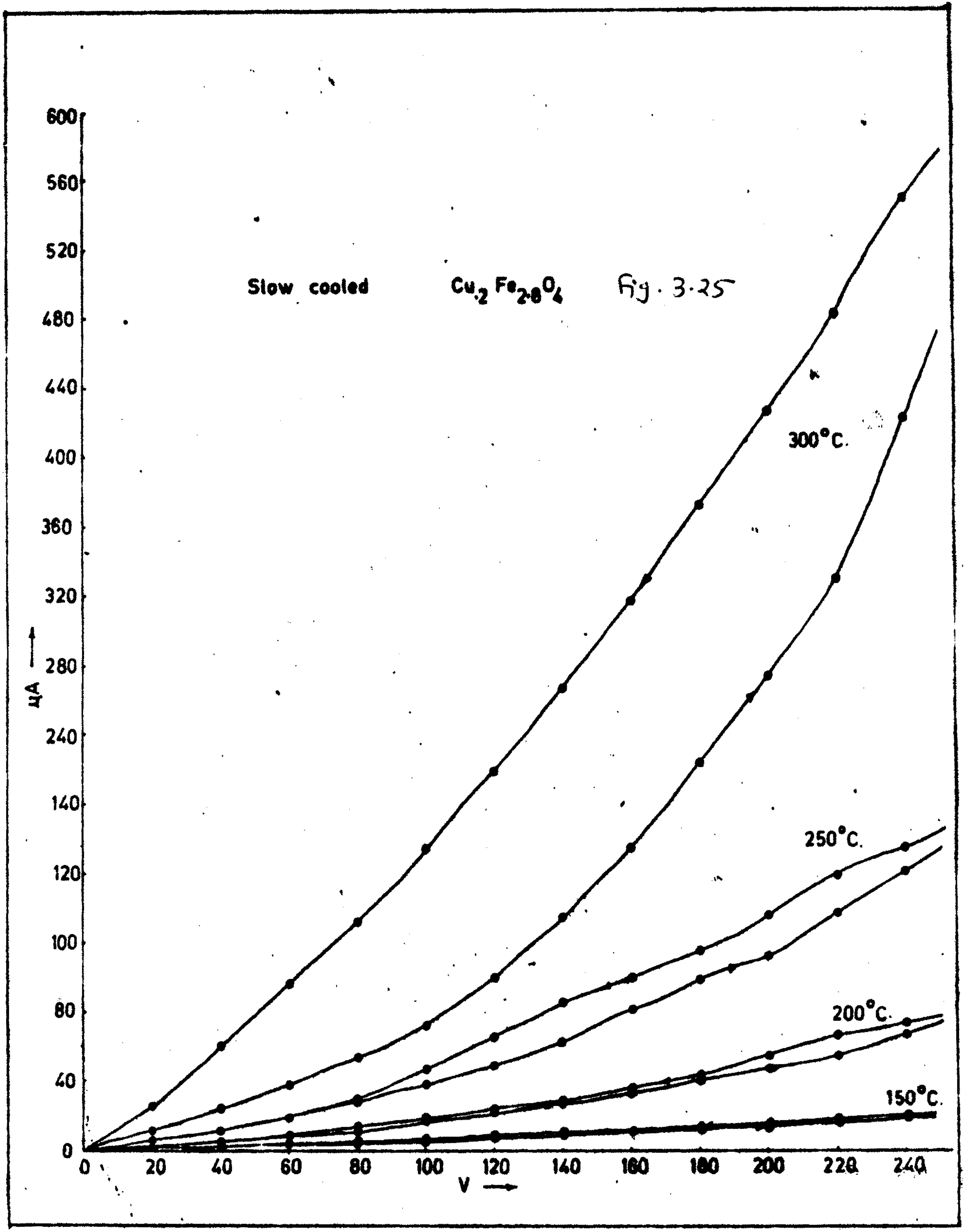

Slow cooled
$Cu_{.2}Fe_{2.8}O_4$
300°C.
250°C.
200°C.
150°C.
µA →
V →
600
560
520
480
440
400
360
320
280
240
140
120
100
80
40
0
0
20
40
60
80
100
120
140
160
180
200
220
240

Fig. 3.25

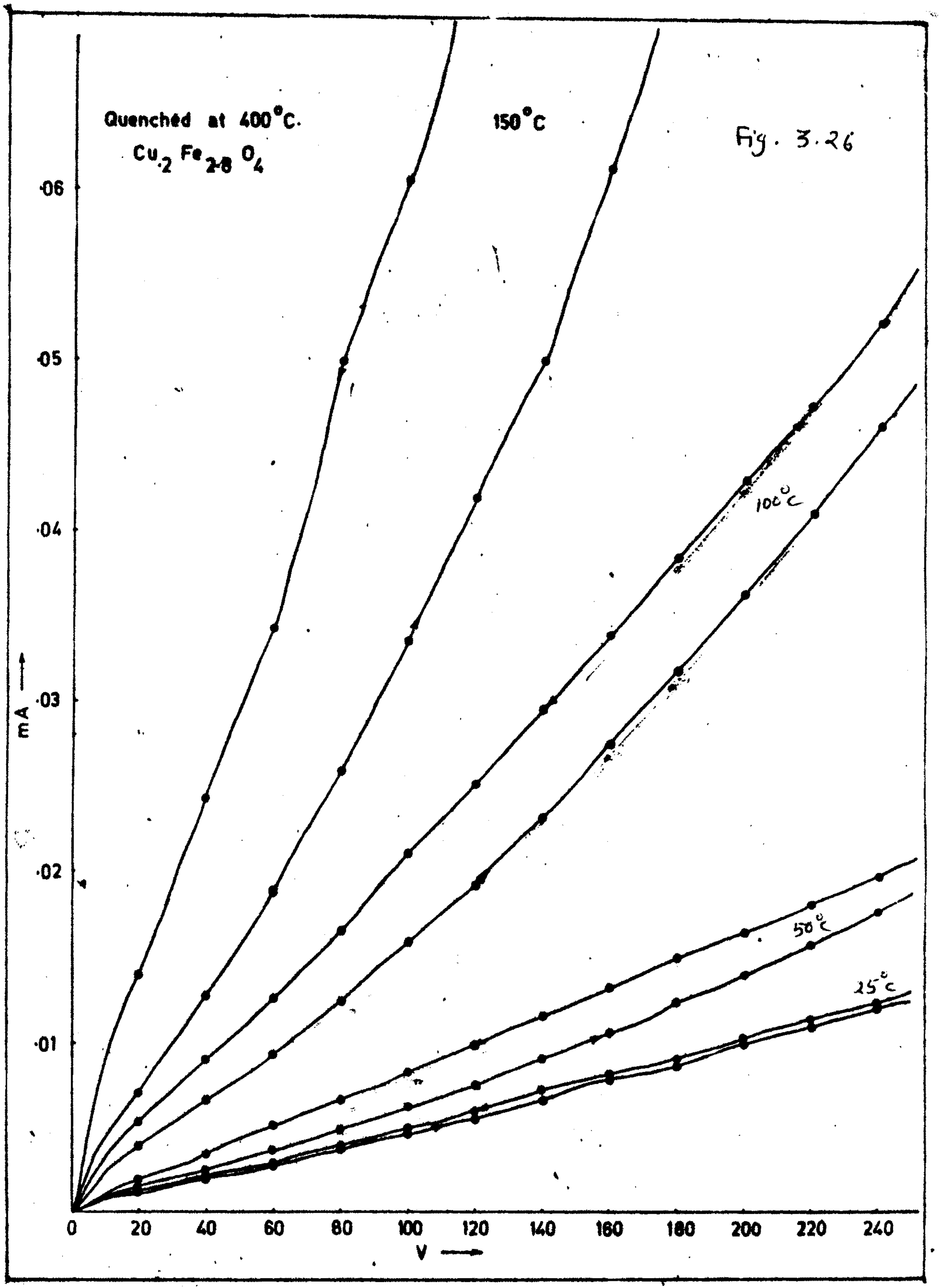

Quenched at 400°C.
Cu.2 Fe2.8 O4
150°C
100°C
50°C
25°C
mA
·06
·05
·04
·03
·02
·01
0
20
40
60
80
100
120
140
160
180
200
220
240
V

Fig. 3.26

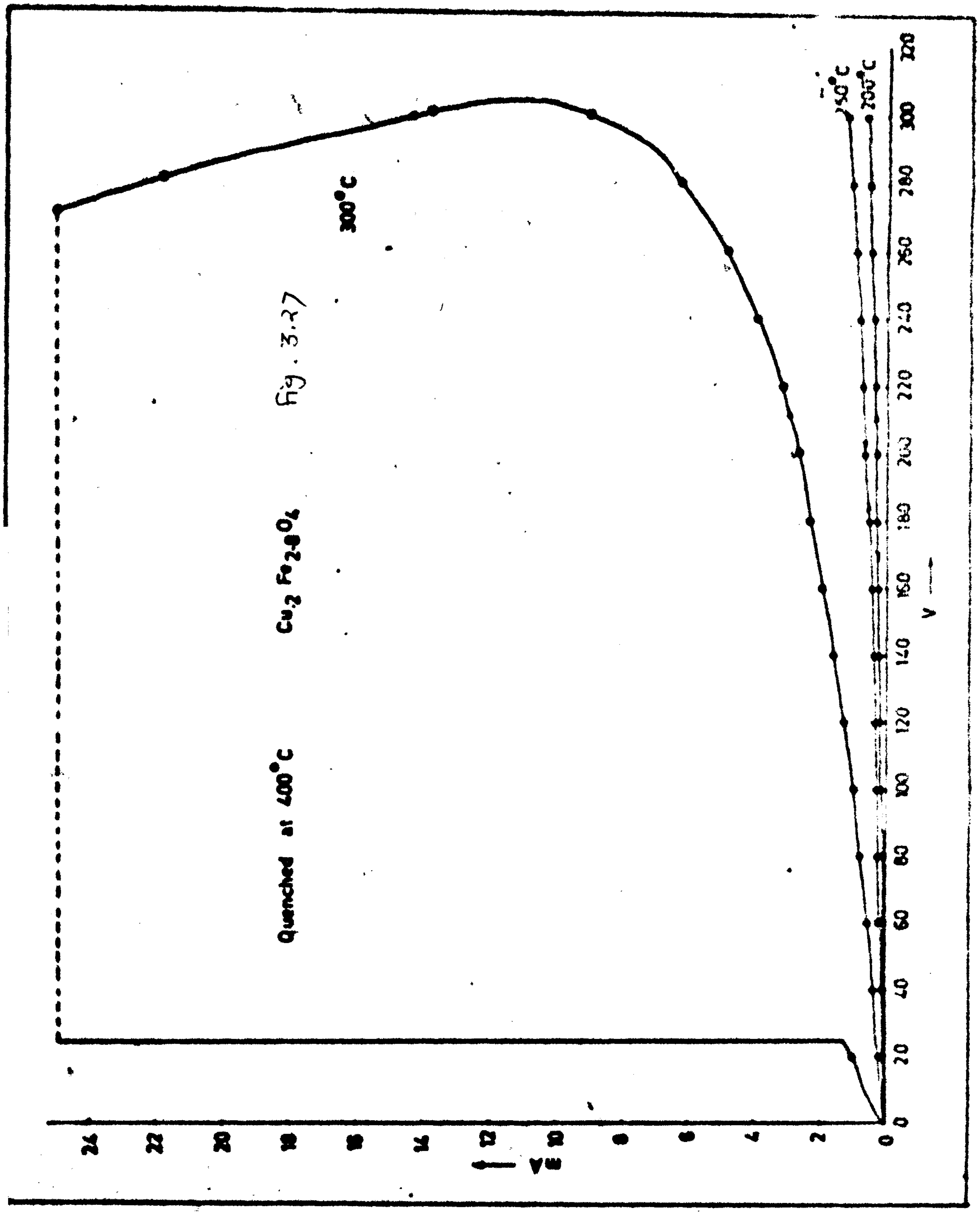
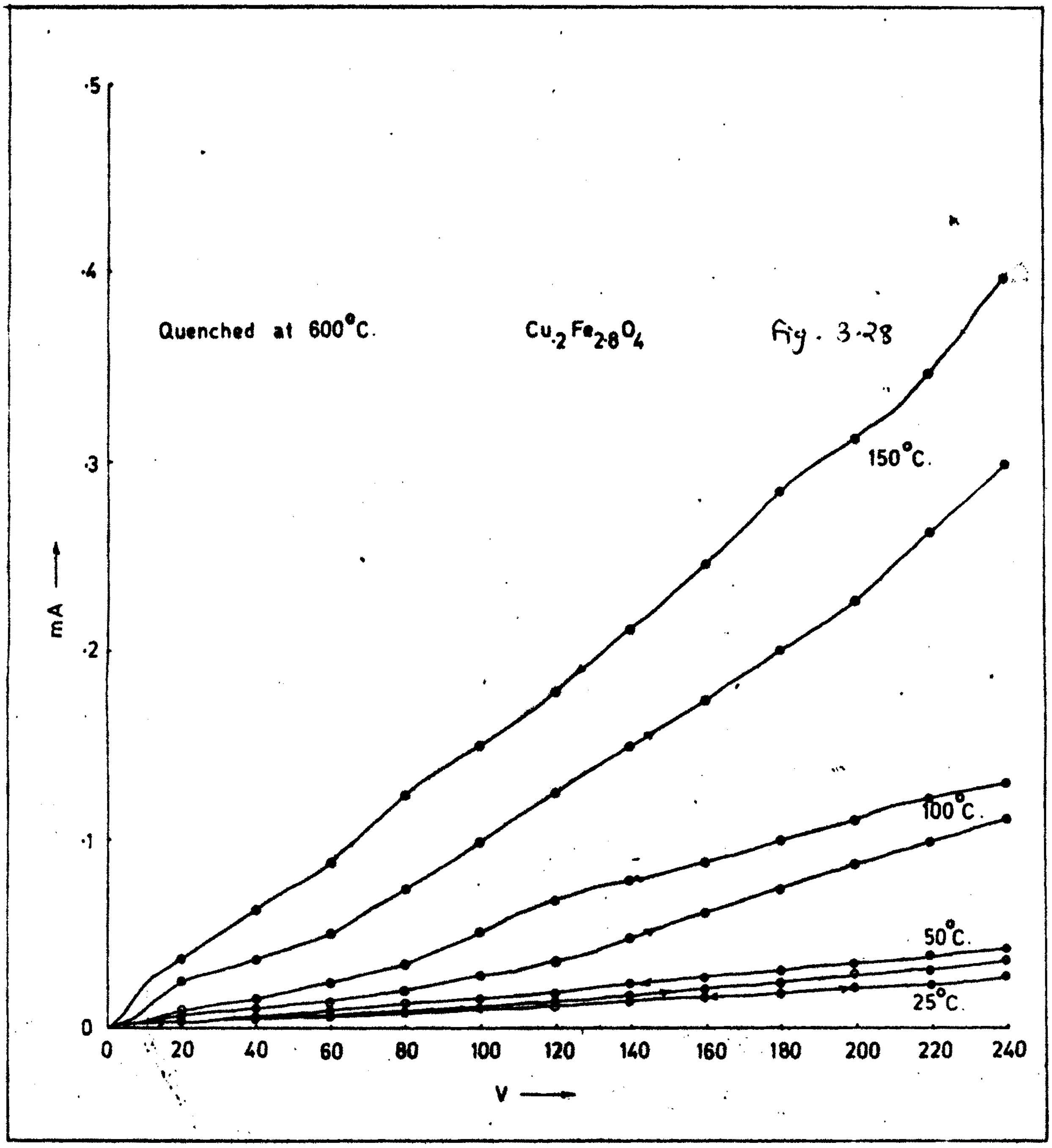
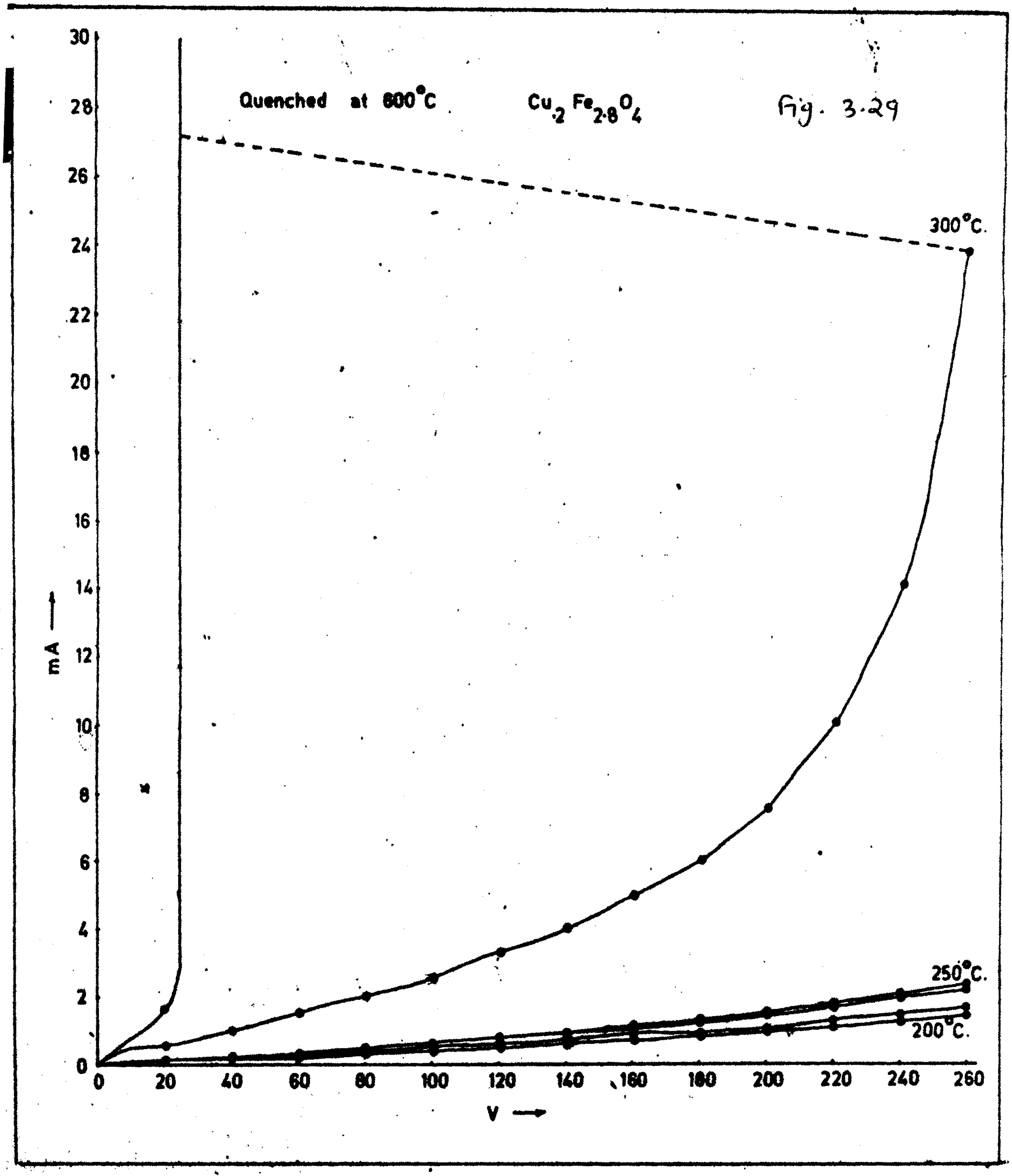
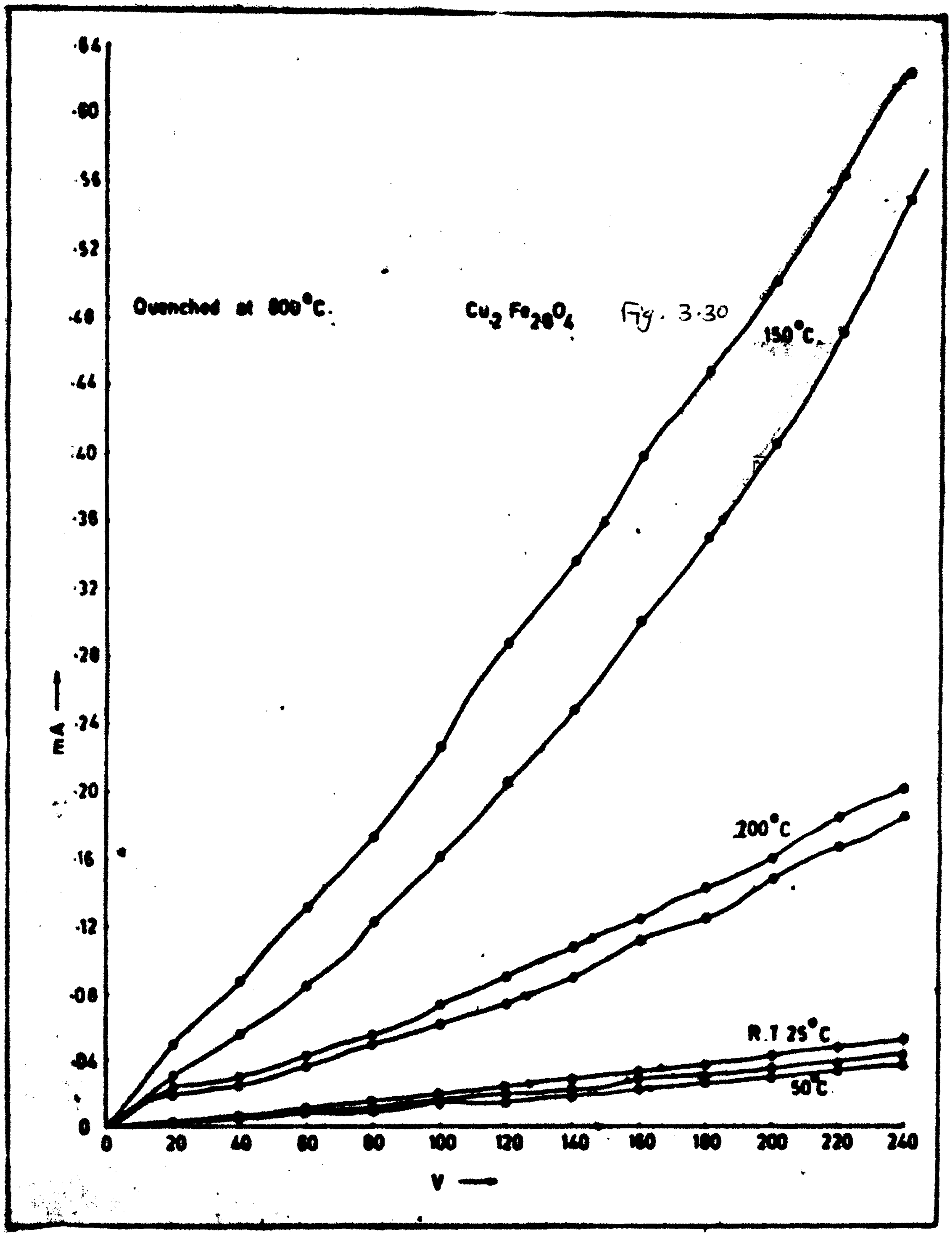

Quenched at 400°C
$Cu_{.2}Fe_{2.8}O_4$
300°C
250°C
200°C
mA ⟶
0
2
4
6
8
10
12
14
16
18
20
22
24
V ⟶
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320

Fig. 3.27


Quenched at 600°C.
$Cu_{.2}Fe_{2.8}O_4$
Fig. 3.28
150°C.
100°C.
50°C.
25°C.
mA
V
0
·1
·2
·3
·4
·5
0
20
40
60
80
100
120
140
160
180
200
220
240


Quenched at 600°C
Cu.2 Fe2.8 O4
Fig. 3.29
300°C.
250°C.
200°C.
mA →
V →
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
0
20
40
60
80
100
120
140
160
180
200
220
240
260


Quenched at 800°C.
$Cu_2Fe_{28}O_4$
Fig. 3.30
150°C.
200°C
R.T 25°C
50°C
mA
V
0
·04
·08
·12
·16
·20
·24
·28
·32
·36
·40
·44
·48
·52
·56
·60
·64
0
20
40
60
80
100
120
140
160
180
200
220
240

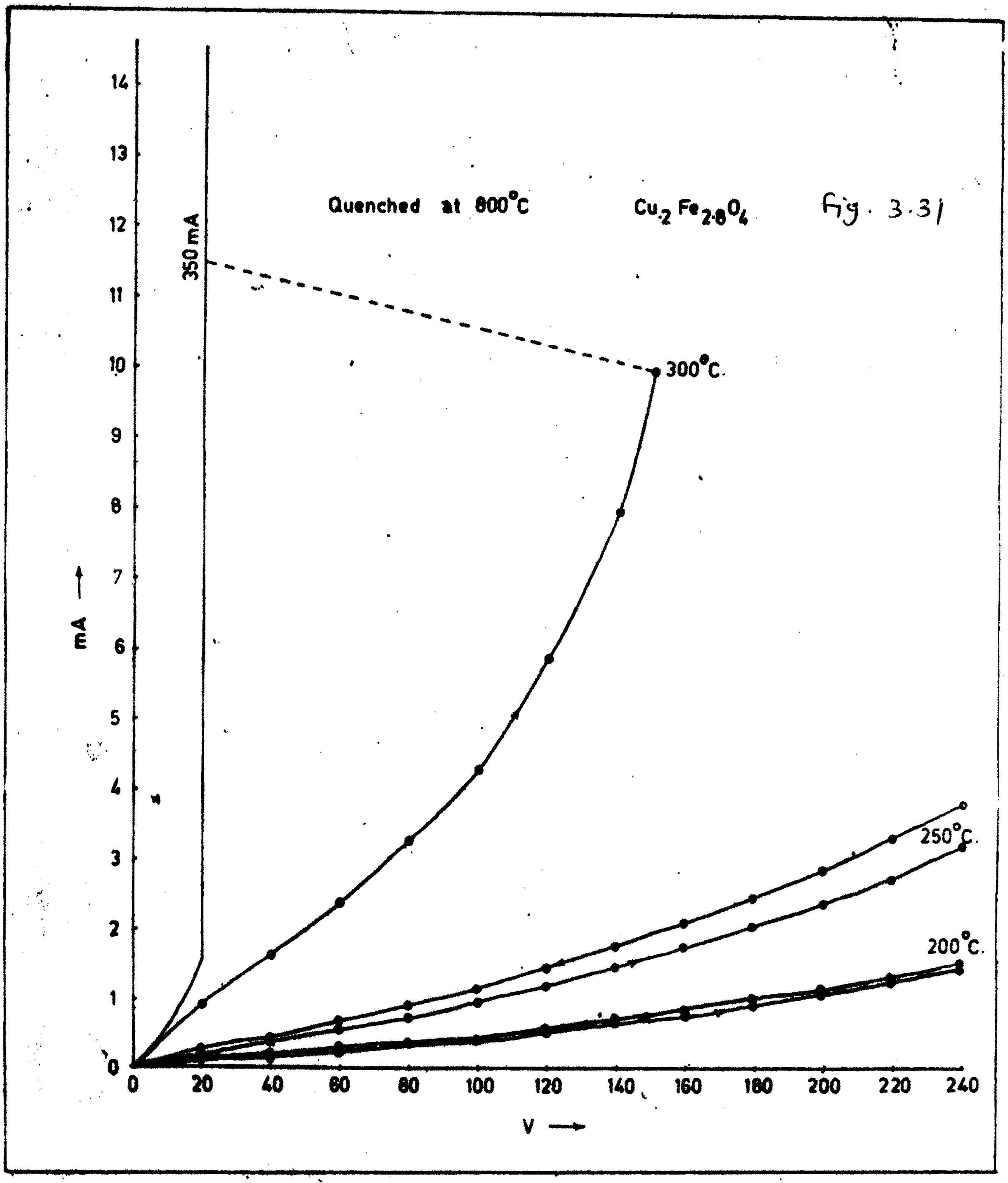

Quenched at 800°C
$Cu_{.2}Fe_{2.8}O_4$
350 mA
300°C.
250°C.
200°C.
mA →
V →
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
0
20
40
60
80
100
120
140
160
180
200
220
240

Fig. 3.31

the first and second or successive cycles i.e. the first cycle is repeatative in case of slow cooled sample of this composition; while the switching cycle after the first breakdown does not repeat in case of quenched samples, quenched from 400°C, 600°C and 800°C. Non-stoichiometric copper ferrite with composition $Cu_{0.4}Fe_{2.6}O_4$ exhibits cubic structure at room temperature. In this case the switching may be therefore attributed to the Joule self-heating alone. However Kulkarni and Patil[17] while studying $CuFe_2O_4$ on Mossbauer effect, have predicted a transformation at about 90°C attributing it to the Jahn-Teller distortion of Cu^{+2} ion. Hence, though in case of this composition the switching may be due to the Joule self-heating, the Jahn Teller distortion cannot be neglected.

In Figs.3.21 to 3.23 are given the I-V characteristics for the quenched non-stoichiometric samples having composition $Cu_{0.4}Fe_{2.6}O_4$. The table 3.5 indicates the first switching currents observed at different switching temperatures for the quenched samples of composition $Cu_{0.4}Fe_{2.6}O_4$ quenched from 400°C, 600°C and 800°C. Following the discussion made for the quenched samples of composition $Cu_{0.8}Fe_{2.2}O_4$, these samples also exhibit the semiconductive properties. It can also be observed from table 3.1 that the first switching temperature goes on decreasing as the quenching temperature increases. The P-N conversion enhanced by the cation migration predicted by N.Nanba and S.Koyabashi[13] in case of stoichiometric quenched samples can also be attributed to quenched samples of composition $Cu_{0.4}Fe_{2.6}O_4$. Following the same argument the conduction may be attributed to electron hopping mechanism between Fe^{+2} - Fe^{+3} ions on B sites with predominant role of Joule self-heating. However, Kulkarni and Patil[17] studying the Mossbaur effect in case of $CuFe_2O_4$ predict the transformation at about 90°C attributed to Jahn Teller distortion of Cu^{+2} ions. Therefore though in case of these quenched samples of composition $Cu_{0.4}Fe_{2.6}O_4$, the switching may be due to Joule self-heating and P.N.conversion the Jahn Teller distortion cannot be neglected.

In case of $Cu_{0.2}Fe_{2.8}O_4$ generally speaking, the switching is not observed in the temperature range below 300°C. But the switching was observed for quenched samples of this composition at 300°C and 330°C. Their I-V characteristics are shown in figs.3.24 to 3.31. However, we have not studied these samples beyond the first break down temperatures and therefore at high field and higher temperatures some data may be obtained which, referring to the results for samples of composition $Cu_{0.4}Fe_{2.6}O_4$ may support the switching occuring due to the Joule self-heating linked with P-N conversion.

In the previous sections the electrical switching observed in different samples of the system $Cu_xFe_{3-x}O_4$ has been discussed and it was attributed to the structural transformation during electrical switching together with Joule-self heating.

In figs. 3.41 and 3.42 the diffractograms of the compositions $CuFe_2O_4$ and $Cu_{.4}Fe_{2.6}O_4$ obtained after switching have been given. In Chapter II the diffractograms of these samples before the first break down are given in Figs.2.4 and 2.7. It can be noticed that the reflecting planes are shifted to different angles. The details of calculation of the crystal structure after switching in these samples are given in Tables 3.7 and 3.8. The observed and calculated 'd' values agree fairly well. The values of lattice constants are also given. It can be seen that in stoichiometric copper ferrite $CuFe_2O_4$ the axial ratio changes from greater than one to less than one i.e.

$$c/a_{(\text{before switching})} > 1 > c/a_{\text{after switching}}$$

This observation clearly indicates that the electrical switching is associated with structural transformation. However, this structural change may be occurring due to Jule-self heating during the experiment within the bulk. A structural transformation in the slow cooled copper ferrite, when heated is reported at about 340°C.

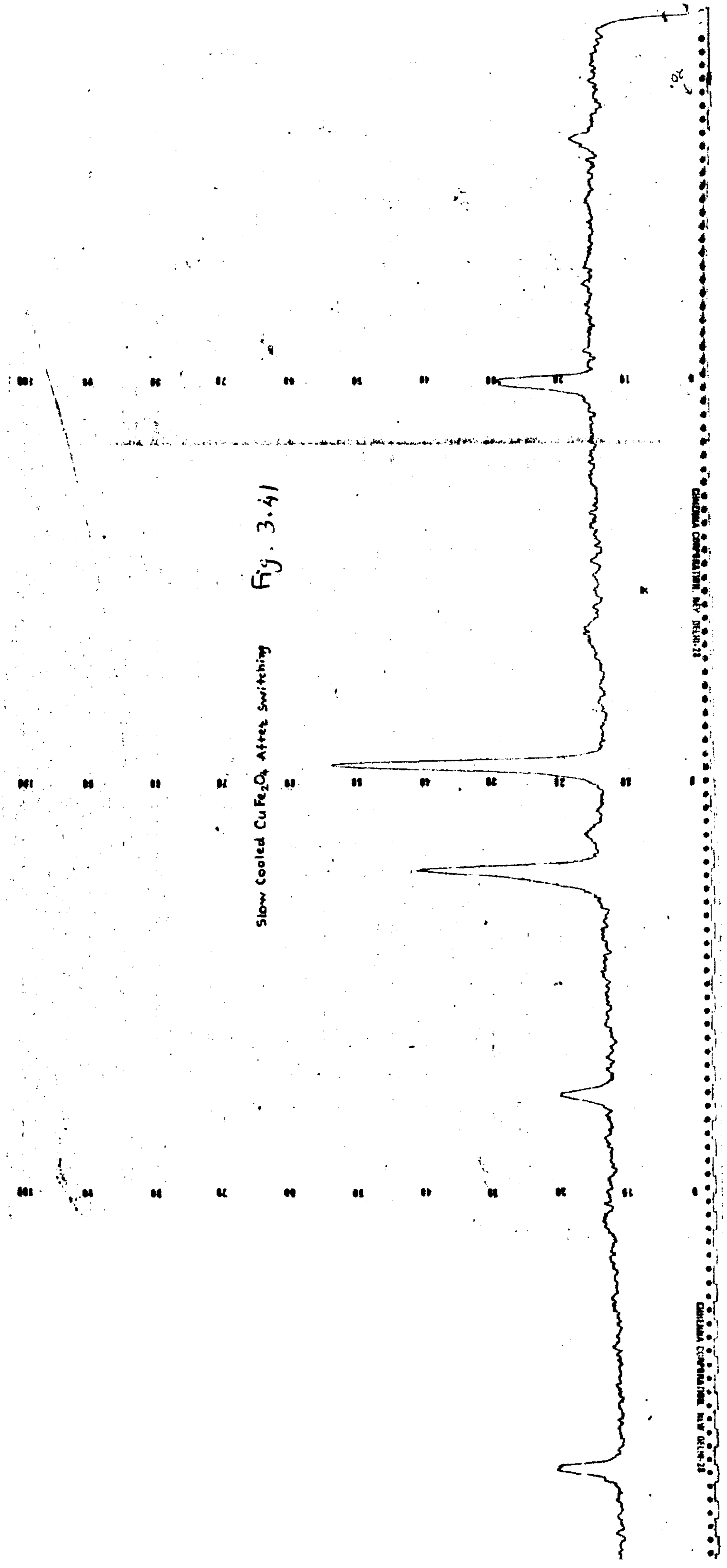
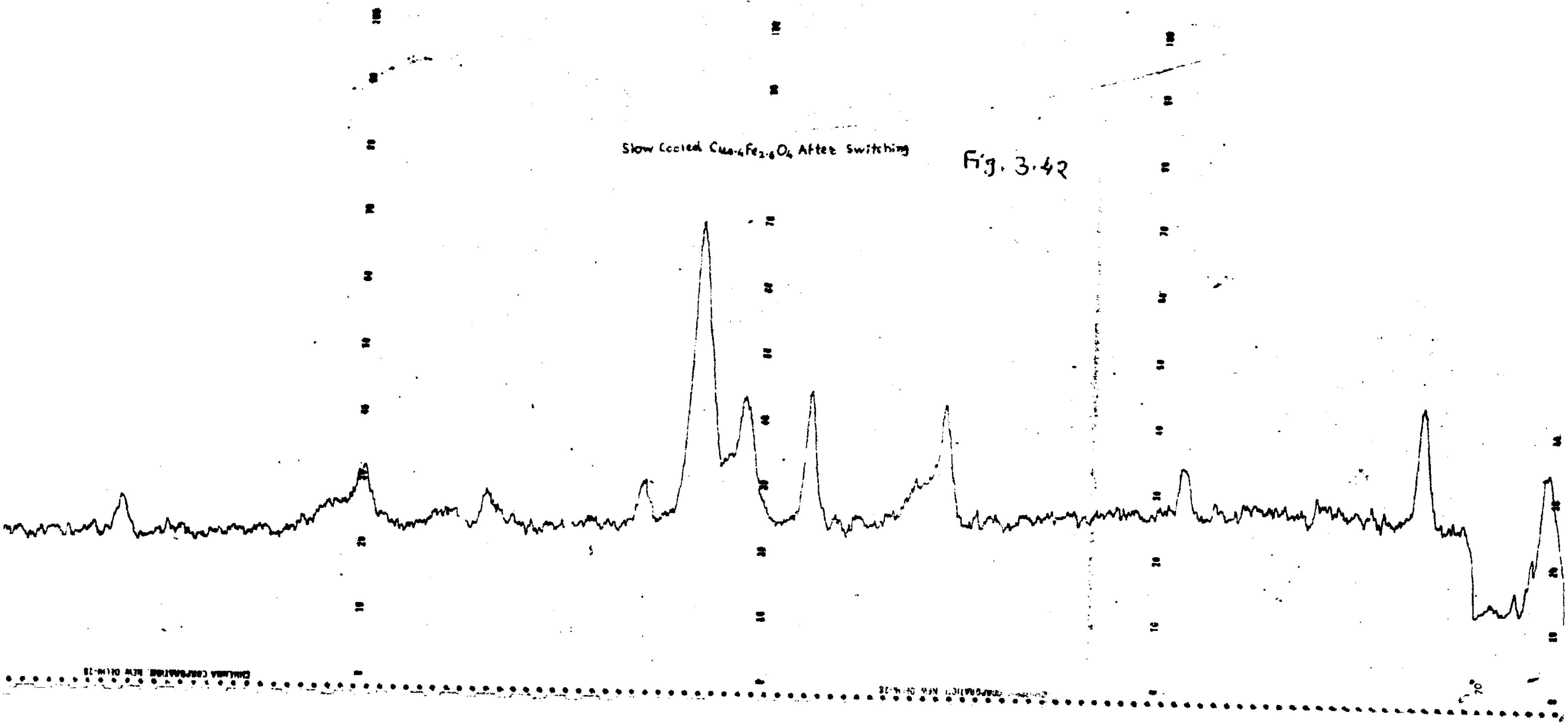

Slow Cooled $CuFe_2O_4$ After Switching
2θ
0
10
20
30
40
50
60
70
80
90
100
CAMERA CORPORATION NEW DELHI-28

Fig. 3.41



Slow Cooled $Cu_{0.4}Fe_{2.6}O_4$ After Switching

Fig. 3.42

TABLE NO. 3.7

DATA ON CRYSTAL STRUCTURE OF $Cu_xFe_{3-x}O_4$ FERRITE AFTER SWITCHING

SAMPLE : $CuFe_2O_4$ ($x = 1$)

hkl	din A° Observed	d in A° Calculated	Lattice Constants
111	4.8659	4.8418	
202	3.6999	3.6936	a = 8.4808 A°
310	2.7082	2.6818	c = 8.2066 A°
311	2.5235	2.5491	∴ c/a = 0.9676
004	2.2093	2.2186	
204	1.8448	1.8468	
422	1.6986	1.7214	
440	1.4890	1.4992	
404	1.4547	1.4743	

TABLE NO. 3.8

DATA ON CRYSTAL STRUCTURE OF $Cu_xFe_{3-x}O_4$ FERRITE AFTER SWITCHING

SAMPLE : $Cu_{0.4}Fe_{2.6}O_4$ (x = 0.4)

hkl	d in A° Observed	d in A° Calculated	Lattice Constants
111	4.8660	4.8584	
200	3.7000	3.7011	a = 8.2759 A°
202	2.9856	3.0007	c = 8.7159 A°
103	2.7050	2.7413	
113	2.5862	2.6022	∴ c/a = 1.0531
311	2.5094	2.5065	
222	2.4237	2.4292	
004	2.2117	2.1789	
400	2.0681	2.0689	
420	1.8436	1.8505	
422	1.6965	1.7033	
511	1.5927	1.5956	
440	1.4935	1.4629	

A similar structural transformation from cubic to tetragonal phase after switching has been observed and can be seen from fig.27 and fig.3.42. These are the diffractrograms of the composition $Cu_{.4}Fe_{2.6}O_4$ before and after switching respectively. This compound is cubic in nature when it is slow cooled and after switching it changes to the tetragonal phase with c/a = 1.0531. Thus once again it can be said that the electrical switching in copper ferrite is associated with structural transformation, which in turn may be occuring due to Joule-self heating. Such a peculiar and interesting result has been obtained for the first time and therefore needs a careful and detailed investigation in this direction.

3.5. THE THEORY OF SPACE CHARGE LIMITED CURRENTS

The band theory of solids conclude that an insulator can be characterised by a full valance band separated from an empty conduction band by forbidden energy gap of few electron volts. The conduction in insulators is not possible in either the filled or empty band unless the insulator contains some additional carriers. The carriers may be added either by modulation or generation inside the insulator by some means or may be injected either from metal electrode or from metal insulator[18] contact (the bulk limited process). The simplest conduction mechanism is the direct quantum mechanical tunnelling of electrons from one metal electrode to the other. If an injection of carriers into the conduction band or the tunnelling is not limiting the rate of conduction process in insulators, the building up of space charge of electrons in a conduction band and the formation of trapping centres may oppose the applied voltage and impede the flow of electrons. At low applied voltage, the Ohm's law is obeyed since the injected ~~carrier~~ carriers density remains lower than the thermally generated free carriers density. In the other way, if the injected carriers density becomes greater than the free carriers density, the current becomes space charge limited. Mott and Gurney[19] have explained such deviations from Ohm's law by assuming that, at high electric fields free from the carrier traps the SCL currents formed has the density expressed as

$$J = \frac{9}{8} \cdot \frac{\epsilon \mu V^2}{d^3} \quad \text{A/cm}^2 \qquad \ldots \qquad (3.1)$$

where,

V = the applied voltage,
d = the thickness of the insulator,
μ = the mobility of the carriers,
ϵ = the permittivity or the dielectric constant.

There may be a significant number of lattice defects capable of accepting one or more charge carriers in insulators similar to semiconductors. These charge trapping centres might modify the equilibrium concentration of the carriers and thus the SCL currents flow in an imperfect insulator, Lampert and Rose[20] and Lampert[21] have reviewed and discussed in detail the influence of traps on SCL currents. For a trap distribution whose density decreases as the energy from the band edge increases. The current density relation becomes

$$J = a V^n \qquad \ldots \quad (3.2)$$

where a is constant and n is parameter characteristic of distribution of traps. When the Fermi level rises in a uniform trap distribution, V^n dependence of current density is expected. After the traps are filled the current density will follow a square law again. Then the equation (3.1) for current density becomes,

$$J = \frac{9}{8} \mu N_o e \frac{v}{d} \exp(tV) \qquad \ldots \quad (3.3)$$

where e is the charge of an electron, N_o is the thermal equilibrium carrier concentration, and t is given by

$$t = \frac{\epsilon A}{4 N_t . e d^2 K_B T} \qquad \ldots . \quad (3.4)$$

where N_t is the trap density per unit energy.
The relation for N_t is given by as[22]

$$N_t = \frac{\epsilon A}{4 K_B T} \left(\frac{1}{ed^2} \right) \left[\frac{V}{J} \left(\frac{dJ}{dV} \right) - 1 \right]^{-1} \ldots \quad (3.5)$$

the symbols have their usual meaning.

3.6 RESULTS AND DISCUSSION

The log I versus log V curves for $CuFe_2O_4$ samples have been given in figs. 3.32 to 3.35. The curves are drawn for the composition having stoichiometric proportion only i.e. $CuFe_2O_4$, for which the dielectric constant was known from the literature. However, different samples of the same composition were obtained by giving different heat treatment i.e. slow cooled and quenched at 800°C, 600°C and 400°C. The plots of log I versus log V are plotted at different temperatures. These temperatures are so chosen that the electrical switching is observed in these samples at that temperatures. It can be noted from the nature of the log I versus log V characteristics that the slope of the curves follow an ohmic region ($n=1$) and then changes to a value in a region where n takes the value greater than two ($n>2$). When the slope of log I versus log V characteristics changes from ohmic region ($n=1$) to a value such that $n > 2$, the space charge limited currents are present[22]. Therefore, from the nature of the curves given in figs. (3.32 to 3.35) the SCL currents are confirmed in slow cooled and quenched samples of copper ferrite. It can be further noted that the change over of the slope takes place exhibiting SCL current mechanism and then the electrical break down in the samples takes place at particular voltage. The same study to examine the possibility of existence of SCL currents in other samples having non-stoichiometric compositions was not attempted because the value of

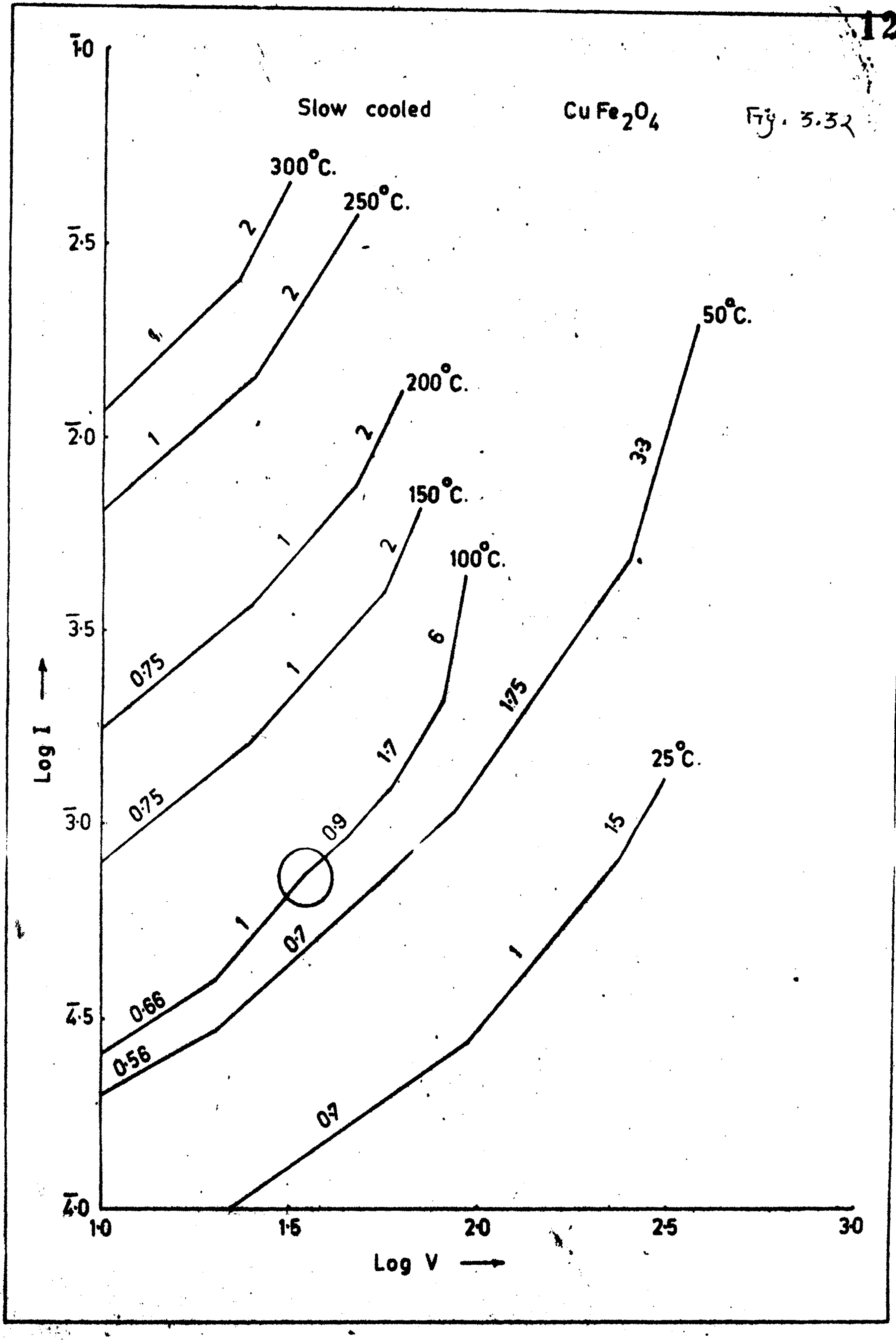
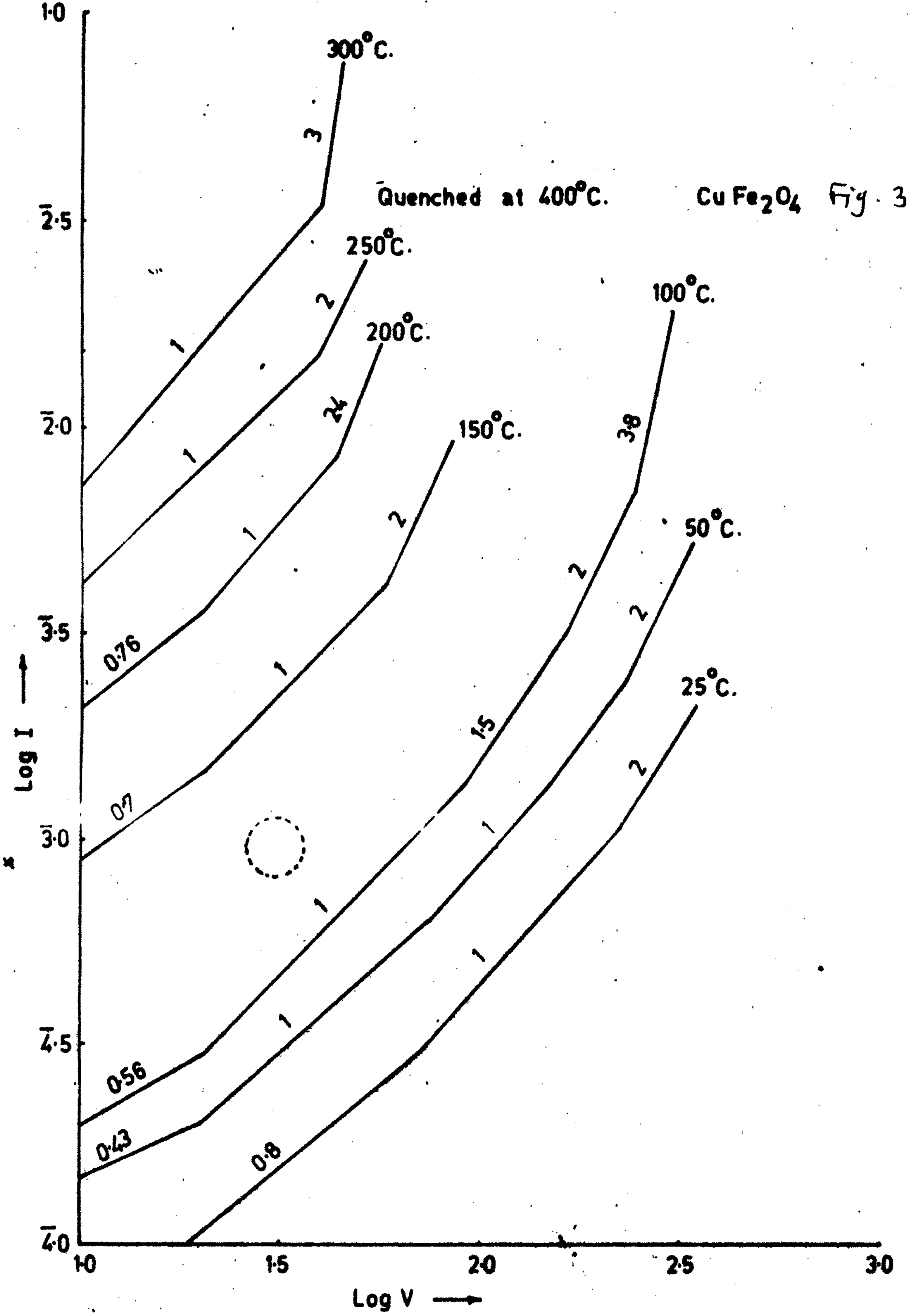
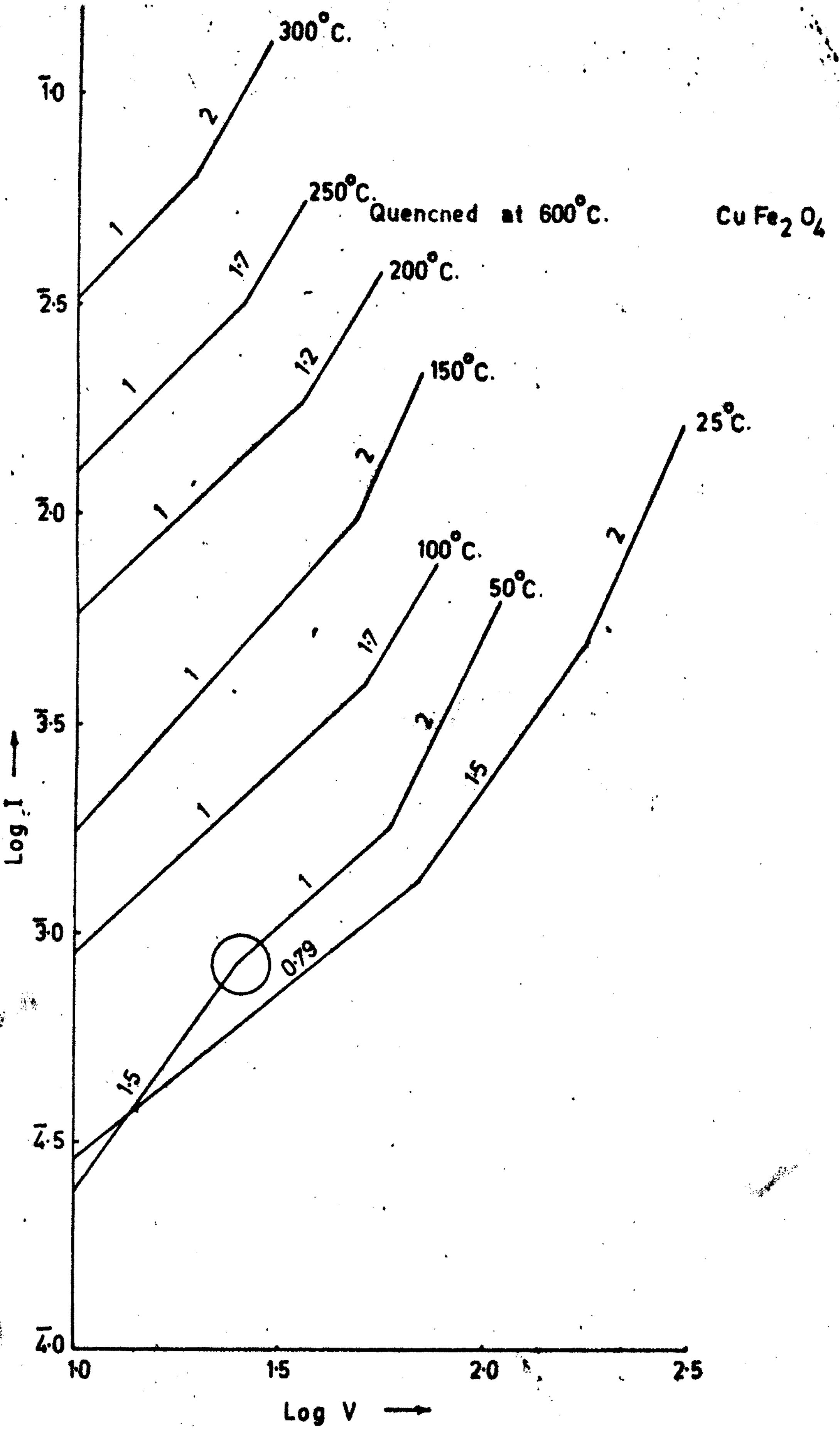
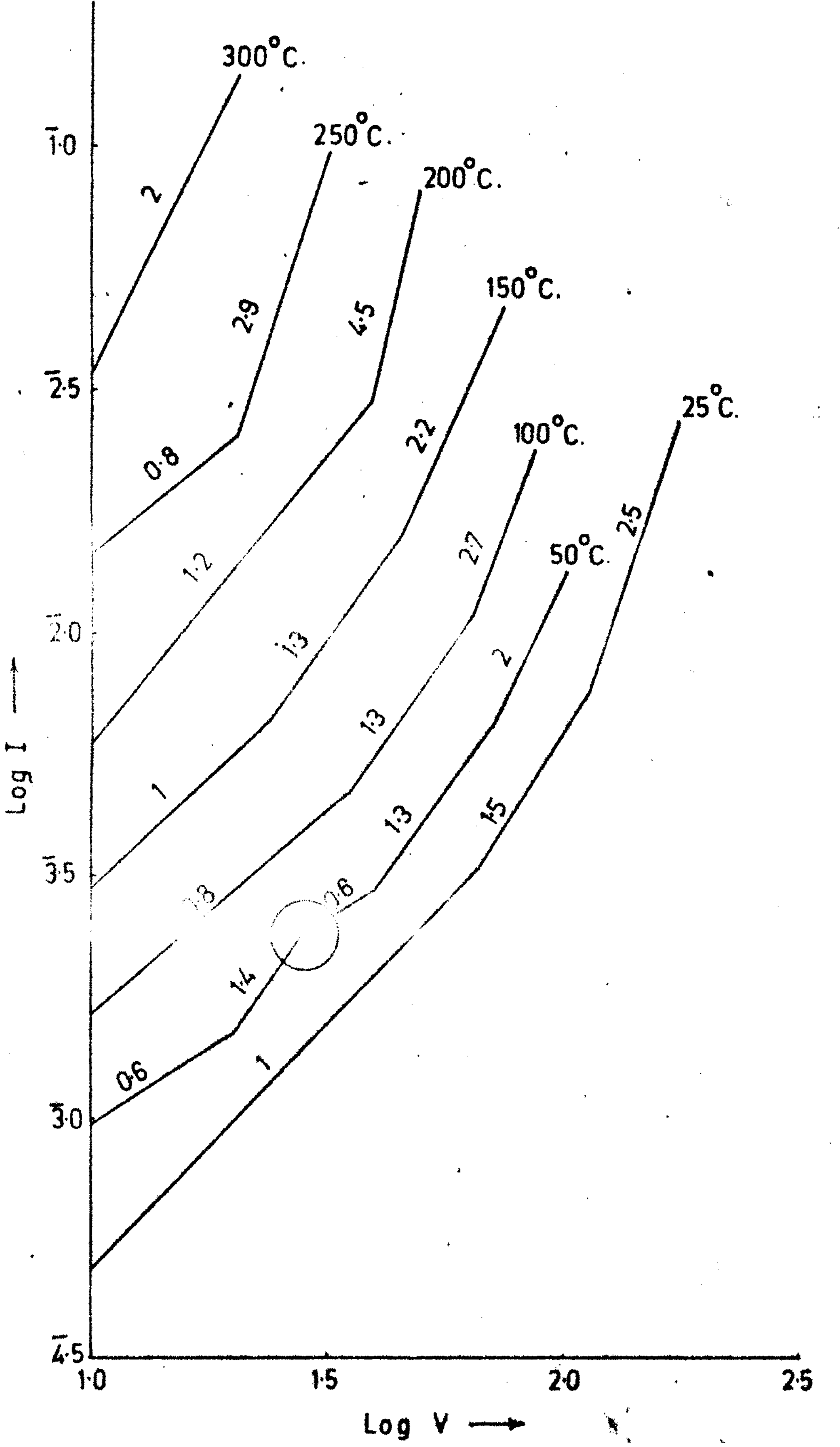

Slow cooled
$CuFe_2O_4$
300°C.
250°C.
200°C.
150°C.
100°C.
50°C.
25°C.
2
1
2
1
2
1
0·75
2
1
0·75
6
1·7
0·9
1
0·66
3·3
1·75
0·7
0·56
1·5
1
0·7
$\bar{1}$·0
$\bar{2}$·5
$\bar{2}$·0
$\bar{3}$·5
$\bar{3}$·0
$\bar{4}$·5
$\bar{4}$·0
1·0
1·5
2·0
2·5
3·0
Log I →
Log V →

Fig. 3.32


Quenched at 400°C. $CuFe_2O_4$ Fig. 3.33


300°C.
250°C.
200°C.
150°C.
100°C.
50°C.
25°C.
Quencned at 600°C.
Cu Fe$_2$ O$_4$
2
1
1·7
1·2
1·5
0·79
$\bar{1}$·0
$\bar{2}$·5
$\bar{2}$·0
$\bar{3}$·5
$\bar{3}$·0
$\bar{4}$·5
$\bar{4}$·0
1·0
1·5
2·0
2·5
Log I →
Log V →

Fig·3·34



Quenched at 800°C. Cu Fe_2O_4 Fig. 3.35

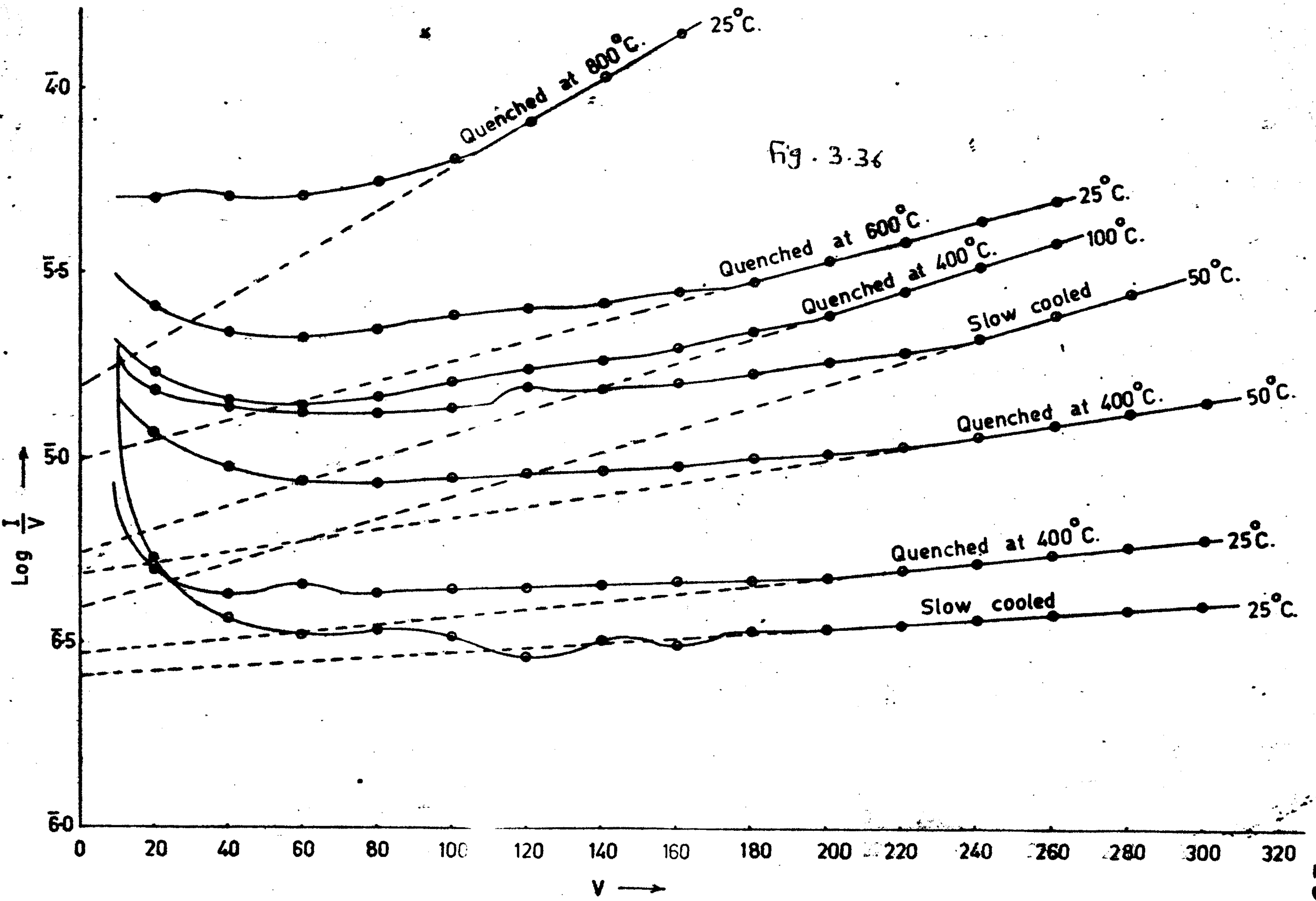

$\overline{4}$·0
$\overline{5}$·5
$\overline{5}$·0
$\overline{6}$·5
$\overline{6}$·0
Log $\frac{I}{V}$ →
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
V →
Quenched at 800°C.
25°C.
Quenched at 600°C.
25°C.
Quenched at 400°C.
100°C.
Slow cooled
50°C.
Quenched at 400°C.
50°C.
Quenched at 400°C.
25°C.
Slow cooled
25°C.

Fig. 3.36

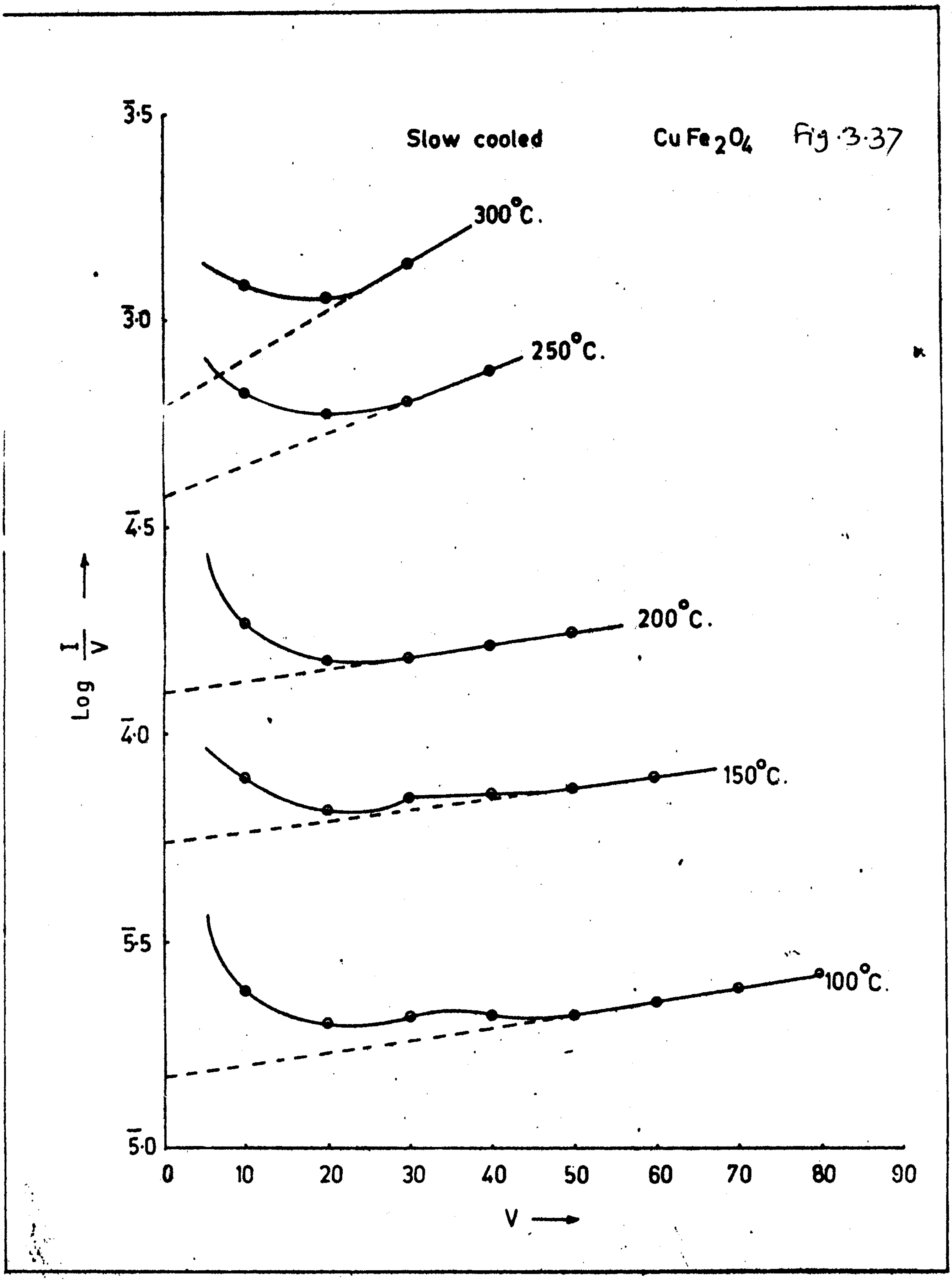
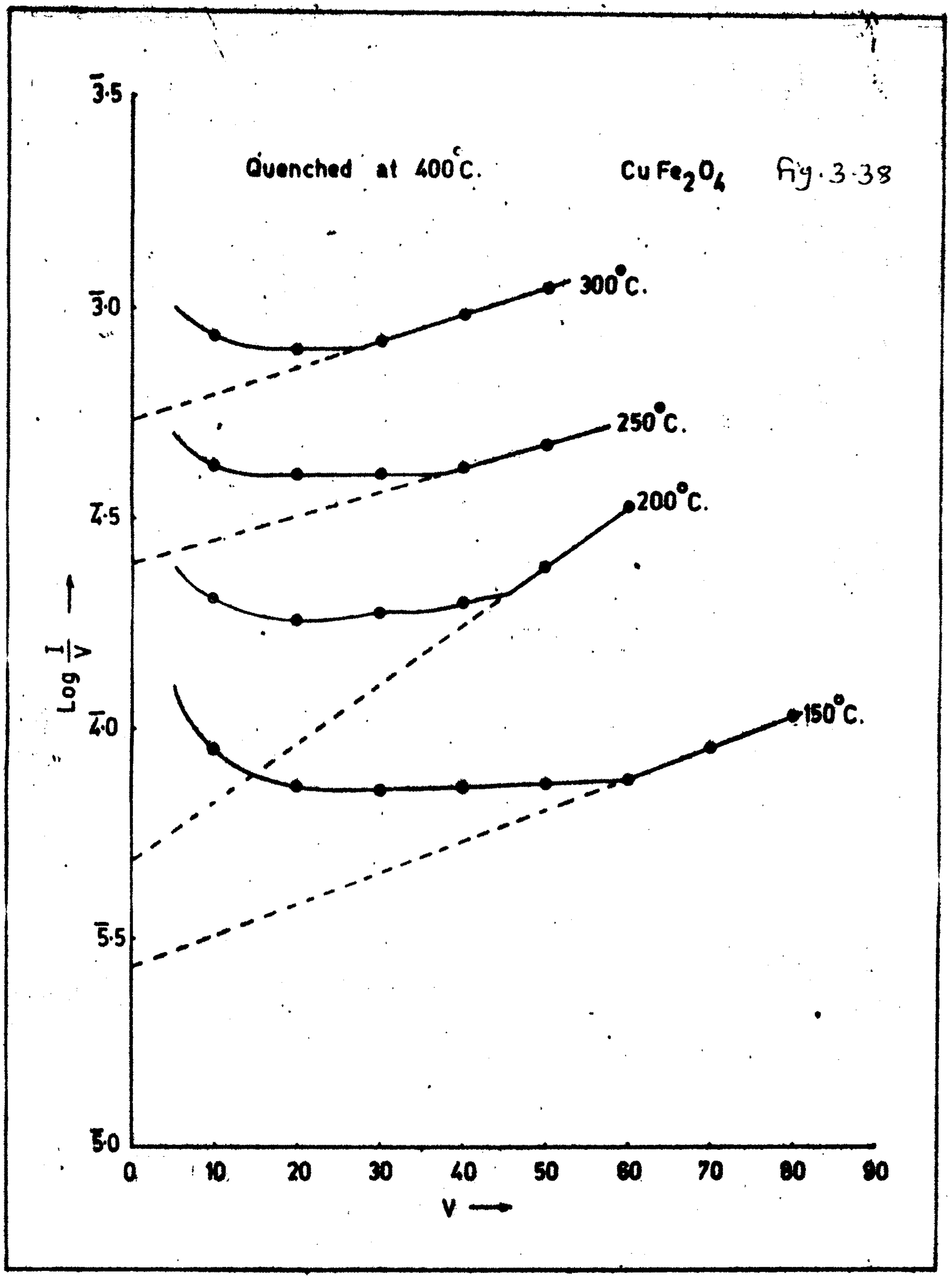
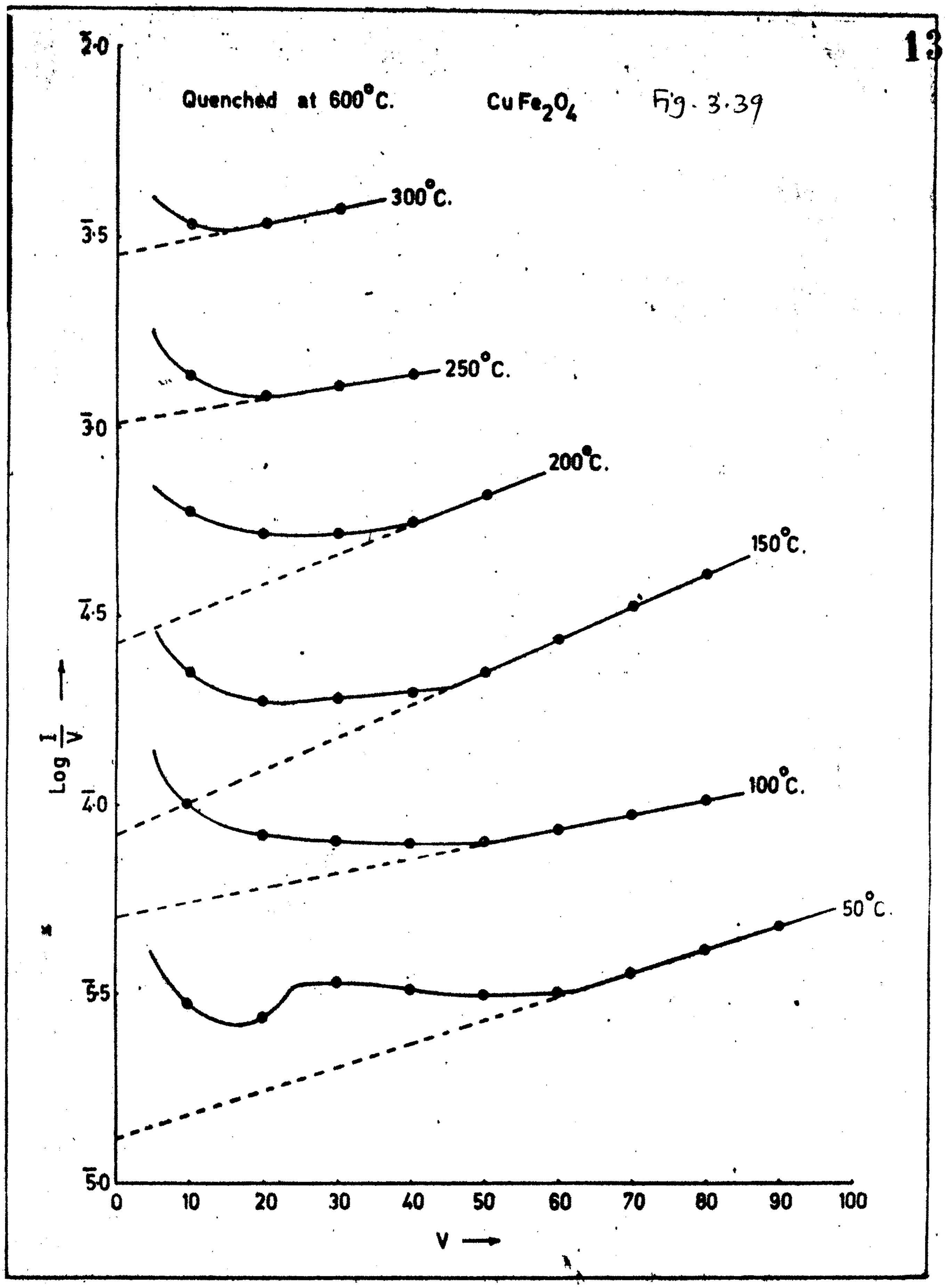
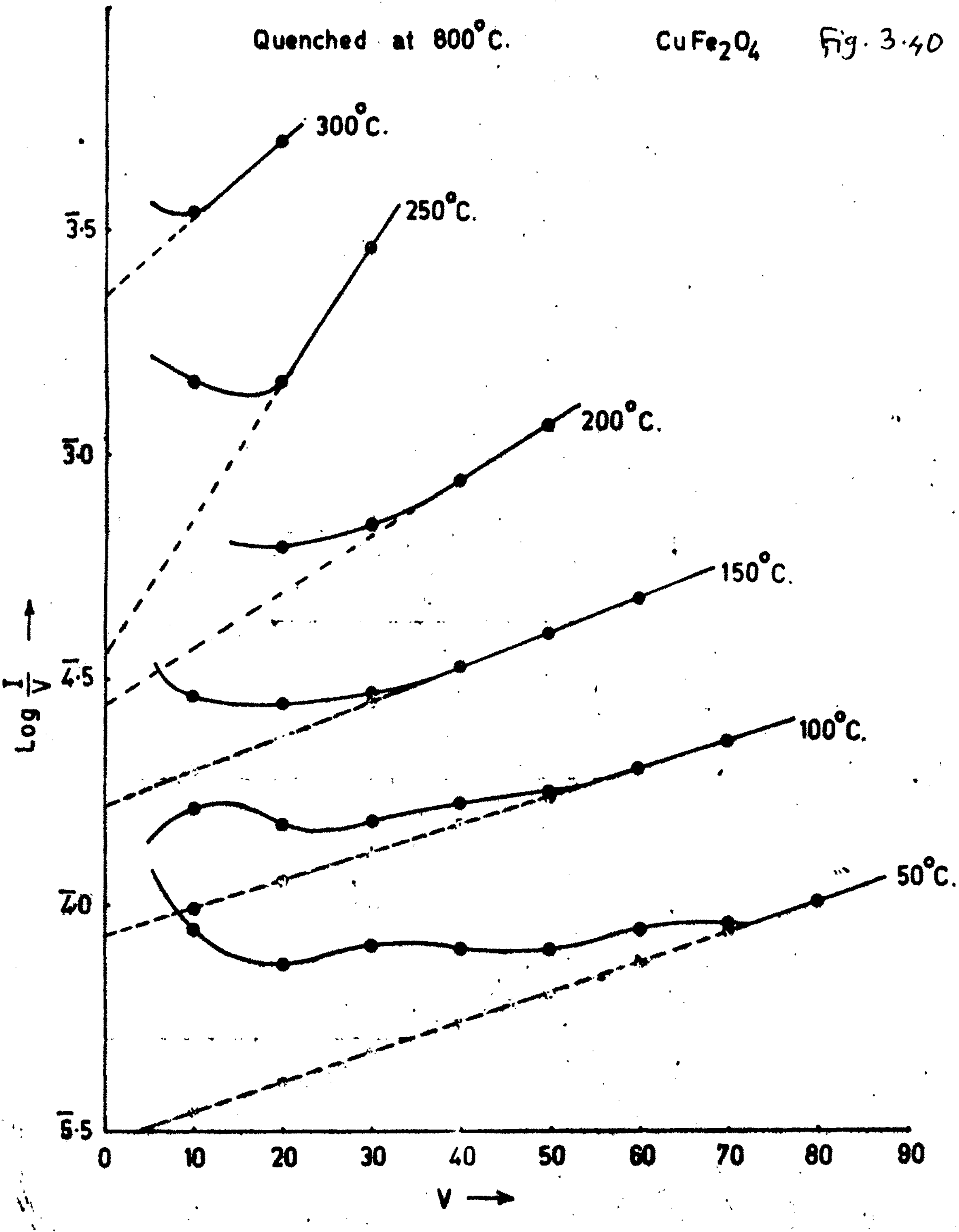

Slow cooled
$CuFe_2O_4$
300°C.
250°C.
200°C.
150°C.
100°C.
$\bar{3}$·5
$\bar{3}$·0
$\bar{4}$·5
$\bar{4}$·0
$\bar{5}$·5
$\bar{5}$·0
Log $\frac{I}{V}$ →
0
10
20
30
40
50
60
70
80
90
V →

Fig.3.37


Quenched at 400°C.
Cu Fe_2O_4
Fig. 3.38
300°C.
250°C.
200°C.
150°C.
$\bar{3}$.5
$\bar{3}$.0
$\bar{4}$.5
$\bar{4}$.0
$\bar{5}$.5
$\bar{5}$.0
Log $\frac{I}{V}$ →
0
10
20
30
40
50
60
70
80
90
V →



Quenched at 600°C. Cu Fe$_2$O$_4$ Fig. 3.39


Quenched at 800°C.
CuFe$_2$O$_4$
Fig. 3.40
300°C.
250°C.
200°C.
150°C.
100°C.
50°C.
$\bar{3}$·5
$\bar{3}$·0
$\bar{4}$·5
$\bar{4}$·0
$\bar{5}$·5
Log $\frac{I}{V}$ →
0
10
20
30
40
50
60
70
80
90
V →

dielectric constant for these compositions were not available.

An alternative check to verify the existence of SCL currents is to see that the graphs of log (I/V) plotted against voltage (V) show a linear relation[22]. In Figs.3.36 to 3.40 are given the log (I/V) versus voltage (V) characteristics for the same samples. It can be noted that the plots exhibit linear relation and thus confirm the space charge limited currents in slow cooled and quenched samples of copper ferrite. This second method can further be made use of in determining the values of $t.N_t$. An attempt was made to calculate these values and compare them with the theoretical values of $t.N_t$. However, it may be brought to the notice that the agreement was not so good; which suggest that the investigation in this direction could be of interest.

Referring to Figs.3.32 to 3.35, a particular point on the log I versus log V curve indicated by an open circle; at 100°C for the slow cooled sample and at 50°C for the samples quenched at 800°C and 600°C respectively. The decrease in slope at this point indicates that the samples transit from CCNR region to VCNR region. This VCNR region exists for very short time and the further increase in the voltage (V) brings the sample back in CCNR region. This study of SCL mechanism in copper ferrite, which exhibits electrical switching, will be of some interest and may reveal some interesting property of the ferrite, however, in the absence of the availability of some parameters, necessary for computation in the literature, all the calculations were not possible.

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