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Temperature Variation of the Magnetic Anisotropy of Graphite

By

K. S. Krishnan and N. Ganguli

With 1 figure



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Temperature Variation of the Magnetic Anisotropy of Graphite.

By K. S. Krishnan and N. Ganguli,
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1. Introduction.

Graphite crystal belongs to the hexagonal system and occurs in the form of a thin flake parallel to the basal plane. The crystal exhibits some remarkable magnetic properties. Whereas its susceptibility along directions in the basal plane, χ_{\perp} , is normal, and has the value $-0.5 \cdot 10^{-6}$ per gm., which is nearly that of diamond, the susceptibility along the hexagonal axis, χ_{\parallel} , has more than 40 times this value, namely about $-22 \cdot 10^{-6}$ per gm., at room temperature¹). This abnormal diamagnetism of graphite along the hexagonal axis is due to its peculiar structure. The carbon atoms are arranged in layers parallel to the basal plane. The atoms in each layer form a regular hexagonal net-work, and are strongly bound to their neighbours in the plane. On the other hand, the binding between adjacent layers, which are rather widely separated, is very weak. Three of the electrons of each carbon atom take part in binding the atom to its three immediate neighbours in the same layer, while the fourth electron is more or less free, and can wander about in the plane of the hexagonal net-work. The large orbits which these odd electrons can execute in the basal plane under the influence of a magnetic field incident along the normal to the plane, explains the abnormal diamagnetism along the latter direction.

Now these "free" electrons probably take part in loosely binding together the adjacent layers of carbon atoms, and any disturbance which alters the distance between the adjacent layers, will naturally interfere with the freedom of these odd electrons, and will therefore tend to diminish the abnormal diamagnetism along the hexagonal axis. In other words, the abnormal part of the diamagnetism of graphite should be markedly structure-sensitive. This is verified experimentally²). On treating the crystal, for example, with a mixture of strong sulphuric and nitric acids, to which has been added a pinch of potassium chlorate—when the crystal swells up to "blue graphite"— χ_{\parallel} diminishes (numerically)

1) Krishnan, *Nature* **133** (1934) 474; Guha and Roy, *Ind. Jour. Phys.* **8** (1934) 345.

2) Krishnan and Ganguli, *Current Sc.* **3** (1935) 472; Ganguli, *Phil. Mag.* **21** (1936) 355.

rapidly from $-22 \cdot 10^{-6}$ to less than $-2 \cdot 10^{-6}$, whereas χ_{\perp} remains practically unaffected. In this treatment it is the distance between the loosely bound adjacent layers of carbon atoms that changes, while the distances between the atoms in any given layer are not altered; i. e. the swelling is confined to one direction, namely the hexagonal axis of the crystal.

A similar effect is observed on treating the crystal with potassium vapour, when it forms a metallic-looking, copper-coloured alloy. Here also the swelling is along the hexagonal axis, and it is the abnormal diamagnetism along this direction that diminishes rapidly, whereas the diamagnetism in the basal plane, which is normal, remains practically unaffected. An indefinite diminution in the size of the crystal, beyond a certain low value, also appears to have a similar effect.

In view of the structure-sensitiveness of the abnormal part of the diamagnetism of the crystal, temperature changes also may be expected to have a large influence. We have therefore made measurements of the principal susceptibilities of the crystal over a large range of temperatures, from the temperature of liquid oxygen, -183°C , to about 800°C . The present paper gives an account of these measurements¹).

2. Measurements of Magnetic Anisotropy at Low Temperatures.

Since one of the principal susceptibilities of the crystal, namely χ_{\parallel} , is much larger than the other, χ_{\perp} , and since the difference between the two is easier to measure accurately than either of them separately, we have made measurements of the anisotropy $\chi_{\parallel} - \chi_{\perp}$, and of the smaller susceptibility χ_{\perp} , at different temperatures.

We shall take up first the low temperature measurements of the anisotropy. The method of measurement adopted is essentially the same as that described in a recent paper²) on the measurement of the magnetic anisotropies of some paramagnetic crystals at low temperatures. The crystal is suspended at the end of a calibrated quartz fibre inside a thin-walled copper cylinder which is kept deeply immersed in the liquid bath of a cryostat. The liquid used for the bath is petroleum ether of low boiling point, kept in a large Dewar cylinder. The bath is kept continually stirred, and its temperature is maintained steady at any desired value by automatic control by a constant-volume air-thermometer of thin-walled copper, immersed completely in the bath. There

1) A preliminary report of the results was published in *Nature*, **139** (1937) 155.

2) Krishnan, Mookherji and Bose, in course of publication in *Phil. Trans. Roy. Soc. A*.

are two electrical circuits, one through the motor of an air pump which can suck slowly liquid oxygen into a small copper chamber immersed in the bath, and the other through a small heating coil, also immersed in the bath. One or the other of the two circuits is automatically closed according as the volume of the air in the controlling thermometer is higher or lower than a certain pre-adjusted value, depending on the temperature at which it is desired to maintain the bath.

Below about -140°C the petroleum ether becomes very viscous, and hence unsuitable as a bath liquid. We could therefore work at only one temperature below this, namely the boiling point of oxygen. For this temperature, liquid oxygen is used directly as the bath liquid, in place of petroleum ether, and is allowed to evaporate freely at atmospheric pressure; no temperature control is necessary in this case.

Measurements of the temperature of the crystal are made with a copper-constantan thermocouple, one junction of which is inside the crystal chamber, just below the crystal, and the other is kept at the temperature of melting ice. The thermocouple is calibrated by keeping the former junction at the following temperatures:— (1) the temperature of liquid oxygen boiling at atmospheric pressure, namely $-183.0^{\circ}\text{C} + (p - 760) \cdot 0.0126^{\circ}\text{C}$, where p is the atmospheric pressure in mm. of mercury; (2) the temperature of a mixture of solid carbon dioxide and ethyl ether, namely -78.64°C ; (3) the temperature of the room, measured with a calibrated mercury thermometer; (4) the boiling point of water at atmospheric pressure. A four-constant formula, of the type $E = at + bt^2 + ct^3 + dt^4$, is used to express the relation between the temperature t of the measuring junction of the thermocouple, in degrees centigrade, and the observed potential difference E between its two junctions.

The magnetic measurements are made by the torsional method described in earlier papers from this laboratory. The crystal is suspended inside the copper-tube immersed in the cryostatic bath, mentioned previously, with its plane vertical. The suspension for the crystal consists of two parts. The upper part is a fine quartz fibre, which has been calibrated previously, and the lower part is a thick glass fibre, sufficiently stout in comparison with the quartz fibre to be regarded as rigid. The whole length of the quartz fibre is above the cryostat, and is practically at room temperature all the time, so that its torsional constant is independent of the temperature of the cryostat. The whole of the cryostatic arrangement is placed between the flat pole-pieces of a large electromagnet, so that the crystal may be in the centre of the field.

The upper end of the quartz fibre is attached centrally to the pin of a graduated torsion-head. The torsion-head is initially adjusted so that when the crystal takes up its natural orientation in the magnetic field, namely with its plane along the field, the torsion on the fibre is zero. If the torsion-head is now slowly rotated from this position there will come a stage when the equilibrium of the crystal in the field becomes unstable and the crystal suddenly turns. If α_c is the total angle by which the torsion-head has been rotated from its original position, then the anisotropy $\chi_{\perp} - \chi_{\parallel}$, per gm., will evidently be given by the relation

$$\lambda = \frac{\alpha_c - \pi/4 - \sigma}{\cos 2\sigma}, \tag{1}$$

where

$$\sin 2\sigma = \frac{1}{2\lambda}, \tag{2}$$

and λ stands for $\frac{mH^2}{2c} (\chi_{\perp} - \chi_{\parallel})$; m is the mass of the crystal, H is the magnetic field and c is the torsional constant of the fibre.

Since α_c is large in our measurements, corresponding to 3 or 4 rotations of the torsion-head, the expression for λ reduces to the simple form

$$\lambda = \alpha_c - \pi/4.$$

Three different crystals were measured and the results are collected together in Table I.

Table I.

I crystal		II crystal		III crystal	
Temp. °K	$\chi_{\perp} - \chi_{\parallel} \cdot 10^6$	Temp. °K	$\chi_{\perp} - \chi_{\parallel} \cdot 10^6$	Temp. °K	$\chi_{\perp} - \chi_{\parallel} \cdot 10^6$
293.6	21.2	301.2	21.0	295.6	21.0
270.6	22.0	272.8	21.9	272.1	21.9
252.9	22.6	241.8	23.0	209.1	24.7
231.2	23.4	212.2	24.2	189.9	25.5
211.4	24.7	186.4	25.4	169.0	26.4
191.8	25.3	160.6	27.0	146.2	27.4
165.4	26.8	137.1	28.0	130.0	28.3
148.9	27.3	90.1	29.1		
90.1	28.8				

IV crystal
new measurements
T $\Delta\chi \times 10$
302.3 21.0
277.2 22.0
245.9 23.2
212.5 24.6
189.2 25.5
167.1 26.5
140.0 27.7
119.0 28.8
93.7 29.6

3. Measurements of Anisotropy at High Temperatures.

For the high temperature measurements the crystal is suspended inside a large-sized tube of unglazed porcelain, closely wound on the

The results of the high temperature measurements on the anisotropy are given in Table II. The crystals are all different from those used in the low temperature measurements.

4. Measurement of χ_{\perp} .

In view of the small value of χ_{\perp} , and its sensitiveness to small traces of iron which are usually present as impurity in graphite crystal, and the large temperature variation of the disturbing effect of the iron impurity, only rough measurements were made on χ_{\perp} . The crystal was suspended with its plane vertical, at the end of a long quartz fibre, in an inhomogeneous part of the magnetic field, so that the plane of crystal may be along the field and perpendicular to the direction of its gradient. The crystal was inside the copper tube of the cryostat in the low temperature measurements, and inside the heated porcelain tube in the high temperature measurements.

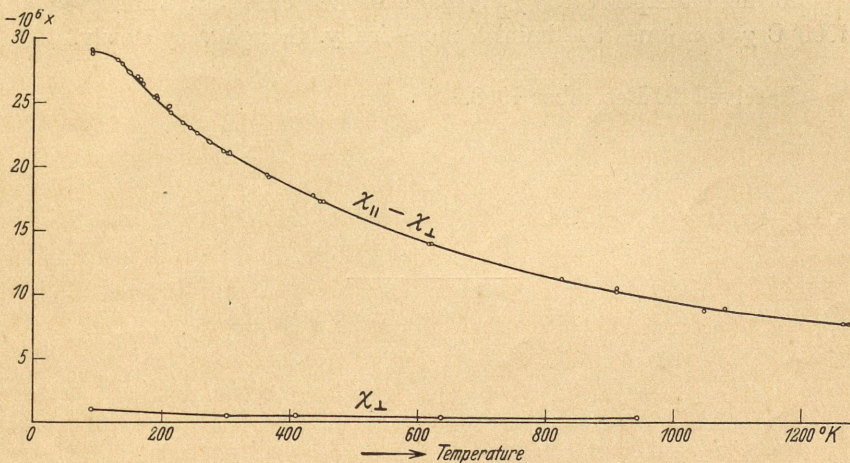


Fig. 1.

The motion of the crystal along the direction of the field gradient when the current through the magnet coils is switched on, is followed by watching through a low power microscope the shift of the suspension fibre at a point as low as possible, i. e. where it emerges from the crystal chamber. The shift is read directly on the eye-piece scale of the microscope.

Owing to the small value of χ_{\perp} , the movement of the crystal in the field is small, and we may therefore take the susceptibilities at different temperatures to be roughly proportional to the lateral shifts

of the suspended crystal, or to the lateral displacements of the fibre in the field of view of the microscope, produced by switching on the current through the magnet coils. The results are given in Table III.

Table III.

Temp. °K	90	301	409	637	943
$\chi_{\perp} \cdot 10^6$	1.0	0.5	0.5	0.4	0.4

5. Temperature Variation of the Principal Susceptibilities.

The values of $\chi_{\perp} - \chi_{\parallel}$ and of χ_{\perp} , at different temperatures are plotted in Fig. 4. As will be seen from the graphs, both χ_{\parallel} and χ_{\perp} increase numerically as the temperature is lowered, χ_{\perp} , however, remaining always very much smaller than χ_{\parallel} . At the temperature of liquid oxygen the curve for χ_{\parallel} tends to flatten, suggesting that it may not increase much as we go to still lower temperatures.

At high temperatures χ_{\perp} is more or less constant, while even at 1000°C χ_{\parallel} continues to diminish numerically, though very slowly.

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Taking T_0 as 520°K , and that the
 one free electron (1 per atom), is capable of
 motion only in the basal plane, its sp.
 heat ~~will be given by~~ can be readily
 obtained with the help of the Table
 given in Stoner's paper.

Electronic sp. heat for 1 elec. per atom

$\frac{T}{T_0}$	T	C_v/R	$\frac{T}{T_0}$	T	C_v/R
.05	26	.245	.5	260	1.258
.10	52	.477	.6	312	1.309
.15	78	.679	.7	364	1.345
.20	104	.840	.8	416	1.371
.25	130	.962	.9	468	1.391
.30	156	1.055	1.0	520	1.406
.35	182	1.125	1.2	624	1.427
.40	208	1.180	1.4	728	1.442
.45	234	1.223	1.6	832	1.452
.50	260	1.258	1.8	936	1.460
			2.0	1040	1.465

14 34

$$f = \frac{\lambda}{\lambda_e \epsilon_0}$$

$$T_{\text{ref}} \quad \lambda_0 = 30$$

$$T_0 = 506^\circ$$

$\frac{T}{T_0}$	T	$\Delta\lambda$ Calcd 20/f	$\Delta\lambda$ Obsd	λ/T	Difference Cal - Obs
.15	759.0 101.2	29.4 28.8	29.9	98.8 79.1	- .4
.20	126.5	28.1	28.5	96.0	- .4
.25					
.30	151.8	27.2	27.6	65.9	- .4
.35	177.1	26.3	26.1	56.5	+ .2
.40	202.4	25.3	24.8	49.4	+ .5
.5	253.0	23.4	22.7	39.5	+ .7
.6	303.6	21.5	20.9	32.9	+ .6
.7	354.2	19.9	19.5	28.2	+ .4
.8	404.8	18.4	18.1	24.7	+ .3
.9	455.4	17.0	17.0	22.0	0
1.0	506.0	15.9	15.9	19.8	0
1.1	556.6	14.8	15.0	18.0	- .2
1.2	607.2	13.9	14.2	16.5	- .3
1.3	657.8	13.1	13.5	15.2	- .4
1.5	759.0	11.7	12.1	13.2	- .4
1.8	910.8	10.1	10.5	11.0	- .4
2.0	1012.0	9.1	9.7	9.8	- .6

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101.5
Jed-o

~~29.4~~

$T_0 = 491$

$\chi_0 = 30.6$

$\frac{T}{T_0}$	T	$\frac{1}{T}$	$\Delta\chi$ calc = $20.4/f$	$\Delta\chi$ obsd	
1.15	736.7	135.7	30.0		
1.20	982	101.8	29.4	29.4	0
1.25	122.8	81.4	28.7	28.7	0
1.30	147.3	67.9	27.8	27.5	+13
1.35	191.9	58.2	26.8	26.3	+5
1.40	196.4	50.9	25.8	25.1	+7
1.5	245.5	40.7	23.8	23.0	+8
1.6	294.6	33.9	22.0	21.2	+8
1.7	343.7	29.1	20.3	19.8	+5
1.8	392.8	25.5	18.7	18.5	+2
1.9	441.9	22.6	17.4	17.2	+2
1.0	491.0	20.4	16.2	16.2	0
1.1	540.1	18.5	15.1	15.3	-2
1.2	589.2	16.5 17.0	14.2	14.4	-2
1.3	638.3	15.6	13.3	13.7	-4
1.4	687.4	14.5	12.6	13.0	-4
1.5	736.5	13.6	11.9	12.4	-5
1.6	785.6	12.7	11.3	11.8	-5
1.7	834.7	12.0	10.7	11.3	-6
1.8	883.8	11.3	10.2	10.7	-5
1.9	932.9	10.7	9.8	10.4	-6
2.0	982.0	10.2	9.3	10.0	-7

issued has been surrendered by the transferor in pursuance of any Order in that behalf made by the Bondholders Incorporation Commission.

If the Directors refuse to register a transfer of any shares, they shall within two months after the date on which the transfer was lodged with the Company send to the transferee notice of the refusal.

All instruments of transfer which shall be registered shall be retained by the Company, but any instrument of transfer which the Directors may decline to register shall, on demand, be returned to the person depositing the same.

35. THE legal personal representatives of a deceased sole holder of a share shall be the only persons recognised by the Company as having any title to the share. In the case of a share registered in the names of two or more holders, the survivors or survivor, or the legal personal representatives of the deceased survivor, shall be the only persons recognised by the Company as having any title to the share.

36. ANY person becoming entitled to a share in consequence of the death or bankruptcy of a member shall, upon such evidence being produced as may from time to time be properly required by the Directors, have the right either to be registered as a member in respect of the share, or, instead of being registered himself, to make such transfer of the share as the deceased or bankrupt person could have made; but the Directors shall, in either case, have the same right to decline or suspend registration as they would have had in the case of a transfer of the share by the deceased or bankrupt person before the death or bankruptcy.

37. WHERE the registered holder of any share dies or becomes bankrupt, his personal representatives or the assignee of his estate, as the case may be, shall, upon the production of such evidence as may from time to time be properly required by the Directors in that behalf, be entitled to the same dividends and other advantages, and to the same rights (whether in relation to meetings of the Company, or to voting, or otherwise), as the registered holder would have been entitled to if he had not died or become bankrupt. Where two or more persons are jointly entitled to any share in consequence of the death of the registered holder, they shall, for the purposes of these Regulations, be deemed to be joint holders of the share.

38. THE guardian of an infant member (in case the Directors elect to treat the holding of shares by an infant as valid) or the committee of a lunatic member may upon producing to the Directors such evidence that he sustains the character in respect of which he proposes to act under this clause or of his title as the Directors think sufficient may, with the consent of the Directors, be registered as a member in respect of such shares or may transfer such shares.

At high temperatures

From the graph
 $-10 \times \frac{1}{\chi} = \frac{125}{1300}$

$$\chi = - \frac{.0104}{T} \text{ per gm.}$$

Equating it to $-\frac{n}{P} \times \frac{\mu^2}{3RT}$, we obtain

$$\frac{n}{P} = \frac{3R \times .0104}{\mu^2} = 5.0 \times 10^{22}$$

using $\left\{ \begin{array}{l} R = 1.379 \times 10^{-16} \\ \mu = 9.250 \times 10^{-21} \end{array} \right.$

Taking the low temp. value $\approx -30 \times 10^{-6}$ per gm and equating it

$$\text{to } - \frac{5.0 \times 10^{22} \times \mu^2}{2RT_0'} \text{ we obtain}$$

$$T_0' = 517^\circ \text{ K}$$

or in round number 520° K

To calculate the value of χ at these temps. Stone [Proc. Leeds Philos. Soc. 3, 403 (1938)] has tabulated the values of $\frac{\mu^2}{\chi_e \epsilon_0}$ for different values of $\frac{T}{T_0}$ ($\epsilon_0 = RT_0'$)

where χ_e is the ^{paramagnetic} suscept. per electron,

χ in cmv notation

$$\chi_e = \frac{3\chi \times \rho}{n}$$

T_0 is taken to be $520 \frac{22}{22}$
as 5.0×10^{22}
n/e

$\frac{T}{T_0}$	$T \frac{10^4}{T}$	$f = \frac{\mu^2}{\chi_e \epsilon_0}$	$\frac{1}{\chi} = f \times \frac{3RT_0}{\cancel{5.0 \times 10^{22}} \times \mu^2}$ $= f \cdot \text{an log. } 4.7015.$	$\chi \times 10^6$
0	0	.6667	3.35×10^4	29.85 ✓
.05	26 384.6	.6681	3.36'	29.77 ✓
.10	52 192.3	.6724	3.38'	29.59 ✓
.15	78 128.2	.6807	3.42'	29.24 ✓
.20	104 96.16	.6937	3.49'	28.65 ✓
.25	130 76.93	.7117	3.58'	27.94 ✓
.30	156 64.00	.7341	3.69'	27.10 ✓
.35	182 54.98	.7603	3.82'	26.17 ✓
.40	208 48.07	.7897	3.97'	25.19 ✓
.45	234 42.74	.8216	4.13'	24.21 ✓
.50	260 38.46	.8557	4.30'	23.26 ✓
.55	286 34.96	.8915	4.48'	22.32 ✓
.60	312 32.05	.9289	4.67'	21.41 ✓
.65	338 29.59	.9674	4.87'	20.53 ✓
.70	364 27.47	1.007	5.06'	19.76 ✓

$\frac{T}{T_0}$	T $\frac{4}{10} \frac{1}{T}$	f	$\frac{1}{\lambda}$	$\lambda \times 10^6$
0.75	390 25.63 ✓	1.048 ✓ 1.405	5.27 ✓ $\times 10^4$	18.98 ✓
0.80	416 24.03 ✓	1.089 ✓	5.48 ✓	18.25 ✓
0.85	442 22.62 ✓	1.131 ✓	5.69 ✓	17.58 ✓
0.90	468 21.37 ✓	1.174 ✓	5.91 ✓	16.92 ✓
0.95	494 20.24 ✓	1.217 ✓	6.12 ✓	16.34 ✓
1.00	520 19.23 ✓	1.261 ✓	6.35 ✓	15.78 ✓
1.05	546 18.31 ✓	1.305 ✓	6.56 ✓	15.24 ✓
1.10	572 17.48 ✓	1.349 ✓	6.78 ✓	14.75 ✓
1.15	598 16.72 ✓	1.394 ✓	7.01 ✓	14.27 ✓
1.20	624 16.03 ✓	1.439 ✓	7.24 ✓	13.81 ✓
1.25	650 15.38 ✓	1.484 ✓	7.46 ✓	13.41 ✓
1.30	676 14.79 ✓	1.530 ✓	7.70 ✓	12.99 ✓
1.35	702 14.24 ✓	1.576 ✓	7.93 ✓	12.61 ✓
1.40	728 13.74 ✓	1.622 ✓	8.16 ✓	12.26 ✓
1.45	754 13.26 ✓	1.668 ✓	8.39 ✓	11.92 ✓
1.50	780 12.82 ✓	1.715 ✓	8.63 ✓	11.59 ✓
1.55	806 12.41 ✓	1.761 ✓	8.86 ✓	11.29 ✓
1.60	832 12.01 ✓	1.808 ✓	9.09 ✓	11.00 ✓

$\frac{T}{T_0}$	T	f	$\frac{1}{X}$	$X \times 10^6$
1.65	858 ^{11.65}	1.855	9.33 ✓ $\times 10^4$	10.72 ✓
1.70	884^{11.51}	1.902	9.57 ✓	10.45 ✓
1.75	910 ^{10.99}	1.949	9.80 ✓	10.21 ✓
1.80	936 ^{10.69}	1.997	10.05 ✓	9.95 ✓
1.85	962 ^{10.40}	2.044	10.28 ✓	9.73 ✓
1.90	988 ^{10.12}	2.091	10.52 ✓	9.51 ✓
1.95	1014 ^{9.86}	2.139	10.76 ✓	9.29 ✓
2.00	1040 ^{9.69}	2.187	11.00 ✓	9.09 ✓
2.1	1092		14.50	} Calculated from series expansion.
2.3	1196		12.46	
2.50	1300		13.41	
2.70	1404		14.36	
2.80	1456		14.83	

See next page.

For values of $\frac{T}{T_0} > 2.00$, for which f values are not given in Stoner's Table, the f 's were calculated in the help of the series

$$f = \frac{T}{T_0} \left[1 + 0.265962 \times \left(\frac{T_0}{T}\right)^{3/2} - 0.005602 \times \left(\frac{T_0}{T}\right)^3 + 0.0001895 \times \left(\frac{T_0}{T}\right)^{9/2} \right]$$

$\frac{T}{T_0}$	$T \frac{f}{1/T}$	f	$1/\chi$	$\chi \times 10^6$
2.0	1040 ^{9.62}	2.187	11.00 $\times 10^4$	9.09
2.1	1092 ^{9.16}	2.288	11.48	8.71
2.3	1196 ^{8.36}	2.474	12.45	8.03
2.5	1300 ^{7.69}	2.667	13.42	7.45
2.7	1404 ^{7.12}	2.862	14.40	6.94
2.8	1456 ^{6.87}	2.958	14.88	6.72
4.0	2080 ^{4.87}	4.1328	20.79	4.81
on the vertical line				
2.0	1040 ^{9.62}	2.0	10.06	9.94
2.5	1300 ^{7.69}	2.5	12.57	7.96
	520 ^{19.23}		5.03	19.88
	650 ^{15.38}		6.28	15.92
				30.00

Experimental values

$$\Delta\chi = \chi_{\perp} - \chi_{\parallel}$$

per gm.

I crystal

II crystal

$\frac{10^4}{T}$	T °K	$\Delta\chi \times 10^6$	$\frac{1}{1000 \Delta\chi}$	$\frac{10^4}{T}$	T °K	$\Delta\chi \times 10^6$	$\frac{1}{1000 \Delta\chi}$
111.0	90.1	28.8	34.7	111.0	90.1	29.1	34.4
67.16	148.9	27.3	36.6	72.95	137.1	28.0	35.7
60.46	165.4	26.8	37.3	62.27	160.6	27.0	37.0
52.14	191.8	25.3	39.5	53.65	186.4	25.4	39.4
47.31	211.4	24.7	40.5	47.13	212.2	24.2	41.3
43.25	231.2	23.4	42.7	41.36	241.8	23.0	43.5
39.55	252.9	22.6	44.3	36.65	272.8	21.9	45.7
36.96	270.6	22.0	45.5	33.20	301.2	21.0	47.6
34.06	293.6	21.2	47.2	32.84	304.5	21.0	47.6
32.84	304.5	21.0	47.6	27.33	365.8	19.2	52.1
27.58	362.5	19.4	51.5	22.43	446	17.3	57.8
22.17	451	17.3	57.8	16.21	617	14.0	71.4
16.11	621	14.0	71.4	10.97	911	10.3	97.1
12.12	825	11.3	88.5	9.55	1047	8.8	114
9.26	1080	9.0	111	7.91	1264	7.8	128

III crystal

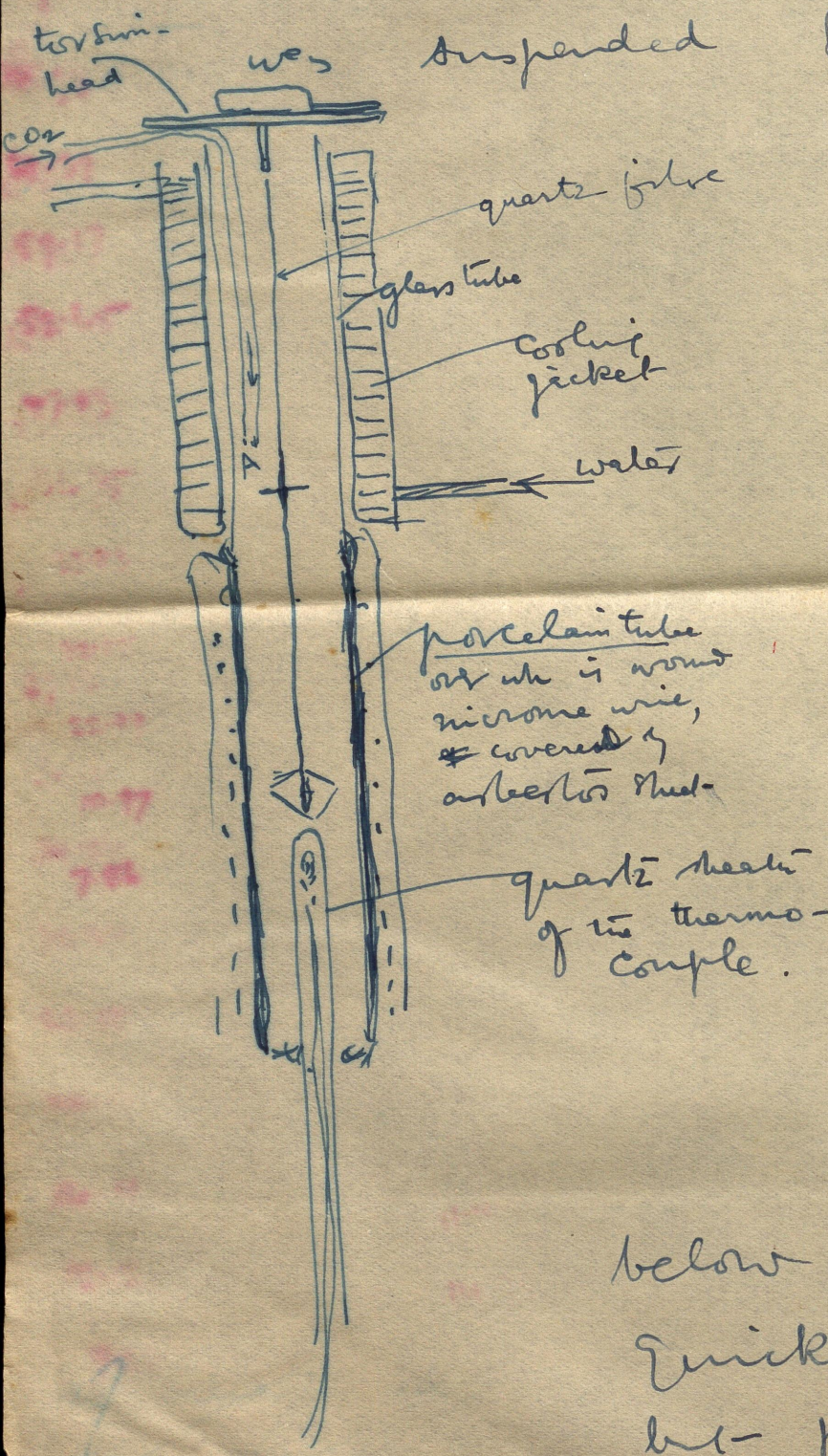
IV (new measurements)

$\frac{10^4}{T}$	T, K	$\Delta X \times 10^6$	$\frac{1}{1000 \Delta X}$	$\frac{10^4}{T}$	T, K	$\Delta X \times 10^6$	$\frac{1}{1000 \Delta X}$
76.93	130.0	28.3	35.3 ✓	10.68	93.7	29.6	33.8 ✓
68.39	146.2	27.4	36.5 ✓	83.49	119.8	28.8	34.7 ✓
59.17	169.0	26.4	37.9 ✓	71.43	140.0	27.7	36.1 ✓
52.65	189.9	25.5	39.2 ✓	55.84	167.1	26.5	37.7 ✓
47.83	209.1	24.7	40.5 ✓	52.85	189.2	25.5	39.2 ✓
36.75	272.1	21.9	45.7 ✓	47.07	212.5	24.6	40.7 ✓
33.83	295.6	21.0	47.6 ✓	40.67	245.9	23.2	43.1 ✓
32.85	304.4	21.1	47.4 ✓	36.08	277.2	22.0	45.5 ✓
22.99	435	17.8	56.2 ✓	33.09	302.3	21.0	47.6 ✓
10.97	911	10.6	94.3 ✓				
7.86	1273	7.8	128 ✓				

X

New high temp means of ΔX for graphite

In all the following measurements the hot chamber in which the graphite cryst. was suspended for the high temp measurement of ΔX was kept filled with CO_2 .



The crystal was introduced only after the heater has been brought to the reqd temp, so as to minimize the time during which the crystal is kept in the hot chamber. Immediately after ΔX measurement the crystal was lifted to the position ^{which is} below the CO_2 jet, and was quickly cooled to room temp. but pass a rapid current of CO_2 . (The ~~time~~ during the heating time was very little CO_2 flow of CO_2 .)

Temp. variation γ meq. anstony of graphite

Cryst no	$\Delta X \times 10^6$ at room temp. 11	T $^{\circ}K$ 2	$\Delta X \times 10^6$ assum room temp. value = 21.0 3	$\frac{1}{1000 \Delta X}$ 4	$\Delta X \times 10^6$ from previous graph 5
<u>I</u>	20.2 ✓ at 26.8 c.	9.42 ✓ 1062 ✓	8.45 ✓ (→ 8.)	118.3 ✓	8.9 ✓
<u>II</u>	20.0 ✓ at 26.2	17.88 ✓ 559 ✓	14.1 ✓ (→ 14.0)	70.9 ✓	15.0 ✓
		12.56 ✓ 796 ✓	11.5 ✓ (→ 11.0)	87.0 ✓	11.5 ✓
		9.12 ✓ 1097 ✓	8.3 ✓ (→ 8.1)	120.5 ✓	8.7 ✓
<u>III</u>	19.7 ✓ at 26.5 c.	22.22 ✓ 450 ✓	17.6 ✓ (→ 17.5)	56.8 ✓	17.3 ✓
		13.89 ✓ 721 ✓	11.8 ✓ (→ 11.7)	84.7 ✓	12.5 ✓
		10.65 ✓ 939 ✓	9.3 ✓	107.5 ✓	10.1 ✓
		8.64 ✓ 1157 ✓	7.6 ✓	131 ✓	8.2 ✓
<u>IV</u>	19.2 ✓	8.92 ✓ 1121 ✓	8.4 ✓	125 124 ✓	
		11.46 ✓ 873 ✓	10.5 ✓	95.1 ✓	
		14.72 ✓ 679 ✓	12.2 ✓	81.9 ✓	

In an atm.
of N_2 gas.

The values in red ink are the values calculated for γ in semi gas $n = 1$ ele per atom & $T_0 = 520^{\circ}K$.

Cryst. no	$\Delta X \times 10^6$ at room temp	T °K	$\Delta X \times 10^6$ lattice value at 300°K = 21.0	$\frac{1}{1000 \Delta X}$
<u>V</u>	20.3 ✓ 14.75 ✓	678 ✓	12.7 ✓	78.7 ✓
	in N ₂ ✓ 11.82 ✓	846 ✓	11.0 ✓	90.8 ✓
	8.93 ✓	1120 ✓	8.1 ✓	123 ✓
<u>VI</u>	not measured in Co ₂ but not change in wt at all	20.20 ✓ 495 ✓	16.0 ✓	62.5 ✓

The value of χ_{eT} at high temps
from the new measurements

$$1062 \times 8.9 \times 10^{-6} =$$

$$1097 \times 8.7 \times$$

$$1157 \times 8.2 \times$$

$$1121 \times 8.1$$

$$1120 \times 8.1$$

E.m.f. of Fe/constantan thermo couple

Emf in millivolts	Temp I.C.T °C	Temp. Roessler + Dahl Nat. Bur. Standards J. Reser. 20,337 (1938)
0	0	0
5	95	
10	186	
15	277	
20	367	362
25	457	
30	546	
35	632	
40	713	711
45	792	
50	871	
55	950	946
60	—	

1. In the calibration of ~~the~~ ^{our} iron constantan couple

E at - { 1) b.p. of water 100°C
 2) m.p. of NaCl 804°C .
 agree with I.C.T values.

Bulb E at - 1) B.P. Sulphur 445°C
 more than I.C.T
 25.35 mv. ~~vs~~ 24.33
 corresp. temp diff = 20° .

2) m.p. CdCl_2 568°C .

$E = 33.68 \text{ mv.}$ I.C.T value = 31.28
 diff = 41°C .

1) Repeat measurement at 804° to find whether thermocouple is unaffected by heating

2) CdCl_2 + Sulphur
 and choose some ~~other~~ fixed pts in this region

$\text{K}_2\text{Cr}_2\text{O}_7$	397.5°C	
$30.5 \text{ NaCl} + 69.5 \text{ Na}_2\text{SO}_4$		637.0
KCl	770.3	Na_2SO_4 884.7
NaCl	800.4	K_2SO_4 1069.1

In the measurement of ΔX

the particular crystal studied showed a
~~distribution in ΔX of~~ the value of ΔX
after the heat treatment was only
0.85 of its value before in treatment

Find whether this is so for all the crystals
or only an accidental result.

• $964.5^\circ - 45^\circ$ at Room Temperature
 919.5° Current = 1.0 Ampere

After the ~~one~~ high temp. measurements

$$\lambda - 45^\circ = 824^\circ - 45^\circ = 779^\circ$$

$$\text{Ratio} = \frac{779}{920} = 84.7\%$$

As measured in the other magnet

$$\text{Original } \lambda = 390.4^\circ$$

$$\text{new } \lambda = 336.7^\circ$$

$$\text{Ratio} = 86.2\%$$

Calibration of an Iron - Constantan Thermocouple

[The Connection in the Potentiometer Box is with the Terminal marked 1 and not with that marked '01]

Temperature of the Hot Junction	Temperature of the Cold J ⁿ	E _{Standard}	E _{Thermocouple}	Galvanometer Scale Reading
Boiling point of Sulfur 444° Barometer Reading 30 inches at 79°F	4°C 2°C	1.0205	0.0254 → 40	Corrected value = 25.3.
		1.0206	0.02535 0.0254	
Corrected temp = 99.9°C Steam. B. Pressure = 29.942 at 79.4°F	0.1°C	1.0202	0.00520	Corrected Value 5.19 Corrected Value = 336.72
		1.0202	0.00520	
Melting point of Cadmium chloride 568°C	0.2°C	1.0221	0.03380	Barometric pressure 29.906 at 80°F.
Melting point of NaCl. <u>800.4°C</u>	0.1°C	1.0206	0.0457	
		1.0206	0.0458	
		1.0206	0.0458	
		1.0205	0.0458	
		1.0205	0.0456	
		1.0205	0.0456	

79
32
47
49

255
26

Correction curve for the Constantan-
iron thermocouple used in the
graphite expts.

emf of cell 1.0183

$\Delta E = \text{Obs} - \text{Table value}$

B. P. Sulphur

1. $\sqrt{\text{Steam bath at } 29.942^\circ \text{ pres}} // \begin{matrix} 99.9 - 0.1 \\ \hline 99.8 \end{matrix}$

$\frac{5.20}{1.0202} \times 1.0183 \text{ mV} = \underline{\underline{5.19 \text{ mV.}}}$

for Table 5.26

$\Delta E = -0.07$

2) B. P. Sulphur

445° C

$E = \frac{25.4 \times 1.0183}{1.0206}$

$= 25.35$

for Table 24.28³³

$\Delta E = \underline{\underline{1.02}}$

20 difference

3) m.p. CdCl2

568°

$E = \frac{33.80 \times 1.0183}{1.0221} = 33.68 \text{ mV.}$

$\Delta E = 2.4 \text{ B}$

calculated for Table 31.28

$\Delta T = 41^\circ$

4) $\sqrt{\text{m.p. NaCl}}$

800°

$\frac{45.7 \times 1.0183}{1.0205} = 45.6$

for Table 45.51

$\Delta X = 0.09$

Taking the values of the thermo e.m.f.
 for the iron-copper couple given in I.C.T.
 as applicable to our thermo couple,
 the correction necessary would be

obsd E mv.	obsd E - I.C.T. value mv.
5.19	- .07
25.35	+ 1.02
33.68	+ 2.40
45.6	+ .09

= 20% diff in temp
 5.5% diff in resist.

max. difference is +2.40 which at this
 temp. ($\approx 570^\circ\text{C}$) will make a difference of $\frac{41^\circ}{1^\circ}$ in temp. and
~~at~~ about 5.4% in ΔX .

45.8 mV corresponds to temp = 80.3°C

$$\Delta X = \frac{21.0 \times 141.6}{390.4} \times 10^{-6} = 7.6 \times 10^{-6}$$

at $T = 10.76^\circ$ $\Delta X = 7.6 \times 10^{-6}$

$$\frac{1}{1000 \Delta X} = 132$$

Rough values

T	ΔX obs.	ΔX from previous graph	Difference
Room temp	(21.0) area		"
225 (235) 498 (508)	15.1	16.2	7%
523 (558) 796 (831)	10.7	11.5	7%
803 (804) 1076 (1077)	7.6 ← 8.9	8.8	15%
650 (690) 923 (963)	8.2 → 9.6	10.2	22%
320 (330) 593 (603)	11.7 - ^{13.8} (14.2)	14.4	21%

21%
12%
80
20
9
27
13

obsd E in mV.	Temp. in I.C.T °C	Correction T ₂ K	T ₁ K old.	Δλ observed
45.8	805 885	1078 1078	8.8 " }	8.9 ✓
38.6	690 660	963 933	✓ 9.8 10.0 }	9.6
18.00	331 319	604 592	14.3 14.4	13.8

Using the correction

Corrected values of temp. given in red ink.

old value too high
too

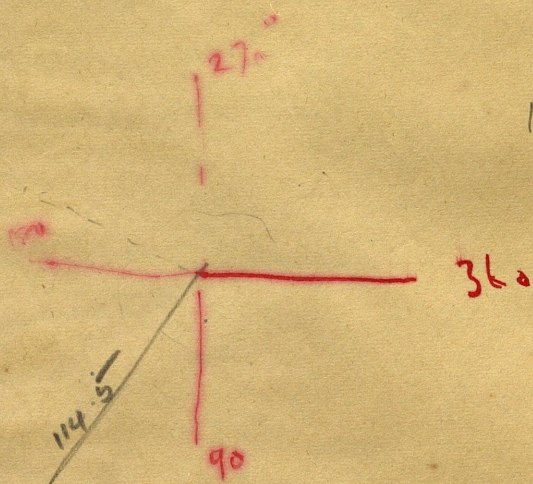
2.5 Amp. = Maximum Current
that can be passed through the magnet

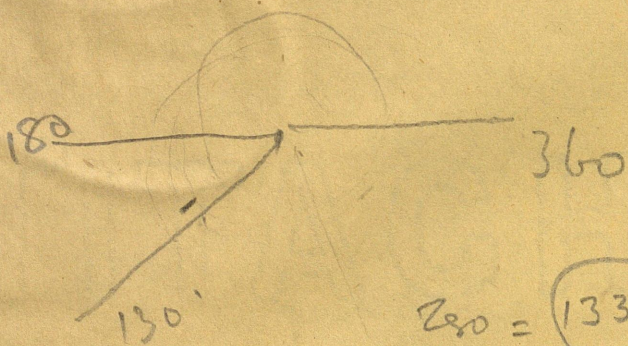
Current in the magnet
= 2.5 Amp.

$E_{Standard}$	$E_{Thermocouple}$	E_s/E_T	E.m.f. Calculated in mV	Temperature in $^{\circ}C$	Initial Reading	No. of Turns	Final Reading	θ	λ	Current through coils
Room Temperature =					114.5	360	192	437.5		
					114.5	360	39.0	436.5	390.4	Nil
					114.5	360		435.5	(21.0) assumed	
1.01840	.01266		12.66	225 $^{\circ}$	114.5	360	83	328.5		
					114.5	360	148	327.5	280.9	1 Amp.
					114.5	360		326.5	(15.1)	
1.01862	.0306		30.6	525 $^{\circ}$	114.5	360	0	245.5		
					114.5	360	229	245.5	198.5	1.5 Amp.
					114.5	360		245.5	(10.7)	
1.01840	.0458	11.5	45.8	803 $^{\circ}$	114.5	360	304	189.5		
					114.5	360	285	189.5	141.6	2.0 Amp.
					114.5	360		189.5	(7.6)	
1.01867	.0386		38.6	650 $^{\circ}$	114.5	360	817	202.5		
					114.5	360	273	202.0	154.3	1.8 Amp.
					114.5	360		201.5	(8.2)	
1.01820	.01800		18.00	320 $^{\circ}$	114.5	360	20	265.5		
					114.5	360	210	265.0	218.2	1.2 Amp.
					114.5	360		267.5	(11.7)	1.2 Amp.

After the expt θ at room temp
was 382.8 $\lambda = 336.7$

which is only 86% of the
original value of 390.4 !!
Has the crystal been partly
oxidized?





Zero = $\textcircled{133\frac{1}{2}}$

140
- 13

$\textcircled{127}$

138 $\textcircled{2}$ 302

$\textcircled{129}$

Temp -
27.3°C

$\textcircled{2}$ 316

$$\begin{array}{r} 307 \\ 130 \\ \hline 177 \\ 720 \\ \hline 897 \end{array} \checkmark$$

$\textcircled{12}$
 $\textcircled{893}$

$$\begin{array}{r} 720 \\ 130 \\ 40 \\ \hline 890 \end{array} \checkmark$$

$$\begin{array}{r} 720 \\ 160 \\ \hline 880 \end{array}$$

$\textcircled{893}$

$$\begin{array}{r} 720 \\ 140 \\ 46 \\ \hline 906 \end{array}$$

$$\begin{array}{r} 720 \\ 164 \\ \hline 884 \end{array}$$

$\textcircled{893}$

$$\begin{array}{r} 720 \\ 138 \\ 44 \\ \hline 902 \end{array}$$

E Standard.

1.0270

1.0276

E. Thermocouple.

0.04973

0.04975

138 \rightarrow 360
90
138 \leftarrow 360
189

$$\begin{array}{r} 360 \\ 138 \\ \hline 222 \\ 90 \\ \hline 312 \end{array}$$

$$\begin{array}{r} 360 \\ 51 \\ \hline 309 \end{array}$$

$\textcircled{311}$

Zero = $\textcircled{137}$

$E_{mF} = 49.74 \times \frac{1.0183}{1.0273} = 49.29 \text{ mV}$

wh corresponds according to I.C.T table to 86°C

$$\text{At } 27.3^\circ \text{C} \quad \lambda = \alpha = 893 - 45 = 848^\circ$$

$$\text{At } 86^\circ \text{C} \quad \alpha = 311 - 45 = 266^\circ \quad \lambda = 264.4$$
$$= 266$$

Take ΔX at room temp as 21.0×10^{-6}

$$\text{at } 86^\circ \text{C} = 1133^\circ \text{K} \quad \Delta X = \frac{21 \times 264.4}{848} = 6.55 \times 10^{-6}$$

from the graph 8.4

At the end of the expt -

$$138 \rightarrow 80$$

$$\frac{720}{58}$$

$$\alpha = 665 - 45^\circ$$

$$138 \rightarrow 190$$

$$\frac{720}{52}$$

$$= 620^\circ$$

$$\frac{21.0 \times 264.4}{620} = 8.95$$

The Real ΔX at the higher temp

shd be betw 6.55 + 8.95.

~~7.8~~ 550

(8.0) approx.

ΔX of Graphite at high temp.

Torsion const. of fibre = $\frac{\text{angle } 0.4186}{5.46^2} = \text{angle } 2.9442$
 0.879

At 26.8°C $\alpha = 1104 - 45^\circ = 1059 = \lambda$ $m = .0205$

$\therefore \Delta X = \frac{\pi \times 1059}{90} \times \frac{c}{.0205 \times [2800^2]} = 20.2 \times 10^{-6}$
 per gm.

~~27~~ [2800]

~~after the expt $\alpha =$~~

With a different suspension, and different field

Temp.	α	λ	m
26.8	572 1410-45	1365	.0205

E.m.f. = $\frac{45.5 \times 1.0183}{1.0300} = 45.0 \text{ mV.}$

Temp. using i.c.f. values
 $= 792^\circ\text{C} = 1065^\circ\text{K}$ $572.5 - 45 = 527.5^\circ$ 525°

26.4°C	after the expt - 1360-45	1315	.0198
----------------------	--------------------------	------	-------

$\frac{1365}{1315} = 1.038$

$\frac{205}{198} = 1.035$

\therefore The diminution of ΔX after the high temp treatment is wholly due to loss of wt. of crystal, owing

due to oxidation, which is apparently
is not completely prevented by the
flooding of the chamber with CO_2 .

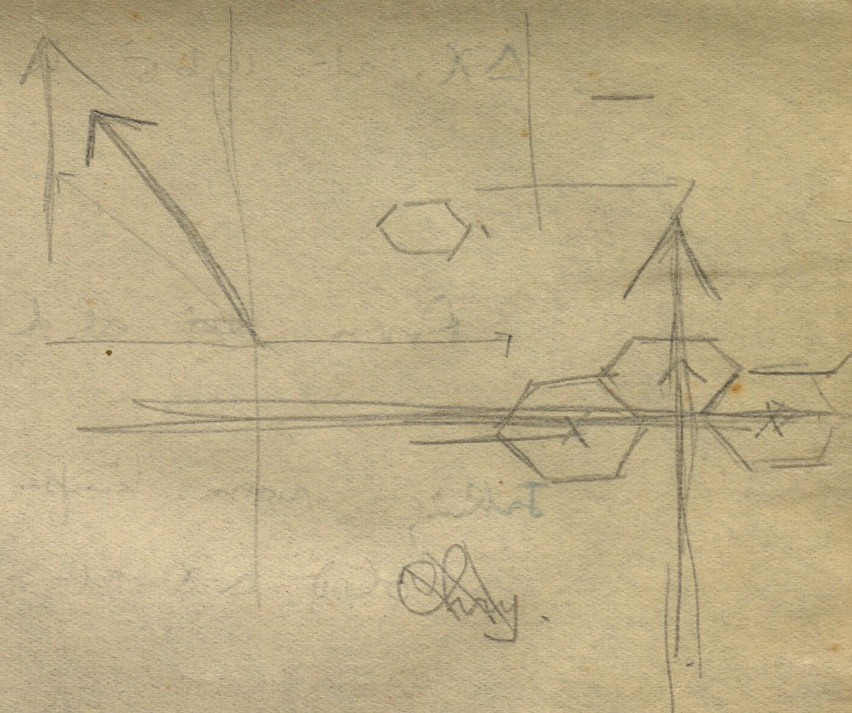
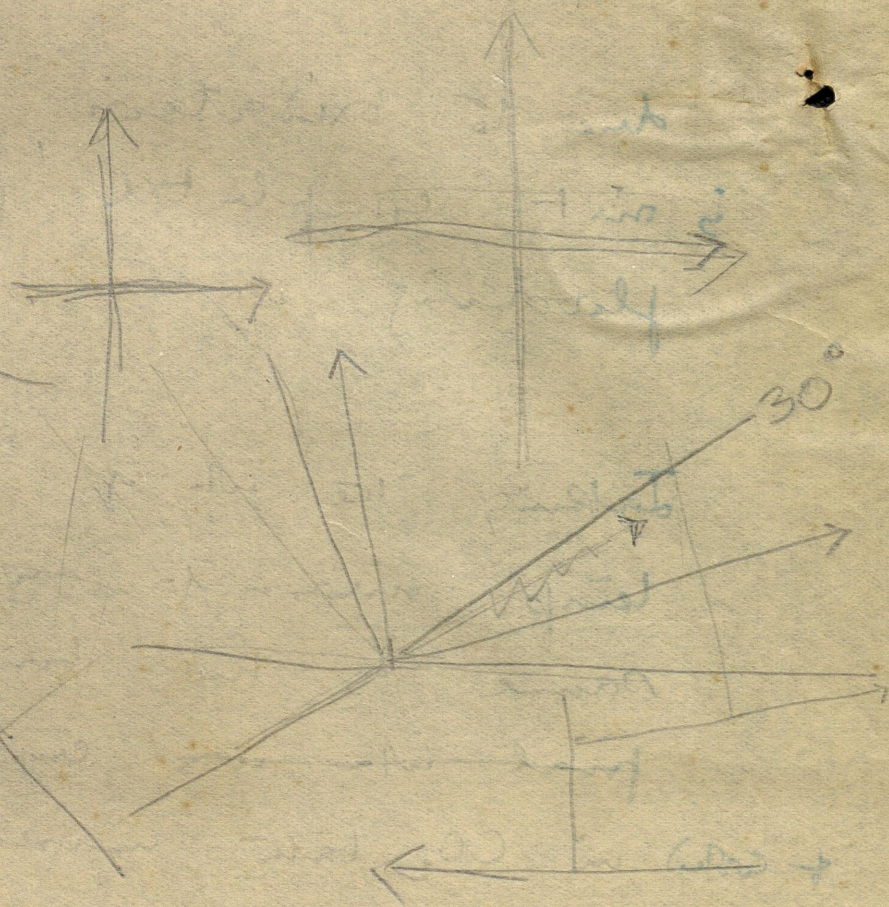
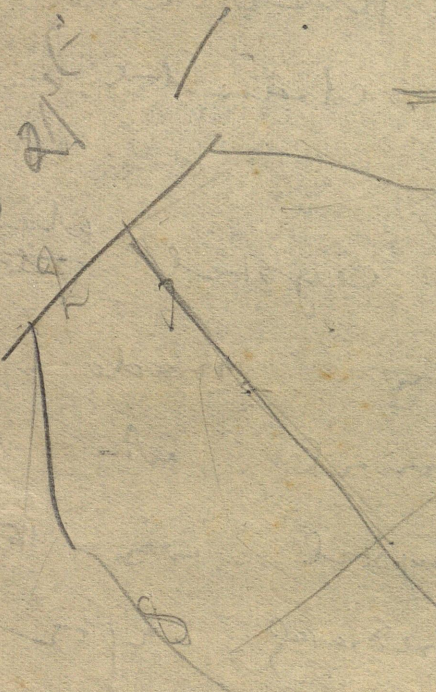
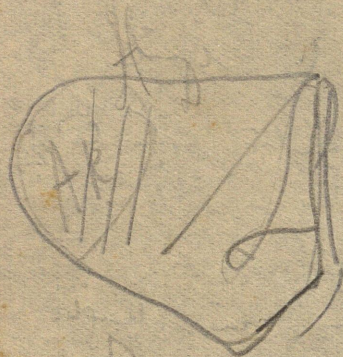
Taking the wt of crystal ~~at~~ ^{when} in high
temp. measmt. was made to be the
same as the final wt., since the
~~final wt.~~ was crystal was taken out
& cooled in CO_2 bath immediately after the high
temp. measmt., we obtain

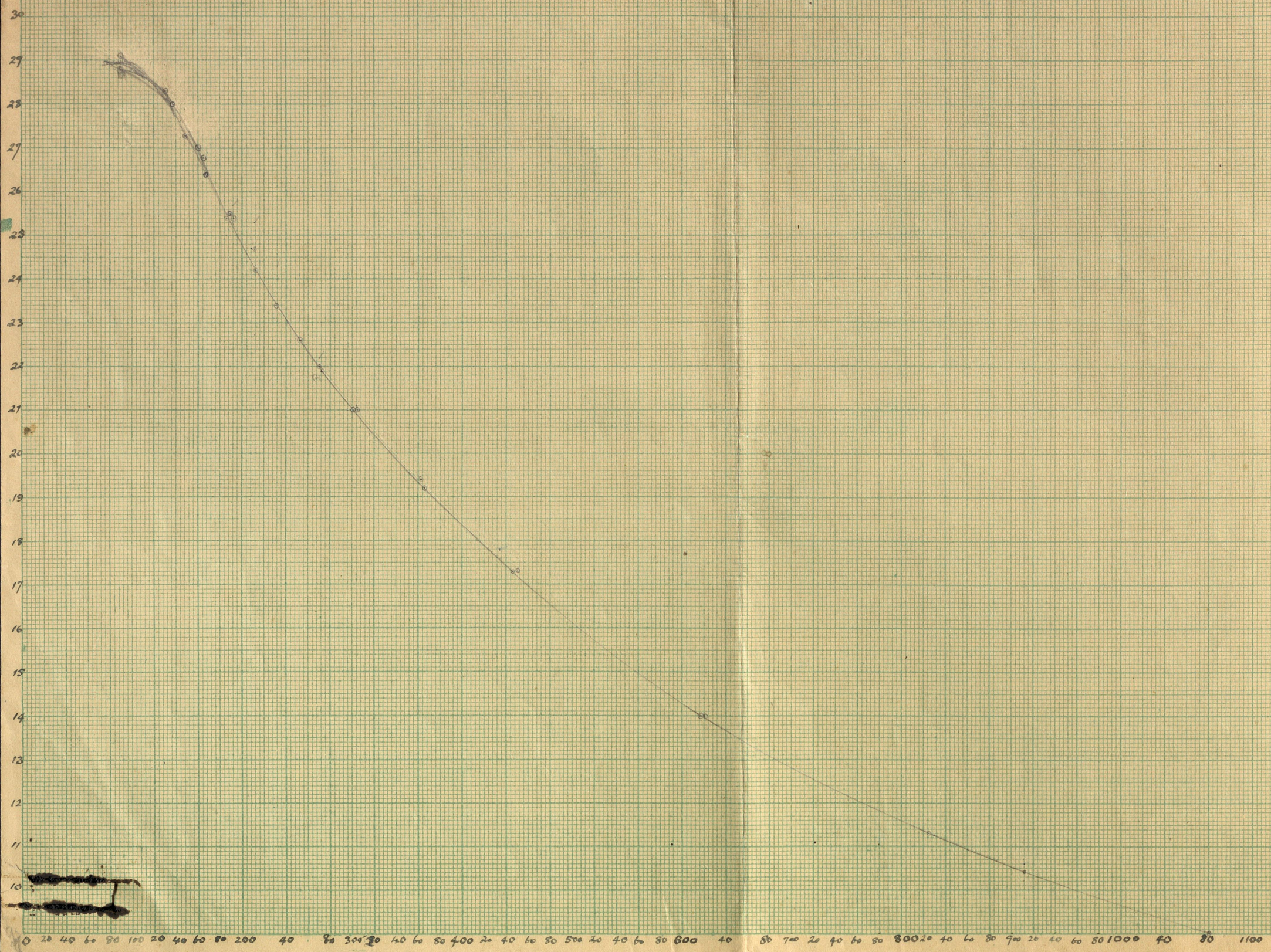
$$\Delta X \text{ at } 1065^\circ \text{K} = \frac{525}{1315} \times 20.2 \times 10^{-6}$$
$$= 8.1 \times 10^{-6}$$

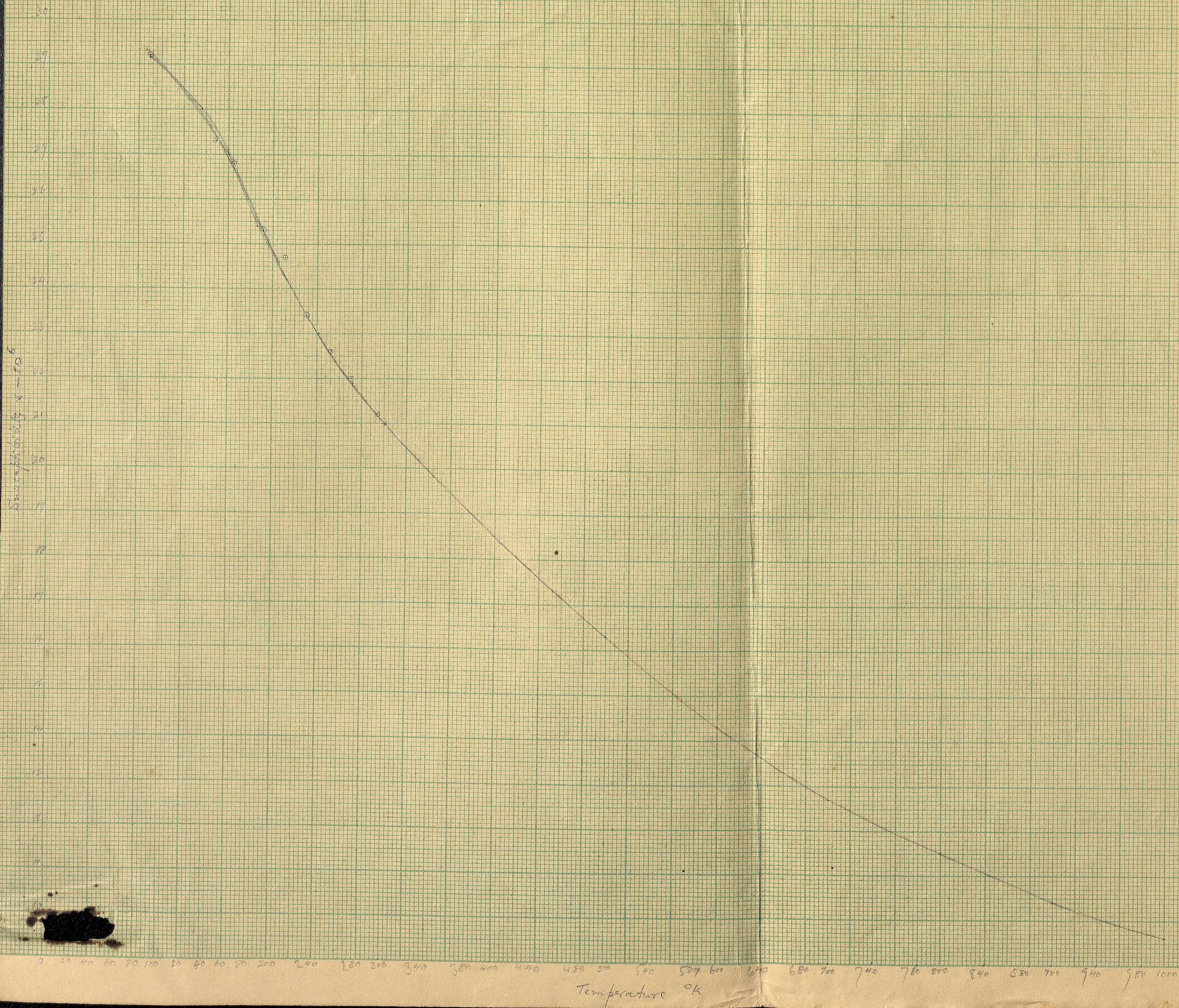
From ~~the~~ old graph 8.9×10^{-6}

Taking room temp. $\Delta X \approx 21.0$
old ΔX at 1065°K wd = 8.4×10^{-6} .

$$\frac{1}{8.4} = .119$$







Absolute Susceptibility at High Temperature

1st Crystal

Temperature	Deflection
28.3°C (Room Temperature)	3.2 (Scale division)
136.0°C	3.15
364.0°C	2.5
670	2.3 or 2.4 " "

2nd Crystal.

27.8 (Room Temperature)	3.2 " "
136°C	2.9 " "
670	2.4 " "

(2nd Crystal) Absolute Susceptibility at Low Temp.

27°C (Room Temperature)	5.2
Liquid Air boiling	11.4

52) 570 (1.1)

28

Fixed Points for Calibration of the Constant Temperature

- (1) Ice melting 0.1
- (2) Steam
- (3) Sulphur " 444.6
- (4) Antimony melting ($t = 630.5$)
- (5) Zinc " ($t = 419.4$)
- (6) Silver " ($t = 960.5$)
- (7) Lead " ($t = 327.4$)
- (8) Tin " ($t = 231.8$)

Low Temperature Measurements:-
Graphite

1st Crystal.

273.1

Pentam Thermometer Readings	E. m. f. of 1 st Standard cell	E. m. f. of 1 st Thermocouple	E Calculated	Temperature °C	θ - 45	Δx x 10 ⁶	Temperature Absolute
20.6°C	1.0064	0.0840	835	20.5	1646	21.2	273.56
-2.3°C	1.0072	0.0102	-101	-2.6	1707	22.0	270.45
-19.1	1.0090	0.0795	-788	-20.2	1751	22.6	252.89
-39.5	1.0172	0.1621	-1594	-41.9	1818 2018	23.4	231.72
-59.9	1.0370	0.2382	-2297	-61.7	1914	24.7	211.34
-79.7	1.0380	0.3057	-2945	-81.3	1968	25.3 (25.4)	191.78
-106.1	1.0012	0.3757	-3754	-107.7	2082	26.8	165.34
-120.1	1.0013	0.4221	-4216	-124.2	2121	27.3	148.89
-183°						29.2 28.8	90.1
							θ - 45 = 1063 at 30°C θ - 45 = 1464 at -183°

2nd Crystal.

29.1	1.0227	0.1187	1161	28.1	726	21.0	301.7
2.5	1.0227	0.0142	-13.9	-0.3	757	21.9	272.78
-21.7	1.0264	0.1243	-1211	-31.3	794	23.0	241.78
-49.4	1.0264	0.2328	-2271	-60.9	837	24.2	212.72
-76.0°C	1.0220	0.3190	-3121	-86.7	878	25.4	186.34
-104.0°C	1.0286	0.4014	-3902	-112.5	932	27.0	160.56
-128.5	1.0241	0.4633	-4523	-136.0	967	28.0	137.01
-183°C						29.15 29.08	90.1
							θ - 45 = 405 at 30.3° θ - 45 = 562 at -183°C

Graphite

Low Temperature measurements

with no selection

t °C	T Temp. °K	c_{meas} °K	$\Delta\chi \times 10^6$	t	$\frac{c_{crystal}}{T}$	$\Delta\chi$
-138 - 5 = -143	135	130	28.3	-138 - 5 = -143		28.9
-122.2 - 4.6 = -126.8	150.8	146.2	27.4	-119.5 - 4.3 = -123.8		27.9
				-102.5 - 3.0 = -105.5		26.9
-101.0 - 3.0 = -104.0	172.0	169.0	26.4			
-80.7 - 2.4 = -83.1	192.3	189.9	25.5 _s	-78.5 - 2.3 = -80.8		25.7
-61.7 - 2.2 = -63.9	211.3	209.1	24.7	-60 - 2.1 = -62.1		25.3
				-39 - 2 = -41 -41		24.3
				-19 - 1 = -20		23.0
-0.9 ✓	272.1 261.0		21.9	-2 ✓		22.2
+22.6 ✓	295.6		21.0			
				25.5 ✓		21.0

omit this set

High Temperature measurements

I crystal			II crystal			III crystal		
t °C	T °K	$\Delta\lambda$ $\times 10^6$	t	T	$\Delta\lambda$	t	T	$\Delta\lambda$
						31.4	304.4	21.1
31.5	304.5	21.0	31.5	304.5	21.0			
89.5	362.5	19.4	92.8	365.8	19.2			
			92.5			161.8	434.8	17.9
			173.1	446.9	17.3	162		17.8
			(172.7)					
177.9	450.9	17.6 (17.3)	344.3	617.3	14.0			
348	621	14.0						
552	825	11.3						
(551)			638	911	10.2 (10.4)	638	911	10.6
			774	1047	8.8			
807	1080	9.0						
			991	1264	7.8			
						1000	1273	7.8

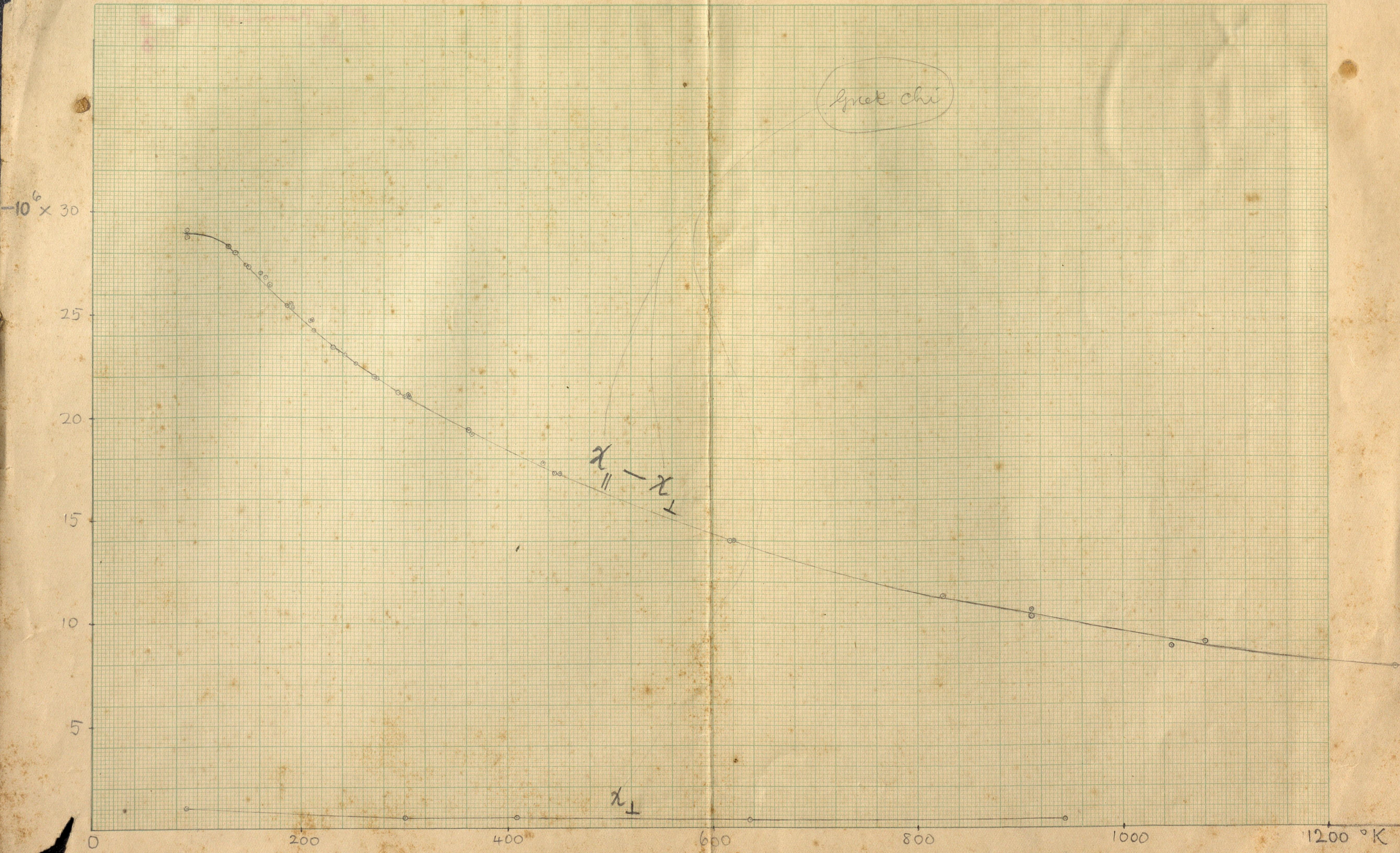


Fig. 1. → Temperature

Temperature variation of the magnetic anisotropy of graphite

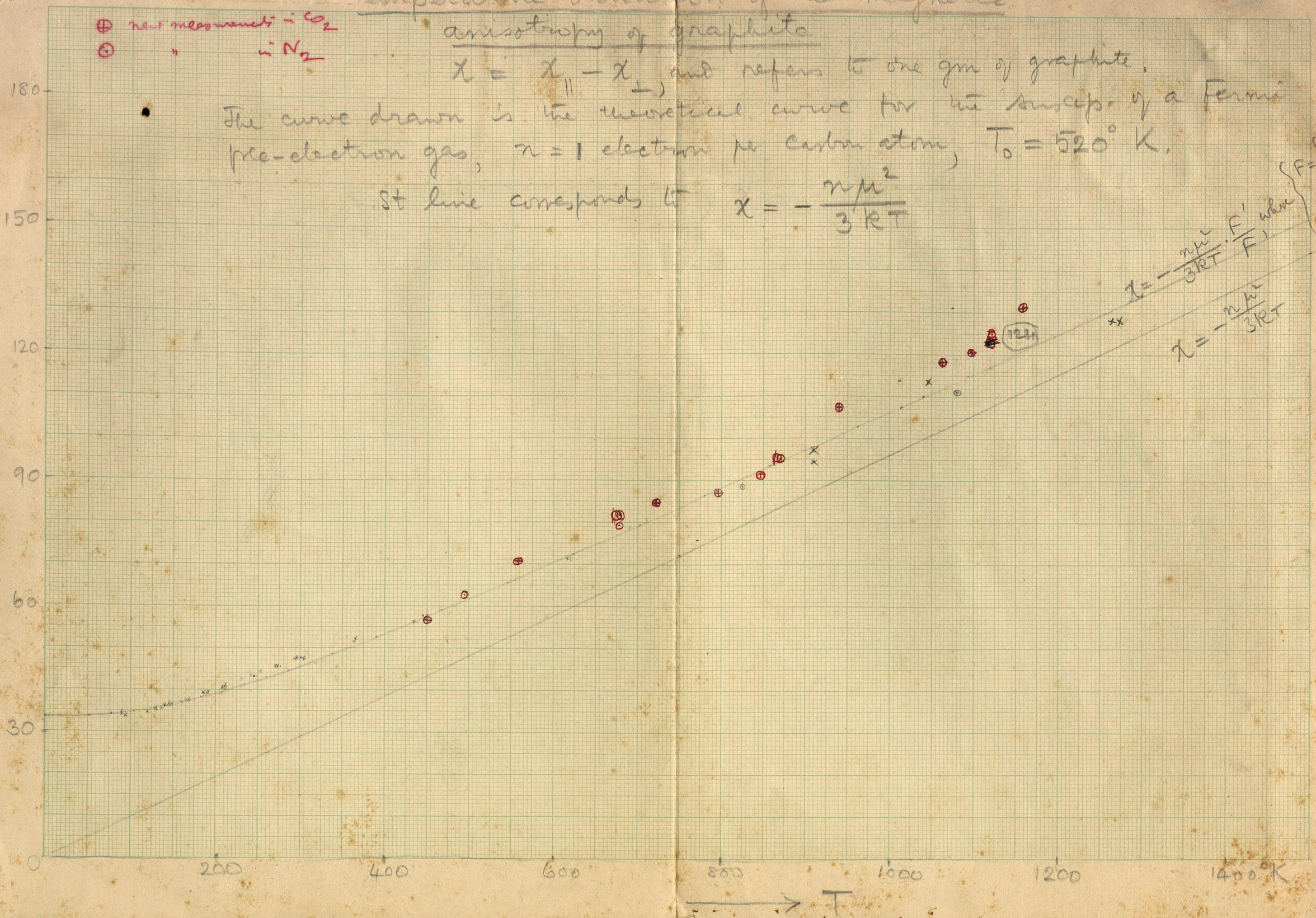
⊕ new measurements in CO₂
 ⊙ " " " in N₂

$\chi = \chi_{\parallel} - \chi_{\perp}$, and refers to one gm of graphite.

The curve drawn is the theoretical curve for the suscep. of a Fermi pre-electron gas, $n = 1$ electron per carbon atom, $T_0 = 520^\circ \text{K}$.

St line corresponds to $\chi = -\frac{n\mu^2}{3RT}$

1000χ



$$F = \int_0^{\infty} \frac{x^2 dx}{e^{x - \mu} + 1}$$

$$F' = \frac{\partial F}{\partial \mu}$$

$$\chi = -\frac{n\mu^2}{3RT} \cdot \frac{F'}{F}$$