THERMAL EXPANSION OF DIAMOND

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1. Introduction

It is well known that the coefficient of thermal expansion of a solid behaves qualitatively in the same manner as the specific heat, becoming constant at high temperatures, but reducing to zero as the temperature approaches the absolute zero. Grüneisen (1912) who was the first to draw attention to this fact derived the following relation connecting the coefficient of thermal expansion α and the specific heat C_v of simple solids:—

$$\alpha = \frac{\gamma \chi_0 C_v}{V_0}, \tag{1}$$

where $\chi_0 =$ the compressibility

$V_0 =$ the atomic volume

and $\gamma =$ a constant independent of temperature.

Taking the value of γ as $1 \cdot 1$ for diamond and its specific heat values as given by a single Debye function corresponding to a characteristic temperature of 1860, Grüneisen (1926) satisfactorily explained the existing data on the thermal expansion of diamond due to Röntgen (1912) which covered the range of temperature from 84° T. to 350° T. Although the Grüneisen's relation is found to be valid over this range, a satisfactory test of the relation should require data over a wider range of temperature. Accurate measurements of the heat capacity of diamond have already been made by Pitzer (1938) over the range of temperature from 70° T. to 300° T. and by Magnus and Hodler (1926) from 273° T. to 1100° T., while the thermal expansion of diamond does not appear to have been investigated above 350° T. In view of the importance of the Grüneisen's relation in the theory of the solid state and its bearing on the nature of the vibration spectrum of a crystal, it was considered desirable to obtain data on the thermal expansion of diamond in order to test the validity or otherwise of the Grüneisen's relation for diamond at high temperatures. In the present investigation* the thermal

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expansion of diamond has been studied over the range of temperature from 300° to 873° T.

2. Technique of Study

As the expansion of diamond is rather small compared with that of ordinary solids and as the specimens available for study were in the form of thin plates, direct determination of the thermal expansion by the interferometric method could not obviously be made with any reasonable degree of accuracy. The X-ray diffraction method was therefore employed and the variation of lattice spacings with increase of temperature was measured and the coefficient of thermal expansion calculated. The technique of study was rather different from that usually adopted, being designed to enable the small expansion of diamond to be measured accurately. It was based on the use of a beam of characteristic X-rays from a copper target diverging from a fine slit and falling on the crystal nearly at the Bragg angle for surface reflection. The photographic film recording the reflections was kept at a considerable distance from the latter. With a perfect crystal like some specimens of diamond, the characteristic X-ray reflections would appear as sharp lines, the width of which being nearly independent of the distance of the film from the crystal, would be determined by the fineness of the slit used. From the observed displacements of the $CuK\alpha_1$ and $K\alpha_2$ reflections when the temperature of the crystal was raised, the relative change in crystal spacing could be evaluated. The observed shift being directly proportional to the crystal-film distance, a very high degree of accuracy could be attained by increasing the latter.

3. Description of Apparatus

Camera.—Fig. 1 represents a horizontal cross-section of the X-ray camera employed in the present investigation. It consisted of a fine lead slit S (4 mm. high and 0·09 mm. wide) which was kept facing and close to the window of a Coolidge demountable X-ray tube provided with a copper target. At a distance of about 5 cm. from the slit was placed a single circle goniometer G. The goniometer was so adjusted that its vertical axis was accurately parallel to the height of the slit. To the axial rod of the goniometer was fixed a fused quartz tube with a drawn out end. The crystal to be examined was held firmly in a slot at the drawn out end. The quartz tube was long enough to ensure that its lower end was not sensibly heated up while the crystal itself was raised to the desired temperature by being enclosed in a small electrically heated chamber or furnace. The latter which is not shown in Fig. 1 formed a separate unit which could be lowered over the crystal after all the necessary settings and adjustments have been made. To

the lower end of the goniometer axis were fixed two wooden arms about a meter in length, each one subtending an angle $2\theta_B$ with the line joining the slit to the crystal (see Fig. 1). θ_B is the Bragg angle for 111 reflection of diamond using CuKα radiations and has the value 21° 58'. Each arm carried a film holder (F_1 and F_2) which could be clamped at any desired distance from the crystal. The films were always kept normal to the reflected beam. A Hartmann diaphragm H provided with three holes was supported in front of each film holder as shown in the figure. With the aid of this diaphragm three sets of X-ray reflections could be recorded in juxtaposition on the same film.
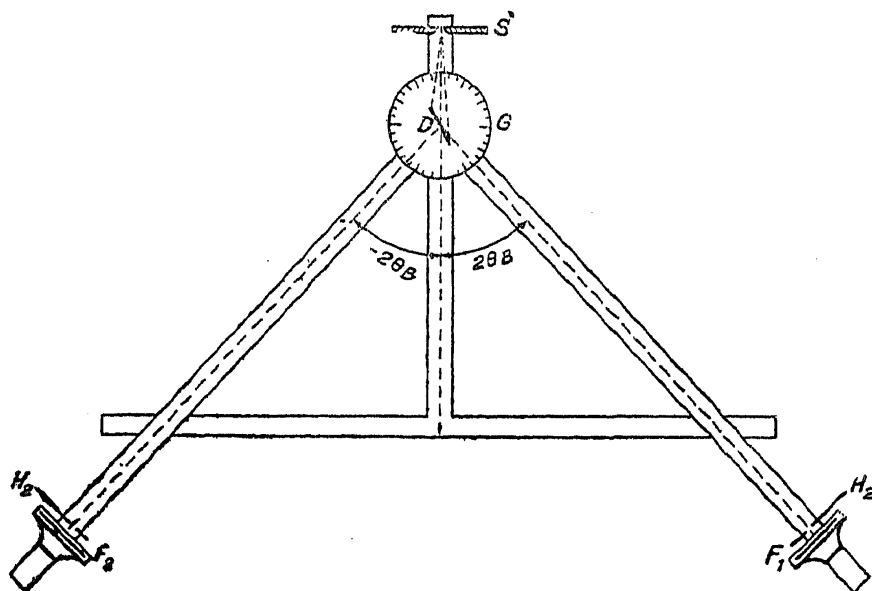

FIG. 1. X-Ray Camera

The Furnace.—The constant temperature chamber consisted of a thin steel cylinder about $2\frac{1}{2}''$ long and $\frac{1}{2}''$ bore. In order to permit free passage of X-rays over a wide angle through the centre of the heater, two segments about $\frac{1}{4}''$ high were cut away from the centre of the tube leaving two narrow ribs connecting the top and bottom halves of the tube. To improve the uniformity of temperature within the chamber these segments were then closed by pieces of extremely thin aluminium foil (0·007 mm. thick). The steel part of the tube was covered with a mica sheet and the heating coil was wound over the mica and set in position with the aid of a mixture of alumina and sodium silicate solution and finally covered over with asbestos. Thick aluminium foil was then stuck on the outside of the furnace in order to minimise heat losses due to radiation. The top of the furnace was closed by an iron disc to which was screwed a thin metal tube. The latter was cemented on to a pyrex glass tube which was in turn fixed to the adjustable arm of a vertical stand. After placing the furnace in position above the crystal, it could be lowered vertically into the right position by means of a

rack and pinion arrangement. The orifice at the bottom of the tube was partially closed by the quartz tube which supported the diamond to be studied. The furnace had a low heat capacity so that the required temperature could be reached within a conveniently short time.

4. DETAILS OF THE EXPERIMENT

Calibration of the Furnace.—As it was not possible to have a thermocouple inside the furnace to record the temperature of the crystal during exposures, the constant temperature chamber was calibrated beforehand. A calibrated nichrome constantan thermocouple was supported vertically through a silica tube similar in size and shape to the one used for supporting the crystal in the actual experiment. In order to measure the temperature of the air space within the furnace it was lowered over the silica tube containing the thermocouple such that the hot junction was at the position subsequently to be occupied by the crystal. A steady current from a set of accumulators was then passed through the heating coil. The current was measured on a good calibrated ammeter. The thermocouple was directly connected to a millivoltmeter. When the steady state was reached which usually took about 15 to 20 minutes, the readings of the ammeter and the millivoltmeter were noted. From the latter reading, the temperature of the chamber was evaluated. On removing the furnace and replacing it, the temperature as recorded by the thermocouple was reproduced to $\pm 1°$ C. As the temperature of the leads had no influence on the temperature recorded by the hot junction, it can be assumed that the thermocouple recorded the true temperature of the air space inside the furnace. The experiment was repeated with various heating currents and the steady temperature attained in each case was noted. A curve showing the relation between the heating current and the steady temperature inside the furnace up to 650° C. was drawn. The furnace was recalibrated after a set of experiments and it was found that the calibration curve remained unaffected even after a lapse of six months. From the calibration curve the values of the heating current correct to the nearest readable division on the ammeter for temperatures as close to 100°, 200°, 300°, 400°, 500° and 600° C. as could conveniently be arranged were read off. The steady temperatures corresponding to these values of the heating current were accurately determined by experiment. They were 105°, 205°, 300°, 405°, 505° and 605° C. While measuring the variation of the lattice spacings the crystal was maintained successively at these temperatures.

Selection and Mounting of the Diamond.—As already remarked in Section 2, in order to attain a high degree of accuracy in the measurement

of the change of lattice spacing with temperature, it is necessary to use a piece of diamond which is the nearest approach to the perfect crystal. Recent measurements of Ramachandran (1944) on the angular divergence of X-ray reflections in different diamonds have shown that diamonds which are opaque to the ultra-violet and which exhibit least fluorescence have the least angular divergence the value of which is just a little more than that for an ideal crystal. Accordingly, diamond (N.C. 76) which had these characteristics was selected for the present investigation from Sir C. V. Raman's personal collection. It was in the form of a triangular plate, about 0·9 mm. thick, with its faces parallel to the octahedral cleavage planes.

The mounting of the diamond on a suitable support presented some difficulty. It was necessary to make the mounting sufficiently robust to withstand temperature changes without an accompanying change in the setting of the diamond. Any displacement of the diamond caused by the yielding of the support when the temperature of the latter was raised would produce a spurious shift of the X-ray reflection. After some trials, it was found that the use of a fused quartz tube for supporting the diamond and of a silicate dental cement for mounting it completely eliminated spurious effects up to a temperature of 500° C. In the range of temperature from 500° to 600° C. there was a slight effect which was corrected for by taking photographs of the X-ray reflections by rotating the crystal holder by twice the Bragg angle.

The plate of diamond was mounted such that its surface (111) planes were exactly in the vertical plane and were parallel to the vertical axis of rotation of the goniometer. It was then set roughly at the Bragg angle for surface reflection of copper $K\alpha$ radiations. When the diamond was bathed in the divergent beam of X-rays, the characteristic $CuK\alpha$ line appeared in the distorted (111) X-ray topograph recorded on a film kept normal to the incident beam at a short distance from the crystal. The film holder was moved away and kept normal to the incident beam at a distance of 80 cm. from the diamond. A trial photograph was taken without the Hartmann diaphragm. The $CuK\alpha_1$ and $K\alpha_2$ reflections appeared on the film as sharp lines separated by about 0·9 mm. The exposure time was adjusted so that the image recorded on the film was just clearly visible. It was of the order of 10 minutes. No intensifying screen was used for photographing the reflections.

Using the Hartmann diaphragm, three sets of X-ray reflections were recorded in juxtaposition on the same film, the middle one with the diamond heated up to a known temperature and the top and bottom ones as controls

at room temperature. The room temperature photographs were taken one before and the other after the high temperature exposure. During the experiment the camera was not disturbed. The goniometer was then turned through twice the Bragg angle, *i.e.*, 43° 56′, so that reflections could occur at the second face of the diamond. With this setting and keeping another film at a distance of 80 cm. from the crystal (see Fig. 1), a series of three photographs were recorded in juxtaposition on it, the middle one with the diamond heated up to the same temperature as before and the top and bottom ones as controls at room temperature. In this manner the experiment was repeated for temperatures 205°, 300°, 405°, 505° and 605° C. As the shift of the X-ray reflection was smaller than the width when the temperature of the crystal was raised from 28° to about 100° C., it was evaluated in the following way. First the shift due to the rise of temperature from 28° to 300° was determined followed by that due to the rise of temperature from 105° to 300° C. The difference gave the displacement due to an increase of temperature from 28° C. to 105° C. The X-ray films were measured under a cross slide micrometer.

5. CALCULATION OF THE THERMAL EXPANSION COEFFICIENT

When the temperature of the crystal is raised, its setting with reference to the camera might get altered giving rise to a spurious displacement of
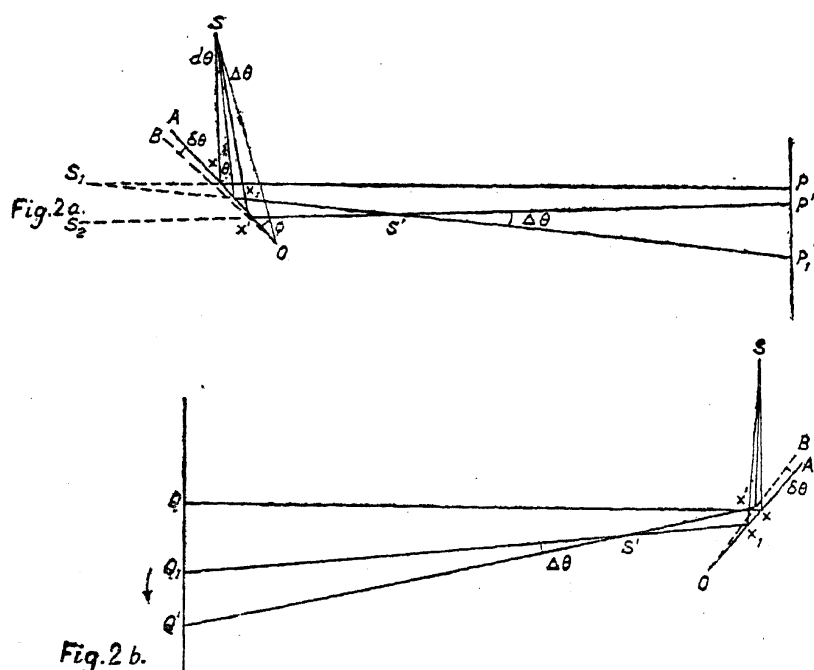
FIGS. 2 *a* & 2 *b*

the X-ray reflection. The observed shift would therefore be the sum of the displacement due to the change in the Bragg angle caused by the increase

:tice spacing and the spurious displacement due to the change in the
g of the crystal. By taking measurements for two different goniometer
gs as described in the previous section, the spurious effects are easily
lated.

is the slit and OA the front surface of the diamond in the first setting.
e room temperature the reflection appears at P or Q on the film (see
2 *a* and 2 *b*). S_1 is the image of S in the plane of the diamond. When
mperature is raised by $t°$ C., let the change in the lattice spacing be *dl*
le corresponding change in the *Bragg angle dθ*.

$$\text{since } 2l \sin \theta = \lambda, \quad d\theta = \frac{dl}{l} \tan \theta. \tag{2}$$

vould produce a displacement *x* of the X-ray reflection on the photo-
c film. *x* is equal to $(R + L) d\theta$, where R and L are the distances of
ystal from the slit and the film respectively. Provided the setting of
/stal remains unchanged, the reflection will appear at P_1 and Q_1 for the
;oniometer settings such that $PP_1 = QQ_1 = x = (R + L) d\theta$ (see
2 *a* and 2 *b*).

it us suppose that at the higher temperature the setting of the crystal
:ference to the camera is altered. Any vertical movement of the crystal
own plane caused by the expansion of the support will not affect the
ntal displacement of the X-ray reflection. Rotation of the plate
a vertical axis and/or a displacement normal to itself would, on the
land, adversely affect the observed shift of the X-ray reflection. Let
pose that the diamond rotates through an angle $\delta\theta$ about the point
le direction indicated in Figs. 2 *a* and 2 *b*. A reference to the two
shows at once that the displacements of the X-ray reflection for the
nd $- \theta_B$ settings are given by x_1 and x_2,

$$x_1 = (L + R) d\theta - (L - R) \delta\theta$$
$$x_2 = (L + R) d\theta + (L - R) \delta\theta.$$
$$\therefore \quad x = \frac{x_1 + x_2}{2} = (L + R) d\theta$$

le mean value of x_1 and x_2 gives the actual displacement due to the
in the Bragg angle.

nilar results are also obtained for any displacement of the diamond
to itself (see Figs. 3 *a* and 3 *b*). It will be noticed that the displace-
of the X-ray reflection due to the rotation or displacement of the dia-
ire in the same sense for both the settings while those due to the
spacing variation are in opposite directions for the two settings.

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Fig.3a

Fig 3b
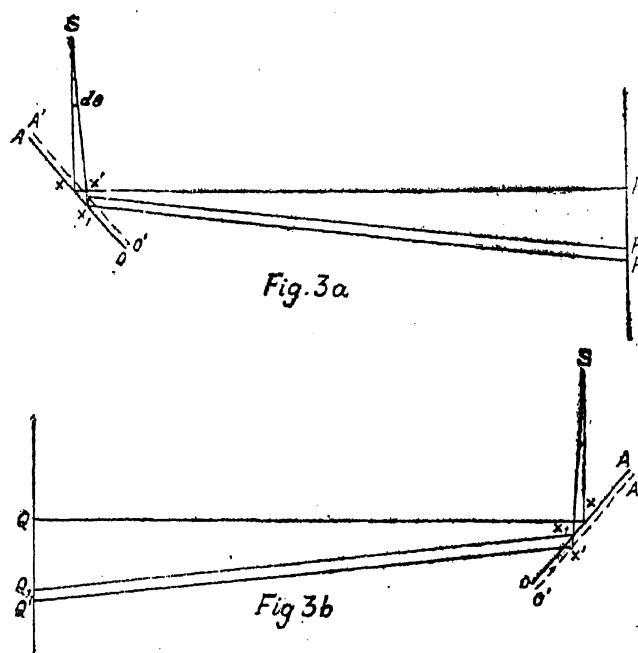
FIGS. 3 *a* & 3 *b*

Let x_0 be the separation of $K\alpha_1$ and $K\alpha_2$ reflections. Then

$$x_0 = (L + R) \frac{d\lambda}{2\,l\cos\theta}.$$

where $l =$ the lattice spacing and $d\lambda$ is the wavelength separation of $CuK\alpha_1$ and $CuK\alpha_2$.

$$\frac{x}{x_0} = \frac{d\theta \cdot 2l\cos\theta}{d\lambda}. \tag{3}$$

From equations (2) and (3) we get

$$\frac{x}{x_0} = \frac{dl}{l} \cdot \frac{\lambda}{d\lambda}. \tag{4}$$

The increase in lattice spacing dl for a rise of temperature of $t°$ is given by

$$dl = l \cdot \frac{x}{x_0} \frac{d\lambda}{\lambda} \tag{5}$$

and the mean coefficient of linear expansion is given by

$$\frac{\alpha}{3} = \frac{1}{t} \cdot \frac{dl}{l} = \frac{1}{t} \cdot \frac{x}{x_0} \cdot \frac{d\lambda}{\lambda}. \tag{6}$$

Thus the final expression for the coefficient of thermal expansion involves a term $\frac{x}{x_0}$ which could be accurately measured, λ the mean wavelength of the CuKα doublet and $d\lambda$ the wave-length separation. The values of λ and $d\lambda$ have been accurately determined by the earlier workers. The expression for α does not, however, involve the distance of the film from the crystal or the slit.

6. Results

Typical photographs of the X-ray reflection showing the progressive displacement of the lines as the temperature is raised are reproduced in Plate V.

Table I

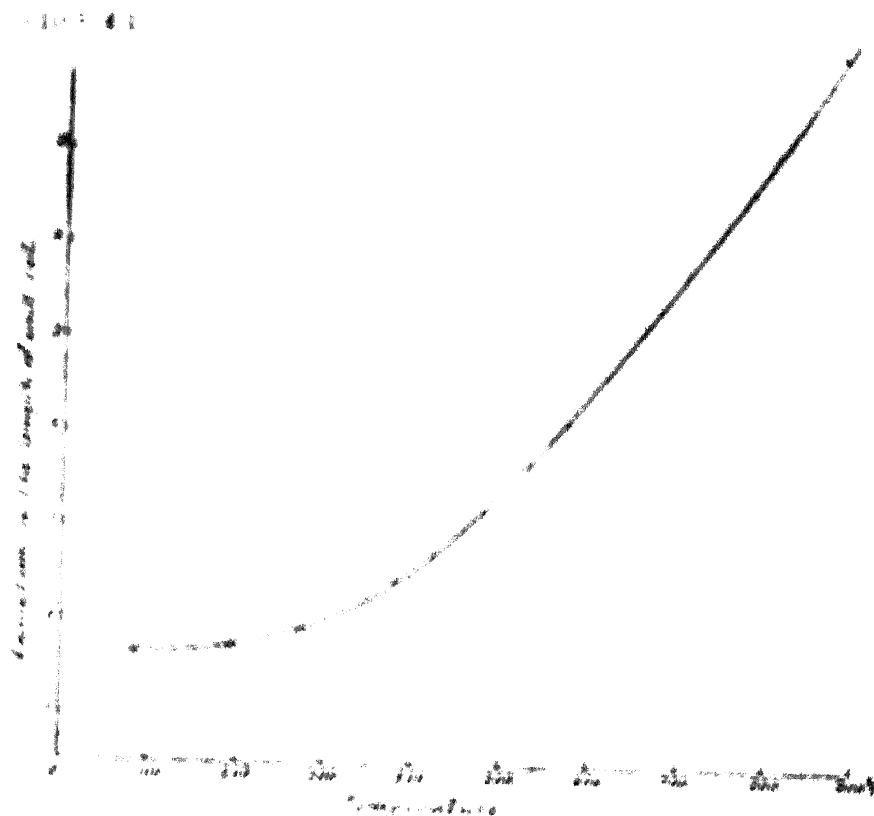| Temperature (°C)	s_1	s_2	Mean shift $\frac{s_1 + s_2}{2}$	Change in lattice constant $\Delta a \times 10^5$
				1.17 Å

Fig. 4. Change of lattice constant as a function of temperature. Dots are author's values, and crosses are those calculated from the data of Röntgen

Table I gives the values of the displacements of the X-ray reflections in terms of the separations s_0 of the $K\alpha_1$ and $K\alpha_2$ lines. As already indicated in Section 4 the displacements of the reflections are nearly the same for both the settings of the goniometer up to a temperature of 505°C, i.e. 778 T. The

increase of lattice-constant is calculated using equation (5) for the different temperature ranges and the values are given in column 5 of Table I. The lattice constant a at room temperature, i.e., at 18° C. (291° T.) is taken as 3·55970 Å.U. The wave-lengths of $CuK\alpha_1$ and $CuK\alpha_2$ are taken as equal to 1·537395 and 1·541232 Å.U. respectively. In Fig. 3 the temperature of the diamond is plotted against the change of lattice-spacing taking the value at 28° C. (301° T.) as the standard. The portion of the curve below 301° T. was drawn using the data on the thermal expansion coefficients for this region recorded by Röntgen (1912) and quoted by Grüneisen (1926).

Mean coefficient of cubic expansion (α) over the ranges of temperature of about 100° has been evaluated using equation (6). The results are shown in the 3rd column of Table II. Those above the dotted line are taken from the determinations of Röntgen (1912). The curve showing the variation of the mean coefficient of volume expansion with temperature is reproduced in Fig. 4. The coefficient increases rapidly in the beginning and finally tends. to a steady value at very high temperatures.

7. DISCUSSION

The mean values of the atomic heat for the different ranges of tempera ture have been obtained by interpolation from the data of Pitzer (1938) below 273° T. and from the data of Magnus and Hodler (1926) above that temperature. These are given in column 5 of Table II.

TABLE II

Temperature Range °T.	$\frac{x}{x_0}$	Mean value of $a \times 10^6$	Calculated values of a using Grüneisen's value for γ	Mean value of Atomic Heat C_v	$\gamma = \dfrac{aV_0}{X_0 C_v}$
84·8–194·1	..	0·54	0·50	0·233	1·19
194·1–273·2	..	1·74	1·86	0·866	1·03
273·2–296·2	..	2·91	2·91	1·351	1·10
296·2–328·1	..	3·51	3·45	1·605	1·12
328·1–351·1	..	4·35	4·02	1·870	1·19
301–378	·045	4·36	4·08	1·870	1·20
378–478	·087	6·51	5·8	2·627	1·27
478–573	·108	8·52	7·55	3·307	1·31
573–678	·138	9·84	8·78	3·874	1·30
678–778·	·145	10·86	9·47	4·329	1·28
778–878	·157	11·76	10·03	4·657	1·29

Using the observed values of C_v and those of the coefficient of thermal expansion in equation (1), the values of γ for the different ranges of tempera ture have been evaluated. These are given in column 6 of Table II. The atomic volume V_0 is taken as equal to 3·42. The value of χ at 0° T. is not

known. The value of χ at 20° C. given by Adams (1921) as $0 \cdot 16 \times 10^{-12}$ cm.^{2}/dyne has been used in the evaluation of γ. The difference between χ_{293} and χ_0 would be very small for a crystal of extremely low compressibility like diamond. The results presented in Table II go to show that γ, far from being independent of temperature, varies with temperature. Its value increases steadily from about $1 \cdot 03$ in the temperature range 194–273° T. to $1 \cdot 31$ in the range 478–573° T. Above 'this temperature the value decreases slowly.

Taking γ to be independent of temperature and equal to $1 \cdot 1$ as suggested by Grüneisen, Saksena (1944) has calculated the thermal expansion coefficients
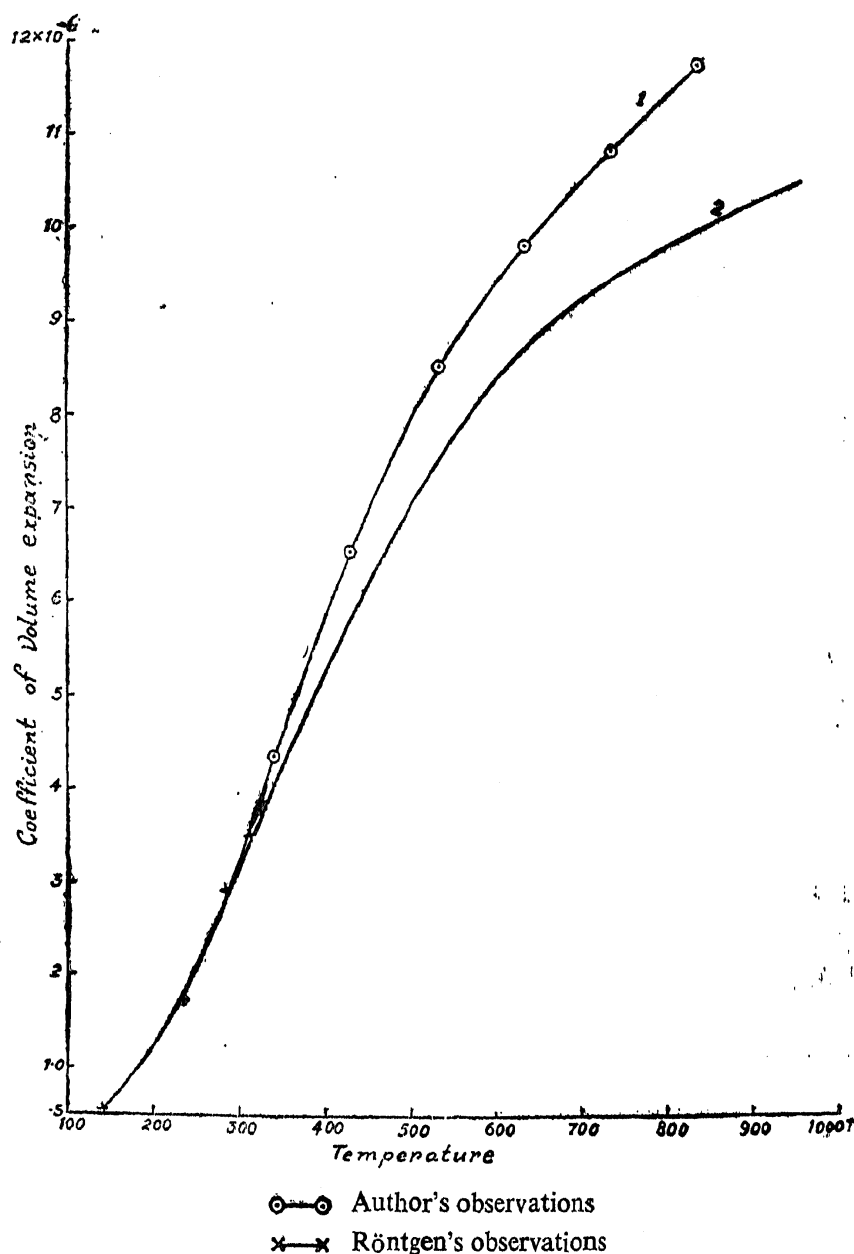

○—○ Author's observations

✕—✕ Röntgen's observations

Fig. 5. Mean coefficient of expansion as a function of temperature
Curve 1: Experimental; Curve 2: Theoretical on the basis of $\gamma = 1 \cdot 1$

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of diamond for different ranges of temperature using equation (1). His results are given in column 4 of Table II. The variation of the thermal expansion coefficient with temperature to be expected on the basis of Grüneisen's relation is graphically represented by curve 2 in Fig. 5. There is fairly good agreement between the observed and calculated values of the coefficient of thermal expansion in the lower ranges of temperature, whereas at the higher temperatures the observed values are definitely higher, e.g., to the extent of about 18% at about 600° C.

The author wishes to express his grateful thanks to Sir C. V. Raman for the loan of the diamond and also for his kind interest in the work.

8. SUMMARY

Using the X-ray method, the change in the lattice spacing of diamond with temperature has been measured over the range of temperature from 28° C. to 605° C. The technique employed is rather different from that usually adopted, being designed to enable the rather small expansion of diamond to be measured accurately. The increase in the lattice constant at ordinary temperatures is small, while it is very rapid at higher temperatures. From the observed changes in lattice constant, the mean coefficients of volume expansion for different ranges of temperature have been deduced. The coefficient of volume expansion of diamond varies from $4 \cdot 36 \times 10^{-6}$ in the range $301° - 378°$ T. to $11 \cdot 76 \times 10^{-6}$ in the range $778° - 878°$ T. Using the observed values of the coefficient of thermal expansion and the existing data on the atomic heat, the Grüneisen's constant γ which is the ratio $\frac{a V_0}{x_0 C_v}$ has been evaluated. V_0 is the atomic volume and χ_0 the compressibility of diamond. It is shown that γ is not a constant, but increases from about $1 \cdot 1$ at low temperatures to about $1 \cdot 3$ at 600° T. and falls again slowly as the temperature is raised.

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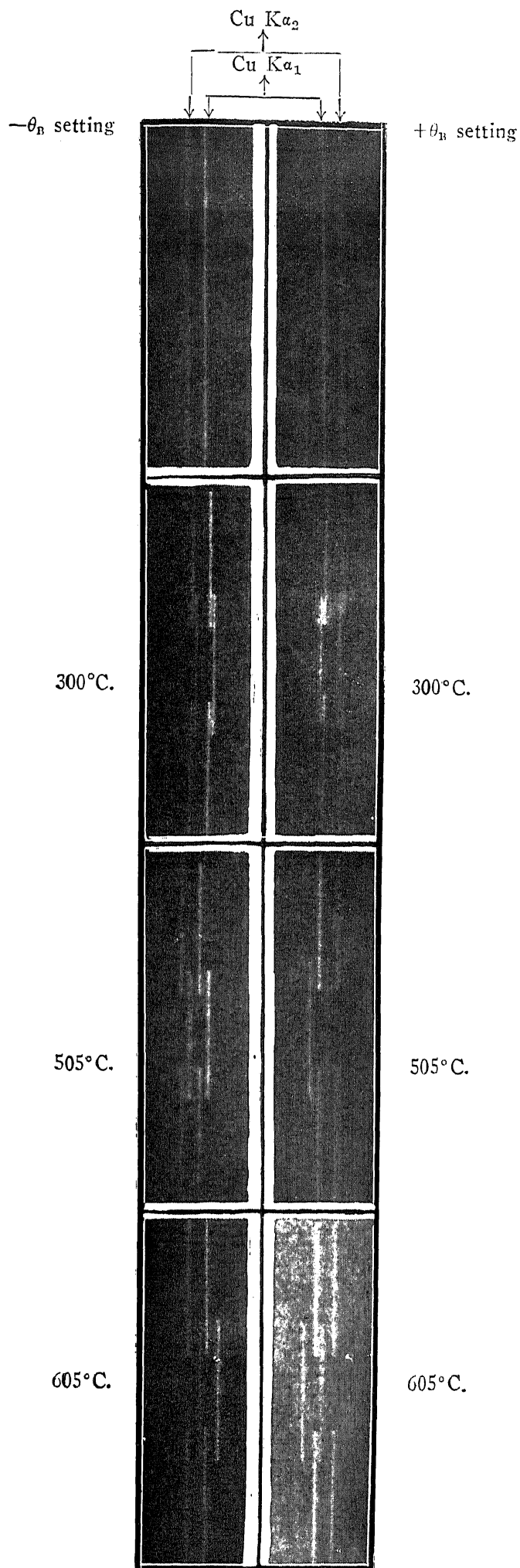|	
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FIG. 6

Thermal Expansion of Diamond