

X-Ray Investigations on the Thermal Expansion of Solids

Part 1.

By

Gunji Shinoda.

(Received February 8, 1933)

The thermal expansion coefficients and the lattice constants of some metals were determined by X-ray method and obtained the following results: expansion coefficient (10^{-6})...Al ($\alpha=22.9$), Sn ($\alpha_{11}=45.8$, $\alpha_{\perp}=25.7$), In ($\alpha_{11}=45.0$, $\alpha_{\perp}=11.7$), Zn ($\alpha_{11}=64.5$, $\alpha_{\perp}=10.8$), Tl ($\alpha_{11}=72$, $\alpha_{\perp}=9$) and lattice constant...Sn ($a=5.824$ A. U., $c/a=0.5415$), In ($a=4.581$ A. U., $c/a=1.077$).

Introduction

X-ray determinations of the thermal expansion coefficients of solids are based upon measurements of the changes in lattice constants at various temperatures and were made, some years ago, by Becker¹ who used Debye-Scherrer's powder method for W, Si and their compounds. As these expansion coefficients are very small, he was obliged to determine mean coefficients between room temperature and about 1000°C. This method is very convenient for finding the coefficient of a very small specimens. But if the melting point or the transformation temperatures of the specimen is not high enough, we must measure very small changes in the lattice constant. For this purpose high resolving power is necessary and therefore, a glancing angle of nearly 90° is convenient. But when the specimen consists of a large number of micro-crystals, as in the powder method, the lines in the photographs are somewhat diffuse and consequently we cannot determine their positions accurately. If the specimens are annealed, crystal grains grow gradually and these lines become discontinuous and at last

1. Z. Phys. 40. (1927) 37.

groups of very small and sharp spots. These spots are produced by reflections of characteristic rays and their widths are narrow enough to make it possible to estimate slight changes caused by small differences of temperatures. Consequently, the determinations of the expansion coefficients become easier. Moreover, if we know the rate of the changes of the distances about several atomic planes we can calculate the expansion coefficient for each direction of the crystal axis without using their single crystals.

Method of the Experiment

The X-ray tube used was Seemann's gas ion tube with a copper anticathode and was excited by a transformer. Two kinds of cameras were used. One was an ordinary Dehlinger camera having a slit of 1 mm. The object of the somewhat large aperture is to obtain slightly converging rays. The other camera is shown in Fig. 1. This camera has an inner plate-holder which can be moved up and down in an outer case to take photographs at each temperature separately. The furnace for heating the specimen was made of brass and, as shown in Fig. 2, the upper part of it has a hole through which it is filled

Fig. 1.

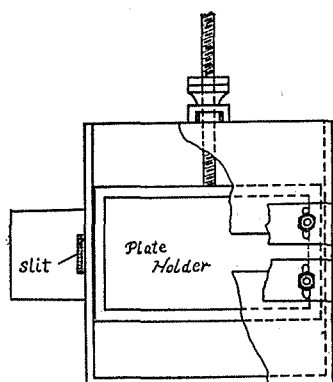
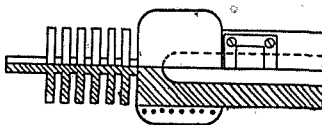


Fig. 2.



with oil and in which a thermometer is inserted. Heating is done electrically by nichrome wires wound around the central part of the furnace and the lower part of it is in the form of a radiator to protect the plate-holder from the heat of the furnace. A portion of one side of the furnace is shaved till the inner hole appears and the specimen, usually a foil, is stuck on it, covered with cellophane, and fastened by a steel frame. The inner side of the specimen is in contact with the

oil in the hole, oil-tightness being secured by the steel frame. Therefore the temperature of the specimen must be nearly equal to that of the oil.

From the well known Braggs' formula $n\lambda = 2d \sin \theta$ we can see immediately that

$$\frac{\Delta d}{d} = \cot \theta \cdot \Delta \theta \dots\dots\dots(1)$$

where Δd is a small variation of d and $\Delta \theta$ a small variation of θ , n being taken as 1. If the specimen is placed at the centre of a circular film, we have

$$\frac{\Delta d}{d} = \frac{1}{2r} \cot \theta \cdot \Delta l \dots\dots\dots(2)$$

where r is the radius of the film and Δl is the displacement of the line, l being the distance between the line and the zero position. But in our case this becomes

$$\frac{\Delta d}{d} = \frac{1}{r} \cot \theta \frac{1}{1 + \left(\frac{l}{r}\right)^2} \Delta l \dots\dots\dots(3)$$

because, instead of the film, a plate perpendicular to the direction of the X-ray beam was used and the positions of the crystal grains were not altered. Accordingly, the X-ray beam must be somewhat converging, as in Seemann's wedge method, and this was secured by the diffuseness of the focus of the anticathode and the width of the slit.

For a cubic crystal the thermal expansion coefficient will be obtained by dividing $\frac{\Delta d}{d}$ by the difference in the temperatures, and for tetragonal, rhombic and hexagonal crystals respectively, we have the following relations,

$$\frac{\Delta d}{d} = \frac{1}{1 + (h'c')^2} \left\{ \frac{\Delta a}{a} (h'c')^2 + \frac{\Delta c}{c} \right\} \dots\dots\dots(4)$$

for tetragonal, where $c' = \frac{c}{a}$ and $h'^2 = \frac{h^2 + k^2}{l^2}$

$$\frac{\Delta d}{d} = \frac{1}{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}} \left\{ \frac{h^2}{a^2} \frac{\Delta a}{a} + \frac{k^2}{b^2} \frac{\Delta b}{b} + \frac{l^2}{c^2} \frac{\Delta c}{c} \right\} \dots\dots\dots(5)$$

for rhombic and

$$\frac{\Delta d}{d} = \frac{1}{1 + (h'c')^2} \left\{ \frac{\Delta a}{a} (h'c')^2 + \frac{\Delta c}{c} \right\} \quad \dots\dots\dots(6)$$

for hexagonal where $c' = \frac{c}{a}$ and $h'^2 = \frac{4}{3} \cdot \frac{h^2 + hk + k^2}{l^2}$

So that if we know $\frac{\Delta d}{d}$ with regard to several atomic planes, we can calculate $\frac{\Delta a}{a}$, $\frac{\Delta b}{b}$ and $\frac{\Delta c}{c}$ which correspond to the expansions of the a -, b - and c -axis respectively. Also the linear expansion coefficient can be calculated from these values.

Cubic System

ALUMINIUM¹. There is no point in determining the expansion coefficients of cubic crystals by this method except when the materials are somewhat uncommon and it is difficult to obtain fairly large specimens. Therefore, the author investigated Al only to test whether this method is reliable or not. The specimen used was a foil 15×10^{-3} cms. thick, and the result obtained for (511) was $\Delta l = 3.95 \times 10^{-2}$ cms. (temperature range: $30^\circ - 90^\circ$) Therefore if we take the lattice constant of Al as 4.040 A. U. we have $22.9 \cdot 10^{-6}$ per deg. C., the distance r between the plate and the specimen being 4.02 cms. This number nearly coincides with $23.8 \cdot 10^{-6}$ given in Landolt-Boernstein's table and so, we can see that this method is reliable.

Tetragonal System

TIN². According to Mark and Polanyi³ white tin has a double body-centred tetragonal lattice of $a = 5.84$ A. U. and $c = 3.15$ A. U.. In the present experiment the lattice constant was determined by means of the lines reflected from (114), (104), (701) planes etc., $CuK\alpha$ radiation being used, and the following results were obtained:

-
1. Al. 99.8 %.
 2. Merk, pure granul.
 3. Z. Phys. 18 (1923) 75

Table I.

$r=4$ cms.

Indices of Planes	114	104	701	640	361	413
l : Distances cms.	1.01	1.50	2.70	2.91	4.25	4.53
$\sin \theta$ (10^{-4} obs.)	9924	9841	9563	9510	9180	9120
$\sin \theta$ (10^{-4} calc.)	9926	9838	9554	9517	9182	9114

Then we have the following quadratic formula

$$\sin^2 \theta = 0.017416(h^2 + k^2) + 0.05943 l^2 \quad \text{for } CuK_{\alpha 1}.$$

Therefore the lattice constant becomes

$a=5.824$ A. U., $c=3.154$ A. U. and $c/a=0.5415$ and the number of atoms in a unit cell, n , becomes

$$n = \frac{107.0 \cdot 7.306 \cdot 10^{-24}}{1.649 \cdot 118.7 \cdot 10^{-21}} = 3.994 \doteq 4$$

The changes in the distances of the atomic planes produced by temperature were determined with regard to some of these planes and the thermal expansion coefficients were calculated. The range of temperature taken was from 34° to 194° . The results obtained are shown in plate I and table II;

Table II.

$r=5.10$ cms.

Indices of Planes	114	104	701	640
Δl per $1^\circ\text{C}.$ (10^{-4} cms.)	15.3	18.0	6.4	6.9
$\frac{\Delta l}{l}$ (10^{-6})	39.6	61.4	26.4	28.8

Therefore from eq. (3) and by means of the method of least squares we get

$$\alpha_{11} = 45.8 \times 10^{-6}, \alpha_{\perp} = 25.7 \times 10^{-6} \quad \text{and} \quad \alpha = 32.4 \times 10^{-6}.$$

These are somewhat larger than Bridgeman's¹ $\alpha_{11} = 30.50 \times 10^{-6}$ and $\alpha_{\perp} = 15.45 \times 10^{-6}$.

INDIUM². Indium has a face-centred tetragonal lattice and its lattice constants are given as $a=4.58$ A. U., $c=4.86$ A. U. and

1. Proc. Am. Acad. Arts, Sci. 60 (1925) 305.
2. Dr. Peters & Rost.

$\frac{c}{a}$ 1.06 (Hull and Davey¹). To confirm these results, the lattice constants were first determined by $Cu K_{\alpha}$ radiation and the following results were obtained :

Table III.

 $r=4.02$ cms.

Indices of Planes	351	244	153
λ : cms.	1.13	1.93	2.03
$\sin \theta$ (10^{-4} obs.)	9906	9754	9734
$\sin \theta$ (10^{-4} calc.)	9914	9761	9754

Therefore, we have

$$\sin^2 \theta = 0.028195(h^2 + k^2) + 0.024307 l^2$$

for $K_{\alpha 1}$, and $a=4.581$ A. U., $c=4.933$ A. U. and $c/a=1.077$.

The density calculated from these values becomes 7.319, the atomic weight of In being taken as 114.8, and nearly coincides with 7.314 given by Richards and Sameshima².

The determination of the thermal expansion coefficients was also carried out with regard to these planes and the results are shown in table IV and plate 3.

Table IV.

 $r=4.02$ cms.

Indices of Planes	351	244	153
Δl (10^{-2} cms.)	2.53	3.52	2.58
Δl per 1°C . (10^{-4} cms.)	3.95	5.50	4.09
Range of Temperature	$23^{\circ}-87^{\circ}$	$23^{\circ}-87^{\circ}$	$23^{\circ}-86^{\circ}$
$\frac{\Delta \lambda}{\lambda}$ (10^{-6})	12.5	25.2	19.3

Therefore we have

$\alpha_{11}=45.0 \times 10^{-6}$, $\alpha_{\perp}=11.7 \times 10^{-6}$ and $\alpha=22.8 \times 10^{-6}$ between 23° and 87°C . This α differs considerably from Fizeau's³ 45.9×10^{-6} (50°) but it is very interesting that his value nearly agrees with my α_{11} .

1. Phys. Rev. 17 (1921) 571.
2. Landolt-Börnstein's table.
3. Landolt-Börnstein's table.

Δl for (153) plane was next measured and the result obtained was 4.50×10^{-2} cms. between 28° and 85°C . Then we have $\frac{\Delta d}{d} = 41.4 \times 10^{-6}$ for this plane and that calculated from the above results becomes 42.3×10^{-6} which nearly coincides with the value observed.

Hexagonal System.

ZINC. Hull and Davey's¹ result shows that Zn has a hexagonal close-packed lattice of $a=2.680$ A. U., $c=4.966$ A. U. and $c/a=1.86$.

The thermal expansion coefficients along each crystal axis were determined by Grüneisen and Goens², and Bridgeman³ and their results were $\alpha_{11}=63.0 \times 10^{-6}$, $\alpha_{\perp}=14.2 \times 10^{-6}$ and $\alpha_{11}=57. \times 410^{-6}$, $\alpha_{\perp}=12.6 \times 10^{-6}$ respectively. In the present experiment the (006) and (106) planes were studied and the following results were obtained (table V. and plate 5.).

Table V.

$r=4.02$ cms.

Indices of Planes	106	006
Δl (10^{-2} cms.)	8.11	14.50
Δl per 1°C . (10^{-3} cms.)	1.33	1.27
Range of Temperature	$31^\circ-92^\circ$	$31^\circ-145^\circ$
$\frac{\Delta d}{d}$ (10^{-6})	58.4	64.5

Therefore we have $\alpha_{11}=64.5 \times 10^{-6}$, $\alpha_{\perp}=10.8 \times 10^{-6}$ and $\alpha=28.7 \times 10^{-6}$ between 31° and 118°C . But the second number is not very reliable and the first one rather coincides with that of Grüneisen and Goens than with Bridgeman's.

THALLIUM⁴. α -thallium, which is stable at room temperature, has a hexagonal close-packed lattice of $a=3.450$ A. U. and $c/a=1.600$ (Sekito⁵) and its expansion coefficient was recently determined by Schulze⁶ who obtained 29.4×10^{-6} between 0° and 100°C . As this metal

1. loc. cit.
 2. Z. Phys. 26 (1924) 235 & 250
 3. Loc. cit.
 4. Kahlbaum.
 5. Z. Krist. 74 (1930) 189.
 6. Z. Metallkunde 22 (1930) 308.

easily oxidizes and its oxide is soluble in glycerine, the specimen, 0.5 mm. in thickness, was put in a cellophane envelope, which was filled with glycerine and then sealed. This envelope was mounted on the furnace and heated as usual and the following results were obtained, (table VI).

Table VI.

 $r=4.02$ cms.

Indices of Planes	124	305
Δl (10^{-3} cms.)	10.1	7.0
Δl per 1°C . (10^{-3} cms.)	1.71	1.19
Range of Temperature	$32^\circ-91^\circ$	$32^\circ-91^\circ$
$\frac{\Delta d}{d}$ (10^{-6})	41.1	30.7

As this specimen cannot be heated up to the transformation temperature, the crystal grains were not very large, and therefore we were obliged to use the ordinary Debye-Scherrer method of large angle of reflection (plate 5). The above results give us

$$a_{111} = 72 \times 10^{-6}, a_{\perp} = 9 \times 10^{-6} \text{ and } a = 30 \times 10^{-6} \text{ between } 32^\circ \text{ and } 91^\circ\text{C.}$$

Now α -Tl is transformed into β -Tl at 225° and the crystal structure of the latter is a face-centred cubic lattice of $a=4.841$ A. U. Therefore, in this $\alpha \rightarrow \beta$ transformation, a hexagonal close-packed lattice is transformed into a face-centred cubic lattice, like Co and Ce, and evidently the basal plane of the hexagonal lattice is transformed into the (111) plane of a face-centred cubic lattice. The distance between two adjacent atoms and the spacing, d , of a (111) plane of a face-centred cubic crystal are $\frac{a}{\sqrt{2}}$ and $\frac{a}{\sqrt{3}}$ respectively, where a is the lattice constant. As these correspond to a and $\frac{c}{2}$ of a hexagonal lattice formed from a face-centred cubic lattice by simple translation, we have $\frac{c}{a} = \frac{2a}{\sqrt{3}} / \frac{a}{\sqrt{2}} = 1.633$. But if we put $a_{111} = 72 \times 10^{-6}$, $a_{\perp} = 9 \times 10^{-6}$ and $\frac{c}{a} = 1.600$, $\frac{c}{a}$ of α -Tl becomes $1.600 \frac{(1 + 72 \cdot 10^{-6} \cdot 200)}{(1 + 9 \cdot 10^{-6} \cdot 200)} = 1.620$ at the transformation temperature. This nearly coincides with the above number, and therefore we can conclude that this transformation occurs when $\frac{c}{a}$ of α -Tl becomes the ratio of twice the spacing d to the distance between two adjacent atoms of a (111) plane of β -Tl.

1. Sekito, Loc. cit.

Summary

The results obtained in the above experiment may be summarized as follows :

Elements	Range of Temperature	$\alpha_{11}(10^{-6})$	$\alpha_{\perp}(10^{-6})$	$\alpha(10^{-6})$
Al	30°-90°	—	—	22.9
Sn	34°-194°	45.8	25.7	32.4
In	23°-87°	45.0	11.7	22.8
Zn	31°-118°	64.5	10.8	28.7
Tl	32°-91°	72	9	30

In conclusion the author wishes to express his hearty thanks to Dr. M. Ishino, the director of the laboratory, and also to Prof. S. Tanaka for their kind guidance and the interest they have taken in this research.

Physical Laboratory,
The Osaka University of Engineering.

Nov. 16, 1932.

Gunji Shinoda

Plate

Plate 1, Al.

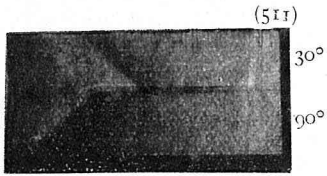


Plate 3, In.

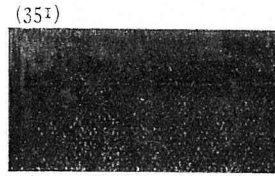


Plate 2, Sn.

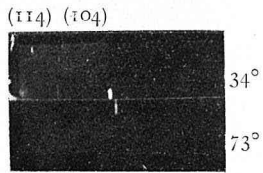


Plate 4, Zn.

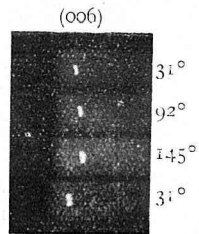


Plate 5, Tl.

