As was mentioned in § 2(c), the scanning area used in our densitometer was 0·03 mm.$^2$.

The densities at which $G$ was determined varied from 0·6 to 1·0 for the different films. Since $G$ depends somewhat on the density, and may also depend on the age of the film, the values listed in Table 1 should only be taken as semi-quantitative indications. It is evident, however, that in general the granularity increases with the film speed, and that, when a scanning area of 0·03 mm.$^2$ is used, the density fluctuations caused by the film grain are only 1–2 %, even for fast films.

### (e) Absorption of Cu radiation

The 'film factor', $F$, by which the intensity of monochromatic X-rays is reduced when passing through the film, is of interest when the multiple-film technique is applied. This factor was measured by means of a Geiger counter for Cu radiation reflected by a monochromator crystal. The values of $F$ are listed in Table 1 for the various types of film; the standard deviation in these values is approximately 2%. The data refer to films without envelopes or interleaving papers; the absorption of a sheet of paper amounts to about 5%.

The absorption of Mo radiation is much smaller than that of Cu radiation, and has not been measured. When using the multiple-film technique with Mo radiation, however, films of different speeds may be superimposed (Iball, 1954).

### (f) Characteristic curves

Since for low densities the effective density $D_{eff.}$ is approximately proportional to the X-ray exposure $E$, $D_{eff.}$ was plotted against $E$, and not against $\log E$. The shapes of the characteristic curves are indicated in the last columns of Table 1, in which the relative exposures required to obtain effective densities of 0·2, 0·4, ..., 2·0 respectively are listed. For each film the exposures were scaled in such a way that the exposure corresponding with the effective density 1·0 became equal to 100. A perfectly linear relationship between $D_{eff.}$ and $E$ is thus represented by the numbers 20, 40, ..., 200. An impression of the deviation from linearity can be obtained by looking at the numbers listed, although it may be preferable to plot them against the $D_{eff.}$ values. The accuracy of the numbers listed is different for the various effective densities, and is such that, for instance, the difference between the characteristic curves of the films 39 and 40 is at the limit of significance.

For practically all films it appeared that the $D_{eff.}$ versus $E$ curve had the same shape for Cu and Mo radiation. Only in four cases was there an indication that the curve for Mo radiation was more nearly linear than that for Cu radiation. The numbers listed in Table 1 refer to Cu radiation.

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# X-ray Study of the Allotropic Modifications of Calcium Metal

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It is shown by means of Debye–Scherrer photographs that for the metal calcium three allotropic modifications occur, namely α-Ca, cubic face centred; β-Ca, hexagonal close packed; and γ-Ca, cubic body centred, the transition points lying at about 250° C. and 450° C. The observed lattice constants of the three modifications are closely related to those of the analogous modifications of strontium.

## 1. Introduction

Earlier investigations concerning the structures of the allotropic modifications of calcium were carried out by Graf (1933, 1934); Ebert, Hartmann & Peisker (1933) and Bastien (1934, 1935). In his first paper Graf reports two modifications, a cubic face-centred (f.c.c.) and a cubic body-centred (b.c.c.) structure, stable respectively below and above 450° C. Ebert *et al.* also found two modifications, a f.c.c. structure stable below 450° C. and a hexagonal close packed (h.c.p.) structure stable above this temperature.

In his second paper Graf indicates that there are three modifications, the transition temperatures being 300° C. and 450° C. Again the α-modification, stable below 300° C., is f.c.c., whereas the γ-modification, stable above 450° C., is h.c.p. The structure of the β-phase, which is stable between these temperatures,

is not mentioned. In Graf's opinion, the structures of the phases depend strongly upon the purity of the calcium used. Impure calcium would have the b.c.c. structure above 450° C.

Bastien confirms the results given by Graf, although he gives slightly different values for the transition temperatures (260° C. and 440° C.). He also does not state the structure of the $\beta$-phase.

Sheldon & King (1949) studied the phase diagram of the system calcium–barium and found that all compositions between the two components crystallize from their melts as a continuous series of solid solutions. From this they conclude that both metals have the same structure (b.c.c.) just below their melting points. This conclusion is in contradiction with those of Graf (1934), Ebert et al. (1933) and Bastien (1934, 1935), unless we consider the solid solutions of barium in calcium as 'impure' calcium. As this seems not very reasonable, we thought it worth while to investigate once again the structures of the three modifications of calcium, the purpose being the determination of the structure of the $\beta$-phase and to find out whether Graf or Sheldon & King were right in their conclusions about the structure of calcium just below its melting point.

## 2. Experimental part

### 2(a). Preparation of the specimens

At first, specimens for X-ray investigation were prepared from filed calcium in evacuated pyrex or quartz capillaries. It turned out, however, that on heating at elevated temperatures (above 500° C.) the calcium acts on glass and quartz, the reaction being:

$$2Ca + SiO_2 \rightarrow 2CaO + Si .$$
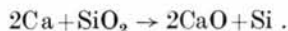
The silicon formed during this reaction can give various alloys with calcium. For this reason it is impossible to use filed calcium in a pyrex or quartz capillary as a specimen. To overcome this difficulty, the following technique was applied. A pyrex tube, with the cup of a ground glass joint at one end, was drawn out thinly at the other end. The thin end of this tube was closed by melting and the cup was connected to the socket of the joint of a vacuum pump. Hereafter a small iron cylinder was turned on a lathe with an external diameter equal to the internal diameter of the pyrex tube (about 1 mm.). At one end of this iron cylinder a hole was drilled in which a small piece of calcium was mounted. The calcium was also turned

to a diameter of 0·6 mm. During the machining, the specimen was kept under paraffin oil to prevent oxidation.

After washing in petroleum ether, the small calcium cylinder held in the iron holder was inserted into the carefully dried pyrex tube. The pyrex tube was evacuated ($10^{-6}$ mm. Hg) and fused off. In this way the calcium is prevented from touching the glass walls of the pyrex tube and it was possible to make X-ray photographs at elevated temperatures.

### 2(b). Apparatus

The X-ray diffraction photographs were made in a Plessey high-temperature camera after the Debye–Scherrer method. Mo $K$ radiation was used, because radiation with a longer wave-length did not pass through the rather thick walls (about 0·5 mm.) of the pyrex tube with sufficient intensity. The rather intense background on the photographs also originates from the pyrex tube.
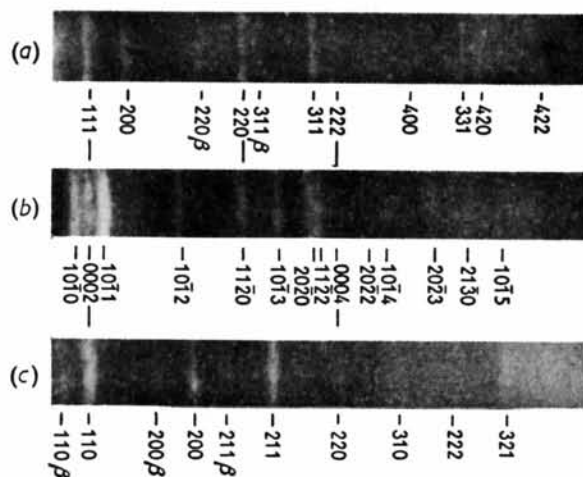
### 2(c). Results

The results are shown in Fig. 1.



Fig. 1. (a) $\alpha$-Ca (f.c.c.). Room temperature.
(b) $\beta$-Ca (h.c.p.). 300° C.
(c) $\gamma$-Ca (b.c.c.). 500° C.

The calculation of the lattice constants was not very accurate because the high-angle reflexions are missing on the photographs, the intensity decreasing rapidly with increasing angle of reflexion. The lattice constants are listed in Table 1.

Table 1. Lattice constants

| | a | | c | | Temperature (°C.) |
|---|---|---|---|---|---|
| | * | † | * | † | |
| $\alpha$-Ca f.c.c. | 5·56 Å | 5·56 Å | — | — | c. 20 |
| $\beta$-Ca h.c.p. | 3·94 Å | 3·94 Å | 6·44 Å | 6·46 Å | c. 300 |
| $\gamma$-Ca b.c.c. | 4·38 Å | 4·43 Å (?) | — | — | c. 500 |

* Present work.     † Graf.

Table 2

| Structure | Plane | Spacing | Calcium | | Cobalt | | Zirconium | |
|---|---|---|---|---|---|---|---|---|
| | | | Spacing (Å) | Ratio | Spacing (Å) | Ratio | Spacing (Å) | Ratio |
| $\alpha$ = f.c.c. | (111) | $\frac{1}{3}a\sqrt{3}$ | 3·21 | 1·00 | 2·04 | 1·00 | — | — |
| $\beta$ = h.c.p. | (0002) | $\frac{1}{2}c$ | 3·22 | | 2·04 | | 2·58 | 1·01$_5$ |
| $\gamma$ = b.c.c. | (110) | $\frac{1}{2}a\sqrt{2}$ | 3·10 | 1·04 | — | | 2·55 | |

Table 3

| | F.c.c. | H.c.p. | | B.c.c. |
|---|---|---|---|---|
| | $a$ (Å) | $a$ (Å) | $c$ (Å) | $a$ (Å) |
| Ca | 5·56 (c. 20° C.) | 3·94 | 6·44 (c. 300° C.) | 4·38 (c. 500° C.) |
| Sr | 6·07 (25° C.) | 4·31 | 7·05 (248° C.) | 4·84 (614° C.) |
| Ratio | 0·91 | 0·91$_5$ | 0·91 | 0·90$_5$ |

Table 4. *Atomic radii of calcium and zirconium*

Calcium

f.c.c. $\frac{1}{2} \times \frac{1}{2}a\sqrt{2} = \frac{1}{4} \times 5\cdot56\sqrt{2} = 1\cdot97$ Å
h.c.p. $\frac{1}{2} \times a = \frac{1}{2} \times 3\cdot94 = 1\cdot97$ Å
b.c.c. $\frac{1}{2} \times \frac{1}{2}a\sqrt{3} = \frac{1}{4} \times 4\cdot38\sqrt{3} = 1\cdot90$ Å

Zirconium

—

$\frac{1}{2} \times a = \frac{1}{2} \times 3\cdot24 = 1\cdot62$ Å $\Big\}$ c. 860° C.
$\frac{1}{2} \times \frac{1}{2}a\sqrt{3} = \frac{1}{4} \times 3\cdot61\sqrt{3} = 1\cdot56$ Å

## 3. Discussion

The main difficulty encountered in this work was the measurement of the temperature of the specimen during the X-ray exposure. For this reason we were not able to measure the transition temperatures with precision and therefore the temperatures given above have not to be considered as such. In our opinion they can be determined far better after the method used by Bastien. On the other hand, Graf, and also Ebert *et al.*, apparently could not measure the temperature of the specimen with great accuracy and we think it quite possible that in his first investigation Graf measured just above the second transition point and thus found the b.c.c. structure, whereas in his second investigation he measured just below this point and consequently found the h.c.p. structure.

An interesting point is the calculation of the spacings of the closest packed layers of the different phases. From the orientation relationships found for 'martensitic-type' transformations between allotropic modifications with respectively f.c.c.–h.c.p. lattices (cobalt), h.c.p.–b.c.c. lattices (zirconium) and b.c.c.–f.c.c. lattices (iron–carbon, iron–nickel) it appears that the closest packed planes (111) f.c.c., (0001) h.c.p. and (110) b.c.c. occupy parallel positions and have approximately equal spacings (Burgers, 1934a; see also Bowles & Barrett, 1952).

Although we have not been able to study the transformation of single crystals of calcium, and for this reason do not know whether the orientation relationship between the three calcium modifications obeys the same laws as found for the individual lattice-pairs mentioned above, we would not be surprised if this were actually the case (cf. Burgers, 1934b). In Table 2 we show the distance of the closest packed layers in the three calcium structures, together with the corresponding values for cobalt and zirconium. It is at once evident that there exists a close correspondence between the various values.

Further evidence for the conception that the transformations of calcium are closely related to those mentioned above can be obtained by comparing the lattice constants of the modifications of strontium metal (Sheldon & King, 1953; cf. also Rinck, 1952) with those found for calcium. Strontium too has three modifications, namely f.c.c. $\alpha$-strontium, h.c.p. $\beta$-strontium and b.c.c. $\gamma$-strontium. It turns out that the ratio of the lattice parameters for the different phases is fairly constant (Table 3).

Finally, the atomic radii of calcium (half the distance between two atoms in a closest packed layer) are approximately the same for the three structures. The difference between the values calculated for the h.c.p. and the b.c.c. structures corresponds again to those found for zirconium (Table 4).

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