Table 1. *Crystallographic data*

| Compound | Space group | *a* (Å) | *b* (Å) | *c* (Å) | $\alpha$ | $\beta$ | $\gamma$ | Density (g.cm.$^{-3}$) Obs. | Density (g.cm.$^{-3}$) Calc. | *Z* |
|---|---|---|---|---|---|---|---|---|---|---|
| Cinchonine sulphate | $P_1$ | 9·4 | 14·1 | 7·0 | 95·5° | 90° | 97° | 1·31 | 1·31 | 1 |
| Cinchonidine | $P2_12_12_1$ | 11·0 | 20·9 | 7·1 | — | — | — | 1·22 | 1·20 | 4 |
| Cinchonidine sulphate | $P1$ | 9·5 | 10·3 | 6·5 | 93·5 | 104 | 100 | 1·47 | 1·48 | 1 |
| Quinine dihydrobromide | $P2_12_12$ | 14·2 | 23·6 | 7·0 | — | — | — | 1·53 | 1·52 | 4 |
| Quinine benzenate | $P2_1$ | 9·7 | 25·3 | 9·7 | — | 109 | — | 1·16* | 1·19 | 4 |
| Quinamine hydrochloride | $P2_12_12_1$ | 13·2 | 16·6 | 8·8 | — | — | — | 1·27 | 1·26 | 4 |
| Dihydroquinamine | $P2_12_12_1$ | 10·8 | 25·5 | 6·2 | — | — | — | 1·21 | 1·21 | 4 |
| Dihydrocinchonamine hydrochloride | $P2_1$ | 9·5 | 9·9 | 9·8 | — | 98 | — | — | 1·21 | 2 |

* See text.

### Dihydroquinamine, $C_{19}H_{26}O_2N_2$

The crystals used were needles elongated along [001]. The Laue symmetry is *mmm* and the space group is uniquely determined as $P2_12_12_1$ by the systematic absences.

### Dihydrocinchonamine hydrochloride, $C_{19}H_{26}ON_2 . HCl$

The crystals were ill-formed plates. The Laue symmetry is $2/m$ and reflexions ($0k0$) are systematically absent when $k$ is odd, so that the space group is either $P2_1$ or $P2_1/m$. Since cinchonamine itself is optically active (Henry, 1949, p. 465) the space group is uniquely determined as $P2_1$. The crystals were of such poor quality that the density could not be measured accurately. The density was calculated for the formula unit quoted above.

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## Coefficients of thermal expansion for face-centered cubic and body-centered cubic calcium.*

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Pearson (1958) has made a critical survey of the available information on the allotropic behavior of calcium metal and has concluded that above room temperature calcium exists in only two allotropic modifications, f.c.c. and b.c.c. The present work was undertaken in order to determine the coefficients of thermal expansion of these two allotropes. The determination was accomplished by comparing measured values of the *d*-spacings from individual X-ray reflections at different temperatures. The diffraction data were taken on a Geiger-counter diffractometer modified in the manner of Chiotti (1954) for high temperature work. The apparatus allows the use of bar specimens which can be maintained under an inert atmosphere of purified helium. Copper radiation was employed. Values of $2\theta$ were measured with a precision of $\pm 0{\cdot}025$ degrees. Values of the *d*-spacings computed from the $2\theta$ measurements were fit to the equation

$$d_{hkl} = d_{0,\,hkl}\,(1+\alpha T)$$

by the method of least squares.

Values for the linear coefficient of thermal expansion of the f.c.c. phase are shown in Table 1. Each value is based upon five to nine experimental points. The greater thermal attenuation of intensity for higher angle reflections accounts for the trend toward narrowing temperature range and reduced precision with increasing Bragg angle. The weak intensity due to the low multiplicity of the 600 reflection made the effect of thermal attenuation particularly severe for that reflection.

Table 1. *Measured coefficients of thermal expansion for* f.c.c. *calcium*

| *hkl* | $\alpha \times 10^6$ per °C. | Temp. range (°C.) |
|---|---|---|
| 511 | $22{\cdot}4 \pm 0{\cdot}4$ | 26–371 |
| 531 | $22{\cdot}5 \pm 0{\cdot}4$ | 26–371 |
| 600 | $21{\cdot}9 \pm 1{\cdot}2$ | 26–164 |
| 620 | $21{\cdot}9 \pm 0{\cdot}6$ | 26–253 |
| 533 | $22{\cdot}8 \pm 0{\cdot}8$ | 26–253 |
| Average | $22{\cdot}3 \pm 0{\cdot}2$ | |

In the case of the b.c.c. only six reflections were observed. Of these, only the (211) reflection persisted at elevated temperatures with sufficient intensity and with a significantly large shift in position to be usable to calculate a meaningful coefficient of thermal expansion. The value obtained from the (211) reflection in the range 467–603 °C. was $(33{\cdot}6 \pm 1{\cdot}6) \times 10^{-6}$ per °C. A very rough

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* Contribution No. 699. Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission.

check of this value was obtained from the only two reliable $d_{310}$ values which were obtained at 467 °C. and at 523 °C. Calculation of the expansion coefficient from these two points gave a value of $33\times10^{-6}$ per °C.

The measured values for the linear coefficient of expansion for the f.c.c. phase are in good agreement with the values of $22{\cdot}5_2\times10^{-6}$ per °C. reported by Erfling (1942) for the range 20–40 °C. and of $22{\cdot}0\times10^{-}{}_{9}$ per °C. reported by Cath & Steenis (1936) for the range 0–300 °C. but is somewhat lower than the value of $25\times10^{-6}$ per °C. obtained by Bridgman (1920). All three of these latter values were obtained by dilatometric measurements. No expansion data were available for comparison with the present value for the b.c.c. phase.

Reference values for the lattice parameters were obtained by extrapolating lattice parameters calculated from the individual reflections against the function proposed by Nelson & Riley (1945). For the f.c.c. phase a value, $a_0$(26 °C.) = 5·5884±0·0002 Å, was obtained and for the b.c.c. phase a value, $a_0$(467 °C.) = 4·480±0·005 Å, was obtained. Calculation of the volumes per atom for the two phases, based upon these lattice parameters and the measured coefficients of expansion, shows that the volume change at the transition temperature, ~450–460 °C., is quite small. Indeed, the extremes of the quoted precisions are sufficient to cause the volume change at transition to shift from a contraction to an expansion. On the basis of volume considerations it might reasonably be expected that the transition should be relatively insensitive to pressure.

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## Structure cristalline des orthovanadates et orthoarseniates de baryum et de strontium.

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L'étude de certains vanadates et arséniates mixtes (Durif, 1957*a*, 1957*b*) dont la préparation nécessitait l'emploi comme matière première des orthovanadates et orthoarséniates de baryum et de strontium, nous a montré que la littérature cristallographique ne faisait pas mention de ces derniers composés, pourtant bien connus au point de vue chimique.

Ces quatre composés ont été préparés par calcination prolongée à 600 °C. des mélanges $X_2O_5+3MO$ ($X$ = V, As; $M$ = Sr, Ba).

Les diagrammes Debye–Scherrer montrent que ces quatre composés sont isotypes, rhomboédriques et appartiennent au type de structure décrit par Zachariasen (1948) pour les orthophosphates correspondants:

$$Ba_3(PO_4)_2 \quad \text{et} \quad Sr_3(PO_4)_2\,.$$

Le Tableau 1 rassemble leurs principales caractéristiques cristallographiques. La maille rhomboédrique renferme une seule unité $M_3(XO_4)_2$ avec la répartition atomique suivante:

| | |
|---|---|
| $1M$ en $1(a)$ 0, 0, 0. | 2O en $2(c)\pm(x,x,x)$ |
| $2M$ en $2(c)\pm(x,x,x)$ | 6O en $6(h)\pm(x,x,z;\ x,z,x;\ z,x,x)$ |
| $2X$ en $2(c)\pm(x,x,x)$ | |

En l'absence de monocristaux nous n'avons procédé à aucun essai de mesure des différents paramètres de positions.

Tableau 1. *Orthovanadates et orthoarseniates de baryum et de strontium*

Groupe d'espace: $D_{3d}^5$–$R\bar{3}m$

| Formules | $a_h$ | $c_h$ | $a_r$ | $\alpha_r$ | $V_{\text{mol.}}$ | $D_x$ (g.cm.$^{-3}$) |
|---|---|---|---|---|---|---|
| $Sr_3(VO_4)_2$ | 5,621 Å | 20,14 | 7,458 | 44° 17′ | 183,7 Å$^3$ | 4,426 |
| $Sr_3(AsO_4)_2$ | 5,581 | 19,98 | 7,399 | 44° 19′ | 179,6 | 4,969 |
| $Ba_3(VO_4)_2$ | 5,783 | 21,34 | 7,859 | 43° 10′ | 206,0 | 5,142 |
| $Ba_3(AsO_4)_2$ | 5,753 | 21,18 | 7,804 | 43° 15′ | 202,3 | 5,627 |

Tableau 2. *Depouillement d'un diagramme de vanadate de strontium*

| *hkl* | $I_{\text{obs.}}$ | $d_{\text{obs.}}$ | $d_{\text{calc.}}$ | *hkl* | $I_{\text{obs.}}$ | $d_{\text{obs.}}$ | $d_{\text{calc.}}$ |
|---|---|---|---|---|---|---|---|
| 101 | *f* | 4,59 Å | 4,72 Å | 205 | *F* | 2,06 Å | 2,08 Å |
| 104 | *mf* | 3,43 | 3,49 | 1,0,10 | *F* | 1,841 | 1,860 |
| 105 | *F* | 3,04 | 3,09 | 211 | *f* | 1,819 | 1,832 |
| 110 | *F* | c. 2,76 | 2,81 | 119 | *m* | 1,736 | 1,749 |
| 202 | *mf* | 2,33 | 2,36 | 125 | *F* | 1,663 | 1,672 |
| 009 | *mf* | 2,21 | 2,24 | 300 | *F* | 1,611 | 1,622 |
| 204 | *mf* | 2,16 | 2,19 | 0,2,10 | *F* | 1,542 | 1,550 |
| 116 | *mf* | 2,13 | 2,15 | 220 | *F* | 1,401 | 1,404 |