

## THE CRYSTAL STRUCTURE OF CALCIUM.

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## SYNOPSIS.

*Crystal Structure of Calcium.*—The X-ray pattern obtained with powdered calcium shows that the atoms are arranged in a face-centered cubic lattice. The side of the elementary cube is 5.56 Å. The Ca atoms in Ca have therefore the same arrangement as in CaO and CaF<sub>2</sub>; but in the fluoride and oxide the atoms are respectively 2 and 14 per cent. closer together than without the fluorine and oxygen.

CALCIUM has generally been considered hexagonal, partly, perhaps, from analogy with magnesium and zinc. The only reference given by Groth<sup>1</sup> is an observation of Moissan,<sup>2</sup> that it forms hexagonal plates or rhombohedra, and shows hexagonal growth forms.

The X-ray analysis shows it to be face-centered cubic.

The analysis was made by the X-ray powder photograph method previously described.<sup>3</sup> Pure Electrolytic Calcium was ground in a ball mill to very fine powder, and exposed to Monochromatic rays from a molybdenum tube. The specimen was mounted in a glass tube about 3 mm. in diameter. The lines on the film were very wide (nearly 5 mm.) and some of them quite faint. In spite of this, the independent measurements on either side of the center (columns 2 and 4 respectively, table I) agree with each other within  $\frac{1}{2}$  per cent., and the planar spacings calculated from their average agree with the theoretical spacings within  $\frac{1}{3}$  per cent. in every case except two, where the deviation is 1 per cent. The full data is given in the table.

Since calcium oxidizes rapidly in air, it seemed possible that the very fine powder used in this experiment was entirely oxidized, and that the above values were due to CaO. A second sample was therefore prepared, consisting of coarse filings from a cast rod of electrolytic Ca, kept in rotation during exposure. This gave lines identical with those in Table I.

As a final check, a photograph was taken, using a tube whose lower half was filled with fine Ca powder, and the upper half with dry CaO. A septum of thin brass prevented overlapping of the scattered rays. This photograph is reproduced in Fig. 1. It shows that the patterns of

<sup>1</sup> Groth, *Chemische Krystallographie*, Vol. 1.

<sup>2</sup> Moissan, *C. R.*, 127, 585, 1898; *Ann. Chim. Phys.*, 18, 303, 1899.

<sup>3</sup> *PHYS. REV.*, 10, 661, 1917.



From the lines in the upper half of Fig. 1, it is evident that the Ca atoms in CaO are also in face centered cubic arrangement, but that the cube is *smaller* than that of pure Ca. The oxygen atoms *not only take up no room, but actually pull the Ca atoms 14 per cent. closer together, without changing their arrangement.*

The Ca atom in CaO is a  $\text{Ca}^{++}$  ion, with the same number of electrons, and presumably the same shape, as an atom of argon. It is probable that the Ca atoms in metallic calcium are also  $\text{Ca}^{++}$  ions, the two extra electrons going into the lattice as free electrons in the same positions as the  $\text{F}^-$  ions in  $\text{CaF}_2$ . This is made plausible by the fact that the distance between Ca atoms in  $\text{CaF}_2$ , where they are also in face-centered arrangement, differs by only 2 per cent. from that in metallic Ca (side of elementary cube in  $\text{CaF}_2 = 5.43 \text{ \AA}.$ ). The free electrons are slightly less effective than the  $\text{F}^-$  ions in pulling the Ca atoms together, due probably to their great mobility. The  $\text{F}^-$  ions, like the  $\text{O}^{--}$  ions in CaO, fit into the Ca lattice without increasing its dimensions. Their dimensions appear to be smaller than those of the holes left in the Ca lattice by closest possible packing of Ca atoms.

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Fig. 1.

Lime above; calcium below.