

⁷ Wulf, *Ibid.*, **14**, 609 (1928).

⁸ "Molecular Spectra in Gases," *Bull. Nat. Res. Council*, No. 57, p. 232.

⁹ Füchtbauer and Holm, *Phys. Zeitschr.*, **26**, 345 (1925); von Wartenberg, *Ibid.*, **11**, 1168 (1910).

¹⁰ For references to this see footnotes 1 and 3 in preceding article by author.

¹¹ Warburg, *Berl. Ber.*, p. 300 (1918).

¹² Coehn and Stuckardt, *Z. f. phys. Chem.*, **91**, 722 (1916); Bonhoeffer and Steiner, *Ibid.*, **122**, 287 (1926); Tingey and Gerke, *J. Am. Chem. Soc.*, **48**, 1838 (1926); Bernard Lewis, *J. Phys. Chem.*, **32**, 270 (1928); Bonhoeffer and Farkas, *Z. f. phys. Chem.*, **132**, 235 (1928).

† *Note added in proof*—See, however, the recent paper by Bonhoeffer and Farkas, *Z. f. phys. Chem.*, **134**, 337 (1928) for another interesting possibility.

THE CRYSTAL STRUCTURES OF THE ALKALINE EARTH METALS

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Prior to the investigation here reported the only one of the alkaline earth metals which had been satisfactorily subjected to x-ray crystal analysis was calcium. Hull¹ reported a face-centered cubic lattice with an edge length of 5.56 A.U. Most of the difficulty with strontium and barium seems to have been in a method of preparation of the pure metals. In the present work calcium, strontium and barium were prepared with purities exceeding 99.9% and subjected to analysis of crystalline structure by the Hull powder method of x-ray spectrography.

The results of Hull on calcium were fully substantiated both as to type of lattice and constant.

Barium was prepared by subliming the metal from a mixture of barium oxide and aluminum in a vacuum sublimation furnace, the product being handled in an atmosphere of argon to avoid oxidation.² The samples for x-ray analysis were prepared by first pressing the sublimed crystals into a cylindrical pellet in a steel die, and then rolling the pellet into a sheet using oil to protect the metal from oxidation during the process of rolling. The thin sheets were then cut into very narrow ribbons under oil and quickly sealed into thin pyrex tubes with sodium chloride which served as a standard for measurement of the diffraction pattern. Several excellent spectrograms with sharp lines over the whole length of the film and free from fogging were obtained.

Analysis of the spectrograms shows that barium crystallizes in the cubic system, the unit cell of which contains two atoms, and whose constant is

5.04 A.U. The intensities of the lines are in agreement with those calculated for the *body-centered* cubic lattice. The density calculated from the above data is 3.52 which compares well with the value 3.5 given in the International Critical Tables and 3.64 obtained from density determinations made with very pure barium wire.³

Specimens of pure strontium were prepared in analogous fashion, the utmost precaution being employed to prevent oxidation, though this metal is not so easily oxidized as is barium. Instead of obtaining the sharp spectra observed for barium, the films were all considerably fogged and showed at the most seven ill-defined diffraction lines. Repeated efforts were made to increase grain size by mechanical and heat treatment, and to chill the specimen in liquid air, but the spectra were not improved. Inasmuch as the $K\alpha$ -rays of molybdenum (42) may excite the fluorescent $K\alpha$ -rays of strontium (38), spectra were also obtained with copper $K\alpha$ rays from a Hadding-Siegbahn tube, again without improvement.

Since the announcement of these results were made at the Saint Louis meeting of the American Chemical Society in April, a paper has appeared by Simon and Vohsen⁴ presenting the results of crystal analyses of the alkali metals and of strontium (the authors state that they had been unable to prepare pure barium). They assign a face-centered cubic lattice to strontium, with the constant 6.03 A.U. They believe that an hexagonal modification may be possible at high temperatures, since optical examination indicates that neither calcium nor strontium crystallize in the regular system. The spectra obtained in the present work do not correspond to any cubic lattice. Of the seven measurable lines possibly two might be made to agree with the structure published by Simon and Vohsen. Inasmuch as strontium is a transition step between calcium (face-centered cubic) and barium (body-centered cubic) it is perhaps not strange that it should behave in anomalous fashion with a transition point between two or more modifications at room temperature. Impurities or oxide layers cannot be said to be the cause of poor diffraction as has recently been demonstrated for potassium, for the metal upon chemical analysis was found to be more than 99.9% pure. The work is being continued with renewed interest in the light of the new work of Simon and Vohsen. Upon the basis of the present results it may be predicted that radium should crystallize on the body-centered cubic lattice.

¹ *Physical Rev.*, **17**, 42 (1921).

² A. J. King, Doctorate Thesis, Syracuse University, 1927. Danner, *J. Am. Chem. Soc.*, **46**, 2382 (1924). Ruff and Hartman, *Zeit. anorg. Chem.*, **133**, 29 (1924). Biltz and Huttig, *Ibid.*, **114**, 241 (1920). Dafert and Miklanz, *Monatsch.*, **34**, 1685 (1913). Guntz and co-workers, cf. *Bull. soc. Chim.*, **35**, 709 (1924).

³ King, loc. cit.

⁴ *Zeit. physikal. Chem.*, **133**, 165 (1928).