[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

THE CRYSTAL STRUCTURE OF BARIUM

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In 1921 Hull[2] determined the crystal structure of calcium, for which he reported a face-centered cubic lattice with a parameter of 5.56 Å. at room temperature. Prior to the beginning of the investigation here reported the structure of barium and strontium had not been determined, but recently a paper has appeared by Simon and Vohsen[3] presenting the results of their measurement of the lattice structure of strontium, to which they assign a face-centered cubic structure having a unit edge of 6.03 Å.

Optical measurements of calcium and strontium at room temperature indicate that these metals do not crystallize with cubic symmetry, but with hexagonal symmetry. Since x-ray data do not confirm this, it is possible that a polymorphic transformation occurs above room temperature, leaving the external appearance of the crystals unchanged.

Barium with a purity of 99.9% was used for the x-ray study of this metal. This was prepared by a method described elsewhere.[4] The samples for x-ray analysis were prepared by pressing the metal into a cylindrical bar in a steel die, then rolling this into a thin foil under dry oil in order to protect the foil from oxidation as far as possible. The foil was cut into narrow ribbons and carefully sealed in pyrex tubes with pure sodium chloride, which served as a standard for the measurement of the diffraction pattern. The sodium chloride and the metal were separated so that their spectrograms were adjacent along the center of the film. Although soft metals are known to recrystallize at room temperature, random orientation of the crystallites was assured by annealing the sample at 120°. Since the spectrograms show no lines which could be ascribed to barium oxide, it is evident that this method of procedure is satisfactory and that oxidation is at most but superficial.

The powder spectrograms were taken with the General Electric x-ray diffraction apparatus. This is provided with a Coolidge x-ray tube containing a molybdenum target and with quadrant cassettes which contain zirconium dioxide filters, so that only the Mo-K_α radiation is effective.

The x-ray data agree very well with those for a body-centered lattice with two atoms in the unit cell, the unit edge of which is 5.015 ± 0.003 Å. The relative intensities of the lines compare favorably with those calcu-

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[1] National Research Fellow.

[2] Hull, *Phys. Rev.*, **17**, 442 (1921).

[3] Simon and Vohsen, *Z. physik. Chem.*, **133**, 165 (1928).

[4] A. J. King, "Doctorate Thesis," Syracuse University, **1927**; Danner, THIS JOURNAL, **46**, 2382 (1924); Biltz and Hüttig, *Z. anorg. Chem.*, **114**, 241 (1920); Dafert and Miklanz, *Monatsh.*, **34**, 1685 (1913); Guntz and co-workers, *Bull. soc. chim.*, **35**, 709 (1924).

TABLE I

POWDER PHOTOGRAM OF BARIUM FOIL

Line	Rel. intens.	Calcd. intens., rel.	Plane, *hkl* (*n*)	d_{hkl}, calcd., Å.	d_{hkl}, meas., Å.	a_0, Å.
1	10	10	110(1)	3.5467	3.556	5.028
2	2	2.25	100(2)	2.5085	2.510	5.020
3	7	5.5	112(1)	2.0478	2.050	5.020
4	3	2	110(2)	1.7733	1.773	5.014
5	2	3	130(1)	1.5860	1.584	5.012
6	1	0.75	111(2)	1.4477	1.447	5.013
7	4	4	132(1)	1.3402	1.339	5.014
8	1	2.3	114(1) 110(3)	1.1819	1.181	5.011
9	0.75	2.3	120(2)	1.1214	1.121	5.013
10	1	Weak	233(1)	1.0693	1.069	5.015
11	1	Weak	112(2)	1.0236	1.023	5.012
12	1	Weak	105(1) 134(1)	0.9835	0.983	5.015
13	0.75	V. weak	125(1)	.9157	.915	5.012
14	0.5	V. weak	305(1)	.8600	.860	5.015

$a_0 = 5.015 \pm 0.003$ Å.

lated for this type of lattice. The density, 3.58, calculated from x-ray data further corroborates this assumption and is in harmony with the values 3.66 and 3.64 obtained by actual measurement.[5] The atomic radius of barium is found to be 2.171 Å., whereas the closest approach of the ions of barium in barium fluoride is only 2.684 Å. This is not in conformity with the hypothesis of constant atomic radii, but is of the same magnitude as that of calcium, 1.963 Å., as determined by Hull, and of strontium, 2.131 Å., calculated from the data of Simon and Vohsen.

In view of the disagreement between optical data and x-ray measurements, further studies are being undertaken to ascertain the possible existence of other modifications of the alkaline earth metals at higher temperatures. The work of Simon and Vohsen shows that but one form of strontium exists between room temperature and 100° absolute.

Ebert and Hartmann[6] have recently published the results of their study of the crystal structure of barium. Their results verify those of the authors. A preliminary paper on this subject[7] has apparently escaped their attention.

An investigation of the binary systems calcium–barium, calcium–strontium and barium–strontium is at present under way and will be published in a subsequent paper.

Summary

1. The crystal structure of very pure barium has been found to be body-centered cubic with a parameter of 5.015 ± 0.003 Å.

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[5] King, ref. 4; Richards, Hall and Mair, THIS JOURNAL, **50**, 3304 (1928).

[6] Ebert and Hartmann, *Z. anorg. Chem.*, **179**, 418–420 (1929).

[7] Clark, King and Hyde, *Proc. Nat. Acad. Sci.*, **14**, 617–618 (1928).

2. The atomic radius calculated from these data is 2.171 Å. at room temperature.

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PARTIAL MOLAL HEAT CAPACITIES AND RELATIVE PARTIAL MOLAL HEAT FUNCTIONS IN SOLUTIONS OF MOLTEN METALS

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There exist in the literature no data on the partial molal properties of solutions of molten metals. There is likewise a great dearth of experimental work from which such data may be calculated. It seems worth while, therefore, to put on record the following results for the partial molal heat capacities and relative partial molal heat functions of Pb–Sb and Bi–Cd solutions calculated from the work of Wüst and Durrer.[1] By direct calorimetric measurements these investigators have determined the values of the specific heats of the above solutions at different concentrations from which the partial molal heat capacities may be determined. They have also obtained the heats absorbed per gram in going from the pure solid components to the liquid solution at the eutectic temperature, for different concentrations. From these data the relative partial molal heat functions may be calculated.

Relative Partial Molal Heat Functions

Consider a solution made up of components a and b. Let $H = E + PV$ be the total heat function of the solution. Then the partial molal heat function h_a of component a in the solution is defined as $(\mathrm{d}H/\mathrm{d}n_a)_{PTn_b}$ where the n's are the number of moles of the respective components in the solution. If h_a^0 is the value of h_a in some arbitrarily chosen reference state, $\bar{h}_a = h_a - h_a^0$ is called the relative partial molal heat function. It is convenient to choose for the reference state the infinitely dilute solution of a in b.[2]

Consider a system composed of some pure a and some solution. Let some of the a go from the pure phase into the solution. If Q is the heat absorbed by the system, then the molal heat of solution of a is defined as $l_a = (\mathrm{d}Q/\mathrm{d}n_a)_{PTn_b}$. Knowing l_a we may calculate $\bar{h}_a$ from the relation

$$\bar{h}_a = l_a - [l_a]_{n_a = 0} \qquad (1)$$

Finally, when $\bar{h}_a$ is known, $\bar{h}_b$ can be calculated from

$$\int_{n_a = 0}^{n_a} \mathrm{d}\bar{h}_b = - \int_{n_a = 0}^{n_a} \frac{n_a}{n_b}\,\mathrm{d}\bar{h}_a \qquad (2)$$

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[1] "Forschungsarbeiten auf dem Gebiete des Ingenieurwesens," Heft 241 (1922).

[2] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, pp. 87–95.