The Crystal Structure of Alloys of Zinc with the Alkali and Alkaline Earth Metals and of Cadmium with Potassium

J. A. A. Ketelaar

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The binary system of sodium and zinc is remarkable for the fact, that these metals form a compound notwithstanding the very low mutual solubility in the liquid state. Moreover the only compound contains about 3 percent Na, corresponding to $NaZn_{11-12}$. Compounds of about the same composition are reported for some of the other systems mentioned in the title.

The x-ray investigation by the powder method with Cu $K\alpha$ and Cr $K\alpha$ radiation revealed the same cubic structure for the alloys of zinc with Na, K, Ca, Sr and Ba and of cadmium only with K. No phase corresponding to the compounds with zinc was found in the other systems of cadmium.[1] Large crystals were obtained by slowly cooling down a large amount of molten KCd_{13}. Single crystal diagrams were made by oscillation round the cube edge and round the diagonal of the cube face. The dimensions of the elementary cell are:

$NaZn_{13}$	$a=12.25_5\pm0.005$A	$CaZn_{13}$	$a=12.13\ \pm0.005$A
KZn_{13}	$a=12.33_5\pm0.005$A	$SrZn_{13}$	$a=12.21_5\pm0.005$A
KCd_{13}	$a=13.78_5\pm0.005$A	$BaZn_{13}$	$a=12.33\ \pm0.005$A.

The number of atoms in the elementary cell was calculated from the density as 111, 113 and 111, respectively, for KCd_{13}, $NaZn_{13}$ and $CaZn_{13}$.

The structure is based on the face-centered lattice, as follows from the period observed in the direction of the diagonal of the cube face. As all reflections hhl with l uneven are absent the space group will be either O_h^6 or T_d^5.[2] Only the general positions of T_d^5 or 96 (i) in O_h^6 are possible for the cadmium atoms since many reflections with odd indices are strong. The position 96 (i) of O_h^6 is a special case having $x=0$ of the general positions of T_d^5.

T_d^5 96(h): xyz $x\bar{y}\bar{z}$ $\frac{1}{2}+x\,z\,y$ $\frac{1}{2}+x\,\bar{z}\,\bar{y}$ $(+000, 0\frac{1}{2}\frac{1}{2}, \frac{1}{2}0\frac{1}{2}, \frac{1}{2}\frac{1}{2}0)$
$\bar{x}yz$ $\bar{x}\bar{y}z$ $\frac{1}{2}-x\,z\,y$ $\frac{1}{2}-x\,z\,\bar{y}$.

The position 96 (i) in O_h^6 is a special case of this with $x=0$.

A discussion of the possible values of the three parameters x, y, z with regard especially to the intensities of the reflections $h00$ leads strictly to only one possible set: $x=0$, $y=2/16$, $z=3/16$. The value found for x indicates that the true space group will be O_h^6. As O_h^6 (and also T_d^5) contains no 4- but only two 8-equivalent positions the constitution can only be: 8 potassium and 8+96 cadmium atoms, corresponding to the formula KCd_{13}. A decision between both 8-equivalent positions can also be made from the observed intensities. So the structure is:

O_h^6 K 8(a): $\frac{1}{4}\frac{1}{4}\frac{1}{4}$, $\frac{3}{4}\frac{3}{4}\frac{3}{4}$ $(+000, 0\frac{1}{2}\frac{1}{2}, \frac{1}{2}0\frac{1}{2}, \frac{1}{2}\frac{1}{2}0)$
Cd 8(b): 000, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ $(+000, 0\frac{1}{2}\frac{1}{2}, \frac{1}{2}0\frac{1}{2}, \frac{1}{2}\frac{1}{2}0)$
Cd 6(i): $0yz$ etc. (see above).

The best accordance between observed and calculated intensities is obtained with the parameter values ($x=0$) $y=0.117\pm0.003$, $z=0.183\pm0.003$.

The spatial arrangement is thus, that each Cd atom on the 96-equivalent position is surrounded by ten other Cd atoms and one K atom. There are five Cd at distances of 2.90–2.99A and five Cd at 3.12–3.22A, in accordance with the values found in pure cadmium: six at 2.97A and six at 3.29A. A Cd atom in the 8-equivalent place is surrounded by 12 Cd atoms at 2.99A. Each K atom has 24 neighboring Cd atoms at 3.98A as compared with 3.90A for the sum of the radii.

The number of electrons contained in the inscribed sphere of the first Brillouin zone (531) was calculated, following the theory of Jones,[3] to be 216.8; that is 1.94 electron pro atom. This ratio calculated directly from the composition has the value 1.93 for $NaZn_{13}$ etc., resp. 2.00 for $CaZn_{13}$ etc. It seems that the compounds $NaZn_{13}$ etc. may be designed as a Hume-Rothery compound with the typical ratio 27/14. The isomorphism between the alkali and the alkaline earth compounds of zinc seems quite remarkable.

J. A. A. KETELAAR
Laboratory for Inorganic and Physical Chemistry,
University, Leyden,
The Netherlands,
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[1] The compound KHg_{11} is also cubic, but with a different structure; the cell containing 36 atoms.
[2] *International Tables for the Determination of Crystal Structures.* (Chemical Catalog Co., New York.)
[3] H. Jones, Proc. Roy. Soc. **144A**, 225 (1934).