

## New CsCl-Type Intermediate Phases in Binary Alloys Involving Rare-Earth Elements\*

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To further work on intermediate phases having the CsCl-type structure in binary alloys involving one rare earth, fifteen additional phases in alloys of rare earths with Zn, Cd, Hg, In, and Tl are described in this paper.

### INTRODUCTION

ABOUT eighty intermediate phases having the CsCl-type structure have been reported in binary alloys involving one rare-earth element.<sup>1-7</sup> Fifteen additional phases in alloys of rare earths with Zn, Cd, Hg, In, and Tl are described in this paper.

### EXPERIMENTAL

In this experiment, the rare-earth metals were of purity greater than 99.9%. The purity of the alloying elements was greater than 99.999%, except for Hg which was only 99.9% pure. The components (total weight about 3 g) were melted by induction in sealed tantalum tubes, 0.95 cm o.d. and 5 cm long under argon atmosphere. Chemical analysis was not performed, but the small weight losses (less than 1%) give reliability to the assumption that the actual composition of the alloys was within  $\pm 2\%$  of the nominal one. All alloys were melted at least twice to insure homogeneity of the melt. The rate of heating of the component had to be kept below a certain limit to avoid the explosive effect of fast exothermic reactions of the components. After melting, additional precautions were taken to prevent reaction with air, and powder specimens for x-ray diffraction analysis were prepared in an argon-filled dry box. X-ray diffraction patterns were obtained using a 114.6-mm-diam camera and CuK radiation with a Ni filter. Lattice parameters were computed using the Nelson-Riley extrapolation and the uncertainties varied from specimen to specimen depending on the sharpness of the back-reflection lines. In some cases the differences in the scattering factors of the rare-earth and the alloy-

ing element was small, and the existence of a CsCl structure (rather than a disordered body-centered structure) could not be firmly established. The lattice parameters of the CsCl phases found in this investigation are given in Table I, together with previously reported results. Uncertainties in lattice parameters are also listed except when they were not explicitly given in the original paper.

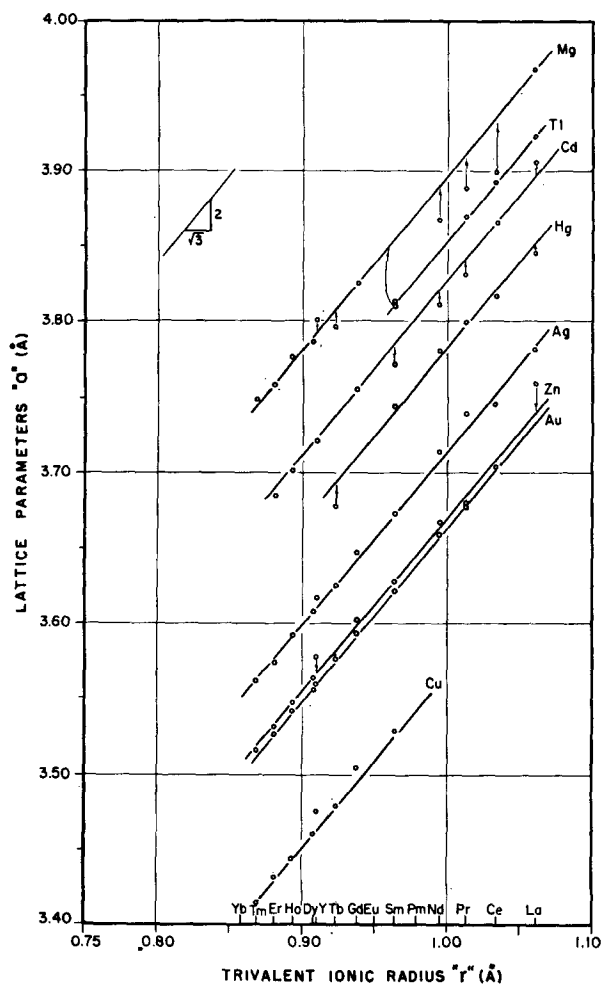


FIG. 1. Relationship between the lattice parameters of CsCl phases and the trivalent ionic radius of the rare-earth ion. For unknown reasons, some of the results for phases containing magnesium taken from Ref. 2 and marked with arrows do not agree with the expected linear relationship.

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<sup>2</sup> K. A. Gschneidner, Jr., *Rare Earth Alloys* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1961).

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<sup>5</sup> N. C. Baenziger and J. L. Moriarty, Jr., *Acta Cryst.* **14**, 948 (1961).

<sup>6</sup> A. E. Miller and A. H. Daane, *Trans. AIME* **230**, 568 (1964).

<sup>7</sup> J. W. Cable, W. C. Kochler, and E. O. Wollan, *Phys. Rev.* **136**, A240 (1964).

TABLE I. Lattice parameters of CsCl intermediate phases and corresponding  $K_M$  values.

	Cu	Ag	Au	Mg	Zn	Cd	Hg	In	Tl
Y	3.476 (1)	3.617 (2)	3.559±2 (4)	3.80 (2)	3.577±3 (3)	3.722±2			
La		3.781 (2)		3.976 (2)	3.759 (2)	3.905 (2)	3.845 (2)		3.922 (2)
Ce		3.746 (2)		3.899 (2)	3.704 (2)	3.865 (2)	3.816 (2)		3.893 (2)
Pr		3.739 (2)	3.68±1 (4)	3.888 (2)	3.678 (2)	3.830 (2)	3.799 (2)		3.869 (2)
Nd		3.714 (2)	3.659±4 (4)	3.867 (2)	3.667±2 (3)	3.811 (2)	3.780 (2)		
Sm	3.528±2 (3)	3.673±3 (4)	3.621±2 (4)	3.810 (2)	3.627±1 (3)	3.771 (2)	3.744 (2)		3.813 (2)
Eu						3.800±2			
Gd						3.951±2			3.975±3
Tb	3.505 (2)	3.6476 (5)	3.593±2 (4)	3.824 (6)	3.602±4 (3)	3.755±3			
Tb	3.480±4 (3)	3.625±3 (4)	3.576±2 (4)	3.796 (6)	3.576±4 (3)	3.725±2	3.678 (7)		
Dy	3.460±3 (3)	3.608 (2)	3.555±2 (4)	3.786 (6)	3.563±3 (3)	3.711±2			
Ho	3.445±1 (3)	3.592±3 (4)	3.541±2 (4)	3.776 (6)	3.547±3 (3)	3.701±2			
Er	3.432 (2)	3.547±2 (4)	3.527±2 (4)	3.758 (6)	3.532±3 (3)	3.685±1			
Tm	3.414±1 (3)	3.562±2 (4)	3.516±3 (4)	3.749 (6)	3.516±3 (3)	3.663±5			
Yb					3.629±1	3.8086±5	3.735±2	3.808±1	3.828±4
$K_M$ (Å)	2.090±2	2.215±5	2.172±2	2.370±5	2.178±2	2.310±5	2.275±5		2.336±2
$R_{12}$ (Å)	1.276	1.442	1.439	1.598	1.379	1.543	1.570		1.712

### CORRELATION BETWEEN LATTICE PARAMETERS AND TRIVALENT IONIC RADII OF RARE-EARTH ELEMENTS

In previous investigations of the CsCl-type phases involving rare-earth elements, it was pointed out that a linear relationship exists between the lattice parameters of these phases and the trivalent ionic radii of the rare earths. This relationship was first pointed out by Iandelli<sup>8</sup> for NaCl-type phases and was subsequently extended to CsCl-type phases.<sup>3,4</sup> In the CsCl structure, the closest approach between atoms is along the diagonal of the cube. If it is assumed that the radius of the rare-earth element is that of the trivalent ion, the space available for the metallic ion is specified by  $a\sqrt{3}-2R_R$ , in which  $a$  is the lattice parameter and  $R_R$  the radius of the rare-earth trivalent ion. This distance, called  $2K_M$  has been computed for all the phases reported here and was found to be constant for a given metallic ion within the experimental uncertainties. The average values of  $K_M$  for each metallic ion and their deviation from the average are given in Table I. If the value of  $K_M$  is constant, the lattice parameters of the CsCl phases involving a given metallic ion should fall on straight lines having a slope of  $2/\sqrt{3}$ , and this is actually the case, as shown in Fig. 1.

<sup>8</sup> A. Iandelli, in *Rare Earth Research*, E. V. Kleber, Ed. (The Macmillan Company, New York, 1961), p. 135.

The results of this investigation lead to the conclusion that if the rare-earth ion actually enters into the CsCl structure with its trivalent ionic radius, the hard-sphere model (with contact between ions) cannot be applied to these phases. It is indeed obvious that the metallic ion cannot occupy all the available space specified by the distance  $K_M$ , since twice this value is always greater than the lattice parameter of a given phase. If it is assumed that the metallic ions enter the CsCl structure with their generally accepted radii for coordination twelve<sup>9</sup> ( $R_{12}$  given in Table I) the structures are not closely packed along the (111) direction.

The lattice parameters of the CsCl phases involving ytterbium and europium were not considered in the previous discussion, because they do not fit the straight-line relationships shown in Fig. 1. In order to bring the ytterbium and europium CsCl-phases lattice parameters in line with the other compounds, it would be necessary to assume ionic radii somewhere between those of the divalent and the trivalent ions. This would lead to a fractional valence of  $2.2\pm 0.1$  for both ytterbium and europium. It is not surprising that Yb and Eu differ from the other rare earths in the CsCl phases, since they are among the only three rare earths (Ce, Eu, and Yb) for which the lanthanides contraction is violated.

<sup>9</sup> F. Laves, in *Theory of Alloy Phases* (American Society for Metals, Cleveland, Ohio, 1956), pp. 131, 132.