

## CsCl-Type Compounds in Binary Alloys of Rare-Earth Metals with Gold and Silver\*

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In binary alloys of silver with Sm, Tb, Ho, and Tm, and of gold with Y, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, and Tm, intermediate phases containing stoichiometric proportions of the two metals were found to crystallize into the CsCl (B2)-type structure. The lattice parameters of these phases are reported and a correlation has been found between these lattice parameters and the trivalent ionic radii of the rare-earth metals.

### I. INTRODUCTION

**E**IGHT binary alloys containing stoichiometric compositions of silver and metals of the rare-earth group have been reported to have the CsCl-type crystal structure. In the present investigation, CsCl-type phases have been found in four additional silver alloys, and in ten gold alloys.

### II. EXPERIMENTAL PROCEDURE

The alloys were prepared by induction-melting stoichiometric amounts of the elements in tantalum crucibles under an atmosphere of argon. Gold and silver had a purity greater than 99.99% and all the rare-earth metals were approximately 99.9% pure, according to the manufacturers. Y and Nd were received from the Michigan Chemical Corporation, Gd from the Atomic Energy Commission, and the others from the American Potash and Chemical Corporation. For all the gold alloys, a strongly exothermic reaction took place as soon as the gold started melting. Such a reaction was not observed during the melting of silver alloys. A rather crude estimate of the melting temperature of the alloys was obtained by observation of the melt with an optical pyrometer and a significant difference was found between the gold and the silver alloys. For the gold alloys, the melting temperature was in all cases between 1200° and 1500°C, whereas all of the silver alloys melted in the range of 800° to 1000°C.

The structure of the alloys was investigated by x-ray diffraction using a Debye-Scherrer camera 114.6 mm in diameter and nickel-filtered copper  $K_{\alpha}$  radiation. Since the high angle lines were not resolved, an average wavelength of 1.54178 Å was used for copper  $K_{\alpha}$ . Lattice spacings were obtained from extrapolation against the Nelson-Riley function.

The structure studies were performed on specimens taken from the solidified ingots and also on specimens rapidly cooled from the liquid state by a recently developed technique described previously.<sup>1</sup> In this technique, a small amount of alloy (about 30 mg) is

melted in a tantalum insert held within a graphite support which is heated by induction. The molten globule is then subjected to a pressure wave originating in a helium shock tube, and is ejected at high speed onto a copper target. An argon atmosphere is kept around the crucible and target to reduce the contamination of the molten alloy by oxygen and nitrogen. Thin flakes can be easily removed from the copper target and are suitable for obtaining x-ray powder patterns.

### III. RESULTS AND DISCUSSION

Results of the crystal structure analysis of the alloys studied in this investigation are summarized in Table I. The alloys are tabulated in the order of increasing atomic

TABLE I. Lattice parameters of the CsCl-type compounds of rare-earth elements with silver and gold.

Compound	Reference	Lattice Parameter (Å)	Remarks
YAg	2	3.617	
LaAg	3	3.781±13	
CeAg	3	3.746±7	
PrAg	4,5	3.739	
NdAg	6	3.714	
SmAg	a	3.673±3	F-S <sup>b</sup>
GdAg	7	3.6476	
TbAg	a	3.625±3	F-S
DyAg	7	3.608	
HoAg	a	3.592±3	F-S
ErAg	a	3.574±2	F-S d
ErAg	3	3.58	
TmAg	a	3.562±2	F-S d
YAu	a	3.559±2	F <sup>c</sup> d
PrAu	a	3.68 ±1	F d
NdAu	a	3.659±4	F
SmAu	a	3.621±2	F
GdAu	a	3.593±2	F
TbAu	a	3.576±2	F-S d
DyAu	a	3.555±2	F-S d
HoAu	a	3.541±1	F-S d
ErAu	a	3.527±2	F-S
TmAu	a	3.516±3	F-S

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<sup>1</sup> P. Duwez and R. H. Willens, *Trans. Met. Soc. AIME* **227**, 362 (1963).

<sup>a</sup> This paper.

<sup>b</sup> F-S means that a structure was obtained in fast- and slow-cooled alloys.

<sup>c</sup> F means that the structure was obtained only in fast-cooled alloys.

<sup>d</sup> Superlattice reflections were observed.

number of the rare-earth metals involved, and previously reported CsCl structures are given with proper references.<sup>2-7</sup> The variation in the uncertainty in the lattice parameter, given in Table I, is due mostly to estimated errors resulting from lack of sharpness of the x-ray diffraction lines. The alloys covered in the present investigation did not always have the CsCl structure in the "as-cast" condition, and fast quenching from the melt was required to bring up this crystal structure. As shown in Table I, the five alloys of gold with Y, Pr, Nd, and Sm, and Gd were in this class. The exact reason for the behavior is not known. Two possible explanations may be advanced: the first one is that the CsCl phase may be an equilibrium high-temperature phase which decomposes very rapidly on relatively slow cooling; the second one is that the CsCl structure is a metastable phase which can be obtained only under extremely rapid cooling from the liquid phase. Such metastable phases (not of the CsCl type, however) have been previously reported in the literature,<sup>8,9</sup> and thus it is possible that the CsCl phases in the five gold alloys obtained only by fast quenching might not be found when the equilibrium phase diagrams of these binary systems are worked out. In fact, the CsCl structure was reported not to exist in the YAu alloy,<sup>2</sup> but was found in this investigation by rapid quenching. With the exception of TmAu, ErAu, TbAg, and HoAg, the lattice parameters of the phases reported in Table I were obtained from diffraction patterns of the quenched alloys because even if the CsCl phase was present in the "as-cast" ingot, the diffraction lines were in all cases sharper in the rapidly cooled alloys. This sharpness is possibly due to the fact that alloys quenched from melts are more homogeneous than those as-cast ingots.

In reviewing the literature on previously reported CsCl structure in silver-rare-earth alloys, it was found that very little quantitative data were given on the actual intensity of the superlattice lines which must be observed in order to claim a CsCl structure rather than a body-centered cubic disordered structure. Among the fourteen alloys reported here as having the CsCl structure, superlattice lines were actually observed in seven (see Table I). However, because of their stoichiometric compositions, it appears reasonable to assume that the other alloys (as well as those reported in the literature) also have the CsCl structure, although no direct proof can be given at this time. The data for two alloys, YAu

TABLE II. Calculated ( $I_c$ ) and observed ( $I_0$ ) relative intensities for YAu and TmAg phases.

$hkl$	YAu		TmAg	
	$I_c$	$I_0^a$	$I_c$	$I_0^a$
100	16.1	m	5.2	vw
110	100.0	vs	100.0	vs
111	5.2	vw	1.6	...
200	17.7	m	17.3	w
210	7.2	vw	2.3	vw
211	35.5	s	35.3	s
220	10.9	w	10.7	w
300,221	3.6	vw	1.1	...
310	15.9	m	15.7	m
311	2.3	vw	0.7	...
222	4.4	vw	4.4	vw
320	2.0	vw	0.6	...
321	25.5	m	25.0	md
400	3.5	vw	3.4	vw
410,322	4.9	vw	1.5	vw
411,330	30.0	wd	24.9	md
331	3.4	vw	1.0	...
420	27.9	wd	26.2	wd

<sup>a</sup> s = strong, m = medium, w = weak, v = very, d = diffuse, ... = not observed.

and TmAg, are given in Table II in which the visual intensities of the diffraction lines are compared with calculated intensities assuming a CsCl structure. The agreement is reasonably good.

The lattice parameters of the CsCl-type phases given in Table I seem to follow a trend with increasing atomic number of the rare-earth metals. In addition, the parameter of a silver alloy is in all cases greater than that of the corresponding gold alloy. A good correlation was found when the lattice parameters of the CsCl-type phases were plotted against the radii of the trivalent rare-earth ions computed from their sesquioxides and

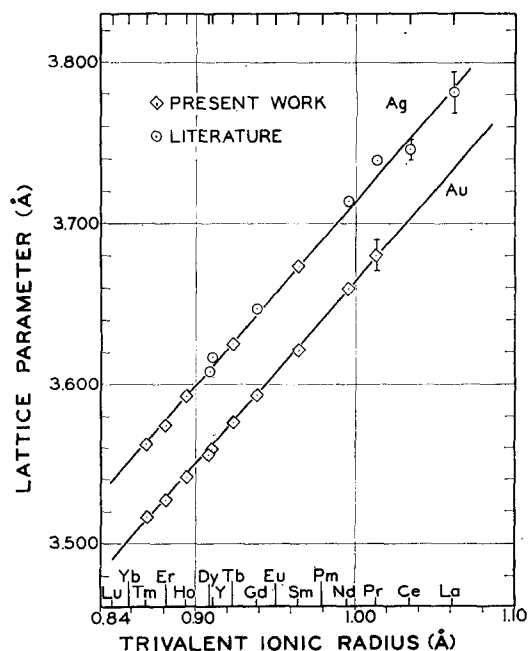


Fig. 1. Lattice parameters of the CsCl-type compounds.

<sup>2</sup> A. E. Dwight, *Trans. AIME* **215**, 283 (1959).

<sup>3</sup> K. A. Gschneidner, Jr., *Rare Earth Alloys* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1961), p. 278.

<sup>4</sup> A. Iandelli, *Att. Congr. Intern. Chim.* 10th Congr. Rome **2**, 688 (1938).

<sup>5</sup> A. Iandelli, in *The Physical Chemistry of Metallic Solutions and Inter-metallic Compounds* (Chemical Publishing Company, Inc., New York, 1960), Vol. 1, p. 376.

<sup>6</sup> R. Ferro, *Gazz. Chim. Ital.* **85**, 888 (1955).

<sup>7</sup> N. C. Baenziger and J. L. Moriarty, Jr., *Acta Cryst.* **14**, 948 (1961).

<sup>8</sup> H. L. Luo and W. Klement, Jr., *J. Chem. Phys.* **36**, 187 (1962).

<sup>9</sup> W. Klement, Jr., *J. Inst. Metals* **9**, 27 (1961).

halides.<sup>10,11</sup> As shown in Fig. 1, the lattice parameter increases linearly with the ionic radius and the scatter of the data is somewhat less for gold than for silver. A similar correlation has been reported by Iandelli<sup>11</sup> for compounds of the NaCl type involving rare-earth metals and VA, and VIA elements.

An interpretation of this correlation is not attempted at the present time, but a side observation might be of interest. The fact that all the unit cell sizes of the gold compounds lie below those of the silver compounds in Fig. 1, indicate that the gold-to-rare-earth bonding is

<sup>10</sup> D. H. Templeton and C. H. Dauben, *J. Am. Chem. Soc.* **76**, 5237 (1954).

<sup>11</sup> A. Iandelli, in *Rare Earth Research*, edited by E. V. Kleber (The Macmillan Company, New York, 1961), p. 135.

stronger and probably more ionic in character than the silver bonding. This statement is strengthened by the facts that in the melting operation a very strong exothermic reaction was observed in all the gold-containing binary alloys, and no such reaction was observed in the silver alloys; and that gold is more electronegative than silver.

It is also interesting to speculate on the lattice parameters of other not yet found CsCl-type structures in alloys of rare earths with gold and silver. If the correlation shown in Fig. 1 holds, the lattice parameters of these phases would be as follows: ScAg, 3.43±1; PmAg, 3.687±5; LuAg, 3.536±5, ScAu, 3.38±1; LaAu, 3.74±1; CeAu, 3.70±1; PmAu, 3.640±3; LuAu, 3.488±3.

### Single- and Double-Deformation Faults in Face-Centered Cubic Crystals\*

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The diffraction effects of a double-deformation fault (extrinsic fault) are readily derived for small faulting probabilities by using a faulted sequence with a layer added and subtracted. Let  $\alpha'$  and  $\alpha''$  be the probabilities for single- and double-deformation faults. If both types of faulting are present, with  $\alpha'$  and  $\alpha''$  both small and independent, the peak broadening depends upon  $\alpha' + \alpha''$ , the peak shift depends upon  $\alpha' - \alpha''$ , and there is a peak asymmetry proportional to  $\alpha''$  which is similar to that produced by twin faulting.

#### I. INTRODUCTION

A SINGLE-DEFORMATION fault in a face-centered cubic crystal is represented by Fig. 1(a). The diffraction effects have been given by Paterson,<sup>1</sup> by Warren and Warekois,<sup>2</sup> and by Warren.<sup>3</sup> A double-deformation fault (extrinsic fault) is represented by Fig. 1(b), and the diffraction effects for this type of faulting have been given by Johnson.<sup>4</sup> We call  $\alpha'$  the probability of a single-deformation fault, and  $\alpha''$  the probability of a double-deformation fault. With the restriction that  $\alpha'$  and  $\alpha''$  are both small and independent, it is possible to obtain in a very simple way the diffraction effects when both types of faulting are present. We assume that the faulting occurs on only one set of 111 planes, and that the fault extends across the coherently diffracting domain. Following the notation of Warren and Warekois,<sup>2</sup> we introduce hexagonal axes  $A_1A_2A_3$ , with  $A_1A_2$  in the 111 plane and  $A_3$  normal to the plane. In terms of the cubic axes  $a_1a_2a_3$  and the cubic indices  $hkl$ , the corresponding

hexagonal axes and indices are given by

$$\begin{aligned} A_1 &= -a_1/2 + a_2/2 + 0 & H &= -h/2 + k/2 + 0, \\ A_2 &= 0 - a_2/2 + a_3/2 & K &= 0 - k/2 + l/2, \\ A_3 &= a_1 + a_2 + a_3 & L &= h + k + l. \end{aligned} \tag{1}$$

#### II. EFFECT OF DOUBLE-DEFORMATION FAULTS ONLY

For simplicity in presentation, we consider first the case for double-deformation faults only, where  $\alpha''$  is assumed to be small. The double fault, represented by

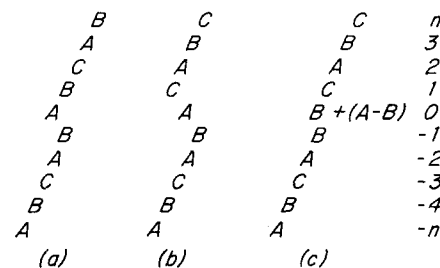


FIG. 1. Faults in the sequence of 111 layers in an fcc crystal: (a) single-deformation fault; (b) double-deformation fault, and (c) alternative representation of a double-deformation fault.

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<sup>1</sup> M. S. Paterson, *J. Appl. Phys.* **23**, 805 (1952).  
<sup>2</sup> B. E. Warren and E. P. Warekois, *Acta Met.* **3**, 473 (1955).  
<sup>3</sup> B. E. Warren, *Prog. Metal Phys.* **8**, 147 (1959).  
<sup>4</sup> C. A. Johnson, *Acta Cryst.* (to be published).