

## The $\gamma$ -Brass Structure at High Pressure

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(Received 13 December 1979; accepted 10 March 1980)

### Abstract

The effect of high pressure on the so-called vacancy-rich structure of intermetallic phases  $\gamma$ -Ag<sub>5</sub>Zn<sub>8</sub> and  $\gamma$ -Cu<sub>5</sub>Zn<sub>8</sub> has been studied by X-ray diffraction using a diamond-anvil cell. Contraction of the unit-cell volume is unexpectedly small with  $K_0$  (initial bulk modulus) =  $109 \pm 2$  GPa for  $\gamma$ -Ag<sub>5</sub>Zn<sub>8</sub> and  $123 \pm 3$  GPa for  $\gamma$ -Cu<sub>5</sub>Zn<sub>8</sub>. No appreciable change is detected in the relative intensities of diffraction lines, indicating that the framework of the atomic arrangements remains unchanged even in the reduced volume. The stability of the  $\gamma$ -brass structure is discussed in the light of the 26-atom-cluster packing model of Bradley & Jones [*J. Inst. Met.* (1933), 51, 131–162].

### Introduction

The  $\gamma$ -brass phase is known as one of the classical electron compounds, frequently found at the electron-atom ratio ( $e/a$ ) of 21/13 in binary alloy systems. The structure of  $\gamma$ -brass has cubic symmetry and is described as an array of  $3 \times 3 \times 3 = 27$  body-centered cubes with two atoms missing and with the remaining atoms arranged in an ordered manner but displaced slightly (Hume-Rothery & Raynor, 1954). Brass-like alloys with  $\beta$  phase, having the  $A2$  (b.c.c.)-type structure, generally form at a composition corresponding to  $(e/a) = 3/2$  and, in order to keep the structure stable beyond this value of electron-atom ratio, vacancies are introduced into the lattice (Schubert, 1973) which provide places available for the excess valence electrons. The  $\gamma$ -brass structure is thus regarded as one of the variants of the vacancy-containing  $A2$ -type structure. As a result of the introduction of vacancies, the density of the  $\gamma$ -brass structure is lower than that of the  $A2$ -type structure.

The purpose of the present study is to investigate how this vacancy-rich structure behaves under compression. Pressures in excess of 15 GPa have been applied to  $\gamma$ -Ag<sub>5</sub>Zn<sub>8</sub> and  $\gamma$ -Cu<sub>5</sub>Zn<sub>8</sub>, two typical intermetallic phases with the  $\gamma$ -brass structure, using a diamond-anvil cell, and X-ray diffraction patterns taken at elevated pressures have been examined. The

results of this high-pressure experiment are reported here.

### Experimental procedures

The alloy samples were prepared by melting appropriate weighed amounts of the constituent metals in an evacuated silica tube. The purity of the metals was silver 99.99%, copper 99.999% and zinc 99.999%. After homogenizing treatment, fine alloy powders were obtained by filing the ingots. Silver-zinc alloy powders were then annealed at 770 K for two days and at 670 K for five days. An X-ray diffraction pattern showed the alloy to be  $\gamma$  phase with the lattice constant  $a = 9.351 \pm 0.003$  Å. The value is slightly larger than that given by Marsh (1954) for Ag<sub>5</sub>Zn<sub>8</sub>, indicating that the composition of our alloy is rich in silver by one atomic percent. For copper-zinc alloy powders annealed at 870 K and subsequently at 770 K, the lattice constant was measured to be  $a = 8.859 \pm 0.003$  Å which was in agreement with the reported value for Cu<sub>5</sub>Zn<sub>8</sub> (Pearson, 1967).

The diamond-anvil cell is the same as that used in the previous studies (Iwasaki, 1978*a*, 1980). No details are given here about the experimental techniques for taking high-pressure X-ray diffraction patterns, except for several modifications adopted in the present study. (a) A high-power X-ray generator with rotating anode was employed, which was operated at 55 kV and 300 mA. With filtered Ag  $K\alpha$  and Mo  $K\alpha$  radiation, it took 20 h to take a diffraction pattern which could be used for the structural investigation. (b) The initial ratio of the gasket-hole diameter to the anvil-face diameter (0.5 mm) was chosen to be 0.3, a little smaller than that formerly adopted. The presence of a small gasket hole resulted in a reduction in pressure gradient in the alloy sample and less broadening of diffraction lines at very high pressures. At the same time, however, it gave a few extra lines from the gasket material (Inconel). (c) In order to check the presence of preferred orientation of crystal grains in the sample, the diamond anvil, which otherwise remained fixed, was oscillated during exposure using a device recently constructed (Iwasaki, 1978*b*). No appreciable preferred orientation was

detected for the present packing of alloy powders and therefore most of the diffraction patterns were taken at the normal setting of the anvil.

### Experimental results

Fig. 1 shows a series of X-ray diffraction patterns of  $\gamma\text{-Ag}_5\text{Zn}_8$  subjected to compression. Eight diffraction lines are observable in the pattern taken at 10.2 GPa. Table 1 lists the intensities of the diffraction lines measured on the X-ray film with a microdensitometer. Because of overlapping by the line from the internal pressure marker (NaCl), the intensity of line 422 cannot be measured. In the fourth column of Table 1 are shown the calculated intensities,  $|F|^2mLP$  ( $F$  structure factor,  $m$  multiplicity factor and LP Lorentz-polarization factor), using the positional parameters  $x(\text{Ag}_I)$ ,  $x(\text{Ag}_{II})$ ,  $x(\text{Zn}_I)$ ,  $x(\text{Zn}_{II})$  and  $z(\text{Zn}_{II})$  given by Marsh (1954). For the  $\gamma$ -brass structure there are other possible reflections in the diffraction-angle range here concerned, but they have smaller calculated intensities and are not shown in the table. An approximate agreement between observed and calculated intensities suggests that the values of the positional parameters remain almost unchanged on compression to 10.2 GPa, although the accuracy of intensity measurements in the powder method does not necessarily rule out the possibility of small variations. Intensity calculations have then been made in which the positional parameters are slightly varied in a number of ways and changes in the relative peak heights of the diffraction lines have been examined. The parameters which give a larger change in the peak heights are  $x(\text{Ag}_I)$  and  $z(\text{Zn}_{II})$  and

their 'uncertainty' can be estimated to be  $\pm 0.008$ , while that of the other parameters is  $\pm 0.01$ . Intensity measurement on single-crystal specimens would determine whether the atoms were slightly displaced or not on compression.

The diffraction patterns taken at 16.4 and 24.2 GPa, shown in Fig. 1, look much the same as that taken at 10.2 GPa, except for a shift of the lines towards the high-diffraction-angle side. It can therefore be concluded that the framework of the atomic arrangements in  $\gamma\text{-Ag}_5\text{Zn}_8$  is stable under very high pressure and this intermetallic phase does not show any tendency to

Table 1. Observed and calculated intensities of diffraction lines from  $\gamma\text{-Ag}_5\text{Zn}_8$

No.	<i>hkl</i>	$I_{\text{obs}}$ (at 10.2 GPa)	$I_{\text{calc}}^*$
1	211	10	9.5
2	222	—	1.3
3	321	—	1.7
4	330, 411	100	100
5	332	5	2.5
6	422	(-) <sup>†</sup>	4.4
7	442, 600	15	12.2
8	532, 611	5	2.3
9	631	—	1.9
10	444	8	4.7
11	543, 550, 710		
12	552, 633, 721	25	20.9
13	554, 741, 811	10	10.1
14	644, 820		

\* The diffraction lines whose calculated intensities are smaller than 1.0 are omitted.

<sup>†</sup> Overlapping with NaCl line.

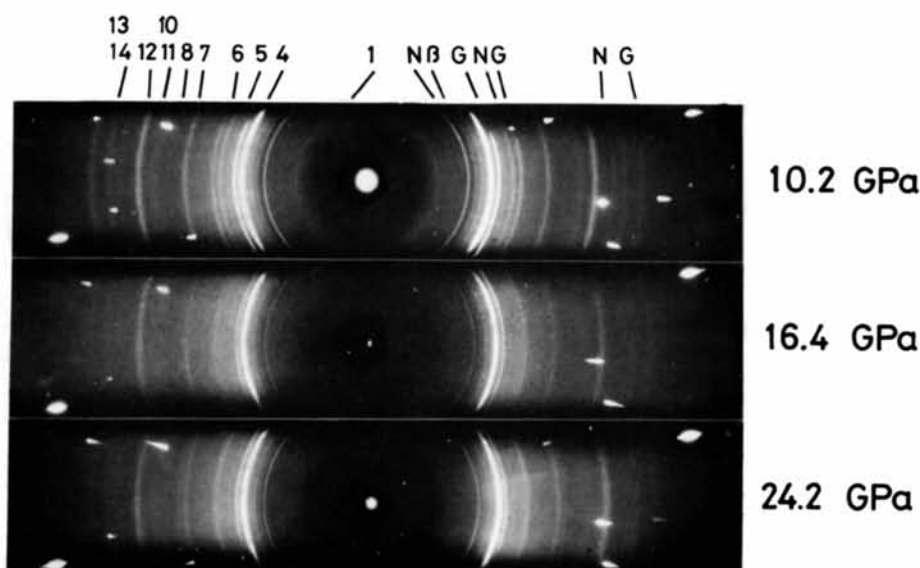


Fig. 1. X-ray diffraction patterns of  $\gamma\text{-Ag}_5\text{Zn}_8$  at elevated pressures. Filtered Ag  $K\alpha$  radiation was used. Indices of the diffraction lines numbered 1 through 14 are shown in Table 1.  $N$  and  $G$  represent the lines coming from NaCl and the gasket, respectively.

transform into a phase which has a more closely packed structure.

From the shift of the diffraction lines, the pressure dependence of the lattice parameter,  $a$ , has been determined, and this is shown in Fig. 2.  $a$  is normalized to the value  $a_0 = 9.351 \text{ \AA}$  at atmospheric pressure. The bars attached to the data points represent estimated errors of the measurements. Compression to a pressure of 24.2 GPa reduces the lattice parameter of  $\gamma\text{-Ag}_5\text{Zn}_8$  by 5%. It may be noted that the contraction of the unit cell is as small as that for silver metal with an ideally close-packed structure, 5.2% at 26.5 GPa (Mao, Bell, Shaner & Steinberg, 1978).

X-ray diffraction experiments on  $\gamma\text{-Cu}_5\text{Zn}_8$  have given similar results: *i.e.* no significant change in the relative intensities of the diffraction lines and small compressibility of the lattice parameter. Fig. 3 shows the lattice parameter as a function of pressure.

Least-squares fitting of the unit-cell volume to the well-known Birch–Murnaghan equation,

$$P = \frac{3}{2}K_0 \left[ \left( \frac{V_0}{V} \right)^{7/3} - \left( \frac{V_0}{V} \right)^{5/3} \right] \times \left\{ 1 - \xi \left[ \left( \frac{V_0}{V} \right)^{2/3} - 1 \right] \right\},$$

gives  $K_0$  (bulk modulus at 0 GPa) =  $109 \pm 2$  GPa and  $\xi = -0.36 \pm 0.11$  for  $\gamma\text{-Ag}_5\text{Zn}_8$ . For  $\gamma\text{-Cu}_5\text{Zn}_8$ ,  $K_0 = 123 \pm 3$  GPa and  $\xi = 0.45 \pm 0.17$ . These bulk moduli are considerably larger than  $K_0 = 59$  GPa of the parent zinc metal (Plendel & Gielisse, 1970). The coefficient of the higher-order term  $\xi$  is related to the pressure derivative of the bulk modulus  $K'_0$  through an equation  $\xi = \frac{3}{4}(4 - K'_0)$  (Birch, 1947), which gives  $K'_0 = 4.5$  and 3.4 for  $\gamma\text{-Ag}_5\text{Zn}_8$  and  $\gamma\text{-Cu}_5\text{Zn}_8$ , respectively.

### Discussion

As was stated above, the  $\gamma$ -brass structure has been regarded by many researchers as the vacancy-contain-

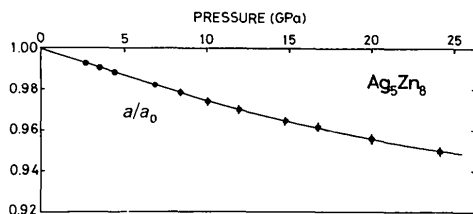


Fig. 2. Pressure dependence of the lattice parameter of  $\gamma\text{-Ag}_5\text{Zn}_8$ .  $a_0 = 9.351 \text{ \AA}$ .

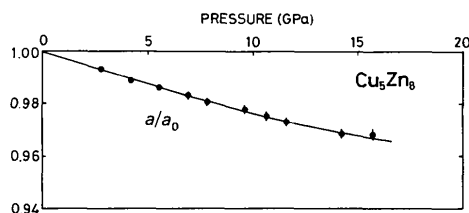


Fig. 3. Pressure dependence of the lattice parameter of  $\gamma\text{-Cu}_5\text{Zn}_8$ .  $a_0 = 8.859 \text{ \AA}$ .

ing structure. The present X-ray measurements have shown that the structure exhibits strong resistance against compression with a  $K_0$  value nearly the same as that of the noble metals. In order to explain the high stability of the structure one must resort to another structural viewpoint which was originally given by Bradley & Jones (1933). According to their view, the large cubic lattice of the  $\gamma$ -brass structure is regarded as a quasi- $A2$ -type lattice with one cluster of atoms centered at the cube corner and the other at the body center. The cluster contains 26 atoms which build outward from the center an inner tetrahedron, an outer tetrahedron, an octahedron and a cuboctahedron, as illustrated in Fig. 4. Silver or copper atoms occupy the sites on the outer tetrahedron and octahedron, while zinc atoms occupy those on the other polyhedra. This type of configuration is shown (Pearson, Brandon & Brizard, 1976) to give as many unlike-atom contacts as possible. The packing fraction defined as a ratio of the total volume of atom spheres to the unit-cell volume is 0.642 and 0.662 respectively for  $\gamma\text{-Ag}_5\text{Zn}_8$  and  $\gamma\text{-Cu}_5\text{Zn}_8$ , which are comparable with the value 0.680 for the ideal  $A2$ -type structure. The  $\gamma$ -brass structure is therefore one of the compact arrangements of atoms of dissimilar sizes with the composition ratio 5:8.

When pressure is applied to the  $\gamma$ -brass structure, the interatomic distances are seen to be nearly uniformly decreased. Since the packing fraction of  $\gamma\text{-Ag}_5\text{Zn}_8$  is a little smaller than that of  $\gamma\text{-Cu}_5\text{Zn}_8$ , the compressibility of the former is expected to be larger than the latter and this is in accordance with the observations in the present X-ray measurements. If the 26-atom cluster is regarded as a big atom, the behavior of the  $\gamma$ -brass structure seems to be similar to that of the  $A2$ -type structure of the transition metals, in which atom cores are in contact with each other. The  $\gamma$ -brass structure is small in its compressibility and stable even at very high pressures, as is the  $A2$ -type structure of vanadium, chromium, niobium and molybdenum.

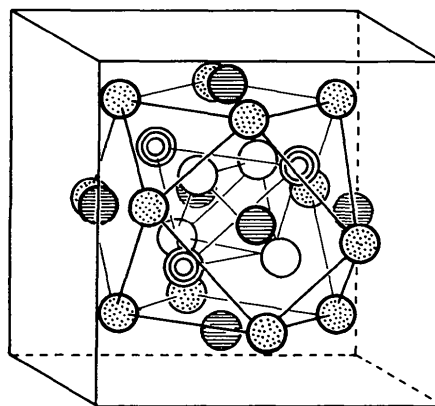


Fig. 4. Cluster of 26 atoms in the  $\gamma$ -brass structure. Open circles represent inner tetrahedron, concentric circles outer tetrahedron, dotted circles cuboctahedron and hatched circles octahedron (after von Heidenstam, Johansson & Westman, 1968).

The observed high resistance against compression of the  $\gamma$ -brass structure may suggest that the bonding is partly of covalent type. On the basis of the measurements of several electronic properties, Menth (1967) showed that the  $\gamma$  phase in the copper-zinc system should be regarded as a semimetal. If this interpretation is correct, the force which holds the atomic clusters firm will be a direct bonding between atoms. In order to clarify the character of the bonding, however, further investigation, both theoretical and experimental, is necessary.

The assistance of Mr H. Harada in operating the high-power X-ray generator RU-500 is greatly acknowledged. The present work has partly been supported by a Grant-in-Aid for Scientific Research.

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## The Structure of Tricaesium Octacyanomolybdate(V) Dihydrate, $\text{Cs}_3\text{Mo}(\text{CN})_8 \cdot 2\text{H}_2\text{O}$ – a New Stereochemical Configuration for $[\text{M}(\text{CN})_8]^{n-}$ Ions

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(Received 20 April 1978; accepted 28 February 1980)

#### Abstract

The crystal structure of  $\text{Cs}_3[\text{Mo}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$  has been determined by single-crystal X-ray diffraction. The compound crystallizes in the monoclinic space group  $P2_1/m$  with two molecules in a unit cell of dimensions  $a = 8.682$  (6),  $b = 14.198$  (9),  $c = 8.477$  (7) Å and  $\beta = 117.91$  (10)°. The final  $R$  value for all the observed reflections was 0.039. The Mo atom is coordinated to eight cyano groups in a geometric form which can be best described as a 4,4-bicapped trigonal prism. The mean Mo–C and C–N distances are 2.17 (2) and 1.14 (2) Å respectively. Two distinct classes of  $\text{Cs}^+$  ions are present, having cubic and 4,4,4-tricapped trigonal-prismatic environments respectively.

#### Introduction

$\text{Cs}_3[\text{Mo}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$  and  $\text{Cs}_3[\text{W}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$  (in contrast to the other alkali-metal salts) can be used as analytical primary standards as a result of their high stability (Basson, Bok & Grobler, 1974).

The  $[\text{M}(\text{CN})_8]^{n-}$  ions ( $M = \text{Mo}$  or  $\text{W}$ , and  $n = 3$  or 4) are also of great spectroscopic and crystallographic interest (Lippard, 1967). Various spectroscopic investigations, of which the Mössbauer studies have proved to be the most successful (Clark, Gancedo, Maddock & Williams, 1975), have been carried out to determine the geometries of these ions in the solid state and in solution, often with contradictory results. X-ray crystallographic studies have provided examples of dodecahedral ( $D_{2d}$ ) as well as square-antiprismatic ( $D_{4d}$ ) configurations for  $[\text{M}(\text{CN})_8]^{n-}$  ions (Basson, Bok & Leipoldt, 1970; Corden, Cunningham &

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