Modulated structure of β-brass CuZn compressed to 90 GPa

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Abstract. Cu–Zn is a classic example of an alloy system displaying a sequence of phases along an alloy composition, called Hume-Rothery phases. The crystal structure of these phases is determined by valence electron concentration (that is the average number of valence electrons per atom), and the lowering of the electronic energy is considered the key factor for the structure stabilization. Using powder x-ray diffraction, we study the \textit{E}-phase of an equiatomic CuZn alloy in its body-centered cubic (bcc) phase in the pressure range up to 90 GPa and find a transformation to a modulated trigonal structure at around 40 GPa. We analyze the structural distortion of bcc CuZn by looking at the configuration of the Brillouin zone of the bcc and the trigonal structures and their interaction with the Fermi surface. We demonstrate that the stabilization of the complex high-pressure structure can be explained with the Hume-Rothery effect.

1. Introduction

Several complex crystal structures have been reported recently in elemental metals under pressure (see reviews [1-3]), including incommensurately modulated and host-guest structures. The traditional explanation of the pressure-induced complexity of the alkali and alkali-earth metals suggests an s-d electron transfer (see review [4]). However, the observation of a large number of structural transformations and a variety of structural types in alkali metals under pressure prompted consideration of other factors that might be responsible for the formation of these phases [2]. Thus, for the complex cubic structure of Li with 16 atoms in the unit cell that appears at around 40 GPa, as well as the long period superstructures of Rb and Cs with 52 and 84 atoms in the unit cell, respectively, a Hume-Rothery mechanism has been suggested to be responsible for the stability of these structures [2]. Formation of a Brillouin-Jones zone with many planes in a close contact with the Fermi surface leads to an opening of an energy pseudo-gap and lowering of the electronic energy, which provides minimization of the lattice energy.

Hume-Rothery effect has been known to stabilize complex phases in some binary alloys (for example Cu–Zn) at ambient pressure. Cu–Zn is a classic example of an alloy system displaying a sequence of phases along the alloy composition, called Hume-Rothery phases. The crystal structure of these phases and their boundaries of stability along the alloy composition are determined by valence electron concentration (that is the average number of valence electrons per atom) [5].
Here, in the first row, the sequence of the Hume-Rothery phases is shown as observed along the alloy composition, where fcc stands for face-centered cubic, bcc – for body-centered cubic, and hcp – for hexagonal close-packed structures. In the second row, the upper boundaries of stability of these phases are shown using valence electron concentration that is directly related to the alloy composition, with the number of valence electrons equal to 1 for Cu and 2 for Zn. The stability of these phases is attributed to the Brillouin zone - Fermi surface interaction, i.e. it is caused by the Hume-Rothery effect. This interaction between the Brillouin zone and Fermi surface increases with pressure. On compression, the electronic contribution to the energy dominates over the electrostatic contribution (the former goes as $V^{-2/3}$, the latter as $V^{-1/3}$, with $V$ denoting the volume), and the electronic energy is lowered by the appearance of new Bragg planes near the Fermi surface as the system adopts structures of lower symmetry. Thus, this stabilization factor becomes more important on compression.

In this respect, it is interesting to study the stability of Hume-Rothery phases in Cu-Zn under pressure. One can expect a phase transition in the $\alpha$- and $\beta$-phases with fcc and bcc structures, respectively, to more complex phases due to an enhancement of Hume-Rothery effect on compression. Indeed, our recent preliminary results on phase stability of Cu–Zn alloys to 50 GPa showed that $\alpha$-phase started to transform to a more complex phase at 17 GPa, $\beta$-phase also started to transform at 37 GPa, while $\gamma$-phase with a complex cubic structure remained stable to the maximum pressure of that study [6].

In subsequent work [7], we studied pressure effects on the $\beta$-phase (bcc structure), collecting diffraction data with improved quality and also to much higher pressure of 90 GPa. We observe diffraction patterns corresponding to a structural distortion of the bcc phase above 40 GPa, that show splitting of the main bcc reflections and appearance of the additional weak reflections. Here we report a tentative structure solution of this high-pressure phase on the basis of a trigonal modulated structure and attribute its formation and stability to the enhanced Hume-Rothery effect.

2. Experimental details
The $\beta$-phase of a Cu–Zn alloy with the composition Cu – 50at%Zn (further denoted as CuZn) was prepared by melting the proper amounts of Cu and Zn of 4N purity in evacuated silica tubes. It has a body-centered cubic (bcc) structure. Whether or not this alloy is chemically ordered, cannot be established from x-ray diffraction, as Cu and Zn have nearly identical atomic scattering factors for an x-ray beam. The alloy was studied under pressure using angle-dispersive x-ray diffraction with synchrotron radiation (beam line 16-ID-B (HPCAT) at the APS in the Argonne National Laboratory. The sample was loaded in a symmetrical Mao-Bell cell in a sample chamber of the rhenium gasket together with nitrogen as a pressure-transmitting medium. To determine the pressure, we used in situ fluorescence measurements of ruby chips loaded in the sample chamber [8]. After closing the cell with the sample and nitrogen, the pressure in the cell was measured as 44.5 GPa. Diffraction patterns from CuZn were collected from 44.5 GPa to 90.0 GPa, the maximum pressure reached in this study. A focused monochromatic beam of wavelength $\lambda = 0.3678$ Å was used and the data were recorded on a MAR image plate. Diffraction data were integrated azimuthally using FIT2D [9], and structural information was extracted from a Lebail fit to the full profile using JANA2000 [10]. Cell parameters and the value of the modulation wavevector were obtained from the least-square fit of main and modulation reflections using the U-FIT [11].

3. Results and Discussion
A body-centered cubic (bcc) phase was observed in CuZn up to 37 GPa in our previous studies [6], before the splitting of the main reflections started to be evident. In the present experiment, the splitting of the (110), (211) and (220) bcc reflections is observed from 44.5 GPa, the lowest pressure of this experiment, while the (200) does not split during the compression (Fig. 1).
On pressure increase to 46 GPa, additional reflections with weak intensity start to appear. This is at slightly higher pressure than observed in our previous experiment [6], where the additional reflections appeared at 37 GPa. The difference probably arises from the fact that we used a different pressure transmitting medium (liquid nitrogen) in this experiment which is known to give a better quasi-hydrostatic pressure transmitting medium in comparison to the ethanol-methanol mixture used in previous experiment [6]. In the present experiment, one extra reflection appears above 46 GPa (Fig. 1a). Above 66 GPa, many more extra lines are visible, which could be interpreted as a transition to a more complex phase or that it is still the same phase and the extra reflections were too weak to be observed at lower pressure. The splitting of the main reflections and weak additional reflections are clearly visible on the 2D diffraction image of CuZn at 90 GPa (Fig. 1b). The lines from nitrogen, used as pressure transmitting medium, can be tracked using data from [12]. \(\varepsilon\)-N\(_2\) transforms at 62 GPa to zeta-phase, where a strong line appears at around 1.88 Å, overlapping with the first group of strong reflections of CuZn at 62 GPa. It shifts to 1.83 Å at 90 GPa and can explain a weak reflection observed in our data at 1.83 Å. There are no diffraction peaks from rhenium gasket in any of the spectra.

Summarising our present results and combining them with those from [6], we conclude that the bcc CuZn phase transforms at 41(4) GPa to a more complex high-pressure phase, where the main reflections split and the extra weak reflections appear.

![Figure 1](image.png)

**Figure 1.** (a) Pressure dependence of the d-spacings observed for the CuZn alloy in its bcc phase and the high-pressure phase, which is shown to be trigonal modulated. The d-spacings of the bcc phase are shown with solid squares (data are taken from [6]) and their indexing is given; the main reflections of the trigonal modulated phase are shown with solid diamonds and the weak superstructure reflections – with open diamonds. Dotted lines show the calculated positions of Re, used as a gasket material, to demonstrate that these positions do not overlap with the sample reflections. (b) 2D diffraction image from CuZn alloy at pressure of 90 GPa, with two insets showing an enlarged view on the first strong group of reflections that consists of a splitted main peak (corresponding to the (110) peak of bcc) and superstructure reflections.

First, we describe our attempt to account for the splitting of the bcc reflections. As the positions and the intensities of the main peaks of the high-pressure phase are close to those of bcc phase, we have searched for a structure that would be a slight distortion of the bcc structure. A possible cell that describes the splitting is a rhombohedral distortion of the bcc with \(a_r = 2.270\) Å and \(\alpha = 109.28^\circ\) at 90 GPa (close to the ideal value for bcc \(\alpha = 109.47^\circ\)) with one atom in the unit cell in the position
1 \alpha \ (0 \ 0 \ 0) \ of \ the \ space \ group \ R-3m. \ In \ the \ hexagonal \ setting, \ the \ lattice \ parameters \ are \ a = 3.703(3) \ \AA, \ c = 2.292(3) \ \AA \ with \ three \ atoms \ in \ the \ unit \ cell \ in \ the \ position \ 3\alpha \ (0 \ 0 \ 0), \ (1/3 \ 2/3 \ 2/3) \ and \ (2/3 \ 1/3 \ 1/3). \ A \ similar \ rhombohedral \ distortion \ has \ been \ proposed \ for \ the \ bcc \ structure \ in \ elemental \ vanadium \ under \ pressure \ [13], \ with \ no \ additional \ reflections \ observed. \ If \ we \ now \ search \ for \ a \ superstructure \ to \ describe \ the \ additional \ weak \ reflections \ of \ CuZn, \ however, \ no \ suitable \ solution \ can \ be \ found. \ We \ search \ for \ a \ solution \ creating \ a \ modulated \ superstructure \ using \ (3+1)-dimensional \ superspace \ groups \ [14]. \ The \ corresponding \ (3+1)D \ superspace \ group \ R-3m(00\gamma) \ does \ not \ give \ any \ suitable \ solutions \ for \ any \ value \ of \ the \ modulation \ vector \ \gamma. \ This \ is \ why \ we \ need \ to \ choose \ a \ different \ basic \ structure.

A \ trigonal \ structure \ with \ the \ same \ lattice \ parameters \ but \ with \ lower \ space \ group \ P-3m \ and \ atoms \ in \ the \ positions \ 1\alpha \ (0 \ 0 \ 0) \ and \ 2d \ (1/3 \ 2/3 \ 1/3) \ and \ (2/3 \ 1/3 \ 2/3) \ (inset \ in \ Fig. \ 2) \ also \ describes \ the \ positions \ of \ the \ main \ reflections \ (see \ upper \ row \ of \ tick \ marks \ in \ Fig. \ 2). \ Similar \ distortion \ of \ the \ bcc \ structure \ is \ known \ for \ Ti \ and \ Zr \ at \ the \ \beta \ \to \ \omega \ \ phase \ transition \ (see \ [1] \ and \ references \ therein). \ This \ solution \ predicts, \ however, \ several \ reflections \ with \ zero \ intensity \ that \ are \ not \ observed \ in \ the \ experiment. \ In \ attempt \ to \ describe \ the \ positions \ of \ superstructure \ reflections \ we \ construct \ a \ modulated \ structure \ with \ the \ corresponding \ (3+1)D \ superspace \ group \ P-3m1(00\gamma). \ The \ value \ of \ \gamma \approx 0.2 \ predicts \ positions \ of \ the \ modulated \ reflections \ that \ describe \ the \ observed \ additional \ weak \ reflections \ in \ CuZn \ at \ 90 \ GPa \ (see \ lower \ row \ of \ tick \ marks \ in \ Fig. \ 2). \ The \ refined \ value \ of \ the \ modulation \ vector \ is \ \gamma = 0.202(2) \ at \ 90 \ GPa, \ which \ was \ obtained \ from \ a \ least-square \ fit \ of \ main \ and \ modulation \ reflections \ using \ the \ U-FIT \ program \ [11]. \ One \ unsplit \ main \ reflection \ ((200) \ in \ the \ bcc \ setting) \ was \ used \ for \ the \ refinement \ together \ with \ several \ non-overlapping \ modulation \ reflections. \ Analysis \ of \ the \ superspace \ group \ symmetry \ shows \ that \ the \ modulation \ wave \ has \ a \ non-zero \ component \ along \ the \ trigonal \ axis, \ and \ the \ atoms \ can \ be \ shifted \ only \ along \ the \ trigonal \ axis.

**Figure 2.** Integrated diffraction pattern of the CuZn alloy sample in the high-pressure phase at 90 GPa. Indexing on the basis of the long-period supercell with the five-fold c-axis is shown. The indices in black correspond to the main reflections, while the indices in italic grey correspond to the superstructure reflections. The upper row of reflections shows the calculated positions for the main reflections, and the lower row shows the superstructure (or modulated) reflections. (Inset) The basic trigonal structure of the high-pressure phase of CuZn with the cell outlined with solid lines, shown in relation to the bcc structure outlined with dashed lines.
At 90 GPa, the refinement of the structural parameters of CuZn for the trigonal solution in the P-3m1(00γ) superspace group are: \( a = 3.703(3) \) Å, \( c = 2.292(3) \) Å, \( γ = 0.202(2) \). The value of the modulation vector equal 1/5 within the error, and that means that this modulated structure can be described by a long-period cell with the 5-fold c-axis. The resulting lattice parameters are \( a = 3.703 \) Å and \( c = 11.460 \) Å. All observed reflections can be now re-indexed with three integer hkl’s (space group P3), as shown in Fig. 2.

The reason for the structural distortion of the bcc phase and appearance and stability of the modulated trigonal structure can be understood within the Hume-Rothery mechanism. We analyze the structural distortion of the bcc phase CuZn by looking at the configuration of the Brillouin zone of the bcc and the trigonal structures and their interaction with the Fermi surface using the program BRIZ\[15\]. The number of planes in the Brillouin zone increases (Fig. 3); zone filling with electronic states increases from 75% (bcc) to 81% (trigonal structure). This brings more of the lower-energy electrons in states of higher density and the overall electronic energy is expected to be reduced. These factors indicate an enhancement of the Hume-Rothery mechanism under pressure.

We note, that a known example of a formation of a long-period superlattice in an alloy is the CuAu-II phase\[16,17\], and its stability has also been described using the Hume-Rothery effect. There are, however, differences to the present case of the high-pressure modulated structure of CuZn. CuAu has one valence electron per atom forming a tetragonal structure, and its superlattice is stabilized by adjusting an existing strong plane of the Brillouin zone to the Fermi surface to minimise the electronic energy. CuZn has on average valence electron concentration of 1.5 forming a bcc phase (Hume-Rothery phase). The displacive modulation found in the present work under pressure leads to a formation of new planes in the Brillouin zone (Fig. 3) that causes further reduction of the electronic energy.

**Figure 3.** The configuration of the Brillouin zone and the Fermi sphere for the bcc structure (left) and the modulated trigonal structure (right).
4. Summary and conclusions.
We have reported a structural distortion of the bcc phase of CuZn at pressures above 40 GPa and proposed a tentative structure solution based on a modulated trigonal cell. The analysis of the interaction of the Brillouin-Jones zone and the Fermi sphere showed a pressure-induced enhancement of the Hume-Rothery effect as a mechanism for structure stabilization. These findings are relevant to the understanding of the formation and stability of the high-pressure phases of Li that have been suggested to stabilize due to the Hume-Rothery mechanism [2].

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