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2005 J. Phys.: Condens. Matter 17 7955

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# Stability of Hume-Rothery phases in Cu–Zn alloys at pressures up to 50 GPa

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Received 10 June 2005, in final form 22 August 2005

Published 2 December 2005

Online at [stacks.iop.org/JPhysCM/17/7955](http://stacks.iop.org/JPhysCM/17/7955)

## Abstract

The crystal structure of the  $\gamma$ -brass phase  $\text{Cu}_5\text{Zn}_8$  is confirmed with single-crystal x-ray diffraction and CCD detector to be cubic with 52 atoms in the unit cell, space group  $I\bar{4}3m$ , and the refined atomic positions are in good agreement with previously reported data. The structural behaviour of  $\alpha$ -(fcc),  $\beta$ -(bcc), and  $\gamma$ -brass ( $cI52$ ) phases of the Cu–Zn alloy system has been studied under pressure using diamond anvil cells and powder x-ray diffraction with synchrotron radiation. The appearance of additional peaks in the diffraction patterns of  $\alpha$ - and  $\beta$ -phases indicates the beginning of transitions to new phases at 17 and 37 GPa, respectively. The complex cubic  $\gamma$ -brass phase is observed to be stable up to at least 50 GPa. The bulk modulus  $K_0$  was determined as 140(4) GPa for  $\alpha$ -, 139(5) GPa for  $\beta$ -, and 121(2) GPa for  $\gamma$ -phase assuming  $K'_0 = 4$ . The structural stability of brass phases of the Cu–Zn system under pressure is discussed in terms of a Hume-Rothery mechanism.

## 1. Introduction

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 electron concentration (that is the number of valence electrons per atom) [1]:

$$\begin{array}{ccccccc} \alpha(\text{fcc}) & \rightarrow & \beta(\text{bcc}) & \rightarrow & \gamma(\text{complex cubic}) & \rightarrow & \varepsilon(\text{hcp}) \\ 1.35 & \rightarrow & 1.5 & \rightarrow & 1.62 & \rightarrow & 1.75 \text{ (electron/atom)}. \end{array}$$

Similar phase sequences exist in other binary alloy systems containing noble and polyvalent metals [2]. The stability of crystal structures at certain electron concentrations in these alloys was explained by the Hume-Rothery concept [3, 4]. The criterion of stability for a crystal structure is a contact of a Brillouin zone (BZ) plane to the Fermi surface (FS), where the FS is considered to be a sphere in the nearly-free electron approximation. The formation of an

energy pseudo-gap at the BZ boundary lowers the kinetic energy of the valence electrons and accounts for the stability of the structure.

The  $\gamma$ -phase of Cu–Zn alloy with the composition  $\text{Cu}_5\text{Zn}_8$  has a complex cubic structure with 52 atoms per unit cell, space group  $I\bar{4}3m$  (Pearson symbol  $cI52$ ), and the lattice parameter 8.86 Å [5]. The  $\gamma$ -brass structure can be regarded as a  $3 \times 3 \times 3$  supercell of a body-centred cubic (bcc) structure. In this supercell, two out of 54 atoms are removed and the remaining 52 atoms are slightly displaced from their ideal positions. The packing fraction of the  $\gamma$ -brass structure, defined as a ratio of the total volume of atom spheres to the unit cell volume, equals 0.655 (or 0.662 [6]), which is smaller than the value of 0.68 for the bcc structure. One can therefore expect a phase transition under pressure from the ‘vacant’ or open  $\gamma$ -structure to a more close-packed structure. The  $\gamma$ -brass  $\text{Cu}_5\text{Zn}_8$  phase has been previously found to be stable under pressure up to 16 GPa [6]. The question arises about the stability of the  $\gamma$ -brass structure at higher pressures, also in comparison with the structural stability of the close-packed phases  $\alpha$  and  $\beta$ .

In our present work, we studied the complex cubic structure of the  $\gamma$ -brass  $\text{Cu}_5\text{Zn}_8$  phase together with the *fcc* structure of the  $\alpha$ -brass  $\text{Cu}_{75}\text{Zn}_{25}$  phase and the bcc structure of the  $\beta$ -brass  $\text{CuZn}$  phase up to pressures of 50 GPa. The study of these phases in the extended pressure range may give us a better understanding of their structural stability at ambient pressure. We discuss the results on Cu–Zn phase stability in the frame of the Hume-Rothery effect.

## 2. Experimental techniques

Alloys of Cu with 25, 50 and 62 at.% Zn were prepared by melting the proper amounts of Cu and Zn of 4N purity in evacuated silica tubes. Single-crystal samples were grown by the Bridgman method. The alloys have been characterized at ambient conditions by means of powder and single-crystal x-ray diffraction and found to correspond to the literature data [5, 7]. The microprobe analysis of the samples has confirmed the corresponding composition of the alloys and also has shown that the phases are homogeneous.

Single-crystal x-ray diffraction data of the  $\gamma$ -brass  $\text{Cu}_5\text{Zn}_8$  sample were collected on the Bruker D8 diffractometer at the Geophysical Laboratory, which is equipped with an APEX CCD detector and an Mo ( $\lambda = 0.7107$  Å) x-ray tube. The structure was solved and refined using direct methods with the programs SMART, RLATT and SAINTPLUS. The result confirmed the structure solution from single-crystal data first reported in [7].

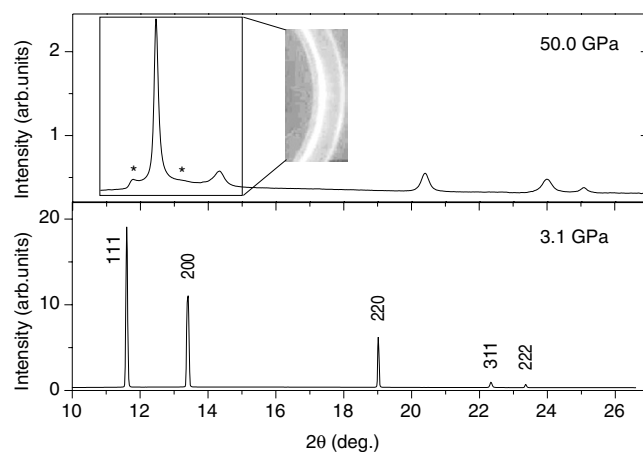
The  $\text{Cu}_3\text{Zn}$ ,  $\text{CuZn}$  and  $\text{Cu}_5\text{Zn}_8$  alloy phases were studied under pressure using powder angle-dispersive x-ray diffraction with synchrotron radiation. Samples were loaded in a symmetrical cell and a 4:1 methanol–ethanol mixture was used as a pressure-transmitting medium. To determine the pressure, we used *in situ* fluorescence measurements of ruby chips loaded in the sample chamber [8]. Powder diffraction data were collected at beam line 16-ID-B (HPCAT) at the Advanced Photon Source, Argonne National Laboratory. A focused, monochromatic beam of wavelength  $\lambda = 0.4237$  and 0.3680 Å was used and the data were recorded on a MAR image plate calibrated with a silicon standard. Diffraction data were integrated azimuthally using FIT2D [9], and structural information was obtained by Rietveld refinement of the integrated profiles [10].

## 3. Results

Single-crystal x-ray diffraction data were obtained for the  $\gamma$ -brass  $\text{Cu}_5\text{Zn}_8$  phase at ambient conditions. A total of 2358 reflections were collected to a resolution of 1.2 Å. These were averaged to give 295 unique reflections with  $F > 2\sigma(F)$ . The final fit to the structure gave

**Table 1.** Structural data on the Cu<sub>5</sub>Zn<sub>8</sub> alloy at ambient conditions. Space group  $I\bar{4}3m$ . Atomic positions refined from our single-crystal data are given in comparison with literature data [7].

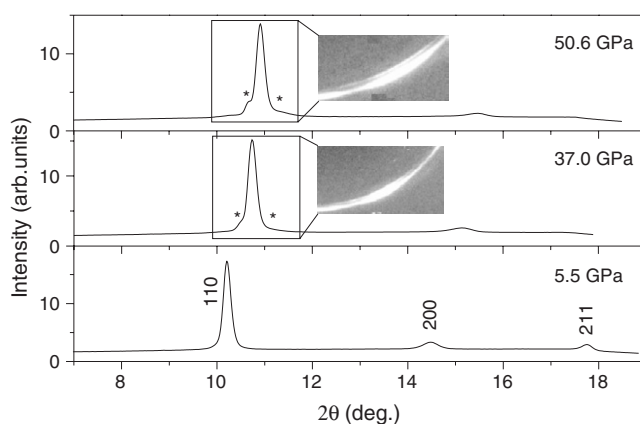
		Literature data [7]			Present data		
		<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>
Cu1	8c	0.8280(4)	0.8280(4)	0.8280(4)	0.8278(1)	0.8278(1)	0.8278(1)
Zn1	8c	0.1089(5)	0.1089(5)	0.1089(5)	0.1095(1)	0.1095(1)	0.1095(1)
Cu2	12e	0.3558(4)	0	0	0.3558(2)	0	0
Zn2	24g	0.3128(3)	0.3128(3)	0.0366(6)	0.3130(1)	0.3130(1)	0.0357(2)

**Figure 1.** Integrated diffraction pattern of the fcc  $\alpha$ -brass phase at 3.1 and 50.0 GPa ( $\lambda = 0.4237 \text{ \AA}$ ). *hkl* indices are given for the fcc phase. Additional diffraction peaks marked by asterisks on the pattern at 50.0 GPa indicate a possible phase transition. A part of diffraction image with the strongest diffraction peak is shown in the inset.

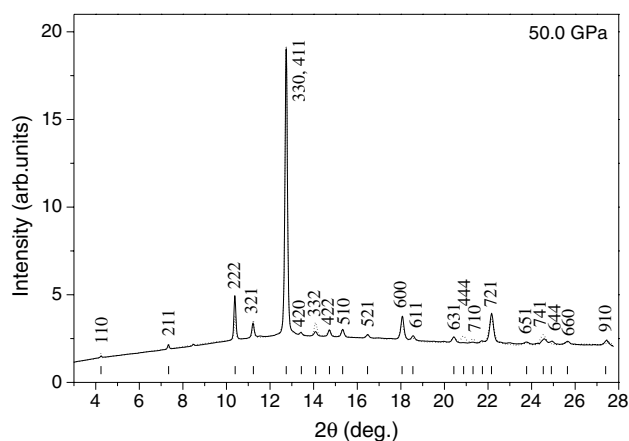
$R_1 = 5.9\%$  and a goodness of fit  $\chi^2$  of 1.134. The crystal structure is confirmed to be body-centred cubic with lattice parameter  $a = 8.856(2) \text{ \AA}$ , space group  $I\bar{4}3m$ , in accordance with [5, 7]. The atomic positions of Cu and Zn atoms are refined and are in agreement with previous single-crystal studies [7], as summarized in table 1.

High-pressure x-ray diffraction studies were performed on powder samples of  $\alpha$ -brass Cu<sub>3</sub>Zn,  $\beta$ -brass CuZn and  $\gamma$ -brass Cu<sub>5</sub>Zn<sub>8</sub> phases to study their structural stability and compressibility. These phases were followed up to 50 GPa, the maximum pressure reached in this study. Diffraction patterns of the fcc  $\alpha$ -phase obtained on pressure increase are shown in figure 1. The diffraction peaks at all pressures can be indexed on the basis of the fcc phase. Some weak features were observed above 17 GPa, implying a possible beginning of a phase transition. Diffraction patterns of the  $\beta$ -brass CuZn alloy are consistent with the bcc structure up to 50 GPa. Some additional features appear above 37 GPa, indicating the beginning of a transition to a new phase, as shown in figure 2. No phase transitions have been observed for the  $\gamma$ -brass up to 50 GPa. Figure 3 shows diffraction pattern of  $\gamma$ -brass at 50 GPa together with Rietveld refinement with atomic positions fixed to the ambient pressure values. The refined lattice parameter of  $\gamma$ -brass at 50.0 GPa is  $a = 8.100(1) \text{ \AA}$ .

The pressure dependence of the atomic volume of these phases is plotted in figure 4. The data were fitted with the second-order Birch–Murnaghan equation. The bulk modulus of  $\alpha$ -brass is  $K_0 = 140(4) \text{ GPa}$ , for  $\beta$ -brass  $K_0 = 139(5) \text{ GPa}$  and for  $\gamma$ -brass  $K_0 = 121(2) \text{ GPa}$ ,



**Figure 2.** Integrated diffraction patterns of the bcc  $\beta$ -brass phase for selected pressures ( $\lambda = 0.3680 \text{ \AA}$ ).  $hkl$  indices are given for the bcc phase. Additional diffraction peaks marked by asterisks on the patterns above pressures of 37 GPa indicate a possible phase transition. Parts of diffraction images with the strongest diffraction peak are shown in the insets.

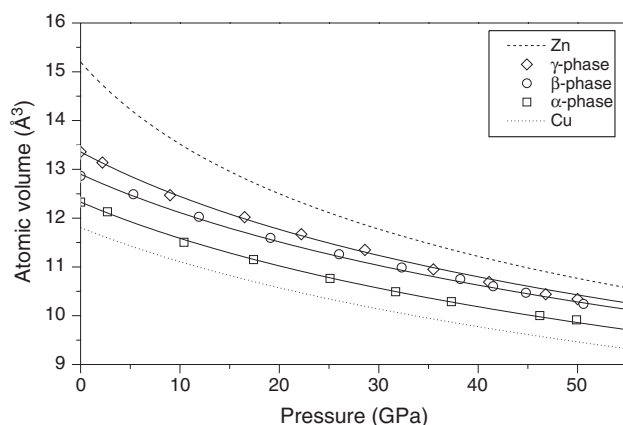


**Figure 3.** Integrated diffraction pattern of the  $\gamma$ -brass phase at 50.0 GPa ( $\lambda = 0.4237 \text{ \AA}$ ) and Rietveld refinement ( $R_p = 3.45$ ;  $R_{wp} = 5.94$ ;  $R_{exp} = 0.01$ ). Solid and dashed lines show experimental and calculated profiles, respectively. Tick marks below the diffraction profile show predicted peak positions. The  $hkl$  indices are shown.

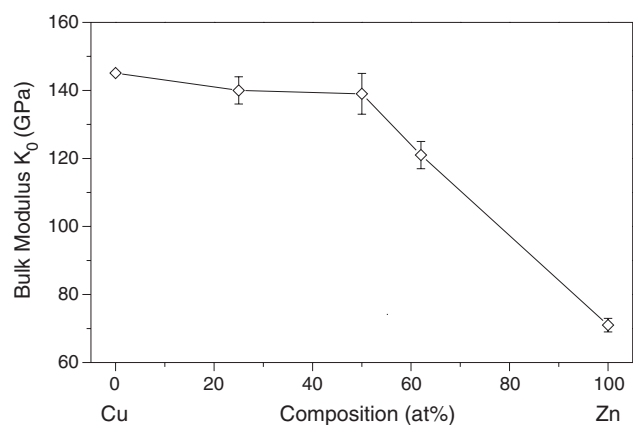
with fixed value  $K'_0 = 4$ . The value of  $K_0$  for  $\gamma$ -brass agrees well with the value of 123(3) reported in [6]. It is found that  $\alpha$ -,  $\beta$ - and  $\gamma$ -phases have a lower compressibility than expected from the average values between constituents (figure 5).

#### 4. Discussion

The criterion of stability for the crystal structures in the Cu–Zn alloy system, as was suggested by Jones [4], is a contact of the Brillouin zone (BZ) plane with the Fermi surface (FS), or the so-called Hume-Rothery effect. Here, the FS is considered to be a sphere within the nearly free electron approximation. The interaction between the BZ boundary and the FS opens a pseudo-gap and reduces the electronic energy, which leads to the lowering of the overall



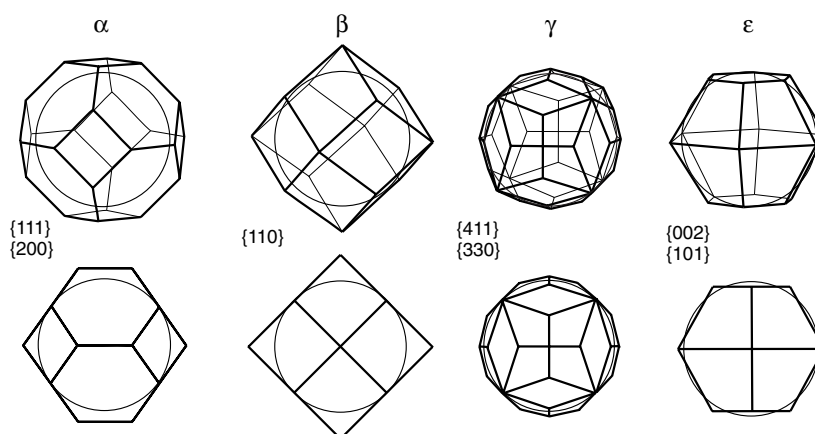
**Figure 4.** The atomic volume as a function of pressure for the  $\alpha$ -,  $\beta$ -, and  $\gamma$ -phases from present work, shown in comparison with literature data for pure elements Cu [11] and Zn [12]. All data are fitted with the second-order Birch–Murnaghan equation of state with  $K_0'$  fixed to 4 to allow comparison.



**Figure 5.** Bulk modulus  $K_0$  at ambient pressure for Cu–Zn  $\alpha$ -,  $\beta$ -, and  $\gamma$ -phases as a function of composition, compared with  $K_0$  values for pure elements. Data are obtained from the fit of the alloy data from present work and data for pure elements from [11, 12] to the second-order Birch–Murnaghan equation of state with fixed  $K_0' = 4$ .

structure energy. In figure 6, the configuration of the BZ and FS is shown for the  $\alpha$ -,  $\beta$ -,  $\gamma$ -, and  $\varepsilon$ -phases of the Cu–Zn alloys. The FS is schematically represented as a sphere with a radius  $k_F = (3\pi^2 z / V_{at})^{1/3}$ , where  $z$  is the number of valence electrons at the phase boundary ( $z = 1.35$  for  $\alpha$ -,  $1.5$  for  $\beta$ -,  $1.62$  for  $\gamma$ -, and  $1.75$  for  $\varepsilon$ -phases), and  $V_{at}$  is the atomic volume determined from the crystal structure. While the first BZ is shown for the  $\alpha$ - and  $\beta$ -structures, an extended Brillouin–Jones zone is shown for the  $\gamma$ -structure, constructed by the planes with the  $hkl$  indices that correspond the diffraction peaks with a large structure factor [4].

Next we discuss the Hume-Rothery effect at high compressions. The crystal-structure energy is usually approximated to consist of an electrostatic term and a band-structure contribution that have the respective scaling  $V^{-1/3}$  and  $V^{-2/3}$  with volume  $V$  (see [13, 14]). The latter contribution is expected to become more important with decreasing volume. This



**Figure 6.** Brillouin zones of Cu–Zn phases with the corresponding Fermi spheres at the boundaries of phase stability. Upper row—common view. Lower row—projections showing the contact of the Fermi spheres and Brillouin zone planes with given  $hkl$  indices (after [4]).

leads to an increase of the energy gap on the BZ planes and an increase of the BZ–FS interaction. Thus, the Hume-Rothery effects are enhanced at high pressure, as proposed by Ashcroft [15].

The proposed enhancement of the Hume-Rothery effect with increasing pressure accounts for the stability of the  $\gamma$ -brass structure up to 50 GPa shown in this study. The relative stability of the  $\alpha$ -,  $\beta$ -, and  $\gamma$ -structures is possibly connected with the relative contribution of the Hume-Rothery effect. For structure stability, it is important to have a BZ with many planes in contact with the FS and consequently a BZ nearly filled with electronic states. For the  $\gamma$ -phase, there are 36 BZ planes (of the  $\{411\}$  and  $\{330\}$  type) that are in contact with the FS, more than in the  $\beta$ -phase (12 planes of the  $\{110\}$  type) and the  $\alpha$ -phase (8 planes of the  $\{111\}$  type) (see figure 6). Also, the BZ of the  $\gamma$ -phase is almost filled (93%), in comparison with 76% zone filling for the  $\beta$ -phase and 62.5% for the  $\alpha$ -phase. The zone filling corresponds to the relative stability of these phases under pressure: no transition was observed for  $\gamma$ -brass up to 50 GPa; the beginning of a transition to a new phase was observed for  $\beta$ -brass at 37 GPa and for  $\alpha$ -brass at 17 GPa. For the  $\alpha$ - and  $\beta$ -phases at compression, a formation of complex structures can be expected, with a BZ containing more planes in contact with the FS and a better filling with electron states. Further studies are required to determine crystal structure of the newly appearing high-pressure phases in the  $\alpha$ - and  $\beta$ -brass alloys, for which evidence was obtained in the present work.

Recent *ab initio* calculations on the  $\text{Cu}_5\text{Zn}_8$  alloy [16] showed the stabilization of the complex  $\gamma$ -brass structure at ambient condition due to a formation of the energy pseudo-gap at the Fermi level by electrons resonating with the BZ planes  $\{411\}$  and  $\{330\}$  and giving rise to standing waves. These studies confirm the importance of the BZ–FS interaction (Hume-Rothery effect) for the stability of this structure. A similar theoretical picture for the  $\gamma$ -brass structure at high pressures is now required. Our experimental result on the stability of the  $\text{Cu}_5\text{Zn}_8$   $\gamma$ -phase to at least 50 GPa confirms the suggestion that the Hume-Rothery effect is enhanced under pressure.

It is interesting to compare the stability of the  $\text{Cu}_5\text{Zn}_8$   $\gamma$ -phase under pressure with the stability of the  $\alpha$ -Mn structure up to pressures of about 140 GPa [17]. Both structures belong to the same space group  $I\bar{4}3m$  and have the same BZ formed by planes  $\{330\}$  and  $\{411\}$ . Although the FS of Mn is quite complex due to the contribution of d-electrons, it does not

seem improbable that the stability of the  $\alpha$ -Mn structure may be for the same reason as the  $\gamma$ -phase of Cu–Zn alloy, i.e. the BZ–FS interaction.

An enhancement of the Hume-Rothery effect under pressure can lead to a formation of high-pressure phases with complex structures. It has recently been suggested that the Hume-Rothery effect explains [18] the appearance and the stability of the complex high-pressure structures in alkali metal Li-*cI16* [19]. It is proposed that the structural distortions from bcc give rise to new diffraction planes forming a BZ boundary close to the FS; interaction between the BZ boundary and the FS opens a pseudo-gap and reduce the overall electronic energy. These effects can also account for the complex, long-period structures Rb-*oC52* and Cs-*oC84* [20, 21] which are related to Li-*cI16*, with additional distortions due to the electron *s*–*d* transfer. The high-pressure phase Li-*cI16*, Rb-*oC52*, and Cs-*oC84* [19–21] thus should be considered as Hume-Rothery phases, similar to the classical Cu–Zn alloy phases. At compression Li shows an increase in resistivity at high temperatures [22] and an appearance and increase of superconductivity [23–25]. The reason for these is probably connected with the enhancement of the Hume-Rothery effect at high pressure.

In the Cu–Zn and other brass alloys, the  $\gamma$ -phase shows an anomalous behaviour of some physical properties, such as resistivity, magnetic susceptibility, Hall effect, magnetoresistance and thermoelectric power, which was accounted for by the band-structure effect associated with the BZ–FS interaction [26]. The observed structural stability of the  $\gamma$ -brass phase under pressure is a further indication on special features of its crystal structure.

In conclusion, we have studied the structure stability of the  $\alpha$ -,  $\beta$ -, and  $\gamma$ -brass phases of the Cu–Zn alloy system up to 50 GPa. We have shown that the close-packed  $\alpha$ - and  $\beta$ -structures begin to transform to new high-pressure phases, and the vacant  $\gamma$ -structure is shown to be stable up to at least 50 GPa. This observation supports the idea of the enhancement of the Hume-Rothery mechanism on compression.

## Acknowledgments

The authors thank M Somayazulu and E Gregoryanz for their assistance with data collection at HPCAT. The financial support by the Russian Foundation for Basic Research under the grant number 04-02-17343 is gratefully acknowledged. The authors acknowledge financial support from NSF, through grant EAR-0217389. The HPCAT facility is supported by DOE-BES, DOE-NNSA (CDAC), NSF, DOD–TACOM, and the W M Keck Foundation. The Advanced Photon Source is supported by the US Department of Energy, Office of Basic Energy Sciences, under Contract No. W-31-109-Eng-38.

## References

- [1] Hume-Rothery W 1926 Researches on the nature, properties, and condition of formation of intermetallic compounds *J. Inst. Met.* **35** 319–35
- [2] Massalsky T B (ed) 1996 *Binary Alloy Phase Diagrams* (Metals Park, OH: American Society for Metals)
- [3] Mott N F and Jones H 1936 *The Theory of the Properties of Metals and Alloys* (London: Oxford University Press)
- [4] Jones H 1962 *The Theory of Brillouin Zones and Electron States in Crystals* (Amsterdam: North-Holland)
- [5] Pearson W B 1967 *Handbook of Lattice Spacings and Structures of Metals and Alloys* (New York: Pergamon)
- [6] Iwasaki H and Okada M 1980 The  $\gamma$ -brass structure at high pressure *Acta Crystallogr. B* **36** 1762–5
- [7] Brandon J K, Brizard R Y, Chieh P C, McMillan R K and Pearson W B 1974 New Refinements of the  $\gamma$  Brass type Structures Cu<sub>5</sub>Zn<sub>8</sub>, Cu<sub>5</sub>Cd<sub>8</sub> and Fe<sub>3</sub>Z<sub>10</sub> *Acta Crystallogr. B* **30** 1412–7
- [8] Mao H K, Xu J and Bell P M 1986 Calibration of the Ruby Pressure Gauge to 800 kbar under quasi-hydrostatic conditions *J. Geophys. Res.* **91** 4673



- [9] Hammersley A P *et al* 1996 Two-dimensional detector software: from real detector to idealized image or two-theta scan *High Pressure Res.* **14** 235
- [10] Kraus W and Nolze G 1996 POWDER CELL—a program for the representation and manipulation of crystal structures and calculation of the resulting x-ray powder patterns *J. Appl. Crystallogr.* **29** 301
- [11] Dewaele A, Loubeyre P and Mezouar M 2004 Equations of state of six metals above 94 GPa *Phys. Rev. B* **70** 094112
- [12] Takemura K 1997 Structural study of Zn and Cd to ultrahigh pressures *Phys. Rev. B* **56** 5170
- [13] Harrison W A 1966 *Pseudopotentials in the Theory of Metals* (New York: Benjamin)
- [14] Heine V and Weaire D 1970 Pseudopotential theory of cohesion and structure *Solid State Physics* vol 24, ed H Ehrenreich, F Seitz and D Turnbull (New York: Academic)
- [15] Ashcroft N 2002 *IUCr XIX: International Union of Crystallography Congress and General Assembly (Geneva, Switzerland, Aug. 2002)*
- [16] Paxton A T, Methfessel M and Pettifor D G 1997 A bandstructure view of the Hume-Rothery electron phases *Proc. R. Soc. London* **A453** 1493–514
- Asahi R, Sato H, Takeuchi T and Mizutani U 2005 Verification of Hume-Rothery electron concentration rule in  $\text{Cu}_5\text{Zn}_8$  and  $\text{Cu}_9\text{Al}_4$   $\gamma$  brasses by *ab initio* FLAPW band calculations *Phys. Rev. B* **71** 165103/1–8
- [17] Fujihisa H and Takemura K 1995 Stability and the equation of state of alpha-manganese under ultrahigh pressure *Phys. Rev. B* **52** 13257–60
- [18] Degtyareva V F 2004 Novel Hume-Rothery phases in simple metals and alloys under high pressure *High Pressure Crystallography* ed A Katrusiak and P McMillan (Dordrecht: Kluwer) pp 447–56
- Degtyareva V F 2003 Brillouin zone concept and crystal structures of sp metals under high pressure *High Pressure Res.* **23** 253–7
- [19] Hanfland M, Syassen K, Christensen N E and Novikov D L 2000 New high-pressure phases of lithium *Nature* **408** 174–8
- [20] McMahon M I, Nelmes R J and Rekhi S 2001 Complex crystal structure of cesium-III *Phys. Rev. Lett.* **87** 255502
- [21] Nelmes R J, McMahon M I, Loveday J S and Rekhi S 2002 Structure of Rb-III: novel modulated stacking structures in alkali metals *Phys. Rev. Lett.* **88** 155503
- [22] Fortov V E, Yakushev V V, Kagan K L, Lomonosov I V, Postnov V I, Yakusheva T I and Kuryanchik A N 2001 Anomalous resistivity of lithium at high dynamic pressure *JETP Lett.* **74** 418–21
- [23] Shimizu K, Ishikawa H, Takao D, Yagi T and Amaya K 2002 Superconductivity in compressed lithium at 20 K *Nature* **419** 597–9
- [24] Struzhkin V V, Eremets M I, Gan W, Mao H K and Hemley R J 2002 Superconductivity in dense lithium *Science* **298** 1213–5
- [25] Deemyad S and Schilling J S 2003 Superconducting phase diagram of Li metal in nearly hydrostatic pressures up to 67 GPa *Phys. Rev. Lett.* **91** 167001
- [26] Mountfield K R and Rayne J A 1983 Electronic properties of bulk copper–aluminum and copper–zinc alloys *Phys. Rev. B* **27** 3263–72