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Structural and elastic properties of β-brass

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Abstract

First-principles calculations have been made for the 50–50 ordered alloy CuZn, β-brass, of the energy per atom in tetragonal structure as a function of the tetragonal lattice parameters a and c. A full-potential electronic-structure program was used with both the local-density approximation (LDA) and the generalized gradient approximation (GGA). Both formulations confirm the existence of a shallow energy minimum (the ground state) at $c/a = 1$ (β-brass has CsCl structure), and reveal the occurrence of a shallow secondary minimum at approximately $c/a = 1.26$. With decreasing electronic charge on the Zn atom this minimum becomes deeper, and moves toward larger c/a values, reaching the value $c/a = \sqrt{2}$ when one full electron is taken away from Zn, i.e., when Zn is replaced with Cu. The three elastic constants of β-brass have been calculated and compared with experiment. The large elastic shear anisotropy of β-brass discussed by Clarence Zener in 1947 has been confirmed in this work, although the anisotropy is not quite as large as the then available experimental data indicate.

1. Introduction

Binary alloys involving a noble metal (Cu, Ag, Au) and either a divalent (Zn, Be, Cd) or a trivalent metal (Al, Ga, Sn) have a β-phase, which in the phase diagram appears immediately to the right of the primary face-centred-cubic (fcc) phase of the pure noble metal [1]. These β-phase alloys have a body-centred-cubic (bcc) structure and satisfy the Hume–Rothery [2] rule as having all the same value of the ratio of valence electrons to atoms (1.5 for these alloys). The prototype, the CuZn alloy, β-brass, is bcc at high temperature with Cu and Zn atoms randomly arranged, and becomes ordered upon cooling (between 454 and 468 °C), with one type of atom occupying the body-centre position and the other type occupying the eight corners of the cubic unit cell. This phase is usually labelled β'. The structure of this phase is CsCl (B2), but we shall keep referring to it as bcc, which is the underlying structure. The bcc designation is particularly appropriate here because β-brass might be considered for some purposes (such as the Hume–Rothery rules) a bcc lattice of atoms with atomic number $Z = 29.5$.

Previous theoretical studies of the CuZn system [3, 4] assumed that the structure was either bcc (CsCl) or fcc and calculated energies as functions of the atomic fraction of Zn atoms to

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determine the more stable structure as the fraction varied. The calculations done in this paper consider only the *ordered* 50–50 CuZn composition, but use the modern total-energy theory which contains all contributions to the system energy, including electron–electron interactions in either the local-density approximation (LDA) or the generalized gradient approximation (GGA). The many approximations of the previous theories are avoided, and it is not necessary to study the relation, used in previous work, of the Fermi level to the density of states. The bcc structure is *proved* to be a stable equilibrium structure by showing that it is a minimum with respect to all small strains. Moreover, a second tetragonal equilibrium structure is found, which is shown to be the modification of the fcc equilibrium state of pure Cu produced by replacement of Cu atoms with Zn. The LDA finds the bcc structure to be the ground state, in agreement with experiment, but the GGA gives the wrong ground state by making the second tetragonal equilibrium state lower by about 0.1 mRy atom^{-1}.

The bcc character of the β-brass structure is interesting because it shows that, starting from pure fcc Cu, the replacement of one half of the atoms of Cu with Zn atoms, which have just one electron more than Cu, is sufficient to change the ground-state structure from fcc to bcc. We will discuss this characteristic of β-brass more extensively below.

A property of β-brass, which is common to all β-phase alloys, is the triangular shape of their stability region in the phase diagram, namely, the fact that the concentration range of the β-phase narrows with decreasing temperature, a fact which would cause the phase to disappear if the critical temperature for ordering did not occur first. This peculiar property of β-phase alloys was explained by Clarence Zener in 1947 [5].

Another property of these alloys is their large elastic anisotropy, namely, a large value of the ratio c_{44}/C' between the shear constant c_{44} for [110] shear in (100) planes and the shear constant $C' = (c_{11} - c_{12})/2$ for $[1\bar{1}0]$ shear in (110) planes. This property was also addressed by Zener in his insightful 1947 paper [5]. At that time β-brass was the only β-phase alloy known to exhibit this property (the c_{44}/C' ratio was believed to be 18), but Zener predicted that the same large anisotropy would be common to all β-phase alloys—a prediction that was later confirmed by experiment [6].

Zener observed that the large elastic anisotropy was a consequence of an 'anomalously low value' of C' and an 'anomalously large value of the c_{44} shear constant'. He could explain the former as the 'direct consequence of the combination of a body-centred-cubic lattice with ions containing only closed shells', but could find 'no satisfactory explanation' for the latter anomaly. We will point out below that the experimental data for c_{44} available to Zener at the time were just incorrect and that in fact c_{44} is quite normal. But Zener's analysis of the C' constant was remarkably insightful at a time when electronic structures calculations were not first principles.

Zener argued that the elastic constants are predominantly determined by two energy terms: (1) the exchange interaction between ions, which in a bcc structure is repulsive when positive ions contain only closed shells, and gives a negative contribution to C'; and (2) the electrostatic interaction between conduction electrons and ions, which always gives a positive contribution to C'. In a hypothetical bcc structure of Cu Zener concluded from the calculations of Fuchs [7] that the negative contribution of the exchange interaction would be larger than the positive contribution of the electrostatic interaction, and therefore in a bcc Cu structure C' would be negative, i.e., 'the lattice would be mechanically unstable'. This prediction was in fact confirmed by recent total-energy calculations on bulk elemental Cu [8]. In β-brass the small value of C' reflects the 'tendency of the ion exchange interaction to render the bcc lattice mechanically unstable' [5] with respect to a (110) shear in the $[1\bar{1}0]$ direction.

The present work addresses both the structural and the elastic properties of β-brass by calculation of the pertinent epitaxial Bain path (EBP), which links bcc and fcc structures, and

of the three elastic constants c_{11}, c_{12} and c_{44} in the bcc ground state with the WIEN97 computer program [9]. The EBP [10,11] as calculated here is a path through tetragonal states which passes through all tetragonal *equilibrium* states, where the energy is a minimum with respect to both a and c, and through tetragonal states that may be produced by epitaxial (biaxial) strain of the equilibrium states. One aspect of the EBP is shown by a plot of the energy/atom as a function of the axial ratio c/a between the two lattice constants c and a that characterize a tetragonal unit cell. The value $c/a = 1$ corresponds to the bcc structure, the value $c/a = \sqrt{2}$ to the fcc structure. We show that the EBP exhibits a shallow minimum at $c/a = 1$, in agreement with the existence of the bcc phase of β-brass. We also show that the calculated elastic constants are in fair agreement with the recent experimental values. We then address the effect on the crystal structure of reducing the electronic charge on the Zn atoms, and show that the EBP progressively changes toward the shape of the EBP of pure Cu for decreasing charge on the Zn atoms.

We describe in section 2 the calculations, in section 3 the results, and in section 4 the conclusions.

2. Calculations

The WIEN97 program [9] uses the full-potential linearized augmented plane wave (FLAPW) method to calculate total energies for a variety of crystal structures and space groups either nonrelativistically (NREL) or relativistically (REL) with electron–electron interactions either in the local-density approximation (LDA) or modified by the generalized gradient approximation (GGA). The program was compiled and executed on a LINUX-based desktop PC. The calculations of the EBP of β-brass were done twice, once with the NREL-LDA and once with the REL-GGA formulation. All calculations assumed a body-centred-tetragonal (bct) unit cell with Cu at the origin at a corner and Zn in the body-centre position, space group $P4/mmm$ (no 123).

As a guide toward determination of the EBP we first calculated the total energy at constant experimental volume for a number of values of c/a from 0.8 to 1.6. The lattice constant of β-brass was taken as $a = 2.9539$ Å (at room temperature) from Pearson's Handbook [12], so that the volume/atom V is 12.887 Å^3 = 86.967 bohr^3. The result is depicted in figure 1, with the solid curve from LDA and the dashed curve from GGA. We note: (1) the minimum at $c/a = 1$ is surprisingly shallow (less than 0.1 mRy); (2) an unexpected minimum occurs at $c/a = 1.23$ for LDA and $c/a = 1.24$ for GGA; the latter almost 0.1 mRy lower than the minimum at $c/a = 1$.

The calculation procedure for the EBP was described in detail in a previous paper [8] and is only briefly summarized here. A value of the lattice constant a was chosen and several (usually five) calculations of the total energy were done for a series of values of the c parameter. A least-squares fit of a cubic polynomial to the five calculated values provided the minimum energy and the value of c that corresponds to the minimum energy. The procedure was then repeated for a number of values of a usually spaced about 2% apart, covering the range of c/a values from 0.8 to 1.6.

The plot of energy (relative to the ground state) versus c/a is shown in the top panel of figure 2, solid curve for LDA and dashed curve for GGA. We note again that the minimum at the experimentally stable phase ($c/a = 1$) is shallow, 0.08 mRy for LDA and 0.02 mRy for GGA, and that the secondary minimum at $c/a = 1.24$ for LDA is only about 0.02 mRy higher, while that at $c/a = 1.28$ for GGA is about 0.07 mRy *lower* than the minimum at $c/a = 1$. The plot of normalized volume V/V_0 as a function of c/a is depicted in the bottom panel of figure 2. The quantity V_0 is the *theoretical* value of the volume of the ground state

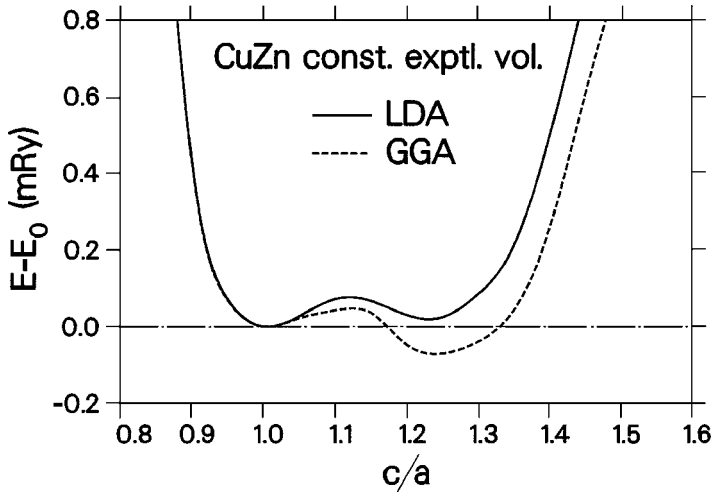

Figure 1. Total energy (referred to the minimum at $c/a = 1$) of CuZn versus the axial ratio c/a at constant experimental volume 86.967 bohr^3. Solid: LDA; dashed: GGA.

(at $c/a = 1$): $V_0 = 82.79$ bohr^3 $= 12.27$ Å^3 for LDA, and $V_0 = 88.41$ bohr^3 $= 13.10$ Å^3 for GGA.

The numerical results are summarized in table 1, which also lists the theoretical and experimental values of the elastic constants. The formulae and procedures for the calculation of c_{11}, c_{12} and c_{44} from the curvature of the energy curves have been given in reference [8].

3. Discussion

Comparison of the calculated lattice constants a_0 and c_0 of the ground state of β-brass with the experimental value (table 1) shows that the GGA (0.5 and 0.7% high) does somewhat better than the LDA (1.8 and 1.2% low), but the occurrence of a minimum *lower* than the ground state in the GGA energy curve is clearly a defect that the LDA curve does not have. Nevertheless, the revealed existence of a tetragonally metastable phase of β-brass for $c/a \sim 1.26$ is new. We show below that this phase is a far-removed relative of the fcc phase ($c/a = \sqrt{2}$) of elemental Cu.

With regard to the elastic constants, comparison between calculated and observed values is somewhat obscured by the fact that the experimental values show notable scatter, although on average the GGA results do better than the LDA. But the LDA and the GGA values of the C' shear stiffness coefficient are close to one another, and so are the values of the ratio c_{44}/C'. The latter turn out to be less than one half the value which misled Clarence Zener in 1947, a value which was based on the only then-available measurements of Good [13]. The data reported in table 1 show that Good's value of C' falls in the general range of the other experimental values, but it is the value of c_{44} that is abnormally larger than the others, and for which obviously Zener could find 'no satisfactory explanation' [5]. Nevertheless, Zener's contention that the elastic anisotropy (the ratio c_{44}/C') of β-brass is abnormally large (even if not as large as 18.6) is still valid, and so is his explanation for the small value of the C' shear. (For comparison, a random selection of data from reference [14] shows that the value of c_{44}/C' is 0.58 for CsCl; 1.7 for Al, Ge, Rh; 3.2 for Cu; 2.4 to 3.3 for CuGe alloys and Cu_3Au; etc.)

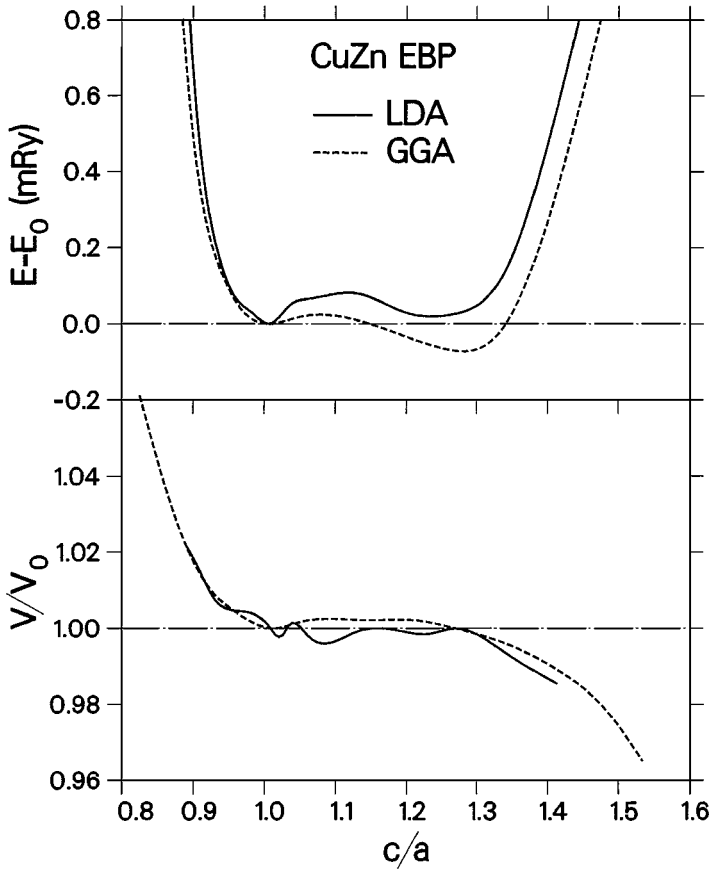

Figure 2. Epitaxial Bain path of CuZn. Top: energy (referred to the minimum at $c/a = 1$) versus axial ratio c/a. Bottom: normalized volume V/V_0 (V_0 = theoretical volume) versus c/a. Solid: LDA; dashed: GGA.

We now consider the shape of the EBP of β-brass and in particular the comparison with that of elemental Cu. The EBP of Cu [8], we recall, exhibits a deep energy minimum at $c/a = \sqrt{2}$ (the fcc phase), a maximum at $c/a = 1$ and a shallow minimum at $c/a = 0.93$ (a tetragonally metastable bct phase). The EBP of β-brass (figure 2, top) has a shallow minimum at $c/a = 1$ (the bcc, or CsCl phase) and no feature at $c/a = \sqrt{2}$. (Note that for β-brass the state at $c/a = \sqrt{2}$ is *not* fcc, owing to the fact that the atom at the origin and the atom at the body-centre of the unit cell are different—the structure has then tetragonal symmetry of the CuAu type.) As mentioned in the introduction, this remarkable change between the two EBP's is obtained merely by replacing one half of the Cu atoms, in a Cu crystal, with Zn atoms, which have just one electron more than Cu.

To examine more closely the nature of this transition from Cu to CuZn, we studied the effect of subtracting some fraction of an electron from the Zn atom, thereby making the Zn atom more 'like' Cu. We did this by calculating the EBP of a fictitious 50–50 alloy CuZn* between Cu and a new atom, Zn*, which has some fraction of one electron less than the 30 electrons normally present in a Zn atom. We considered two cases: CuZn*, with Zn* having atomic number $Z = 29.98$, i.e., 0.02 electrons *less* than Zn; and CuZn**, with Zn** having atomic number $Z = 29.9$, i.e., 0.1 electrons less than Zn. The corresponding

Table 1. Calculated and experimental lattice parameters and elastic constants of β-brass (CuZn). The calculations were done with the WIEN97 (FLAPW) program [9] both in the nonrelativistic LDA and in the relativistic GGA: a_0 and c_0 are the parameters of the unit cell, in Å units; V is the volume per atom, in Å^3; the c_{ij} are elastic constants, in Mb; $C' = (c_{11} - c_{12})/2$ is the shear modulus, in Mb.

	Theory		
Quantity	LDA	GGA	Experiment
a_0	2.900	2.968	2.954[a]
c_0	2.918	2.974	2.954[a]
V	12.27	13.10	12.89
c_{11}	1.647	1.337	0.52[b] 1.40[c] 1.21[d] 1.31[e]
c_{12}	1.398	1.084	0.34[b] 1.09[c] 1.02[d] 1.15[e]
c_{44}	1.125	0.907	1.73[b] 0.83[c] 0.93[d] 0.92[e]
C'	0.138	0.127	0.093[b] 0.155[c] 0.095[d] 0.080[e]
c_{44}/C'	8.2	7.1	18.6[b] 5.4[c] 9.8[d] 11.5[e]

[a] Reference [10] (Pearson).
[b] Calculated from the values of the elastic moduli s_{ij} at 24 °C in reference [11] (Good).
[c] Data at 4.2 °K from reference [13] (McManus).
[d] Graphical extrapolation to 0 °K of data in reference [14] (Young and Bienenstock).
[e] Graphical extrapolation to 0 °K of data in reference [15] (Prasetyo *et al*).

EBP's are depicted in figure 3 (as calculated with GGA), together with the EBP's of CuZn and Cu (the latter from reference [8]). We see that the effect of reducing the electronic charge in the partner of Cu in the alloy is noticeable even when the reduction is minute: the secondary minimum in the EBP of CuZn moves to lower energies and larger c/a values (from $c/a = 1.28$ in CuZn to 1.29 in CuZn* and 1.32 in CuZn** on its way to $\sqrt{2}$ in elemental Cu), while the ground-state minimum in CuZn moves toward smaller c/a values, from 1 in CuZn to 0.99 in CuZn*, 0.97 in CuZn**, and eventually 0.93 in elemental Cu (see figure 4).

In summary, modern first-principles total-energy electronic theory is shown to check the remarkable insight of Clarence Zener about the unusually small value of C' for β-brass. The modern theory is also able to establish that c_{44} is normal, as Zener suspected, and to find a

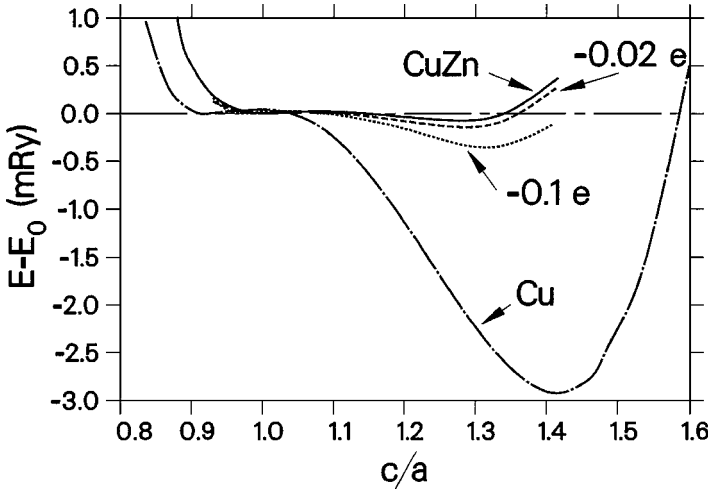

Figure 3. Effect of electron density on the structure of β-brass. The figure shows four EBP's, energy/atom (referred to the minimum at $c/a = 1$) versus axial ratio c/a: one curve for CuZn (solid); one for CuZn* (dashed), Zn* is a fictitious atom with 0.02 electrons less than Zn; one for CuZn** (dotted), Zn** has 0.1 electrons less than Zn; and one for elemental Cu (dash-dotted, from reference [8]).

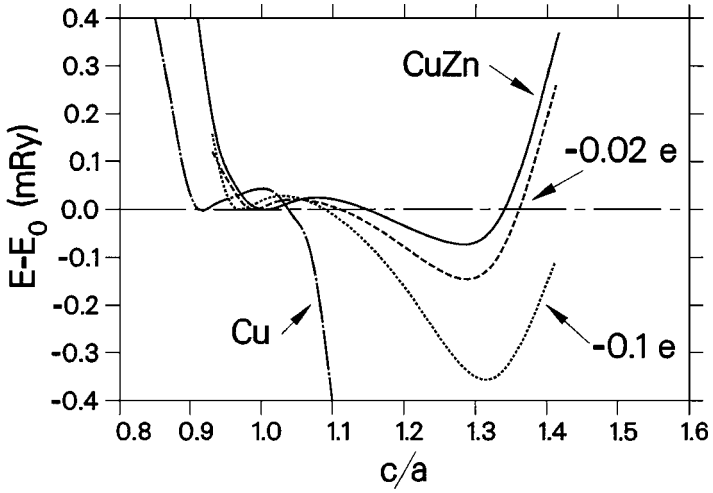

Figure 4. Enlarged view of the range around $c/a = 1$ in figure 3 showing the movement of the tetragonal equilibrium state from $c/a = 1$ in β-brass to $c/a = 0.93$ in Cu.

tetragonally metastable state of β-brass that is the remnant of the fcc ground state of Cu when the electron density is increased.

Acknowledgment

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References

[1] Massalski T B, Okamoto H, Subramanian P R and Kacprzak L (ed) 1990 *Binary alloy phase diagrams* (Materials Park, Ohio: ASM International)
[2] Hume-Rothery W 1936 *The Structure of Metals and Alloys* (London: Institute of Metals)
[3] Evans R, Lloyd P and Mujibur Rahman S M 1979 *J. Phys. F: Metal Phys.* **9** 1939
[4] Paxton A T, Methfessel M and Pettifor D G 1997 *Proc. R. Soc. Lond.* **453** 1493
[5] Zener C 1947 *Phys. Rev.* **71** 846
[6] Murakami Y and Kachi S 1974 *Jap. J. Appl. Phys.* **13** 1728
[7] Fuchs K 1935 *Proc. R. Soc.* **A151** 585
Fuchs K 1936 *Proc. R. Soc.* **153** 622
Fuchs K 1936 *Proc. R. Soc.* **157** 444
[8] Jona F and Marcus P M 2001 *Phys. Rev.* B **63** 094113
[9] Blaha P, Schwarz K and Luitz J 1997 *WIEN97*, Vienna University of Technology, improved and updated UNIX version of the original copyrighted WIEN code which was published by
Blaha P, Schwarz K, Sorantin P and Trickey S B 1990 *Comput. Phys. Commun.* **59** 399
[10] Alippi P, Marcus P M and Scheffler M 1997 *Phys. Rev. Lett.* **78** 3892
[11] Marcus P M and Alippi P 1998 *Phys. Rev.* B **57** 1971
[12] Villars P and Calvert L D 1985 *Pearson's Handbook of Crystallographic Data for Intermetallic Phases, Am. Soc. Metals* (Materials Park, OH: ASM International), p. 2040
[13] Good WA 1941 *Phys. Rev.* **60** 605
[14] Simmons G and Wang H 1971 *Single Crystal Elastic Constants and Calculated Aggregate Properties: A Handbook* (Cambridge, MA: MIT Press)
[15] McManus G M 1963 *Phys. Rev.* **129** 2004
[16] Young P L and Bienenstock A 1971 *J. Appl. Phys.* **42** 3008
[17] Prasetyo A, Reynaud F and Warlimont H 1976 *Acta Metall.* **24** 1009