

A first-principles study of the Hume-Rothery electron compounds

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2002 J. Phys.: Condens. Matter 14 1275

(<http://iopscience.iop.org/0953-8984/14/6/314>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.27

The article was downloaded on 17/05/2010 at 06:08

Please note that [terms and conditions apply](#).

A first-principles study of the Hume–Rothery electron compounds

F Jona and P M Marcus

Department of Materials Science and Engineering, State University of New York, Stony Brook, NY 11794-2275, USA

Received 30 July 2001, in final form 14 November 2001

Published 1 February 2002

Online at stacks.iop.org/JPhysCM/14/1275

Abstract

First-principles total-energy band-structure calculations have been performed on ordered Cu–Zn compounds with variable electron concentrations, or, equivalently, Zn concentrations, from pure Cu to 50% Zn and above. There are two total-energy minima of the compounds in the body-centred tetragonal structure at each Zn concentration. These minima correspond to the low-temperature α - and β' -phases of the Cu–Zn alloy system, which forms Hume–Rothery electron compounds. Lattice constants as functions of Zn concentration agree well with experiment. Elastic constants reveal the stability ranges of Zn concentration in each phase. The α -phase, which is face-centred cubic for Cu, becomes tetragonal (like CuAu) for finite Zn concentration, and remains stable to slightly beyond 50% Zn. The β' -phase, which becomes stable with the CsCl structure at 35% Zn, remains stable with that structure indefinitely for Zn concentrations up to and above 50%. The energy difference between the β' - and the α -phases, which is always less than 1 mRy atom⁻¹, becomes negative at 47.5% Zn, hence the phase line between the ($\alpha + \beta'$) two-phase region and the pure β' -region must be above 47.5% Zn, consistent with the experimental value of 48% Zn.

1. Introduction

In his seminal work on alloy systems Hume–Rothery discussed how simple solid solutions may give rise to so-called intermediate phases, one class of which he called *electron compounds* [1]. These are compounds in which the appearance of a particular structure requires a particular value of the ratio e/a of valence electrons to atoms. In alloys involving Cu, Ag or Au on one hand and Zn, Cd, Al, In or Sn on the other, similar phases usually occur for different atomic concentrations, but for about the same value of e/a . This statement is mentioned in the literature as one of the Hume–Rothery rules for electron compounds. Hume–Rothery writes ([1], p 229) that for $e/a = 1.5$ the structure of the electron compounds is body-centred cubic (bcc in the disordered state, CsCl in the ordered state); for $e/a = 1.61$, it is of the γ -brass type;

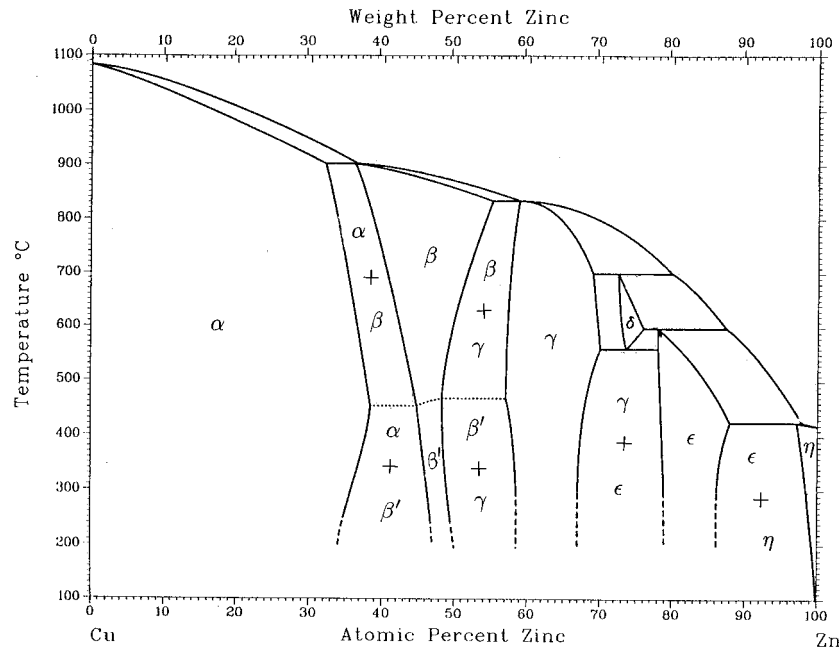


Figure 1. Cu–Zn phase diagram (adapted from Thaddeus B Massalski *Alloy Phase Diagrams* 2nd edn, vol 2, ASM International 1990, Materials Park, Ohio 44073, USA).

and for $e/a = 1.75$ it is hexagonal close-packed (hcp) [1]. The prototype of these so-called β -phase alloys is the copper–zinc system, which is the subject of this study.

The temperature–concentration phase diagram of the Cu–Zn system, reproduced in figure 1, shows that at low temperatures phase-lines occur in pairs at Zn concentrations which mark the boundaries of two-phase regions separating single-phase regions. For the α - and β' -phases (the prime denotes the ordered phase) these boundaries are approximately at 35 and 48% Zn. Between these boundaries mixtures of 35% α - and 48% β' -phases are observed with amounts varying continuously from all 35% α - to all 48% β' -phases. Only α -phases with up to 35% Zn are observed, and only β' -phases with more than 48% Zn are observed. Other pairs of phase lines occur for ($\beta' + \gamma$), ($\gamma + \epsilon$) and ($\epsilon + \eta$) two-phase regions. We study here the stability ranges of the α - and β' -phases, which must therefore include up to 35% Zn for α and more than 48% Zn for β' , and we draw some limited theoretical conclusions about the positions of the two ($\alpha + \beta'$) phase-lines.

Previous theoretical studies of electron-compound formation in CuZn and other β -phase alloy systems span a range of more than 60 years, which includes early work by Jones [2], a study by Zener [3] of elastic anisotropy in β -brass (50% Zn), and, more recently, the band-structure approach of Paxton *et al* [4]. Our calculations avoid the rigid-band approximation used in [4], and replace the band-structure energy by the total energy.

In a previous paper [5] we have verified with first-principles total-energy band-calculations the shear weakness of β -brass that was discussed by Zener in 1947 [3]. Here we extend the calculation of the shear weakness of the β' -phase to Cu–Zn alloys with Zn concentrations less than that in β -brass. We determine the Zn concentration at which the weakness turns into instability, i.e. we find a stability limit in Zn concentration for the phase in CsCl structure of such alloys. We also determine the change in lattice parameter of both the α - and β' -phases as a function of Zn concentration to compare with available experimental data.

Following the Hume–Rothery concept of electron compounds, in which the electron concentration determines the structure, we introduce a continuous sequence of ordered alloys CuZn^* (with 50% Zn^*) where Zn^* has a fractional atomic number Z^* between 29 (Cu) and 30 (Zn) and beyond. At each Z^* the compound CuZn^* is studied in tetragonal structure, with Cu (Zn^*) in the corners and Zn^* (Cu) in the body-centre position. The equilibrium states of tetragonal CuZn^* can then be calculated from first principles, as was performed for the compound CuZn (which corresponds to $Z^* = 30$) in [5]. Both the α - and β' -phases at that value of Z^* can be determined, and their lattice constants, elastic constants, relative energies and stabilities can be found, along with some conclusions about the positions of the phase-lines.

The procedures followed for the present calculations are described in section 2, the results in section 3 and the conclusions are discussed in section 4.

2. Calculation procedures

A convenient way to treat tetragonal structures (lattice parameters a and c) and find the minima of the total energy $E_t(a, c)$ is to seek a special path in the tetragonal plane (coordinates a and c , or $V = ca^2/2$ and c/a) which goes through the minima. One such path, called the epitaxial Bain path (EBP) [6], is found by minimizing the energy E_t with respect to c at each a , corresponding to equilibrium in pseudomorphic epitaxy on a square-net substrate with lattice constant a . Detailed procedures for the calculations are given in [7]. The EBPs that we show here are plots of the energy E_t along this path versus the axial ratio c/a : the value $c/a = 1$ indicates bcc (or CsCl) structure, the value $c/a = \sqrt{2}$, fcc structure.

We calculate the EBP for each of a number of selected Cu–Zn compounds with varying Zn content. As mentioned in the introduction, we model such compounds by ordered CuZn^* alloys, where Zn^* is an artificial atom with fractional atomic number Z^* . When Z^* varies from 29 to 30 and beyond, the fractional Zn concentration f varies from 0 to 0.5 and beyond, and the number of valence electrons per atom $n \equiv e/a$ varies from 1 to 1.5 and beyond. The descriptions of the electron concentration are related by¹ $n = 1 + f$ and $Z^* = 29 + 2f = 27 + 2n$; the atomic per cent of Zn is $100f$.

The calculations are performed on a LINUX-based desktop computer with the WIEN97 program [8] in the nonrelativistic mode within the local-density approximation (LDA). The GGA correction was shown in [5] to give the wrong ground state for CuZn [5]. The α -phase in the GGA calculation was 0.07 mRy/atom lower than the β' -phase, whereas the LDA calculation found the α -phase to be 0.02 mRy/atom higher. In [5] both GGA and LDA results for lattice constants and elastic constants are given, but since this paper is concerned mainly with phase stabilities, only the more reliable LDA was used. Once the EBP is calculated we know the values of the parameters a_0 and c_0 for which energy minima occur. There are usually two minima, one at or around $c/a = 1$, the near-bcc equilibrium state, associated with the β' -phase, and one at or around $c/a = \sqrt{2}$, the near-fcc equilibrium state, associated with the α -phase.

We are interested in testing the stabilities of the equilibrium phases. This test requires calculations of the elastic constants, since the stability conditions are, for cubic crystals [9]

$$c_{11} > |c_{12}| \quad c_{11} + 2c_{12} > 0 \quad c_{44} > 0 \quad (1)$$

and for tetragonal crystals [7]

$$c_{11} > |c_{12}| \quad Y'c_{33} \equiv (c_{11} + c_{12})c_{33} - 2c_{13}^2 > 0 \quad c_{44} > 0 \quad c_{66} > 0. \quad (2)$$

¹ For an alloy with $f\%$ Zn and $(1 - f)\%$ Cu, $n = 1 - f + 2f = 1 + f$. Defining $\delta Z^* = Z^* - 28$ as the number of valence electrons in Zn^* then $n = (1 + \delta Z^*)/2$, i.e. $Z^* = 27 + 2n$.

The calculations of the elastic constants require determinations of the curvature of the energy as a function of strain for selected deformations of the unit cell, as described in [7]. In the present case we mostly did not calculate *all* the elastic constants, because we found that the constants c_{11} , c_{12} , c_{33} , c_{44} and c_{66} are always positive. Instabilities, when they occur, are due to failure of the first condition in (1) and of either (or both) of the first two conditions in (2). For the β' -phase it is therefore necessary, and in the bcc or CsCl structure sufficient, to determine the sign of the quantity $C' \equiv (c_{11} - c_{12})/2$, which is a shear modulus for cubic crystals. The focus on C' simplifies the task of determining stability, because a calculation of C' can be done directly, without need for separate calculations of c_{11} and c_{12} .

The procedure for the calculation of C' consists in determining the curvature at the cubic state of the energy function obtained by applying a particular small strain to the cubic structure. Consider the strain energy density for small deformations of a cubic crystal around the cubic equilibrium state

$$\frac{E}{V_0} = \frac{1}{2} c_{11}(\epsilon_1^2 + \epsilon_2^2 + \epsilon_3^2) + c_{12}(\epsilon_2\epsilon_3 + \epsilon_3\epsilon_1 + \epsilon_1\epsilon_2) + \frac{1}{2} c_{44}(\epsilon_4^2 + \epsilon_5^2 + \epsilon_6^2) \quad (3)$$

where V_0 is the volume per atom and c_{ij} and ϵ_i are the elastic constants and strains in matrix notation [9], pp 133, 134. Applying a volume-conserving strain $\epsilon_1 = \epsilon_2$; $\epsilon_3 = -2\epsilon_1$; $\epsilon_4 = \epsilon_5 = \epsilon_6 = 0$, E becomes a function of a :

$$\frac{E}{V_0} = 3(c_{11} - c_{12})\epsilon_1^2 = 6C'\epsilon_1^2 = 6C'\left(\frac{a - a_0}{a_0}\right)^2 \quad (4)$$

whence by differentiation and with $V_0 = a_0^3/2$:

$$C' = \frac{1}{6a_0} \left(\frac{\partial^2 E}{\partial a^2} \right)_{a=a_0}. \quad (5)$$

We calculate five energies for five different values of $\epsilon_1 = \delta a/a_0$, namely -2 , -1 , -0.2 , $+1$, $+2\%$ (0% is avoided so that all calculations are for tetragonal, noncubic, structures). A least-squares fit of a cubic polynomial to the five energy values as functions of a allows the calculation of the second derivative in (5). All energies are total energies, but we drop the t subscript.

The elastic constant Y' appearing in (2) for tetragonal structure is given by the curvature of $E^{\text{EBP}}(a)$ at equilibrium. The relation is found by a procedure similar to that used above for C' for cubic structure, but starting from the energy density for strained tetragonal structure. The derivation is given in [7], section 2 of the appendix (which does not derive (5) for C'), to give

$$Y' = \frac{1}{c_0} \left(\frac{\partial^2 E^{\text{EBP}}(a)}{\partial a^2} \right)_{a=a_0, c=c_0}. \quad (6)$$

The elastic constant Y' might be called the epitaxial Young modulus, since it relates epitaxial stress in the basal plane to epitaxial strain in the basal plane for tetragonal structures, according to

$$\sigma_1 = Y' \epsilon_1 \quad (7)$$

where σ_1 is the stress, and $\epsilon_1 = \epsilon_2$, $\epsilon_3 = \epsilon_4 = \epsilon_5 = \epsilon_6 = 0$, which corresponds to isotropic epitaxial or biaxial strain.

3. Results

Figure 2 shows a comparison between calculated and experimental [10–14] lattice constants (in the form of the side of the equivalent cube) of the α - and β' -phases as functions of Zn

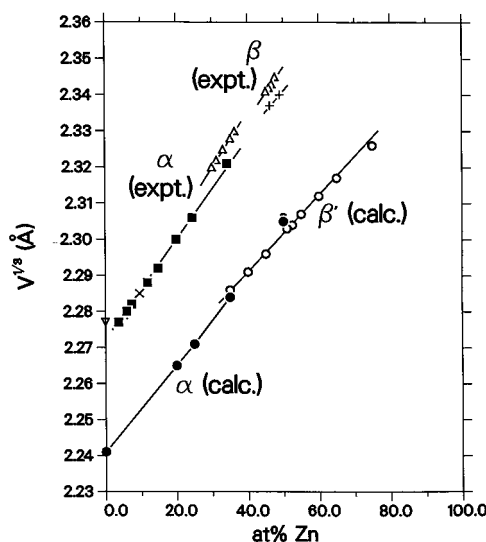


Figure 2. Experimental and theoretical lattice constants of the α -, β and β' -phases as functions of Zn concentration. The ordinate is the cube-root of the atomic volume (i.e. the side of the equivalent cube). The experimental data are cited by Pearson [10] as due to: full squares [11]; x signs [12]; up triangles [13]; + signs [14]; down triangle [9]. The open and full circles are calculated values from this work.

concentration. The agreement in both phases over the observable range of each is very good, allowing for the usual overbinding of the LDA, which makes the theoretical values about 1–2% smaller than the experimental. Reference [7] shows that for the Cu α -phase the LDA value of $V^{1/3}$ is 1.6% lower than experiment, and the GGA value is 0.5% higher. Reference [5] shows that for the CuZn β' -phase the LDA value is again 1.6% lower than experiment, and the GGA value is 0.4% higher. So the trends in lattice constant with Zn concentration are similar for LDA, GGA and experiment.

We show in figures 3(a) and (b) a few selected EBPs (energy versus c/a) for different values of Z^* . In figure 4 we plot the values of C' for the near-bcc phases with different Z^* values. In figure 5 we show the energy difference of the α - and β' -phases as a function of Z^* .

The top curve in figure 3(a) is the Cu EBP ($Z^* = 29.0$), already published in [7], drawn here with the zero of energy at the first minimum, the near-bcc phase at $c/a = 0.93$. After a maximum at $c/a = 1$, the second minimum, at $c/a = \sqrt{2}$, marks the fcc ground state of bulk Cu. We recall that the near-bcc phase is unstable: $c_{11} < c_{12}$ (see [7]), hence $C' < 0$; bcc Cu is also clearly unstable, since the maximum at $c/a = 1$ means that $Y' = (c_{11} - c_{12})(c_{11} + 2c_{12})/c_{11} < 0$.

The other EBPs in figure 3(a) have been drawn with the same energy scale as that for Cu, in order to facilitate comparisons. The second curve in figure 3(a) is the EBP of CuZn* with $Z^* = 29.4$, hence 20% Zn and $n = 1.2$. The near-bcc phase has moved to $c/a \sim 0.95$: it is still unstable ($C' < 0$, see figure 4), while the near-fcc minimum is now at $c/a = 1.397$, still stable. This result is consistent with the phase diagram (figure 1), which shows that at 20% Zn we are in the α region. Note that in our ordered compound CuZn* the α -phase is not fcc, but rather tetragonal.

With increasing Z^* (i.e. increasing Zn concentration), the near-bcc minimum moves toward the maximum at $c/a = 1$, and for $Z^* = 29.7$ (i.e. 35% Zn and $n = 1.35$) it merges

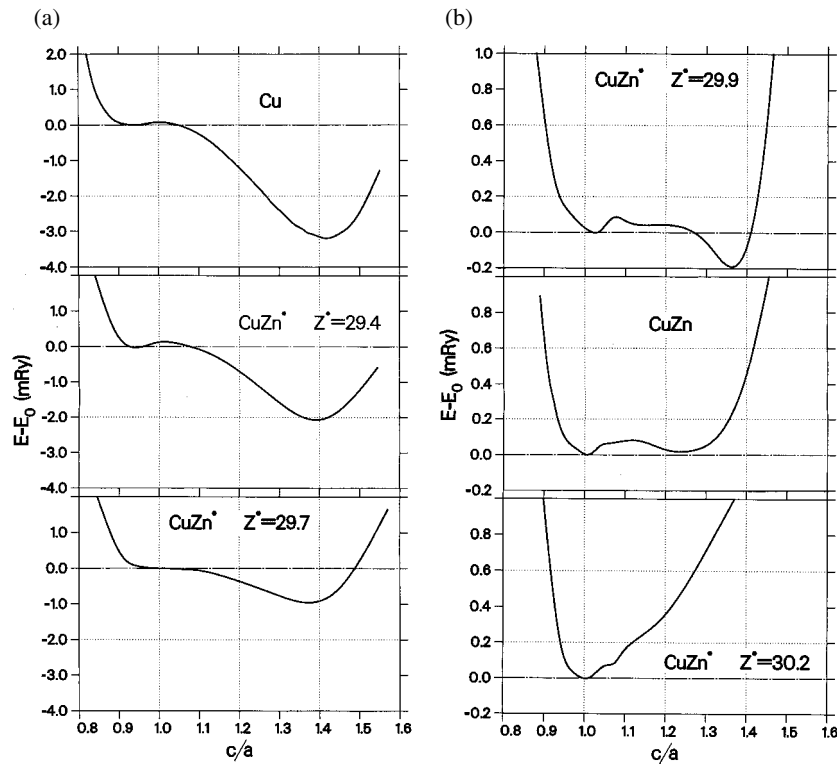


Figure 3. (a) EBP of Cu and of CuZn* with $Z^* = 29.4$ and 29.7 . The ordinate is the energy/atom referred to the near-bcc phase. (b) EBP of CuZn* with $Z^* = 29.9$, 30.0 (CuZn) and 30.2 . The energy scale is magnified five-fold with respect to that in figure 3(a).

with the maximum creating a horizontal inflection point at $c/a = 1$ (see the third curve in figure 3(a)), while the near-fcc minimum is now at $c/a = 1.363$. This composition marks the beginning of the stable β' -phase, since Y' and $C' = 0$. Above $Z^* = 29.7$, C' rises abruptly and shows a different analytic character from the smooth curve below $Z^* = 29.7$.

With increasing Z^* the minimum in the EBP remains at $c/a = 1$ and the maximum is now at $c/a > 1$, as demonstrated by the top curve in figure 3(b) for $Z^* = 29.9$ (45% Zn, $n = 1.45$). (Note that in figure 3(b) the energy scale is magnified five times with respect to that in figure 3(a).) This phase is now stable: the value of C' is positive (see figure 4). There is still a second minimum of about the same depth at $c/a \sim 1.36$: the α -phase and the β' -phase coexist.

The second EBP in figure 3(b) is that of CuZn ($Z^* = 30.0$), already published in [5]. The near-fcc minimum has now shifted to $c/a \sim 1.23$, but is still locally stable (see [5]), i.e. it is metastable, the β' -phase and the α -phase still coexist.

However, a very small increase of Z^* above 30.0 (already at $Z^* = 30.02$) produces an EBP in which there is only one minimum: the β' -phase at $c/a = 1$. The near-fcc phase no longer exists. Thus, the end of the α -phase is found to occur slightly above $Z^* = 30.0$. An example of this situation is shown in the third curve of figure 3(b), for $Z^* = 30.2$ (60% Zn, $n = 1.6$).

Figure 4 is a plot of $C'(Z^*)$ for CuZn* at the first minimum of the EBP. For $Z^* < 29.7$ the elastic constant $C' < 0$ and the tetragonal phase is unstable. As noted above, when Z^* approaches 29.7, a horizontal point of inflection develops in the EBP at $c/a = 1$, the curvature $Y' = (c_{11} - c_{12})(c_{11} + 2c_{12})/c_{11}$ goes to 0, as does C' . For $Z^* > 29.7$, $C' > 0$, the minimum

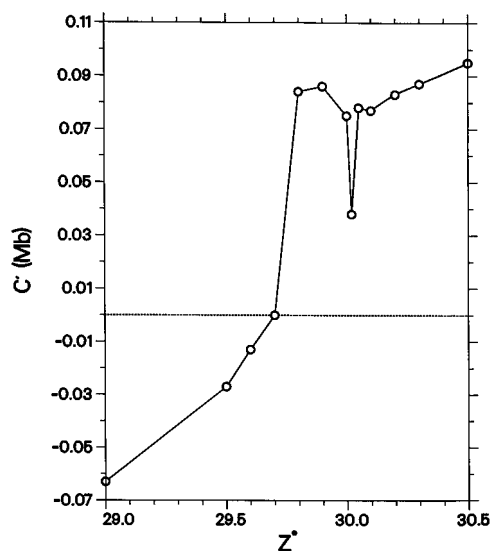


Figure 4. Elastic constant C' as a function of Z^* for the β' -phase of a number of CuZn^* alloys. Negative values of C' indicate instability.

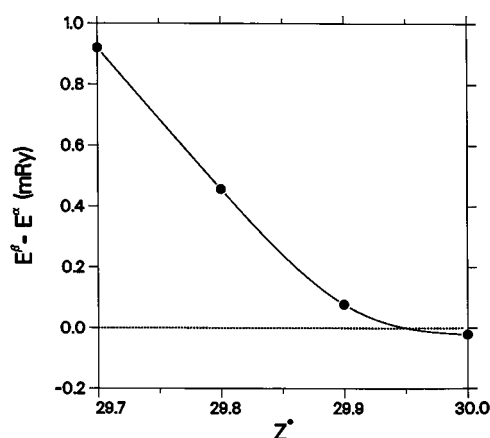


Figure 5. Difference in total energy between the β' -phase and the α -phase versus Z^* . The β' -phase has lower energy for $Z^* > 29.95$.

in the EBP is at $c/a = 1$, and the β' -phase is cubic (CsCl structure) and stable. In the vicinity of $Z^* = 30.0$ the C' values seem to show abrupt changes. The accuracy of the calculations is not sufficient to establish a clear trend, but always $C' > 0$. Above $Z^* = 30.1$, C' increases monotonically.

The α -phase at the near-fcc minimum has been called stable in the discussion above when it becomes tetragonal. The second stability condition in (2), $Y' > 0$, is clearly satisfied for Z^* from 29.0 to 30.0. We note that the first condition in (2) is also satisfied at the minimum, e.g., some typical values are (in Mb) $C' = 0.360$ ($Z^* = 29.0$ [7]); $C' = 0.348$ ($Z^* = 29.5$); and $C' = 0.524$ ($Z^* = 30.0$). An instability in which $Y' > 0$, but $C' < 0$, is shown by the body-centred tetragonal minimum of Cu at $c/a = 0.93$ ($Y' = 0.443$, $C' = -0.072$ [7]).

4. Discussion

The agreement between calculated and observed lattice constants of both the α - and β' -phases shows that the CuZn* electron compounds can describe the behaviour of actual Cu–Zn alloys as the Zn concentration varies. Hence other physical properties of these alloys that depend on the valence-electron concentration are plausibly also reliably determined, such as elastic constants and stability limits. Note that the CuZn* model of electron compounds avoids the rigid-band approximation used in previous theories of CuZn phases [4], because the band structure is recalculated at each Zn concentration and, in fact, at each tetragonal structure. Some comments about the relation between this treatment of CuZn phases and previous approaches are made in [5], in the introduction.

The EBP calculations as functions of Z^* show that the β' -phase becomes and remains stable and cubic (CsCl) at 35% Zn on up to 50% Zn and beyond. A general argument can be made that the β' -phase *must* be cubic (CsCl) and (meta)stable at all Zn concentrations above 50% on up to 100% Zn, although other phases will have lower energies in various concentration ranges. The general argument states that if there is only one minimum in the EBP for tetragonal CuZn* compounds, as appears to be the case for $Z^* > 30$, that minimum must be at $c/a = 1$ and continues the β' -phase with $Y' > 0$. A symmetry argument proves that at a cubic structure the energy along the EBP is stationary, hence must be a minimum or a maximum². The only stationary point is the minimum, which therefore must be at the one cubic point $c/a = 1$. The cubic CsCl structure is always locally stable, by (1), because the curvature at the minimum is positive, hence by (6) Y' , hence C' , are positive. The observed β' -phases between 48 and 51% Zn (the beginning of the $\beta' + \gamma$ two-phase region) are clearly within the theoretical stability range of the β' -phase, which then satisfies the Hume–Rothery $n = 1.5$ rules.

The EBP calculations also show that the α -phase exists and is locally stable from 0% to just above 50% Zn, which includes the observed range of α from 0 to 35% Zn; in the ordered compounds CuZn*, the α -phase is tetragonal, except for pure Cu. At 50% Zn the α -phase appears to exist and be stable and to have an energy close to that of the β' -phase, hence might be stabilized by pseudomorphic epitaxy on a substrate with a theoretical lattice constant $a = 2.71 \text{ \AA}$ (which becomes $a = 2.75 \text{ \AA}$ when corrected for the overbinding produced by the LDA on using the value for Cu). At the Z^* value at which the α -phase disappears the EBP maximum and the α -phase minimum come together to create a horizontal point of inflection with zero curvature (as in the β' -phase at $Z^* = 29.7$), hence $Y' = 0$, and the α -phase has become unstable.

The EBP calculations permit some limited conclusions about the Zn concentrations at the phase lines, which correspond to the particular compositions of the α and β' phases in equilibrium with each other. Then at the two phase lines the chemical potentials $\mu = \partial E(Z^*)/\partial Z^*$ in the two phases are equal, and the free energies (at zero temperature) $G(Z^*) = E(Z^*) - \mu Z^*$ are equal. The condition $G^\alpha(Z^{*\alpha}) = G^{\beta'}(Z^{*\beta'})$ corresponds to a common tangent to the two $E(Z^*)$ curves with slope $\mu = [E^{\beta'}(Z^{*\beta'}) - E^\alpha(Z^{*\alpha})]/(Z^{*\beta'} - Z^{*\alpha})$. Unfortunately, the total energies $E_t^\alpha(Z^*)$ and $E_t^{\beta'}(Z^*)$ determined by the EBP calculations are not suitable for this tangent construction. The total energies are dominated by very large changes in core energies as Z^* changes, and the core energies are not the same as the core energies of true Zn atoms. What is needed for the tangent construction is cohesive or bonding energy as a function of Z^* .

² At all points on an EBP, $[\partial E(a, c)/\partial c]_a = 0$ by construction. At a point of cubic symmetry, $\partial E/\partial a = \partial E/\partial c$, hence $\partial E/\partial a = 0$, and first derivatives of E vanish for all changes of a and c at that point, including along the EBP. Note that $c/a = \sqrt{2}$ is not a point of cubic symmetry when Zn* is different from Cu (more generally, when the atom at the body-centre is different from the atom at the origin), hence the EBP is not flat at $c/a = \sqrt{2}$ for $Z^* > 29$.

However, there is one accurate result about cohesive energies that can be obtained from the total energies. At each Z^* the difference in total energy between α - and β' -phases is the same as the difference in cohesive energy, hence relevant to the tangent construction. In figure 5 this energy difference $E^{\beta'} - E^{\alpha}$ is plotted versus Z^* . Figure 5 shows that the cohesive-energy difference is zero (i.e. the cohesive energy of the β' -phase goes below the cohesive energy of the α -phase) at $Z^* = 29.95$ or 47.5% Zn. Any tangent to the β' -phase cohesive energy must contact the β' -curve at a concentration greater than 47.5% Zn, which is consistent with the observed value of 48% Zn for the β' -phase in the two-phase region.

With regard to the contact point of the common tangent on the α -curve, we note first that since we know from experiment that a common tangent does exist, hence we expect that the α -phase energy curve will have a shape with positive curvature between Cu and CuZn. If the curvature does not vary much, the common tangent will contact the α -curve at a Zn concentration closer to CuZn than to Cu, since the tangent must head toward the β' curve, which is below but very close to the α curve above 47.5% Zn. Then the contact point would be at Zn concentrations above 25%, the halfway point between Cu and CuZn, which is consistent with the experimental value of 35% Zn. In [3], Zener constructs energy curves for the α - and β -phases as functions of electrons/atom from calculations by Jones. The common tangent has points of contact at 41% Zn for α and 45% Zn for β . However, the difference in energy between β and α at 35% Zn in [3] is more than two orders of magnitude larger than the 1 mRy/atom shown in figure 5.

In summary, first-principles total-energy calculations have been made on ordered Cu–Zn compounds with variable electron concentrations in tetragonal structure. The two equilibrium states of the tetragonal structure give the α - and β' -phases at each electron concentration, and various properties of the phases. These properties include the lattice constants, which compare favourably with measurements, the stability limits and the elastic constants of the phases, and some conclusions about the positions of the low-temperature phase lines in the phase diagram. The procedures followed here could be applied to other phases of Cu–Zn and possibly to other β -phase alloy systems. In particular, rather similar calculations could be made for the hcp phases ϵ and η of Cu–Zn.

Acknowledgments

We gratefully acknowledge partial support of this work by the National Science Foundation with grant DMR0089274. We thank François D'Heurle for discussion of the meaning of phase lines. P M Marcus thanks IBM for providing facilities as an Emeritus member of the Thomas J Watson Research Centre.

References

- [1] Hume-Rothery W 1926 *J. Inst. Metals* **35** 309
see also Hume–Rothery W, Smallman R E and Haworth C W 1969 *The Structure of Metals and Alloys (Institute of Metals Monograph No 1, London)*
- [2] Jones H 1937 *Proc. Phys. Soc. A* **49** 250
- [3] Zener C 1947 *Phys. Rev.* **71** 846
- [4] Paxton A T, Methfessel M and Pettifor D G 1997 *Proc. R. Soc. A* **453** 1493
- [5] Jona F and Marcus P M 2001 *J. Phys.: Condens. Matter* **13** 1
- [6] Alippi P, Marcus P M and Scheffler M 1997 *Phys. Rev. Lett.* **78** 3892
Marcus P M and Alippi P 1998 *Phys. Rev. B* **57** 1971
- [7] Jona F and Marcus P M 2001 *Phys. Rev. B* **63** 094113

-
- [8] 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)
 - [9] Nye J F 1957 *Physical Properties of Crystals* (Oxford: Clarendon)
 - [10] Pearson W B 1967 *A Handbook of Lattice Spacings and Structures of Metals and Alloys* (New York: Pergamon)
 - [11] Owen E A and Roberts E W 1939 *Phil. Mag.* **27** 294
 - [12] Hume-Rothery W, Raynor G V, Reynolds P W and Packer H K 1940 *J. Inst. Met.* **66** 209
 - [13] Beck L H and Smith C S 1952 *J. Metals* **4** 1079
 - [14] Johansson A and Westgren A 1933 *Metallwirt.* **12** 385