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Modelling the thermodynamic data for hcp Zn and Cu-Zn alloys– an *ab initio* and Calphad approach

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Abstract

The phase diagrams of systems between zinc and elements such as Cu, Ag and Au show two distinct hcp phases on the Zn side of the system. Because of this, it is difficult to model the thermodynamic properties of these phases within a single dataset. As a result it is common to assess the data for these systems with two hexagonal phases, a phase HCP_A3 with a near ideal c/a ratio and the terminal solid solution of Zn with an anomalously high value for this ratio designated as HCP_ZN. We have examined the effect of additions of Cu on the enthalpy of mixing and lattice parameters of HCP_ZN in order to verify, using *ab initio* calculations, the origin of the above mentioned thermodynamic model for the alloy. The analysis of the calculations allows us to suggest a possible alternative to the state-of-the-art two hcp phases approach akin to the magnetic model used with success within the CALPHAD modelling.

Introduction

Nearly all the assessments of thermodynamic data for alloy systems published over the last 25 years have been based on the SGTE pure element data published in 1991¹. With a few exceptions they were derived on the basis of well-established critical assessments of the data for the stable phases supplemented by data for the unstable or metastable phases derived by Saunders et al.^{2,3}. While such data have been extremely successful forming the basis of many private, public and commercial databases⁴⁻¹¹, they are now in need of revision partly in the light of new experimental data but also because there is the need and the opportunity to inject more insights from theoretical physics into the way in which data are modelled. These were the subject of intense discussions reviewed in Refs. ¹²⁻¹⁸.

One particular issue that is still unresolved is how to handle the difficulties posed by zinc and cadmium based solutions and in particular for systems involving Zn with elements such as Ag, Cu and Au where the phase diagram shows two single phase regions for the hcp phase separated by a miscibility gap. The region close to Zn has an anomalous distorted structure with an axial c/a ratio which is rather higher than the ideal value of 1.633 resulting from a specific electronic contribution to the Gibbs energy for Zn rich compositions. The other hcp phase, which is still rich in Zn but contains rather more Ag, Cu or Au, has a c/a ratio much closer to the ideal value of 1.633. At present, a convention is adopted whereby the two distinct phases would be modelled using separate datasets.⁸ The phase with the near ideal c/a ratio is modelled as forming continuous solid solutions with elements which crystallise in the hcp structure and designated as HCP_A3. In contrast, the solid solution based on Zn is thought to have such a markedly different structure as to warrant its own phase name – HCP_ZN. Recently this issue was discussed in some detail by Schmid-Fetzer and Hallstedt.¹⁹ They suggested strongly that

this designation should be reversed, that is the Zn terminal solid solution should be HCP_A3. We believe that neither approach is correct. Using the Cu-Zn system as a model, we in this paper attempt to give greater understanding of its thermodynamic properties through the use of *ab initio* calculations and suggest a possible alternative approach, which removes the need to model Zn (and Cd) based alloys with two distinct datasets.

The Problem

The essence of the problem is shown in Figure 1, which is the phase diagram for the Cu-Zn system calculated from the critically assessed thermodynamic data of David et al.²⁰. On the Zn-rich side, there are two single phase regions, which the authors designate as the ϵ and η phases. Both of these phases are, in fact, hcp phases although they have very different lattice constants as indicated by the c/a ratio. The phases are very close in composition to pure zinc and it is nearly impossible to generate a single set of parameters for thermodynamic modelling of the phases, which represents all the known experimental data. As a consequence David et al.²⁰ and, before them, Kowalski and Spencer²¹, described the thermodynamics of the system with two distinct hcp phases.

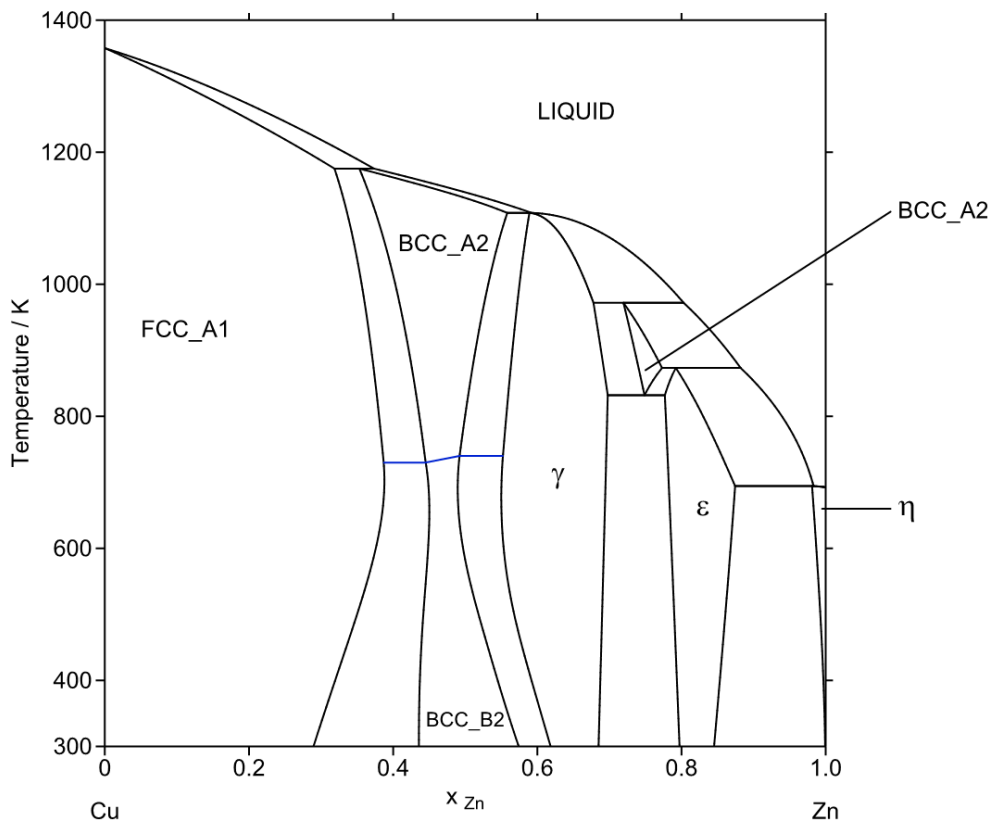


Figure 1. Phase diagram for the Cu-Zn system calculated using the data from the assessment of David et al.²⁰ The blue line represents the second order transformation from BCC_B2 to BCC_A2.

This problem is not restricted to the Cu-Zn system. Other systems such as the Ag-Zn and Au-Zn show exactly the same behaviour in terms of the appearance of two hexagonal phases in the Zn rich part of the binary phase diagram and this is mirrored in the changes in lattice spacing as shown in Figure 2. This figure shows the variation of the c/a ratio as a function of the Zn mole fraction for the Cu-Zn, Ag-Zn and Au-Zn system from the work of Massalski and King²².

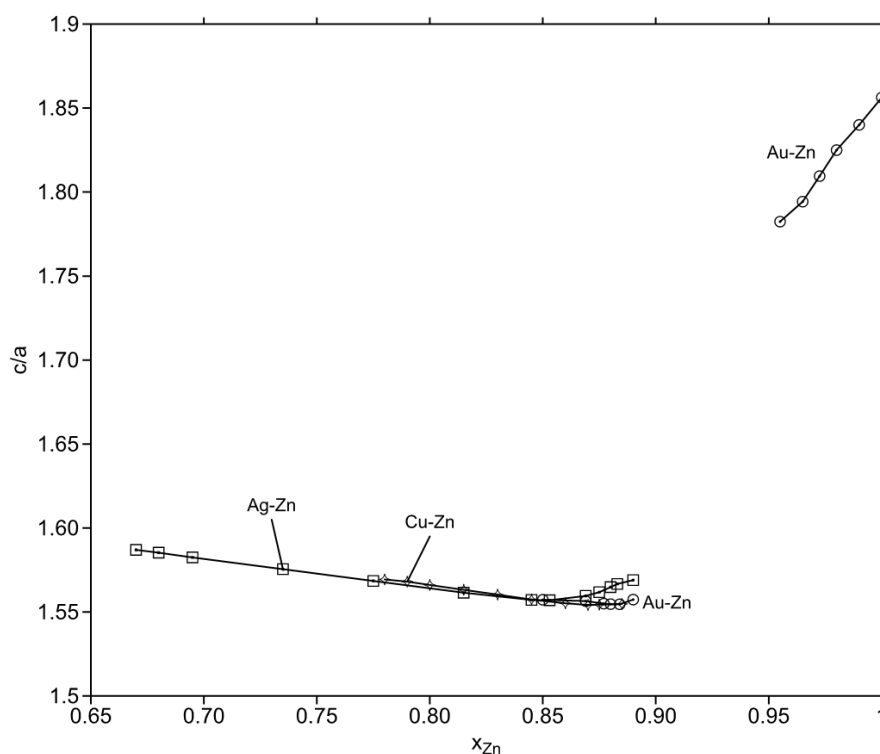


Figure 2. The variation of the c/a ratio as a function of the Zn mole fraction for the Ag-Zn, Cu-Zn and Au-Zn systems.

This should be compared with Figure 3 which shows the c/a ratio calculated using DFT for 0 K across the whole composition range for Cu-Zn alloys.

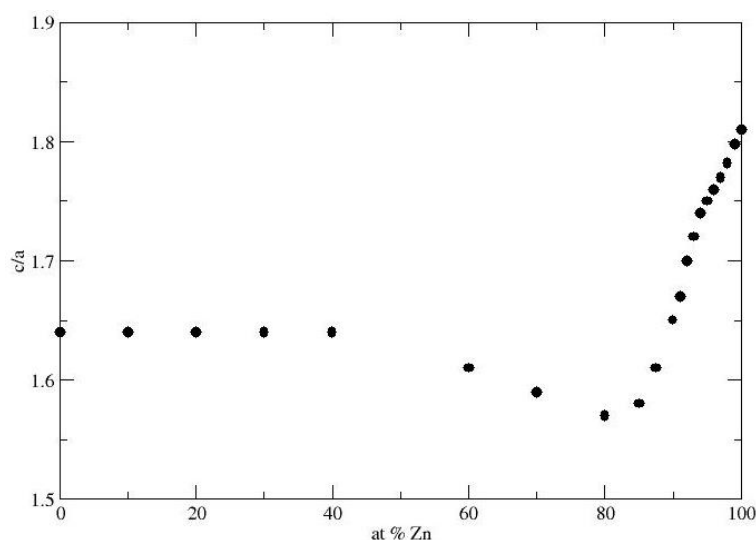


Figure 3. c/a ratio for hcp Cu-Zn alloys calculated using ab initio EMT-CPA method for 0 K across the whole range of compositions. Details of calculations are presented in section Applied Ab initio Methods below.

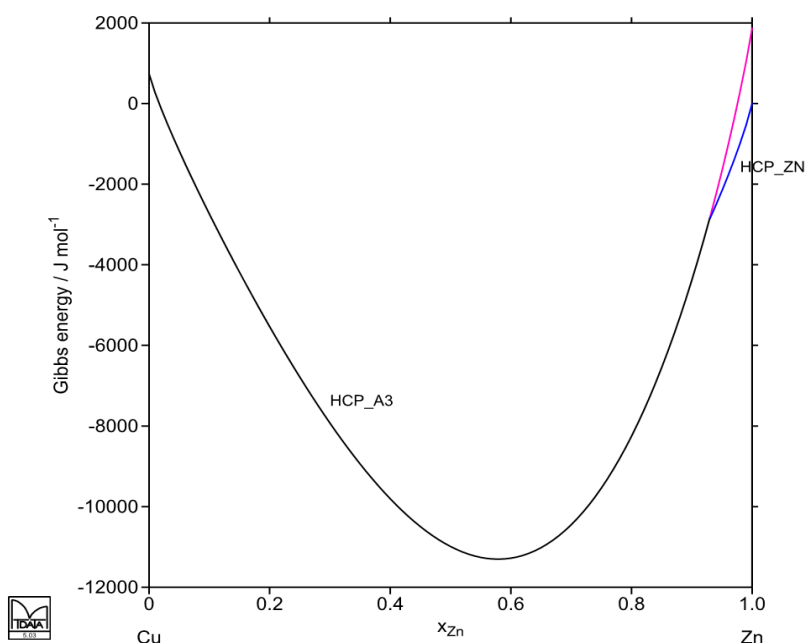
It is useful at this stage to compare Figure 2 with values for the c/a ratio for other elements which crystallise in the hcp structure. The values in Table 1 are taken from King²³.

Table 1 c/a ratios at 25°C for variety of elements crystallising in the hcp structure²³.

Element	c/a ratio	Element	c/a ratio	Element	c/a ratio	Element	c/a ratio
Be	1.568	Hf	1.5811	Ru	1.5826	Tm	1.5700
Cd	1.8856	Ho	1.5702	Sc	1.5921	Y	1.5711
Co	1.6232	Lu	1.5832	Tb	1.580	Zn	1.8576
Dy	1.5732	Mg	1.6236	Tc	1.605	Zr	1.5928
Er	1.5692	Os	1.5316	Ti	1.5875		
Gd	1.5910	Re	1.6147	Tl	1.5989		

These values clearly identify that Zn and Cd are anomalous in their behaviour. This is now understood quite clearly as being due to a stabilisation of the hcp phases of Zn and Cd as a result of electronic effects. The effect is illustrated in Figure 4. Figure 4a shows the variation of Gibbs energy of the hexagonal phase of the Cu-Zn system at 700 K with composition calculated based on the critically assessed data from Spencer and Kowalski²¹. As the hcp phase is stable only for Zn rich compositions the diagram is to some extent conjectural.

For the most of the composition range the Gibbs energy may be expected to behave normally in a similar fashion to other solution phases such as the fcc phase or the liquid phase. Close to pure Zn there is an additional stabilisation of the hexagonal phase from electronic effects. This Zn-rich portion of the diagram is expanded in Figure 4b.



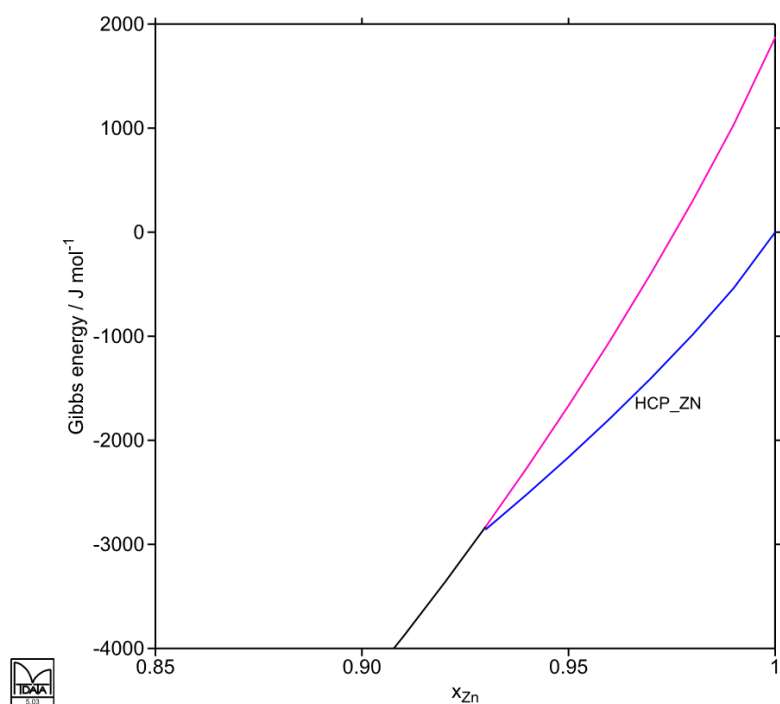


Figure 4. (a) Variation of the Gibbs energy of the hcp phase in the Cu-Zn system showing the normal parabolic behaviour for most of the composition range but with extra stabilisation close to pure Zn. (b) an enlargement of Figure 4(a) for compositions close to pure Zn.

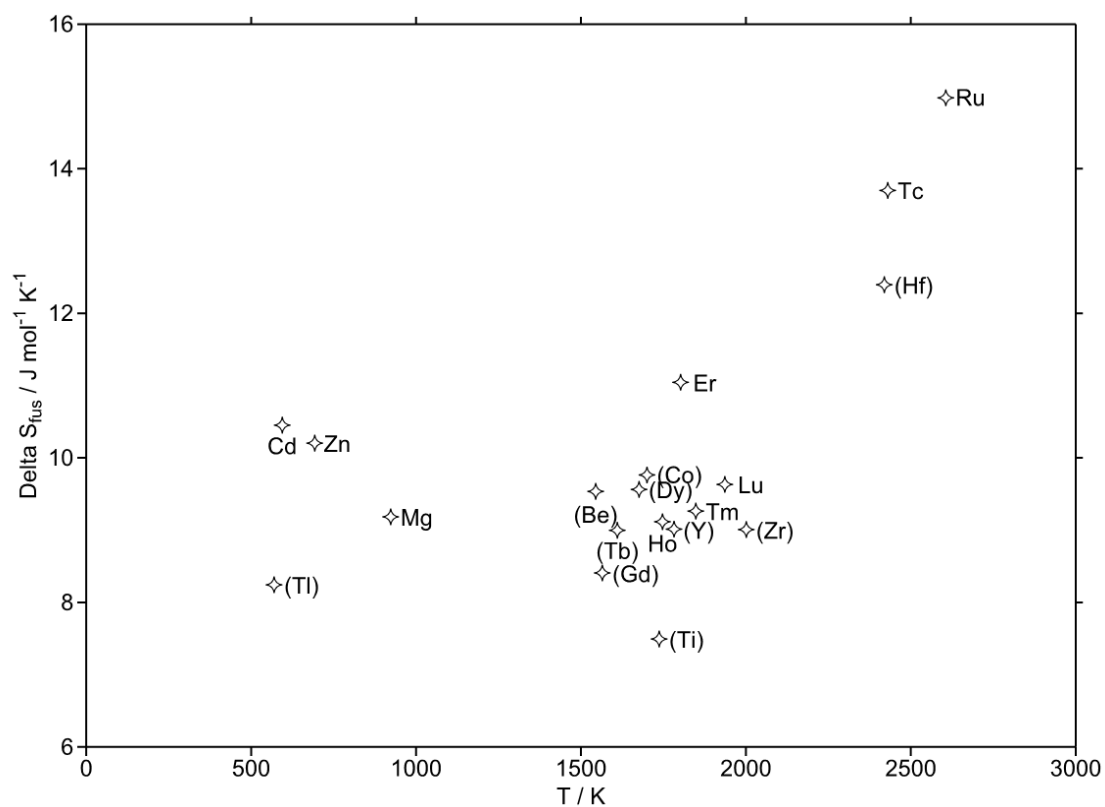


Figure 5. The entropy of fusion for a number of hcp metals plotted against the temperature of fusion. Zn and Cd clearly show up as being anomalous.

This effect can also be seen in Figure 5 which shows the entropy of fusion of a number of hcp metals plotted against their temperature of fusion. There is a trend for the entropy of fusion to be higher for those elements, which melt at higher temperatures. Clear exceptions to this trend are Cd and Zn, which have rather higher entropies of fusion than would be expected from their melting points indicating that the form with the anomalous c/a ratio should have both a lower enthalpy and a lower entropy than the form with an ideal c/a ratio.

Figure 4 implies the existence of a hexagonal Zn phase with an ideal c/a ratio. However is this a true metastable state? This question has been addressed by Vitos et al.²⁴, who, using *ab initio* calculations, identified both forms of Zn-based alloys with Cu (*i.e.* with ideal and non-ideal c/a ratios) as either stable or metastable phases, depending on Cu concentration. However, the Exact Muffin-Tin orbitals (EMTO) method they used employs the spherical approximation for the crystal potential, which could affect a conclusion based on tiny energy differences, in fact at the limit of the accuracy of *ab initio* calculations at that time. More precise calculations employing state-of-the-art first-principles methods with full non-spherical treatment of the crystal potential are certainly desirable. Besides, only one value at 7 at.% Cu concentration was published so far for the difference in enthalpy between the two forms of Zn-based alloys calculated from first-principles.²⁴ Such information could be obtained from *ab initio* calculations for a broad range of Cu-Zn alloy compositions.

Kowalski and Spencer²¹ estimated the difference in thermodynamic properties between the two forms assuming that the ideal hexagonal form for Zn should have thermodynamic properties similar to those of the fcc phase which were already reasonably well established. These values are shown on Figures 6 and 7 and are fairly consistent with the experimental thermodynamic properties and also with the extensive partial Gibbs energy data from David et al.²⁰ for the two phase equilibria between the ϵ phase with both the η phase and with the liquid phase. Figure 6 shows the partial Gibbs energy of Zn in the ϵ phase relative to pure crystalline Zn along with experimental data for the Cu-Zn system from Olander²⁵, for the Ag-Zn system from Straasland and Masson²⁶ and for the Au-Zn system from Anantamula²⁷. Similarly Figure 7 shows the assessed enthalpy difference between Zn in the ϵ phase and pure crystalline Zn with experimental data for the Cu-Zn and Ag-Zn systems from Blair and Downie²⁸. All three system have been assessed with the ϵ and η phases modelled separately^{20,21,29,30}. While it is difficult to draw too many conclusions from extrapolated values, if the enthalpy difference between Zn in the ϵ and η phases is larger in magnitude than the Gibbs energy difference *i.e.* there is also an entropy difference, it may be possible that at some temperature the two phases might have the same Gibbs energy.

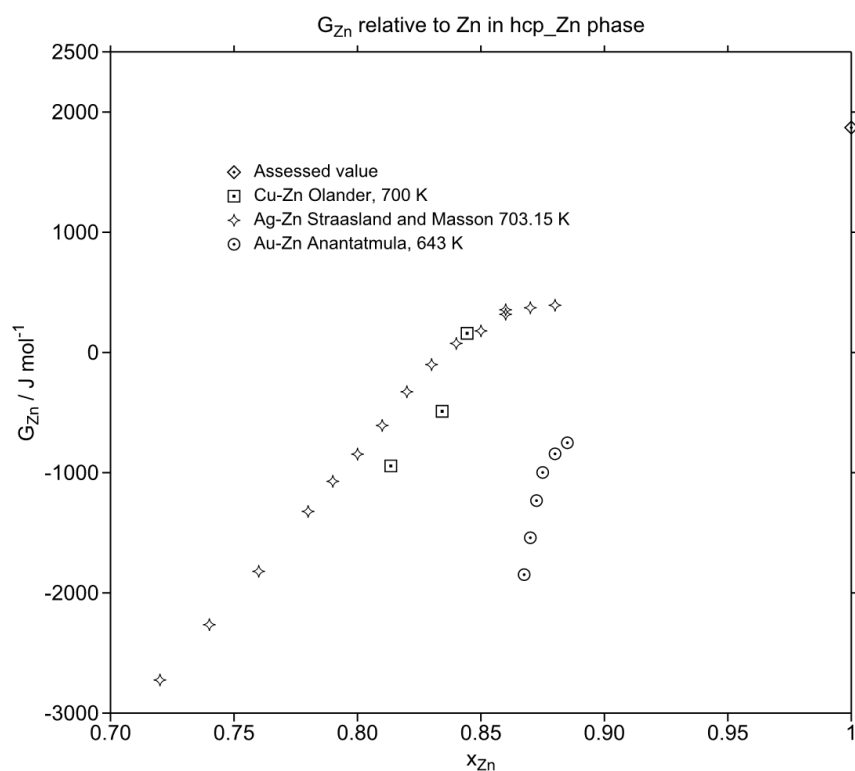


Figure 6. Experimental partial Gibbs energies of Zn for Cu-Zn, Ag-Zn and Au-Zn systems in the hcp phase. An extrapolation of the data to pure zinc would provide an estimate of the difference in Gibbs energy between the two phases. The diagram also shows the assessed value

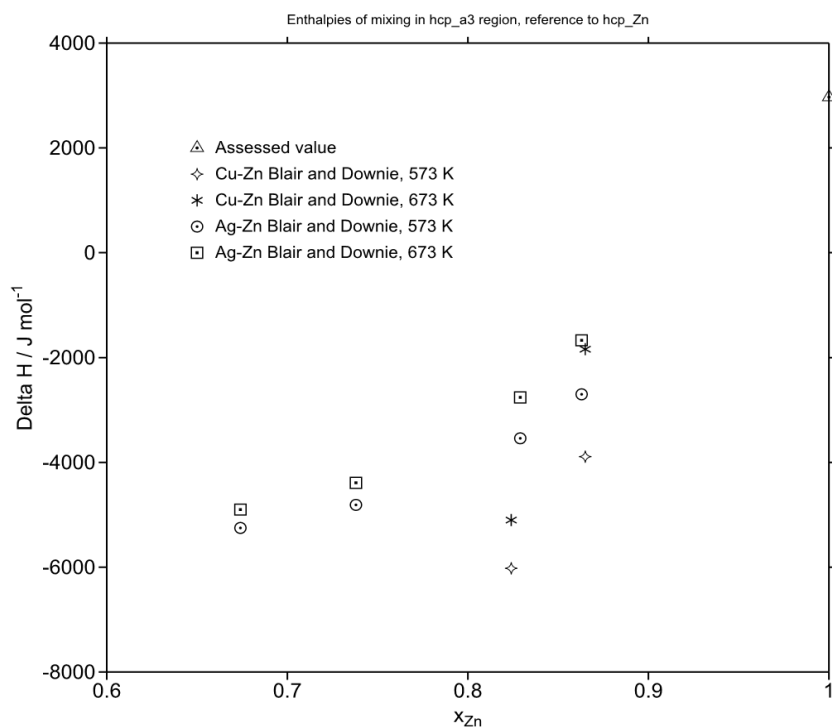


Figure 7. Experimental enthalpies of mixing for Cu-Zn, Ag-Zn and Au-Zn systems in the hcp phase. An extrapolation of the data to pure zinc would provide an estimate of the difference in enthalpy between the two phases. The diagram also shows the assessed value

Applied ab initio methods

Calculations were carried out using an all-electron projector-augmented wave (PAW) method³¹ as implemented in the Vienna Ab initio Simulation Package (VASP) code^{32,33}. Note that this technique does not impose any approximation on the shape of the crystal potential. The generalized gradient approximation (GGA)³⁴ was used for treating electron exchange-correlation effects. The energy cut-off for plane waves included in the expansion of wave functions was set at 500 eV. For total energy calculations, the tetrahedron method with Blochl corrections has been used. Sampling of the Brillouin zone for pure Zn was done using a gamma-centred scheme on a grid of 30x30x30 k-points. For alloys containing 3.125 and 6.25 at % of Cu we have used a supercell with 16 and 32 atoms respectively. For a 16-atom cell a predetermined accuracy of 0.001 eV was achieved on a grid of 19x19x13 k-points, for the second supercell a grid of 16x16x6 k-points was chosen for calculations. Internal positions of atoms in each supercell studied in this paper were fully relaxed until the Hellmann-Feynman forces^{35,36} acting on all the atoms were about 0.001 eV/Å.

To find the equilibrium values of the lattice parameters and to construct a colour map of the energy dependence for pure Zn and alloys in the Cu- Zn system, calculations were performed with the volume per atom variation in the range 12 to 16 Å³/atom in 0.12 increments and the variation in the c/a ratio in the range 1.6 to 1.95 in 0.01 increments.

Additional calculations of the mixing enthalpy of a continuous series of disordered alloys at more concentrations were carried out within the framework of the density functional theory using the software package EMTO in the coherent potential approximation³⁷⁻³⁹. Exchange-correlation effects in an electron gas were taken into account in the generalized gradient approximation³⁴. The basis set of wave functions included s-, p-, d-, f-orbitals. The integration over the irreducible part of the Brillouin zone was carried out using a grid of 31x31x19 k-points in the reciprocal space. While integrating over the energy in the complex plane, 20 points were taken on the semi-circular contour. The convergence of energy with these calculation parameters was at 10⁻⁷ eV.

Figure 8 shows the energy as a function of c/a and volume per atom calculated using PAW-VASP. The global minimum, $a = 2.65$ Å, $c/a = 1.90$, $V=15.30$ Å³/atom, agrees fairly well with the experimental data ($a = 2.66$ Å, $c/a = 1.86$). In our full potential calculations we find only one minimum on the potential energy surface. This indicates that there is only one stable hcp phase of pure Zn and that this has an anomalously large value of the c/a ratio. There is also no indication of the existence of a metastable hcp Zn with c/a ratio close to the ideal value. On the other hand, the overall energy dependence in Fig 8 is abnormal. The shape of the iso-energy surfaces around the minimum (shown by the dark blue colour) is elongated along the c/a direction with a slight tilt to the right (towards the volume increase). Thus, though we do not observe a competing hcp phase in the system, the tendency towards the presence of the second minimum can be identified on the potential energy surface. In addition, it is seen that at high pressures the system tends to adopt an ideal value of c/a . This tendency is confirmed in Fig. 9. Note that our results for the pressure dependence of the c/a ratio, as well as the equation of state (Fig. 10) for pure Zn agree well with experiment and earlier calculations, confirming the reliability of the potential energy surface in Fig. 8.

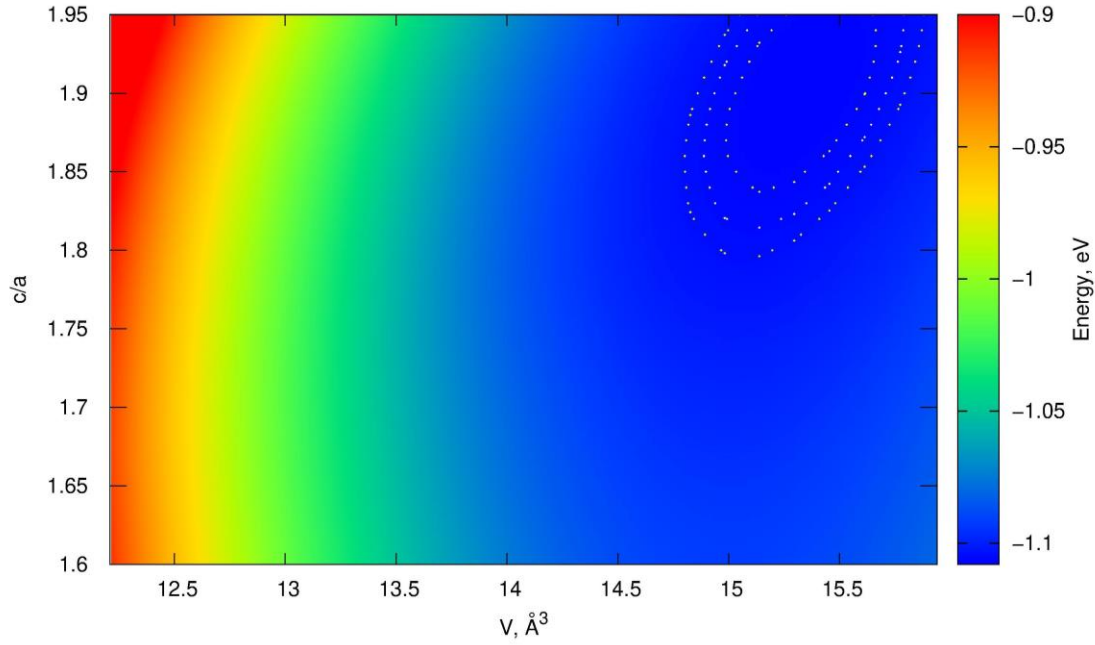


Figure 8. Total energy for the hcp Zn as a function of the volume per atom and hexagonal axial ratio, c/a calculated within PAW-VASP. Dotted iso-energy lines are placed around the global energy minimum with steps of 0.001 eV.

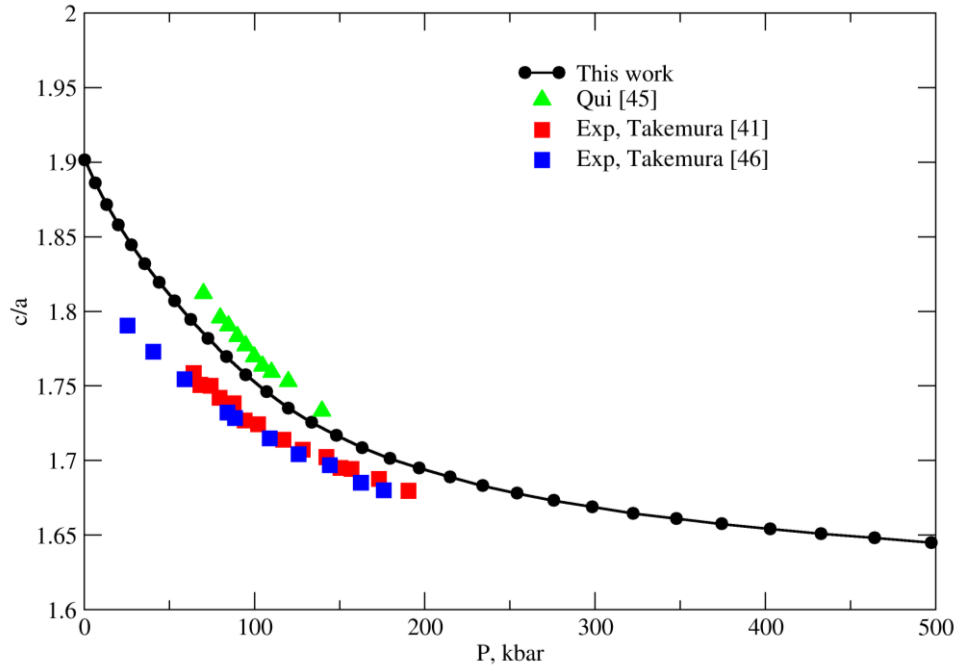


Figure 9. Calculated c/a ratio for pure Zn from *ab initio* calculations for 0 K as a function of pressure. These show that at high pressure Zn tends to adopt an ideal c/a ratio. The experimental points and results of previous theoretical calculations are included for comparison^{41, 45, 46}.

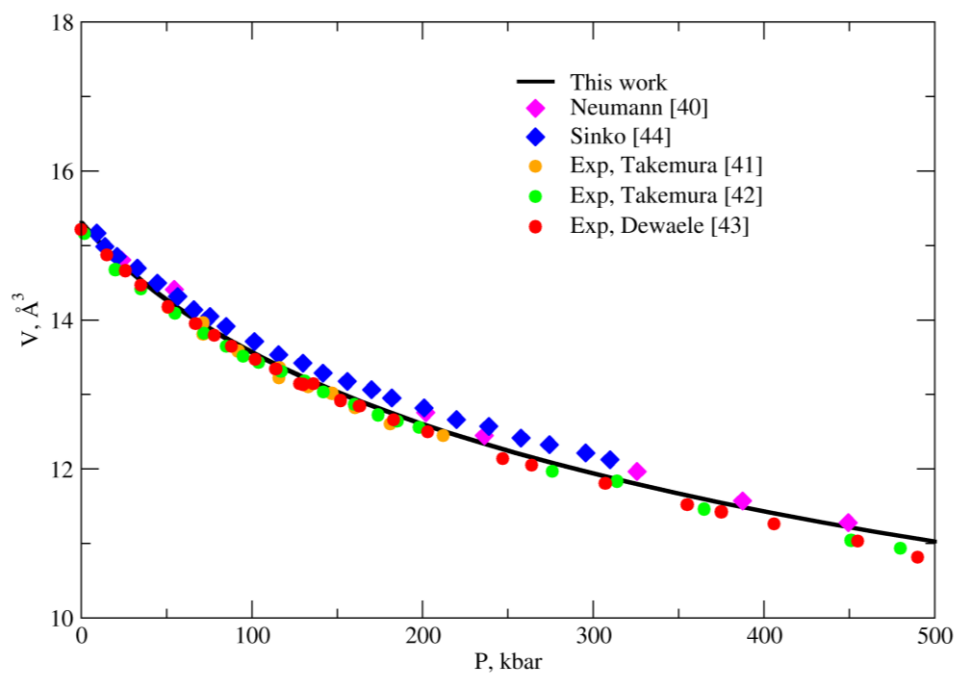
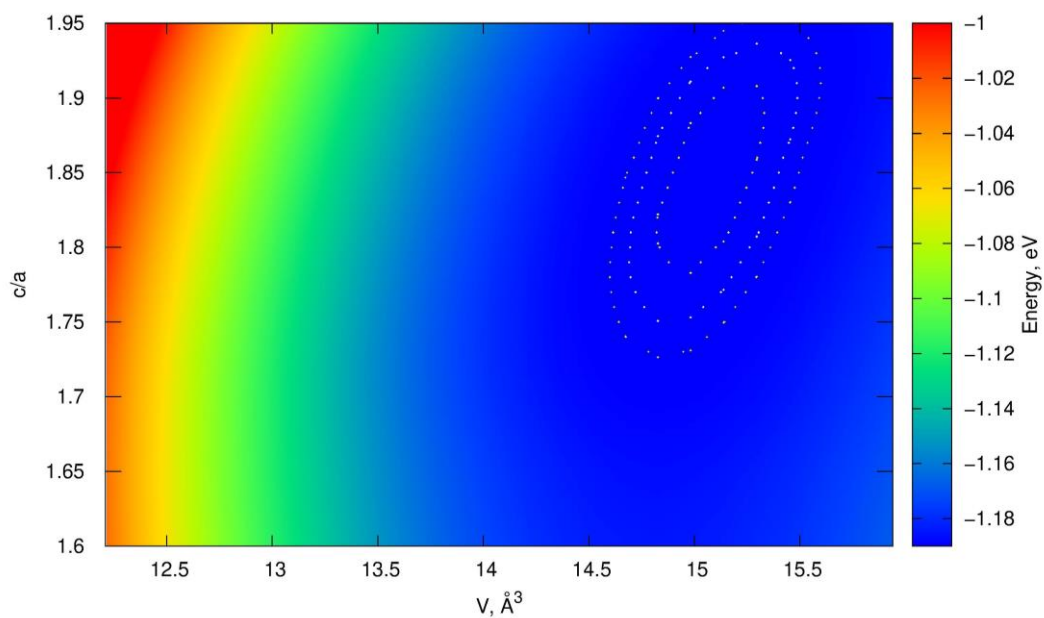


Figure 10. Calculated volume per atom of Zn at 0 K from *ab initio* calculations. The high pressure region represents Zn in an ideal c/a ratio. The experimental points and results of previous theoretical calculations are included for comparison ⁴⁰⁻⁴⁴.



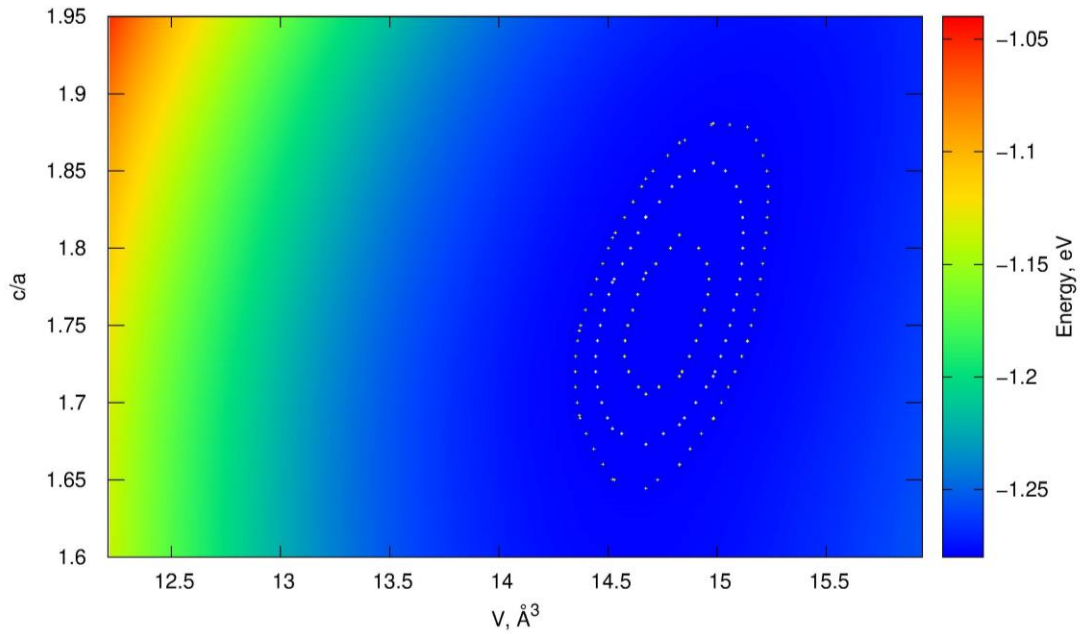


Figure 11. Total energies for the $\text{Zn}_{96.875}\text{Cu}_{3.125}$ (a) and $\text{Zn}_{93.75}\text{Cu}_{6.25}$ (b) random alloy as a function of the volume per atom and the hexagonal axial ratio, c/a , calculated with PAW-VASP. Dotted iso-energy lines are placed around the global energy minimum with steps of 0.001 eV.

Two specific Cu-Zn alloys were modelled in a similar way using supercells containing 32 and 16 atoms. At a Cu 3.125 at% concentration the alloy nears the solid solution boundary, and its lattice parameter changes insignificantly compared to pure Zn ($a = 2.66 \text{ \AA}$, $c/a = 1.86$.) However, as we can see on Figure 11a the gradient near the minimum values becomes less steep compared to pure Zn, it remains noticeably elongated, with the same tilt to the right (towards the increase in volume). An alloy with a Cu concentration of 6.25 at% (Figure 11b belongs to the two-phase region (a mixture of η and ϵ phases). The equilibrium value of the lattice parameter for this alloy is $a = 2.69 \text{ \AA}$ and $c/a = 1.76$, which is much closer to the ideal c/a ratio. The energy dependence against c/a shows the presence of only one global minimum, which is less pronounced in this case than in the alloy with a Cu concentration of 3.125 at%. It becomes clear that the formation of the second minimum does not occur. Previous calculations³⁸ demonstrated the existence of a local minimum corresponding to the ϵ -phase, which becomes more energetically favourable with increasing concentration of copper. In our calculations we can see that with the increase of Cu concentration the region of the minimum values becomes less elongated and gradually "slips" from the abnormally high c/a to lower values, closer to the ideal ratio.

Using the numerically efficient EMT-CPA method, the mixing enthalpy of the disordered hcp alloys of the Cu-Zn system was calculated over the complete concentration range. Figure 12 shows the results of this calculation. The reference states are fcc Cu and hcp Zn. The mixing enthalpies obtained by the EMT-CPA method and by the PAW method are in good agreement with each other. Note that in EMT-CPA, calculations of the short-range order effects are neglected. They should slightly decrease the enthalpy of mixing at finite temperatures⁵¹. Giving this, ab initio results appear to be in good agreement with experiment and make it possible to analyse the behaviour of the mixing enthalpy of a continuous series of disordered alloys. Moreover, Fig. 12 shows the first-principles data obtained at ideal c/a ratio in addition to the

mixing enthalpies calculated for the optimized values of the c/a ratio. It is clearly seen that near the composition corresponding to 90 at% Zn, the mixing enthalpy, calculated for the optimized c/a ratio, has an inflection, which correlates to the coexistence of two phases in this region. Moreover, Fig. 12 shows that there is excellent agreement between the assessed difference in enthalpy between stable Zn (with a non ideal c/a ratio) and Zn with an ideal c/a ratio.

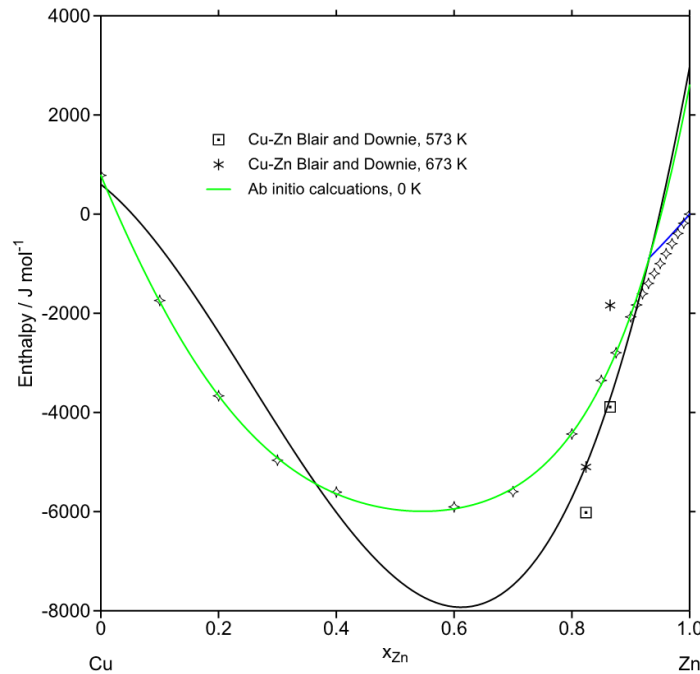


Figure 12. Mixing enthalpy of hcp Cu-Zn alloys with optimized (diamonds) and ideal (green line) c/a ratio calculated from first principles using EMTO-CPA method for $T=0$ K as in Figure 11, fitted according to a Redlich Kister expression. Superimposed is the assessed enthalpy of mixing from using the data of Kowalski and Spencer (black line)²¹. The blue line is the calculated enthalpy of mixing in the two phase region between the two hcp phases. The reference states are fcc Cu and hcp Zn. The experimental points from Blair and Downie²⁸ are included for comparison.

Calphad modelling

The comments of Schmid-Fetzer and Hallstedt

Over the last 25 years it has been the practice in the CALPHAD community to model these two distinct phase regions with different thermodynamic datasets although it is recognised that it would be best if a model could be devised which represent data for both regions within a single dataset. The conventional Redlich-Kister power series expansion is unfortunately not nearly good enough for this purpose. The phase with the anomalous, highly non-ideal c/a ratio has been labelled HCP_ZN, leaving the region with the more ideal c/a ratio to be designated as HCP_A3, the same designation we also use for elements such as Mg, Co, Tl, Ti etc.

Recently Schmid-Fetzer and Hallstedt¹⁹ strongly suggested that the η phase, the Zn terminal solid solution should be designated as HCP_A3, instead of the ϵ phase. They draw heavily in their arguments on the fact that in the Mg-Cd system where both components crystallise in the

hcp structure, there is continuous solid solution. This is in spite of the fact that Cd also has an anomalous c/a ratio like Zn. Their argument is that Mg is the prototype for the hcp_{A3} phase structure and, since it and Cd form a continuous series of solid solutions, Cd must also be designated as HCP_{A3}. Since Zn and Cd are similar, Zn must also have a HCP_{A3} designation. Consequently the ϵ phase in the Cu-Zn, Ag-Zn and Au-Zn system, if they are to be modelled as separate phases should be designated, according to their argument, as an hcp variant.

We believe that their arguments are not valid. Firstly, figure 4 shows the expected variation of the Gibbs energy of the hcp phase of the Cu-Zn system with composition also showing the extra stability for compositions close to pure Zn arising from electronic effects. For the nearly all the composition range the c/a ratio can be expected to be near ideal. Although the curves in Figures 4 are, to some extent, schematic they are strongly supported by our *ab initio* data (Fig. 12). Consider now the solution of Mg in such a phase. One could imagine that the thermodynamic properties for the composition range with a near ideal c/a ratio would be relatively easy to model. However one might expect that the thermodynamic properties of a solution of Mg in Zn with the anomalous c/a ratios would display unusual variation with composition. Secondly in the Cd-Mg system which Schmid-Fetzer and Hallstedt¹⁹ use to justify their suggestion, the variation of the c/a ratio with composition is much less marked than in the Cu-Zn, Ag-Zn and Au-Zn systems⁴⁷. It is therefore likely that any anomalous behaviour in the thermodynamic properties would be spread over a wide composition range reflecting the more gradual change in c/a ratio. Of course, to support the above discussion the Cd-Mg system should be the subject of a future study.

Similarity to magnetic anomalies

In many respects the extra stability gained by Zn by assuming an anomalous c/a ratio is equivalent to a magnetic contribution to the Gibbs energy. In systems such as Co-Cr, Co-Mn, Co-V and Fe-Ni, the strength of the magnetic contribution coupled to the steep variation of the Curie temperature with composition may lead to the existence of a so-called 'Nishizawa horn'⁴⁸, a miscibility gap between a ferromagnetic region and a paramagnetic region of the same phase. For other systems the magnetic effect may show up as a small perturbation in the phase boundaries only. To some extent this seems similar to the occurrence of miscibility gaps in Zn systems and it is appealing to see whether the model used so successfully for magnetic materials can be adapted to represent the effect on the thermodynamic properties on these systems.

The approach used with some success within the CALPHAD community over the past 30 years for the magnetic contribution to the thermodynamic properties was suggested by Hillert and Jarl⁴⁹ based on the work of Inden⁵⁰. Its adoption would require the definition of some critical temperatures akin to the Curie temperature i.e. in this case where the Gibbs energies of both forms (ideal and anomalous c/a ratios) are the same. For Zn this should be in the region of 3000 K according to the assessed data and the experimental information given in Figures 6 and 7. For the other elements this critical temperature should be very negative such that the variation of this critical temperature with composition should give rise to the miscibility gap (Figure 13). The magnitude of thermodynamic contribution would also be expected to change with composition just as the magnetic contribution varies.

The red line in Figure 13 shows schematically the expected variation of the critical temperature with composition. It should be emphasised that there is no magnetic anomaly in the hexagonal phases in the Cu-Zn system but there is an electronic contribution to the thermodynamic properties which is dependent on composition, pressure and probably temperature. In the Cu-Zn system the transition between the two hexagonal phases is first order in nature. However it is possible that in other systems there could be a second order phase transition. In the Cd-Mg system it seems as if the c/a ratio varies in a much less dramatic way compared to other systems such as Cu-Zn. Might the anomaly be seen here in careful measurements of enthalpies of mixing or the heat capacity? A full understanding of this phenomenon will require further *ab initio* calculations and experimental studies on a wider range of systems before a model equivalent to the magnetic contribution can be recommended. An exploration of this approach will be the subject of a future study.

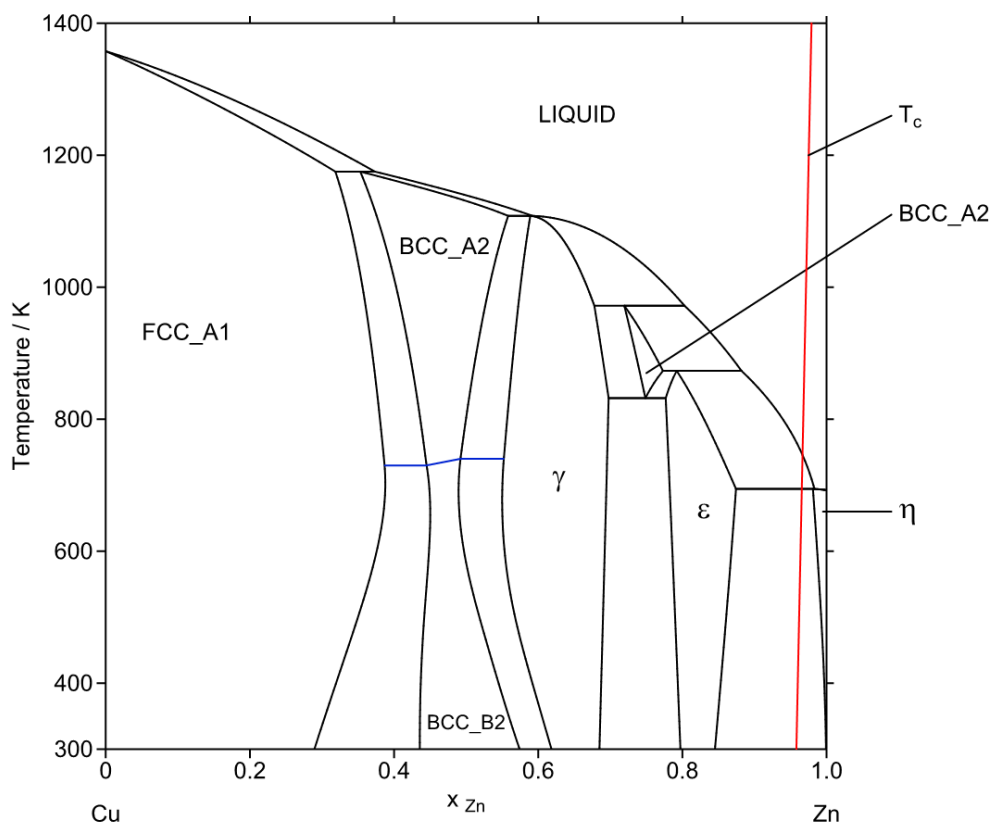


Figure 13. Calculated phase diagram for the Cu-Zn system showing the expected variation of the critical temperature marking the position of the sharp change in c/a ratio. The blue line represents the second order transformation from BCC_B2 to BCC_A2.

Conclusions

The effect of the c/a ratio on the thermodynamic properties of the hexagonal phase in zinc based solid solutions has been explored. It is argued that the approach adopted by the CALPHAD community for the past 25 years is correct whereby the zinc and cadmium terminal (η phase) solid solutions are designated as HCP_ZN in contrast to the ϵ phase which is designated as

HCP_A3. A potential approach whereby both phases can be modelled using a single dataset based loosely on the familiar magnetic model, is recommended and will be the subject of a future investigation. Further experimental calorimetry is needed to obtain a better understanding of the difference in enthalpy between the pure Zn and the form with the hypothetical form with a more ideal c/a ratio and this will be supported by *ab initio* calculations.

Data Availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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