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Anomalous behavior of lattice parameters and elastic constants in hcp Ag-Zn alloys

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The observed c/a lattice parameter of hcp solid solution $Ag_{1-x}Zn_x$ shows anomalous behavior in both ϵ $(0.68<x<0.87)$ and η $(x>0.95)$ phases. We investigate the nature of these anomalies by performing *ab initio* exact muffin-tin orbitals total energy calculations for hcp $Ag_{1-x}Zn_x$ random alloys. The peculiar features in crystal structure and elastic constants are mapped out in detail, and where experimental data are available they excellently agree with the theoretical results. The sharp variation in c/a obtained for $x=0.87$ is explained by an almost zero resistance to c/a variations at constant volume, giving a deformation path with a very low energy barrier connecting the ϵ and η phases. The rapid decrease of c/a in Zn-rich alloys, on the other hand, is found to have a band energy origin.

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The crystal structure gives the key to many properties of solid materials. Unusual structural properties that can be subtly tuned by chemical composition or external conditions are of great interest.[1–3] Most elemental metals crystallizing in the hexagonal close packed (hcp) lattice have an axial ratio c/a that is close to the "ideal" value 1.633 obtained in a stacking of rigid spheres. Zn and Cd are exceptions, with $c/a=1.86$ and 1.89, respectively. Here we focus on the striking variations in c/a on alloying, as exhibited in the Ag-Zn solid solutions. The hcp structure is the thermodynamically most stable phase of $Ag_{1-x}Zn_x$ in two separate regions: in the ϵ phase from about $x=0.68$ to $x=0.87$ and in the η phase when $x>0.95$. Experiments[4–6] show that c/a decreases very rapidly on alloying in the η phase (Fig. 1). In the ϵ phase c/a is somewhat lower than the ideal value,[4] first slowly decreasing as a function of Zn content, followed by a sudden and pronounced upturn close to the phase boundary. Contrasting this, the volume per atom varies slowly and monotonically in the hcp Ag-Zn lattice, with values for the intermediate ϵ phase agreeing well with a simple interpolation from pure Ag to the Zn-rich η phase.

It is our purpose in this report to demonstrate that modern computational quantum mechanics is able to describe and predict the anomalous concentration dependence of lattice parameters and elastic properties of low symmetry structures. We give a detailed account of how the crystal structure of hexagonal Ag-Zn varies with the composition, and relate this variation to peculiarities in the elastic behavior. Since theoretical calculations can be performed on metastable phases, we cover the entire composition range from pure hcp Ag to pure hcp Zn, thus obtaining a complete picture of the structural and elastic anomalies. We find that the sharp increase of c/a in the ϵ phase is related to the change of the compressibility mechanism. As opposed to this, the rapid decrease of c/a in η phase on adding Ag is governed by the kinetic contribution to the total energy. Based on our theoretical elastic constants we show that the ϵ and η phases remain mechanically stable around and slightly beyond the phase boundaries. Within the two-phase-field region these phases are in thermodynamic equilibrium with a deformation path between them having a very low energy barrier. This suggests that at these compositions the hcp phases of the Ag-Zn alloy are close to mechanical instability.

Our total energy calculation is based on the density functional theory.[7] The one electron equations were solved using the recently developed exact muffin-tin orbitals (EMTO) method,[8–10] and the generalized gradient approximation (GGA)[11] was used for the exchange-correlation term. The

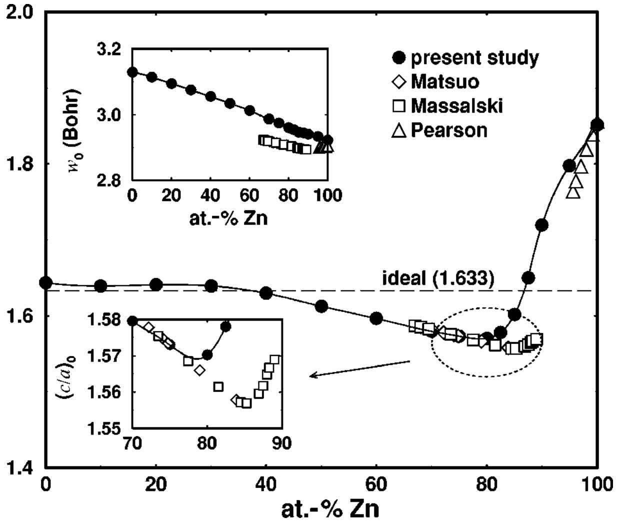

FIG. 1. Concentration dependence of the theoretical (present study) equilibrium axial ratio $(c/a)_0$ in hcp $Ag_{1-x}Zn_x$ alloys. The upper inset shows the calculated equilibrium atomic radii w_0 as a function of Zn content. In the lower inset the rapid upturn of $(c/a)_0$ near 82% Zn is illustrated. Experimental data are from Matsuo (Ref. 6), Massalski (Ref. 4) and Pearson (Ref. 5).

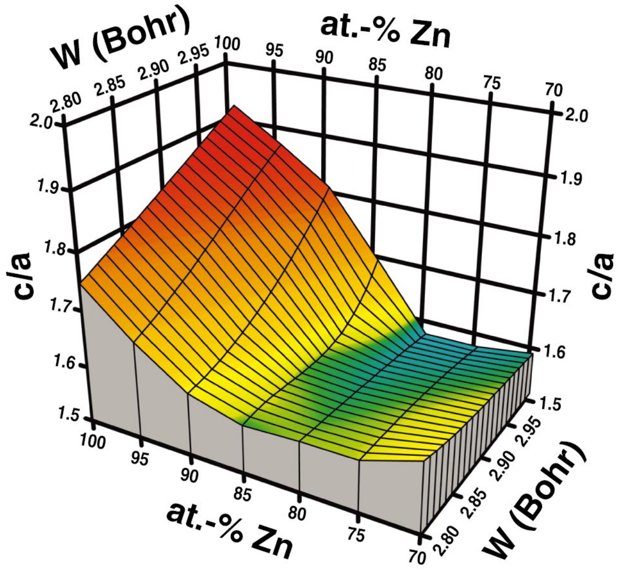

FIG. 2. (Color) Theoretical axial ratios (c/a) of hcp Ag-Zn random alloys plotted against chemical composition (at.-% Zn) and average atomic radius (w).

substitutional disorder was treated within the coherent potential approximation (CPA),[12–14] neglecting the short range order and local relaxation effects. The EMTO-CPA method has been successfully used in the *ab initio* study of the bulk properties of metallic alloys, semiconductors and oxides.[2,3,9,10,14–19]

For each concentration x in $Ag_{1-x}Zn_x$ the theoretical equilibrium average atomic radius w_0 and axial ratio $(c/a)_0$ were determined by minimizing the total energies $E(w,c/a)$ of hexagonal structures calculated for five different atomic volumes and seven c/a ratios close to the energy minimum. The bulk modulus B was obtained from an exponential Morse fit at the energy minima.[20] The five hexagonal elastic constants $c_{11}, c_{12}, c_{13}, c_{33}$ and c_{44} were obtained from the bulk modulus, $B=[c_{33}(c_{11}+c_{12})-2c_{13}^2]/C$, the logarithmic volume derivative of c/a, $R \equiv d\ln(c/a)_0/d\ln V_0=-(c_{33}-c_{11}-c_{12}+c_{13})/C$, where $C\equiv c_{11}+c_{12}+2c_{33}-4c_{13}$ and $V_0=4\pi w_0^3/3$, and three isochoric strains, as described in Ref. 21. The ratio of the linear compressibilities parallel and perpendicular to the c axis was obtained as $K\equiv K_{\parallel}/K_{\perp}=(c_{11}+c_{12}-2c_{13})/(c_{33}-c_{13})$. All calculations were done at the theoretical lattice parameters.

To assess the accuracy of the EMTO-CPA method in the present system[22] we compare in Table I the theoretical results obtained for the $Ag_{0.3}Zn_{0.7}$ random alloy with experimental data.[6] The deviation between the theoretical and experimental equilibrium atomic radius and c/a are 2% and 0.2%, respectively. These discrepancies are typical for what has been obtained for elemental transition metals[23,24] using the GGA for the exchange-correlation functional.[11] The calculated elastic constants are somewhat small when compared with the measured values, but the relative magnitudes are well reproduced by the present theory. The overall agreement between theory and experiment is very satisfactory, especially if one notes that the total energy minimum is very shallow in Ag-Zn alloys (Fig. 4, later), which makes the calculation of elastic properties numerically difficult.

TABLE I. Theoretical (present results) and experimental (Ref. 6) equilibrium atomic radius w (units of Bohr), hexagonal axial ratio c/a, and elastic constants (units of GPa) of the hcp $Ag_{0.3}Zn_{0.7}$ random alloy.

	w_0	$(c/a)_0$	c_{11}	c_{12}	c_{13}	c_{33}	c_{44}
Theory	2.98	1.579	110	56	63	129	27
Experiment	2.92	1.582	130	65	64	158	41

Figure 1 shows the theoretical $(c/a)_0$ ratio for hcp $Ag_{1-x}Zn_x$ alloys in the whole range of concentrations $0\leqslant x\leqslant 1$. Experimental data taken in the ϵ[4,6] and η phases[5] are also included. Where a comparison with experiments is possible there is an excellent agreement between theory and experiment, which further testifies the accuracy to which our *ab initio* approach can describe structural properties of Ag-Zn random alloys. In contrast to the rapid changes in $(c/a)_0$, the equilibrium atomic radii w_0 follow, to a good approximation, Vegard's rule over the entire concentration range (see the upper inset in Fig. 1).

In order to understand the conspicuous sharp upturn of $(c/a)_0$ near the upper concentration limit of the ϵ phase, we have calculated the volume dependence of c/a for different concentrations. Figure 2 shows c/a as a function of the atomic radius w and chemical composition in the concentration range of interest. An important feature in the volume dependence of c/a is seen: for $x\lesssim 0.8$ c/a slightly decreases with volume, whereas for $x\gtrsim 0.8$ it shows the behavior characteristic of pure Zn.[25] There is a narrow concentration range around 82% Zn where the volume dependence of c/a is nearly flat. The parameter R, describing the logarithmic volume derivative of c/a near the equilibrium structure, has an almost constant value of -0.2 in the Ag-rich part of the ϵ phase. However, at about 82% Zn there is a change in the sign of R, followed by a marked increase. This variation in R imposes a transition in the linear compressibility ratio K. For $x\lesssim 0.82$ we have $K<1$, i.e., the a axis is more compressible than the c axis. For these compositions K shows a weak concentration dependence, which correlates well with the

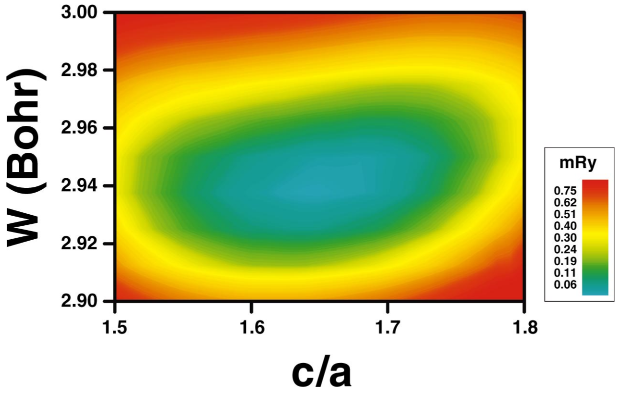

FIG. 3. (Color) Total energy (units of mRy) of the $Ag_{0.125}Zn_{0.875}$ alloy as function of atomic radius (w) and hcp axial ratio (c/a). The energies are plotted relative to the energy minimum.

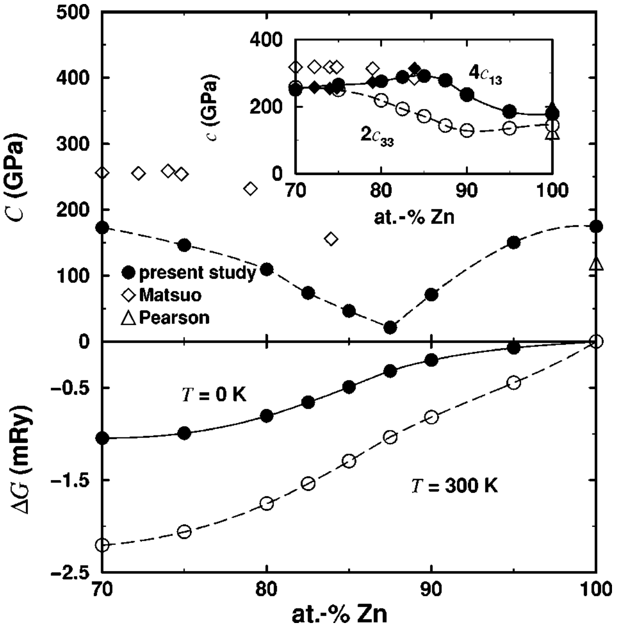

FIG. 4. Upper panel: calculated elastic constant $C \equiv c_{11}+c_{12}+2c_{33}-4c_{13}$ (inset: $2c_{33}$ and $4c_{13}$) of hcp Ag-Zn alloys as functions of concentration. Lower panel: the Gibbs energy of formation for hcp Ag-Zn random alloys for temperatures of 0 (solid line) and 300 K (dashed line).

trend of the axial ratio from Figs. 1 and 2. At concentrations above ~82% Zn K becomes larger than 1 and increases rapidly with x. The hardening of a axis relative to c axis causes the upturn in the $(c/a)_0$ already within the thermodynamic stability field of the ϵ phase.

In the vicinity of 88% Zn the total energy variation becomes very small when the volume is kept at V_0 and c/a is changed around its equilibrium value $(c/a)_0$. This is illustrated in Fig. 3, where the total energy of the random $Ag_{0.125}Zn_{0.875}$ alloy is plotted relative to the energy minimum as a function of w and c/a. Close to the equilibrium radius of this alloy, $w_0=2.94$ Bohr, the energy changes by only few tens of μRy when going from $c/a=1.55$ to $c/a=1.75$. The flatness of the $E(w,c/a)$ function can be seen at other volumes as well. Collating this energy map with that obtained for the $Cu_{0.07}Zn_{0.93}$ random alloy (Fig. 3 of Ref. 14) we conclude that the very shallow minimum around the equilibrium appears as a result of the superposition of two shallow energy minima near $c/a \approx 1.64$ and $c/a \approx 1.7$, corresponding to the ϵ and η phases, respectively. At this concentration the ϵ and η phases are in thermodynamic equilibrium, with a barrier of the order of μRy between the two energy minima.

The variation of $E(w,c/a)$ with c/a at constant volume, calculated for the equilibrium structure, is described by the elastic constant C.[21] In the upper panel of Fig. 4 the concentration dependence of the theoretically derived C is compared with the experimental data.[5,6] Although there is an almost constant shift between theoretical and experimental values,[6] the observed trend in $C(x)$ is well captured by the *ab initio* theory. The pronounced minimum in $C(x)$ around 88% Zn appears as a result of the noticeable variations of $2c_{33}$ and $4c_{13}$ terms from the expression of C with concentration (see the inset of Fig. 4).

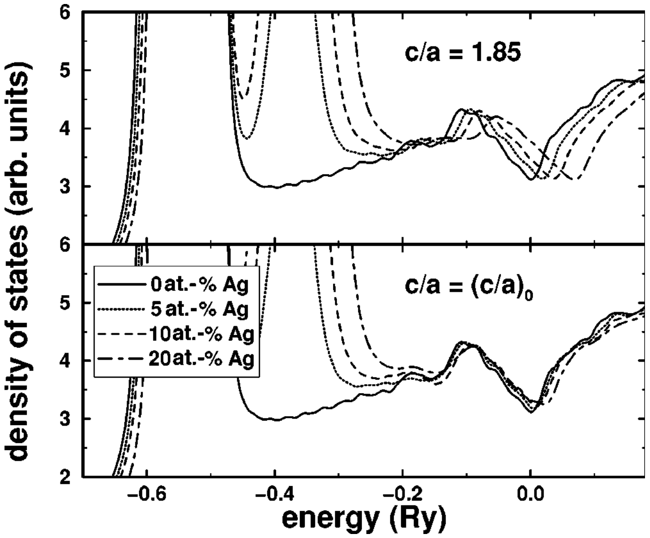

FIG. 5. The total density of states of $Ag_{1-x}Zn_x$ random alloys ($x=1, 0.95, 0.9$ and 0.8) calculated at the equilibrium volumes and $c/a=1.85$ (upper panel) and $c/a=(c/a)_0$ (lower panel). The equilibrium volumes and $(c/a)_0$ are shown in Fig. 1.

The calculated trend of the elastic constant $C(x)$ shows that hcp random Ag-Zn alloys may have a mechanical instability, or be very close to such a behavior, at about 88% Zn. Using our calculated total energies we estimated the Gibbs energies of formation $\Delta G(x)$[26] of Ag-Zn random alloys at $T=0$ and $T=300$ K. This is shown in the lower panel in Fig. 4. From the shape of $\Delta G(x)$ we determine the stability limits of the ϵ and η phases. We find that the theoretical two-phase-field region decreases from $0.77 \lesssim x \lesssim 1$ at $T=0$ K to $0.83 \lesssim x \lesssim 0.96$ at $T=300$ K, which is in qualitative agreement with the phase diagram information.[27] Thus, the softening of the hexagonal phases along the c axis, i.e., $C(x) \rightarrow 0$, will occur already inside two-phase-field region in the phase diagram, where in fact a single hcp phase is metastable and separates into ϵ and η phases.

Finally, we address the question of the rapid decrease of $(c/a)_0$ on adding Ag to η phase. The relatively large values of the calculated elastic constant $C(x)$ in Zn-rich Ag-Zn alloys (Fig. 4) and its smooth and moderate decrease with Ag content rules out an elastic origin. Since a similar rapid decrease of $(c/a)_0$ is seen in alloys between other noble metals and Zn or Cd,[28] a decisive role of the atomic size on crystal structure is also unlikely. In pure Zn the electrostatic energy, that favors the ideal c/a ratio, was found[29–31] to be suppressed by the band energy contribution, and a pronounced well in the density of states at the Fermi level stabilizes the large c/a of Zn. The present density of states for few Zn-rich $Ag_{1-x}Zn_x$ alloys, calculated at the theoretical equilibrium volumes, are shown in Fig. 5. At $c/a=1.85$ (upper panel) the Ag addition pushes the pseudo-gap near the Fermi level towards larger energies. When c/a is released (lower panel) the alloys find their equilibrium by bringing back the pseudo-gap to the Fermi level, which in turn is realized at $(c/a)_0 < 1.85$ (Fig. 1). Therefore, we find that the anomalous $(c/a)_0$ ratio in Zn-rich η phase has the same electronic origin as the one reported[29–31] in the case of pure Zn, namely, minimizing the band energy contribution to the total energy. With increasing Ag content, i.e., decreasing s electron density, the distortion-promoting band energy maintains its dominant role, and a reduced axial ratio minimizes the total energy.

In summary, using the EMTO-CPA *ab initio* total energy method we have obtained a complete description of the variation in the crystallographic unit cell dimensions of hcp Ag-Zn alloys. In particular, we have studied the exceptional variations in the c/a axis ratio and in the hexagonal elastic constants. The calculated behavior at intermediate concentrations (the ϵ phase) and at the Zn-rich end (the η phase) is in excellent agreement with experiments in these thermodynamically stable phases. The sharp upturn in c/a (in our calculations at about 82% Zn) is explained with reference to the axial ratio landscape when c/a is plotted as a function of the atomic volume and concentration. In the two-phase-field region the η and ϵ phases have different c/a ratios, but with almost the same total energy separated by a very small energy barrier. This is also manifested as an almost vanishing elastic constant corresponding to the isochoric hexagonal deformation. The rapid decrease of c/a in the η phase is found to be a consequence of the dominating role of the band energy term in the total energy.

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[22] In the self-consistent EMTO-CPA total energy calculations the one-electron equations were solved within the scalar-relativistic and frozen-core approximations. The Green's function was calculated for 21 complex energy points distributed exponentially on a semi-circular contour. The EMTO basis set consisted of the s, p and d orbitals. The total charge density was expanded in terms of spherical harmonics including terms up to $l_{max}=10$. For the calculation of the hexagonal axial ratios and the elastic constants in the irreducible wedge of the Brillouin zones $2500-7000$ k-points were used, depending on the particular crystal symmetry.

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