Origin of the Modulated Phase in Copper-Gold Alloys

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Statistical modulated phases which occur at high temperature in a number of alloy systems such as copper-gold cannot be explained either in an axial Ising model or by using arguments based on Fermi surface–Brillouin zone interactions. Instead we argue that these phases are stabilized by local disordering at antiphase boundaries. We back up our statements with precise density functional calculations in the local density approximation. [S0031-9007(96)02099-6]

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It is a curious fact that many compounds and polytypes exist in *modulated phases* in which periodic arrays of stacking faults or antiphase boundaries (APBs) modulate an otherwise small unit cell. These fall into two classes: "rational" structures (e.g., polytypes in SiC [1], or Ag_3Mg [2], in which the period M (number of small unit cells separating the modulating planar defects) is an integer and the defects are perfectly flat; and "statistical" structures (e.g., in Cu-Au or Cu-Pd alloys), which are usually high temperature phases, in which M can be an irrational number, or *average* period, often depending on stoichiometry. In the latter case, the defects are observed to be stepped—or wavy on the scale of tens of lattice constants [3]. We offer here a new explanation for the origin of statistical modulated phases after demonstrating the difficulties inherent in current theories. We find that the proper control parameter for determining the stability and period is not the nesting vector or Ising parameter, but instead depends on the ordering temperature of the alloy. As an example, we use the stoichiometric CuAu intermetallic compound.

An equiatomic mixture of Cu and Au is disordered on a face centered cubic (fcc) lattice at high temperature T. At low T the crystal orders into the CuAu-I structure in which the Cu and Au atoms occupy alternate (002) layers of the underlying fcc lattice. In a narrow intermediate temperature range there appears the CuAu-II phase [4]. Its structure is CuAu-I modulated by an array of APBs with an average separation of five fcc lattice spacings along the b axis; Fig. 1. Important experimental observations are: (i) CuAu-II is a high T phase which is accessible by heating or cooling through a first order transition [5]. (ii) The period of the APBs is statistical rather than rational [3]. (iii) M is found to increase both in the Au-rich and Cu-rich non-stoichiometries [3]. (iv) A *reduction* of M to as low as 1.5 is found upon large additions of impurities [5]. (v) High T modulated phases are observed in all Cu-Au alloys with greater than 25 at. % Au [3].

These observations would argue for a statistical mechanical explanation based on some alloy Hamiltonian with an order parameter, or an axial Ising model; and these indeed form the basis of some recent theories of modulated phases [7]. A more popular, and far older explanation is given in terms of Fermi surface–Brillouin zone interactions, in which the modulated structure is stabilized by Fermi surface nesting [5]. Although it is hardly likely that nesting can be occurring at all stoichiometries above 25% Au; that the theory would predict CuAu-II to be the ground state; and that the Fermi surface is smeared out at high T; the nesting argument remains popular, and recent calculations using first principles band structures show there are indeed parallel sheets of Fermi surface in CuAu-I and that the associated **k** vector is consistent with measured average periods [8]. Further confusion arises from mean field alloy Hamiltonian calculations which reveal a first order transition from disordered to a modulated phase $\langle M \rangle$ with $M \approx 2$ (rather than 5 as it should be), although electronic structure effects such as nesting are *neglected* in the semiclassical, parameterized Hamiltonian [7].

It is clear that to resolve this conflict one needs reliable total energy calculations, a problem for which the local density approximation in density functional theory is ideally suited [9]. We have now made the first systematic calculations and are able to show decisively that (1) Fermi surface nesting does *not* lower the internal energy of CuAu-II relative to CuAu-I, and (2) there is no explanation for the transition within an axial Ising model. There is a spectacular effect of atomistic and lattice relaxation, which has largely been neglected in previous work. We offer a new explanation for the appearance of modulated phases at high T which is based in a clear physical picture.

The Kohn-Sham equations are solved using full-potential LMTO [10] as described in Ref. [11]. To converge the tiny energy differences, especially for lattice and atomistic relaxations, we use modified tetrahedron integration [12] and a very fine mesh of **k** points of 20 divisions along the reciprocal lattice directions parallel to the a and c axes and $(20 + M)/M$ divisions along the b axis, which is M times longer. The calculations are very demanding and in the cells having $M > 4$ we do the relaxations with the Harris-Foulkes approximation [13] and make a self-consistent calculation of the final structure. We use direct energy minimization [14] rather

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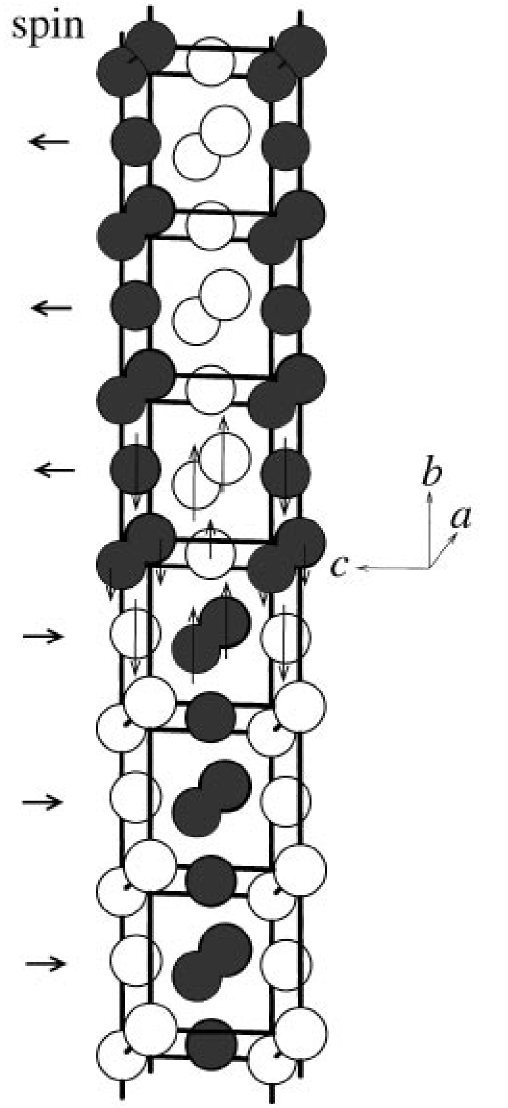

FIG. 1. Part of the CuAu-II unit cell near the APB. The spins associated with each CuAu-I unit cell are shown to the left and those atomistic relaxations greater than $0.1a_0$ are shown by arrows over the atoms; arrow lengths are roughly proportional to the distances moved. Crystal directions are also shown.

than minimization with forces and stresses. We then take a novel approach which allows us to demonstrate points (1) and (2) simultaneously.

We focus on the APB energy and make successively larger supercells in which the APBs are separated by one, two, $\ldots M \ldots$ unit cells of the CuAu-I structure. In the language of the axial Ising model, these are unit cells of the structures denoted $\langle 1\rangle, \langle 2\rangle, \ldots \langle M\rangle \ldots$ or $\ldots \uparrow\downarrow \ldots, \ldots \uparrow\uparrow\downarrow\downarrow \ldots$, etc. [6]. The "ferromagnetic" ground state CuAu-I $(\ldots \uparrow \ldots)$ is denoted $\langle\infty\rangle$. CuAu-II is $\ldots \uparrow\uparrow\uparrow\uparrow\uparrow\downarrow\downarrow\downarrow\downarrow\downarrow \ldots$, or $\langle 5\rangle$. The axial next nearest neighbor Ising (ANNNI) model might provide a description of the ferromagnetic to modulated to disordered transitions since the mean field ANNNI model phase diagram has just that structure; and for certain values of the ANNNI parameters, J_1 and J_2, one sees $\langle\infty\rangle$ to $\langle 5\rangle$ to disordered transitions [6]. These J_n are the parameters that appear in the expression for the total energy per four-atom layer of the structure $\langle M\rangle$ in the axial Ising model

$$E^{\langle M\rangle} = E_0 - M^{-1} \sum_{i}^{M} \sum_{n}^{\infty} J_n s_i s_{i+n}, \qquad (1)$$

where the spin s_i in layer i is ± 1 and E_0 is the nominal energy of an isolated layer. The energy of the APB in the structure $\langle M\rangle$ is $\gamma^{\langle M\rangle} = (1/ac)(ME^{\langle M\rangle} - ME^{\langle\infty\rangle})$ (a and c are lattice parameters). By taking the limit as $M \to \infty$ and using (1), the energy of the isolated APB is $(1/ac)(2J_1 + 4J_2 + 6J_3 \ldots)$, which is quite slowly converging unless the $|J_n|$ diminish rapidly with n. One expects an ANNNI description of the phase transitions if (i) only J_1 and J_2 are significantly large, (ii) $J_1 > 0$ so that the ferromagnetic ground state is stable, and (iii) $J_2 < 0$ to ensure "competing interactions" in the ANNNI phase diagram [6]. A corollary of (iii) is that the plot of $\gamma^{\langle M\rangle}$ against M has a negative initial slope (i.e., $\gamma^{\langle 1\rangle} > \gamma^{\langle 2\rangle}$), since $ac\gamma^{\langle 1\rangle} = 2J_1$ and $ac\gamma^{\langle 2\rangle} = 2J_1 + 4J_2$ in the next nearest neighbor approximation.

To begin with, we look at the APB energy as a function of M in a fixed lattice calculation, in which the lattice parameters are taken to be $a = c = 1$ and $b = 2M$ (in units of $a_0 = 3.86$ Å) and in which no relaxation of atomic positions is allowed. The results are shown in Fig. 2(a). As expected from the axial Ising description, γ converges only slowly with M. Furthermore, since

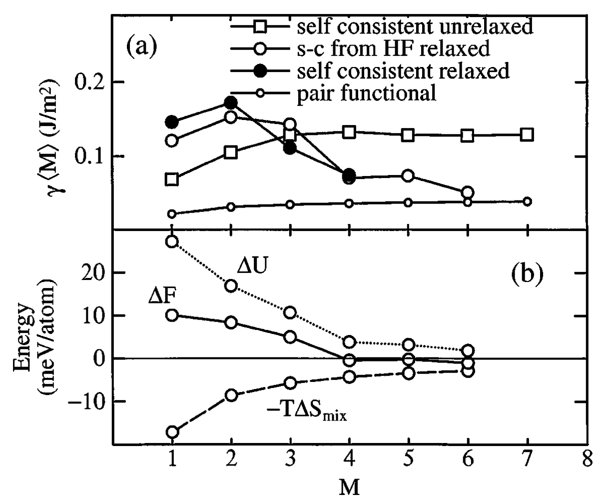

FIG. 2. (a) Self-consistent APB energies in supercells in which the APBs are separated by M units cells of CuAu-I, unrelaxed and relaxed; and from relaxations in the Harris-Foulkes (HF) approximation. (The relaxed energies can be higher than the unrelaxed because the energy of the CuAu-I structure is also lowered by relaxation.) Also shown are relaxed APB energies using the pair functional. (b) Internal energy per atom $\Delta U = (E^{\langle M\rangle} - E^{\langle\infty\rangle})/4$ and free energy per atom $\Delta F = \Delta U - T\Delta S_{\mathrm{mix}}$ at $T = 600$ K and taking the order parameter at the APB to be $\eta = 0.7$.

the initial slope is positive, both J_1 and J_2 are positive. Therefore based on static electronic structure, *the ANNNI model cannot predict the occurrence of the CuAu-II phase.* There is also clearly no special stability associated with the $M = 5$ structure that one would expect from the Fermi surface nesting theory. There may, of course, be parallel flat bands [8], but whether or not these lead to a lowering of energy can be determined only by a total energy calculation such as the present one. In other words special stability requires both nested bands *and* a large matrix element connecting them, and in this case the conditions are clearly not met.

We have then repeated these calculations while simultaneously relaxing the lattice parameters a, b, and c, and allowing all atoms to move independently, but in the b direction only. As Fig. 1 shows, the atomistic relaxations amount to a buckling of the atomic planes closest to the APB. These relaxations are only degrees of freedom for $M > 2$, and Fig. 2(a) shows the dramatic lowering of γ that accompanies these. We view this as an *electronic* consequence of relaxations driven by the large size difference between Cu and Au atoms, by comparison with pair functional calculations. The relaxed lattice calculations show a non-uniform convergence of γ and hence the Ising parameters, so a picture based on an axial Ising model is again not appropriate.

We have taken care to use the most precise density functional approach in order to be able to settle clearly points (1) and (2) above. However, the bonding in Cu-Au is not so subtle that an empirical pair functional model may not also be instructive. In order to come to an understanding of the origin of the modulated phases, we have used the same pair functional as previously used to study order-disorder phenomena in the Cu-Au system [15]. [The pair functional reproduces the isolated APB energy to within a factor of two [Fig. 2(a)] as well as the relaxed APB structure, and describes well the ground state properties of CuAu-I and the order-disorder transition [16].] In Ref. [15] it was found that significant predisordering ("wetting") occurred at a grain boundary and *this is the clue to understanding the modulated structures.* New Monte Carlo simulations shown in Fig. 3 now show wetting at the APB in CuAu-I at $T = 600$ K, so that the order parameter η is reduced to about 0.7 at the APB. In an ideal solution the entropy of mixing per atom of the structure $\langle M \rangle$ is $\Delta S_{\text{mix}} = M^{-1}k[-\eta \ln \eta - (1 - \eta)\ln(1 - \eta)]$, where k is Boltzmann's constant. For $T = 600$ K this is plotted in Fig. 2(b) and added to the internal energy per atom to give the free energy difference ΔF between structure $\langle M \rangle$ and CuAu-I. The very small energy differences and the approximate entropy mean that our results are semi-quantitative, but a very clear picture is evident: One could write the free energy of the unit cell of $\langle M \rangle$ as $ME^{\langle\infty\rangle} + (ac\gamma - TS_{\text{mix}}) + E_{\text{int}}$; the interaction energy between APBs (which vanishes as M increases) is positive and provides a *repulsion,*

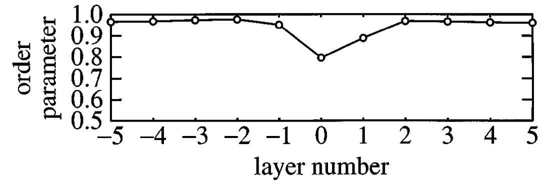

FIG. 3. Order parameter η at $T = 600$ K at planes on either side of an APB in the $\langle 5 \rangle$ structure.

but the term in parentheses at a certain T becomes negative and, coupled with the repulsion, stabilizes a *periodic* array of APBs. In our simple treatment we are neglecting the T dependence of the internal energy.

Our conclusions are as follows. CuAu-I is the ground state structure and there is no energy lowering by introducing periodic, perfect APBs, either by Fermi surface nesting or by ANNNI-like competing interactions. However, close to T_c the appearance of APBs *locally wetted* will lower the free energy and, due to their repulsion, stabilize a structure of periodic APBs. The reason that a new phase must form, rather than the gradual appearance of more APBs as the temperature increases, is that these defects arise from shifts in whole blocks of crystal and can be produced only within a crystal by a specific dislocation mechanism. The effect of wetting will be less in nonstoichiometric compositions since the crystal between the APBs will also have an increased entropy and hence M would be expected to be larger as observed. We cannot account for observations [5] in alloys with large impurity concentrations in which M is found to be as low as 1.5, but we believe these go beyond the realm of a dilute alloy theory and do not fall within the purview of our supercell results. However, our picture does account for all other experimental facts listed at the outset.

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