Electronic structure of ordered and disordered Cu-Ag alloys

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We present a study of the electronic structure of Cu-Ag alloys. This work includes total-energy evaluations, band structure, and density of states (DOS) determinations using the augmented-plane-wave method for the \( L_{12} \), \( B_1 \), and \( B_2 \) structures. We also study the corresponding disordered phases of these alloys by the tight-binding coherent potential approximation. Our results confirm the \( B_2 \) and \( L_{12} \) (Cu reach) as the stable structures of these systems. We compare the DOS with experiment and other calculations, and confirm the absence of both magnetism and superconductivity in these alloys. Finally we estimate charge transfer for these alloys from Cu to Ag.

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I. INTRODUCTION

In the process of obtaining the phase diagram of Cu-Ag, Cu-Au, and Ag-Au alloys, Wei et al.\(^1\) calculated by the linear-augmented-plane-wave method the band structure of the ordered \( A_nB_{4-n} \), \( (n=0, 1, 2, 3, 4) \) compounds. The results from ordered compounds were used in Ref. 1 via a three-dimensional Ising model, to obtain thermodynamic properties. Here we present in more detail the calculations of the band structure of Cu\(_3\)Ag and CuAg, using the semirelativistic (excluding spin-orbit coupling) augmented-plane-wave (APW) method. In addition we have used the tight-binding coherent-potential approximation (TB-CPA) in order to obtain the density of states (DOS) of the disordered alloys Cu\(_{0.75}\)Ag\(_{0.25}\) and Cu\(_{0.50}\)Ag\(_{0.50}\). We compare the DOS and other related properties with other calculations and experiment, when available. We have adjusted the APW muffin-tin sphere sizes in order to obtain charge transfers\(^2\) consistent with CPA and experiment.

Cu\(_3\)Ag crystallizes in the \( L_{12} \) structure (fcc unit cell with Ag at the corners and Cu at the face centers). By total-energy minimization we determined the lattice constant to follow Vegard’s rule closely. For CuAg we performed calculations in the CsCl and NaCl structures. It turned out that CuAg has lower total energy in the CsCl (\( B_2 \)) than in NaCl (\( B_1 \)). For the disordered alloys in the TB-CPA formalism, an energy shift is necessary for meaningful comparison with experiment. We have established a shift-determining procedure based on the \( d \)-band separation of the well-known Cu\(_3\)Au, which we consider as a prototype (see, for example, Refs. 2 and 3). For the ordered alloys, Wertheim, Mattheiss, and Buchanan\(^3\) proposed a shift of the Fermi level \( E_F \) in order to agree with experiments. A similar procedure was followed here, arising again from the prototype Cu\(_3\)Au. For the CPA calculations we used lattice constants that obey Vegard’s rule, although this underestimates both the experimental and the theoretical values;\(^4\) for Cu\(_{0.75}\)Au\(_{0.25}\) we performed a calculation with the experimental lattice constant (7.1 a.u. vs 7.07 a.u. from Vegard’s rule), and found no appreciable difference.

We found that disordering decreases DOS at \( E_F \), \( N(E_F) \), contrary to Cu-Au alloys.\(^5\) A study of Cu\(_{0.95}\)Ag\(_{0.05}\) by the Korringa-Kohn-Rostoker (KKR) cluster CPA method reveals essentially a Cu fcc DOS with a small Ag peak at 6.8 eV below \( E_F \).\(^6\) Another KKR-CPA study\(^7\) for Cu\(_{0.50}\)Ag\(_{0.50}\) shows a DOS at 2 eV below \( E_F \), and a Ag component at 6 eV below \( E_F \). We make comparisons with these available studies.

II. METHODOLOGY

The band structure of the ordered alloys was calculated with the APW method,\(^8\) where the core levels are treated fully relativistically as atomic levels, and the outer 11 elec-

![FIG. 1. The heat of mixing per atom as a function of the atomic volume for Cu-Ag alloys.](image-url)
TABLE I. Equilibrium lattice parameters (bohr) and bulk moduli (Mbar).

<table>
<thead>
<tr>
<th>Element/structure</th>
<th>Lattice constant</th>
<th>Bulk modulus</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Expt.</td>
<td>Other calc.</td>
</tr>
<tr>
<td>Cu fcc</td>
<td>6.83</td>
<td>6.673</td>
</tr>
<tr>
<td>Ag fcc</td>
<td>7.73</td>
<td>7.611</td>
</tr>
<tr>
<td>CuAg B2</td>
<td></td>
<td>5.688</td>
</tr>
<tr>
<td>CuAg B1</td>
<td></td>
<td>9.900</td>
</tr>
<tr>
<td>Cu3Ag L12</td>
<td></td>
<td>7.10</td>
</tr>
</tbody>
</table>

C. Reference 1.

FIG. 2. (a) The band structure of ordered Cu3Ag at the equilibrium lattice constant. (b) The total and the d-site-decomposed DOS.
two-center Slater-Koster parameters are treated as adjustable parameters, obtained by experimentation on our prototype Cu₃Au revealed that an appropriate on-site parameter shift would yield equal d-band separations in both the ordered and the disordered alloys.

III. RESULTS

In Table I we give the calculated lattice parameters and the corresponding bulk moduli for the ordered compounds and for reference the corresponding values for the pure elements. Our total energy results are given in Fig. 1, which shows the heat of mixing per atom, calculated by subtracting the percentage of the energy of fcc crystals Cu and Ag from the total energy of the alloy. In agreement with previous calculations, the L1₂ and B2 structures are shown to be the stable structures for the corresponding Cu-Ag alloys.

A. Ordered Cu₃Ag

Previous studies of Cu₃Ag address the issue of determining phase diagrams, but do not provide any details about the band structure per se, which would permit comparisons with our work. Our APW total-energy minimization yielded a L1₂ lattice constant of 7.008 a.u., in close agreement to other studies. The band structure and the DOS are shown in Fig. 2. The d band extends from 7.1 to 1.6 eV below E_F, and consists of mainly two parts, the lowest Ag part between 7.1 and 4.1 eV, and the upper Cu part between 4.1 and 1.6 eV below E_F. Ag has some small-d component in the Cu part, extending up to 1.5 eV below E_F. The Cu d band remains essentially the same as in the pure fcc Cu, while the Ag d band develops some d interaction with Cu and narrows by approximately 1 eV upon alloying. The Ag t₂g and e_g components are reversed compared to the pure Ag fcc. The semirelativistic separation between the low-lying Ag t₂g and e_g peaks is 0.55 eV. The main interactions are Ag(e_g)-Cu(s) and Ag(t₂g)-Cu(p), with a slight hybridization between Ag(e_g)-Cu(e_g)-Ag(s)-Cu(p), the Cu d states being essentially unmixed. In summary we can say that Ag loses its pure fcc character and it is influenced by its simple cubic environment; it interacts mainly with Cu s and p orbitals with a weaker d interaction between Cu and Ag. The Ag s states interact with Cu p states while hybridizing weakly with Ag e_g states.

B. Disordered Cuₐ₀.₇₅Agₐ₀.₂₅

We calculated Cu₀.₇₅Ag₀.₂₅ in the fcc structure by using the TB-CPA and SK parameters of pure Cu fcc and Ag fcc. We shifted the Cu on-site parameters by −0.08 Ry to match the Cu-Ag d-band separation in the ordered Cu₃Ag. The CPA DOS are given in Fig. 3. The whole valence band extends up to 9.5 eV below E_F, and consists of two parts, the Cu part between 1.3 and 4.3 eV below E_F and the Ag part between 4.3 and 6.8 eV below E_F. These features are maintained in the APW DOS of the ordered Cu₃Ag, calculated directly in the L1₂ structure, but the CPA DOS is smoother. Takano, Imai, and Fukuchi calculated with the KKR cluster CPA method the DOS of Cu₀.₀₅Ag₀.₉₅. Compared to the DOS of this alloy we can see some similarities: the existence of the Cu and Ag parts 3.4 and 2.0 eV wide, respectively, with comparable Cu and Ag peak positions separated by 3.4 eV.

FIG. 3. Total, Cu-site, and Ag-site DOS’s of Cu₀.₇₅Ag₀.₂₅.
C. Ordered CuAg

Since our calculations reveal that CuAg in the CsCl structure is more stable than NaCl, in Fig. 4 we present the band structure and DOS (total and angular momentum site-decomposed) in the CsCl structure. We see again the simple cubic symmetry characteristic that the lowest Ag $t_{2g}$ and $e_g$ components are reversed compared to the pure Ag fcc. The DOS shows two rather separated parts, the lowest Ag part and the upper Cu part. The valence bands extend up to 9 eV below $E_F$. The Ag $d$ part extends essentially between 6.8

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Cu</th>
<th>Ag</th>
</tr>
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<tbody>
<tr>
<td>Pure metal (fcc)</td>
<td>0.74</td>
<td>0.35</td>
</tr>
<tr>
<td>Cu$<em>{0.75}$Ag$</em>{0.25}$</td>
<td>0.69</td>
<td>0.47</td>
</tr>
<tr>
<td>CuAg</td>
<td>0.49</td>
<td>0.39</td>
</tr>
<tr>
<td>Cu$<em>{0.5}$Ag$</em>{0.5}$</td>
<td>0.67</td>
<td>0.42</td>
</tr>
</tbody>
</table>
and 3.4 eV below $E_F$, but there is also some mixing with the Cu $d$ part, which extends between 4 and 1.5 eV below $E_F$. The Cu $e_g$ states do not hybridize appreciably with Ag $d$ states, whereas the Cu $t_2g$ states interact mainly with Ag $t_2g$ states. Besides that, the Cu $p$ states have some interaction with Ag $e_g$ states, while some Ag $s$ and $p$ states interact slightly with Cu $p$ and $d$ states.

D. Disordered Cu$_{0.50}$Ag$_{0.50}$

We determined TB parameters corresponding to bcc Cu and Ag, and applied an energy shift in the CPA of $-0.08$ Ry as in Cu$_{0.75}$Ag$_{0.25}$. The resulting DOS is shown in Fig. 5 to consist of two broad features. The lower represents mainly Ag states located at about 6 eV below $E_F$, and the upper part represents Cu states centered at about 2 eV below $E_F$. The Cu peak is slightly narrower and higher than the Ag peak.

E. Densities of states at the Fermi level

The DOS at $E_F$, $N(E_F)$, is related to the specific-heat coefficient $\gamma$. For the Cu-Ag alloys it is shown in Fig. 6. We find a decrease of $N(E_F)$, and $\gamma$ upon disordering for the 25% composition, but an increase for the 50% composition. In Table II we list the values of the total $N(E_F)$ as well as the components of the constituent atoms for the ordered compounds. If we account for the number of atoms in each unit cell, all of the ordered compounds have nearly the same $N(E_F)$. The Fermi velocity $V_F$, also listed in Table II, is $1.29\times10^8$ cm/s in CuAg and $1.46\times10^8$ cm/s in Cu$_3$Ag. These values of $V_F$ are comparable to those of the pure elements. In Table II we also give the electron-phonon interaction parameters $\eta$ determined in the rigid muffin-tin approximation. These values are similar to those of the pure elements, and much smaller than the values of $\eta$ in typical superconducting materials, predicting no superconductivity. Finally, in Table II we list the Stoner criterion for magnetism $I_F N(E_F)$. These values are far from the value of 1.0 needed for the occurrence of magnetism, predicting paramagnetism.

F. Charge transfer

The APW analysis for the charge transfer depends on the size of the muffin-tin (MT) spheres. If equal MT spheres and an equipartition of the interstitial electrons are assumed, the results show the opposite direction of charge transfer than the CPA. On the other hand, if we use unequal MT spheres, which are proportional to the pure fcc elemental size, and if we partition the interstitial electrons proportionally to the volume of the unequal MT spheres, we find a charge transfer in very good agreement with our CPA results. In order to clarify this subject we performed similar APW and CPA calculations for the well-known Cu$_3$Au, and obtained the same trends concerning the charge transfer. Actually, the experiment shows that in Cu$_3$Au upon alloying there is a charge transfer from Cu to Au consistent with electronegativity arguments. In addition, Kuhn and Sham observed that the increase of the overall Au charge occurs in such a way so that the $d$ charge decreases, while the $s$ and $p$ charges increase. We find that our CPA calculation, which does not suffer from the ambiguity of the choice of the relative size of the muffin-tin spheres, agrees well with experiment. Hence, unequal MT spheres, appropriately determined as above, are necessary to describe the correct charge transfer. It should be emphasized that the band structure, and DOS, have very weak dependences on the relative size of the MT spheres. In Table III we give the charge transfer with unequal MT spheres for the Cu-Ag alloys.

![FIG. 5. Total, Cu-site, and Ag-site DOS's of Cu$_{0.50}$Ag$_{0.50}$.](image1)

![FIG. 6. The DOS around $E_F$ for Cu-Ag alloys.](image2)
IV. SUMMARY

In summary, with the intent to complement previous studies, we presented comprehensive calculations of the electronic structure of Cu-Ag alloys equally balanced between total-energy results and band-structure analysis. Our study includes ordered and disordered phases of these compounds using the APW and CPA methods, respectively.

ACKNOWLEDGMENTS

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