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Electronic structure of ordered and disordered Cu alloys: Cu_3Pd, Cu_3Pt, and Cu_3Au

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We present a relativistic study of the electronic structures of both ordered and disordered Cu_3Pd, Cu_3Pt, and Cu_3Au alloys. The electronic-structure calculations were performed with use of the fully relativistic Korringa-Kohn-Rostoker (KKR) and KKR–coherent-potential-approximation methods for the ordered and disordered phases, respectively. We focus on the changes in the electronic structure due to disorder and by isoelectronically replacing the 4*d* element Pd by the 5*d* element Pt and then its neighbor Au. We also discuss controversies concerning the electronic structure of the disordered Cu_3Pd alloy.

I. INTRODUCTION

The electronic properties of Cu alloys have been extensively studied, experimentally and theoretically. In particular, this work has provided an important testing ground for theories of alloy phase stability. Recently, there has been an effort to phrase theories in terms of the alloys' underlying electronic structure.[1] To this end, in this paper, the electronic band structures of Cu_3Pd, Cu_3Pt, and Cu_3Au are calculated in both their ordered and disordered phases. In particular, we focus on the changes in the electronic structure by isoelectronically replacing the 4*d* element Pd by the 5*d* element Pt and then by moving in the 5*d* row from Pt to its neighbor Au. While such a systematic investigation has its obvious merits, each of those alloy systems is interesting in its own right.

The Cu_3Au system is the canonical example of an order-disorder phase transformation[2] and the temperature-dependent changes in the electronic structure, as this transition is traversed, have been monitored by angle-resolved photoemission measurements.[3] Also, it has been extensively studied, allowing some comparison.[3-8] Both Cu-Pd and Cu-Pt show some fascinating incommensurate ordering phenomena.[9] Measurements of x-ray, neutron-, and electron-diffuse-scattering intensities find peaks as a function of momentum transfer. Moreover, these peaks vary smoothly with concentration. Gyorffy and Stocks[10] have proposed a theoretical framework in which such an incommensurate ordering effect derives from the existence of well-defined parallel sheets of the Fermi surface of the compositionally disordered alloy. This theory has been successfully applied to copper-rich Cu-Pd alloys. To date, similar applications to Cu-Pt and Cu-Au have not been made owing to the importance of relativistic effects in these alloys.

We show here a fully relativistic study of the electronic structures of both ordered and disordered Cu_3Pd, Cu_3Pt, and Cu_3Au alloys. We are able to see how the relativistic effects build up as the 4*d* component is replaced by a 5*d* component and how these change the disordering effects on the electronic structure. As a side issue to this systematic study, we also address the controversy which has surrounded the electronic structure of the disordered Cu_3Pd alloy.

In the next section we discuss the bonding of the ordered Cu_3Pd, Cu_3Pt, and Cu_3Au compounds. The third section compares the densities of states of the ordered and disordered alloys, while in Sec. IV the spectral functions are analyzed. This latter section provides a guide for temperature-dependent, angle-resolved photoemission studies. In the last section we compare these calculations with other work, both experimental and theoretical, on the electronic structure of Cu_3Pd and Cu_3Au. Finally, we draw some overall conclusions.

II. BONDING

We performed self-consistent-field–linear muffin-tin orbitals method–atomic-sphere-approximation (SCF-LMTO-ASA) calculations[11] within the Hohenberg-Kohn-Sham local-density-approximation (LDA) formalism for the ordered Cu_3Pd, Cu_3Pt, and Cu_3Au alloys. These LDA calculations should describe the bonding properties in these compounds. Indeed, from the cohesive energy (i.e., the electronic energy of an alloy minus the sum of energies of its constituent atoms) of Cu_3Pd, Cu_3Pt, and Cu_3Au versus the percentage deviation of the experimental lattice constant, the theoretical lattice constant is in very good agreement with the experimental ones: 0.4% too big for Cu_3Pd, 1.8% too big for Cu_3Pt, and 1.0% too big for Cu_3Au.

In these calculations we use atomic spheres of equal radii for Cu and its solutes, Pd, Pt, and Au. This might not take adequately into account that Pd, Pt and Au are bigger atoms. We also calculated the total energy per unit cell for Cu_3Pd as a function of percentage of Pd volume. Nevertheless, we find that the optimum Pd volume occurs at 30%, indicating that our choice of 25% is reasonable.

The overall excellent description of the bonding in this Cu compound series suggests that the underlying potential functions may give a good description of the electronic structure in these compounds. We put the LMTO-ASA potentials in muffin-tin form for use in the relativistic KKR (Ref. 12) and KKR-CPA (Ref. 13) codes to study the electronic structure of the ordered and disordered alloys. (KKR denotes Korringa-Kohn-Rostoker; CPA denotes coherent-potential approximation.)

In Fig. 1 we plot the phase shifts calculated from these muffin-tin potentials. A striking feature from Fig. 1 is that the resonance energies of the solute *d* orbitals are significantly lowered with respect to those of Cu as Pd is replaced by Pt, which is then replaced by Au in these alloys. Another interesting feature is the sizable increase in the spin-orbit splittings as the atomic number of the minority species is increased.

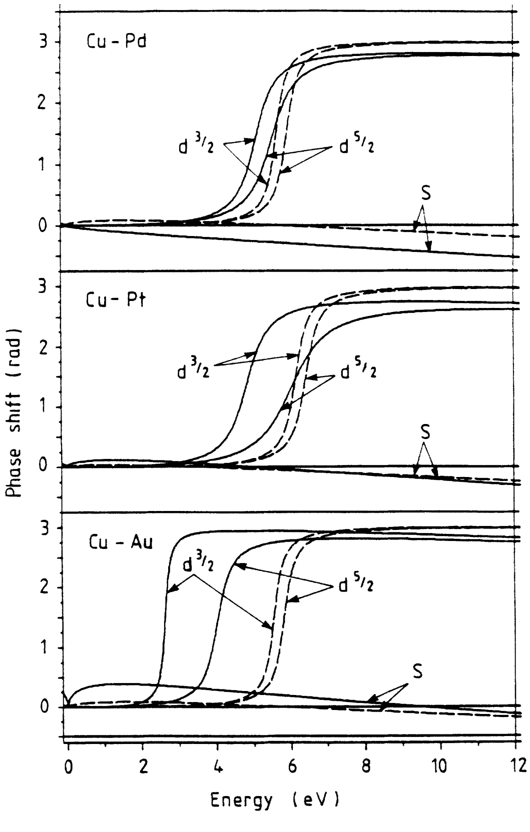

FIG. 1. Relativistic *s* and *d* phase shifts of Cu (dashed line) and Pd, Pt, and Au (solid line), in Cu_3Pd (top), Cu_3Pt (middle), and Cu_3Au (bottom), respectively.

The increase in the splitting of the Cu *d* resonance with the solute's *d* resonance will lead to an increasing tendency to split off solute *d* states from the bottom of the Cu *d* band. While the solute's *d* resonance moves to higher binding energy, the nature of the solute's *s* phase shifts also changes. From being negative in Pd, it becomes positive for Pt and Au: the *s* states are being pulled down in energy by the large relativistic mass-velocity and Darwin effects.

III. DENSITIES OF STATES

We calculated the densities of states of ordered and homogeneously disordered Cu alloys using the same muffin-tin potentials. We used the relativistic KKR and relativistic KKR-CPA methods. In the case of the relativistic KKR-CPA (RKKR-CPA) method use was made of the recent improvements in solving for the KKR-CPA equations.[13] Here, a stable numerical scheme is used to solve the KKR-CPA equations, which preserves their double-point-group symmetry at each stage in the iteration process. This overcomes problems that have been encountered with previous relativistic KKR-CPA calculations[4] of Cu-Au alloys. Reference 4 presented calculations of the relativistic densities of states of both ordered and disordered Cu_3Au alloys. The results for the ordered alloy were identical to those we present here. Although we have used the same LMTO ordered alloy potentials in our RKKR-CPA study of the disordered alloy as Ref. 4 [their Fig. 1(b)], we obtain only qualitatively similar results. We conclude that the discrepancies indicate the relative inaccuracy of the numerical scheme used in the earlier work to solve the RKKR-CPA equation.[13] Reference 4 also described how a self-consistent potential was constructed for the disordered alloys and assessed the effects of such self-consistency. We are unable to reaffirm these conclusions, however, since they are based on an interpretation of differences between densities of states which cannot, in our opinion, be reliably resolved using the earlier numerical scheme.

The multiple-scattering description of both the ordered- and disordered-material calculations makes the comparison between the ordered and disordered electronic structures particularly meaningful. From an inspection of the phase shifts in the preceding section, we anticipated the solute's states to move to higher binding energy as the atomic number increases, together with an increase in the spin-orbit-splitting effects. The densities of states of Fig. 2 confirm this. In Fig. 2 the total and site-decomposed density-of-states (DOS) functions for the disordered phase are compared with the total DOS of the ordered one. An examination of Fig. 2 from top to bottom shows the features at the bottom of the band building up and splitting as the spin-orbit effects grow.

The DOS functions in the ordered and disordered phases have similar features. The effect of disorder mainly smears out the sharp peaks present in the DOS spectra of the ordered phase. This disorder smearing is more pronounced at the bottom of the band than in the Cu-

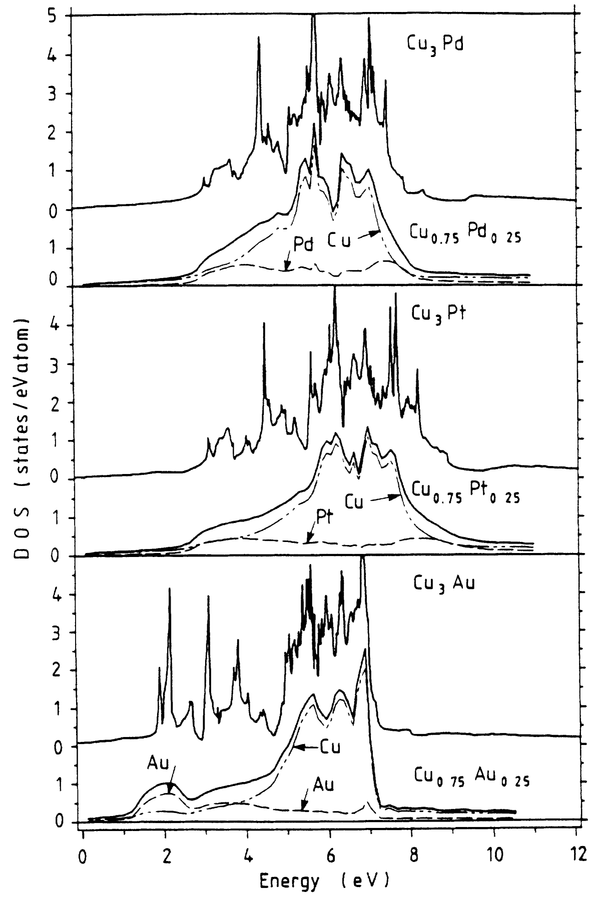

FIG. 2. Relativistic densities of states of ordered and disordered Cu_3Pd (top), Cu_3Pt (middle), and Cu_3Au (bottom). The density of states of the disordered alloy is site-decomposed.

dominated region of the DOS at the top of the band. A more detailed analysis of this energy-dependent disorder smearing will be made in the next section when we discuss the spectral functions. We remark that there is no shift of the DOS-related features between the ordered and disordered states. This confirms *a posteriori* our ansatz of using the same potential functions in these systems in both the ordered and disordered phases when studying the electronic structure. Moreover, these "disordered" calculations agree well with fully-SCF-KKR-CPA calculations for Cu_3Pd in which potential functions were obtained from self-consistent calculations of the disordered state.[14]

In conclusion, by increasing the atomic number of the solute in Cu from Pd to Pt to Au, we see an increasing tendency to split off a solute band from the common *d* band in these compounds and alloys. These common-*d*-band systems show no chemical shifts between the disordered and ordered phases. The effect of disorder is mainly an energy-dependent broadening of the DOS.

IV. SPECTRAL FUNCTIONS

In Fig. 3 we compare the bands of ordered Cu, Cu_3Pd, Cu_3Pt, and Cu_3Au along the [100] and [111] directions of the simple-cubic Brillouin zone. By replacing one of the Cu atoms in elemental, simple-cubic Cu (four atoms per unit cell) [Fig. 3(a)] by a Pd atom [Fig. 3(b)], degeneracies at the high-symmetry points Γ, *R*, and *X* are lifted. In the case of the *sp* bands, these degeneracies are lifted only slightly, whereas in the case of the *d* bands the effect is more pronounced. For example, the *sp* band crossing E_f in the Γ*R* direction has its degeneracy only slightly lifted when substituting one Cu by a Pd. This also remains the case for substituting one Cu by a Pt [Fig 3(c)] or a Au [Fig. 3(d)]. The reason for this is that the *s* and *p* scattering channels for the Cu, Pd, Pt, and Au are very similar, as shown in the phase-shift plot of Fig. 1.

We anticipated that the states with predominant *d* character will be substantially affected by the substitution of one of the Cu atoms by a Pd, Pt, or Au. In Fig. 1 we saw the splitting of the Cu *d* resonance from the solute's *d* resonance increasing and moving to higher binding energy when going from Pd to Pt and to Au. Inspection of the states at the Γ point reveals that the amount by

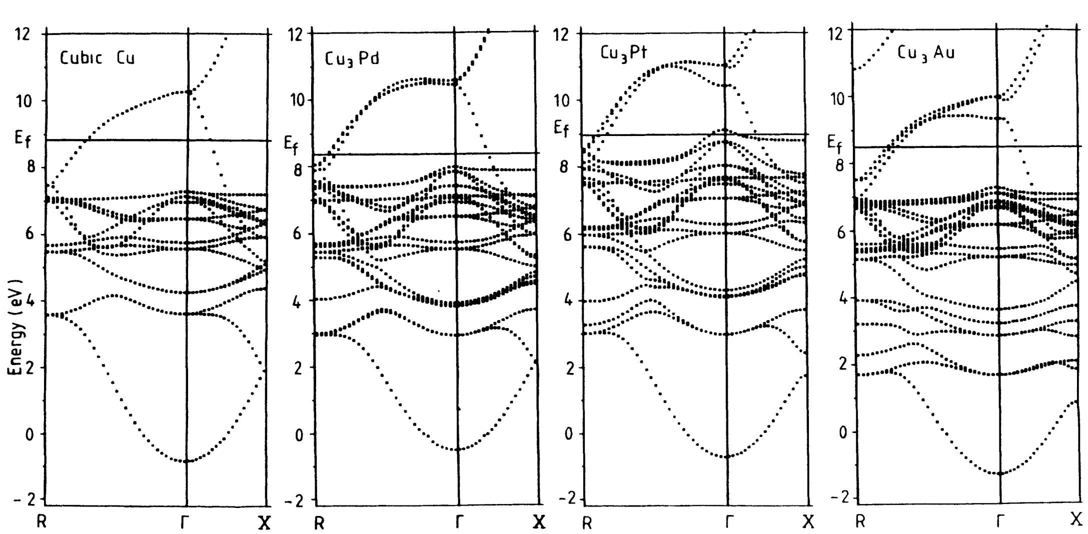

FIG. 3. Relativistic KKR band structures of simple-cubic Cu, Cu_3Pd, Cu_3Pt, and Cu_3Au.

which the degeneracies of the *d* states are lifted increases from Pd to Pt and to Au. For example, the third-lowest-energy eigenvalue at the Γ point has its degeneracy lifted in ever-increasing amounts when going from Pd to Pt and to Au. This effect is *k* dependent and therefore the topology of the bands also changes. The second energy eigenvalue at the Γ point moves down in energy towards the first one in the series Cu→Pd→Pt→Au. This will give rise to the growth of the DOS at the bottom of the common *d* band when going through the series.

At the top of the *d* band at the Γ point, at the seventh, eighth, and ninth energy eigenvalues, we see an increase in width from 0.3 to 1.1 to 1.7 eV, and then a decrease in the case of Cu_3Au to 0.7 eV. However, as seen from the density-of-states pictures in Fig. 2, this does not correspond to the splitting off of Pd and Pt bands from the top of the *d* bands. On the other hand, the band edge at the top of the *d* bands in Cu_3Pt and Cu_3Pd is not as steep as in Cu_3Au.

From the band structures of Fig. 3, we identified the states which give rise to the buildup of the states at the bottom and top of the common *d* band. What happens

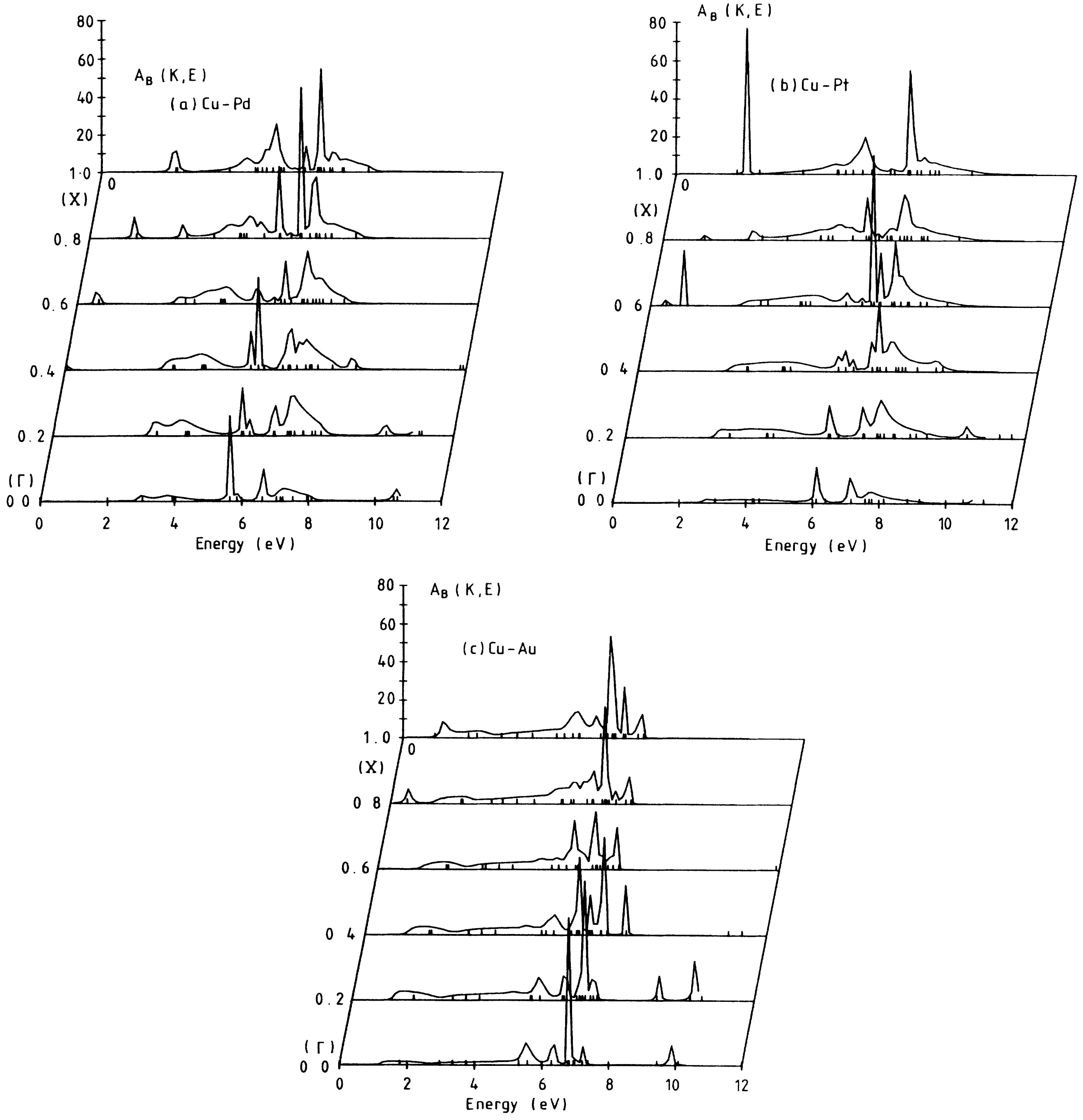

FIG. 4. Bloch spectral functions of the disordered alloys in the Γ*X* direction, compared with the energy bands of the ordered alloys (shown as tic marks).

now to these states when we disorder the compound? In Figs. 4 and 5 we compare the spectral functions of disordered Cu_3Pd, Cu_3Pt, and Cu_3Au with the band structures of the ordered compounds. The tic marks on the abcissa of the spectral functions denote the position of the ordered alloy's bands. We see that, wherever there are tic marks, there is structure in the spectral functions. In other words, disorder does not shift the states in these Cu alloys.

However, the widths of the structure of the spectral functions varies considerably as a function of K and E. There are some simple trends concerning this behavior. For the same reason that chemical substitution does not change the *sp*-dominated states substantially, disorder broadening for these states is also quite small. Disorder affects the *d*-dominated states strongly and significantly broadens them. In the case of Cu_3Pt and Cu_3Pd this disorder broadening occurs at the bottom and top of the common *d* band, while in Cu_3Au it mostly affects the bottom of the common *d* band. This explains why the disordered Cu_3Au alloy has nearly the same sharp band edge at the top of the common *d* band as in the ordered com-

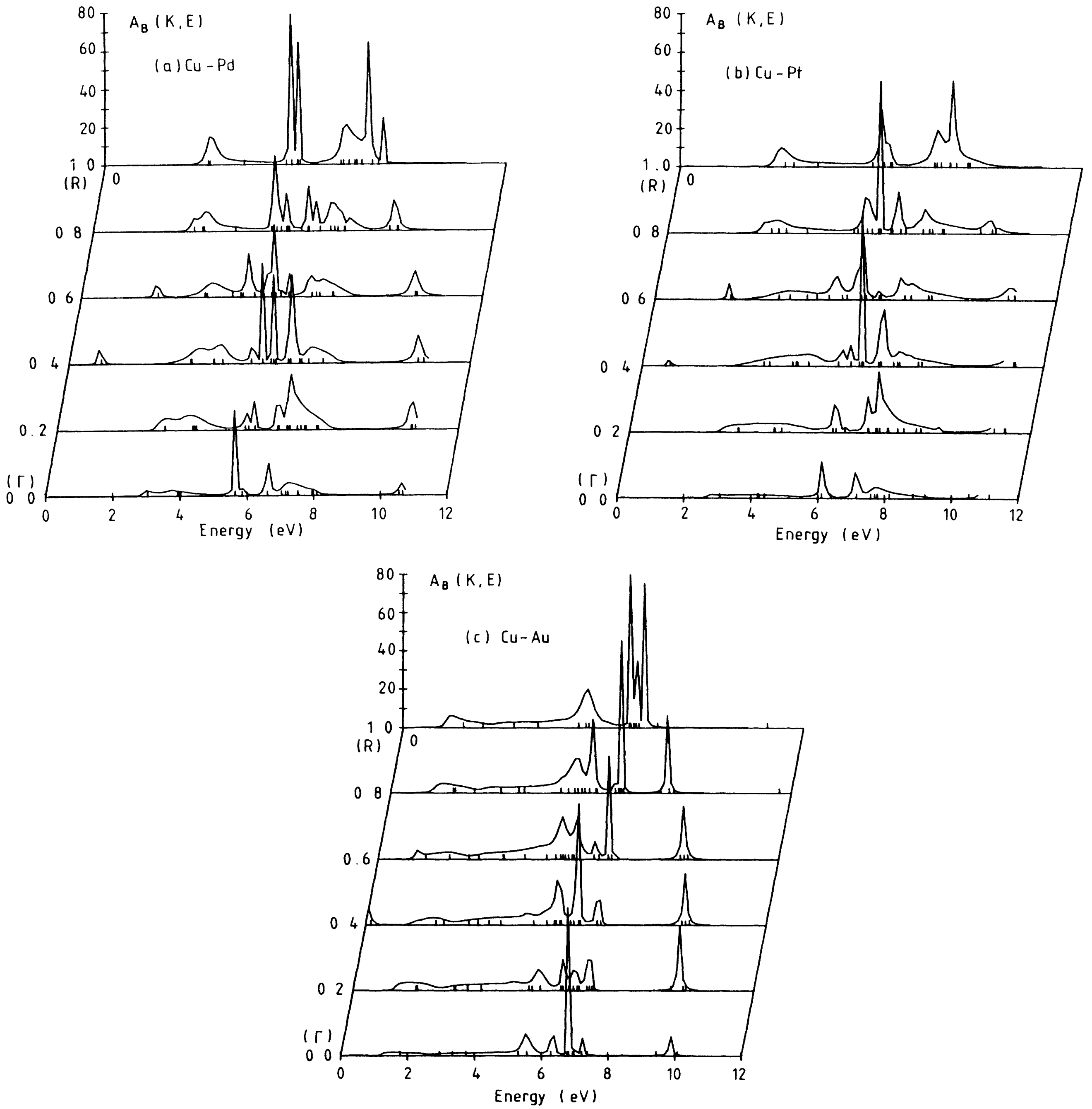

FIG. 5. Bloch spectral functions of the disordered alloys in the ΓR direction, compared with the energy bands of the ordered alloys (shown as tic marks).

pound, and why for both ordered and disordered Cu_3Pt and Cu_3Pd this band edge is much gentler. Again, the phase shifts offer a simple explanation for this: at approximately 8 eV the Cu and Au d resonances look more similar than the Cu and Pd or Cu and Pt resonances.

V. COMPARISON WITH EXPERIMENT

Numerous spectroscopic studies of the electronic structure of Cu_3Au and Cu_3Pd have been performed recently. All these studies focused on the bandwidth and the nature of the hybridization of the solutes Pd and Au with Cu. Unfortunately, the experimental studies of these two systems and their interpretations have been done quite separately, and what was considered a fundamental discrepancy with band theory regarding the solute's bandwidth in Cu_3Pd was dismissed as a minor discrepancy in Cu_3Au. With d bands of elemental Cu, Pd, and Au (and also Pt) spanning the same energy range (Cu from -2 to -5 eV below E_F, Pd from E_F to -5 eV below, and Au from -2 to -8 eV below E_F), the question arises of what happens when we alloy Pd and Au with Cu?

Previous studies have proposed various models for the electronic structure of Cu_3Au. For example, the Cu_3Au d band is a simple superposition of elemental Au and Cu.[15] More recently, Eberhardt *et al.*[16] analyzed ultraviolet-photoemission data as a superposition of elemental Cu with a spin-orbit-split atomic doublet of Au. The present band-theoretical calculations, and also the previous calculations by Skriver and Lengkeek,[5] Jordan *et al.*,[3] Davenport *et al.*,[6] Weinberger *et al.*,[4] Wertheim,[7] and Wertheim *et al.*,[8] all agree on the picture of hybridizing Cu and Au states giving rise to a common d band with the Au states dominating at the bottom of the d band and Cu at the top. Angle-resolved photoemission experiments of Wang *et al.*[17] have been able to map out some of the bands of Cu_3Au, but more detailed analysis of the experimental data is needed. These authors concluded that the band theory was giving a reasonable description of the Cu_3Au experimental data. Also, x-ray-photoemission-spectroscopy (XPS) measurements have been performed by Wertheim *et al.*[8] and suggest that band theory provides a good description of the experimental data, provided that a surface narrowing of the solute's d band is taken into account. Weinberger *et al.*[4] performed XPS calculations for ordered (and also disordered) Cu_3Au, neglecting this surface narrowing, and obtained good agreement with the experimental curves of Dicenzo *et al.*[18] after shifting the Fermi energy by 0.7 eV. Similar shifts are obtained by Wertheim *et al.*[8] (0.65 eV) and Krummacher *et al.*[19] (0.6 eV).

Our calculated spectral functions for disordered Cu_3Au (Figs. 4 and 5) show that the main effect of disorder is an energy-dependent broadening of the bands. This broadening is most pronounced at the bottom of the d band, where the Au-related states dominate. This broadening, however, extends over the whole d-band width. This has been seen experimentally in the work of Jordan *et al.*[3] A detailed comparison with this angle-resolved photoemission data is in the process of being carried out. Wertheim *et al.*[8] also see this disordering broadening extending over the whole bandwidth. Also in agreement with our calculations is that the fact that there is no change in d-band width between the ordered and disordered phases of Cu_3Au.

While much detailed work still needs to be done on Cu_3Au, the consensus is that Cu_3Au is a common d-band alloy whose electronic properties are considered to be well understood. This is in stark contrast with the situation in Cu_3Pd.

Spectroscopic studies of Cu_3Pd have given rise to some controversy. On one hand, for disordered Cu_3Pd Winter *et al.*[4] conclude that the alloy has a common d band and that there is good agreement between the electronic structure calculated by the KKR-CPA and the experimental data of Hedman *et al.*[20] Positron-annihilation studies by Debowska and Rudzinka-Girulska[21] are also consistent with $Cu_{1-x}Pd_x$ being a common-d-band alloy. Moreover, the Fermi-surface–spanning vector of these KKR-CPA results was used by Gyorffy and Stocks[5] to explain successfully the separation of the diffuse x-ray spots. All the above evidence suggests that the KKR-CPA gives an excellent description of the electronic structure of Cu_3Pd. In contrast, Wright *et al.*[22] recently performed ultraviolet-photoemission-spectroscopy (UPS) experiments as a function of photon energy using the Cooper minimum to extract the partial densities of states for disordered Cu_3Pd, and concluded that the KKR-CPA overestimates the Pd density of states at the bottom of the d band. They argued against a surface narrowing of the Pd states in their data as the possible source of discrepancy between theory and experiment, pointing out that the effect would have to be substantially larger than seen in elemental Cu, Ag, or Au. They considered the differential expansion of the Cu lattice around a Pd site, as seen by extended x-ray-absorption fine structure (EXAFS), as the reason for the Pd d-band narrowing. It is difficult to include this differential expansion in a first-principles calculation. Model calculations "see" a narrowing, but the effect is too small.[23] This issue might be resolved by an experimental study of ordered Cu_3Pd, which could be compared to our results. Our calculations show that the Pd d-band width is unaffected by the order-disorder transformation. This is contrary to the interpretation of Weightman *et al.*[24] which should give rise to an increase in the Pd bandwidth when lowering the temperature through the order-disorder transformation: Upon ordering, the differential expansion around the Pd sites should disappear and, therefore, the Pd bandwidth should increase. In addition, it is hard to reconcile such a large differential expansion effect in Cu-Pd with an apparently negligible effect in Cu-Au. We conclude that another cause has to be found for this narrowing of the Pd d band.

Soft-x-ray calculations also overestimate the Pd bandwidth in Cu_3Pd.[25] It has the same root cause, which is the self-energy, generated by electron-electron interactions, of the hole state in the excited many-electron system.[26] It should not be confused with a disorder effect. Moreover, a recent systematic study[27] indicates that for elemental Rh, Pd, and Ag, for example, good agreement with high-resolution XPS data is obtained only after including a phenomenological self-energy correction whose imaginary part increases with binding energy—this has the effect of suppressing the contribution from the bottom of the band.

VI. FUTURE WORK AND CONCLUSIONS

While Cu_3Pd and Cu_3Au belong to the same category of common-*d*-band alloys, the understanding of their electronic structures is perceived very differently. By studying these systems as a family, we were able to study the broad features of their electronic structures and to argue that nothing is fundamentally wrong with the calculated electronic structure of disordered Cu_3Pd. We propose an experimental study of ordered Cu_3Pd and a comparison with our ordered calculations to uncover the source of the discrepancy of the low-lying Pd states possibly due to differential expansion around a Pd site. We are in the process of performing slab calculations which model a Cu_3Pd surface to investigate the amount of surface narrowing in ordered Cu_3Pd.

We would like to suggest that further experimental work be carried out on Cu_3Pt and thus complete a systematic study of these copper alloys.

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