LETTER TO THE EDITOR

The electronic structure of the CuAu II superlattice

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Abstract. The electronic band structure of the CuAu II superlattice was calculated and compared with the electronic structure of CuAu I as well as with results from low-temperature specific heat experiments. One of the differences found in the present study between the density of states of CuAu II and that of CuAu I concerns the position of the dip in the density of states curve at the Fermi level. This explains the large difference between the electronic specific heat of CuAu II and that of CuAu I and yields excellent agreement with experimental low-temperature specific heat data. The electronic properties of different atomic layers were also studied. Calculated local densities of states show marked differences between successive atomic layers. In the atomic layer nearest to the antiphase boundary the Cu and Au d bands attain their lowest and highest locations respectively and the charge transfer from Cu to Au atom attains its maximum value.

In the equiatomic Cu–Au alloy system there are two well characterised ordered phases: CuAu I and CuAu II [1–3]. According to experiments the electronic specific heat coefficient (γ) is considerably lower in CuAu II than in CuAu I [4]. It is somewhat surprising that such a large effect on γ can arise from rather small changes in crystal structure. The CuAu II superlattice is a modification of CuAu I. The unit cell of CuAu II is obtained by stacking five CuAu I unit cells in a row in the direction of one of the long cell edges and then repeating this unit at five cell intervals, with a simultaneous out-of-step shift at the boundary through the lattice vector $\frac{1}{2}(a + c)$. In addition to the formation of this antiphase boundary, the lattice parameter ratios b/a and c/a and the atomic positions change slightly [3]. The unit cell of CuAu II is shown in figure 1(a). In the present study the lattice parameters and atomic positions were chosen according to the results of the x-ray diffraction experiments of Okamura *et al* [3].

In order to determine how the electronic structure changes during the formation of the CuAu II superlattice, electronic band structure calculations for CuAu II were performed. The scalar-relativistic linear-muffin-tin-orbital method was used, including the combined correction terms and the atomic sphere approximation [5, 6]. The basis function set for the valence electrons consisted of s, p and d functions. The exchange–correlation effects were introduced into the local-density approximation using the Barth–Hedin potential [7]. The core states were determined by self-consistent-field relativistic calculations and were held fixed throughout the self-consistent cycles of the valence electrons. The ratio of Cu and Au Wigner–Seitz radii was assumed to be the same as for elemental Cu and Au metals. The 40 atoms of the unit cell were divided into six groups (Cu I, Au I, Cu II, Au II, Cu III and Au III) according to atomic positions
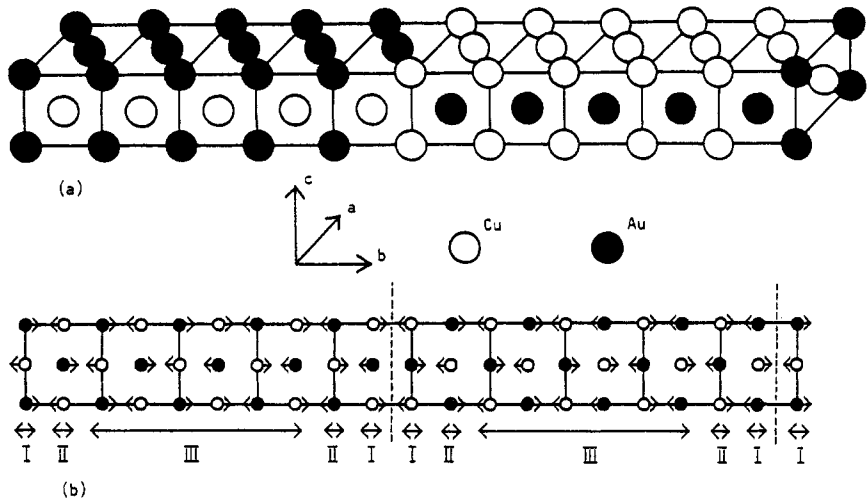
Figure 1. (*a*) Unit cell of CuAu II. (*b*) Atomic arrangement of CuAu II projected on (001) plane; vertical broken lines represent antiphase boundaries. Arrows attached to atoms show directions of displacements determined by Okamura *et al* [3]. Atomic layers I, II and III are also shown.
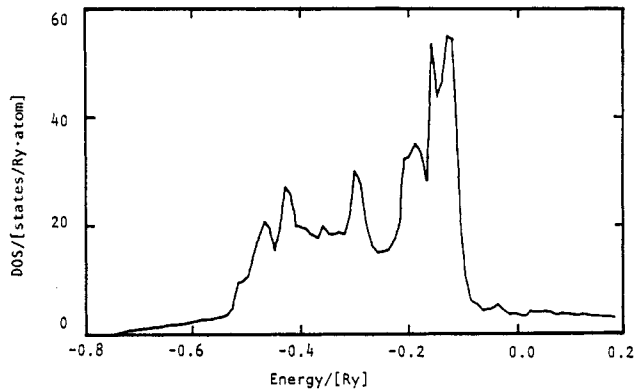

Figure 2. Total density of states of CuAu II.

(figure 1(*b*)). The atomic layers nearest to the antiphase boundaries consisted of type I atoms, the next nearest layers consisted of type II atoms and all other layers consisted of type III atoms. Atoms belonging to the same group were treated as equivalent atoms in the calculations. The potential was iterated to self-consistency on a grid corresponding to 100 k-points in the irreducible section of the Brillouin zone of the simple orthorhombic lattice. The final results were calculated using a grid corresponding to 600 k-points.

The overall shape of the total electronic density of states (DOS) of CuAu II, shown in figure 2, is quite similar to the shape of the DOS of CuAu I [8] . At the middle of the d band there is a dip, dividing the band structure into two distinct sections. As figure 3 shows, the upper section is mainly of Cu type and the lower section of Au type. At the Fermi energy there is a broad dip in the DOS. This dip has a considerable effect on the

Table 1. Characteristic d-band energies relative to Fermi energy: top (A), centre (C) and bottom (B) and electronic density of states per atom at Fermi level ($N(E_F)$). Results for elemental metals and CuAu I are from [8].

Alloy	Atom	A (mRyd)	C (mRyd)	B (mRyd)	$N(E_F)$ (states Ryd^{-1}/atom)
CuAu II	Cu I	−97	−182	−320	3.55
	Cu II	−93	−179	−316	3.66
	Cu III	−92	−178	−316	3.51
	Au I	−156	−325	−527	3.68
	Au II	−157	−326	−528	3.60
	Au III	−162	−330	−532	3.44
CuAu I	Cu	−96	−182	−320	3.63
	Au	−165	−334	−536	4.54
Elemental metals	Cu	−117	−201	−336	4.08
	Au	−131	−303	−508	3.80

low-temperature electronic specific heat in CuAu II as well as in some other Cu–Au alloys [8]. A closer examination of the CuAu II DOS, however, reveals some minor deviations from the DOS of CuAu I, The dip at the middle of the d band is not as deep as in CuAu I and the dip at the Fermi energy lies at higher energies than in CuAu I. As table 1 shows, the whole d band of CuAu II has shifted a few mRyd from the CuAu I d-band position closer to the Fermi level.

In order to determine how electronic properties change from layer to layer in the periodic array of atomic (010) planes (figure 1), the characteristic d-band energies for all six types of atoms were calculated (table 1). The Cu d band in CuAu II shifts gradually to lower energies when passing towards the antiphase boundary, until finally the position of the Cu I d band prectically equals that of the Cu d band in CuAu I. The Au d band in CuAu II behaves in an opposite manner to the Cu d band: the Au d band shifts to higher energies when passing towards the antiphase boundary. For all atomic layers in CuAu II the Cu (Au) d band lies considerably higher (lower) than the d band in the corresponding elemental metal.

To obtain a more detailed idea of the differences in electronic properties between different atomic layers in CuAu II, the local densities of states (LDOS) are shown in figure 3. The LDOS of the s–p band does not change appreciably from layer to layer, whereas the LDOS within the d-band section shows considerable differences between different atomic layers. As figure 3(a) shows, for Cu atoms the DOS mainly increases around the bottom of the Cu section and decreases near the top of the Cu section when passing towards the antiphase boundary. In figure 3(b) the corresponding changes in LDOS are shown for Au atoms. The largest changes occur in the Au section; but contrary to the case of Cu there is a considerable increase and decrease in the DOS within the Au section as a whole when passing towards the antiphase boundary.

Charge transfers between the atomic Wigner–Seitz spheres relative to the corresponding total charge values in CuAu I shows that some portion of the valence electrons of CuAu II has transferred from Cu atoms to Au atoms (figure 4). This charge transfer attains its maximum value in the atomic layer just next to the antiphase boundary, decreasing rapidly towards the inner atomic layers of the antiphase domain.
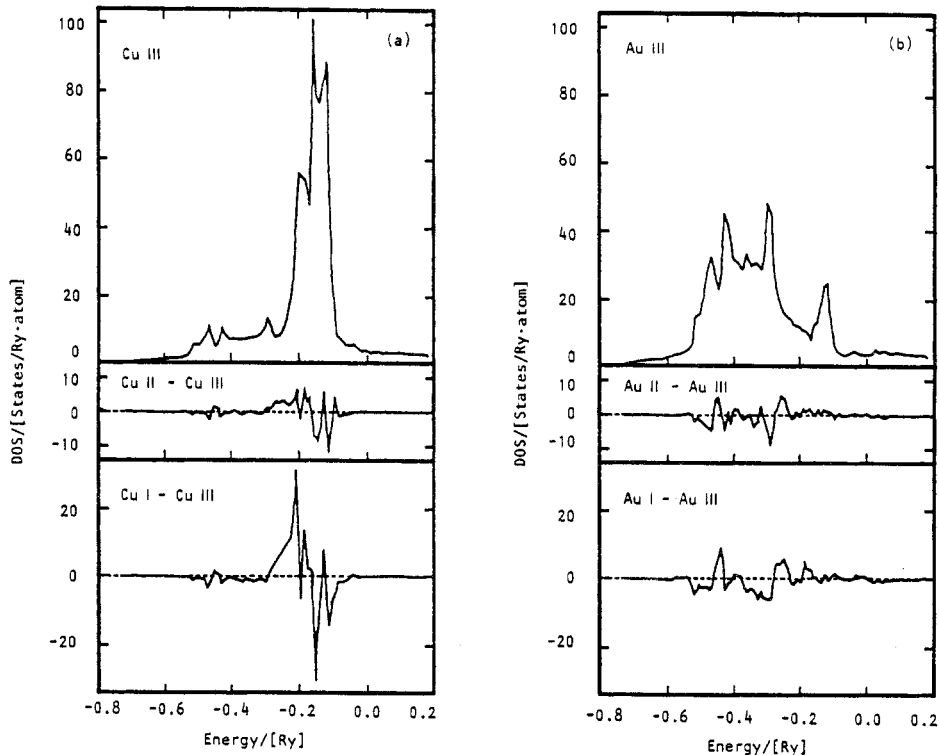
Figure 3. Local partial density of states. (*a*) Local density of states of Cu III (upper panel), difference in local density of states between Cu II and Cu III (middle panel) and between Cu I and Cu III (lower panel) and (*b*) corresponding quantities for Au atoms.
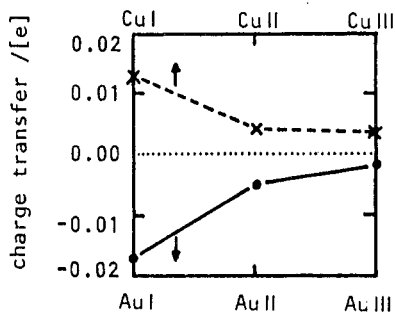

Figure 4. Charge transfers between Cu and Au atoms in CuAu II relative to corresponding charge transfer values in CuAu I.
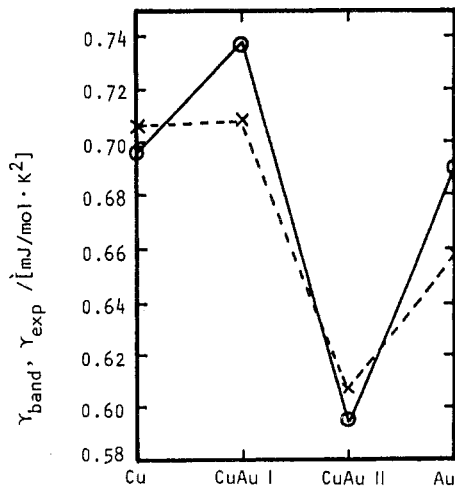

Figure 5. Band structure (γ_{band}) (broken line) and experimental [4] (γ_{exp}) (full line) electronic specific heat coefficients in Cu, CuAu I, CuAu II and Au.

Since the low-temperature electronic specific heat coefficient is proportional to the total electronic density of states at the Fermi level $(N(E_F))$ [9], the above-mentioned minor deviation between CuAu II and CuAu I in the DOS curve near the Fermi energy has a dramatic effect on the γ-coefficient. In figure 5 the present band theoretical specific heat coefficient (γ_{band}) is shown for CuAu II, CuAu I and elemental Cu and Au. There is a major dip in the γ_{band} curve at the CuAu II case. This dip is due to the relative positions of the broad dip in the DOS curve and the Fermi level. In CuAu I the dip in the DOS near the Fermi energy lies just below the Fermi level [8]. In CuAu II this dip has shifted to higher energies, in such a way that the Fermi level has dropped into the dip and thus $N(E_F)$ is considerably lower in CuAu II than in CuAu I. This feature is a global one in CuAu II: the value of local $N(E_F)$ is lower for every atomic layer as well as for every individual atom than $N(E_F)$ in elemental Cu and Au (table 1). The smallest value of local $N(E_F)$ belongs to atoms deeper inside the antiphase domain. With respect to $N(E_F)$ the atoms in the atomic layer just next to the antiphase boundary behave in an opposite manner to those inside the antiphase domain. In the atomic layer next to the antiphase boundary the $N(E_F)$ of Au is higher than that of Cu, contrary to the situation in other layers in CuAu II.

Figure 5 also shows the experimental electronic specific heat coefficient (γ_{exp}) [4]. The trend of γ_{exp} is quite well predicted by the band theoretical result γ_{band}. This agreement between γ_{exp} and γ_{band} supports the assumption that the trend of γ in Cu–Au alloys can be predicted by band structure calculations and that the effect of electron–phonon interaction will be less important as far as the trend of γ is concerned.

In conclusion, the overall shape of the DOS of CuAu II resembles that of CuAu I, but there are certain minor deviations. The deviations at the Fermi level, however, give rise to a large effect on the band structure electronic specific heat, which explains the fact that the experimental low-temperature specific heat of CuAu II is considerably lower than that of CuAu I. The electronic properties of the CuAu II superlattice possess a character near the antiphase boundaries quite different to that inside the antiphase domains.

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