A band theoretical study on the electronic specific heat in the phase transition CuAuI to CuAu II

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Abstract. The linear muffin-tin orbitals (LMTO) method is used to calculate the electronic density of states at the Fermi energy, characteristic d-band energies and charge transfers of CuAu I and CuAu II. It has previously been shown that the large difference observed in low-temperature specific heat between CuAu I and CuAu II is explained quite well by band structure calculations. In this study it is shown that the dominant factor in the change of the electronic specific heat in the phase transition CuAu I → CuAu II is the formation of anti-phase boundaries in CuAu II, the effect of changes in lattice parameters, atomic positions and atomic potentials being less important. The electronic specific heat as a function of the length of the anti-phase domain is also studied.

The structure of equiatomic Cu–Au alloys has been the subject of numerous studies over many decades [1–4]. CuAu alloy annealed below 380 °C acquires a tetragonal $L1_0$ structure (CuAu I). CuAu I is a modified FCC-type structure in which the alternate (002) planes contain either all copper or all gold atoms (figure 1(a)). Due to this layered structure a contraction in the c direction occurs ($c/a = 0.926, a = b = 3.966$ Å [5]). When annealed above 380 °C but below 410 °C a long-period ordered superstructure (CuAu II) is formed. This first example of long-period superlattices was discovered by Johansson and Linde [6] in 1936. The orthorhombic CuAu II superstructure (figure 1(b)) is a modification of the CuAu I structure. The unit cell of CuAu II contains ten cells of the CuAu I type. Half way along the b axis of the cell a phase change occurs. At this anti-phase boundary (APB) the (002) planes containing all gold atoms are opposite to those that contain all copper atoms. The range between these APBs is called an anti-phase domain (APD); the length of this domain is thus half of the lattice parameter b.

The structure shown in figure 1(b) is only a first approximation of the CuAu II lattice. Okamura *et al* [7] have found that copper atoms shift towards the APB and gold atoms shift away from it. These atomic displacements are at most about 0.08 Å. Considerable disordering also takes place in the neighbourhood of the APB. The anti-phase boundaries are not planar but instead have regular step-like [8] or wave-like [9–12] forms (figure 1(c)). The lattice parameters of CuAu II ($a = 3.956$ Å, $b = 39.72$ Å and $c/a = 0.929$ [7]) are also relaxed from the corresponding CuAu I values.

In previous work [13] it was shown that the large difference observed in the low-temperature specific heat between CuAu I and CuAu II [14] can be explained quite well by one-particle band structure calculations. The electronic specific heat coefficient γ is proportional to the total electronic density of states at the Fermi
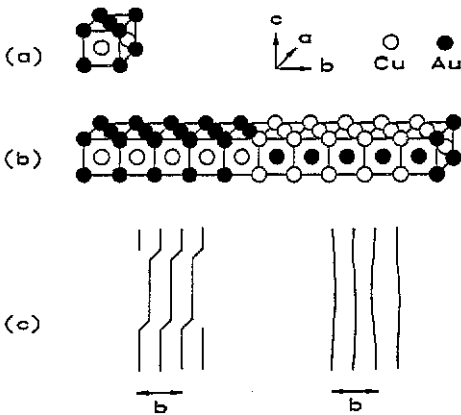
Figure 1. (a),(b) Unit cells of CuAu I and CuAu II, respectively. (c) Cross sections of possible non-planar forms of anti-phase boundaries in CuAu II according to [8] and [11].

energy ($N(E_F)$) (see e.g. [15]):

$$\gamma = \gamma_{band}(1 + \lambda) = \frac{\pi^2 k_B^2}{3} N(E_F)(1 + \lambda)$$

where k_B is the Boltzmann constant and λ is the enhancement factor due to electron–phonon and electron–electron interactions (see e.g. [16]). γ_{band} is the so-called band structure specific heat. Because the difference in γ between CuAu I and CuAu II is accounted for well by $N(E_F)$ alone, this suggests that the change of λ in the transition CuAu I → CuAu II is small.

The purpose of this study was to find the factors that dominate in the change of the specific heat in the phase transition between CuAu I and CuAu II.

The band structure is determined by atomic potentials and crystal structure. The change in the crystal structure in the transition CuAu I → CuAu II can be divided into three different categories: the relaxation of lattice parameters and atomic positions from the corresponding CuAu I values and the formation of APBs. It will be shown that the formation of the anti-phase boundaries in CuAu II is the dominant factor in the change of γ as the transition CuAu I → CuAu II takes place.

The changes in atomic potentials, lattice parameters and atomic positions have been treated in the present calculations without any further approximations than those made in the band calculation method itself. The anti-phase boundary, however, has been approximated by a smooth plane. The disorder near the APB as well as the possible wave-like or step-like form of the APB has been ignored. In principle also these features could be taken into account in the band calculations by using a large unit cell containing several CuAu II cells; but the size of the resulting supercell would be too large for practical band structure calculations. (The unit cell of CuAu II contains 40 atoms.)

In the previous paper [13] the band structure of CuAu II was calculated using 600 k-points in the irreducible section of the Brillouin zone and six non-equivalent atoms in the unit cell. In the present study the number of non-equivalent atoms was increased from six to ten. In the present calculations, the atoms in layers (parallel to the APBs) which are at different distances from the nearest APB are treated as non-equivalent atoms. Increasing the number of non-equivalent atoms was not found to lead to any significant changes in the specific heat. The present calculations were

made using 18 *k*-points in the case of CuAu II, since this seems to be sufficient to show the difference in electronic specific heat between CuAu I and CuAu II. The calculations were performed using the LMTO method [17], utilizing the computer codes implemented by Skriver [18]. The details of the calculations are described in [13].
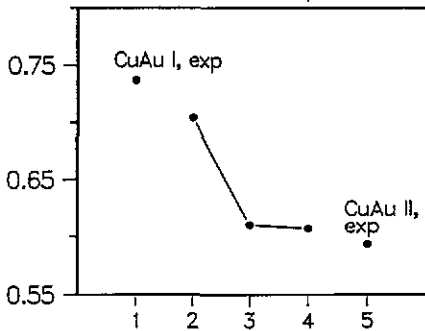

Figure 2. Full curve (cases 2, 3 and 4): the trend of the band structure specific heat coefficient (γ_{band}) of equiatomic CuAu alloy obtained by using different potentials and crystal structures. Case 2: self-consistent result for CuAu I. Case 3: γ_{band} of CuAu II calculated using the atomic potentials of CuAu I (obtained from case 2). Case 4: same as 3 but the potential has been iterated to self-consistency. Cases 1 and 5: the experimental electronic specific heat coefficients of CuAu I and CuAu II, respectively [14].
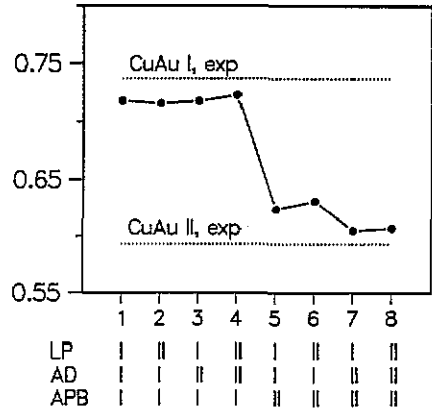

Figure 3. The band structure specific heat coefficient (γ_{band}) as a function of crystal structure in the phase transition CuAu I → CuAu II. The change of crystal structure in this transition was approximated as consisting of three independent steps: (1) change of lattice parameters (LP), (2) atomic displacements (AD) and (3) formation of anti-phase boundaries (APB). If every step can take two values (corresponding to CuAu I and CuAu II) there will be eight different combinations of them. These combinations are shown on the *x*-axis. In three rows (LP, AD and APB) the mark I (II) means that the the corresponding quantity has a value that refers to CuAu I (CuAu II). As the figure shows, there is distinct correlation between the specific heat and the third row (APB) which shows the existence (II) or non-existence (I) of anti-phase boundaries. The dotted lines show experimental electronic specific heat coefficients of CuAu I and CuAu II [14].

Figure 2 shows that the self-consistent atomic potentials of CuAu I substituted in the CuAu II structure give practically the same result for the specific heat as the self-consistent calculation for CuAu II. Thus the change of γ in the phase transition CuAu I → CuAu II is due to changes in crystal structure and not in atomic potentials. The effects on γ due to changes in lattice parameters, atomic positions and the formation of APBs were studied independently. The results are shown in figure 3. There is a distinct correlation between the value of the specific heat and the existence of APBs. The possible correlation of γ with atomic displacements or with changes in lattice parameters is much weaker. A slight correlation with atomic displacements, however, appears with the existence of APBs. Thus the dominant factor in the change of γ during the transition CuAu I → CuAu II seems to be the formation of APBs. Although the change in γ is due to this localized phenomenon in crystal structure, $N(E_F)$ (which determines the specific heat) decreases not only around the APBs but
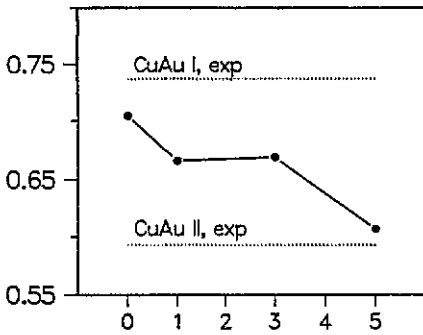
Figure 4. The band structure specific heat coeffi-
cient (γ_{band}) as a function of the length of anti-
phase domains. If this length is zero (five) the
corresponding structure is CuAu I (CuAu II). The
dotted lines show experimental specific heat coeffi-
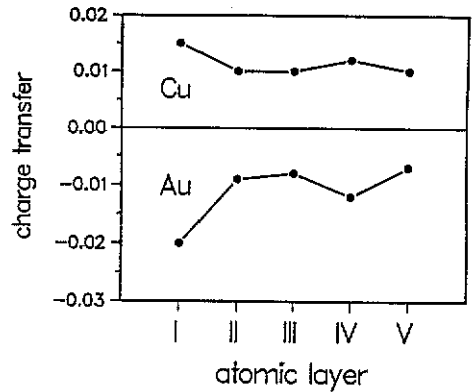cients of CuAu I and CuAu II [14].

Figure 5. Charge transfers between Cu and Au
atoms. Atomic layers are shown on the x-axis.
Layer I is nearest to the anti-phase boundary, layer
II is second nearest and so on.

also throughout the whole crystal [13].

Figure 4 shows specific heat as a function of the length of the APD. The specific
heat decreases as this length increases from zero (CuAu I). Structures with APDs
longer than five have not been investigated, but it is expected that as the length of
these domains increases sufficiently the specific heat will begin to increase and will
eventually approach the value obtained for CuAu I.

Increasing the number of non-equivalent atoms in the present calculations from
six to ten provides more detailed information about the charge transfers inside the
APDs. The results obtained in the previous study [13] are, however, confirmed by
the present calculations: charge transfer between the atomic Wigner–Seitz spheres,
relative to the corresponding total charge values calculated in the CuAu I structure,
shows that some portion of the valence electrons of CuAu II has been transferred
from Cu atoms to Au atoms. This charge transfer attains its maximum value in the
atomic layers immediately adjacent to the APBs, decreasing rapidly towards the inner
atomic layers of the APDs. This charge transfer does not occur only within the same
atomic layer (perpendicular to the b axis); some portion of the Cu electrons inside
the domain have been transferred to the Au atoms lying in the layers next to the
APB. Thus charge transfer does not occur only perpendicular to the b axis but also
parallel to it. In addition to these results, the present calculations show that this
charge transfer oscillates inside the APD: in the fourth atomic layer from the APB
there is a slight increase in the charge transfer (figure 5).

The characteristic d-band energies (table 1) of atoms of all ten different types
(atoms lying in different atomic layers perpendicular to the b axis) in general show
similar trends to those found in [13]: the Cu (Au) d band lies higher (lower) within
the APD than in the atomic layers close to the APB. All d-band energies obtained
from the present calculation, however, are a few mRyd lower than the corresponding
energies given in [13]. The reason for these minor deviations is probably the large
difference in the number of k-points used in the two calculations. The present
calculation, although not as accurate as [13], gives more detailed information about
the d-band shifts: the Cu d band, at the transition from the APB to within the domain,
first rises and then (layers IV and V) slightly sinks again. The Au d band first slightly

Table 1. Characteristic d-band energies relative to the Fermi energy: top (A), centre (C) and bottom (B) and electronic density of states per atom at the Fermi energy ($N(E_F)$) of CuAu II. Numbers I to V refer to the atomic layer in which the corresponding atom is lying. I is nearest to the anti-phase boundary, II is second nearest and so on.

Atom	A (mRyd)	C (mRyd)	B (mRyd)	$N(E_F)$ (states Ryd^{-1}/atom)
Cu I	−102	−187	−324	3.40
Cu II	−100	−185	−322	3.44
Cu III	−94	−179	−317	3.74
Cu IV	−96	−181	−319	3.62
Cu V	−97	−182	−319	3.64
Au I	−161	−330	−531	3.61
Au II	−160	−329	−530	3.38
Au III	−162	−330	−531	3.45
Au IV	−163	−331	−533	3.40
Au V	−165	−333	−534	3.36

rises (layer II) but after that (layers III, IV and V) it sinks monotonically. The local $N(E_F)$ values shown in table 1 also differ slightly from the values presented in [13]; this difference is attributed to the above-mentioned difference in the number of k-points. In spite of this difference, the general trends of local $N(E_F)$ presented in [13] are confirmed by the present calculation, except that the present result for $N(E_F)$ of Cu atoms is higher inside the domains than close to the APB.

In conclusion, the results show that the dominant factor in the change in specific heat in the phase transition CuAu I $\rightarrow$ CuAu II is the formation of anti-phase boundaries in CuAu II. The general trends in charge transfer, d-band positions and local $N(E_F)$ values obtained in the previous study [13] are confirmed by the present calculations, which give more detailed information about these trends due to the increase in the number of non-equivalent atoms in the present calculations from six to ten.

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