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# Theoretical investigation into a long-period anti-phase structure of $\text{Au}_3\text{Zn}$

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**Abstract.** The present work deals with the effect of crystal structure on the electronic properties of  $\text{Au}_3\text{Zn}$  alloys. At high temperatures this alloy has a one-dimensional long-period superstructure. We show that the total electronic density of states (DOS) at the Fermi level is reduced about 25% by the formation of the anti-phase domain (APD) structure. This has an effect on various physical properties since the DOS value at the Fermi level affects, for example, the electrical and thermal conductivity as well as specific heat of solid materials. The reduction of the DOS value at the Fermi level was found to be mainly caused by the d component of Au states and this reduction can be attributed to the splitting of the energy bands in the  $\Gamma$ -X direction in the Brillouin zone. To understand better the physical mechanism behind the deformations of the total DOS we calculate the local partial DOS and electronic band structure of  $\text{Au}_3\text{Zn}$  with and without the APD structure by using the LMTO method. The results obtained are briefly discussed in relation to some experiments, especially with spectroscopic methods.

## 1. Introduction

In the current paper we investigate the electronic properties of the  $\text{Au}_3\text{Zn}$  alloy. At high temperatures (250 °C–415 °C) this alloy has a one-dimensional long-period superlattice structure (H phase) [1, 2]. The unit cell of  $\text{Au}_3\text{Zn(H)}$  is formed by stacking two  $L1_2$  ( $\text{Cu}_3\text{Au}$ -type) cells in a row along the  $c$  axis with an elongation of 2.2% in that direction and then repeating this unit at two-cell intervals with a simultaneous out-of-step shift at the boundary through the lattice vector  $(a + b)/2$  (figure 1). The boundary formed as above is called the anti-phase boundary (APB) and the region between the APBs is called the anti-phase domain (APD).

There are many other alloys which have APD structures. One of these is CuAu II [3, 4], a modification of CuAu I whose structure is  $L1_0$ . In the phase transition CuAu I  $\rightarrow$  CuAu II the electronic specific heat is observed to decrease by about 15%. This decrease in the specific heat has been shown to be caused by the change in the total electronic density of states (DOS) associated with the formation of the APD structure in CuAu II [5]. The purpose of the present work is to find out whether the formation of the APBs has similar effects also in  $\text{Au}_3\text{Zn}$  alloys. Since many physical properties depend on the DOS, we concentrate on the effects of the APBs on the DOS. The APD structure of  $\text{Au}_3\text{Zn(H)}$  is similar to that of CuAu II, except that the length of the APDs in  $\text{Au}_3\text{Zn(H)}$  is only two fifths of that in CuAu II.  $\text{Au}_3\text{Zn(H)}$  differs also from CuAu II with respect to the Au concentration, average number of valence electrons per atom and relative position of the d bands of the constituent elements of the alloy.

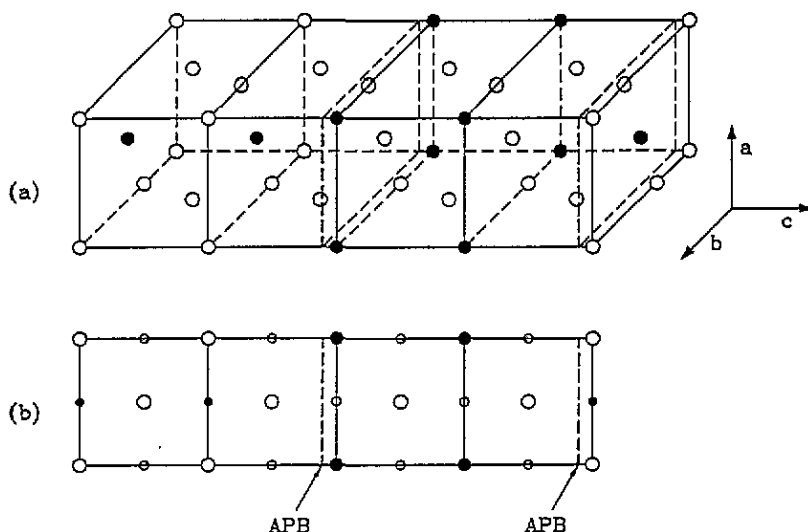


Figure 1. (a) The supercell of  $\text{Au}_3\text{Zn}$  alloy. Black and white spheres correspond to Zn and Au atoms, respectively. (b) The atomic arrangement of  $\text{Au}_3\text{Zn}$  projected on the (100) plane. Large and small spheres refer to the atoms in different atomic planes. Broken lines represent schematic anti-phase boundaries (APBs).

## 2. Methods of calculations

The calculations were performed using the scalar-relativistic linear-muffin-tin-orbital (LMTO) method including the combined correction terms and the atomic sphere approximation [6, 7]. The basis function set for the valence electrons consisted of s, p and d functions. The exchange–correlation effects were introduced within the local density approximation using the von Barth–Hedin potential [8]. The core states were held fixed throughout the self-consistent cycles of the valence electrons. The same atomic Wigner–Seitz (WS) radius was accepted for both Au and Zn atoms. The lattice parameters used in the calculations were  $a = b = 4.000 \text{ \AA}$  and  $c = 16.352 \text{ \AA}$  [9].

At first we made test calculations for pure Au metal using the same kind of unit cell as used in the case of  $\text{Au}_3\text{Zn(H)}$ . Guided by the results of the test calculations we adjusted the calculational parameters to get well converged DOS curves. In the final calculations we used 144  $k$ -points in the irreducible wedge of the tetragonal Brillouin zone and over 300 vectors in the lattice sums both in the real and reciprocal space.

## 3. Results

The present investigation shows that the total DOS of  $\text{Au}_3\text{Zn}$  changes within the whole occupied region due to the formation of the APBs (figure 2). The most marked changes of the DOS are the upward shifts of the whole Zn d band by about 0.1 eV and the bottom of the Au d band by about 0.3 eV, changing of the intensity ratio of the two major peaks in the Au d band region and smoothing of the DOS near to the Fermi level. Due to the APBs the intensity of the DOS in the lower part of the Au d band is increased, whereas the intensity is reduced in the upper part of the Au d band leading to a decreasing general trend with increasing energy of the total DOS in the Au d-band region. Perhaps the most discernible effect of the APBs on the partial DOS curves is the suppression of the striking

hybridization of the Au p DOS and the Zn s DOS with the peak in the Au d DOS at about 2 eV below the Fermi level (figure 3).

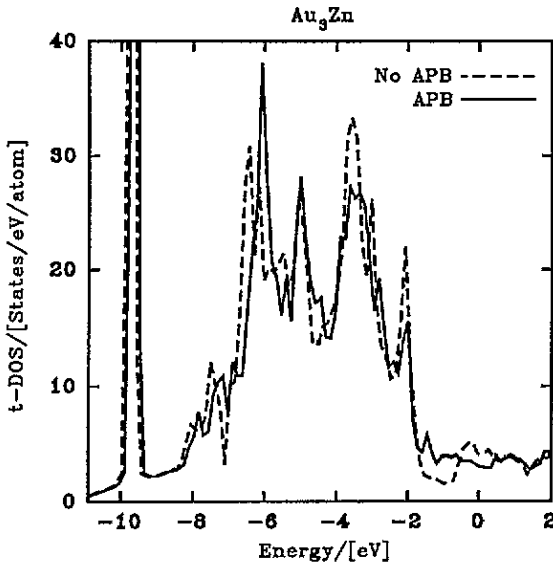


Figure 2. The total density of states (DOS) of  $\text{Au}_3\text{Zn}$  alloy. Solid and broken curves correspond to  $\text{Au}_3\text{Zn(H)}$  structure (APB) and  $L1_2$  structure (no APB), respectively.

The smoothing of the DOS near to the Fermi energy can have significant effects, since many physical properties depend on the DOS value at the Fermi level. The partial DOS curves show that although the smoothing occurs in all partial DOS, over 80% of it is caused by the Au atoms and from that about two thirds comes solely from the Au d DOS. The above behaviour is similar to that found in  $\text{CuAu I}$  where the modifications of the total DOS at the Fermi level, induced by the variation of the  $c/a$  ratio of the lattice parameters, are mainly caused by the d DOS of Au atoms [10]. As figures 4 and 5 show, one can locate the smoothing of the DOS of  $\text{Au}_3\text{Zn}$  near to the Fermi energy in a certain region in the  $k$ -space. The smoothing originates mainly from the X-point region where there exists a flat band which is deformed and split due to the formation of the APD structure. Also in the  $M-\Gamma$  direction there are discernible changes in the band structure near to the Fermi level.

The formation of the APBs in  $\text{Au}_3\text{Zn}$  has only a small effect on the charge transfer between the Au and Zn WS spheres. Zn atoms lose p-type charge and gain s-type charge leading to Zn atoms totally possessing about 2% more electrons in the APD structure than in the  $L1_2$  structure. Considering the nearest-neighbour configuration for the atoms in  $\text{Au}_3\text{Zn(H)}$ , all the Au as well as Zn atoms are equivalent. However, if the second-nearest-neighbour configuration is considered, there are two kinds of Au atom: Au atoms having one or none Zn second-nearest neighbours. Calculations treating the Au atoms as either equivalent or inequivalent give in any case practically the same DOS curves.

#### 4. Discussion

In the following we first discuss the general effects of the APBs on  $\text{Au}_3\text{Zn}$  alloys with comparison to the  $\text{CuAu}$  case, and after that we consider some experimental methods which can be used to verify the theoretical predictions obtained. Although the formation of the

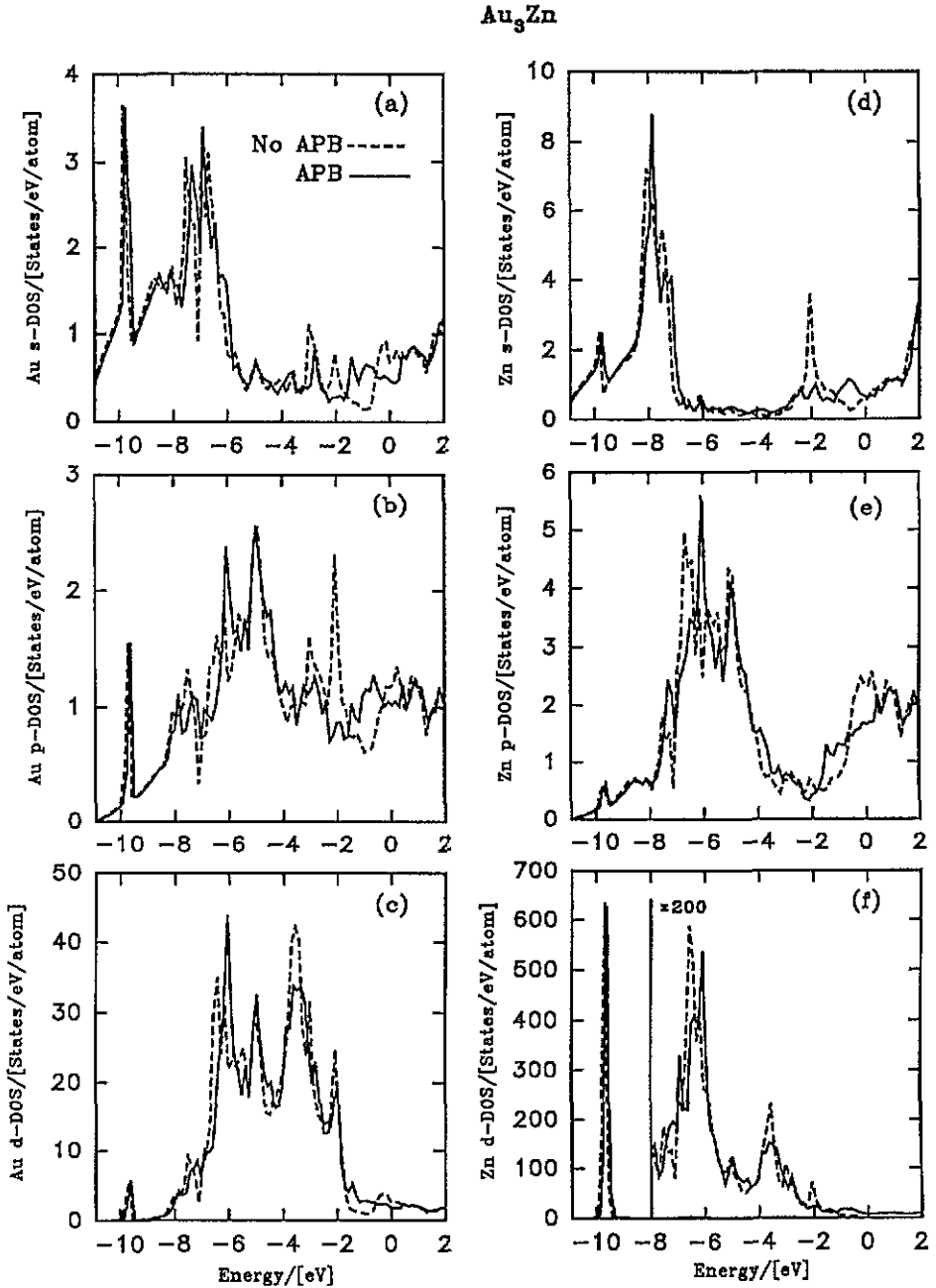


Figure 3. Partial densities of states of Au and Zn atoms in  $\text{Au}_3\text{Zn}$  alloy. Solid and broken curves correspond to APB structure and structure without APBs, respectively. The Fermi level position is 0 eV. Figure 3f contains also 200-fold magnification above  $-8$  eV.

APD structure both in  $\text{Au}_3\text{Zn}$  and  $\text{CuAu}$  alloys does not lead to any large overall changes in the DOS curves, it has a significant effect on the DOS in certain limited energy regions. Our results for  $\text{Au}_3\text{Zn}(\text{H})$  and also for  $\text{CuAu II}$  [5, 11] suggest that the substantial effect of the APBs on the total DOS near to the Fermi level is a common feature among metallic

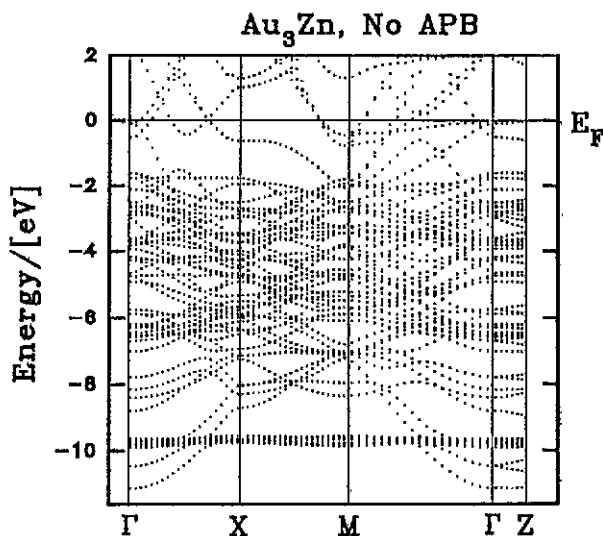


Figure 4. The electronic band structure of  $\text{Au}_3\text{Zn}$  alloy without APBs. Bands are drawn in principal symmetry directions. The Fermi level is shown by a horizontal line.

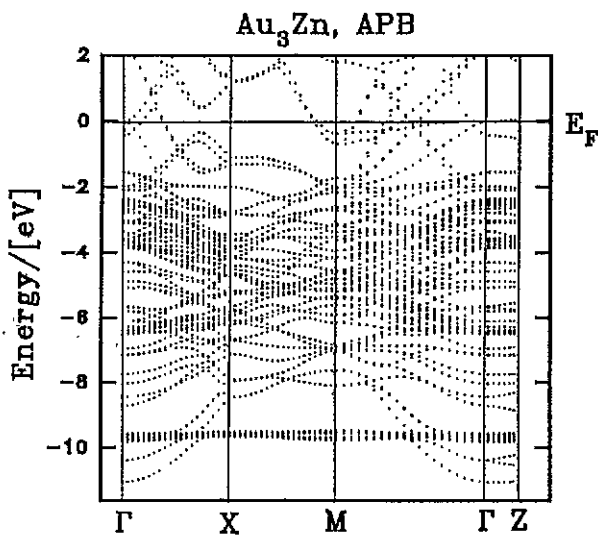


Figure 5. The electronic band structure of  $\text{Au}_3\text{Zn}$  alloy with APBs. Bands are drawn in principal symmetry directions. The Fermi level is shown by a horizontal line.

alloys. Since many important properties of semiconductors and insulators depend on the width of the energy gap, it would be interesting to study what kind of effect long-period superstructures would have on the energy gaps of compound semiconductors and insulators.

Although the formation of the APD structure may cause some small atomic displacements in  $\text{Au}_3\text{Zn}(\text{H})$  the effects of these displacements on the DOS curves are expected to be very small [11]. Besides the induced changes in the DOS near the Fermi level, the other similarity between  $\text{Au}_3\text{Zn}$  and  $\text{CuAu}$  is that the d-band complex is shifted slightly upward in both alloys when the APD structure is formed. However, the calculated charge transfers between the atomic WS spheres are different in  $\text{Au}_3\text{Zn}(\text{H})$  and

CuAu II. The formation of the APD structure increases slightly the valence charge in Au WS spheres in CuAu II whereas the valence charge of Au WS spheres is decreased in Au<sub>3</sub>Zn(H).

In Au<sub>3</sub>Zn alloys the electronic correlation effects are expected to be small since the d bands of the constituent atoms are fully occupied. Therefore, one can predict some experimental phenomena more reliably than in the case of transition metal alloys, for instance [12]. The features found in the DOS of Au<sub>3</sub>Zn alloys can be studied by using various experimental methods. The DOS at the Fermi level can be obtained from low-temperature specific heat measurements provided that the electron-phonon and electron-electron many-body effects can be estimated as well [13–16]. Nuclear magnetic spin-lattice relaxation rate measurements can be used to provide information of the partial DOS at the Fermi level [17, 18].

The DOS near the Fermi level is a useful quantity to study with spectroscopic methods. Here we consider briefly only few of them: x-ray photoelectron spectroscopy (XPS), x-ray emission spectroscopy (XES) and ultraviolet photoelectron spectroscopy (UPS). The XPS measurements probe the occupied total DOS of a system being investigated, in which a hole is created in the valence band by an x-ray quantum. Therefore, it could be possible by this method to verify the predicted shifts of Zn 3d band and the bottom of the Au 5d band as well as the intensities of the peaks in the Au 5d-band region and the structures found between the top of the Au 5d band and the Fermi level. Since the UPS method is more surface sensitive, one has to be careful in preparing the surface of a sample. However, if good-quality surfaces of the Au<sub>3</sub>Zn alloys are available, UPS spectra can be used to analyse the same phenomena as was discussed in the context of XPS spectra, but with a better energy resolution.

Turning to the more bulk-sensitive methods, the shift of the Zn 3d band might be observable in XES  $L\alpha_{1,2}$  spectra or as a quadrupole peak in the XES  $K\beta_{2,5}$  valence band spectra. In XES a specific atom is core ionized in an alloy. The core hole hereby created moves (at the same time or afterwards) to the occupied valence band and an x-ray quantum is observed. This means that the spectrum obtained is site dependent. Furthermore, dipole ( $\Delta l = \pm 1$ ) and quadrupole ( $\Delta l = \pm 2$ ) selection rules (where  $l$  is the angular momentum quantum number) are obeyed which means that the corresponding transition processes give information about the partial DOS.

The distinct peaks in the Zn s DOS (figure 3(d)) and Au p DOS (figure 3(b)) at about 2 eV below the Fermi level are completely washed out in the APD structure. The position of these peaks coincides with the top of the Au 5d band as can be seen in figure 4. This feature in the Au p DOS might be observed by using the XES method. The feature in question is connected with the dip in the total DOS below the Fermi level in the  $L1_2$  structure. This fact will be evident from looking at figure 4 (particularly between  $\Gamma$  and X points). For the  $L1_2$  structure there are far fewer bands available above the peak (–2 eV) of the Au p DOS than for the APD structure.

Considering the mixing of the Zn 3d states with other states at about 10 eV below the Fermi level one finds a strong hybridization in the Au p DOS, but only a weak one in the Zn p DOS. This phenomenon is due to the fact that all the nearest neighbours of Zn atoms are Au atoms in these alloys. This nearest-neighbour effect explains also the strong hybridization of the Zn s and p DOS with the Au d DOS. It is interesting to note that the hybridization effect in the alloy between the Zn 3d states and the Au p DOS can be even stronger than the 3d–4p hybridization in pure Zn metal. Finally, one can conclude that for both structures of the alloy the hybridization between the 4p and 3d states of Zn is very weak at about 10 eV below the Fermi level. In view of the XES  $K\beta_{2,5}$  spectrum of Zn

in the Au<sub>3</sub>Zn alloy there is an energetic coincidence between the dipole 1s→4p transition which is associated with the hybridization effect (figure 3(e)) in question and the quadrupole 1s→3d transition. Therefore, the quadrupole transition may dominate at the bottom of the Zn band.

## 5. Conclusions

The results of the current paper show that the total DOS near to the Fermi level changes significantly due to the formation of the APBs in the Au<sub>3</sub>Zn alloy. The same kind of phenomenon has been found previously in Cu–Au alloys. In both cases the largest changes in the DOS near to the Fermi level were found to be caused by the d DOS of Au atoms. The present investigation suggests that it may be possible to adjust the electronic properties of alloys and compounds by properly changing the long-period crystal structure of the particular system. The structures found in the DOS of Au<sub>3</sub>Zn could also be investigated experimentally using thermophysical and spectroscopic techniques. Also, as far as a short-range order effect is concerned the hybridization between the Zn 3d and Au p DOS depends to a considerable extent on the location of the neighbouring atom species. These features could be experimentally investigated by the XES method.

## Acknowledgments

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