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Study of Electronic and Magnetic Properties of CuPd, CuPt, Cu_3Pd and Cu_3Pt: Tight Binding Linear Muffin-Tin Orbitals Approach

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ABSTRACT

Electronic structure of ordered alloys CuPd, CuPt, Cu_3Pd and Cu_3Pt have been studied using Tight Binding Linear Muffin-Tin Orbitals Atomic Sphere Approximation (TB-LMTO-ASA). For the electronic properties, we have performed band structure calculations. Our findings show that all the systems considered are metallic in nature. To know the contribution of the orbitals in the bands, the system is analyzed via fat bands which reveal most of the contributions on valence band for CuPd, CuPt, Cu_3Pd and Cu_3Pt is from d-orbital and on conduction band is from s and p-orbitals. We have also checked the magnetic properties of the alloys. The density of states for spin up and spin down electrons have found to be same in each and every steps, showing non-magnetic nature of CuPd, CuPt, Cu_3Pd and Cu_3Pt.

Key words: Band structure, TB-LMTO-ASA, Alloys, Density functional theory

INTRODUCTION

The main basis for understanding materials ultimately rests upon understanding their electronic structure (Martin, 2004). The cohesive, electronic, optical, magnetic and super-conducting properties of solids are dominated by the behavior of valence electrons moving in the field of the ion-core of constituent atoms. The development of electronic structure calculations has taken place in several steps. The Tight-Binding Linear Muffin-Tin Orbital method with Atomic Sphere Approximation (TB-LMTO-ASA) (Skriver, 1984; Andersen, 1975; Andersen *et al.*, 1984) is one of the frequently used technique to deal with the electronic properties; especially band structure and density of states of the solids (Kaphle *et al.* 2012, Andersen, 1984; Ganguly *et al.* 2011). In the present work we have used TB-LMTO-ASA method to study the electronic and magnetic properties of different alloys of Copper (Cu), Palladium (Pd) and Platinum (Pt) i.e., CuPd, CuPt, Cu_3Pd & Cu_3Pt. The homogeneous mixture of two or more metals or of metallic elements with non metallic elements is called alloy.

If there is a mixture of only two types of atoms, it is called binary alloy. Binary alloys may be ordered or disordered depending upon atomic positions (Ashcroft & Mermin, 1976; Kittel, 1966). If the atoms are situated by making symmetry in the crystals then they are called ordered alloys and if the atoms are situated randomly in the crystals so that they fail to have crystal symmetry then they are called disordered alloys. Metals and alloys are materials of great scientific as well as practical importance.

With the rapid development of advanced technologies, the demands for the design of components and the production of new materials which are strong, stiff and ductile are increasing. Stable materials responding these requirements are the inter-metallic compounds (Kart *et al.* 2008). They have structural properties which differ greatly from constituent metals. Cu-based inter-metallics have motivated the strong interest in their fundamental properties as they have received considerable attention due to their promising use as catalysts in many technologically important areas and future technology.

MATERIALS AND METHODS

All the systems considered are studied using Tight Binding Linear Muffin-Tin Orbitals Atomic Sphere Approximation (TB-LMTO-ASA). All results are derived from self-consistent calculations based on density-functional theory in the local-density approximation (LDA) (Hohenberg & Kohn, 1964). Throughout the calculation we use the exchange-correlation potential of von Barth and Hedin (Barth & Hedin, 1972). The crystal potential is constructed of over-lapping Wigner-Seitz spheres for each atom in the unit cell. According to the spirit of the tight-binding Linear muffin-tin Orbital method with atomic sphere approximation (TB-LMTO-ASA) procedure, only the energetically higher-lying valence states have been included in the self-consistent calculations of the effective crystal potentiall (Skriver, 1984; Aschroft & Mermin, 1976; Mizutani, 2001). The deeper lying core states are treated as atomic like in the inner states, so called frozen core approximation. The calculations were iterated to self-consistency with an error in total energy less that 10^{-6} Rydberg.

RESULTS AND DISCUSSION

This section includes the results and discussion of the calculations carried out to obtain the band structure and density of states of CuPd, CuPt, Cu_3Pd and Cu_3Pt.

Band Structure of CuPd and CuPt

The energy minimization curve for CuPd is shown in Fig. 1. To deal with CuPd, we used space group Pm-3m (space group No. 221) (Mighell *et al.* 1977). The lattice parameter for the ground state (GS) geometry of CuPd is found to be equal to 2.94 A (5.56 a.u.) which is around 1% less than the experimental result (2.99 Å (5.65 a.u.)). In case of CuPt we have used rhombohedral crystal structure with hexagonal axes (Bornstein, 2009) having space group R-3m (space group No. 166). The c/a ratio for the CuPt alloy is 4.90 (Bornstein, 2009). The lattice parameter is taken to be 3.79 Å (Mohl *et al.* 2011). Further calculations are performed using these optimized parameters.

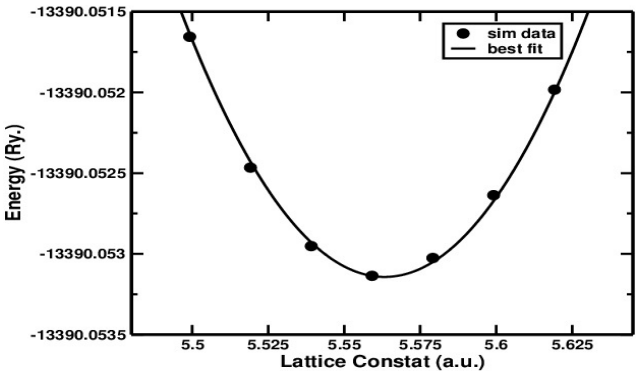

Fig. 1. Plot of Energy vs lattice constant for CuPd.

The band structure of CuPd is shown in Fig. 2. We found eighteen bands with valence band and conduction bands overlapping with each other showing CuPd has a metallic nature. The minimum energy value for the valence band is labeled as 'a', which is found to be -0 .6238 Ry and the maximum value of energy for conduction band, labeled as 'b', is found to be 2.4014 Ry. These are located below and above the Fermi level at Gamma point respectively.

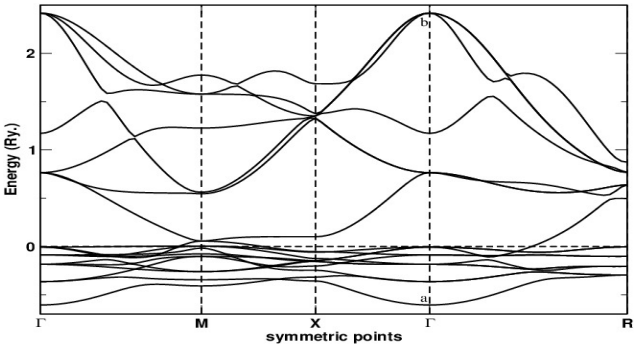

Fig. 2. Band structure of CuPd, horizontal dotted line represents the Fermi level .

To know the orbital contributions of cu and Pd in CuPd which plays an important role for the band-structure, we perform the fat band calculations. The optimized calculations are reflected in Figs. 2 to6. The Fig. 3 shows the contributions of s and p-orbitals of copper in CuPd. This signifies that s and p-orbitals don't contribute much in the band structure of CuPd, even, the contribution of p-orbital to the valence bands is very negligible though has some in the conduction band. Same kind of behavior is observed for s and p-orbitals of palladium in CuPd as in Figs. 4 to 6 show the fat band of d-orbitals of copper and palladium respectively. It is obvious from the Figs. 5 & 6 that the occupancies of the d-orbitals is most significant to the total band structure. The majority of contributions to the valence band is from the d-orbitals of the copper and palladium. It is mainly due to majority of electrons are in d-orbitals of copper and palladium.

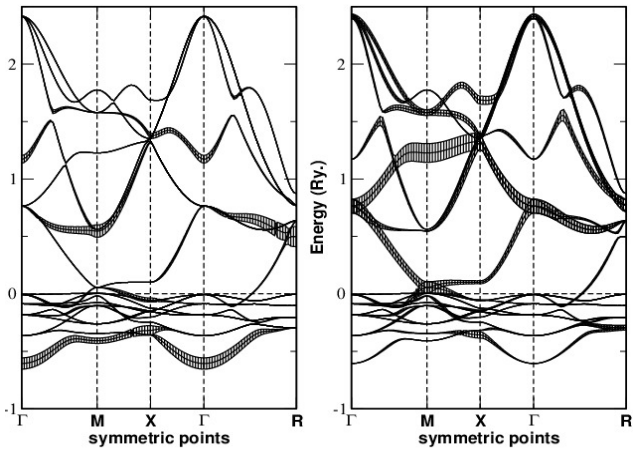

Fig. 3. Fat band structure of s-orbital (left) and p-orbital (right) of Cu in CuPd, horizontal dotted line represents the Fermi level.

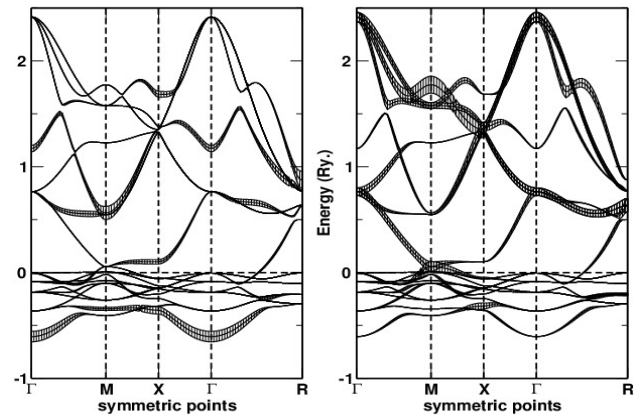

Fig. 4. Fat band structures of s (left) and p-orbitals (right) of Pd in CuPd.

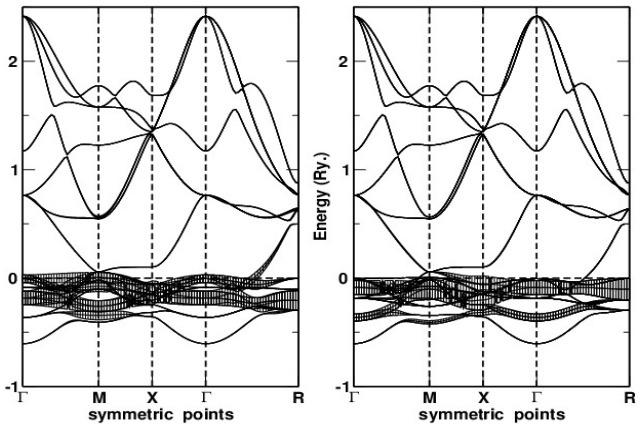

Fig. 5. Fat band structure of t_{2g} (left) and e_g orbitals (right) of Cu in CuPd.

The contributions of t_{2g} and e_g orbitals for Cu and Pd are separately shown in the Figs. 3 & 4 showing that these orbitals has dominated contribution around the Fermi level over s-orbitals and p-orbitals of copper and palladium.

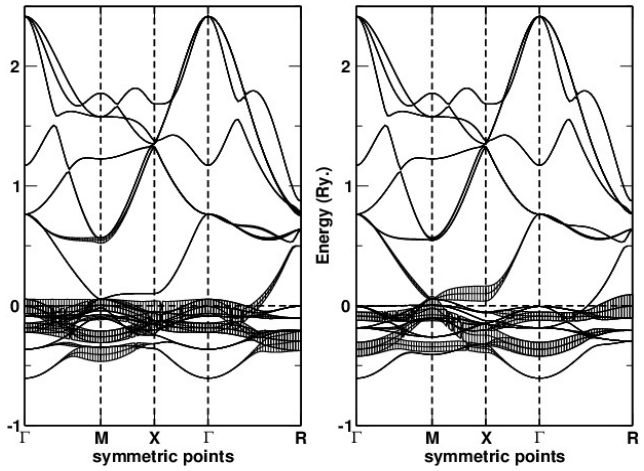

Fig. 6. Fat band structure of t_{2g} (left) and e_g orbitals (right) of Pd in CuPd.

The band structure of CuPt is shown in Fig. 7 which also contains 18 bands including s, p and d orbitals. The minimum energy level in valence band and maximum energy level in conduction band both are observed at -point. We found that the lowermost occupied valence band represented by 'l' with energy -0.2531 Ry and the topmost unoccupied conduction band represented by `i' with energy 0.9576 Ry. From the band structure of the ordered alloy CuPt, we see that the conduction bands and valence bands are overlapping in their energies near Fermi level. This reveals that CuPt forms an ordered state which is metallic in nature.

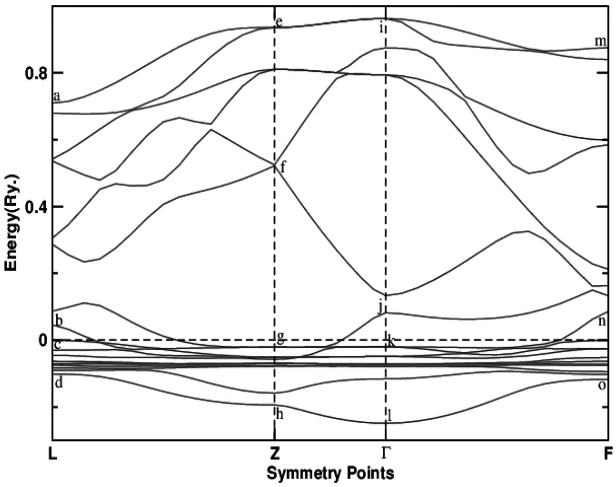

Fig. 7. Band structure of ordered CuPt binary alloy , horizontal dotted line shows Fermi level.

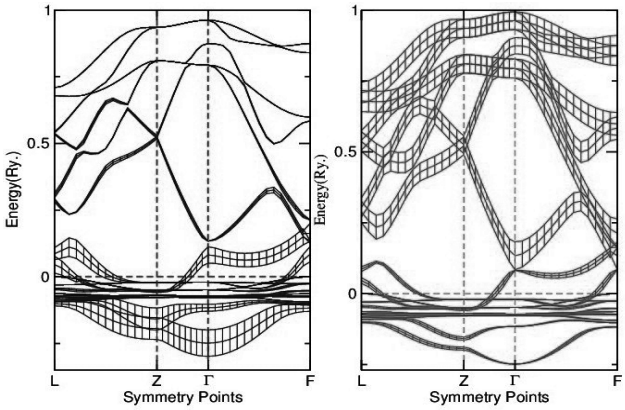

Fig. 8. Fat bands of Cu/s, Pt/s and Cu/p, Pt/p of CuPt respectively, horizontal dotted line represents Fermi level.

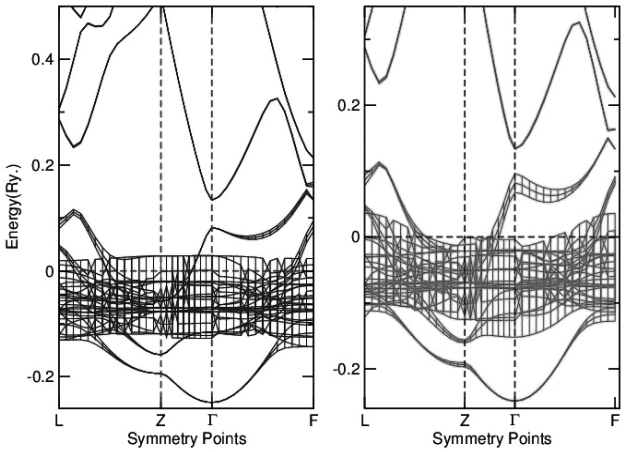

Fig. 9. Fat bands of Cu/t_{2g}, Pt/t_{2g} and Cu/e_g, Pt/e_g orbitals, horizontal dotted line represents the Fermi level.

The electron's occupancy at different orbitals of the atoms in CuPt alloy can be understood by studying the fat-bands. The fat-bands of s and p orbitals of copper and platinum in CuPt are shown in Fig. 8. From Fig. 8, we found that the less electrons are occupied in the p orbitals of Cu and Pt both, below the Fermi level and s-electrons of Cu and Pt in CuPt play little bit contribution than p-electrons of Cu and Pt. We also found that p orbitals of Cu and Pt in CuPt, above the Fermi level are occupied more. The main contribution to the energy bands of CuPt below Fermi level is from d-orbital electrons of both Cu and Pt which can be seen from fat-bands of d orbital of Cu and Pt of CuPt alloy.

The fat-bands of t_{2g} and e_g of d-orbital of Cu and Pt respectively in CuPt alloy is shown in Fig. 9. From the fat-band of Cu/t_{2g}, Pt/t_{2g} and Cu/e_g, Pt/e_g in CuPt, it clearly can be said that most of the electrons below Fermi level are occupied by d orbital electrons. The main contribution to the electronic and magnetic properties of the CuPt comes from these orbitals and plays important role to display major fundamental properties of solids.

Band Structure of Cu_3Pd and Cu_3Pt

The crystal structure of the Cu_3Pd and that of Cu_3Pt alloys both have a face-centered cubic structure of the L12 type (Kourav *et al.* 2007; Schneider, 1944). The Cu atoms occupy the face centers of the cube and Pd occupies the corner sites. The space group are taken as Pm-3m (Space group no.221) for both the cases. From the present calculation the lattice constant of Cu_3Pd for the minimum energy is obtained as 3.63 Å (6.86 a.u.) which is about 1.5% less than experimental observed value i.e. 3.69 Å (6.98 a.u.) (Kart et al. 2008; Pearson, 1967). Similarly the lattice parameter for the lowest energy value of Cu_3Pt is found to be 3.65 Å (6.91 a.u.) which agrees with experimental 3.69 Å (Schneider & Esch, 1944) within 1.08% deviation. The energy minimization curves for both Cu_3Pd and Cu_3Pt are shown in figure 10. All the further calculations are done using these optimized lattice parameters.

The band structure of Cu_3Pd calculated from the present calculations is shown in Fig. 11. We observed are thirty-six bands with valence and conduction bands overlapping with each other, showing Cu_3Pd has metallic nature. The minimum value of energy of valence band is -0.6833 Ry, labelled as 'a' and the maximum value of energy of conduction band is 2.6430 Ry, labelled as 'b' at point. Though not shown in the figure, it is clear that most of valence bands are contributed by the d-orbitals of Cu and Pd, also clear from their electronic configuration, as like in CuPd. Similarly, the band structure of Cu_3Pt calculated from the present calculations is shown in figure 12. It also contains 36 bands contributing s, p, d and f orbitals. The valence and conduction bands overlap with each other showing metallic nature of Cu_3Pt alloy. The maximum energy of the conduction band at point is 3.0338 Ry and minimum energy of valence band at point is -0.9367 Ry.

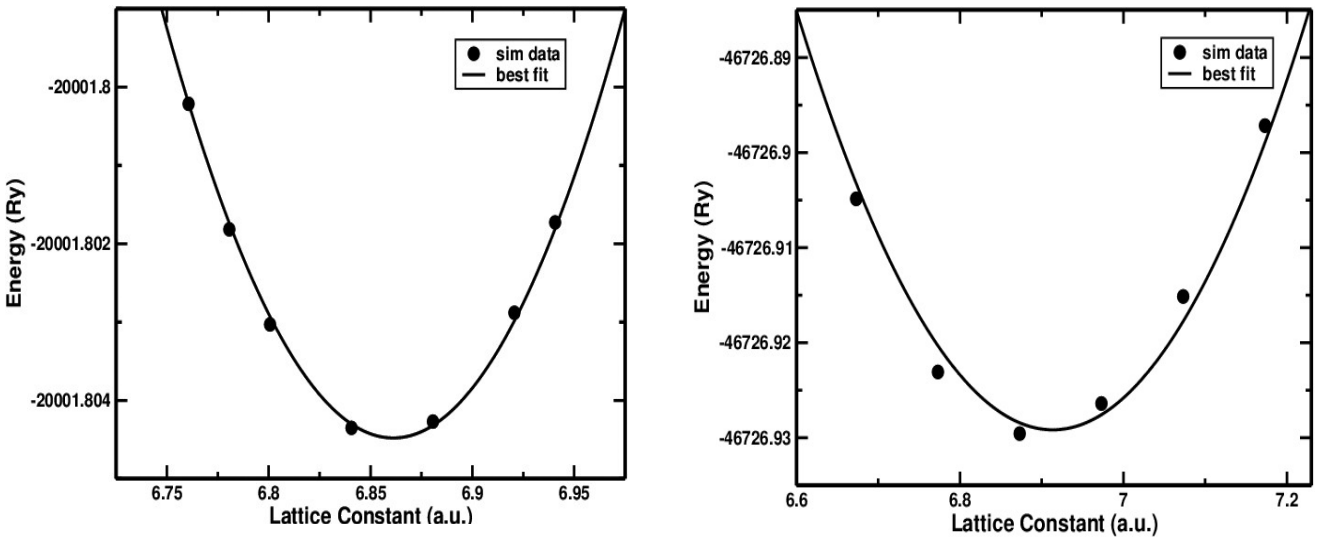

Fig. 10. Plot of Energy vs lattice constant for Cu_3Pd and Cu_3Pt.

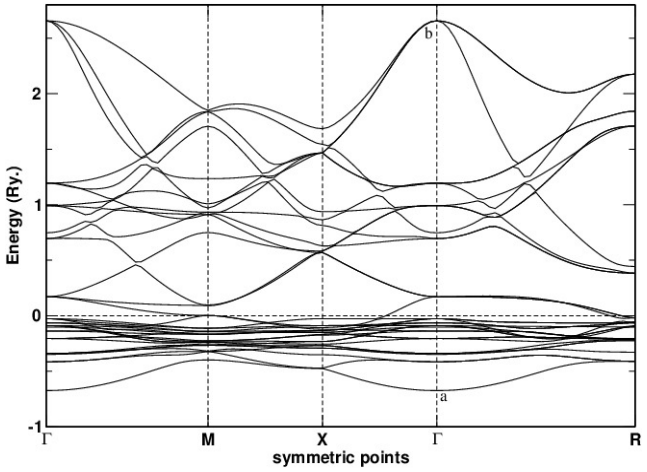

Fig. 11. Band structure of Cu_3Pd, horizontal dotted line represents the Fermi energy level.

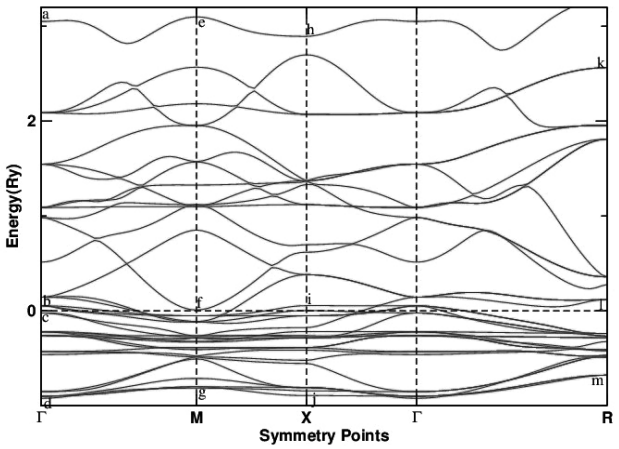

Fig. 12. Band Structure of Cu_3Pt, horizontal dotted line represents the Fermi energy level.

The main contribution in the energy bands occurs from the electrons of d orbitals which has also be reflected from fat-bands calculation (not shown in the Fig.).

Density of States for CuPd and CuPt

The plots of TDOS (total density of states) and PDOS (projected density of states) calculated using optimized parameters and experimentally given structures for Cu_3Pd and Cu_3Pt are shown in Figs. 13 to 17. Fig. 13 represents the TDOS plot of CuPd , showing major contributions on up and down states comes from those d-orbitals of copper and palladium. The total DOS is simply the sum of DOS of all the orbitals of copper and palladium. This plot is due to the results of the charge distribution for s, p and f orbitals which are very less compared to charge on d-orbitals. The total up and down DOS is shown in Fig. 13 showing nonmagnetic in nature. This behavior is due to strong competition between up spin and down spin components so that effective magnetization is zero.

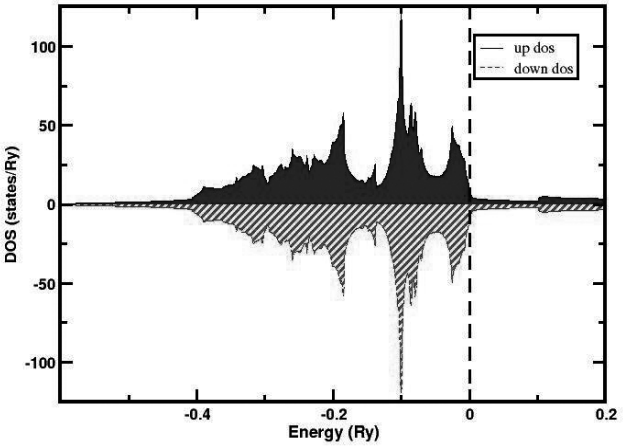

Fig. 13. TDOS of CuPd, vertical dotted line represents the Fermi level.

The low magnetic moment of CuPd can also be explained from the Figs. 13 & 15 where the curve for up and down DOS is almost the same. The calculated DOS from the present calculation is comparable to the DOS calculated by S. Takizawa *et al.* (Takizawa *et al.*, 1991), which is shown in Fig. 14. The contribution of individual DOS of Cu and Pd is shown in Fig. 15. The peaks in the DOS signify the large number of states at the corresponding energy. This can be illustrated from the band structure of CuPd, Fig. 2 and the fat band structure of different orbitals of CuPd Figs. 3 to 6. Relating the figures of fat band structure, band structure and DOS, we see peaks in DOS at certain energies. The energies are the ones where majority of the bands are found in the band structure diagrams and so the large number of electrons can be filled.

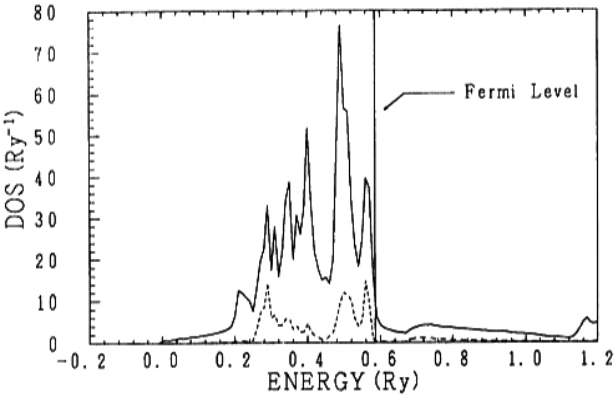

Fig. 14. TDOS of CuPd alloy with the dotted lines showing PDOS for d orbital at the Pd site calculated by Takizawa et. al. using LMTO method (Takizawa *et*

***al.*, 1991).**

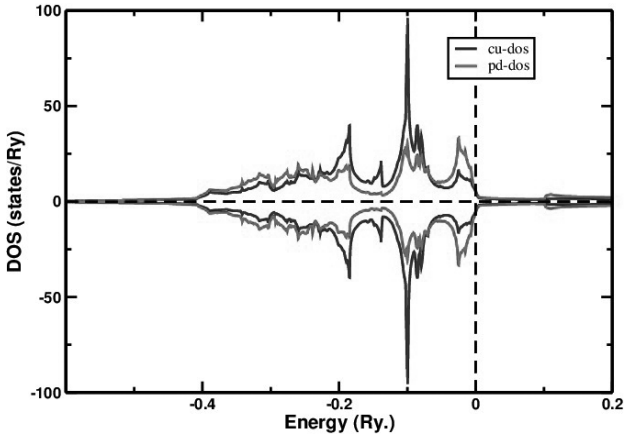

Fig. 15. Density of states of Cu and Pd in CuPd, vertical dotted line represents the Fermi level.

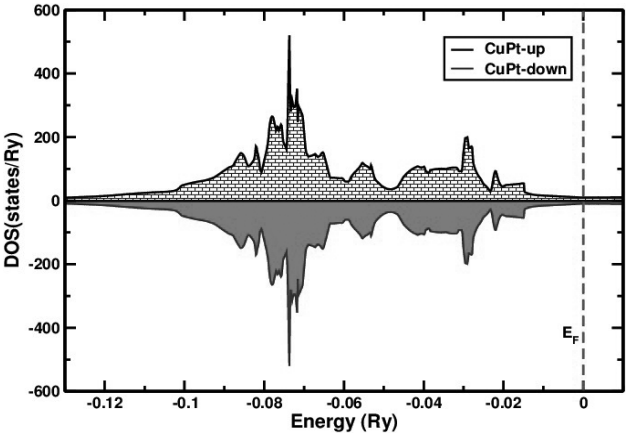

Fig. 16. Plot of density of states for CuPt. Brick stripe represents the DOS of up spin and doted cover represents DOS of down spin.

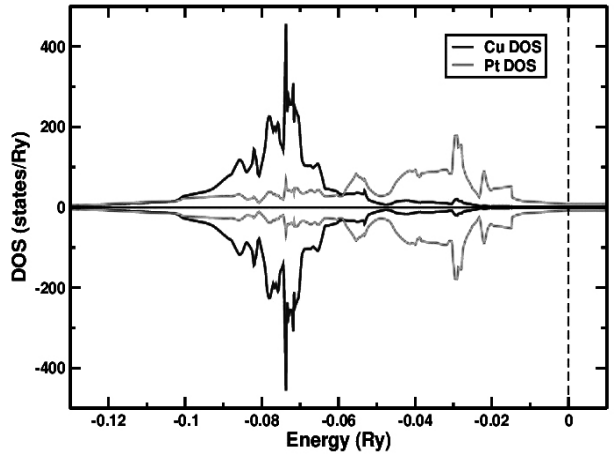

Fig.17. Individual DOS contribution of Cu and Pt in CuPt, Shaded portion represents Pt dos and vertical dotted line represents the Fermi level.

The DOS of CuPt is shown in Fig. 16. The densities of states are plotted taking reference as Fermi energy. From Fig. 16, we found that large numbers of peaks lie below Fermi energy and few peaks are observed above Fermi energy. The highest peak of up spin as well as down spin both lie below the Fermi energy. This shows that most of the orbitals below Fermi level are occupied. The peaks in the DOS signify the large number of states at the corresponding energy. This can be illustrated from the band structure of CuPt (Fig. 7). The contribution of individual atoms (Cu and Pt) in the DOS of CuPt is shown in Fig. 17. The main contribution d-orbitals are found to be dominated to s and p -orbital electrons for both Cu and Pt. From the DOS plot we simply find the magnetic moment. Basically, the magnetic moment is the integration of the difference of the density of states between up and down spin states up to the Fermi level. The magnetic moment of CuPt is found be zero. This is mainly due to cancellation of up and down spins in every steps and points.

Density of States for Cu_3Pd and Cu_3Pt

The plots of DOS calculated using optimized parameter and experimentally given structures for Cu_3Pd and Cu_3Pt are shown in Figs. 18 & 20 respectively. From these Figs., it can be said that the density of electron is more in the d-orbital, showing major contributions on the observed density of states of up and down state comes from those d-orbitals of copper and palladium. This also indicates that the density of charge distribution for s, p and f orbitals is very less compared to d-orbital. The total up and down DOS is shown in Fig. 18.

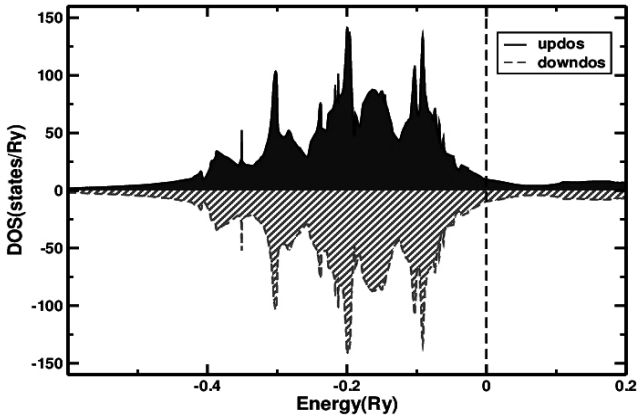

Fig. 18. Density of states of Cu_3Pd, vertical dotted line represents the Fermi level.

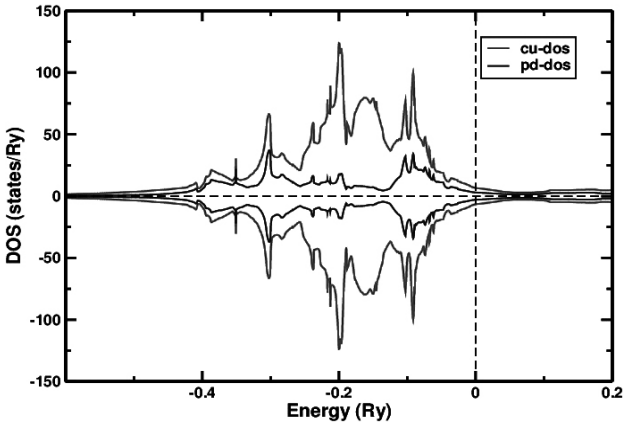

Fig. 19. Density of states of Cu and Pd in Cu_3Pd, vertical dotted line represents the Fermi level.

It is simply the sum of DOS of all the orbitals of copper and palladium. The contribution of individual DOS of Cu and Pd is shown in Fig. 19. The peaks in the DOS signify the large number of states at the corresponding energy. This can be illustrated from the band structure of Cu_3Pd, Fig 11. Relating the figures of band structure and DOS, we found peaks in DOS at certain energies. The energies are the ones where majority parts of the bands are found in band structure diagrams and so the large number of electrons can be filled.

Further, the magnetic moment of the Cu_3Pd is also calculated. The magnetic moment is the integration of the difference between up and down spin states up to the Fermi level. The magnetic moment of Cu_3Pd is found to be zero which reflects equal contributions of up and down spins in all the steps by cu and Pd respectively. The TDOS of Cu_3Pt is shown in Fig. 20. The densities of states are plotted taking reference as Fermi energy. From Fig. 20, we observed that the large number of peaks lie below Fermi energy and few peaks are observed.

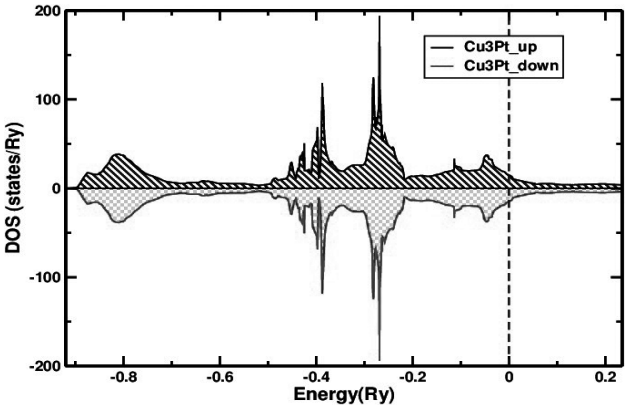

Fig. 20. Plot of density of states for Cu_3Pt. Stripped shade represents the DOS of up spin and checked shade represents DOS of down spin.

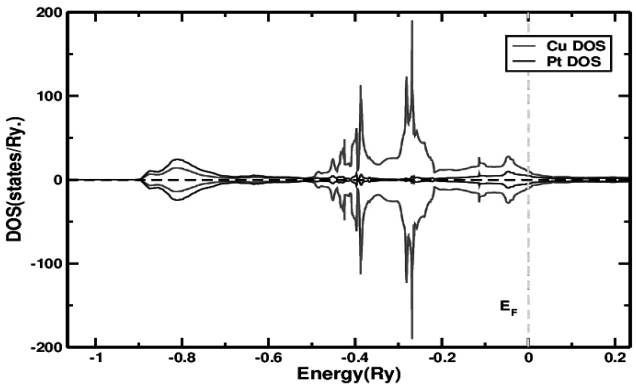

Fig. 21. Individual DOS of Cu and Pt in Cu_3Pt, bold line represents the DOS of Cu and vertical dotted line represents the Fermi level.

above Fermi energy. The highest peak of up spin as well as down spin both lie below the Fermi energy. This shows that most of the orbitals below Fermi level are occupied. The peaks in the DOS signify the large number of states at the corresponding energy. Same situation is also reflected from the band structure of Cu_3Pt (Fig. 12). The contribution of individual atoms (Cu and Pt) in the DOS of Cu_3Pt is shown in Fig. 21.

The main contributions to the magnetic moment of Cu_3Pt come out from d orbitals of both Cu and Pt. However the magnitude of individual up and down spins contributions are canceled during the formation of alloys and reflects the zero magnetic moments indicating that Cu_3Pt is nonmagnetic in nature.

CONCLUSIONS

In the present work, we have studied the band structure and density of states of ordered binary alloys CuPd, CuPt, Cu_3Pd and Cu_3Pt by using TB-LMTO-ASA. We calculated the electronic and magnetic properties of CuPd, CuPt, Cu_3Pd and Cu_3Pt. In ordered binary alloys CuPd & CuPt, we have found 18 bands and in Cu_3Pd & Cu_3Pt, we found 36 & 37 bands respectively with valence and conduction bands overlapping with each other. The band structures show the metallic nature of the systems under study.

Furthermore, we have calculated the fat band structure of CuPd and CuPt. We observed that below Fermi level, most of the bands were occupied with d-orbitals as expected. Above Fermi level, we see that the bands were occupied mostly with s and p orbitals. We also studied the density of states of all the systems. The up and down DOS is found to be nearly same, thus giving the total magnetic moment nearly equal to zero which shows our systems are non-magnetic in nature.

Finally, We are planning to use augmented space

recursion (ASR) method (Mookerjee, 1973; Saha *et al.* 1996; Chakraborty *et al.* 2001 ; Mookerjee, 1973) to deal with disordered calculations of these systems, which are left for the further communication in future.

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