

## Electronic structure calculation of CuMn alloy

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MS received 31 July 1990; revised 30 October 1990

**Abstract.** We have used a fully self-consistent multiple scattering  $X_\alpha$  method within the local density formalism to study the charge distribution, bonding characteristics and the density of states in CuMn alloy. The charge distribution shows almost no ionic character but significant hybridization of  $s$  and  $d$  states is observed near the Fermi level. The crystal field splittings, ionization energies and the excitation energies are calculated and compared with experiments wherever available.

**Keywords.** Electronic structure; alloys.

**PACS Nos** 71·70; 71·20

### 1. Introduction

The study of alloys has been given considerable interest in recent years with the development of computational schemes and experimental techniques. Experiments like transmission conduction-electron spin resonance (Monod and Schultz 1986), de Haas–Van Alphen (Coleridge *et al* 1972), thermodynamic measurements (Ranganathan and Hajra 1988), Microstructure and defect cluster density (Zinkle 1988), nuclear magnetic resonance (Abbas *et al* 1978a, b, 1982), susceptibility measurements and neutron diffraction exist on Cu based alloys with small concentration of transition metal impurity. Theoretical models like localized spin fluctuations (Gruner 1974), scattered wave method (Johnson and Vvedensky 1979), and cluster methods employing linear combination of Gaussian orbitals (Bagayoko *et al* 1986) have been utilized to explain some of the above experiments. Emphasis has been given to the Kondo problem, namely the magnetism of Mn in the non-magnetic Cu host.

In this paper, we study the Cu–Mn alloy and focus our attention on the charge distribution, bonding characteristics and density of states. We use a fully self-consistent multiple scattering  $X_\alpha$  method (Johnson 1967, 1968, 1971) within the framework of local density formalism. Our computation limitations restrict our choice of cluster size. However, size effects have been given considerable attention and the striking similarities of small cluster calculations with those of the bulk are encouraging (Lee *et al* 1984; Khowash 1986; Khowash and Khan 1986).

### 2. Method

The method is based on the division of solid into polyatomic clusters. The cluster chosen is then surrounded by a bigger sphere called the Watson sphere. A fixed radius

is assigned to each type of atom. Experience shows that atomic radius is a good starting point for most covalent solids and ionic radius for ionic solids (Khowash 1986).

To start with, the intra-atomic potential assumed to be in the muffin-tin form, is expressed in terms of spherical harmonics about its own centre

$$V(r) = \sum V_{l,m}(r) Y_{l,m}(r). \quad (1)$$

The single centered wave function within each atomic region is given by

$$\psi_I(r) = \sum C_{l,m} R_{l,m}(E, r) Y_{l,m} \quad \text{for } 0 < r \leq a \quad (2)$$

where  $a$  is the radius of the muffin-tin sphere and  $C$ 's are the partial wave coefficients to be determined. The functions  $R_{l,m}(E, r)$  are solutions of radial Schrödinger equation

$$\left[ -\frac{1}{r} \frac{d}{dr} r^2 \frac{d}{dr} + \frac{l(l+1)}{r^2} + V(r) - E \right] R(E, r) = 0. \quad (3)$$

The solutions are generated by outward numerical integrations. The exchange part of interaction is approximated in the local form as given by Slater (1972)

$$V_{\text{ex}} = -3\alpha \left[ \frac{3}{4\pi} \rho(r) \right]^{1/3}. \quad (4)$$

In the region outside the Watson sphere of radius  $b$ , the potential is again assumed to be spherically averaged and the solution is written as

$$\psi_{II}(r) = \sum C_{l,m} R_l(E, r) Y_{l,m} \quad \text{for } b \leq r < \infty \quad (5)$$

In the interstitial region, the potential is volume averaged and the solution of the Schrödinger equation is

$$\psi_{III}(r) = \sum \sum A_{l,m} k_l(\kappa r) Y_{l,m} + \sum A_{l,m}^0 i_l(\kappa r_0) Y_{l,m} \quad (6)$$

where  $i_l$  and  $k_l$  denote the modified spherical Bessel and Hankel functions. The first term may be thought of as outgoing spherical wave scattered by regions of spherically averaged potential while the second term may be interpreted as incoming spherical wave scattered by extramolecular region. The whole problem now reduces to matching the logarithmic derivatives of the wavefunctions at the sphere boundaries and calculating the coefficients for the next iteration in the process of self-consistency. The name multiple scattering theory comes from the fact that the wave function in the interstitial region is build with wave scattered from the different atomic regions. For further details of the method, classic papers of Johnson (1967, 1968, 1971) may be referred to.

### 3. Results

We use a fully self-consistent field multiple scattering  $X_\alpha$  method in the local density approximation to study the electronic structure of and bonding in CuMn alloy. The fixed parameters utilized in the self-consistent run of the program are the values of  $\alpha$ , the radius of the muffin-tin spheres, and the charge on the Watson sphere. The

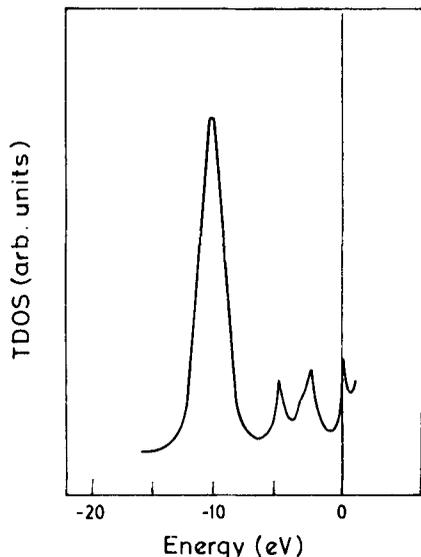
chosen values of  $\alpha$  of 0.71279 and 0.70697 for Mn and Cu, respectively, are due to Schwartz (1976). Since neutral atoms were put together to form the cluster, a net charge of zero electron was promoted to the Watson sphere. The atomic value of radius of Cu was assigned as its muffin-tin radius. The radius of Mn was obtained by subtracting the Cu radius from Cu–Mn bond length, so that the muffin-tin spheres continue to touch one another. Dependence of charge distribution on the atomic radius has been studied in detail for NaCl (Khowash 1986) and it is found that the atomic or the ionic radius is a good starting point for such calculations.

Pure Cu metal has a face centered cubic structure. The Mn atoms when added, in principle, can occupy either the Cu site or go into an interstitial site. Our cluster is composed of a single Mn atom sitting at the centre of the coordinate system (i.e., body centre of the unit cell) surrounded by six Cu atoms occupying the octahedral sites. This choice of cluster symmetry reduces the computational space and time. The other choice demand lower symmetry and/or larger cluster size which is beyond the scope of present computational facilities. The charge distribution in the different regions of the chosen cluster is shown in table 1. The charge in the central region indicates that Mn gives out about 1.29 electrons. The ligand Cu atoms, on the other hand, each gives out approximately 1.17 electrons. The reason for greater amount of electrons given out by the central region over the ligands, is due to the fact that the occupied 4s atomic state of Mn is lower in energy (magnitude) as compared to the occupied atomic 4s state of Cu. The piling up of charge in the interstitial region is a contribution of both kinds of atoms in the cluster and is attributed to the covalency in the alloy.

The nearest neighbour Cu atoms occupy the octahedral sites around the Mn atom and hence the cluster eigenvalues are designated according to the irreducible representation of the octahedral point group. The eigenstates are then filled with electrons from lowest energy upwards, in accordance with Pauli exclusion principle. In the present case, the total number of valence electrons obtained is 73 ( $6 \times 11 = 66$  from six Cu atoms and 7 from Mn atom), from 3d and 4s states of Cu and Mn. The 1s, 2s, 2p, 3s and 3p states in both kinds of atoms are treated as core states. The discrete one electron levels obtained self-consistently as solutions of Schrödinger equation are then broadened with a lorentzian of constant width of 0.4 eV to simulate the bulk density of states. The total density of states of CuMn alloy is shown in figure 1. The Fermi energy in our calculation is pinned at the last occupied or partially occupied state and is indicated, in figure 1, by a vertical line. The peak deep in the valence band is solely from Cu 3d state. Other cluster calculations also reveal a broad Cu 3d band (almost 2.1 eV wide) in the valence band. The Mn 3d states lie mainly at  $-2.8$  eV below the Fermi energy. This band is composed of about 57% Mn 3d and 30% contribution from the interstitial region and 12% from the extramolecular

**Table 1.** Charge distributions in the different regions of the cluster of CuMn alloy in electron units.

Central atom region	23.71
Ligand atom region	27.83
Intersphere region	6.23
Extramolecular region	2.18



**Figure 1.** Total density of states for CuMn alloy relative to the Fermi energy. The vertical line denotes the Fermi energy.

region. The peak lying in between Cu  $3d$  and Mn  $3d$  states is composed of 80% Cu  $4s$ , 10% interatomic and nearly 10% extramolecular contribution. These percentage contributions are directly obtained from the eigenfunctions and the corresponding weights (for the different atoms in the cluster) from the discrete cluster eigenstates obtained as a solution of the self-consistent Schrödinger equation. A comparison with the individual atomic states, at this stage, shows that atomic Cu  $3d$  level is pulled down by approximately 3.8 eV inside the valence band to form the bonding state. The atomic  $4s$  state of Cu formally above the atomic  $3d$  state of Mn is also pulled down to form a peak in between Cu  $3d$  and Mn  $3d$  states. The atomic Mn  $4s$  state, on the other hand, is pushed up by about 0.8 eV towards the Fermi level. A partially filled level of  $e_g$  character is found at the Fermi energy as is also seen by Johnson *et al* (1979) in their calculations. Other calculations (Bagayoko *et al* 1986) find a level of  $a_{1g}$  character at the Fermi level. This  $e_g$  state has a large contribution (about 65%) from the intersphere region and nearly 21% Mn  $3d$  character with traces of Cu  $3d$  character. It is therefore clear that as we move towards the Fermi energy from deep inside of the valence band, the states tend to be more and more delocalized, picking up considerable amount of intersphere charge. These delocalized states near the Fermi energy can be attributed to calvalency in CuMn alloy. It is also possible to calculate the bonding parameter,  $\lambda_\sigma$ , from our self-consistent calculations, since the basis functions used in our calculations are same as molecular orbitals in ligand field theory. In molecular orbital theory, however,  $\lambda_\sigma$  cannot be calculated from first principle. They are usually deduced from matching of parameterized orbital form factors with neutron scattering experimental data or their spin density at the nucleus with nuclear magnetic resonance data. The bonding parameter calculated for CuMn alloy is about 3.1%. Unfortunately, no experimental data is known to us to match with our calculated results. However, a further comparison can be made with that of  $\text{KFeF}_3$  and  $\text{KNiF}_3$ , where  $\lambda_\sigma$  calculated in similar manner have values of 7.55% and 5.88%, respectively,

in good agreement with experimental values of 5.11% and 6.24%, respectively (Khowash 1986). Again, from the charges of the individual spheres it is clear that CuMn system has practically no ionic character and the material is softer than the perovskites discussed above with strong covalent character.

In addition to the bonding parameter,  $\lambda_\sigma$ , the crystal field splitting ( $10Dq$ ), the ionization energy ( $I$ ), and the excitation energies ( $EE$ ) are also calculated. The partially filled  $3d$  state of Mn in CuMn splits into a four-fold degenerate  $e_g$  and a six fold degenerate  $t_{2g}$  state in presence of the ligands giving rise to a crystal field splitting of 1.0 eV. This calculated value of  $10Dq$  goes closely with the calculations of Johnson and Vvedensky (1979) but is almost half the calculated value of Bagayoko *et al* (1982). The ionization energy is obtained by removing the electron from the last occupied state to infinity. According to Koopman's theorem, it is the energy of the last filled state which in the case of CuMn is 6.02 eV. On the other hand, the excitation energy is the energy difference between the last filled state and the first empty state. In the case of semiconductors, this corresponds to the band gap of the materials. The value of the excitation energy calculated for the CuMn alloy is 4.1 eV and is in fair agreement with the experimental (Myers *et al* 1968) value of 5.0 eV.

In summary, we have used a fully self-consistent multiple scattering  $X_\alpha$  method to study the electronic structure, charge distribution and the density of state of CuMn alloy within the local density framework. The covalency and ionicity of the material is discussed both from the charge distribution and density of states point of view. The material shows almost no ionic character with large covalency. The calculated crystal field splitting of 1.0 eV, ionization energy of 6.02 eV and the excitation energy of 4.1 eV are found to be in fair agreement with other calculations and experiments.

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