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Electronic structure of magnetic impurities in copper

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We show that the anomalously small impurity exchange splittings obtained from previously reported multiple-scattering $X\alpha$ cluster calculations for the dilute alloys *CuM* (*M* represents a 3*d* transition metal) were due to incomplete convergence to self-consistency. Proper self-consistent calculations produce exchange splittings that are in excellent agreement with other calculations, which we illustrate with *Cu*Mn. We compare in detail the results of our calculations with those obtained with other approaches and discuss briefly the role of many-body effects in the *CuM* alloy series.

The calculation of electronic structures of dilute transition-metal impurities in a nonmagnetic host is a problem in determining the extent to which the impurity 3*d* electrons maintain an atomic character in the metallic environment. In general terms, the local alloy electronic structure is the result of a competition between the tendency toward localization of the 3*d* charge about the impurity, which is driven by the intra-atomic electronic correlations, and charge delocalization, caused by mixing between the impurity 3*d* orbitals and the conduction electrons of the host. For example, there are well-defined moments associated with several of the transition metals in a copper environment which for chromium and manganese have been observed to prevail well below liquid-helium temperatures.[1] In contrast, the magnetism of the transition metals is almost completely absent in an aluminum environment, with only chromium and manganese showing signs of quasimagnetic behavior in the form of spin fluctuations.[2]

The varied electronic properties of the transition metals in the respective environments underscore the role of the host in determining the local electronic structure of the alloy. The manifold differences between the electronic structures of copper and aluminum are reflected through the bonding among neighboring atoms[3] which, in turn, influences the available bonding channels between the transition-metal impurities and the respective hosts.

The formal approaches to this problem begin from one of two extreme points of view. The Friedel-Anderson virtual-bound-state model[4,5] considers the 3*d* orbitals as resonances in the host conduction band such that even in the case of a magnetic impurity only the gross features of 3*d* atomic character remain. At the other extreme the Schrieffer-Hirst configuration-based model[6,7] asserts that the impurity-host interaction leads to a coupling among different 3*d* occupancies within each of which there is a hierarchy of term, spin-orbit, and crystal-field splittings. The magnetic limit of the Schrieffer-Hirst theory then corresponds to the predominance of one 3*d* configuration over all others, and the model predicts that the aforementioned intra-atomic splittings within this dominant configuration are experimentally observable.[7] The virtual bound-state approach thus places the burden of localization upon the strength of the impurity potential (e.g., the Friedel sum rule[4]), while the configuration-based approach presumes the existence of localized many-electron atomic states whose correlations must be broken down by the conduction electrons.

In a previous paper,[8] a model was developed for the local electronic structure of dilute *CuM* (*M* represents a 3*d* transition metal) alloys based upon the multiple scattering $X\alpha$ (MS-$X\alpha$) method.[9,10] Electronic structure calculations were carried out for nineteen-atom complexes that included the substitutional impurity and the twelve nearest and six next-nearest copper neighbors in the face-centered cubic lattice. The calculations revealed (a) trends in local magnetization and spin occupancy of crystal-field levels that are in agreement with nuclear-magnetic-resonance (NMR) measurements,[11] (b) significant impurity-host *d-d* hybridization, which was subsequently observed in photoemission studies,[12] *but* (c) the reduction of the impurity intra-atomic exchange splitting by an order of magnitude from the atomic value. Here we show that the anomalous result (c) was due to incomplete convergence to self-consistency, and that fully self-consistent calculations yield excellent agreement for the impurity exchange splitting with other cluster calculations,[13] as well as with the self-consistent matching Green's-function calculations of the Jülich group.[14]

In Fig. 1 we show the self-consistent MS-$X\alpha$ spin-polarized energy levels for the nineteen-atom $\mathrm{Cu_{18}Mn}$ cluster, and in Table I we tabulate the spatial charge distributions of the orbitals that transform according to the t_{2g} and e_g irreducible representation of the octahedral (O_h) point group. We see first of all that the total magnetization is $5\mu_B$, which is entirely due to preferential occupancy of the majority-spin $7e_g$ ($2\mu_B$) and $8t_{2g}$ ($3\mu_B$) levels. Furthermore, the exchange splittings of the $7e_g$ (2.08 eV) and $8t_{2g}$ (1.30 eV) levels are in good agreement with that found for *Cu*Mn from Green's function calculations (2.06 eV).[14]

In addition to the exchange splitting we find that the manganese 3*d* levels in $\mathrm{Cu_{18}Mn}$ exhibit four characteristic

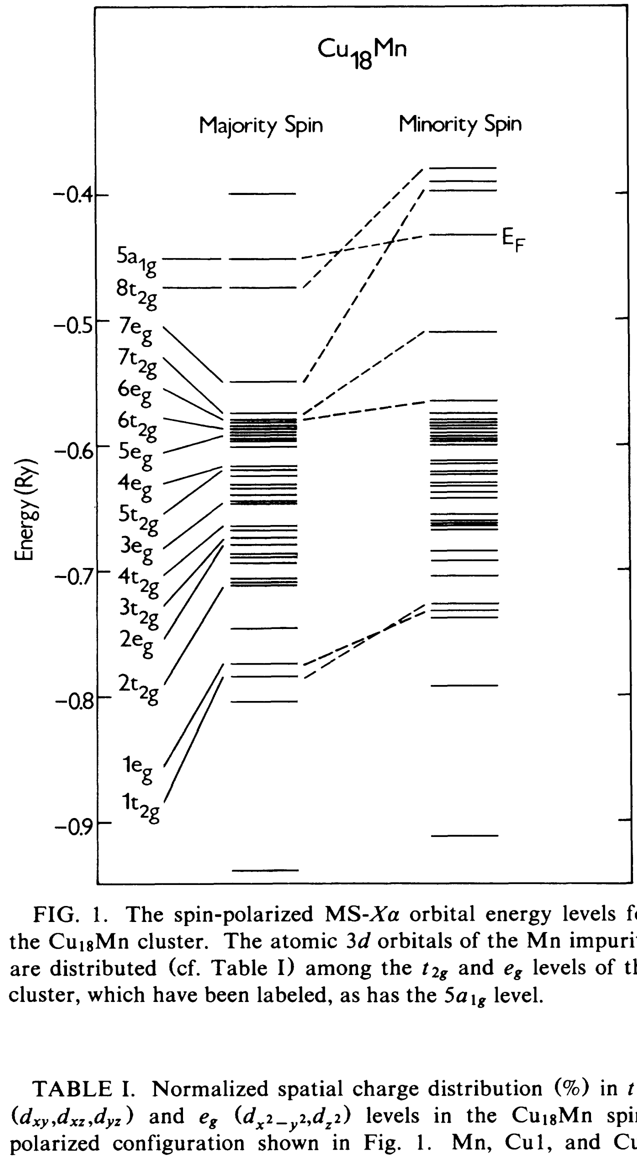

FIG. 1. The spin-polarized MS-$X\alpha$ orbital energy levels for the $Cu_{18}Mn$ cluster. The atomic $3d$ orbitals of the Mn impurity are distributed (cf. Table I) among the t_{2g} and e_g levels of the cluster, which have been labeled, as has the $5a_{1g}$ level.

TABLE I. Normalized spatial charge distribution (%) in t_{2g} (d_{xy},d_{xz},d_{yz}) and e_g ($d_{x^2-y^2},d_{z^2}$) levels in the $Cu_{18}Mn$ spin-polarized configuration shown in Fig. 1. Mn, Cu1, and Cu2 denote manganese, nearest-, and next-nearest neighbor copper muffin-tin spheres, respectively.

	Majority spin			Minority spin		
	Mn	Cu1	Cu2	Mn	Cu1	Cu2
$8t_{2g}$	8	46	21	58	21	4
$7e_g$	11	50	25	75	10	8
$7t_{2g}$	6	30	62	14	44	31
$6e_g$	2	12	84	3	60	28
$6t_{2g}$	6	16	76	0	24	74
$5e_g$	2	11	85	1	7	89
$4e_g$	14	70	13	1	9	87
$5t_{2g}$	14	66	16	2	27	66
$3e_g$	10	78	9	1	93	4
$4t_{2g}$	0	84	15	3	94	1
$2e_g$	16	67	15	1	84	12
$3t_{2g}$	10	88	0	0	84	15
$2t_{2g}$	1	81	15	1	86	11
$1t_{2g}$	48	47	1	7	83	5
$1e_g$	39	47	9	5	74	16

features: (a) localized unoccupied minority-spin $7e_g$ and $8t_{2g}$ levels (Table I); (b) a fairly uniform distribution of impurity $3d$ charge among several levels between the top of the copper $3d$ band and the Fermi level, implying a comparatively broad virtual bound state; (c) enhanced majority-spin occupancy for levels lying in the copper $3d$ bands, increasing toward the bottom of the bands, where the impurity-host bonding levels ($1t_g$ and $1e_g$) lie; and (d) confinement of the influence of the manganese largely to within the impurity unit cell, as evidenced by a comparison of charge distributions and partial-wave characters for the Cu_{19} and $Cu_{18}Mn$ levels. These results are confirmed by the recent calculations of Blaha and Callaway[13] for the $Cu_{18}Fe$ cluster using the spin-density-functional formalism with an uncontracted Gaussian basis set. However, the Green's function calculations of Ref. 14 are in agreement only with the features (c) and (d). Moreover, the photoemission measurements of Hochst, Steiner, and Hufner[12] clearly support (b) and (c). Possible reasons for this discrepancy have been discussed in Refs. 13 and 14, but the issue remains unresolved.

A comment is in order concerning the comparison of cluster and band calculations with regard to the frequently made statement[14] that clusters are incapable of describing the s-d interaction. While the conduction band of copper is described by only three levels ($5a_{1g}$, $7e_g$, and $8t_{2g}$ in Fig. 1), the addition of successively more distant neighbor shells simply causes the nearest- and next-nearest-neighbor charge to be distributed among successively more levels. By truncating the cluster at second neighbors, we are in effect presuming that the s-d coupling does not vary over the width of the conduction band. Thus, while the cluster can account for the gross features of the electronic structure, the finer details, such as the profiles of the virtual bound state, are lost. This important distinction between the two approaches is most apparent for systems near the magnetic instability point (e.g., *Cu*Co), where the details of the host band structure are required for an accurate quantitative characterization of the impurity-host interaction.

One final remark we would like to make concerns many-body effects for magnetic impurities in copper. The strong magnetic limit of the Anderson model[5] is given in terms of the intra-atomic Coulomb integral U and the broadening Δ of the spin-degenerate impurity state by $U/\Delta \gg 1$, which may be generalized to include orbital degeneracy. On the other hand, as discussed in the introduction, the magnetic limit of the Schrieffer-Hirst model corresponds to the prominence of a single $3d$ configuration with an associated hierarchy of atomic fine structure. Accordingly, if we denote the interconfigurational excitation energy by I, and the impurity-$3d$–host bond energy by E_{sd}, then the condition for moment formation becomes $I/E_{sd} > 1$. In other words, if the bonding between the impurity $3d$ levels and the copper is inhibited to a sufficient extent, the impurity forms a quasiatomic state with the residual bonding leading to renormalized atomic structure constants. In fact, NMR data[15] suggest this to be the case for *Cu*Cr and *Cu*V, where, for example, the Cr $3d$ orbital angular momentum and spin-orbit coupling constant are reduced to approximately 80% of their free-ion values.

From a theoretical point of view, a calculation is required that includes the full atomic structure of the impurity from the start. The calculation could be formulated with the Green's-function matching formalism by embedding a highly correlated system in an effective one-electron medium characterized by a band structure.[16] The recent work of Riegel *et al.*,[17] showing, on the one hand, the stability of the $3d^6$ configuration of Fe^{2+} in K, Rb, and Cs, and, on the other, unstable magnetic behavior of Fe in Li, would seem to provide particular impetus for such calculations.

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