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Calculation of magnetization in ordered Ni-Cu alloys

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Results for the magnetic and electronic properties of three artificial, *ordered* geometries for the Ni-Cu alloys indicate three physical mechanisms which suppress Ni magnetization in the alloys. These are as follows: decreased d character of the states at E_F, rounding and loss of structure in the projected Ni density of states, and filling of the d band. These mechanisms are equally applicable to the disordered alloys, and we discuss the modifications introduced by disorder. Results are in good agreement with behavior of the disordered alloys.

I. INTRODUCTION

For almost half a century the magnetic behavior of Ni-Cu alloys has been a model problem in itinerant ferromagnetism. The magnetic and electronic properties of these alloys have been extensively studied both experimentally[1,2] and theoretically.[3–6] The most striking feature is that the magnetic moment *per Ni atom* of the alloys decreases approximately linearly with Cu concentration, from $0.616\mu_B$ for pure Ni to zero at about 60 at. % Cu.

Mott[7] proposed a rigid-band model in which conduction electrons are shared equally among Cu and Ni sites. This results in charge transfer from Cu to Ni, with filling of the Ni minority-spin band, and consequent reduction of magnetization. The theory gives excellent results for the magnetic moment as a function of concentration. However, the very different behavior of alloys of Fe and Co with nonmagnetic metals[8] suggests that the success of the rigid-band model for Ni is fortuitous. More recent experiments[1,9] moreover suggest that d-band filling is less important than local environment effects in reducing the alloy magnetization.

Unfortunately, the fully self-consistent calculation of electronic properties of random transition-metal alloys is not yet feasible, despite recent progress.[10] Some magnetic coherent potential approximation (CPA) calculations have been performed for simple model Hamiltonians,[3–5] but these have not included hybridization between the sp and d bands. Such hybridization is crucial for a realistic physical description, as we see below.

In order to examine the basic physical mechanisms responsible for the extinction of ferromagnetism in the Ni-Cu alloys, and to gain some idea of their relative importance, we have therefore calculated the electronic and magnetic properties of some *ordered* Ni-Cu alloys. Specifically, we consider those geometries which can be represented with a four-atom supercell, the conventional cubic cell for the fcc lattice. These structures are entirely artificial for the Ni-Cu alloy, and in interpreting our results we try to distinguish between those effects which are sensitive to the precise geometry, and those which are not.

We find three distinct effects which are important: The effective exchange interaction is reduced in the alloy, relative to pure Ni, by hybridization of the Ni d band with the conduction band, which increases the partial sp character of the d-like states at E_F; the magnetization is further reduced by changes in the shape of the density of states

(DOS) projected at the Ni sites, and there is some d-band filling, though it cannot be described in a rigid-band model such as Mott's.

II. CALCULATION

We take our Hamiltonian to be the sum of a one-electron term H_0 and an electron-electron interaction term H_{ee}. For H_0 we choose the parametrized tight-binding scheme of Slater and Koster.[11] The Hamiltonian H_0 is written in terms of one- and two-center integrals, which are treated as parameters chosen to fit the bulk band structure. We include s, p, and d orbitals, with interactions up to second-nearest neighbor. For the matrix elements between Ni and Cu in the alloy, we take the geometric mean of the respective Ni-Ni and Cu-Cu matrix elements. The two sets of intersite matrix elements are very similar, so the results are insensitive to the precise scheme for choosing the Ni-Cu matrix elements.

The electronegativities of Ni and Cu are the same to within about 0.1 eV,[12] so we choose the zeros of energy for the two metals so as to line up their bulk Fermi levels. However, the final self-consistent result is not sensitive to physically reasonable ($\sim$0.2 eV) differences in the respective Fermi levels.

For the electron-electron interaction we use a single-site approximation, which has been extensively discussed,[13]

$$H_{ee}=\sum_{i\sigma\sigma'}\sum_{\alpha\beta\gamma\delta} U_{\alpha\beta\gamma\delta}\, c^{\dagger}_{i\alpha\sigma} c^{\dagger}_{i\beta\sigma'} c_{i\gamma\sigma'} c_{i\delta\sigma} , \qquad (1)$$

where $c^{\dagger}_{i\alpha\sigma}$ creates an orbital of symmetry α and spin σ at site i. Intersite Coulomb terms can be neglected here, since results for the single-site approximation are already essentially charge neutral at each site.

We treat H_{ee} in the Hartree-Fock approach; we can, with some approximations, reduce H_{ee} to a simple form for the on-site potential shifts,

$$\begin{aligned}\Delta E_{d\nu\sigma}= & -\tfrac{1}{2}(U-J)\langle m_{d\nu\sigma}\rangle-\tfrac{1}{2}J\langle m_{d\sigma}\rangle \\ & +V_{sd}\langle n_s-n_s^0\rangle+V_{dd}\langle n_d-n_d^0\rangle , \qquad (2)\\ \Delta E_{s\sigma}= & \,V_{ss}\langle n_s-n_s^0\rangle+V_{sd}\langle n_d-n_d^0\rangle .\end{aligned}$$

Here, $\Delta E_{d\nu\sigma}$ is the on-site potential shift for a d orbital of symmetry ν and spin σ, measured relative to the value for the pure paramagnetic metal. By $m_{d\nu\sigma}$ we denote the spin polarization $n_{d\nu\sigma}-n_{d\nu\bar{\sigma}}$ in the d orbital of symmetry ν at a given site, and $m_{d\sigma}\equiv\sum_{\nu}m_{d\nu\sigma}$. The total d occupancy at the site is denoted by $n_d\equiv\sum_{\nu\sigma}n_{d\nu\sigma}$, and the value for the respective pure metal is n_d^0. Quantities for s and p orbitals are similarly defined. In (2), s refers to the entire sp complex.

We define U as the on-site direct Coulomb integral between d orbitals of the same symmetry (rescaled by correlation effects, see below); U' is the integral between d orbitals of different symmetry, and J is the exchange integral. We define $V_{dd}\equiv U'-\frac{1}{2}J$, which gives the effective (repulsive) interaction between d electrons, aside from magnetic effects. We similarly define an effective interaction V_{ss} among sp electrons, and V_{sd} between sp and d electrons. We neglect the on-site exchange integrals other than between d orbitals. The ratios $U{:}U'{:}J$ are taken to be 5:3:1 as suggested by Herring[13]; this incidentally allows us to cancel a term involving $U+J-2U'$. These ratios are not crucial. Similar results are obtained for $J=0$ or $J=U$ as long as the overall magnitude is scaled to give the correct[14] bulk Ni magnetization $\mu=0.616\mu_B$. Such scaling is necessary in any case when we work in the Hartree-Fock approximation, since the *effective* interaction is reduced by correlation effects.[13]

We use Auger data[15] to set V_{dd} for Cu and Ni. The ratios of V_{sd} and V_{ss} to V_{dd} are taken to be the ratios of the atomic values. The value of V_{dd} for Cu is twice that for Ni, so we take all Cu interaction parameters to be twice the corresponding Ni value. This is actually unimportant since the Cu magnetization is always negligible for any reasonable values of the interactions.

We tested this Hamiltonian for pure Ni and found excellent agreement with theory and experiment.[16] We then calculated the electronic properties of the ordered Ni-Cu structures described above. Our Ni_3Cu and $NiCu_3$ structures are generated by replacing one of the four atoms in the conventional cubic cell of Ni or Cu with the other metal. Our NiCu structure consists of alternating (100) layers of Ni and Cu on the underlying fcc lattice. We restrict consideration to only ferromagnetic and paramagnetic states.

Yamashita *et al.*[17] have calculated the DOS's for the ordered alloys considered here, and also for the corresponding random alloys (within the CPA) without spin polarization. The similarity between the ordered and disordered cases is strong, supporting our claim that disorder introduces only quantitative modifications here.

We note that more accurate calculational methods than those used here are currently available. However, since we are treating an artificial system, and one for which the tight-binding approximation is well suited, there is little point in applying such demanding methods here.

III. RESULTS

Our results are summarized in Table I and Fig. 1. For each alloy, Table I gives the number $z_{\text{Ni-Ni}}$ of Ni neighbors at a Ni site, the magnetization μ at a Ni site, the change Δn_d in total d-orbital occupancy at a Ni site relative to pure ferromagnetic Ni, $D_d(E_F)$, the d component of the DOS at E_F at a Ni site, and α, a measure of hybridization effects, which is defined and discussed below and is proportional to the "effective" Stoner exchange parameter.

For the geometries considered, all Ni sites are equivalent. In all cases the moment at a Cu site is negligible, in agreement with experimental results of Medina and Cable.[1] All sites are essentially charge neutral. We omit further discussion of quantities projected at the Cu sites.

In Fig. 1 we show the contribution to the alloy DOS from d orbitals at a Ni site for each spin. This projected DOS is based on a finite wave-vector sample (i.e., 5832 points in the full simple-cubic Brillouin zone of the four-atom cell for Ni_3Cu). The DOS is smoothed by convolution with a Gaussian of full-width at half-height equal to 0.01 Ry.

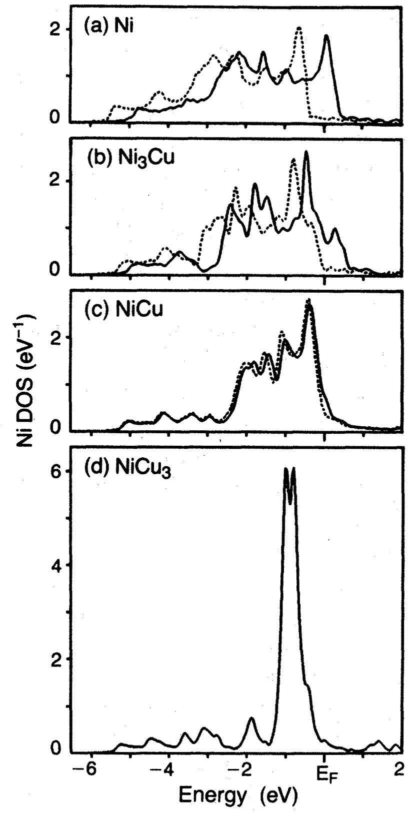

FIG. 1. The d-orbital component of the local DOS *per Ni atom,* projected by spin at the Ni site. (a) for pure Ni. (b) for Ni_3Cu. (c) for NiCu. (d) for $NiCu_3$. See text for alloy geometries. Solid line represents minority spin, and dashed line represents majority spin.

Some simple trends are immediately evident from Table I. The magnetization of course decreases with increasing Cu concentration. Our results for the Ni magnetic moments of the two ferromagnetic alloys are in excellent agreement (within $0.04\mu_B$ per Ni atom) with experimental results of Medina and Cable,[1] interpolated to 25 and 50 at. % Cu. This agreement may be regarded in part as fortuitous, though, in view of the artificial geometries used here.

TABLE I. Electronic and magnetic properties of Ni in ordered Ni-Cu alloys. All quantities defined in the text.

Alloy	$z_{\text{Ni-Ni}}$	μ (μ_B)	Δn_d	$D_d(E_F)$ (eV^{-1})	α
Ni	12	0.62	0	1.77	0.97
Ni_3Cu	8	0.47	0.07	0.93	0.88
NiCu	4	0.09	0.15	1.20	0.79
$NiCu_3$	0	0.00	0.22	0.58	0.35

There is a significant filling of Ni d orbitals in the alloy, relative to pure Ni. This filling Δn_d is approximately linear in the number of Cu neighbors. The d-band filling is due to narrowing of the projected Ni d-band with reduced Ni-Ni coordination. The d band is centered well below E_F, so as it narrows, it pulls below E_F and becomes fuller. This is possible because charge neutrality can be maintained at only moderate cost in energy by transferring electrons from the sp band to the d band at the Ni site. This mechanism for d-band filling is suggested by results of calculations for the random paramagnetic Ni-Cu alloy[6] using a non-self-consistent potential. We find that this effect is modified by self-consistency but not eliminated, as it would be in a calculation which omitted the *sp* band. Note that this is completely unrelated to the Mott rigid-band picture. Charge transfer is between *sp* and *d* bands projected at the Ni site, *not* between Ni and Cu. Also, the driving force for charge transfer is band narrowing, which is absent in a rigid-band model. Most important, the *d*-band filling accounts for only a fraction of the change in magnetization.

A major cause of the reduced magnetization is evident in Fig. 1. In the alloy, the upper edge of the *d* band becomes rounded, for reasons discussed below. This reduces the DOS at E_F, and hence the magnetization. In the Stoner rigid-band model, a ferromagnet with a "square" band (constant DOS with sharp cutoff) is always saturated at $T=0$, i.e., for an almost full band there are no majority-spin holes left. With a rounded upper band edge some majority-spin holes can remain, reducing the magnetization. We believe this DOS "shape" effect to be a crucial factor for magnetism in Ni alloys, and the failure to mimic the detailed shape of the alloy DOS is the major barrier to relating our results quantitatively to the random alloy.

For the real metal or alloy, the *d* bands hybridize with the *sp* band. The effective exchange field felt by a state is approximately proportional to the magnetization, and to the degree of *d* character of the state. For the Ni-Cu alloy, the magnetization is localized at the Ni sites, so the effective exchange potential felt by a state is proportional to its *d* character at the Ni sites. We therefore define a quantity α which measures the average fraction of a state at the Fermi level, which is derived from *d* orbitals at Ni sites. To be precise, we define

$$\alpha \equiv \frac{\sum_\nu W_\nu^2 \delta(E_F - E_\nu)}{\sum_\nu W_\nu \delta(E_F - E_\nu)} , \tag{3}$$

$$W_\nu \equiv \sum_{im} |\langle \phi_{im} | \nu \rangle|^2 , \tag{4}$$

where $|\nu\rangle$ is an eigenstate of the system (either spin) of energy E_ν, normalized to unity in the unit cell, and ϕ_{im} is a *d* orbital of symmetry *m* at Ni site *i* in the cell.

A more obvious parameter might have been

$$\frac{\sum_\nu W_\nu \delta(E_F - E_\nu)}{\sum_\nu \delta(E_F - E_\nu)} .$$

However, this is simply the fraction of the DOS at E_F which derives from Ni *d* orbitals. Such a definition would give no measure of the degree of *hybridization* between *sp* and *d* bands. Our parameter α defined by (3) is equal to 1 if the Ni *d* band at E_F uncouples from the conduction band, regardless of the relative magnitudes of the components of the DOS (the Cu *d*-band contribution at E_F is negligible). On the other hand, if $D_d(E_F)$ derives from states with only partial *d* character, α is reduced.

In fact, it is easy to show that for the Stoner rigid-band model, given a *d* band hybridized with a conduction band (whose spin polarization and exchange interaction may be neglected), the Stoner susceptibility formula

$$\chi = 2\mu^2 N (1 - IN)^{-1} , \tag{5}$$

should be replaced by

$$\chi = 2\mu^2 N_d (1 - \alpha I N_d)^{-1} , \tag{6}$$

where N_d is the *d* component of *N*, the one-spin DOS at E_F, *I* is the Stoner exchange parameter for the *d* band alone, and α is defined by (3). Thus, α is the correct measure of the reduction in the effective exchange interaction due to hybridization, at least in the paramagnetic case where (5) holds.

Returning to Table I, we see that the Ni_3Cu structure has a moment per Ni atom which is 23% less than the Ni bulk. The change in α is modest, and for the pure Ni DOS [Fig. 1(a)] this reduction in the effective exchange strength would probably result in little change in magnetization. Half the loss of magnetization results from *d*-band filling, if we assume all the extra *d* electrons go into the minority-spin band.

Another effect which reduces the magnetic moment is easily seen in Fig. 1(b). The projected DOS at the Ni site has become rounded relative to pure Ni. The large DOS at the top edge of the *d* band, characteristic of the ideal fcc structure, is greatly reduced in the alloy. This effect is clearly seen in non-self-consistent calculations for the random paramagnetic alloy,[6] and we have mentioned how this DOS rounding tends to reduce magnetization. The change in the DOS has two causes: the reduced local order and the fact that the Cu *d* band is lower in energy than the Ni *d* band. The latter factor results in *energy-dependent* narrowing of the projected Ni *d* band. The states at the top of the Ni *d* band interact least with the Cu *d* band (due to the larger energy denominator), so these states are the most "narrowed" towards the band center, relative to pure Ni, reducing the DOS at the top of the band. In fact, near E_F the interaction with the Cu *d* band can almost be neglected; only the effect of the conduction band remains. If we artificially remove the Cu *d* orbitals from the Hamiltonian, the shape of the Ni DOS well below E_F changes but the behavior near E_F, the magnetization, and the charge transfer are all affected surprisingly little. Thus as regards magnetism, the Cu *d* level may be considered crudely as an almost inert core.

The effect of reduced local order is drastic. For the ideal fcc structure, the sharp features at the upper edge of the *d* band are caused by the very flat bands encountered along various lines (e.g., *WX* and *WL*) in the Brillouin-zone faces. Any reduction in symmetry (and, *a fortiori,* any disorder) lifts this degeneracy, and in general suppresses that sharp peak at the top of the fcc *d* band, which is so conducive to ferromagnetism in pure Ni.

The *sp-d* hybridization produces a related but more subtle effect, a "smearing" of the *d*-orbital component of the DOS. Some *d* holes are hybridized into high-energy states of mostly *sp* character, which cannot contribute significantly to the spin polarization. In the alloy this effect is stronger than in bulk Ni, because of the larger *sp* DOS per Ni atom at E_F. The number of "effective" *d* holes per Ni atom is thus reduced. This behavior is analogous to that found in Anderson's model[18] for a magnetic impurity.

For the 50-50 alloy, consisting of alternate (100) layers of Ni and Cu, each Ni atom has only four Ni neighbors and the magnetic moment has almost vanished. In fact, it is surprising that any moment remains, since experimentally the moment vanishes at 60 at.% Cu, with each Ni atom having about five Ni neighbors on the average. The reason for this apparent discrepancy can be seen in Fig. 1(c). Because of the highly ordered geometry, the projected *d*-band DOS at the Ni site shows sharp peaking at the top of the band. The small Ni-Ni coordination also narrows the band, further increasing the DOS at E_F, which is anomalously large (Table I). Even so, this structure is only precariously magnetic. For a less symmetric structure with the same Ni-Ni coordination, the upper band edge would be less sharp, $D(E_F)$ would be smaller, and the system would be paramagnetic.

To illustrate this point, we note that in another calculation[19] using the same Hamiltonian, we found that a Ni atom at a (100) Ni-Cu interface has a moment $0.28\mu_B$. In that case the Ni-Ni coordination at the site is 8, as for the Ni_3Cu structure here, yet the high-symmetry Ni_3Cu alloy has a much larger Ni moment, $0.47\mu_B$. We should add that the local symmetry of the structure may affect not only the DOS but also the degree of hybridization of the local *sp* and *d* bands.

For the $NiCu_3$ structure, the Ni atom has no Ni neighbors, and the situation is similar to the low-Ni-concentration limit. The Ni DOS is extremely narrow, but E_F lies in the high-energy tail of the DOS, so $D_d(E_F)$ is quite small, and the alloy is paramagnetic. Also the very small value of α (Table I) indicates that the small $D_d(E_F)$ derives from states with a large *sp* character, i.e., highly hybridized states.

A final comment is in order concerning the effect of the filling of the Ni *d* band. For small Cu concentrations, it is reasonable to think of these extra electrons as going primarily into the minority-spin *d* band, reducing μ by roughly Δn_d. Near the critical concentration, however, the spin splitting is small and $D_\uparrow(E_F) \approx D_\downarrow(E_F)$, so the extra charge is shared nearly equally between the two spins. The notion that the majority-spin *d* band is full in Ni arises from neglect of hybridization, and is misleading in this context. In the alloy the notion loses all validity.

To the extent that *d*-band filling is important in the near-critical regime of concentration, it is because such filling pushes E_F further into the high-energy tail of the *d* band, where the DOS is quite small, even for a very narrow band, as in Fig. 1(d).

IV. CONCLUSION

By calculating the electronic and magnetic structure of some artificially ordered Ni-Cu alloys, we have distinguished three mechanisms responsible for the reduced magnetic moment per Ni atom in the Ni-Cu alloy relative to pure Ni. These are *d*-band filling due to band narrowing, changes in the shape of the site-projected local DOS, and *sp-d* hybridization, which reduces both the effective exchange interaction, for states at E_F, and the number of effective *d* holes, as the Cu concentration is increased. All three factors are important. The shape of the DOS is the factor most sensitive to the disordered nature of the real alloy; however, a self-consistent potential is required to position correctly the *d* band, which is crucial in determining both *d*-band filling and hybridization, i.e., the effective exchange interaction strength.

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