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Application of coherent potential approximation to Ni-rich Ni-Cu alloys*

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The electronic structure of Cu-Ni alloy has been studied for up to 50 at.% of Cu concentrations in the Ni-rich domain, using the coherent-potential approximation. Results are presented in both the paramagnetic and ferromagnetic phase. Reasonable agreements with the experimental results on charge transfer, specific heat, Curie temperature, and the magnetic moments are obtained. The calculation lends support to the minimum-polarity model of Lang and Ehrenreich.

I. INTRODUCTION

The effect of alloying a magnetic metal like nickel with nonmagnetic impurities in the form of copper has been of both theoretical and experimental interest for a long time. Experimentally it has been observed that the magnetic moment of the alloy disappears in the vicinity of 60 at.% Cu concentration. This transition from the ferromagnetic to the paramagnetic phase had led the theoreticians to believe in Mott's[1] rigid-band model of the alloy. According to this model it is believed that the density of states of a pure crystal remains unchanged as another component is added to form an alloy. The only effect of adding the impurity is to allow the electrons to redistribute equally between the host (Ni) sites and the impurity (Cu) sites, thereby shifting the position of the Fermi level. Earlier experimental evidence on nickel led one to believe that, in the metallic state, it has 0.6 unfilled d-electron states per atom. Thus this band is just full when Cu concentration reaches 60 at.%, because Cu has one additional electron per atom. However, during the last decade evidence has been piling up which suggests that this explanation might just have been due to a combination of circumstances which gave a correct answer, starting from an incorrect hypothesis. In 1968 Lang and Ehrenreich[2] undertook a formidable many-body calculation, in which they treated the effects of the interactions of the d electrons in the t approximation, using a short-range model Hamiltonian due to Hubbard,[3] Kanamori,[4] and Gutzwiller.[5] They found that a careful analysis of the rigid-band approximation would give a pole in the zero-temperature static paramagnetic susceptibility at a concentration of Cu around 10 at.%.[6] This shows that the ferromagnetic Curie temperature T_C becomes zero for this concentration of Cu, rather than at 60 at.%. They went on to calculate the pressure dependence of the Curie temperature, and compared the predictions of the rigid-band model with the experimental measurements by Okamoto *et al.*[7] They found that the rigid-band model would predict an increase in the Curie temperature with the pressure, rather than the observed decrease.

Further failures of the rigid-band model were noticed when accurate measurements of the low-temperature specific heats were made in both the magnetic and nonmagnetic phases of the alloy. The Fermi-level density of states $\rho(E_F)$ calculated from the specific-heat coefficient γ shows sharp disagreement with the predictions of the rigid-band model. More direct evidence on the subject comes from the recent photoemission experiments by Hüfner *et al.*[8] The experimental $\rho(E_F)$ are in sharp disagreement with the prediction of Mott's theory.

Lang and Ehrenreich[2] proposed an alternative model, referred to as the "minimum-polarity model."[9] According to this model there is little charge transfer from Cu to Ni sites on alloying, and the constituents retain their atomic configurations of ($3d^{10}4s$) and ($3d^{9}4s$), respectively. Thus, in contradistinction to the rigid-band model, where each site has appreciable ionic character, the minimum-polarity model demands local charge neutrality at each site. X-ray emission data of Blokhin *et al.*[10] corroborate that the number of d holes in Ni is substantially larger than 0.6—it being approximately 1.1.

A practical way to calculate the density of states of an alloy, which is valid in the intermediate concentrations of the impurities, was proposed by Soven,[11] and subsequently put into a mathematically rigorous form by Velický, Kirkpatrick, and Ehrenreich.[12] Considering a single band, the latter authors wrote down a coupled nonlinear equation for the one-particle self-energy function Σ. Stocks *et al.*[13] used the coherent-potential approximation (CPA) to calculate the density of states for the paramagnetic Ni-Cu alloys, starting with a realistic density of states for the host material. Subsequently Hasegawa and Kanamori[14] considered various Fe-based alloys, where the impurity too was magnetic. They included the correlations between the *d* electrons, within Hubbard's model of intra-atomic and intraorbital interactions,[3] in the Hartree-Fock scheme. While this provided a way to estimate the effects of such electron interactions, these authors took idealized density-of-states curves by simplifying the state-density curve of Connolly[15] in such a way that the height and the width of their linearlized curve corresponded approximately to the major peak of Connolly's calculation. Because of this the calculations were not expected to provide quantitative estimates of the properties of the alloys considered by them. Recently Levin *et al.*[16] calculated the spin susceptibilities of Ni-Rh and Ni-Pd alloys using the CPA density of states.

In this work we have undertaken an extensive calculation of the Cu-Ni alloys in the Ni-rich region. Thus our emphasis has been on the ferromagnetic phase of the alloys, even though we have considered both phases for completeness. Kirkpatrick *et al.*[12] have studied the density-of-states function of this alloy within the framework of CPA in a simple model. Since we can expect the effect of *d*-electron interactions to be very important here, we have considered a model which included intra-atomic and interorbital interactions, considered within the Hartree-Fock theory. We calculate the spin-dependent self-energies by solving the CPA equations for each spin. The input density of states is taken in its full detail from the recent tight-binding calculations of Callaway and Wang.[17] The scheme of the paper is as follows.

In Sec. II we write down the model Hamiltonian and discuss the strengths of the various electron interactions. Also in this section we review briefly the coherent-potential approximation and write down the relevant formulas. In Sec. III we give the method of calculation, and set up the numerical algorithm for both the paramagnetic and ferromagnetic calculations. Section IV gives the results for the paramagnetic state. By calculating the paramagnetic susceptibility as a function of the temperature and concentration, we also get information on the instability towards the ferromagnetic regime. Section V discusses the results for the ferromagnetic phase, where we calculate such properties as the magnetic moment and ferromagnetic specific heat. By extrapolating the magnetic-moment curve we also obtain information regarding its paramagnetic instability as a function of concentration.

II. THEORETICAL BACKGROUND

A. Hamiltonian for alloy

We shall be concerned basically with the contribution of the *d* electrons to the various magnetic properties of the alloy. Both the constituents being transition metals, we need to consider Hamiltonians which are appropriate to the case of electrons in considerably narrow bands (the *d* band).

A suitable model Hamiltonian has been introduced by Hubbard,[3] Kanamori,[4] and Gutzwiller.[5] In this model one considers only the correlations between *d* electrons to be of any importance, and, because of screening by the conduction electrons, such correlations are once again confined to the carriers in the same atomic site. The simplest of the Hamiltonians is the one in which all interorbital interactions are neglected, and is given by the following expression:

$$\mathcal{H}=\mathcal{H}_0+\sum_{i\mu} U_\mu N_{i\mu\uparrow}N_{i\mu\downarrow} \ , \tag{2.1}$$

where $\mathcal{H}_0$ represents the renormalized single-particle Hartree-Fock energy,

$$\mathcal{H}_0=\sum_{\substack{ij\\ \mu\mu'\sigma}} T_{ij}^{\mu\mu'} C_{i\mu\sigma}^\dagger C_{j\mu'\sigma} \ , \tag{2.2}$$

$$T_{ij}^{\mu\mu'}=\int d^3r\, \varphi_\mu^*(\vec{\mathrm{r}}-\vec{\mathrm{R}}_i)\left(\frac{-\nabla^2}{2m}+V_p(\vec{\mathrm{r}})\right)\varphi_{\mu'}(\vec{\mathrm{r}}-\vec{\mathrm{R}}_j) \ , \tag{2.3}$$

μ and μ' being the fivefold degenerate orbital indices and $\hbar=1$. Here $\varphi_\mu(\vec{\mathrm{r}}-\vec{\mathrm{R}}_i)$ is an orbital of symmetry μ centered at $\vec{\mathrm{R}}_i$, $V_p(\vec{\mathrm{r}})$ is the periodic potential of the rare-gas cores, and $C_{i\mu\sigma}$ and $C_{i\mu\sigma}^\dagger$ are the conventional electron annihilation and creation operators. $U_\mu \equiv (\mu\mu|V|\mu\mu)$ is the intra-atomic intraorbital interaction,

$$(\mu_1\mu_2|V|\mu_3\mu_4)=\int d^3r\, d^3r'\, \varphi_{\mu1}^*(\vec{\mathrm{r}})\,\varphi_{\mu2}^*(\vec{\mathrm{r}}') \times \frac{1}{|\vec{\mathrm{r}}-\vec{\mathrm{r}}'|}\,\varphi_{\mu3}(\vec{\mathrm{r}})\,\varphi_{\mu4}(\vec{\mathrm{r}}') \ . \tag{2.4}$$

We shall denote this Hamiltonian as case (i).

The second model Hamiltonian [case (ii)] to be considered is one in which we consider the *d* carriers as holes, in which we include the effect of interorbital interactions. The model is the same as proposed by Lang and Ehrenreich, except that we do not distinguish between the separate t_{2g} and e_g symmetries, as do these authors. The Hamiltonian is written

$$\begin{aligned}\mathcal{H}=\mathcal{H}_0&+U\sum_{i\mu} N_{i\mu\uparrow}N_{i\mu\downarrow}-J\sum_{i,\,\mu\neq\mu'}\vec{\mathrm{S}}_{i\mu}\cdot\vec{\mathrm{S}}_{i\mu'}\\ &+\tfrac{1}{2}(U'-\tfrac{1}{2}J)\sum_{\substack{i,\,\mu\neq\mu'\\ \sigma,\sigma'}} N_{i\mu\sigma}N_{i\mu'\sigma'}\\ &+J'\sum_{i,\,\mu\neq\mu'} C_{i\mu\downarrow}^\dagger C_{i\mu\uparrow}^\dagger C_{i\mu'\uparrow}C_{i\mu'\downarrow} \ . \end{aligned} \tag{2.5}$$

$\vec{\mathrm{S}}_{i\mu}$ is the spin operator for the electron (i,μ), whose components are given by

$$S^{+}_{i\mu}=C^{\dagger}_{i\mu\uparrow}C_{i\mu\downarrow}\ ,$$
$$S^{-}_{i\mu}=C^{\dagger}_{i\mu\downarrow}C_{i\mu\uparrow}\ , \qquad (2.6)$$
$$S^{z}_{i\mu}=\tfrac{1}{2}(N_{i\mu\uparrow}-N_{i\mu\downarrow})\ .$$

The Coulomb matrix elements involved in (2.5) are

$$(\mu\mu|V|\mu\mu)=U\ ,\quad (\mu\mu'|V|\mu\mu')=U'\ ,$$
$$(\mu\mu'|V|\mu'\mu)=J\ ,\quad (\mu\mu|V|\mu'\mu')=J'\ , \qquad (2.7)$$

where by dropping the orbital indices from the U, J, etc., we have tacitly assumed equivalence of the orbitals. This is obviously erroneous, but nevertheless it might provide a general understanding of the situation where interorbital interactions are included. In any case, as we shall discuss shortly, the estimates of U, U', etc., are highly controversial and hence this assumption is not entirely unreasonable.

At this stage, we shall talk briefly about the magnitudes of the various parameters that have entered into our models. There has been considerable dispute over the value of U, which depends on the amount of screening of the intraorbital interactions provided by the conduction electrons. We refer the reader to an extensive discussion given by Herring.[18] Herring himself estimates it to be ~5 eV, while Kanamori takes it to be ~7.6 eV. Herring's estimate of U' and J is 3 and 1 eV, respectively, while Kanamori[4] gives J as 0.6 eV, but does not speculate on the value of U'. Lang and Ehrenreich[2] found that taking the U' and J to be the values given by Herring leads to a rather low value for the pressure gradient of the Curie temperature for Ni, and they parametrize U to be 3.9 eV to be consistent with the available experimental data on dT_C/dP. Because of the apparent confusion we shall consider various combinations of U, U', and J in the course of our numerical computation.

B. Coherent-potential approximation

We shall employ a variation of the coherent-potential approximation developed by Velický *et al.*[12] to describe the alloy of Cu and Ni considered here. The variation is necessitated by the spin dependence of the self-energy because of the ferromagnetic interactions, and does not alter any of their theoretical details.

Because of the single-site nature of their theory we have to reduce our Hamiltonians (2.1) and (2.5) to a one-body random problem. The kinetic-energy part $\mathcal{H}_0$ is rewritten as follows:

$$\mathcal{H}_0=\sum_{i\mu\sigma}\epsilon_{i\mu}C^{\dagger}_{i\mu\sigma}C_{i\mu\sigma}+\sum_{\substack{i\neq j\\ \mu\sigma}}{}' t_{ij}C^{\dagger}_{i\mu\sigma}C_{j\mu\sigma}\ , \qquad (2.8)$$

where $\epsilon_{i\mu}$ is the single-particle energy, which is either ϵ_{Cu} or ϵ_{Ni} depending upon the atom occupying the site i. The transfer integrals t_{ij} are taken to be independent of the individual sites i and j and to depend on the separation $|\vec{R}_i-\vec{R}_j|$. It is further assumed that the quantities ϵ_{Cu}, ϵ_{Ni}, and t_{ij} do not depend upon the relative concentrations of Cu and Ni.

The interaction part of the Hamiltonian is reduced into one-body problems in the Hartree-Fock approximation. This is done by writing down the equation of motion for the single-particle operator $C_{i\mu\sigma}$, and linearizing the resultant equation of motion.

For case (i), it gives

$$\mathcal{H}_{\text{int}}=\sum_{i\mu}U_i\langle N_{\mu\bar{\sigma}}\rangle N_{i\mu\sigma}\ , \qquad (2.9)$$

which can be absorbed into $\mathcal{H}_0$ by defining spin-dependent energies $\epsilon_{i\mu\sigma}$ through

$$\epsilon_{i\mu\sigma}=\epsilon_{i\mu}+U_i\langle N_{\mu\bar{\sigma}}\rangle\ . \qquad (2.10)$$

For case (ii), a similar procedure gives

$$\epsilon_{i\mu\sigma}=\epsilon_{i\mu}+\tilde{U}\langle N_{\mu\bar{\sigma}}\rangle-J\sigma\sum_{\mu'}{}'\langle S^{z}_{i\mu'}\rangle+\tilde{J}\sum_{\mu'\sigma'}{}'\langle N_{i\mu'\sigma'}\rangle\ , \qquad (2.11)$$

where the primes on the summations indicate that the term $\mu'=\mu$ is excluded from the sum, and

$$\tilde{U}=U-U'\ ,\quad \tilde{J}=U'-\tfrac{1}{2}J\ . \qquad (2.12)$$

Having reduced the problem to the case of single-site Hamiltonians, we can closely follow Velický *et al.* The relevant formulas are reproduced, taking care of the spin dependence of the quantities involved. We consider Ni and Cu alloyed in the ratio $y:x$, such that $y+x=1$.

The single-particle properties of the system are derived from a study of the Green's function

$$G(Z)=(Z-H)^{-1}\ . \qquad (2.13)$$

The effective Hamiltonian characterizing the average crystal is defined by

$$\langle G(Z)\rangle=(Z-H_{\text{eff}})^{-1}\ . \qquad (2.14)$$

The matrix elements of H_{eff} are given by

$$\langle\mu k\sigma|H_{\text{eff}}|\mu k'\sigma\rangle=\delta_{k,k'}[S(k)+\Sigma^{\mu}_{\sigma}(Z)]\ , \qquad (2.15)$$

where $S(k)$ are the matrix elements of $\sum'_{ij\mu}t_{ij}C^{\dagger}_{i\mu\sigma}\times C_{j\mu\sigma}$, which is diagonal in the Bloch representation, and the self-energy $\Sigma^{\mu}_{\sigma}(Z)$ is spin-dependent and is given in the CPA by the following equation:

$$\Sigma^{\mu}_{\sigma}(Z)=(x\epsilon^{\sigma}_{\text{Cu}}+y\epsilon^{\sigma}_{\text{Ni}})-[\epsilon^{\sigma}_{\text{Cu}}-\Sigma^{\mu}_{\sigma}(Z)][\epsilon^{\sigma}_{\text{Ni}}-\Sigma^{\mu}_{\sigma}(Z)]\times F^{\mu}_{\sigma}(Z)\ , \qquad (2.16)$$

where $F^{\mu}_{\sigma}(Z)$ is defined by

$$F^{\mu}_{\sigma}(Z)=\int_{-\infty}^{+\infty}\rho^0(E)/[Z-\Sigma^{\mu}_{\sigma}(Z)-E]\,dE\ , \qquad (2.17)$$

$\rho^0(E)$ is the density of states corresponding to the band structure $S(k)$. Henceforth we will drop the superscript μ, assuming it to be understood. The total density of states of the disordered system $\rho_\sigma(E)$ determined through

$$\rho_\sigma(E) = -(1/\pi)\,\mathrm{Im}[F_\sigma(Z)]_{Z=E+i0^+} \tag{2.18}$$

gives the total number of electrons per atomic orbital,

$$N_{i\sigma} = \int_{-\infty}^{+\infty} \rho_\sigma(E) f(E)\, dE \ , \tag{2.19}$$

where $f(E)$ is the Fermi function. The partial density of states ρ_{Cu} or ρ_{Ni} is obtained through the relation

$$\rho_A^\sigma(E) = -\frac{1}{\pi}\mathrm{Im}\, \frac{F_\sigma(Z)}{1-[\epsilon_A^\sigma - \Sigma_\sigma(Z)]\, F_\sigma(Z)}\Bigg|_{Z=E+i0^+} \tag{2.20}$$

($A=$ Cu or Ni). It obeys the charge-conservation sum rule

$$\rho_\sigma(E) = x\rho^\sigma_{\mathrm{Cu}}(E) + y\rho^\sigma_{\mathrm{Ni}}(E) \ . \tag{2.21}$$

III. METHOD OF CALCULATION

We are concerned basically with the ferromagnetic regime and therefore will restrict ourselves to a nickel-rich system. The host material will be taken to be nickel with the effect of alloying being described by the coherent-potential approximation. Thus to start with we require a reliable density of states of nickel. There have been several band-structure calculations on nickel, and on choosing a reliable band structure we examined these calculations to find out how well they explain the important physical properties of metallic nickel. We require both the paramagnetic and the ferromagnetic density of states, because as the copper concentration increases the ferromagnetic Curie temperature of the alloy drops from its value 633 °K for the case of pure nickel to less than 200 °K for 40 at.% Cu concentration. Thus at room temperatures, even at intermediate concentrations of copper, the paramagnetic phase of the alloy is as important as the ferromagnetic one.

Recently Callaway and Wang[17] did a self-consistent calculation of energy bands in ferromagnetic nickel using the tight-binding method. The crystal potential of their work was generated from a superposition of overlapping charge densities, the atoms being in the $(3d)^9(4s)^1$ configuration. Incorporating a Kohn-Sham-Gasper[19,20] type of exchange they obtained very satisfactory results for the Fermi-surface properties. The number of d holes is assumed to be 1, which is consistent with recent calculations of the number of free electrons in Ni by Blokhin *et al.*[10] using the x-ray emission data.

We have taken the density of states of Wang and Callaway and subtracted out from it the contribution due to the conduction electrons, assuming the s-d hybridization to be small and assuming a parabolic band structure for the s-electrons. This is clearly an approximate procedure, and a proper account of the s-d mixing must be taken in a better calculation. Pure nickel will be assumed to have 1 d hole per atomic site, whereas pure copper will be considered to have a closed d shell. This, along with the magnetic-moment data from Wang and Callaway's calculation, immediately fixes the average number of majority and minority spins per nickel site. The unit of energy is taken to be half the bandwidth of nickel. For the case of the Hamiltonian with only intraorbital interaction, the value of U is taken to be 5 eV. In real life there is no reason to assume that the strength of interaction U is the same for both types of metals. However, our information about U to data is so incomplete that making such a distinction seems rather meaningless. For the case of the Hamiltonian with the interorbital (but intra-atomic) interaction, we consider two sets of parameters suggested by Herring: $U=5$ eV, $U'=3$ eV, $J=1$ eV; and $U=3.9$ eV, $U'=3$ eV, and $J=1$ eV. Further, it is convenient to define the zero of energy such that

$$\epsilon_\mu^{\mathrm{Cu}} = -\epsilon_\mu^{\mathrm{Ni}} = \tfrac{1}{2}\delta \ , \tag{3.1}$$

which defines δ as the separation between the d resonances of Cu and Ni, in the absence of any electron-electron interaction. This is therefore the atomic resonance separation given by a band-structure calculation. The orbital dependence of δ is very small and is to be neglected. We have calculated the position of the d resonance of Ni for the band-structure calculation of Wang and Callaway, and have taken the corresponding value of Cu from Stock *et al.*[13] For a fixed set of parameters U, J, and J', we can then obtain $\epsilon^{\mathrm{Ni}}_{i\mu\sigma}$ and $\epsilon^{\mathrm{Cu}}_{i\mu\sigma}$ by using the formulas (2.10) and (2.11).

In actual computation, we determine the real and the imaginary part of the coherent potential $\Sigma_\sigma(E)$ by using trial values of $N_{i\sigma}$. The simultaneous nonlinear equations in $\mathrm{Re}\Sigma(E)$ and $\mathrm{Im}\Sigma(E)$ are solved numerically by using the two-dimensional Newton-Raphson method until the convergence is one part in a thousand. The number of electrons per site is then recalculated using these values of real and imaginary $\Sigma(E)$ and the whole cycle repeated. Very fortunately, there is very little charge transfer from Cu to Ni sites on alloying, a fact well borne out in our calculation. Thus when the first cycle of calculation is completed $N_{i\sigma}$'s are already determined to an error of less than 1.5%.

IV. RESULTS FOR NONMAGNEITC STATE

Calculations were carried out, starting with Wang and Callaway's input density of states for

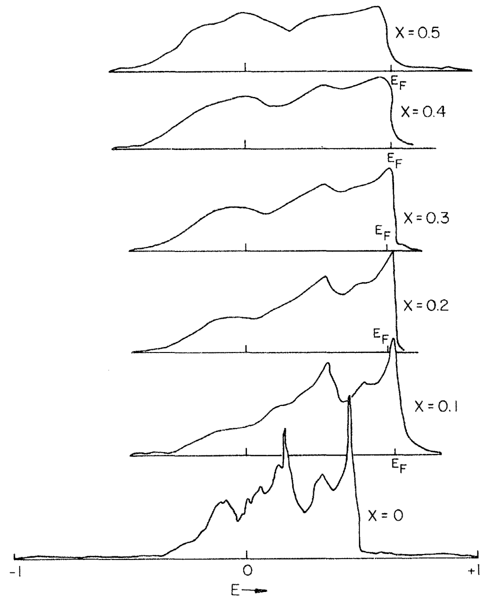

FIG. 1. Total density of state of Cu-Ni alloys for various concentrations for $U=5$ eV.

paramagnetic nickel (bottom of Figs. 1 and 2). The temperatures were fixed at slightly higher than the phenomenological Curie temperatures of the copper-nickel alloys, so that we are in the paramagnetic regime. Figure 1 shows the alloy density of states for $U=5$ eV, and the corresponding results with $U=3.9$ eV, $U'=3$ eV, and $J=1$ eV are shown in Fig. 2. It is observed that even for small concentrations the structures seen in the pure-nickel band tend to smooth out and the peaks become less sharp, and for concentrations around 50 at.% copper, the alloy band shape is almost flat, with only the remnants of the two major nickel peaks still barely identifiable. It is also found that when the interorbital interactions are included this effect is more pronounced than in the case with only the intraorbital electron interactions. These density of states have been compared with the experimental optical density of states obtained by Seib and Spicer, and show the general qualitative features of the experimental curves. Stocks *et al.* have given detailed discussion of such comparison for the noninteracting case, and the shape of the density of states does not change very much in the presence of electron interactions. In Fig. 3 we have shown the partial density of states of Ni and Cu, which show the energy distributions at the Ni and Cu sites. It is seen that the electrons at the impurity (Cu) sites spread toward the higher energies (away from E_F) and the opposite picture appears for the host sites. The partial energy distribution is affected by two factors. The first is the energy difference δ between the mean energies at the copper and nickel sites, and the second is the abrupt change in the amplitude of the wave function from a host site to the impurity site. If the wave function has a large amplitude at the nickel site, the resulting cost of band energy will offset any gain in energy, due to the fact that $\epsilon^{Cu} > \epsilon^{Ni}$. The electron-interactions U, J, etc., affect these

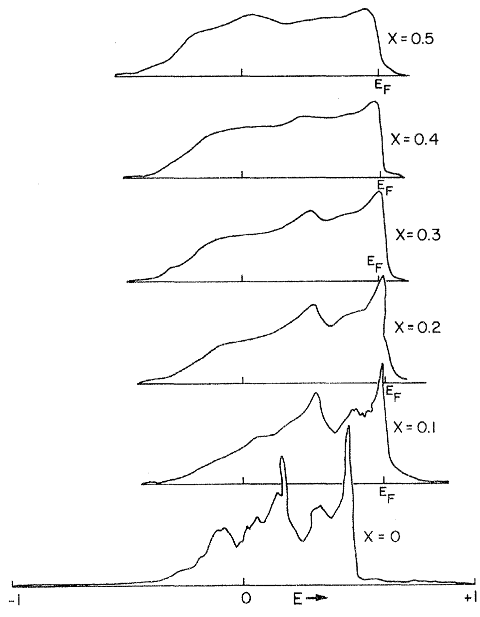

FIG. 2. Density of states of Cu-Ni alloys for $U=3.9$ eV, $U'=3$ eV, and $J=1$ eV. Fermi energy is denoted by E_F.

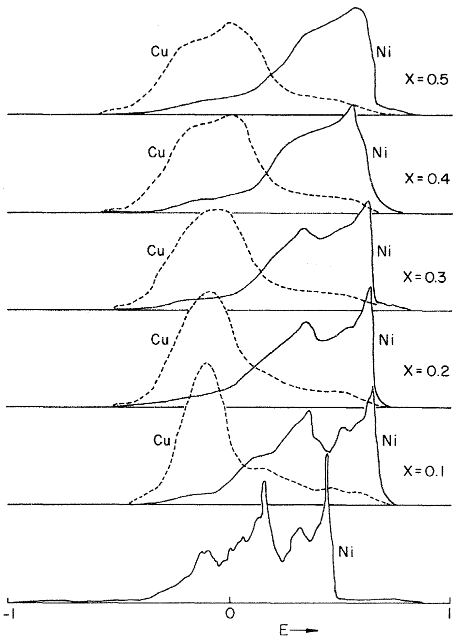

FIG. 3. Partial density of states at Cu and Ni sites. Parameters correspond to $U=3.9$ eV, $U'=3$ eV, and $J=1$ eV.

marginally because, since their strengths are the same at both Ni and Cu sites, they tend to influence the wave functions of Ni and Cu in similar fashion. For low copper concentration, the local density of states at the Cu site has a rather conspicuous peak in the region away from the Fermi energy, which is approximately Lorentzian in shape. As concentration increases this band becomes more and more flat, and gradually overtakes the secondary peak of pure nickel. The positioning of the impurity sub-band at energies removed from the Fermi energy would suggest that the number of electrons at the Cu site is less than that in the case of pure Cu. However, the height of the peak in the low-concentration region and the spread in the high-concentration region offsets this and the integrated density of states does not vary from its value in pure Cu by more than 2.5%. Figure 4 gives the integrated density of states i.e., average number of electrons) for both Ni and Cu for two sets of parameters. We find that the electron transfer from Cu and Ni is small. Mott in 1935 had introduced the rigid-band model, according to which it is believed that the electrons redistribute equally among the lattice sites. This explained the ferromagnetic to paramagnetic transition in Cu-Ni alloy as a function of concentration, if we assume that Ni has 0.6 holes per site. However, the pressure dependence of the Curie temperature shows a qualitatively incorrect behavior. Our calculation lends credence to the "minimum-polarity model" of Varley[9] and of Lang and Ehrenreich,[2] according to which the charge transfer on alloying is negligible. As we shall see later, as in the case of the minimum-polarity model, our calculation gives a rather strong correlation effect, which makes the ferromagnetism disappear for copper concentrations above 40 at.%.

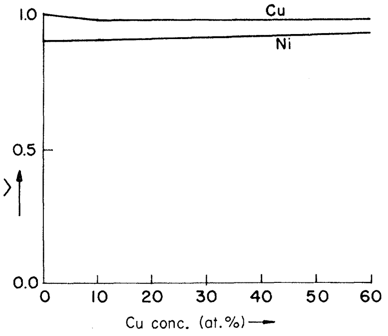

FIG. 4. Total number of d electrons per atom, $\langle N_i \rangle$, at Ni and Cu sites.

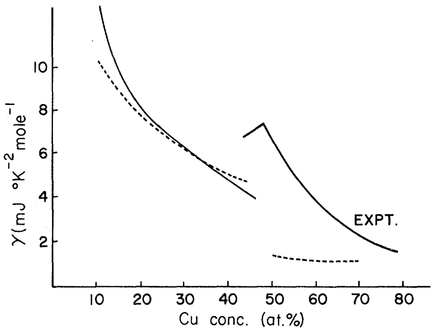

FIG. 5. Low-temperature specific heat in the paramagnetic region. Continuous curve corresponds to $U=5$ eV, and the broken curve to $U=3.9$ eV, $U'=3$ eV, and $J=1$ eV.

We have also computed the low-temperature specific heats of the Cu-Ni alloy as a function of the concentration. The results are presented in Fig. 5. We have deliberately not attempted to make any comparison here with the experimental data for two reasons. First, at temperatures at which most of these experiments are conducted (~ 1.2–4.2 °K), the alloy is in the ferromagnetic phase. Second, the density-of-states curves are peaked sharply near the Fermi energy, and the specific heat depends crucially on an accurate determination of $\rho(E_F)$. Thus even though we have provided the experimental specific-heat coefficient for Cu concentrations > 43 at.%, no special importance should be attached to the actual theoretical numbers. However, it should be remarked that even within our accuracy the value of γ seems rather low. This is presumably because of the fact that for such concentrations of copper, we can no longer regard the effect of alloying as being given by considering copper as an impurity in nickel. A proper description in this region cannot be provided by starting with either Ni or Cu.

We have also calculated the paramagnetic susceptibility of the Cu-Ni alloy for various concentrations as a function of temperature. Regarding the carriers as holes, we have used the expressions for the susceptibility obtained by Lang and Ehrenreich within the so-called T approximation. They express the static susceptibility for both the models in terms of the density of states, and the interaction strengths U, J, and U' only.

For the case of the usual Hubbard model ($U \neq 0$, $J=U'=0$) they obtain the static susceptibility χ_{i} (assuming all orbitals to be equivalent) as

$$\chi_{\mathrm{i}} = 10 N \mu_B^2 F / (1 - U_{\mathrm{eff}}^{(1)} F) , \tag{4.1}$$

and for the second case (U, U', $J \neq 0$)

$$\chi_{\mathrm{ii}} = 6 N \mu_B^2 F / [1 - (U_{\mathrm{eff}}^{(2)} + 2 J_{\mathrm{eff}}) F] , \tag{4.2}$$

where

$$F = \int_{-\infty}^{+\infty} d\epsilon \, \rho(\epsilon) \left(\frac{\partial f(\epsilon)}{\partial \epsilon_F} \right) , \tag{4.3}$$

$$U_{\mathrm{eff}}^{(1)} = \frac{U}{1+UK} , \tag{4.4}$$

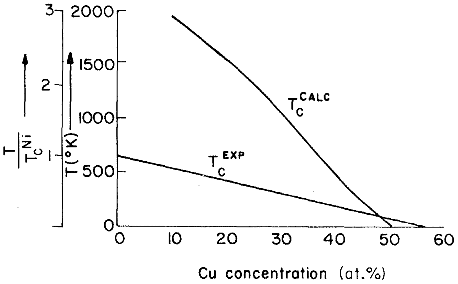

FIG. 6. Ferromagnetic Curie temperature as a function of concentration of Cu.

$$U_{\text{eff}}^{(2)}=\frac{U+(U+2J)(U-J)K}{[1+(U+2J)K][1+(U-J)K]}, \tag{4.5}$$

$$J_{\text{eff}}=\frac{1}{2}\left(\frac{U'+J}{1+(U'+J)K}-\frac{U'-J}{1+(U'-J)K}\right), \tag{4.6}$$

and

$$K=\frac{1}{2}\int_{-\infty}^{+\infty} d\epsilon\, \rho(\epsilon)\, \frac{[1-f(\epsilon)]^2}{\epsilon}\ . \tag{4.7}$$

In (4.3) and (4.7), the energies ϵ are measured from the energy of the bottom of the d bands (X_1) for case (i) where the carriers are electrons, and from the top of the conduction bands (X_5) for case (ii), in which the charged carriers are the holes in the threefold degenerate t_{2g} sub-band. The instability towards the ferromagnetic state is determined by the denominators of χ_{I} and χ_{II} being zero. Figure 6 gives the Curie temperature of the alloy as a function of concentration. The theoretical curves do not end at the Curie temperature of pure Ni, when extrapolated. This is because in the limit of extremely low concentration localized magnetic moments appear, and the calculation of T_C for the metal becomes independent of the vanishing of the determinant of X. A rather detailed discussion of this point has been given by Hasegawa and Kanamori,[14] in their description of the Fe-Ni system. For comparison's sake we have also drawn the experimental Curie temperature due to Ahren *et al.*[21] The temperature where the denominator of χ vanishes does not exist for concentrations of Cu $\geqslant$ 50 at.%. The general agreement of the theoretical curve with the experimental one is very poor, a fact that seems to be an inherent inadequacy of the CPA, in that Hasegawa and Kanamori[14] also obtained a similar-shaped curve for the Fe-Ni system. The concentration at which the Curie temperature vanishes is approximately 50 at.%, which is lower than the experimentally observed value of 57 at.%. We stress once more that the conclusion for concentrations $\geqslant$ 50 at.% seems to be rather dubious, and, as in the case of Hasegawa and Kanamori,[14] indicative of a spurious first-order phase transition at $T=0$, which is not observed experimentally.

V. FERROMAGNETIC PHASE

Figure 7 shows the density of states for the Ni-Cu alloys up to 50 at.% Cu concentration. Once again, we have used the recent density of states due to Callaway and Wang.[17] We have presented the results for the case $U=5$ eV. Not much more information from the structure of the density of states can be obtained for the other set of parameters used in our calculations. For all three sets of parameters, however, the Fermi energy E_F lies above one of the spin bands (referred to as the majority spin band), so that this band is full. The other band (or the minority band) is only partially occupied, giving a net magnetization. As the concentration of Cu increases beyond 20 at.%, however, the majority spin band starts to cross and spread away from the Fermi level, and a small number of holes start appearing in this band. Because of the cost involved in our computation, we had limited ourselves to steps of 10 at.% in Cu concentration. We were unable to obtain any ferromagnetic solution by the iterative method employed here for 60 at.% of concentration of Cu. This is in agreement with the disappearance of ferromagnetism around 57 at.% Cu. As in the paramagnetic case, we find that, except for the major peaks towards the Fermi energy, which are still identifiable for large Cu concentration, both the

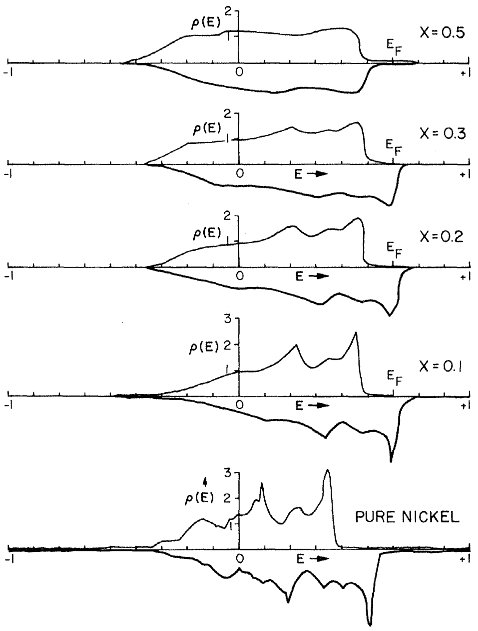

FIG. 7. Density of states for up and down spins for the ferromagnetic alloy. Note that the majority spin band spreads across the Fermi level for $c \gtrsim 0.3$.

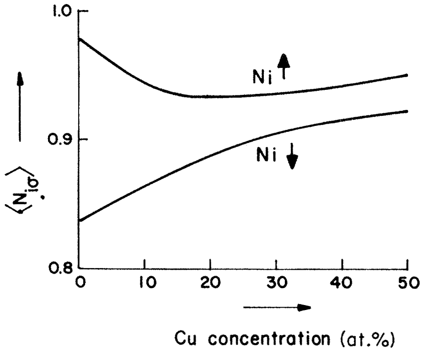

FIG. 8. Average number of *d* electrons per atoms of spin σ per site, $\langle N_{i\sigma} \rangle$, in the ferromagnetic state.

majority and the minority spin bands are deformed considerably. We have also calculated the integrated density of states for Cu and Ni, for both the spin states, from their partial density of states, and the results are reproduced in Fig. 8. Once again the calculations lend support to Lang and Ehrenreich's[2] minimum-charge-transfer hypothesis.

Figure 9 compares the calculated magnetic moment of the alloy with the experimental measurements of Ahren *et al.* As expected, the magnetic moment decreases with the addition of the nonmagnetic Cu atoms. The calculated values are somewhat lower than the experimental ones. Figure 10 shows the average magnetic moment at the nickel site for concentrations of Cu up to 50 at.%. Recent neutron-scattering measurements[22,23] reveal the existence of giant magnetic moments ($\sim 8-10\mu_B$). Assuming that the spin moments on a nickel atom depend upon the local atomic environment, we can understand our low values of the Ni moments on the basis of clustering of the Ni atoms. For example, for 30 at.% Cu concentration, our value for $\mu_{\text{Ni}} \sim 0.22$ indicates clusters containing 30–40 Ni atoms. Nickel clusters of approximately this size may be expected on a statistical basis[24] in the given concentration range.

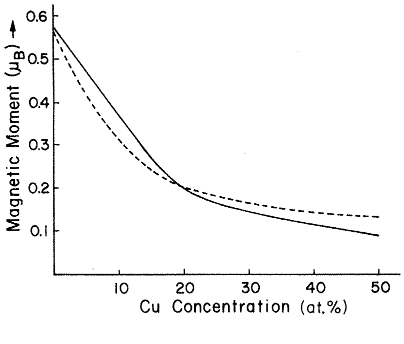

FIG. 9. Total magnetic moment of the Cu-Ni alloys.

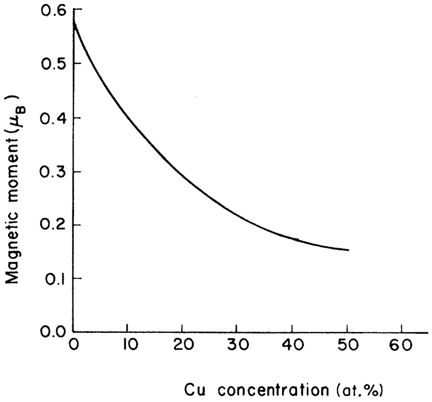

FIG. 10. Average magnetic moment at the Ni site for the ferromagnetic alloy. This curve corresponds to the parameters $U=3.9$ eV, $U'=3.0$ eV, and $J=1$ eV.

Figure 11 gives the measured specific heat in the ferromagnetic region, compared with that calculated from the density of states on the Fermi surface. Experimentally one observes a large specific-heat anomaly near the critical concentration region. This rather large contribution has been interpreted to be due to electron-magnon interaction in the ferromagnetic regime,[25] and also due to paramagnons in the region of $T > T_C$.

VI. DISCUSSION

We have seen that while the one-band CPA gives a reasonable qualitative description of the alloy properties, in both the ferromagnetic and paramagnetic regions, it still falls short of providing a totally satisfactory description. Most of the problem is due to the formation of local clusters, which eludes our discussion of the system as a totally disordered system. In particular properties like the partial magnetic moments, which depend more on the local configuration, are very unsatisfactory. A proper description should also account for the many-body interaction beyond the Hartree-Fock scheme.

An alternative modification is to consider a multiband CPA. Some preliminary nonquantitative

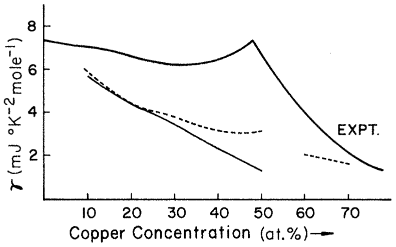

FIG. 11. Ferromagnetic specific heat of Cu-Ni alloy.

steps have already been taken in this direction.[26] As Cu concentration increases, our description of the alloy starting from a pure Ni host becomes less and less satisfactory. Ideally, in the Cu-rich region, the density of states of Cu provides a good starting point, and therefore in the intermediate concentration range we should take a statistical sum of the properties obtained by starting with Ni and Cu separately.

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