Densities of States in Cu-Rich Ni-Cu Alloys by the Coherent-Potential Approximation: Comparisons with Rigid-Band and Virtual-Crystal Approximation

G. M. Stocks, R. W. Williams,† and J. S. Faulkner
Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

(Received 10 December 1970)

It is shown that the coherent-potential approximation is capable of explaining the densities of states of Cu-rich Ni-Cu alloys as obtained from recent photoemission experiments. The coherent-potential approximation predicts the formation of a separate Ni *d* band for these alloys, this being consistent with the qualitative picture of Friedel-Anderson virtual bound states. This picture cannot be obtained from either the rigid-band model or the virtual-crystal approximation.

The recent photoemission data of Seib and Spicer[1] for Cu-Ni alloys at high Cu concentrations (13, 23, and 38% Ni in Cu) give a clear description of the behavior of the density of states as a function of concentration. The main feature of these experimental data is the appearance of a subsidiary emission peak between structure originating from the *d* bands of Cu and the Fermi energy. This peak is ascribed by Seib and Spicer to Ni *d* levels. A second important feature is that the high-energy emission edge of the Cu *d* states does not change its position with respect to the Fermi energy as the Ni concentration is increased. Neither of these features can be explained even qualitatively by either the rigid-band model or the virtual-crystal approximation, hitherto the most widely used models for alloy calculations. As Seib and Spicer point out, the features are qualitatively those expected for a Friedel-Anderson[2-5] virtual-bound-state model. This model meets difficulties when the impurity concentration becomes finite, and no specific predictions have been made as to the position of the impurity sub-band, although Seib and Spicer use the forms of the equations to parametrize their results. Here we present a calculation using the coherent-potential approximation (CPA)[6-8] which explains semiquantitatively the above features of the experimental photoemission data and gives a sound theoretical picture of the electronic states in Ni-Cu alloys of arbitrary concentration.

On the addition of Ni impurities to Cu the CPA predicts the formation of a *d* sub-band of approximately Lorentzian shape between the main *d* band and the Fermi energy. The nature of the states in each sub-band can be identified since it is possible in the CPA to calculate the partial *d* densities of states resulting from Cu sites, $\rho_{\mathrm{Cu}}{}^d(E)$, and from Ni sites, $\rho_{\mathrm{Ni}}{}^d(E)$, together with the total density-of-states function $\rho(E) = \rho^s(E) + \rho_{\mathrm{Cu}}{}^d(E) + \rho_{\mathrm{Ni}}{}^d(E)$, where $\rho^s(E)$ is the density of states for the *s*-like band. Utilization of this analysis reveals that the Lorentzian sub-band results almost entirely from Ni sites while the main sub-band results similarly from Cu sites. As the concentration of Ni is increased the CPA shows how the Ni sub-band grows at the expense of the Cu sub-band, gradually developing structure and finally evolving into the Ni *d*-band structure in which the Fermi energy lies. During this process the Cu sub-band changes its position with respect to the Fermi energy of the alloy very little, merely becoming smaller and structureless. This behavior is in marked contrast to the rigid-band model which predicts that the alloy density-of-states function remains as that for pure Cu, and that as the electron-to-atom ratio is decreased with the addition of Ni the Fermi energy approaches the *d* band at a more or less uniform rate. The predictions of the virtual-crystal approximation are qualitatively the same as the rigid-band model. It is clear that the CPA provides a working alternative to these qualitatively incorrect models.

Kirkpatrick, Velický, and Ehrenreich (KVE)[8] have performed a calculation using the CPA on some Ni-rich Ni-Cu alloys and have obtained reasonable agreement with experimental photoemission data for these systems, but if this work is extended directly to Cu-rich alloys there is little agreement with the photoemission results detailed above. However, we do not regard this as a shortcoming of either the CPA in general or the particular model of KVE. Rather it is a result of an inadequacy associated with the crystal potential which KVE used to describe pure paramagnetic Ni, an inadequacy which was irrelevant to the application of their model to the Ni-rich alloys. In this paper we show how a reappraisal of the above undesirable feature based on our own Korringa-Kohn-Rostoker (KKR)[9] band-theory calculations leads straightforwardly to the applicability of the KVE model to Ni-Cu alloys of arbitrary concentration.

In the model of KVE the effects of alloying on the d bands of the parent metals are treated in a tight-binding sense extended in the framework of the combined interpolation scheme of Hodges and Ehrenreich[10,11] (HE) to treat s-d hybridization and orbital degeneracy. An important parameter in the analysis of the model is the splitting δ between the d bands of the parent metals. The energy of the d-band scattering resonance E_0 (in the notation of the HE interpolation scheme) determines the position of the d bands with respect to the energy $E(\Gamma_1)$ of the bottom of the s band. Since the s bands in Cu and Ni are essentially identical, the s band is assumed to be unchanged on alloying, and hence δ can be taken as the energy separation between the d-scattering resonances when referred to $E(\Gamma_1)$, i.e., $\delta=[E_0{}^{\mathrm{Cu}}-E^{\mathrm{Cu}}(\Gamma_1)]-[E_0{}^{\mathrm{Ni}}-E^{\mathrm{Ni}}(\Gamma_1)]$, the superscripts denoting atomic species.

In their consideration of Ni-rich alloys KVE based their interpolation Hamiltonian on that for pure Ni. Similarly when considering Cu-rich alloys we have based the interpolation Hamiltonian on that for pure Cu. A single interpolation Hamiltonian could be devised which would extrapolate from pure Cu to pure Ni by giving the parameters other than δ in the interpolation Hamiltonian some reasonable concentration dependence. However, since the differences in these off-diagonal elements between pure Cu and pure Ni are rather small, based on our calculations, it is not necessary to adopt such a procedure. Thus, as we shall see, the important distinction between the present interpolation Hamiltonian and that used by KVE is in the much larger value which we obtain for δ and not in the rather minor differences in the off-diagonal elements.

Although there are many approximations in the model, the most serious in respect of the present application is an approximate decoupling scheme introduced to bring the equations into a two-level tight-binding form which can be treated simply in the CPA and thus circumvent the difficulties associated with orbital degeneracies in the d bands. The approximation is clearly adequate when δ is small compared with the bandwidth, but it is not obvious that the decoupling is valid in the case of large δ where a near split-band regime may be expected, as in the present case. However our calculation reveals that this approximation is not as restrictive as expected. The problem is worst at band edges where the imaginary part of the self-energy becomes significant, but the error is still probably only of the order of 0.01 Ry. Since, because of lack of experimental precision, we are only interested in the gross features of the density of states we continue to use this decoupling procedure.

Other important parameters in the interpolation Hamiltonian are those governing the s-d hybridization. As Anderson[3] and Heine[12] have pointed out, this is an important interaction in controlling the width of the d bands. Seib and Spicer[1] incorrectly dismissed the CPA for explaining their data arguing that the CPA did not properly include s-d hybridization; since the CPA as applied here includes hybridization effects in setting up the interpolation Hamiltonian as indicated above, it does a priori include significant effects of this interaction. The excellent agreement with experiment for the Cu-rich alloys indicates that this means of taking the interaction into account is adequate.

Of the available energy-band calculations for Ni and Cu, KVE chose to use the calculations of Burdick[13] for Cu and Hanus[14] for Ni as a base for their CPA calculation. We have used neither of these calculations, relying on potential functions generated by us for the present application; however, substitution of the Burdick Cu calculation for ours leaves the results reported here essentially unchanged. Although it is known that the Chodorow potential used by Burdick for Cu gives good agreement with experiment for Fermi-surface parameters,[9] we have generated a superior potential by using the Mattheiss[15] prescription, Herman-Skillman[16] wave functions, and Slater[17] exchange. This potential is essentially that of O'Sullivan, Switendick, and Schirber[16] and gives agreement with experimental de Haas–van Alphen data to <1%. The density of states calculated from this potential agrees well in its main features with photoemission data for Cu.

The most reasonable potential we have found for nickel was generated in the same way as the copper potential above using a $(3d)^{9.4}(4s)^{0.6}$ starting atomic configuration. The density-of-states function for Ni is characterized, disregarding spin splitting, by two sharp peaks below the Fermi energy. For the above Ni potential the upper peak is located 0.08 eV below E_{F} and the two main peaks have a splitting of 1.64 eV; the corresponding numbers for the Hanus potential are 0.0 and 1.9 eV, respectively. Probably the most reliable experimental optical density-of-states

(ODS) data on pure Ni are those of Eastman and Krolikowski[19] (see Ref. 1) who locate the high-energy peak 0.2 eV below E_F and obtain a value of 1.7 eV for the splitting between the peaks, in reasonable accord with the values obtained using the present potential. However, this indication of the adequacy of the present nickel potential should not be considered very significant in itself. Rather, the overall reasonableness of the results obtained for the pure metal and Cu-Ni alloy densities of states should, in conjunction with the above points, be regarded as substantiating the correctness of the general features of the potential function.

Having obtained reasonable potentials for Cu and Ni at lattice parameters appropriate to pure metals, energy-band calculations were performed using the KKR method, and the CPA calculations were performed from this base. The present potential functions for Ni and Cu give $\delta = -0.134$ Ry. In the calculations which follow, the difference between this value and that of -0.06 Ry obtained by KVE using the Hanus Ni potential is nontrivial.

At this point it is worth noting that Pierce and Spicer[20] have recently demonstrated the extreme insensitivity of the results of the photoemission experiment to the magnetic state of Ni. From our point of view this has two important ramifications. Firstly, it lends weight to the use we have made of the ODS as a guide to our selection of a potential function for Ni. Secondly, in order to be consistent with their experimental observations Pierce and Spicer conclude that the spin-splitting parameter is required to be <0.03 Ry at E_F, a value small compared with our calculated value of δ. Thus the effects of spin splitting on the gross features of the alloy densities of states even in Ni-rich alloys should be small.

CPA calculations have been performed for the density of states on a series of Ni-Cu alloys, using the value of δ determined above. For Ni-rich alloys the qualitative features elucidated by KVE still obtain. A sample result obtained for a Cu-rich alloy is shown in Fig. 1, this being for a 13% Ni-87% Cu alloy. There is good overall agreement between theory and experiment, since the magnitude of the structure in the experimental data is probably of little significance. The agreement obtained for other Cu-rich alloys (23 and 38% Ni in Cu) is similarly very good.

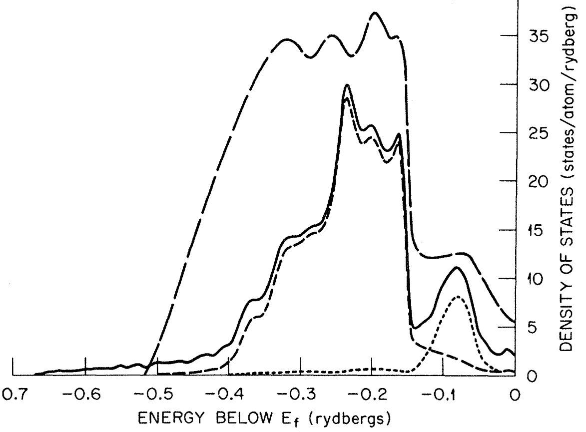

FIG. 1. The density of states in a random 87% Cu-13% Ni alloy. The curves are as follows: Full line, total density of states, $\rho(E)$; dashed line, density of d states at Cu sites, $\rho_{\mathrm{Cu}}{}^{d}(E)$; dotted line, density of d states at Ni sites, $\rho_{\mathrm{Ni}}{}^{d}(E)$. These are theoretical curves given by the CPA. The outer curve gives the experimental "optical density of states"; for this curve the scale is arbitrary. The theoretical curve has been moved slightly such that the edge at ≈ -0.16 Ry coincides with experiment.

If the theoretical curves for the alloys are compared with the curve for pure Cu several points beyond those previously discussed emerge. Fine structure on the density-of-states curve is rapidly damped out with increasing impurity concentration. Indeed, this is intuitively obvious and has already been noted by KVE for Ni-rich alloys. Also the structure on the Cu sub-band is preferentially damped at the top of the band; the high density-of-states peak which occurs for pure Cu at the top of the d band is very rapidly damped such that it is only a small spike as shown in Fig. 1. For a 23% Ni-77% Cu alloy this peak is damped to a shoulder; for a 38% Ni-62% Cu alloy there is no trace of this peak. This behavior appears to be in keeping with the data of Seib and Spicer.

Figure 2 shows how the position of the high-energy edge in the host sub-band changes with respect to the Fermi energy as the impurity concentration is increased. The curve marked "rigid band" was obtained by using the Cu density-of-states function and allowing the filling of states according to the electron-to-atom ratio appropriate to the alloy under consideration. The curve marked "virtual crystal" was obtained from the density-of-states functions for alloys having a potential function $V_{\mathrm{alloy}} = cV_{\mathrm{Cu}} + (1-c)V_{\mathrm{Ni}}$, where V_{Cu} and V_{Ni} are the potential functions appropriate to Cu and Ni, respectively. The virtual-crystal approximation was invoked at the stage of the HE interpolation scheme rather than

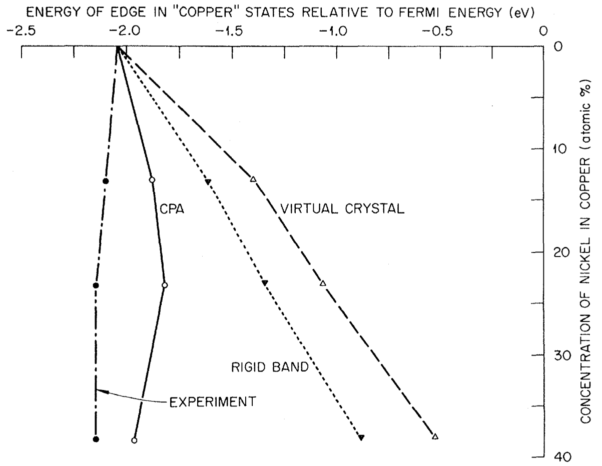

FIG. 2. The energy at its half-height of the high-energy edge in the Cu sub-band measured relative to the Fermi energy. The curves CPA, rigid-band, and virtual-crystal were obtained from calculated densities of states while the experimental curve was taken from energy-distribution curves at an incident photon energy of 10.2 eV. The experimental curve has been moved uniformly 0.06 eV such that theory and experiment coincide for pure Cu.

in the generation of the original potential functions. As can be seen from the rigid-band and the virtual-crystal curves, the prediction is that the edge approaches the Fermi energy at an approximately uniform rate, in clear contrast to experimental observation. The combined error ($\approx$0.2 eV) of the experimental results and the present CPA calculation leaves the two in reasonable accord. That the host sub-band remains in the same position relative to $E_{\rm F}$ is a direct consequence of the appearance of the reasonably high density-of-states impurity sub-band near to $E_{\rm F}$. Thus decreases in the electron-to-atom ratio as the Ni concentration is increased can easily be accommodated by small changes in the position of $E_{\rm F}$ with respect to the Cu sub-band.

As has been indicated earlier, Seib and Spicer interpreted the photoemission data as being consistent with a Friedel-Anderson virtual-bound-state mechanism. Indeed, the predictions of the CPA are consistent with this interpretation. As can be seen from Fig. 1 the impurity sub-band is quite Lorentzian at low concentrations and the impurity sub-band only develops structure at Ni concentrations on the order of 40%. On the basis of these calculations the impurity sub-band is located 0.68 and 0.79 Ry above the top edge of the host sub-band for the 13 and 23% Ni alloys, respectively. The corresponding experimental values are 0.74 and 0.81 Ry. The theoretical half-widths of the impurity sub-bands for the 13 and 23% Ni alloys are 0.034 and 0.042 Ry, respectively, the experimental values being 0.040 and 0.048 Ry. These parameters are in good agreement considering the joint experimental and theoretical uncertainties.

Finally it should be noted that calculation of $\rho_{\rm Ni}{}^d(E)$ and $\rho_{\rm Cu}{}^d(E)$ reveals that the total charge on Cu and on Ni sites in the above Cu-rich alloys remains essentially the same as in the pure parent metals, in agreement with the minimum-polarity hypothesis of Lang and Ehrenreich[21] and the findings of KVE.

---

*Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

†Present address: Electrical Engineering Department, University of Vermont, Burlington, Vt. 05401.

[1] D. H. Seib and W. E. Spicer, Phys. Rev. B 2, 1676, 1694 (1970).

[2] J. Friedel, Can. J. Phys. 34, 1190 (1956), and J. Phys. Radium 19, 573 (1958).

[3] P. W. Anderson, Phys. Rev. 124, 41 (1961).

[4] R. Riedinger, J. Phys. Chem. Solids 31, 2087 (1970).

[5] R. Riedinger and F. Gautier, J. Phys. Chem. Solids 31, 2099 (1970).

[6] P. Soven, Phys. Rev. 156, 809 (1967), and 178, 1136 (1969).

[7] B. Velický, S. Kirkpatrick, and H. Ehrenreich, Phys. Rev. 175, 747 (1968).

[8] S. Kirkpatrick, B. Velický, and H. Ehrenreich, Phys. Rev. B 1, 3250 (1970).

[9] J. S. Faulkner, H. L. Davis, and H. W. Joy, Phys. Rev. 161, 656 (1967).

[10] L. Hodges, thesis, Harvard University, 1966 (unpublished).

[11] L. Hodges, H. Ehrenreich, and N. D. Lang, Phys. Rev. 152, 505 (1966).

[12] V. Heine, Phys. Rev. 153, 673 (1967).

[13] G. A. Burdick, Phys. Rev. 129, 138 (1963).

[14] J. G. Hanus, Massachusetts Institute of Technology Solid State and Molecular Theory Group Quarterly Progress Report No. 44, 1961 (unpublished).

[15] L. F. Mattheiss, Phys. Rev. 133, A1399 (1964).

[16] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, N. J., 1963).

[17] J. C. Slater, Phys. Rev. 81, 385 (1951).

[18] W. J. O'Sullivan, A. C. Switendick, and J. E. Schirber, Phys. Rev. B 1, 1443 (1970).

[19] D. E. Eastman and W. F. Krolikowski, Phys. Rev. Lett. 21, 623 (1968).

[20] D. T. Pierce and W. E. Spicer, Phys. Rev. Lett. 25, 581 (1970).

[21] N. D. Lang and H. Ehrenreich, Phys. Rev. 168, 605 (1968).