preparing the sample used in this study. The use of the Varian E-4 EPR spectrometer which is maintained by Mr. J. Anderson is also greatly appreciated. We would also like to thank Mr. G. Hénein for many helpful discussions throughout this investigation. This work was supported under the National Science Foundation–Materials Research Laboratory program through the Materials Research Center of Northwestern University under Grant No. DMR-76-80847.

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Complete Solution of the Korringa-Kohn-Rostoker Coherent-Potential-Approximation Equations: Cu-Ni Alloys

G. M. Stocks
Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

and

W. M. Temmerman
H. H. Wills Physics Laboratory, University of Bristol, Bristol, United Kingdom

and

B. L. Gyorffy[a]
Brookhaven National Laboratory, Upton, New York 11973
(Received 24 March 1978)

We report on calculations of the electronic states in disordered $Cu_c Ni_{(1-c)}$ alloys based on a complete solution of the coherent-potential approximation for a muffin-tin model of the alloy potential [Korringa-Kohn-Rostoker coherent-potential-approximation (KKR-CPA)]. The computational effort required is modest on the scale of that involved in band-structure calculations for many atoms per unit cell. The calculated densities of states are in good agreement with the results of photoemission and other experiments. The adequacy of previous approximate KKR-CPA and averaged t-matrix calculations is discussed.

Experience with simple models[1,2] over the past decade indicates that the coherent-potential approximation (CPA)[3] gives a sufficiently good description of electronic states in random alloys to warrant calculations based on first-principles crystal potentials similar to those used for perfect crystals. However, because of the computational complexities, until recently little progress has been made towards implementing such a scheme. In this Letter we present the first complete solutions of the CPA equations for a non-overlapping muffin-tin model of the crystal potential [KKK (Korringa-Kohn-Rostoker)-CPA] for three $Cu_c Ni_{(1-c)}$ alloys. While correcting some

of the details the results generally confirm those obtained by Temmerman, Gyorffy, and Stocks[4] who used a simplified version of the theory in order to facilitate the calculation. However, they are qualitatively different from the results of the non–self-consistent form of the theory, namely the average t-matrix approximation (ATA).[5]

In the muffin-tin model of the crystal potential we assign, within touching spheres, spherically symmetric potential functions v_A and v_B to the sites occupied by the atomic species A and B, respectively. In the interstitial region the potential assumes a constant value V_{MTZ}. The CPA *Ansatz* is to construct a system of effective scattering centers, characterized by effective scattering amplitudes $f_{c,L}$ ($L \equiv l, m$), from which the configurational averaged properties of the real system may be calculated. The effective scattering amplitude is determined from the self-consistency condition[6]:

$$f_{c,L}^{-1}(\epsilon) = c f_{A,L}^{-1}(\epsilon) + (1-c) f_{B,L}^{-1}(\epsilon) - \sqrt{\epsilon}\,[f_{A,L}^{-1}(\epsilon) - f_{c,L}^{-1}(\epsilon)]\,\tau_{LL}^{c,00}(\epsilon)\,[f_{B,L}^{-1}(\epsilon) - f_{c,L}^{-1}(\epsilon)], \quad (1)$$

where the scattering amplitudes $f_{\alpha,L} = \sin\delta_l^{\alpha} \times \exp(i\delta_l^{\alpha})$, corresponding to the site potentials v_α, are determined at each energy ϵ by the phase shifts δ_l^{α} with $\alpha = A$ or B, and $\tau_{LL}^{c,00}(\epsilon)$ is the "on-energy shell" site-diagonal matrix element of the "scattering path operator." For an infinite ordered array of $f_{c,L}$'s it is given by

$$\tau_{LL'}^{c,00}(\epsilon) = \frac{1}{\Omega_{BZ}} \int_{BZ} d^3q\,[t_c^{-1} - G(\vec{q}, \epsilon)]^{-1}|_{LL'}, \quad (2)$$

where the angular momentum matrix elements of $t_c(\epsilon)$ and $G(q, \epsilon)$ are $t_{c,L}(\epsilon) = -(\sqrt{\epsilon})^{-1} f_{c,L}$ and $G_{LL'}(q, \epsilon)$, the KKR structure constants. The details of the theory are given in Ref. 6.

The major difficulty encountered in the self-consistent solution of Eqs. (1) and (2) is the necessity for repeated evaluation of the Brillouin-zone integral involved in Eq. (2) for various guesses of the $f_{c,L}$'s. Until now this appeared too forbidding and it has been suggested that one should not attempt to solve Eqs. (1) and (2) but rather use the average t-matrix approximation $f_L^{ATA} = c f_{A,L} + (1-c) f_{B,L}$ to calculate ensemble-averaged observables.[5,6]

Recently two approximate solutions of Eq. (1) have been obtained. In the first,[7] $\tau_{LL'}^{c,00}(\epsilon)$ is approximated by its value at the central site of a finite cluster of effective scatterers rather than for the infinite array implied in Eq. (2). In the second method[4] the atomic-sphere approximation (ASA) of Anderson[8] is used to simplify Eqs. (1) and (2). The results of the cluster CPA appear best convergent for the d bands at high energy (relative to V_{MTZ}) when the electron wavelength is much smaller than the cluster size. The ASA-CPA works best for tightly bound bands at low energies in closed-packed systems (certainly fcc and probably hcp). These techniques have been used to obtain results for CuNi, AgPd, and NbMo alloys that are useful for explaining recent experiments. Although they are not as generally applicable as the full CPA, these techniques were found to give better results than the ATA.

It is the purpose of this Letter to show that the approximations involved in cluster CPA and ASA-CPA can be avoided with little extra computational effort and that Eqs. (1) and (2) can be solved directly. As an example we show some results for the Cu-Ni alloy system.

We proceed by direct evaluation of Eq. (2) for some initial guess of the $f_{c,L}$'s. On successive iterations of Eqs. (1) and (2) updated values of the $f_{c,L}$'s are obtained via the Newton-Raphson method. The evaluation of Eq. (2) is carried out by performing integrations along directions emanating from the Brillouin zone center. A summation is then made over directions. The directions and weights are chosen either by the special-directions method of Bansil[9] and of Fehlner and Vosko[10] or by a prism method based on the constant-energy search pattern of Faulkner, Davis, and Joy.[11]

Prior to the commencement of the iteration process the KKR structure constants $G_{LL'}(\vec{q}, \epsilon)$ are fitted to polynominals after a term $\sum_{\vec{K}_n} Z_{LL'}/(\epsilon - |\vec{q} + \vec{K}_n|^2)$ has been subtracted from each $G_{LL'}$ in order to remove the free-electron singularities. The summation is over those reciprocal lattice vectors $\vec{K}_n$ which contribute a singularity along the q direction under consideration. Evaluation of the $G_{LL'}(\vec{q}, \epsilon)$ for a particular energy and wave vector is thus reduced to a few additions and multiplications. From this point on the present calculations are no more time consuming than the approximate ASA-CPA calculations of Temmerman, Gyorffy, and Stocks.[4]

We have solved Eqs. (1) and (2) for the effective scattering amplitudes $f_{c,L}$ (or alternatively $\tau_{LL}^{c,00}$) at some 50 energies for each of three $Cu_cNi_{(1-c)}$ alloys having $c = 0.77$, 0.50, and 0.81. Central to establishing the accuracy of the solution $f_{c,L}$'s is the accuracy to which the Brillouin-

zone integral in Eq. (2) can be evaluated. Evaluation of Eq. (2) using the 13 special directions of Bansil,[9] the 21-direction Gaussian formula of Fehlner and Vosko,[10] as well as 36 and 136 uniformly distributed directions shows that the self-consistent $f_{C,L}$ based on the 13 special directions of Bansil are convergent to better than 1% (often better than 0.2%). This is adequate for determining the density of states and Bloch spectral density.[4] We feel that it would be necessary to go beyond the 13-direction method only for special purposes, e.g., accurate determination of Fermi surface properties.

For $c=0.77$ and 0.19 the self-consistent $f_{C,\alpha}$'s are essentially identical with those of the ASA-CPA calculation of Temmerman *et al.*[4] This was expected since the atomic-sphere approximation is particularly good for describing the d bands of fcc metals. However, it should be stressed that the present method removes all the restrictions imposed by the ASA on the systems which can be treated, while it does not significantly increase the computational effort required to perform the calculations.

Having obtained the $f_{C,L}$'s, it is a simple matter to calculate a number of interesting quantities. The average integrated density of states is given by[6]

$$N(\epsilon)=N^0(\epsilon)-\frac{\mathrm{Im}}{\pi}\left\{\frac{1}{\Omega_{\mathrm{BZ}}}\int d^3q \ln\| t_{C,L}{}^{-1}\delta_{LL'}-G_{LL'}(\vec{q},\epsilon)\| \right.$$
$$\left.-(1-c)\ln\frac{\| t_{A,L}{}^{-1}-\langle t_L{}^{-1}\rangle\|}{\| t_{A,L}{}^{-1}-t_{C,L}{}^{-1}\|}-c\ln\frac{\| t_{B,L}{}^{-1}-\langle t_L{}^{-1}\rangle\|}{\| t_{B,L}{}^{-1}-t_{C,L}{}^{-1}\|}\right\}, \quad (3)$$

with $\langle t_L{}^{-1}\rangle = c t_{A,L}{}^{-1}+(1-c)t_{B,L}{}^{-1}$ and with $N^0(\epsilon)$ the integrated density of states for free electrons. In Fig. 1 we show the average density of states $n(\epsilon)$, obtained by numerical differentiation of $N(\epsilon)$, for the three concentrations considered. The Cu and Ni muffin-tin potentials underlying these calculations are those used by Temmerman, Gyorffy, and Stocks.[4] For all three concentrations the prominent structures in $n(\epsilon)$ are in accord with uv and x-ray photoemission experiments[12] and with the hybrid tight-binding, nearly-free-electron calculations of Stocks, Williams, and Faulkner (SWF).[1] The gradual switch from a split-band regime at low Ni content to the modified virtual crystal behavior at high Ni content is clearly evident. In the $Cu_{0.19}Ni_{0.81}$ alloy, calculation of the component densities of states shows that the two peaks at -0.01 and -0.12 Ry arise from Ni sites and are rounded versions of the two peaks in pure Ni which occur at these energies. In $Cu_{0.50}Ni_{0.50}$ there is a broad structureless "Ni" peak which extends from E_F to 0.12 Ry below E_F and a more structured "Cu" peak which extends from 0.15 to 0.35 Ry below E_F. The Ni peak is centered around 0.04 Ry, and the Cu peak is centered around 0.18 Ry below E_F; this is good agreement with the values of 0.04 and 0.20 Ry for the corresponding structures seen in photoemission experiments.[12]

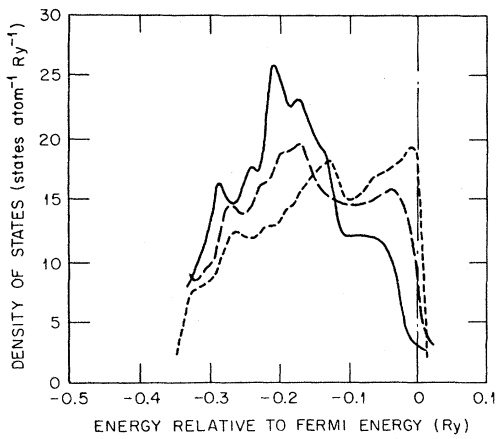

FIG. 1. Densities of states for three Cu-Ni alloys. $Cu_{0.77}Ni_{0.23}$, solid line; $Cu_{0.50}Ni_{0.50}$, dashed line; $Cu_{0.19}Ni_{0.81}$, dotted line. The zero of energy is the Fermi energy.

The density-of-states curve for $Cu_{0.77}Ni_{0.23}$ of Fig. 1 shows the expected Ni impurity band between E_F and the main Cu d-band complex. However, the Ni impurity band is less split off than either the calculation of SWF or results of photoemission experiments would have it. As was pointed out by SWF for very Cu-rich alloys, unlike Ni-rich alloys, the degree to which the impurity band is split off is very sensitive to the splitting between the d-scattering resonances of the Cu and Ni site potentials or alternatively the parameter δ of SWF. The extreme sensitivity to δ persists in the KKR-CPA. The potentials used in the calculation of Fig. 1 correspond to $\delta=0.107$, 0.110, 0.112 Ry for $c=0.77$, 0.50, 0.81. In Fig. 2 we show results for $Cu_{0.77}Ni_{0.23}$ based on Cu and Ni site potentials for which $\delta=0.134$, the value used by SWF. For the adjusted potentials

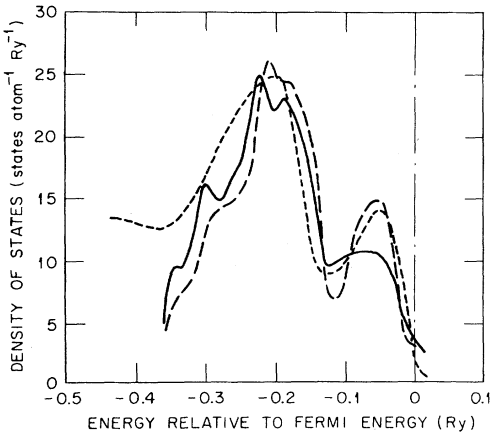

FIG. 2. Densities of states for $Cu_{0.77}Ni_{0.23}$. Full line, KKR-CPA results for the potentials chosen such that $\delta = 0.134$. Dashed line, model calculation of SWF (Ref. 4). Dotted line, experimental EDC taken from Shevchik and Penchina (Ref. 12).

the Ni impurity level is more clearly detached from the Cu *d*-band complex. Also shown in Fig. 2 are the corresponding results taken from SWF and an energy distribution curve for an incident photon energy of 40.2 eV taken from the photoemission experiments of Shevchik and Penchina.[12] The positions of the Ni impurity band and the Cu band are now in good agreement both with the work of SWF and with the results of the photoemission experiments. However, some differences between the KKR-CPA calculation and the model calculation remain. In the former the Ni impurity band is rather flat and is skewed to high energy; in the latter it is Lorentzian with a sharp dip between the Ni band and the Cu band. These differences are due largely to the fact that *sd* hybridization effects are correctly included within the present CPA calculation whereas in the calculation of SWF they are neglected. The extra structure seen in the KKR-CPA calculation (and ATA)[5] on the low-energy side of the Cu *d*-band complex reflects the fact that at energies well below the *d*-scattering resonance of the Cu-site potential the impurity scattering is very weak, and hence the host states are well defined and can give rise to sharp peaks in the density of states. In the single-parameter calculations of SWF all low-weight structures in the pure metal densities of states are smeared out on alloying.

The differences between the present results and those of the ATA calculations of Bansil, Schwartz, and Ehrenreich[5] (BSE) are worthy of some comment. The density-of-states curves for $Cu_{0.19}Ni_{0.81}$ and $Cu_{0.50}Ni_{0.50}$ of Fig. 1 and $Cu_{0.77}Ni_{0.23}$ of Fig. 2 should be compared with the corresponding curves of Figs. 7–9 of BSE. For $Cu_{0.19}Ni_{0.81}$ the ATA gives a clearly resolved Cu-related structure at the bottom of the Ni band. That this structure is not present in the CPA reflects the fact that the CPA effective scattering amplitude has only a single "virtual-crystal"–like resonance while the ATA scattering amplitude has a double resonance—one at the resonance energy of the Cu potential, one at the resonance energy of the Ni potential. For both $Cu_{0.50}Ni_{0.50}$ and $Cu_{0.77}Ni_{0.23}$ in the CPA the high-energy Ni band is less structured than in the ATA. This results from intersite *dd*-interaction effects in the CPA which broaden the Ni resonance in the effective scattering amplitude and push it to higher energies relative to the ATA. That the ATA omits this *dd*-repulsion effect also accounts for the excessive erosion of the top of the Cu *d*-band complex in $Cu_{0.77}Ni_{0.23}$.

In this Letter we hope only to have established that calculations of the properties of disordered substitutional alloys based on a full implementation of the muffin-tin model of the CPA are possible for an amount of computational effort that is less than had generally been supposed necessary and that these calculations give a good description of the effects of alloying on the densities of states in the Cu-Ni system. In conclusion we would like to emphasize that the aim of the KKR-CPA goes far beyond the density of states. Once the effective scattering amplitude has been determined, most properties that are usually calculated for pure metals can be obtained without further complications. More detailed comparison of the results with angle-resolved photoemission, soft x-ray emission, and Fermi-surface experiments has been left to other publications.

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[a]Permanent address: H. H. Wills Physics Laboratory, University of Bristol, Bristol, United Kingdom.

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Magnetic Ordering in Single-Crystal Praseodymium Induced by Uniaxial Stress

K. A. McEwen
Department of Pure and Applied Physics, University of Salford, Salford M5 4WT, United Kingdom

and

W. G. Stirling
Institut Laue-Langevin, 38042 Grenoble-Cedex, France

and

C. Vettier
Laboratoire Louis Néel, Centre National de la Recherche Scientifique, 38042 Grenoble-Cedex, France, and Institut Laue-Langevin, 38042 Grenoble-Cedex, France
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Neutron inelastic scattering techniques have been used to examine the dispersion relations for magnetic excitons propagating on the hexagonal sites of double-hcp Pr when uniaxial stress is applied along the $[1\bar{2}10]$ direction. The mode of lowest energy (longitudinal optic) along ΓM was found to exhibit a clear soft-mode behavior with increasing stress. Elastic satellite reflections corresponding to long-range magnetic ordering in a longitudinally modulated structure were observed: at 800 bars the Néel temperature is 7.5 K.

Praseodymium metal has the double-hexagonal close-packed (dhcp) crystal structure. It is well known that the Pr ions ($J = 4$) experience a crystal field which produces singlet ground states at both the locally hexagonal and cubic sites. Pr is a particularly interesting singlet ground-state system since the coupling between the ions on the hexagonal sites is just below the critical value for an induced-moment system.[1] Magnetic ordering may, however, be induced by alloying with small amounts of Nd. Lebech, McEwen, and Lindgård[2] found that $Pr_{1-x}Nd_x$ single crystals exhibited magnetic ordering in a sinusoidally modulated structure with the moments in the basal plane.

Neutron inelastic-scattering studies of Pr have been made by Rainford and Houmann[3] and more recently by Houmann *et al.*[4] They interpreted the majority of the excitations they observed at low temperatures in terms of magnetic excitons, composed of linear combinations of transitions from the ground state $|J = 4, J_z = 0\rangle$ to the first excited states $|4, \pm 1\rangle$ on those sites with local hexagonal symmetry. The lowest energy mode along the Brillouin-zone direction ΓM has a pronounced minimum at approximately the same wave vector (0.25 Å^{-1}) as that describing the longitudinally modulated structure observed in $Pr_{1-x}Nd_x$.

The coupling between the magnetic excitons and the phonons in Pr has been considered by Jensen.[5] This coupling is substantial because of the large orbital angular momentum ($L = 5$) of the Pr ions. From an analysis of the magnetic field dependence of the exciton energies, Jensen deduced a value of 30 meV/ion for the second-order

