

⁷D. W. Ross, unpublished calculation (cf. Ref. 3, Appendix C). The important point is that the resonant contribution to the growth or damping rate contains the average along a field line of $\Phi \cos(m\omega_b \int dl/v_{||})$ which is small because of the oscillating cosine factor.

⁸Here, m is the closest integer to $lq(r)$. The mode is not assumed to be of the form $e^{im\theta}$ but instead slowly varying along the field line at each radius.

⁹R. Z. Sagdeev and A. A. Galeev, Dokl. Akad. Nauk SSSR 180, 839 (1968) [Sov. Phys. Dokl. 13, 562 (1968)].

Density of States in CuNi Alloys

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X-ray photoemission spectroscopy has been used to measure the valence band of CuNi alloys. The results are in good agreement with theoretical predictions based on the coherent-potential approximation.

The nature of the electronic state of transition metals and alloys remains a subject of discussion.¹ There are mainly two quite distinct approaches to this problem: The first is the rigid-band model which makes no distinction between the different constituents of the alloy and attributes a common band to all electrons. The second is the virtual-bound-state model (preferred for dilute impurities) which assumes screening of the host electrons at the site of the impurity. Neither of these two limiting models can fully describe the actual situation. Though many experimental facts favor the virtual-bound-state model, its application is difficult in the case of concentrated alloys, especially when the magnetic electrons have much itinerant character as, for example, in CuNi alloys.² Soven³ and Velický, Kirkpatrick, and Ehrenreich⁴ have therefore used the coherent-potential approximation (CPA) to describe the electronic properties of binary alloys. The results of these calculations are very promising, and invite comparison with experimental results.

The CuNi system may be regarded as one of the test cases for theoretical descriptions of magnetic alloys.⁵ This system had long been considered the prototype alloy whose magnetic properties are explained by the rigid-band model. Yet simple theoretical considerations^{6,7} and much recent experimental evidence^{5,8-12} show the inadequacy of that model for the CuNi system. Ehrenreich and co-workers^{4,6,7,13} find that an approach based on the CPA (which they call the minimum polarity model) does indeed account much more satisfactorily for the experimental observations. Recently Stocks, Williams, and Faulkner¹⁴ have re-examined the CuNi problem using the CPA,

following the work of Kirkpatrick, Velický, and Ehrenreich.¹³ We report here x-ray photoemission spectroscopy (XPS) data for the density of states of NiCu alloys and compare them with the theoretical predictions and with other measurements. These include (1) the specific-heat measurements of Gupta, Cheng, and Beck,⁸ which strongly favor a CPA description; (2) the very extensive uv-photoemission data of Seib and Spicer^{9,10} which were originally interpreted in terms of the virtual-bound-state model, but can indeed be very well interpreted^{13,14} in the CPA; and (3) the extensive x-ray-emission investigation of Clift, Curry, and Thompson,¹¹ who found that the sharing of electrons between Cu and Ni is small but were unable to determine the form of the density of states.

Experiments using uv photoemission spectroscopy (UPS) and XPS measure similar properties, but with some important differences. Their relation can be described as follows: The systematic studies of Eastman¹⁵ have made it apparent that for photon energies below ≈ 30 eV the photoemission "joint densities of states" show strong dependence of both peak heights and positions on exciting energy; for energies > 30 eV, peak positions and relative heights show only little change with exciting energy and are indeed very similar to those obtained in XPS experiments as can be seen in valence spectra of Au, Fe, Cu, and Ni.^{15,16} Thus it can be assumed that for $E > 30$ eV the density of final states contributes no structure and that UPS and XPS experiments measure approximately the valence-band density of states. To get the "true" density of states, two corrections have to be applied to these data. The transition probabilities are a function of the energy

of the initial state, varying by about $\sim 10\%$ over the width of the d band in Ni.¹⁷ It is at present impossible to correct for this effect. Secondly, the transition probabilities are quite different for d , p , and s electrons. However, since we are here only interested in the d -electron density of states, this effect does not concern us. The photoemission data of Seib and Spicer,^{9,10} which were taken with excitation energies $E \leq 11.6$ eV, have to be considered in the light of these facts. These measurements nevertheless show unambiguously that the rigid-band model cannot be used to describe the CuNi system.

We have taken XPS spectra of CuNi alloys with

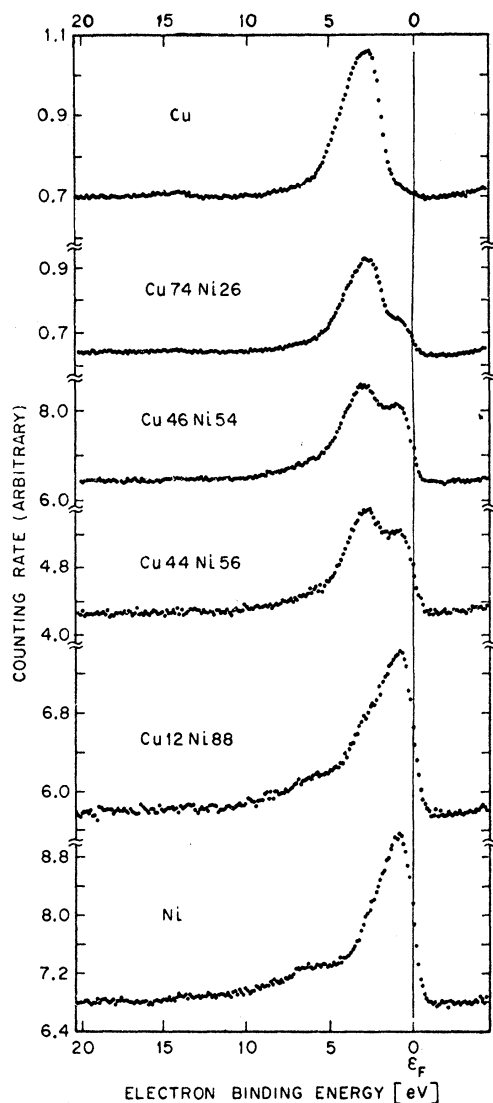


FIG. 1. XPS valence-band spectra for NiCu alloys. The Fermi energy was determined, with a Au sample, as the position where the $6s$ band is down to half its height.

a Varian model IEE 15 spectrometer using $Mg K\alpha$ radiation. The surfaces of the samples were cleaned before the measurements by argon ion sputtering to remove oxygen and carbon impurities from the surface. The spectra in Fig. 1 clearly show that the positions of the Cu and Ni d states remain the same to ± 0.2 eV in the whole alloy series. At all concentrations, except in pure Cu, there is still a considerable density of states at the Fermi energy. The density relative to that of pure Ni is shown in Fig. 2. These results have a fairly large uncertainty because of the limited resolution of the instrument (1.2 eV) and because the density of states has a steep slope at the Fermi energy. This is especially serious for the point at the highest Cu concentration.

Figure 1 shows clearly that the density of states of CuNi alloys can, to a very good approximation, be made up by superimposing those of Ni and Cu. This means that there is indeed only a very limited sharing of electrons by the two constituents. Thus the basic assumption underlying the minimum polarity model⁶ is very well substantiated by the experimental facts. The density of states at the Fermi level, which in the simplest formulation of the model should decrease linearly with increasing Cu concentration,^{6,7} also follows these predictions. With the present experimental accuracy one cannot distinguish between the results of the improved calculations^{13,14} and those of the most simple formulation of the model,^{6,7} Fig. 2. The present results are in agreement with the

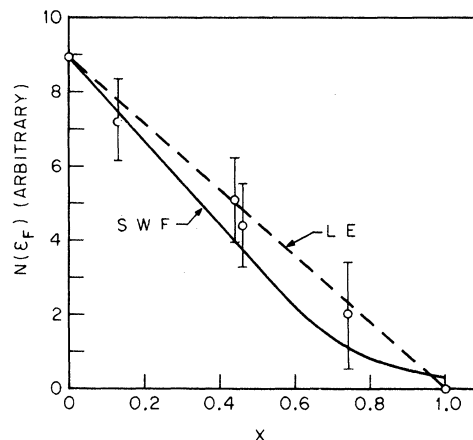


FIG. 2. Density of states (in arbitrary units) at the Fermi energy deduced from spectra in Fig. 1 for $Cu_x - Ni_{1-x}$ alloys. Also shown are the theoretical predictions of Lang and Ehrenreich, Ref. 6 [LE; $N(\epsilon_F, x) = (1-x) \times N(\epsilon_F, 0)$] and Stocks, Williams, and Faulkner, Ref. 14 (SWF).

soft-x-ray emission experiments.¹¹ These measurements could not reveal the form of the density of states but did show convincingly that there is very little sharing of electrons in these alloys. It is more difficult to comment on the UPS work.^{9,10} Stocks, Williams, and Faulkner¹⁴ find that the optical density of states reflects quite well certain features of the theoretical density of states, especially two main peaks in the optical density of states (one associated with the Ni *d* states and the other associated with the edge of the Cu *d* band) which show no shift with concentration. As for other features of these data it has to be kept in mind that UPS results taken at low exciting energy yield only a joint density of states including effects of the final density of states of the excited electrons. The XPS technique so far has insufficient resolution to show the details of the structure present in the UPS spectra and in the calculations. More detailed information about the structure in the density-of-states curves and their theoretical interpretation can come only out of UPS experiments at higher energy or XPS experiments at higher resolution.

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¹C. Herring, in *Magnetism*, edited by G. T. Rado and

H. Suhl (Academic, New York, 1966), Vol. 4.

²S. H. Tang, P. P. Craig, and T. A. Kitchens, *Phys. Rev. Lett.* **27**, 593 (1971).

³P. Soven, *Phys. Rev.* **156**, 809 (1967), and **178**, 1136 (1969).

⁴B. Velický, S. Kirkpatrick, and H. Ehrenreich, *Phys. Rev.* **175**, 747 (1968).

⁵P. A. Beck, *Met. Trans.* **2**, 2017 (1971).

⁶N. D. Lang and H. Ehrenreich, *Phys. Rev.* **168**, 605 (1968).

⁷S. Kirkpatrick, B. Velický, N. D. Lang, and H. Ehrenreich, *J. Appl. Phys.* **40**, 1283 (1969).

⁸U. P. Gupta, C. H. Cheng, and P. A. Beck, *Phys. Rev.* **133**, A203 (1964).

⁹D. H. Seib and W. E. Spicer, *Phys. Rev. Lett.* **20**, 1441 (1968).

¹⁰D. H. Seib and W. E. Spicer, *Phys. Rev. B* **2**, 1676, 1694 (1970).

¹¹J. Cliff, C. Curry, and B. J. Thompson, *Phil. Mag.* **8**, 593 (1963).

¹²C. G. Robins, H. Claus, and P. A. Beck, *Phys. Rev. Lett.* **22**, 1307 (1969).

¹³S. Kirkpatrick, B. Velický, and H. Ehrenreich, *Phys. Rev. B* **1**, 3250 (1970).

¹⁴G. M. Stocks, R. W. Williams, and J. S. Faulkner, *Phys. Rev. Lett.* **26**, 253 (1971), and *Phys. Rev. B* **4**, 4390 (1971).

¹⁵D. E. Eastman, in *Proceedings of the Conference on Electron Spectroscopy*, Asilomar, California, September, 1971 (to be published).

¹⁶N. V. Smith and M. M. Traum, *Phys. Rev. Lett.* **27**, 1388 (1971).

¹⁷J. R. Cuthill, A. J. McAlister, M. L. Williams, and R. E. Watson, *Phys. Rev.* **164**, 1006 (1967).

Anisotropic Behavior of Dilute Au:Dy Alloys: Observation of the Γ_8 (Quartet) Resonance*

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We report the first observation of a Γ_8 (quartet) resonance in a metal (Au:Dy). The field for resonance determines the relative magnitude and sign of the crystal-field parameters, $B_4/B_6=1300\pm 30$, to be compared with that found for Ag:Dy alloys, ≤ 340 . The linewidth yields an exchange-coupling parameter $J_{fs}=0.14\pm 0.05$ eV, slightly larger than for Au:Gd and Au:Er alloys, and slightly smaller than for silver-based alloys.

We report the first observation of a Γ_8 (quartet) resonance of a localized moment in a metal. Electron-paramagnetic-resonance experiments were carried out on single crystals of Au:Dy alloys. The field for resonance was anisotropic, obeying the usual symmetry rules appropriate to a Γ_8 quartet. Fitting with the predictions of crystal-field theory yields a precise value for the

magnitude of the ratio (and relative sign) of the fourth- to sixth-order crystal-field coefficients. A formula is presented for the linewidth of the Γ_8 resonance caused by exchange relaxation to the conduction electrons, yielding a value for the localized conduction-electron exchange coupling. Comparisons of the exchange coupling and the crystalline-field parameters are made with sil-