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Electronic structure of Fe, Co, and Ni impurities in Pd

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A photoemission study of the valence bands of the dilute alloys *Pd*Fe, *Pd*Co, and *Pd*Ni is presented. We use the Cooper minimum effect to estimate the local density of states on the impurity site. The behavior of transition-metal impurities in a transition-metal matrix is shown to be very different from their behavior in *s-p* metals. Our conclusion is that the Fe and Co 3*d* states are mixed with states throughout the Pd 4*d* band, while the Ni contribution to the spectra is dominated by a peak of (minority) 3*d* states near the Fermi level.

I. INTRODUCTION

The alloys of 3*d* transition-metal impurities in Pd have fascinating magnetic properties, which have attracted scientific attention for more than half a century, especially because of the unusually large "giant" magnetic moment (for *Pd*Fe up to $12.6\mu_B$) that can be attributed to the impurity[1-5] (see Ref. 6 for a review of experimental results). Since the susceptibility of Pd metal is strongly enhanced, dissolving small quantities (<0.1 at. %) of Mn, Fe, or Co in Pd is sufficient to cause a ferromagnetic state at low temperature.[6] Neutron scattering experiments have demonstrated that magnetically polarized Pd atoms around the impurity carry the larger part of the giant moment. Such a polarization cloud may consist of 200 host atoms.[7] Also, for the system of Ni dissolved in Pd, giant moments have been reported. But ferromagnetic order does not exist here below a critical concentration of approx. 2 at. % Ni.[5,8] This contrasts with the properties of the dilute alloys of the other late 3*d* transition metals in Pd that order ferromagnetically with seemingly no lower limit to the impurity concentration.[6] The occurrence of a giant moment in a Pd alloy depends critically on the polarization of the Pd 4*d* band and thus on the interaction between the impurity and the neighboring host atoms. Detailed experimental data on the density of states at the impurity site and especially on the degree of mixing with the Pd states should therefore contribute to an understanding of the impurity-induced effects.

The purpose of this paper is to provide data on this question from photoemission investigation of the valence bands of the dilute alloys *Pd*Fe, *Pd*Co, and *Pd*Ni. To extract information about the local density of states on the impurity, part of these measurements have been done at the Cooper minimum in the Pd 4*d* cross section. A Cooper minimum only exists for orbitals with one or more nodes in their radial wave functions (e.g., for 4*d* and 5*d*, but not 3*d* levels). It occurs when the overlap integral coupling initial state and outgoing continuum wave changes sign with changing kinetic energy of the photoelectron.[9,10] Cooper minima are broad so that the choice of photon energy is not critical, and for the Pd 4*d* levels it is at ~ 130 eV.[10,11] Complete cancellation of the cross section, however, does not occur as the outgoing electron can have either $l+1$ or $l-1$ character. The effect is nevertheless sufficiently strong to constitute a useful tool for the identification of partial densities of states[12] or, as in our case, to highlight impurity contributions.

II. EXPERIMENTAL

The polycrystalline alloys *Pd*Fe, *Pd*Co (10 at.% 3*d* transition metal), and *Pd*Ni (5 and 10 at.% Ni) were prepared by arc melting and subsequent vacuum annealing. X-ray diffraction was used to check that the samples were in single phase. The low-energy photoemission experiments were performed at BESSY (Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung) and in Brookhaven. Typically the experimental resolution varied between 200 mV at 50 eV and 500 mV at 130 eV photon energy. The photoemission spectra were taken at normal incidence of light on the sample surface, electrons with take-off angles between 0° and ~40° of normal were collected, and count rates were normalized with respect to the photon flux.[11,13] The relative photon flux was determined by measuring the electron yield from a gold foil positioned in the monochromatized beam.

The samples were cleaned by scraping *in situ* before each measurement. Since the base pressure was about 10^{-10} torr the buildup of surface contamination was small, as judged from the absence of notable photoemission peaks in the binding-energy range 6–12 eV and parallel XPS studies under similar conditions. Prolonged measurements, if necessary, were done in several sessions with repeated scraping before each run. XPS spectra of Pd and impurity core levels were recorded at different electron take-off angles to check that there was no significant segregation of transition metal to or from the surface.

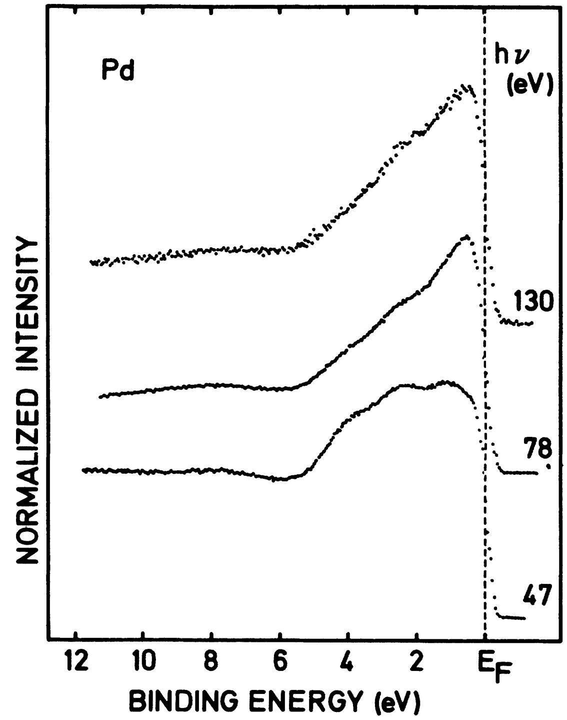

FIG. 1. Photoemission spectra of the valence band of Pd metal, taken at different photon energies. The spectra have been normalized to give the same peak height.

III. RESULTS AND DISCUSSION

Photoemission spectra of the valence band of Pd metal, recorded at different photon energies, are shown in Fig. 1. Spectra were recorded at many other photon energies and these are representative of the general trends. Note that the spectra have been normalized to the maximum intensity in Fig. 1, and that the absolute intensity of the 130-eV spectrum is much lower than that at 47 eV. The structure near the Fermi level E_F is due to the Pd valence band; its width of ~5 eV and the high density of states (DOS) at E_F are in good agreement with band-structure calculations (see, e.g., Refs. 14 and 15). The change of shape of the Pd spectra with photon energy is at least partly related to the change in electron energy loss function with energy and need not concern us here.

Figure 2 presents the valence band spectra of *Pd*Fe, measured at different photon energies. In order to derive conclusions about the local density of states on the impurity we first compare these spectra with those of Pd metal.

At 47 eV photon energy we observe for *Pd*Fe as well as for the other alloys a broad valence-band structure comparable to that of Pd metal. Although, especially near the Fermi level structural differences are noticeable, it is very difficult to interpret these differences in terms of impurity contributions, because they are so weak. Also at photon energies around 80 eV there is a strong resemblance between the spectra of the dilute alloy and that of the pure host. The main difference is that the valence

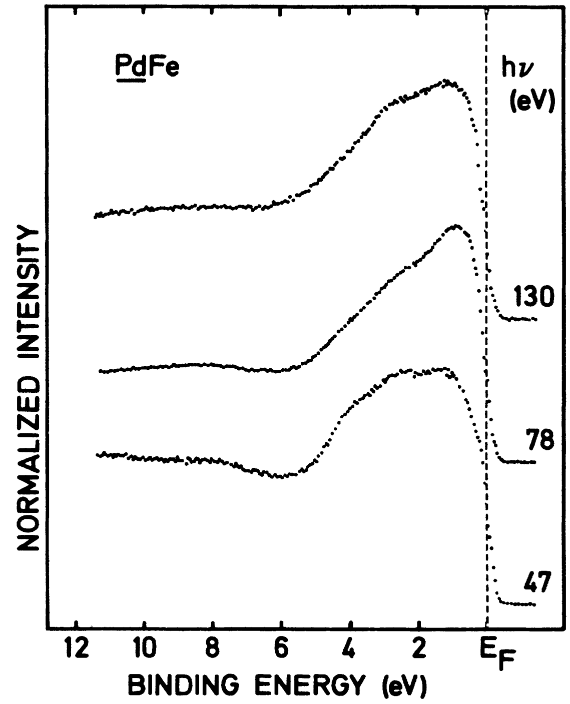

FIG. 2. Photoemission spectra of the valence band of the dilute alloy *Pd*Fe at different photon energies. Normalization as for Fig. 1.

bands of *Pd*Fe and also of *Pd*Co and *Pd*Ni (not shown) are broadened with respect to the band of pure Pd. It is only at the Pd 4*d* Cooper minimum around 130 eV that the clear differences between the spectra of the different alloys justify clear conclusions regarding the impurity contributions. We see, for instance, that the *Pd*Fe valence-band spectrum at 130 eV has a much broader appearance than that of Pd itself at the same energy. The spectra of the *Pd*Ni alloy are more peaked at E_F, even with only 5 at. % Ni, and those of *Pd*Co are intermediate in character.

Our problem now is how to separate out the contributions from the impurity and the host, and for this two methods are available. One is subtraction of the spectra at $h\nu=47$ or 78 eV from the spectra at 130 eV where the Pd 4*d* contribution is minimized. We found the results of this procedure unsatisfactory because of uncertainties introduced by the high binding energy (low kinetic energy) background and the normalization procedure. Instead, we chose to compare the spectra of Pd and the alloys at 130 eV, where the *relative* contributions of the 3*d* metals are maximized. These data are given in Fig. 3, where the spectra have been normalized to the photon flux. Note that the spectra of the alloys are nearly twice as intense as those of pure Pd, which means that at ~ 130 eV, the 3*d* impurities contribute nearly 50% of the spectral weight, because the Pd 4*d* cross section is so low. Note also that the background height at ~ 10 eV below E_F, mainly due to inelastic losses, is increased in intensity as well.

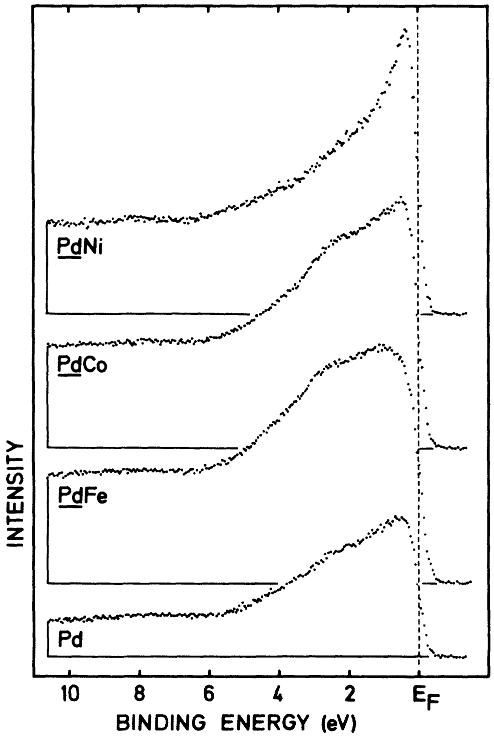

FIG. 3. Photoemission spectra at $h\nu=130$ eV of Pd metal and *Pd*M alloys. The spectra have been normalized to the photon flux from the monochromator and the Pd spectrum has been multiplied by 0.9 to allow for the change in Pd atomic concentration.

The difference spectra, *Pd*M minus Pd (where M indicates transition metal), for all three 3*d* transition-metal impurity systems are given in Fig. 4. We label these as the spectra due to M in Pd because the Pd photoemission cross section at the Cooper minimum is essentially determined by the 4*d* wave function inside the atomic sphere and to a large extent independent of the solid-state environment. Thus, changes in the 4*d* cross section should not produce the large observed increase in photoemission intensity. We are aware that the label "Fe in Pd" is an approximation and would be invalid if the Fe produced a massive change in the host DOS. However, we argue that the changes in the Pd host DOS, as a result of the 3*d* impurities, are not large because there are only small changes in the spectra at $h\nu=47$ and 78 eV, where the Pd 4*d* contribution dominates (see Fig. 2). The uncertainties associated with our procedure are not sufficient to negate the following conclusions.

First, the Ni impurity produces a large enhancement of the density of states near the Fermi level, which must be associated with the Ni partial density of states. The satellite in the Ni contribution is not as pronounced as for the core levels.[16]

Secondly, a similar enhancement at the Fermi level is found in Co, but here there is also an enhancement of the partial density of states at positions deeper in the band (approximately down to 3 eV).

Finally, in the case of Fe, the prononuced peak at the Fermi level is wiped out by extra intensity spread throughout the whole Pd band. This is particularly strong at about 3 eV below the Fermi level. We again attribute these changes to the local density of states on the Fe impurity.

This is not the first photoemission investigation of dilute alloys with transition-metal impurities (see, e.g., Refs. 17–23), but there is a marked difference to most published work in that we have studied systems for which the host is also a transition metal, and where therefore the impurity resonance lies in the middle of the host *d* band and not in an *s*-(*p*) band. This explains why our results show usually rather broad partial densities of state for the impurity site while the published data have been dominated by sharp peaks situated in the host *s*-(*p*) band. In the Anderson model the shape of the impurity partial density of states depends on the strength of mixing which in turn depends on two factors: the density of host states and the hybridization potential mixing the impurity state with the host states. The density of host states in our systems is the host *d* state density and this density is very high. For a transition-metal impurity in an *s*-(*p*) host the host density of states is low because the *s*-(*p*) band is broad and there are only two *s* states per host atom instead of the ten *d* states. A discussion of the *d* impurity in *d* host systems is more useful in terms of the Clogston-Wolff model,[3,21,24] in which the host-host (*d*-*d*) and the host-impurity (*d*-*d*) hybridization potentials are assumed equal, and the special character of the impurity is in the energy difference Δ between the host *d* band "centroid" and the impurity state. When the host *d* band is more separated from the impurity state, i.e., for large Δ, the amount of mixing is smaller. This applies for instance to $3d$ transition-metal impurities in noble metals, in which case it is not easy to isolate the amount of mixing experimentally.[21] For each of the systems *Pd*Fe, *Pd*Co, and *Pd*Ni, on the other hand, the majority states on the impurity lie in the host d band, although their positions with respect to the Pd d band centroid may vary slightly. These changes are strong enough to cause differences in the partial density of majority spin states on the impurities, as calculated in the local spin-density formalism,[25,26] and also in the higher binding energy part of the $3d$ contribution which we have extracted through the difference spectra in Fig. 4. The position for the minority states is more complex. For Fe the exchange splitting is large enough to push most of the minority $3d$ weight to energies above the Pd $4d$ band, while for Co and Ni in Pd the strongest weight in the minority band is calculated to be at the top of the Pd band.[26,27] The peak we see growing at the Fermi level in going from *Pd*Co to *Pd*Ni in Fig. 4 is actually to be attributed to states with minority character. We will make a more complete comparison with theory at a later date, but we have drawn in Fig. 4 the total density of Fe impurity states, calculated by Oswald *et al.* for Fe in a Pd host.[26] The general features are in good agreement, the maximum is several eV below the Fermi level, and the states are spread over a large energy range. Agreement in detail is not as good, for we find no peak at approximately 4 eV as indicated in the calculations and the general shape is not precisely reproduced. We cannot say at this stage if this is an experimental artifact or due to more fundamental effects, such as an energy dependence of the self-energy correction,[28,29] lattice distortion around the impurity site, or the high experimental impurity concentration. For Ni in Pd the sharp peaking of the Ni density of states near the Fermi level, which we find, clearly confirms the results of the calculations by Akai[27] and Oswald *et al.*[26] Thus, in general, we conclude that the results presented in Fig. 4 support the validity of the approximation used to calculate the local density of states for magnetic impurities. Where we have been able to make studies at lower concentrations (*Pd*Ni, 5 at. % Ni) we find no significant difference, but we would caution against drawing rigid conclusions from differences in fine details between our results and calculated data.

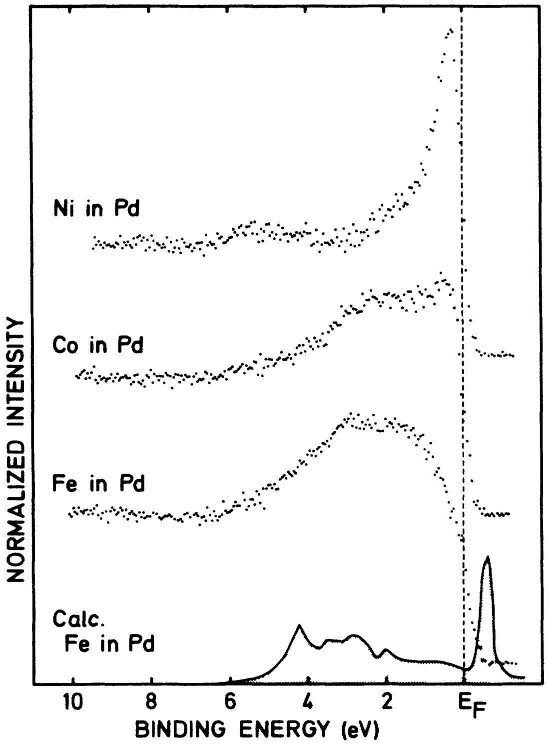

FIG. 4. Difference spectra, obtained from the spectra in Fig. 3, for the valence bands of the dilute alloys *Pd*Ni, *Pd*Co, and *Pd*Fe at $h\nu = 130$ eV. Also shown is the calculated DOS for an Fe impurity in Pd from Ref. 26.

IV. CONCLUDING REMARKS

In this paper we have presented an experimental investigation of the local DOS at a $3d$ transition-metal impurity in Pd. Our results for Fe, Co, and Ni impurities show that the impurity states are much more strongly mixed with the host states than is the case for $3d$ metal impurities in noble, or other s-(p) metal hosts. Our results, furthermore, suggest that the majority $3d$ state character is spread throughout the whole Pd band, but that, by contrast much of the minority character is concentrated in a fairly narrow energy range near the top of, or actually above the Pd $4d$ band. We suggest that it is the strong trend in the position and the width of this minority $3d$ peak from Fe to Co to Ni that is largely responsible for the differences in the magnetic behavior of these three dilute systems.

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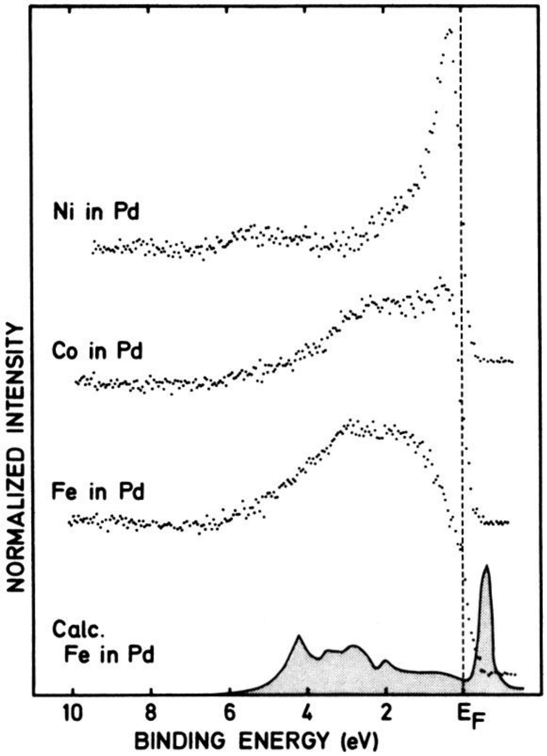

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