Photoemission investigation of the electronic structure of Fe-Pd and Fe-Pt alloys

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A photoemission investigation of Fe-Pd and Fe-Pt transition-metal alloys, using ~ 50–150-eV synchrotron radiation, is presented. We consider in particular the spectral distribution of Fe states when approaching the dilute limit. By means of the Cooper minimum in the $4d$ and $5d$ photoionization cross section, we identify structures that have mainly Fe minority- or Fe majority-spin character. The relative position of these peaks is discussed in terms of the covalent interaction between Fe $3d$ and Pd or Pt d states. Also, the strong resemblance between the distribution of Fe states in the Pd-based and in the Pt-based alloys is demonstrated. We find a consistent behavior of interacting d states towards the dilute limit. It is concluded that the Fe states that are observed in the photoemission spectra of the dilute alloys have mainly majority-spin character and are, because of the covalent interaction with host states, widely distributed over the energy range of the host d band. The Fe minority-spin band, which is centered near the Fermi level, gradually empties with increasing Fe dilution.

I. INTRODUCTION

Among the magnetic properties considered to be characteristic of Fe-Pd and Fe-Pt transition-metal alloys are the anomalously large local magnetic moment on the Fe atoms $(2.8$–$3.1\mu_B)$ and, in particular, the induced moment on the Pd or Pt atom (up to $0.5\mu_B$ per atom).[1-3] The cause of the strong magnetic polarizability of Pd and Pt is the exchange enhanced magnetic susceptibility, which is typical of these metals, and which is related to the large density of states (DOS) at the Fermi level. The dilute alloys *Pd*Fe and *Pt*Fe therefore behave as so-called giant-moment systems: a single magnetic impurity may polarize up to 200 neighboring host atoms[4] and thus is the cause of a magnetic moment as large as $12\mu_B$ per impurity for Fe in Pd or $6\mu_B$ per impurity for Fe in Pt.[5] In general the Fe-Pd and Fe-Pt alloys order ferromagnetically at sufficiently low temperature. The Curie temperature rises smoothly as a function of Fe concentration, and exceeds for the Fe-Pd system room temperature already above 13 at. % Fe.[6] A notable exception is $FePt_3$, which in the atomically ordered phase is an antiferromagnet $(T_N = 170$ K).[7]

In a previous photoemission study of dilute alloys of late $3d$ transition metals Fe, Co, and Ni (10 at. %) in Pd we have discussed the trend in the shape of the local density of states (LDOS) at the impurity site.[8] The LDOS was estimated experimentally by means of a difference technique. The spectrum of pure Pd was subtracted from the alloy spectrum after normalization by means of incident photon flux. The Cooper minimum effect in the photoionization cross section of the Pd $4d$ band was used

to suppress the contribution of the host material in the spectra. Our results indicated that for Ni most spectral weight is concentrated at the Fermi level, while the Co and, in particular, the Fe impurity levels are distributed at higher binding energies. It was concluded that the Fe contribution to the valence-band spectrum of $FePd_9$ consists mainly of majority-spin states, which strongly mix with the Pd $4d$ states. By contrast, much Fe minority-spin character is positioned above the Fermi level as an unoccupied virtual bound state (VBS), which is split off from the host $4d$ band because of the large exchange splitting. Self-consistent calculations of the LDOS at an Fe impurity site in Pd support this conclusion.[9] The increase of weight at the Fermi level in the LDOS of Co and Ni was interpreted as an increasing contribution of occupied minority-spin states at the Fermi level, in line with the decreasing exchange splitting.

The purpose of the present study is to place the distribution of the Fe majority-and minority-spin states in the context of a covalency model of chemical binding in alloys and intermetallic compounds (see, e.g., Refs. 10–13). A comparison of valence-band spectra, obtained by means of x-ray photoelectron spectroscopy (XPS), with self-consistent band-structure calculations, has demonstrated that, even in case of Pd-based alloys with electropositive metals such as Al and V, the experimentally observed filling of the $4d$ band can be explained in terms of covalent admixture of states of the partner element.[13] Excessive charge transfer, therefore, needs not to be involved. We will show in this study how also the photoemission spectra of Fe-Pd and Fe-Pt alloys fit in this general picture, which emphasizes covalent interaction and

mixing between different metallic states.

Since our interest concerns the behavior of the Fe states with increasing dilution, we will consider in particular the Pd- and Pt-rich alloys. Although Fe is electropositive with respect to Pd, the characteristics of band filling associated with Pd are not expected to be as clear as in case of, for example, the Pd-V alloys.[13] We expect strong mixing between Pd and Fe states, an effect complicated by the magnetic behavior of these alloys. It will therefore not be possible *a priori* to separate spectral features originating from Fe and Pd states on a binding energy scale, but we may attempt to estimate their relative weights. In order to assign structures in the spectra, we will therefore refer to a few relevant detailed band-structure calculations, which have been performed by means of an *ab initio* formalism[14] or in terms of a tight-binding scheme.[15]

Essential for this kind of experiment is the Cooper minimum in the photoionization cross section, which is observed for orbitals having one or more nodes in their wave functions, i.e., for the Pd 4d and Pt 5d, but not for the Fe 3d states.[16] Figure 1, compiled from the atomic photoionization cross-section calculations by Yeh and Lindau,[17] shows the broad Cooper-minimum effect in the atomic photoionization cross sections of the Pd 4d and Pt 5d orbital as compared to the weak energy dependence of the Fe 3d cross section. The figure indicates, for example, at what photon energy a favorable Fe 3d to Pd 4d cross-section ratio is to be expected, in order that the contribution of the Pd 4d states to a photoemission spectrum be minimized. It should, however, be kept in mind that solid-state effects, and many-body interactions in general, may affect position and depth of the Cooper minimum.[18] Photoemission investigation with use of Cooper-minimum effect has established itself as a powerful tool in the investigation of the electronic structure of dilute alloys and of compounds in general.[8,18–21] In view

of the photon energies at which the Cooper-minimum effect is usually observed, it should be noted that such investigation has become feasible only with the advent of facilities supplying synchrotron radiation.

II. EXPERIMENT

We have investigated the polycrystalline alloys FePd, FePd$_3$, FePd$_9$ and dilute *Pd*Fe (4 at. % Fe), as well as the isostructural series FePt, FePt$_3$, and FePt$_9$. The alloys were prepared by arc melting the requisite constituents under an Ar atmosphere. X-ray diffraction was used to check that the samples were homogeneous and consisted of a disordered fcc structure, except the two samples of the highest Fe concentration. These samples (FePd and FePt) were found by x-ray diffraction to have crystallized in a disordered tetragonal CuAu type of structure.

The photoemission experiments were performed at the Berliner Elektronen-Speicherring-Gesellschaft für Synchrotronstrahlung using the toroidal grating monochromator TGM2. Angle-integrated photoemission spectra were taken at normal incidence of light using a high-performance ellipsoidal mirror electron-energy analyzer, which was operated at an overall resolution of typically 500 meV.[22] The base pressure was 10^{-10} Torr.

During the experiment the intensity of the incoming monochromated radiation was continuously recorded using the total electron yield from a gold foil positioned in the beam. The normalization of photoemission yield by means of incident photon flux has, in a number of previous studies, been used to determine photoionization cross sections.[18,23–27] Also, an experimental estimate of the LDOS at an impurity site can be obtained by means of this method.[8] The normalized spectral intensity in the valence band is determined by means of standard computational procedures for the subtraction of the electron-loss background.[28] In this was we estimated the relative spectral contribution of Fe states to the valence-band spectrum of dilute *Pd*Fe. Note that we are not dealing with absolute cross-section values here, but only with relative effects. An accurate experimental estimate of relative contributions to the spectra is not possible in the case of small differences in the normalized valence-band spectral intensities, e.g., for a less favorable Fe 3d to Pd 4d cross-section ratio or for increasing Fe dilution.

Special care was taken to prevent surface contamination. The combination of the relatively high surface sensitivity at these photon energies (as compared to x-ray energies used in XPS) and the relatively low photoionization cross section at the Cooper minimum make the photoemission spectra, in particular of Pd metal and Pd-based dilute alloys, very sensitive to surface contamination. The samples were therefore scraped *in situ* in between repeated experimental sessions of data accumulation, each lasting at the most 30 min.

In order to check the surface impurity concentration of the dilute alloys we recorded XPS core-level spectra at different electron takeoff angles after scraping the sample. No indication of significant surface segregation of an atomic species was found.
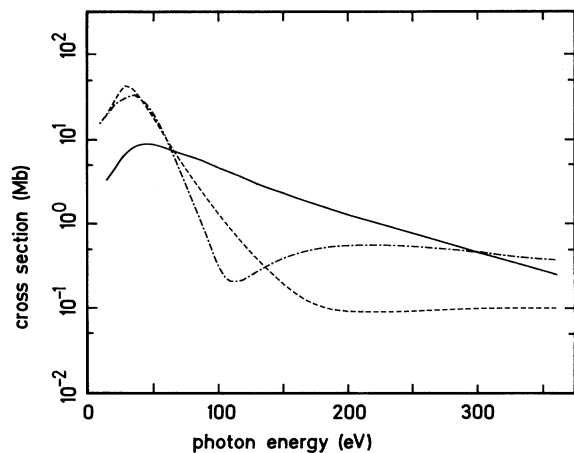

FIG. 1. Atomic subshell photoionization cross sections as a function of photon energy for Fe 3d (solid line) as compared to Pd 4d (dash-dotted line) and Pt 5d (dashed line) orbitals. Data are compiled from Ref. 17.

III. RESULTS AND INTERPRETATION

A. Fe-Pd alloys

Figures 2 and 3 show photoemission valence-band spectra, normalized to equal height, of the Fe-Pd alloys (FePd; FePd$_3$; FePd$_9$; and PdFe, 4 at. % Fe) and of pure Pd, taken at 78 and 130 eV, respectively. The spectra are dominated by structures within 6 eV of the Fermi level and show tailing to a higher binding energy, which is primarily caused by inelastically scattered electrons. Experimental data for the Pd metal and FePd$_9$ have been presented before,[8] but can now be viewed within a wider context.

As is apparent from our data, the valence-band spectra of pure Pd at 78 and 130 eV are similar. The spectral distribution is dominated by the structure representing the Pd 4d band and is characterized by an intensity maximum near the Fermi level (at 0.5 eV). The spectra of the alloys, in particular FePd and FePd$_3$, on the other hand, differ strongly with photon energy. For FePd, for example, two pronounced peaks are observed at 130 eV, while at 78 eV the spectrum consists of a single broad structure with a shoulder at the Fermi level. Even the valence-band spectrum of the dilute alloy (4 at. % Fe), which at 78 eV closely resembles that of elemental Pd, proves to be broadened at 130 eV. We attribute these effects to the

Cooper minimum at 130 eV in the Pd 4d photoionization cross section, which results in a suppression of the contribution of Pd 4d character to the spectra.

From the atomic calculations it follows that the photoionization cross section of the Fe 3d orbital is 10 times larger at 130 eV than the Pd 4d cross section (see Fig. 1).[17] The relative contribution of Fe 3d character to the valence-band spectrum of FePd$_9$ at this photon energy is thus estimated to be 53%. The contribution of s and p states may safely be ignored. The suppression of the contribution of Pd d states to the spectra at 130 eV should thus be considerable and deserves a closer look from an experimental point of view, also because of possible solid-state effects on depth and position of the Cooper minimum.[18] We therefore subtracted the electron-loss contribution from the experimental spectra. By correcting the integrated spectral intensity of the valence band for incident photon flux a normalized spectral intensity was obtained. The normalized intensity for FePd$_9$ was 1.76 times that of pure Pd, so that we may estimate the relative Fe contribution to be 49% of the total intensity in the valence band of FePd$_9$. From this value we have calculated the relative Fe intensity in the spectra of the other alloys. These estimates are listed in Table I together with the relative Fe contribution derived from the theoretical (atomic) cross-section ratio.[17] It is assumed
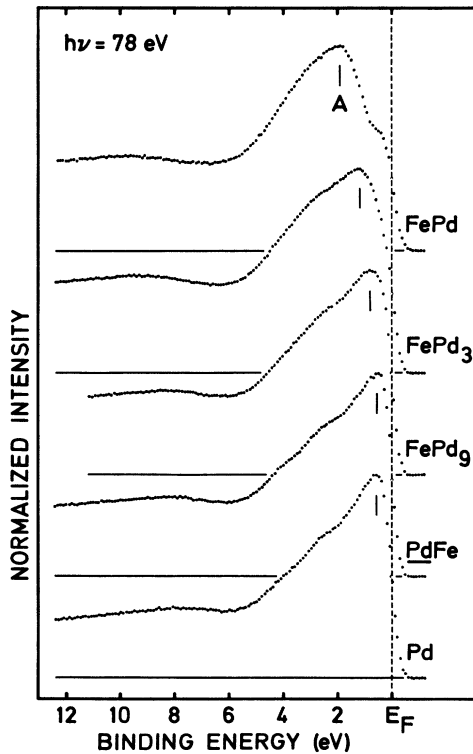

FIG. 2. Photoemission spectra of the valence band of Fe-Pd alloys and pure Pd, taken at 78 eV. Structures in the spectra associated mainly with Pd 4d states are indicated by means of feature A.
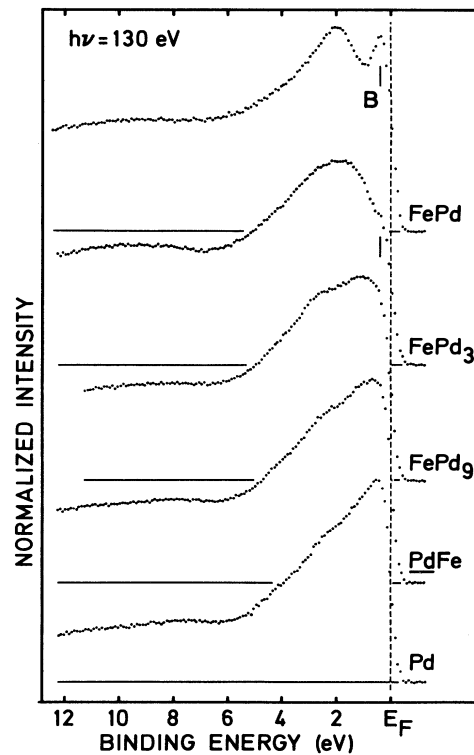

FIG. 3. Photoemission spectra of the valence band of Fe-Pd alloys and pure Pd, taken at 130 eV (the Cooper minimum of the Pd 4d orbital). Structure B is associated with the Fe 3d minority-spin states, which are observable in the spectra of the concentrated alloys.

TABLE I. Estimated relative intensity contribution of Fe states (in %) to the valence-band photoemission spectra of Fe-Pd alloys at 130 eV using the atomic photoionization cross-section tables by Yeh and Lindau (Ref. 17) (Theor.) and data obtained by means of photon flux analysis (Expt.) (Ref. 29).

	Theor.	Expt.
FePd	91	90(4)
FePd$_3$	77	74(8)
FePd$_9$	53	49(10)
*Pd*Fe	30	27(8)
(4 at. %)		

here that the $3d$-to-$4d$ cross-section ratio does not vary with alloy composition. Although the experimentally derived values are comparable to the theoretical estimates, and consequently are an indication of a strong Cooper-minimum effect in these photoemission spectra, it should be noted that a more detailed comparison, aiming at a discussion of, for instance, solid-state effects, is complicated. A larger uncertainty is, for example, related to the formulation of an effective photoionization cross section (including asymmetry parameters which differ for $3d$ and $4d$ orbitals) for electron-energy analyzers with a large acceptance solid angle.[24] The main conclusion from Table I is, nevertheless, that the spectra of FePd$_3$ and, in particular, of FePd at 130 eV (see Fig. 3) show largely spectral intensity originating from Fe d states. Both spectra are characterized by an intensity maximum at 2 eV and a structure near the Fermi level, which in case of FePd consists of a rather pronounced peak. Table I also shows that the Fe states contribute considerably to the spectral intensity even for the Pd-rich alloys (10 and 4 at. % Fe). The structure at the Fermi level, characteristic of the spectra of the more concentrated alloys, is absent at larger Fe dilution.

The photoionization cross section of the Fe $3d$ orbital at 78-eV photon energy according to the atomic calculations[17] is about three times larger than the Pd $4d$ cross section (cf. Fig. 1). For the largely qualitative considerations given here it is sufficient to assume that the valence-band spectra at 78 eV (as shown in Fig. 2) show mainly intensity of Pd d origin. This should certainly be the case for FePd$_3$ and the Pd-based dilute alloys. From a purely phenomenological point of view this assumption is confirmed by the fact that the mutual differences of the spectra of Pd and the dilute alloys at 78 eV are considerably smaller than at 130 eV.

The two structures (near the Fermi level and at 2 eV as indicated by feature A in Fig. 2) that we have identified in the valence-band spectrum of FePd at 78 eV have positions similar to those in the photoemission data at 130 eV. Since the peak at 2 eV dominates the spectrum of FePd at 78 eV, we conclude that the Pd states have most of their weight at higher binding energy, and to a lesser extent mix in with the Fe states near the Fermi level. It is thus observed that a feature in the valence-band spectrum of FePd, which originates from Pd states, has shifted to higher binding energy with respect to its position

for the pure metal. Since the dominating structures in all valence-band spectra at 78 eV can be identified with Pd states, we thus recognize a trend, indicated by means of feature A in Fig. 2, which can be summarized by the shift of a structure, attributed to Pd d states, to higher binding energy upon alloying with Fe.

B. Fe-Pt alloys

Valence-band spectra of Fe-Pt alloys are shown in Figs. 4 and 5. Again we have chosen for a series of spectra taken at the Cooper minimum of Pt (160 eV), as compared to a lower photon energy (82 eV). The minimum in the cross section of the Pt $5d$ orbital extends, as indicated by Fig. 1, from 180 eV over a large energy range. Since this Cooper minimum is rather broad, we expect a strong reduction of the Pt $5d$ to Fe $3d$ cross-section ratio already at lower photon energy. Our choice of 160 eV photon energy is based on the consideration that a clear Cooper-minimum effect is observed, while the decreased signal-to-noise ratio, due to the lower monochromator throughput, is still acceptable. Valence-band spectra taken at photon energies below 82 eV have not been considered because of strong distortion due to resonant enhancement associated with excitation of the Pt $4f$ level.

The spectra of pure Pt at 82 and 160 eV (in Figs. 4 and 5, respectively) show the two pronounced structures, with a valley at about 3 eV in between, typical of the Pt $5d$
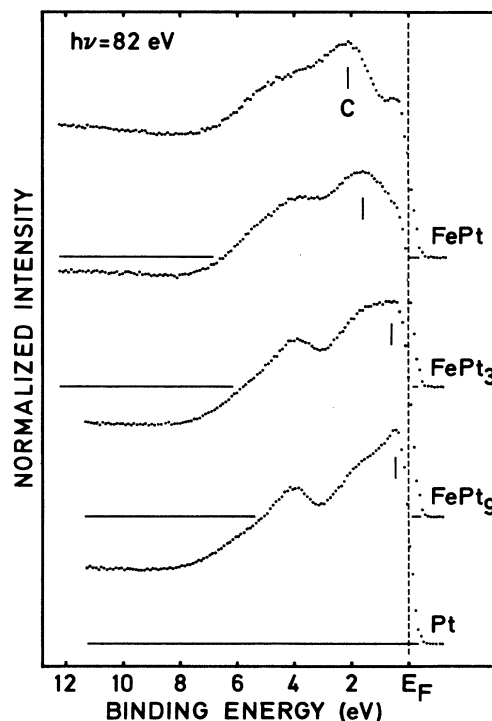

FIG. 4. Photoemission spectra of the valence band of Fe-Pt alloys and pure Pt, taken at 82 eV. Structure C represents features associated with Pt $5d$ states.

TABLE II. Estimated relative Fe contribution (in %) to valence-band photoemission spectra of Fe-Pt alloys at 160 eV, using as in Table I the atomic photoionization cross-section calculations (Theor.) (Ref. 17) and data from photon flux analysis (Expt.).

	Theor.	Expt.
FePt	94	91(3)
FePt$_3$	84	77(7)
FePt$_9$	63	53(9)

band.[30] The structure at the Fermi level is strongly peaked at 82 eV, but flattened out at 160 eV. We attribute this difference to the commonly observed photon-energy-dependent cross-section effects at lower photon energies ($h\nu < 100$ eV).[31]

Table II lists the relative contribution of Fe d states to the valence-band spectra at 160 eV, estimated experimentally and theoretically. The experimental results are based on the normalization of the spectral intensity of the valence bands of FePt$_9$ and Pt metal, and give a clear indication of a Cooper-minimum effect. Again, we see that the valence-band spectra of FePt and FePt$_3$ show mainly intensity originating from Fe states. The strong resemblance between the Cooper-minimum spectra of FePd and FePt is remarkable. The only distinction is a small shift of the high-energy feature (from 2.0 eV in the spec-

FIG. 5. Photoemission spectra of the valence band of Fe-Pt alloys and pure Pt, taken at 160 eV. Feature D indicates the position of Fe $3d$ minority-spin states.

trum of FePd to 2.3 eV for FePt, as shown in Fig. 3). The spectrum of FePt$_3$ is, like that of FePd$_3$, characterized by a shoulder at the Fermi level.

An inspection of Fig. 1 shows that the atomic Fe $3d$ to Pt $5d$ cross-section ratio has reduced from a factor of 15 at 160 eV to a factor of 2 at 82 eV. The peaks observed at 160 eV in the spectrum of FePt have, although unshifted in energy, changed their relative intensity at 82 eV. In addition, we see a third structure at about 5 eV, which is absent in the Cooper-minimum spectrum. Because of the larger spectral contribution of the Pt d states at 82 eV, we conclude that the main structure (at 2.1 eV) originates from Pt states. The spectrum of FePt$_3$ is also dominated by a broad peak (at 1.6 eV), which has mainly Pt d character. Structures, attributed to Pt states and indicated by means of feature C in Fig. 4, are thus seen to shift to higher binding energy with increasing Fe concentration.

IV. DISCUSSION

In summarizing the photoemission results we have seen how at lower photon energy the features that can be identified with Pd or Pt d states shift to higher binding energy upon alloying with Fe. At the Cooper minimum, where Fe d states dominate the spectral distribution, we have observed an agreement in shape between the spectra of FePd$_3$ and FePt$_3$ and, in particular, a strong resemblance between valence-band spectra of FePd and FePt. We consider this as an indication of the similarity in the distribution of the Fe d states in both alloy systems, and thus as additional proof for the common origin of the magnetic and structural properties of these alloys (see, e.g., Ref. 6 and references therein). Keeping in mind the general agreement in the characteristics of the valence-band spectra of both alloy systems, we will discuss separately the concentrated alloys and the dilute systems in the following.

A. Concentrated alloys

We will first compare FePd, FePt, FePd$_3$, and FePt$_3$, and argue that the two structures in the Cooper-minima spectra have mainly Fe majority-spin (at higher binding energy) and Fe minority-spin character (near the Fermi level). Evidence is obtained from the self-consistent calculation of the electronic structure of FePd$_3$ and related transition-metal alloys in the Cu$_3$Au crystal structure by Hasegawa,[14] and from a tight-binding calculation of the band structure of FePt (CuAu crystal structure).[15] The picture offered by these band-structure calculations is that the Fe majority-spin states mix strongly with the Pd or Pt d states, while the Fe minority-spin states are centered near the Fermi level at the top of the 4d or 5d band.

We have summarized the conclusions of these calculations in a simple scheme (Fig. 6), which shows how the Fe 3d and Pd 4d majority- and minority-spin states each are affected by covalent interactions. Note that the effective level of the Fe 3d states is positioned at higher energy with respect to the Pd 4d resonance (Fe is electropositive with respect to Pd). As is indicated by the band-structure calculations, we consider the Fe majority-spin states here
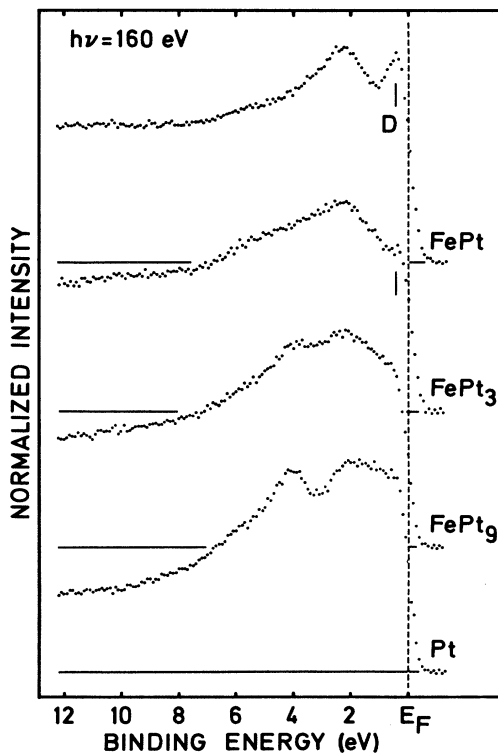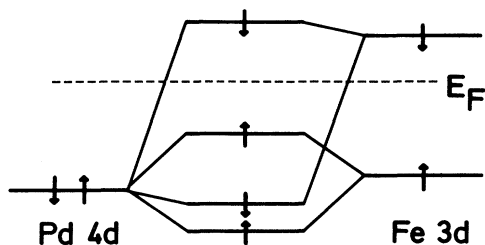
FIG. 6. Schematic energy diagram, indicating the covalent interaction between Fe 3d and Pd 4d states in magnetic Fe-Pd alloys. The position of the Fermi level is indicated approximately. Note that direct Pd-Pd and Fe-Fe interactions are not included in this scheme.

nearly degenerate with the Pd d states. This stresses their strong tendency to mix, since both the bonding and antibonding states have Fe and Pd d weight in nearly equal amounts. The positions of the d resonances of the Fe and Pd minority-spin states, on the other hand, are, because of the large exchange splitting in the Fe 3d states, about 2–3 eV separated in energy. The antibonding states at higher energy are therefore expected to carry most of the Fe 3d minority spin weight. Although this scheme, formulated in terms of a covalent magnetism,[12] strongly simplifies the state of affairs, it demonstrates the distinct distribution of the Pd majority- and minority-spin states, and thus the induced magnetic polarization of the Pd 4d band and the corresponding local moment on the Pd site (which is actually parallel to the moment on the Fe site).

The band-structure calculations furthermore indicate that the Fe majority-spin band is practically filled and that the Fe majority-spin DOS at the Fermi level is negligible. By contrast, the Fe minority-spin states straddle the Fermi level. The calculated Fe minority-spin DOS per unit cell at the Fermi level in $FePd_3$, for example, is comparable to the *total* Pd DOS per unit cell.[14] We therefore conclude that the features at the Fermi level in the Cooper-minimum spectra of the concentrated Fe-Pd and Fe-Pt alloys (indicated as B and D in Figs. 3 and 5, respectively) have mainly Fe minority-spin character, while at higher binding energy largely Fe majority-spin states are observed. The Cooper-minimum effect, therefore, allows the observation of an exchange-split pair of Fe states in the valence-band spectra of the concentrated Fe-Pd and Fe-Pt alloys (25 and 50 at. % Fe). Although photoemission only measures quasiparticle energies associated with the creation of a valence-band hole, we do not expect the self-energy corrections for Fe-Pd and Fe-Pt alloys [in contrast to, for example, metallic Ni (Ref. 32)] to be so large that they would invalidate our largely qualitative conclusions from a comparison with ground-state calculations. Note, for instance, that comparable conclusions concerning the distribution of minority- and majority-spin states in Fe_3Pt were derived in a spin-polarized low-energy photoemission study by Kisker *et al.*[33]

Figure 6 also demonstrates that, because of the co-

valent interaction with electropositive Fe, Pd or Pt d weight tends to accumulate near the bottom of band in the concentrated alloys. This is confirmed by the partial DOS calculations.[14,15] The structures that are experimentally observed at higher binding energy in the spectra of the concentrated alloys at about 80 eV (Figs. 2 and 4) apparently originate from these Pd (Pt) states. The shift of features attributed to Pd or Pt d states to higher binding energy upon alloying with Fe thus agrees with general concepts regarding the electronic structure of alloys of Pd and Pt with electropositive partner elements, although the effects observed are not as pronounced as in case of V-Pd alloys and are complicated somewhat by the magnetic phenomena.[13] The so-called filling of the Pd (Pt) d band is caused by covalent admixture of Fe d states. Note, therefore, that Pd (Pt) d character, of mostly minority-spin character, is always present above the Fermi level, which is the cause of the induced magnetic moment on the Pd (Pt) site.

Since our study deals with disordered alloys, a final remark of this section concerns the effect of disorder on the electronic structure of the Fe-Pd and Fe-Pt alloys. An electron in the majority-spin band will see relatively little disorder since the Pd (Pt) and Fe majority-spin states are nearly degenerate. The distribution of the minority-spin states, on the other hand, is rather sensitive to the nearest-neighbor configuration because of the large exchange splitting. Disorder will therefore cause a smoothing of structure in the largely unoccupied minority-spin band. This is assumed not to affect the present conclusions insofar as they are based on the results of band-structure calculations of ordered compounds.

B. Dilute limit

Structures that can be identified with Fe minority-spin states are, as we have seen above, observed at the Fermi level in the valence-band spectra of the concentrated alloys, but are clearly absent in the spectra of the dilute Pd alloys (10 and 4 at. % Fe). As we have discussed before,[8] this agrees with the fact that in the impurity limit most of the minority-spin weight is located above the Fermi level as a VBS.[9] Our experimental results for the fcc-type Fe-Pd and Fe-Pt alloys therefore demonstrate a consistent behavior of interacting states towards the dilute limit of Fe. Note that, also in the impurity limit, covalent interaction is the mechanism responsible for the distribution of the metallic states (and the magnetic polarization of the neighboring Pd atoms). The behavior of the Fe minority-spin states with increasing dilution can thus be understood in terms of a simple scheme as depicted in Fig. 6. With increasing dilution of Fe (or increasing Fe-Fe interaction) the Fe minority-spin band narrows and tends to localize above the Fermi level. The charge balance on the Fe site is maintained by depletion of minority-spin charge into the Fe majority-spin band, which causes filling of the Fe majority-spin band and an increase of the local magnetic moment. Finally, in the impurity limit the Fe minority spin states are split off from the Pd d band, since their resonance is located at the top of the 4d band. Only about 1.5 minority-spin

electrons, having bonding $3d$ character, mix in with the $4d$ band. This results in the maximum possible local magnetic moment on the Fe site $(3.5\mu_B)$ in the impurity limit.[9] The completely filled Fe majority-spin states therefore constitute the larger part of the Fe states contributing to the photoemission spectra in the dilute limit. These states hybridize with the Pd (Pt) d states and are distributed over a large energy range of the host d band. Our previous experimental estimate of the LDOS at an Fe site, for FePd$_9$, confirms this picture.[8]

A final point deals with finite temperature effects associated with the magnetic properties of these alloys. We have concluded that the experimental spectra agree with our expectations concerning a magnetic state of the impurity atom. The experiments described in this study have been performed at room temperature, which means that only the concentrated compounds FePd, FePd$_3$, and FePt, and certainly not the dilute alloys, were in a magnetically ordered state during experiment. On the other hand, it has been suggested that in itinerant systems a short-range magnetic order as well as a local exchange splitting persist even above the transition temperature. Experimental evidence, mainly from neutron-scattering studies, as well as theoretical arguments have been advanced in favor of this hypothesis.[34] We have checked for temperature-dependent effects in more detail by measuring the valence band of FePd$_9$ ($T_C = 264$ K) also below the transition temperature. These experiments show minor changes in the spectral distribution, which certainly is not compatible with a significant redistribution of states, i.e., with a significant variation of the local exchange splitting. This point is discussed in a forthcoming paper.[35]

V. SUMMARY

This work can be summarized in the following conclusions.

(i) We have shown that the Cooper-minimum effect in photoemission enables the separate observation of Fe majority- and minority-spin states in the valence bands of Fe-Pd and Fe-Pt alloys.

(ii) Experimental investigation of the electronic structure of Fe-Pd and Fe-Pt alloys confirms the common origin of the physical properties of both alloy systems.

(iii) The relative distribution of Fe and Pd (Pt), majority- and minority-spin, d states is explained in terms of the covalent interaction between the different metallic states.

(iv) We observe a consistent behavior of the Fe d states towards the dilute limit. Our experimental results agree with the assumption that the Fe minority-spin band gradually empties with increasing Fe dilution, which anticipates the VBS character of the minority-spin states in the impurity limit.

Of course a more quantitative comparison of theory and experiment, i.e., electronic-structure calculations and experimental spectra, would be desirable. At present, however, such a quantitative comparison seems impossible since accurate DOS calculations of disordered Fe-Pd and Fe-Pt alloys, as well as computations of the energy-dependent photoemission matrix elements at the photon energies employed in this study, are not available. We believe, nevertheless, that the availability of high-quality experimental spectra may stimulate the generation of such data.

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