Split-Off Narrow d-Band States above E_F in Transition-Metal Alloys

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The presence is shown of narrow early–transition-metal d bands in the unoccupied states, sometimes several electronvolts above the occupied states, in alloys of early with late transition metals. The widths of these states are small if the early–transition-metal concentration and the host density of states above E_F are both low. Their relationship to the narrow resonances of impurities in metals and their possible relevance to optical properties are discussed.

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Modern ideas on the electronic structure of a transition-metal impurity atom in a matrix can be considered to date from Friedel's work on phase shifts in the early 1950's and Anderson's work on the impurity Hamiltonian in the early 1960's.[1,2] It is clear from that work that if the transition-metal d levels fall in a region where the host has a low density of states, then a narrow d resonance or split-off state can be formed either above or below E_F. Several years ago photoemission studies of NiCu and PdAg alloys[3] indicated that even in concentrated alloys the rigid-band model was not appropriate and that split-off d bands could occur. Since then most of the spectroscopic and theoretical band-structure studies have concentrated on the occupied states. However, for physical properties the states above E_F are just as important as states below, but less attention has been given to them until recently because of the lack of a fairly direct method of investigating them. Bremsstrahlung isochromat spectroscopy (BIS)[4,5] has recently proved to be an important tool for understanding the role of the f electrons[5] in rare-earth elements and the actinides, where localized resonances are found above E_F. Here we apply BIS to transition-metal alloys in which narrow (now d) band resonances are formed.

Although in the pure early transition metals the d states form broad bands, these are now known[6,7] to become sharp resonances above the Fermi level when the atoms are dispersed as impurities in a matrix with a low density of states. Intermetallic compounds are systems in which intermediate cases can be studied because the early–transition-metal (TM) band is strongly dependent on the number of nearest neighbors of the same kind, which is in turn dependent on the stoichiometry and the crystal structure. To approach the impurity case the early TM element should have no nearest neighbors of its own kind, as for the Cu_3Au structure.[8] With use of the data of Fuggle *et al.*[9] we conclude that to fulfill the condition of a low density of states above E_F, a suitable choice of the other component is a noble metal or a late TM in intermetallic compounds. As we discuss below this combination also often provides the case of split-d-band behavior with the Fermi level nested in the d-band "gap" which can lead to interesting optical properties.

In Figs. 1–3 we give BIS and calculated densities of states (DOS) data for intermetallic compounds which show phenomena above E_F related to the sharp resonances or split-off states of dilute alloys. Other cases where such effects were not found will also be discussed to clarify when they occur. The BIS spectra were recorded at a photon energy of 1486.7 eV and a resolution ~0.65 eV in a UHV system.[10] DOS were calculated with use of the method of augmented spherical waves,[11] and a Gaussian broadening of 0.65 eV was applied to simulate experimental broadening. Samples were prepared by inductive melting under Ar.[9] They were cleaned by scraping in UHV. The intermetallic compounds considered here are ordered, and have a high heat of formation. Consequently, extensive surface segregation is not expected. Within experimental accuracy no deviation from the bulk stoichiometry could be detected at the surface by use of peak intensities of x-ray photoemission spectroscopy (XPS).

Figure 1 shows data for YPd_3 and $TiPd_3$, where there is no nearest-neighbor contact of the Y or Ti atoms. The calculations were made for the Cu_3Au structure in both cases, although $TiPd_3$ has the $TiNi_3$ structure which does differ from Cu_3Au but still has no Ti-Ti nearest neighbors. On the basis of DOS calculations and cross sections, the strong XPS emission from the filled bands can in both cases be attributed to states with mainly Pd d character.[9] The emission falls off strongly towards E_F so that these bands may be considered full. Above E_F, there is a strong background in the BIS spectra, attributed mainly

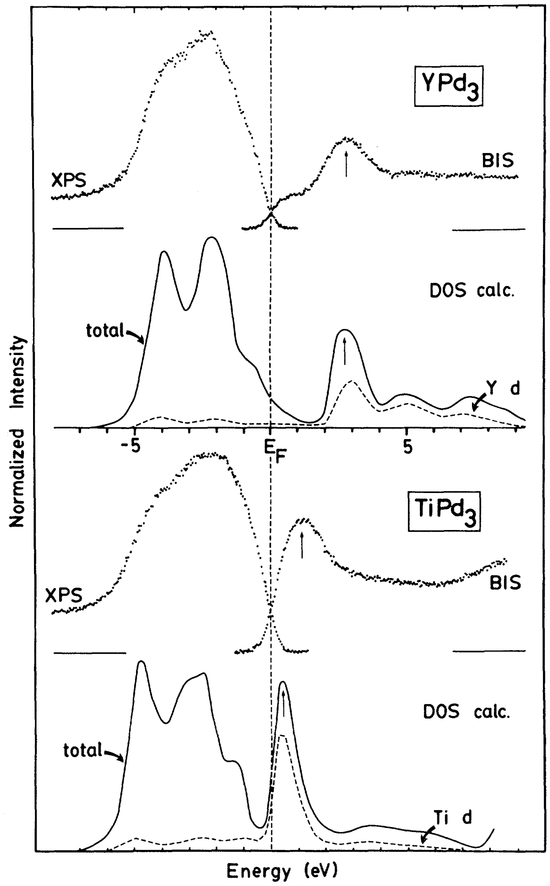

FIG. 1. Experimental ((XPS and BIS) and theoretical densities of states for YPd_3 and $TiPd_3$. No background was subtracted from the experimental spectra. The theoretical DOS curves have been broadened by 0.65 eV; total (full lines) and TM d densities (broken lines) are given.

to *sp* states with a smaller electron-hole pair-creation contribution.[12] Of more interest are the peaks marked with arrows in the BIS spectra of YPd_3 and $TiPd_3$ at about 2.6 and 1.0 eV above E_F. In both cases the DOS calculations indicate that the largest contribution to its weight comes from the early-TM d states.[13] In $TiPd_3$ the peak is closer to E_F because the effective atomic energy level of Ti 3d is lower than that of Y 4d.

The important point is that both BIS measurements and DOS calculations show a large peak in the densities of early-TM states above E_F in compounds with the Cu_3Au structure. To show that this effect is quite general and to give additional support to our conclusions we show results for a series of rare-earth–Pd_3 alloys in Fig. 2. The non-f parts of the valence bands of the rare-earth elements [i.e., $(5d6s)^3$] are similar to Y, and all the alloys crystallize in the Cu_3Au structure.[14] The spectra are dominated by the f states, which in the rare-earth elements are superimposed on a 5d6s band which is 10–12 eV wide.[15] We find in all alloys a peak at 2.3 to 3 eV above E_F, which we interpret in the same way as in YPd_3 or $TiPd_3$. We note that the peak at 2.3 eV in the BIS spectrum of $CePd_3$ caused some confusion when it was first observed[16] because it was not recognized at that time that so much of the Ce 5d spectral weight could be concentrated into a single, relatively narrow, peak.

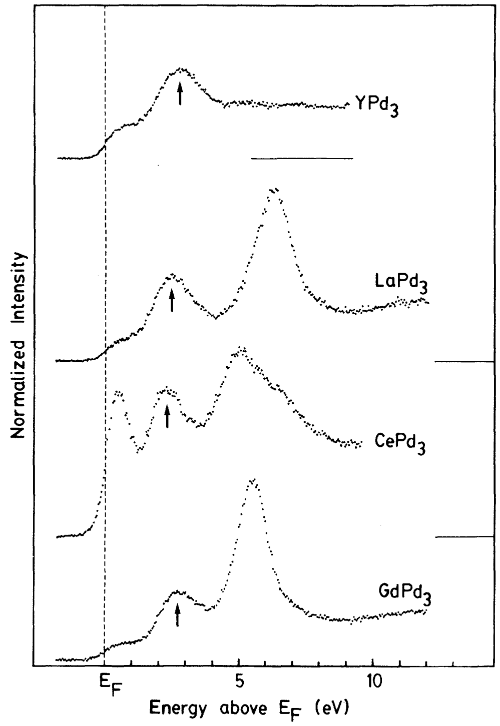

FIG. 2. BIS spectra of RPd_3 compounds with Cu_3Au structure.

We now consider TiNi for which data are shown in Fig. 3. Here the Ti-Ti distance is not increased so strongly in the alloy as compared to the pure metal, so that we do not expect such a pronounced sharpening of the Ti d bands.[8] This is indeed the case. The Ti d peaks are now about 3 eV wide. Also the Ti d DOS is high where the Ni d DOS is low and vice versa, so that the condition for split-off state formation, that the early-TM d levels fall in a region of low matrix DOS, is fulfilled. The split-off character is not so strongly developed in the CsCl structure because the Ti-Ti interactions are stronger than in $TiPd_3$ (but still smaller than in Ti).

Alloys with high early-TM concentration do not

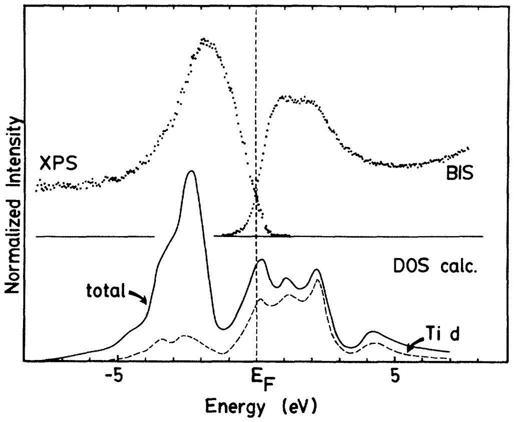

FIG. 3. Experimental and theoretical DOS for TiNi. Details as in Fig. 1.

show split-off band character because the direct metal-metal interactions are too large. Examples like this include R_3Ni, R_7Ni$_3$, and RNi, where R = La or Ce.[17] In CeSn$_3$ or CeAl$_3$ the Ce 5d bands fall in the Sn or Al sp bands which have a relatively high DOS and large hopping integrals, and here again no split-off states are observed.[16] Finally we note an almost trivial example: The DOS spectra of Rh-Pd alloys show only a peak near E_F, which is due to a continuation of the Rh-Pd d bands[18] from below E_F, and there is no split-off state because there is no early TM. These results confirm that to form split-off character above E_F one needs (1) an early TM as one component; (2) low density of states of the other component at the early-TM atomic d energy level; (3) small interactions between the early-TM atoms, which is achieved by low early-TM concentrations and suitable crystal structures.

The behavior of the split-off states above E_F is similar to that of late TM (and noble metals[19]) whose d bands below E_F also narrow considerably when they are diluted into elements with a low DOS near the effective atomic level of the TM.[3,9] Related effects have also been found by photoemission[20] and other studies[21] for earlier TM. For states below as well as above E_F, an increased TM concentration leads to a larger TM-TM interaction, the bands become wider, and describing them as split-off states is less appropriate.

The extent to which narrow split-off states can form above E_F, even from normally well delocalized states, has not been sufficiently appreciated until now. Their occurrence will not be as widespread as below E_F because higher-energy states are less well bound with more extended wave functions and larger hopping and hybridization integrals. Nevertheless our work shows that they do occur quite generally. Materials with a strong DOS peak above E_F and a gap, or very low DOS near E_F, may have interesting optical and transport properties. For instance, it is possible that for CePd$_3$ the relatively low energy cutoff (~1 eV) in the optical reflectivity and the peak in the absorptivity above this energy[22] are related to the gap and the split-off states that we observe. We suggest that the peak may be due to transitions from near E_F into the split-off state with mostly d character at ~2.3 eV. Such an absorption can be pronounced under certain conditions. There may even be possibilities to tailor such materials for certain technological applications where high ir reflectivity and absorption of visible light are desirable.

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virtual bound-state, character.

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