

## Direct Observation of the Exchange-Split Virtual Bound State in Dilute Mn Alloys

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The majority- and minority-spin states of the exchange-split virtual bound state of Mn impurities in Cu and Ag are studied with high-resolution photoemission and bremsstrahlung isochromat spectroscopy. The exchange splitting is found to be close to the atomic value. The majority-spin state is strongly hybridized with the host-metal  $d$  band resulting in its delocalization. The minority-spin states are localized but close to the Fermi level so that a description of the physical properties in terms of a spin Hamiltonian is not appropriate.

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During the past decades the alloys of  $3d$  transition-metal impurities dissolved in a noble-metal matrix have attracted considerable attention of theoreticians and experimentalists. Much work has been done on the Kondo<sup>1</sup> and spin-glass properties,<sup>2</sup> the latest theoretical developments<sup>3,4</sup> being the solution of the Kondo and Anderson<sup>5</sup> Hamiltonians and the development of fast-converging perturbation theories.<sup>6</sup> Although these theories treat the many-body effects on a high level of sophistication, they use model Hamiltonians, the validity of which depends on the relative magnitudes of the various parameters. They also lack a proper description of the band-structure details, especially the occurrence of the strong  $d$  resonance in the noble metals. In recent embedded-cluster<sup>7</sup> and coherent-potential-approximation<sup>8</sup> *ab initio* calculations these band-structure details are included, but exchange correlation is treated in the local density approximation.

The Mn atom is known to have an effective magnetic moment of about  $5\mu_B$  even in solid solution in noble metals.<sup>9,10</sup> Therefore it is probably one of the most beautiful examples of a transition-metal atom with a spin-split state consisting qualitatively of a full majority- and an empty minority-spin  $d$  shell.

The alloys  $AgMn$  and  $CuMn$  have been investigated extensively by means of a large variety of experimental techniques. For the interpretation of the experimental results one has resorted to the use of a Kondo Hamiltonian for which one implicitly assumes that the impurity has only spin degrees of freedom. Or, in other words, one has assumed that the Schrieffer-Wolff<sup>11</sup> transformation of the Anderson Hamiltonian is valid. This transformation is valid if  $r_{\pm} = \Delta_{\pm}/\epsilon_{\pm} \ll 1$ , where  $\Delta$  is the half-

width of the virtual bound state and  $\epsilon_{\pm}$  is its position relative to the Fermi level;  $\pm$  here denote the majority- and minority-spin states.

Although several photoemission studies have been reported,<sup>12-14</sup> we present the first direct measurement of the unoccupied impurity-induced density of states for  $AgMn$  and  $CuMn$  as well as high-resolution photoemission data for the occupied states. We obtain values for the above-mentioned parameters and compare these to theoretical calculations. We conclude that the validity of the Schrieffer-Wolff transformation is highly questionable and that the majority states are delocalized, whereas the minority states are localized as found in Heusler alloys.<sup>15</sup>

The polycrystalline  $AgMn$  samples (5% and 10%) were obtained from the melt and examined metallographically for the presence of secondary phases. The polycrystalline  $CuMn$  samples (1.5%, 5%, 10%, and 15%) were supplied by the University of Leiden group.<sup>16</sup>

The bremsstrahlung-isochromat spectroscopy (BIS) and ultraviolet-photoelectron spectroscopy (UPS) equipment is described elsewhere<sup>17,18</sup> and was operated at resolutions of 0.85 eV and 90 meV, respectively. The base pressure in both chambers was less than  $5 \times 10^{-11}$  Torr. The samples were treated with either Ar-ion etching or scraping, and surface composition was checked with x-ray photoelectron spectroscopy and Auger-electron spectroscopy.

The UPS spectra were corrected for the He I satellite of 23.09 eV and an intensity of 0.017 relative to the main line at 21.22 eV. The energy grids were 0.02 and 0.1 eV for UPS and BIS. The UPS difference spectra were obtained by subtracting the scaled spectra.<sup>19</sup> The BIS difference spectra were obtained

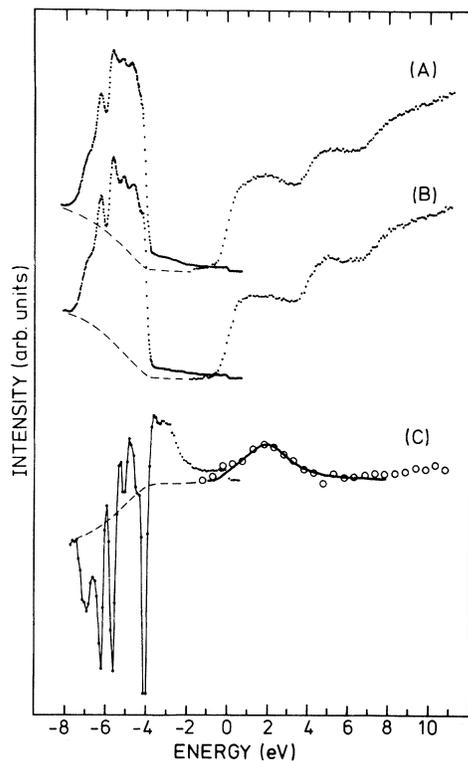


FIG. 1. Curve A,  $\text{Ag}_{0.95}\text{Mn}_{0.05}$  UPS (left) and BIS (right). Curve B, Ag UPS and BIS. Curve C, the dots are the UPS difference spectra; for clarity only the average of five consecutive data points is shown. The thin solid line serves as a guide to the eye. The circles are the BIS difference spectra. The solid line is the fit discussed in the text. All energies are relative to  $E_F$ . The dashed lines are the secondary electron contributions to the spectra.

by scaling to equal intensity at 10 eV and subtracting.

The corrected UPS and BIS spectra of Cu, Ag,  $\text{Cu}_{0.9}\text{Mn}_{0.1}$ , and  $\text{Ag}_{0.95}\text{Mn}_{0.05}$  are shown in Figs. 1 and 2 together with the difference spectra. The structure in the pure-metal BIS spectra has been discussed elsewhere.<sup>20</sup> In the alloy spectra additional structures are observed, the intensity of which is proportional to the Mn concentration.<sup>21</sup> We therefore interpret these structures as the Mn-impurity-induced difference in the spectral distribution. The BIS difference spectra show a Lorentzianlike peak just above the Fermi level which we interpret as the minority-spin Mn  $d$  states. These difference spectra were fitted with a single Lorentzian peak cut off at the Fermi level and convoluted with a 0.85-eV full width at half maximum Gaussian (solid line in Figs. 1 and 2). The Gaussian broadening is due to the experimental resolu-

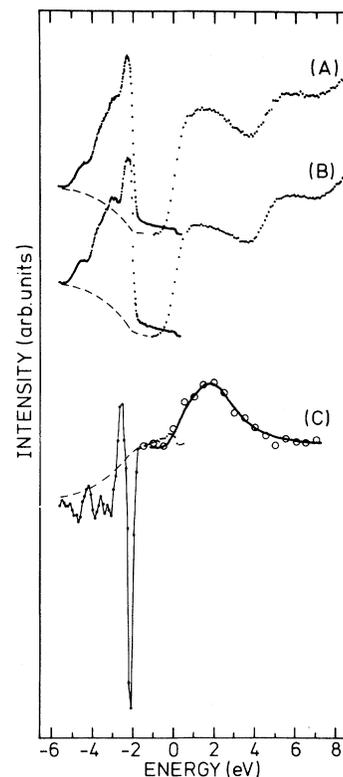


FIG. 2. Curve A,  $\text{Cu}_{0.9}\text{Mn}_{0.1}$  UPS (left) and BIS (right). Curve B, Cu UPS and BIS. Curve C, difference spectra with dots and lines as in Fig. 1.

tion and was determined from the Fermi-level-cutoff part of the spectrum of the pure metals. The minority-spin peak position and Lorentzian broadening are given in Table I.

The UPS difference spectra show in addition to structure just below the Ag  $d$  band in  $\text{AgMn}$  a lot of structure within this band. The positive contribution at about  $-3$  eV in  $\text{AgMn}$  is due to the majority-spin Mn  $d$  states. The strong structure in the Ag  $d$  band is due to two effects: firstly a dilution effect (i.e., removal of Ag)<sup>20</sup> and secondly the presence of Mn  $d$  density of states in the Ag  $d$  band due to hybridization. For the  $\text{CuMn}$  alloys the situation is even more complicated because no extra structure outside of the Cu  $d$  band is observed. The majority-spin Mn  $d$  state must therefore lie inside the Cu  $d$  band. This is not surprising since we expect the majority-spin state in Cu and Ag hosts to be at approximately the same position, which, with use of the  $\text{AgMn}$  value, would put it in the center of the Cu  $d$  band. This is also suggested by comparison of the positions of the minority-spin  $d$  states in  $\text{CuMn}$  and  $\text{AgMn}$ .

TABLE I. Most symbols are discussed in the text.  $n_{\pm}$  is the occupancy of the impurity majority and minority states. In this work it is obtained by integrating the Lorentzian distributions up to  $E_F$ .  $P_{\text{eff}}$  is obtained with the assumption that  $P_{\text{eff}} = g[S(S+1)]^{1/2}$  with  $S = \frac{1}{2}(n_+ - n_-)$ . References (b), (d), and (f) give theoretical data. References (e) give optical data, interpreted *a posteriori*.

	$\epsilon_+$ (eV)	$\Delta_+$ (eV)	$n_+$	$r_+$	$\epsilon_-$ (eV)	$\Delta_-$ (eV)	$n_-$	$r_-$	$P_{\text{eff}}(\mu_B)$
CuMn <sup>a</sup>	...	...	~ 5	...	1.7 ± 0.2	1.4 ± 0.2	1.1 ± 0.1	0.82	4.8
CuMn <sup>b</sup>	...	...	5.0	...	0.79 <sup>c</sup>	0.8 <sup>c</sup>	1.6	1.01	4.3
CuMn <sup>d</sup>	-3.5 <sup>c</sup>	0.16 <sup>c</sup>	4.9	0.05	0.8 <sup>c</sup>	0.64 <sup>c</sup>	1.0	0.8	4.8
AgMn <sup>e</sup>	-3.25	...	...	...	1.6	...	...	...	...
AgMn <sup>a</sup>	-3.1 ± 0.2	0.7 ± 0.1	4.65 ± 0.2	0.23	2.1 ± 0.2	1.2 ± 0.1	0.83 ± 0.1	0.57	4.7
AgMn <sup>f</sup>	-2.6 <sup>c</sup>	~ 0.2 <sup>c</sup>	~ 5.0 <sup>c</sup>	0.07	~ 0.7 <sup>c</sup>	~ 0.6 <sup>c</sup>	~ 1.1 <sup>c</sup>	0.86	4.80

<sup>a</sup>This work.

<sup>b</sup>Ref. 7.

<sup>c</sup>Estimated from the figures.

<sup>d</sup>Ref. 22.

<sup>e</sup>Refs 13 and 23.

<sup>f</sup>Ref. 8.

The absence of a clear peak in the UPS part of the difference spectrum of CuMn indicates that the majority-spin Mn *d* state is spread out over the whole Cu *d* band. A more detailed analysis suggesting this conclusion in terms of model calculations will be presented elsewhere.<sup>21</sup> Here we make the qualitative observation that the majority-spin Mn *d* state in CuMn is strongly delocalized because of hybridization with the Cu *d* band. A similar effect, but less severe, is found for AgMn. The position and half-width of the majority-spin impurity state in AgMn can be determined and are also given in Table I. The energy splitting between the majority- and minority-spin states is found to be 5.2 eV for AgMn which is considerably larger than the value obtained from first-principles calculations (3.5 eV).<sup>7,8</sup>

It is interesting to compare the observed energy splitting to atomic values. If we assume the ground state to be nominally  $d^5 6S$ , the energy splitting is

$$|E_-| + |E_+| = E(d^4 5D) + E(d^6 5D) - 2E(d^5 6S) \\ = F^0 + \frac{4}{14}(F^2 + F^4)$$

according to Slater's atomic table.<sup>24</sup> This is, in a more commonly used notation for magnetic impurities, identical to  $U + 4J$ . From Auger spectra we can also determine the energy of a  $d^3(4F 4P)$  state,<sup>25</sup> from which we find  $F^0 \approx \frac{1}{14}(F^2 + F^4)$  or  $U \approx J$ . Using the values of Table I for  $\epsilon_-$  and  $\epsilon_+$  we get  $F^0 \approx 1$  eV and  $\frac{1}{14}(F^2 + F^4) \approx 1$  eV. The free-atom values are<sup>26</sup>  $F^0 \approx 22$  eV and  $\frac{1}{14}(F^2 + F^4) \approx 1.2$  eV showing again<sup>27-29</sup> that  $F^0$  or  $U$  is strongly reduced from the free-atom value but the term splittings remain atomlike.

As mentioned in the introduction a very important quantity to check the validity of the

Schrieffer-Wolff transformation and the use of a spin Hamiltonian to treat the problem is  $r_{\pm}$ . This quantity is also listed in Table I. We see that the condition  $r \ll 1$  is not really fulfilled for either CuMn or AgMn. This is mainly because the minority-spin state is so close to the Fermi energy. The consequence of this could only be determined by investigating the higher-order terms in the Schrieffer-Wolff transformation.

Using a Lorentzian fit to the spectra we can determine the occupation of the majority- and minority-spin bands as given in Table I. The average magnetic moment is found to be  $4.72\mu_B$  for AgMn which agrees well with measured values ranging from  $4.73\mu_B$  (Ref. 10) to  $5.4\mu_B$ .<sup>30</sup>

In conclusion we have shown the existence of the spin-split virtual bound state in CuMn and AgMn. The splitting is considerably larger than that given by first-principles calculations with an exchange interaction close to atomic values. The close proximity of the minority-spin state to the Fermi level suggests that the use of a spin Hamiltonian for these systems is not appropriate. The absence of a clear peak in the UPS spectrum of CuMn confirms the theoretical idea<sup>7</sup> that the Mn majority *d* state is strongly hybridized with the Cu *d* band. The full noble-metal *d* bands can therefore mediate a superexchange interaction between Mn impurities and may for first and second neighbors even dominate over the usually assumed Ruderman-Kittel-Kasuya-Yosida<sup>31</sup> mechanism.

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<sup>25</sup>Unpublished results. The Auger spectra showed that  $U_{\text{eff}} \approx 0$ . Assuming the  $d^56s$  atomic ground state, we derive for the Auger final states  $U_{\text{eff}}(^4F) = F^0 - \frac{1}{441} \times (72F^2 + 9F^4)$  and  $U_{\text{eff}}(^4P) = F^0 + \frac{1}{441} (63F^2 - 84F^4)$ . The weighted averaging yields  $U_{\text{eff}} = F^0 - \frac{1}{14} (F^2 + F^4)$ .

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