Unveiling the impurity band induced ferromagnetism in the magnetic semiconductor (Ga,Mn)As

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(Ga,Mn)As is a paradigm of a diluted magnetic semiconductor which shows ferromagnetism induced by doped hole carriers. With a few controversial models emerging from numerous experimental and theoretical studies, the mechanism of the ferromagnetism in (Ga,Mn)As still remains a puzzling enigma. In this article, we use soft x-ray angle-resolved photoemission spectroscopy to positively identify the ferromagnetic Mn 3d-derived impurity band (IB) in (Ga,Mn)As. The band appears dispersionless and hybridized with the light-hole band of the host GaAs. These findings conclude the picture of the valence-band structure of (Ga,Mn)As disputed for more than a decade. The nondispersive character of the IB and its location in vicinity of the valence-band maximum indicate that the Mn 3d-derived IB is formed as a split-off Mn-impurity state predicted by the Anderson impurity model. Responsible for the ferromagnetism is predominantly the transport of hole carriers in the IB.

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I. INTRODUCTION

Ferromagnetic diluted magnetic semiconductors (DMSs) are formed by substitution of several percent of cation sites in a host semiconductor by magnetic impurities. Because the carriers in DMSs are considered to mediate the magnetic interaction between the magnetic ions [1], these materials are of key importance for “spintronics” aiming at development of advanced functional devices to control the spin degree of freedom of the carriers. Due to the mediation mechanism, the ferromagnetism (FM) in DMS is called carrier-induced FM. This mechanism is equipped with the capability of manipulating both the electron charge and spin degrees of freedom in functional spintronic devices. The III-V based DMS (Ga,Mn)As is a prototype ferromagnetic DMS, which has been intensively studied from both fundamental and applied points of view [2]. Although the Curie temperature (T_C) of (Ga,Mn)As is at present lower than room temperature, applications of (Ga,Mn)As to functional spintronic devices have been established.

Understanding the mechanism of the carrier-induced FM is of paramount importance for further development of spintronic device applications with DMS. Several theoretical models for carrier-induced FM in (Ga,Mn)As have been proposed [1]. In the limit where the hole carriers are considered nearly free or itinerant, the Zener p-d exchange model has been suggested based on a mean-field theory point of view [3,4]. Here, the Mn 3d acceptor level is located above the Fermi level (E_F) and merges into the valence band (VB) of the host GaAs through its hybridization, leading to the exchange-split VB of host GaAs crossing E_F. This model can explain the carrier-concentration dependence of T_C measured on an electric-field transistor structure using (Ga,Mn)As [5]. In the opposite limit where the hole carriers are strongly localized around the magnetic impurity, the Mn 3d impurity band (IB) model has been proposed [6–9]. Here, in contrast to the Zener model, the IB intersects E_F. This model can explain the experimental results of vacuum-ultraviolet angle-resolved photoemission spectroscopy (ARPES) [10], hard x-ray ARPES [11], and optical spectroscopy suggesting that E_F resides in the IB [12], as well as the results of resonant tunneling spectroscopy indicating that E_F is located above the valence-band maximum (VBM) of the host GaAs [13,14]. Additionally, as a model bridging from the localized hole carriers to the delocalized hole carriers causing the FM, the percolation theory of bound magnetic polarons (BMPs) has been proposed [15,16]. The model well explains the temperature dependence of the transport property of (Ga,Mn)As with low carrier concentration [16], and is likely relevant for an understanding of the nanoscale phase separation [5] and inhomogeneous growth of magnetic domains near T_C [17]. Here, to address the issue of the VB structure involving Mn 3d IB, we report the results of soft x-ray (SX) ARPES measurements of (Ga,Mn)As that take advantage of the enhanced probing depth combined with the elemental and chemical state specificity achieved with this technique [18,19]. Our Ga_{1-x}Mn_xAs samples, with a low Mn concentration just above the onset of FM [8,9], have an advantage in that they provide an authentic picture of FM in Ga_{1-x}Mn_xAs without any ambiguities due to potential formation of MnAs clusters at large Mn concentrations.

II. EXPERIMENTAL

Ga_{1-x}Mn_xAs (x = 0.025) thin films with a thickness of 100 nm were grown on a GaAs(001) substrate at 275°C under ultrahigh vacuum by the molecular beam epitaxy method. To avoid surface oxidation, after the deposition of a
Ga$_{1-x}$Mn$_x$As layer the sample was covered by an amorphous As capping layer with a thickness of 5–10 Å to produce the structure As/Ga$_{0.975}$Mn$_{0.025}$As/GaAs(buffer)/GaAs(001). The Curie temperature $T_C$ of our sample was $\sim 35$ K, as determined by the Arrott plot of the magnetic circular dichroism. The SX-ARPES experiments were conducted at the ADRESS beamline [20] of the Swiss Light Source using the SX-ARPES end station [21]. The measurements were carried through the As capping layer without its thermal desorption, thereby accessing the native (Ga,Mn)As electronic structure without potential formation of MnAs clusters. In the photon energy ($h\nu$) range from 350 to 1000 eV, the combined beamline and analyzer energy resolution varied from 50 to 150 meV. With our experimental geometry [21], the analyzer slit was oriented to lie in the measurement plane. The measurements used linear vertical ($p$) and horizontal ($s$) polarizations of the incident beam. The measurements were performed under ultrahigh vacuum of $5.0 \times 10^{-11}$ mbar at a temperature of 11 K, which essentially eliminated the effects of thermal broadening as well as electron-phonon scattering destroying the coherent spectral weight [21]. The Mn $L_{2,3}$ x-ray absorption spectroscopy (XAS) spectra were measured in the total-electron-yield mode.

III. RESULTS AND DISCUSSION

A. Band dispersion around the $\Gamma$ point

Our Ga$_{1-x}$Mn$_x$As thin-film sample was capped by an amorphous As layer, which well protects a GaAs underlayer against oxidation, exposure to deionized water, and annealing up to 180 °C [22]. In this report, we demonstrate that the use of SX-ARPES with photon energies $h\nu$ towards 1 keV allows the observation of the bulk band dispersion of the Ga$_1$–Mn$_x$As underlayer through the amorphous passivation layer, with any contributions from their interface being hardly seen in the spectra [see also Figs. S1 and S2, and the movie in the Supplemental Material [23]]. Details of the SX-ARPES experiment illustrating its penetrating ability through capping As layers have been published elsewhere [24]. These results exclude any possible surface As capping layer or (Ga,Mn)As/As interface contributions in our ARPES spectra. Hereafter, we shall focus on the bulk electronic structure of (Ga,Mn)As seen in our SX-ARPES experiments.

Figure 1 shows the binding energy ($E_B$) vs momentum ($k$) plots along the $\Gamma$–K–X symmetry line of the Brillouin zone (BZ) measured with $p$ and $s$ polarizations at $h\nu$ of 890 eV. Due to the wave-function symmetry properties, the light-hole (LH) and split-off (SO) bands of the host GaAs show up with the $p$ polarization [Fig. 1(a)], whereas the heavy-hole (HH) band pops up in the image taken with the $s$ polarization [Fig. 1(b)]. The LH and HH bands become almost degenerated along the $\Gamma$–X–$\Gamma$ line, as shown in Fig. 1(c). These dispersive bands form the band manifold characteristic of the GaAs band structure. Our results are consistent with the previous ARPES experiments and band calculations on GaAs [25–27]. Figures 1(d) and 1(e) display the energy distribution curves (EDCs) along the $\Gamma$–K–X symmetry line around the $\Gamma$ point with $p$ and $s$ polarizations, respectively. Note that although the LH and HH bands approach $E_F$ in the vicinity of the $\Gamma$ point, they do not intersect $E_F$ even at their top. The same is observed along the $\Gamma$–X–$\Gamma$ line, as shown in Fig. 1(c). These results provide unambiguous evidence that the VBM of host GaAs is located below $E_F$, which is consistent with the results of resonant tunneling spectroscopy [13] and immediately dismisses the Zener $p$–d exchange model [3,4].

Furthermore, we note a small but finite spectral weight at $E_F$, which is a direct observation of finite density of states at $E_F$ in (Ga,Mn)As. Figure 2 shows a comparison of the EDCs in the vicinity of the $\Gamma$ point between (Ga,Mn)As and pure GaAs. The slope near $E_F$ in (Ga,Mn)As is smaller than that in GaAs, manifesting a finite intensity near $E_F$ in (Ga,Mn)As. This result identifies an additional spectral weight at $E_F$ due to the Mn doping in (Ga,Mn)As. This fact, consistent with the metallic conductivity of (Ga,Mn)As, has been noted in the previous hard x-ray ARPES study with its large probing depth [11] but was missed by all previous low-energy photoemission experiments, including in situ ones [10,11,28,29]. The reason is probably the surface effects: The conventional photoemission experiments on semiconductor surfaces require their special treatment (such as ion sputtering and annealing) to remove the adsorbed surface contamination molecules. As these surface treatments are basically destructive, the
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FIG. 2. (Color online) Comparison of EDCs in vicinity of the Γ point taken at $h\nu = 890$ eV between Ga$_{0.975}$Mn$_{0.025}$As and GaAs thin films. The EDCs of GaAs are shifted to match the band dispersion to that of Ga$_{0.975}$Mn$_{0.025}$As. The momentum $k_z$ is along the Γ-K-X direction and its unit is $2\sqrt{2}\pi/a$, where $a$ is the in-plane lattice constant. (Ga,Mn)As shows additional spectral weight at $E_F$ consistent with its metallic conductivity.

FIG. 3. (Color online) Comparison of the band dispersions between different BZs across $k_z$. The momentum $k_z$ is along the Γ-K-X direction. The band dispersions taken at $h\nu = 650$ eV are determined by fitting the experimental MDCs with the Lorentzian function. The identity of the dispersions measured with different probing depths excludes any significant band bending.

Electronic structure near the surface in these experiments may be different from the bulk. Even in the case of \textit{in situ} photoemission on (Ga,Mn)As [28], the carrier concentration in the vicinity of the surface is possibly suppressed from the bulk one. This observation warrants that the SX-ARPES measurements with their enhanced probing depth reflect the bulk electronic structure of (Ga,Mn)As. No signal from the Mn 3$d$ states can be distinguished from the VB of host GaAs in these spectra taken at high $h\nu$.

It is important to mention a negligible contribution of the band bending near the interface between the amorphous As overlayer and (Ga,Mn)As underlayer. The bending, if it existed, would strongly influence the interpretation of the experimental data described below. Figure 3 compares the band dispersion between different BZs across the $k_z$ direction. The ARPES image was taken at $h\nu = 890$ eV (the seventh BZ). The superimposed points mark peak positions of the momentum distribution curves (MDCs) in the ARPES images taken at $h\nu = 655$ eV (the sixth BZ). Both the dispersive bands look identical, as shown in Fig. 3. Taking into account the increase of the photoelectron mean free path with $h\nu$, this result demonstrates that the band bending near the interface between the (Ga,Mn)As underlayer and amorphous As overlayer is negligible. Additionally, the observation that difference of As 3$d$ core-level peak positions between the surface and the bulk components (see Fig. S2 [23]) is constant as a function of $h\nu$ suggests the negligible contribution of the band bending near the interface. These results imply that even in the vicinity of the interface, $E_F$ is located in the same position of the bulk (Ga,Mn)As underlayer.

B. Mn 3$d$-derived impurity band

The energy position of the Mn 3$d$ states in VB has intensively been debated for more than a decade. To address this issue, we have conducted resonant angle-resolved photoemission spectroscopy (r-ARPES) at the Mn $L_3$ absorption edge. r-ARPES is known to probe the element-specific band dispersion of open-shell $d$ or $f$ electron systems [30,31]. Figure 4(a) shows the XAS spectrum at the Mn $L_{2,3}$ edges of the sample. Previously, the magnetic field dependence of x-ray magnetic circular dichroism (XMCD) has demonstrated that (Ga,Mn)As includes two kinds of Mn components: the intrinsic one, which is most likely due to ferromagnetic substitutional Mn ions, including some of the paramagnetic interstitial Mn$^{2+}$ ions, and the extrinsic one, which is due to paramagnetic oxidized Mn$^{3+}$ ions segregated in the surface region [17,32]. The XAS peak position of the ferromagnetic intrinsic Mn component of 640 eV is different from that of the paramagnetic extrinsic component of 640.5 eV [red and blue vertical lines in Fig. 4(a)] [17]. Accordingly, the resonance enhancement of ARPES measured at $h\nu = 640$ eV should be relevant to the intrinsic components, while the r-ARPES spectrum taken at $h\nu = 640.5$ eV should have almost zero contribution of the ferromagnetic states. Therefore a comparison between the r-ARPES spectra taken at 640 and 640.5 eV will reveal the Mn 3$d$ states of the intrinsic origin which are responsible for the FM.

Figures 4(c)–4(f) show a series of r-ARPES images measured on our (Ga,Mn)As sample under variation of $h\nu$ with $s$ polarization. [No shift of the band dispersion could be seen in the spectra taken at different BZs (see Fig. 3).] Most important to note in the evolution of the r-ARPES images is the Mn $3d$-derived IB which pops up at $h\nu = 640$ eV in the vicinity of $E_F$, as shown in Fig. 4(d), due to the resonance enhancement at the excitation energy of the ferromagnetic intrinsic Mn component, not paramagnetic extrinsic Mn oxides. The resonance at $h\nu = 640$ eV also enhances the intensity around $E_B \sim 3$ eV, which is due to the well-known main peak of the Mn 3$d$ partial density of states [29]. Conversely, the r-ARPES image in Fig. 4(e), taken at $h\nu = 640.5$ eV, which resonates with the paramagnetic Mn component and is nonresonant for the
The red and blue vertical dashed lines correspond to the resonant energy positions of the Mn L3 resonance. With \( h\nu \leq 40 \text{ eV} \) and hard x rays [11], the location of the IB was deeper (\( \sim 0.4 \text{ eV} \) below \( E_F \)) than in our observation and overlapped with the VBM. Furthermore, theoretical calculations subsequent to the vacuum-ultraviolet ARPES [10] suggested that the IB originated from the interstitial Mn impurities [34]. The present observations give unambiguous evidence that the IB is in fact located near the VBM and formed by the intrinsic Mn ions directly related to the FM in (Ga,Mn)As. Even though the intrinsic Mn components include not only the Mn ions substituting for the Ga site, but also partly interstitial Mn ions antiferromagnetically coupled to the substitutional Mn, influence of the interstitial Mn is minor in the r-ARPES spectra because the amount of the interstitial Mn ions is only \( \sim 10\% \) of the total amount of Mn ions in (Ga,Mn)As [35]. We note that although the spectral weight seen at \( E_F \) is small, it must be nonzero because of its disordered character of the IB, which introduces significant energy broadening of this band with its high-energy tail approaching \( E_F \).

In addition, incident light polarization dependence of the r-ARPES signal sheds light on details of the hybridization between the Mn 3d orbital and the ligand bands. Figures 4(g)–4(j) show the Mn L3 r-ARPES series of the (Ga,Mn)As sample taken with \( p \) polarization. The off-resonance image taken at \( h\nu = 638 \text{ eV} \) shows the LH band of host GaAs over the background of nondispersive amorphous As states, as shown in Fig. 4(g). The \( h\nu = 640 \text{ eV} \) resonance of the ferromagnetic intrinsic Mn component enhances the Mn 3d-derived IB in the vicinity of the VB maximum and the Mn 3d partial density of states around binding energy \( E_B \sim 3 \text{ eV} \), as shown in Fig. 4(h). It is important to note here that together with the IB the \( h\nu = 640 \text{ eV} \) resonance also pops up the LH band. These manifest the IB hybridization with the LH band. In contrast, the ARPES images shown in Figs. 4(c)–4(f), taken with \( s \) polarization, which exposes the HH band, do not show any increase of the HH intensity on top of the IB, indicating its insignificant hybridization with the HH band.
band of host GaAs, the difference of the EDCs taken at 640 and 640.5 eV [the green area in Fig. 4(k)], representing the resonant contribution, disperses as a function of \( k \), closely following the LH band. As opposed to the \( p \) polarization, the EDCs taken with \( s \) polarization, which exposes the HH band, show only the \( k \)-independent intensity of the IB, confirming the insignificant hybridization between the IB and HH band. Furthermore, a close look at the resonant tunneling results [14] shows that with incorporation of Mn the LH resonant tunneling peak displaces and the HH peak stays at the same energy. This is fully consistent with our r-ARPES results, which unambiguously identify the hybridization of the Mn IB and the host GaAs band with the HH band.

In addition to the formation of IB, the doped Mn atoms into GaAs also disorder the GaAs lattice, resulting in broadening of the GaAs bands as shown in Fig. 2. This means that although the GaAs bands terminate below \( E_F \), because of their energy broadening there should be finite GaAs weight at \( E_F \), which can in principle contribute to the conductivity. Qualitatively, the disordered GaAs may suppress the carrier-induced ferromagnetism in GaMnAs because the spin information of carriers is smeared by scattering on the GaAs defects. However, competition between the IB and disordered GaAs states may be relevant only for much larger Mn concentrations close to the optimal. Quantitative details regarding the disorder contribution will be addressed in further research of the band dispersion near \( E_F \) with different Mn concentrations.

C. Valence-band structure and origin of ferromagnetism in (Ga,Mn)As

Figure 5(a) shows a summary of the VB structure of (Ga,Mn)As near the \( \Gamma \) point. Here, the positions of the LH, SO, and HH bands were estimated from the Lorentzian broadening of the GaAs bands as shown in Fig. 2. This into GaAs also disorder the GaAs lattice, resulting in the insignificant hybridization between the IB and HH band.
GaAs:Mn (Mn concentration of 1.1 × 10^{17} \text{ cm}^{-3}), \sim 110 \text{ meV}
above VBM estimated from luminescence and electron spin resonance measurements [38,39].

According to the percolation theory of BMPs, the non-monotonic temperature dependence of the transport properties of (Ga,Mn)As is qualitatively explained [16] as due to the hole localization around the Mn ions. From cluster-model calculations of the Mn 2p core-level photoemission spectra [40], the exchange interaction between the d magnetic moment and carrier spin for the split-off state \( N/\beta \) has previously been estimated as \( -1.2 \pm 0.2 \text{ eV} \), where a negative sign means antiferromagnetic magnetic interaction between the 3d moment and carrier spin. In this case, most of Mn 3d character hybridized into the VB goes to the split-off state and forms the IB as the antibonding impurity state [41], the exchange interaction between the Mn 3d magnetic moment and carrier spin. In this case, most of Mn 3d character hybridized into the VB goes to the split-off state and forms the IB as the antibonding impurity state [41], the exchange interaction between the Mn 3d magnetic moment and carrier spin. In this case, most of Mn 3d character hybridized into the VB goes to the split-off state and forms the IB as the antibonding impurity state [41], the exchange interaction between the Mn 3d magnetic moment and carrier spin. In this case, most of Mn 3d character hybridized into the VB goes to the split-off state and forms the IB as the antibonding impurity state [41], the exchange interaction between the Mn 3d magnetic moment and carrier spin. In this case, most of Mn 3d character hybridized into the VB goes to the split-off state and forms the IB as the antibonding impurity state [41], the exchange interaction between the Mn 3d magnetic moment and carrier spin. In this case, most of Mn 3d character hybridized into the VB goes to the split-off state and forms the IB as the antibonding impurity state [41], the exchange interaction between the Mn 3d magnetic moment and carrier spin. In this case, most of Mn 3d character hybridized into the VB goes to the split-off state and forms the IB as the antibonding impurity state [41], the exchange interaction between the Mn 3d magnetic moment and carrier spin. In this case, most of Mn 3d character hybridized into the VB goes to the split-off state and forms the IB as the antibonding impurity state [41], the exchange interaction between the Mn 3d magnetic moment and carrier spin. In this case, most of Mn 3d character hybridized into the VB goes to the split-off state and forms the IB as the antibonding impurity state [41], the exchange interaction between the Mn 3d magnetic moment and carrier spin.

### APPENDIX: SPLIT-OFF MN-IMPURITY STATE INDUCED BY STRONG p-d HYBRIDIZATION

A single transition-metal or rare-earth ion embedded in an infinite lattice of nonmetal ions can be described by the Anderson impurity model [36]. In AIM, the band electron state \( \psi_{eq} \), which has the same symmetry group \( \gamma \) and spin \( \sigma \) as the \( d \) electron state \( \psi_{\gamma q}(q \equiv \gamma \sigma) \), is hybridized with \( \psi_{q} \) [41]. These states are assumed to be orthonormalized:

\[
\langle \epsilon q | \epsilon' q' \rangle = \delta(\epsilon - \epsilon') \delta_{q,q'}, \quad \langle q|q' \rangle = \delta_{q,q'}, \quad \langle \epsilon q | q' \rangle = 0.
\]

(A1)

Using these one-electron orbital bases, the Hamiltonian of the AIM is given by

\[
H = H_d + H_p + H_{pd},
\]

\[
H_d = \sum_{q=1}^{10} \epsilon^0_{dq} c_{q}^\dagger c_{q} + \frac{1}{2} \sum_{q,q'=1}^{10} \langle q q' | v | q'' q''' \rangle c_{q}^\dagger c_{q'}^\dagger c_{q''} c_{q'''},
\]

\[
H_p = \sum_{q=1}^{10} \int_{\epsilon_p - W_p/2}^{\epsilon_p + W_p/2} d\epsilon \epsilon n_{\epsilon q},
\]

\[
H_{pd} = -\sum_{q=1}^{10} \int_{\epsilon_p - W_p/2}^{\epsilon_p + W_p/2} d\epsilon \left[ t_{eq} c_{q}^\dagger c_{q} + t_{eq}^* c_{q}^\dagger c_{eq} \right],
\]

where \( W_p \) is the bandwidth of the ligand-orbital-derived VB centered at \( \epsilon_p \), \( c_{eq}(\epsilon q) \) is the creation (annihilation) operator of the band electron, and \( t_{eq} \) is the transfer integral.

In AIM, the wave function of the one-electron state is a linear combination of the \( d \) and valence-band states as

\[
\tilde{\psi}_q = a_q \psi_{eq} + \int_{\epsilon_p - W_p/2}^{\epsilon_p + W_p/2} d\epsilon' c_{q}^\dagger c_{eq}(\epsilon q),
\]

(A3)

Here, \( a_q \) is the normalization constant. The matrix elements of the Hartree-Fock operator are

\[
\langle \gamma_\uparrow | H_{HF}^{N/\beta} | \gamma_\downarrow \rangle = \epsilon^0_\gamma + 4U' - 4J_H \equiv \epsilon^0_\gamma',
\]

\[
\langle \gamma_\downarrow | H_{HF}^{N/\beta} | \gamma_\uparrow \rangle = \epsilon \delta(\epsilon - \epsilon'),
\]

\[
\langle \gamma_\uparrow | H_{HF}^{N/\beta} | \gamma_\uparrow \rangle = -\epsilon \gamma.
\]

The Hartree-Fock equation for the state \( A3 \) to be solved is given by

\[
(h_{HF} - \epsilon) \tilde{\psi}_\gamma = 0.
\]

(A5)
Then the integral equation for $c_{\gamma \gamma}(\epsilon')$ is given by substituting Eq. (A8) in Eq. (A6):

$$
\int_{\epsilon_{p}+W_{p}/2}^{\epsilon_{p}+W_{p}/2} d\epsilon' \left| t_{\epsilon'\gamma} \right|^2 = \epsilon - \epsilon_d. 
$$

(A9)

Here, $\gamma$ is the $t_2$ level, i.e., $\gamma = d_{xy}, d_{xz}, d_{yz}$. For simplicity, $|t_{\epsilon'\gamma}|^2$ is assumed to be a spheroid within $\epsilon_p - W_p/2 < \epsilon < \epsilon_p + W_p/2$, as shown in the left panel of Fig. 7. The left side of Eq. (A9) has singularities at the edges of the VB ($\epsilon = \epsilon_p \pm W_p/2$), as shown in the right panel of Fig. 7. If the hybridization is strong enough, a crossing point exists between the left side and the right side of Eq. (A9) outside of the VB continuum, and a discrete level, i.e., a split-off state is formed above the VB maximum through the hybridization, as shown in Fig. 7.

Let us consider the electronic structure of a single Mn ion in (Ga,Mn)As. If the Mn ion substituting for the Ga$^{3+}$ site is trivalent Mn$^{3+}$, the charge neutrality condition is satisfied. In contrast, if the Mn ion is divalent Mn$^{2+}$, the ion supplies a hole to the VB to satisfy the charge neutrality condition. Because the hole should have the down-spin, the $d$ spin strongly couples with the spin of the $p$ hole antiferromagnetically. Taking into account the configuration interaction method, the same system can be described from a many-electrons point of view. Assuming that the many-electron ground state $\Psi_{N}^{\uparrow}(d^{4})$ is expanded by wave functions $\Psi(d^{4})$ and $\Psi(d^{4} \downarrow)$, which represent the electronic configurations $d^{4}$ and $d^{4} \downarrow$, an integral equation similar to Eq. (A9) is obtained, where $\downarrow$ denotes a hole in the ligand. Thereby, the discrete split-off state appears below the continuum $d^{4} \downarrow$, as the solution of the integral equation, as well as the one-electron states [41].


