

Correlation effects on the L_3VV Auger line shape of $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$

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The L_3VV Auger spectrum of Mn in $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ has been measured with the use of soft-x-ray excitation. The partial Mn $3d$ density of filled states is obtained from the x-ray photoemission spectra of the binary CdTe and its alloy with manganese. Comparison with theoretical density-of-states calculations shows evidence of crystal-field-split multiplets in the final states of the d^4 configuration. The quasiatomic analysis of the Auger process indicates that the electrostatic interactions are largely screened in the alloy and that the two holes on Mn are uncorrelated. Consequently the shape of the Auger spectrum is simply given by the self-fold of the one-particle projected density of states. The extra-atomic contribution to the relaxation energy is also considered. The spin-spin exchange splitting of the d electrons is found to be 5.2 eV.

INTRODUCTION

$\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ is a semimagnetic semiconductor which belongs to a group of II-VI materials exhibiting a variety of interesting phenomena of fundamental and technological interest.¹ Recently, the energy position of the $3d$ states of Mn has been determined by ultraviolet photoemission measurements^{2,3} and it is the same for other ternary alloys⁴ irrespective of composition. The crystal-field-split e component of the $3d$ states is almost unaffected by the hybridization with the $5p$ -like states of Te and forms a narrow band at ≈ 3.4 eV below the top of the valence band while the t_2 component hybridizes strongly. Earlier photoemission measurements^{5,6} indicated a large delocalization and a strong Mn $3d$ -Te $5p$ hybridization for both components in contrast with the later results. The antibonding Mn $3d$ empty states lie in the conduction band and are split by the exchange interaction J_{dd} .⁷ Theoretical estimates^{8,9} of the projected Mn $3d$ density of filled states indicate a bandwidth smaller than 2 eV, compared to the total valence-band width $W \approx 6$ eV, which raises interesting questions concerning the strength of the electron correlation in this alloy. The Auger process, involving two localized holes in the final state, is a sensitive probe of such correlation energy U .¹⁰ If U is smaller than the one-electron bandwidth ($U \ll W$) the two holes will be largely delocalized and the local two-hole spectrum will resemble the self-convolution of the corresponding one-hole spectra. In the other limiting case ($U \gg W$) a quasiatomic spectrum as in a free atom will be observed.

Generally, the narrowing of the d valence band for an alloyed transition metal gives rise to an increased value of U compared to the pure d metal.¹¹ On the contrary we find that, despite its energy localization, the correlation energy of Mn in these semiconducting alloys is zero as in metallic manganese.¹² This result is based mainly on the position of the Mn $2p_{3/2}$ level measured by x-ray photoemission (XPS) with respect to the corresponding L_3VV Auger process. We first extract the Mn d -like density of the filled states (DOS) from the difference

spectra of CdTe and $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ ($x=0.6, 0.75, 0.85$) valence bands. It consists of a narrow peak located at 3.4 ± 0.2 eV below the top of the valence band and a small contribution delocalized over all the band in good agreement with the photoemission data of Taniguchi *et al.*² Its self-convolution reproduces quite well the measured Auger line shape. A comparison is made with two different calculations of the projected valence DOS's for the ordered $\text{Cd}_{0.4}\text{Mn}_{0.6}\text{Te}$ (Ref. 8) and $\text{Cd}_{0.5}\text{Mn}_{0.5}\text{Te}$ alloys.⁹ A general agreement is found for the position of the Mn e band. The entire Auger profile of the Mn $L_3M_{4,5}M_{4,5}$ transitions is, however, described by the combination of the atomiclike multiplet structure and of the hybridized portions of the Mn band with the Te sp band.

EXPERIMENTAL PROCEDURE

XPS and Auger measurements were performed in a ultrahigh-vacuum (UHV) chamber (Vacuum Generator MK II) under a base pressure better than 5×10^{-10} Torr. The energy resolution of the electrons using a hemispherical analyzer and an Al $K\alpha$ x-ray source was about 1 eV with a pass energy of 20 eV. $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ samples of various Mn concentrations ($x=0, 0.05, 0.15, 0.5, 0.6, 0.75,$ and 0.85) were cleaned by argon-ion etching and sometimes scraped under UHV conditions. The x-ray analysis showed a single zinc-blende phase with a concentration-dependent lattice parameter a which strictly followed Vegard's law up to $x=0.75$. At higher concentrations the system is multiphase with a predominant zinc-blende phase ($a=6.379 \pm 0.003$ Å) and a MnTe_2 cubic phase with $a=6.967$ Å, in agreement with previous determinations.¹³ The local coordination was also checked by means of the extended x-ray-absorption fine-structure spectroscopy (EXAFS).¹⁴

The scanned energy range included the valence band, the $2p_{3/2}$ Mn core level, and the corresponding Auger $L_3M_{4,5}M_{4,5}$ transitions. Because of charging effects, the valence-band-edge position was found to shift slightly from time to time. To overcome this unavoidable prob-

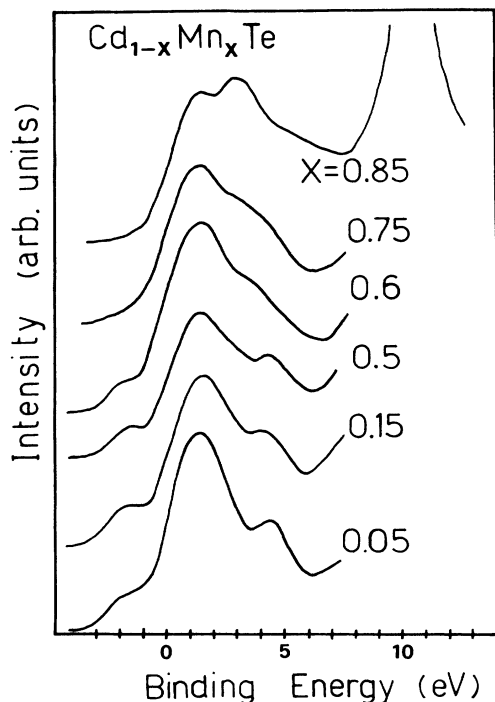


FIG. 1. Valence-band XPS spectra of $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ for increasing Mn content. The reference level is the valence-band maximum. The $4d^{10}$ level is at 10.5 eV binding energy. The Mn $3d$ level is positioned at about 3.5-eV binding energy.

lem the energy scale was referred to the $1s$ level of the residual carbon contaminant (<0.1 monolayer). Figure 1 shows the valence-band spectra of $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ for increasing Mn content. The faint structure below the valence edge, which decreases with decreasing Cd content, is a replica of the Cd $4d^{10}$ level at about 10.5 eV

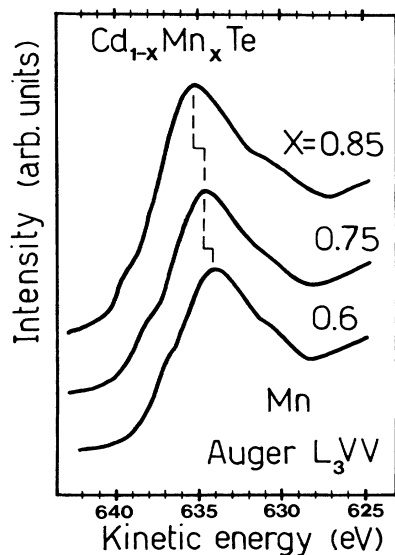


FIG. 2. Measured Auger L_3VV spectra of Mn.

binding energy, excited by the $K\alpha_{3,4}$ satellites.

The spectra up to $x=0.5$ are in good agreement with those previously reported by Webb *et al.*⁵ These authors argued that the Mn $3d$ band should be placed at a binding energy of 3.5 eV but clear evidence for this structure was lacking in their spectra. Our XPS measurements for $x > 0.5$ display clearly an additional structure at this energy which is attributed to manganese. Figure 2 shows the Mn L_3VV Auger spectra in the latter concentration range. The spectra consist of a central main peak with two lateral shoulders. We notice a shift of the central peak of about 1 eV towards lower kinetic energy decreasing the Mn fraction.

DISCUSSION

From previous work on diluted transition-metal alloys it has been established that the Auger process is very sensitive to the impurity-host interactions and to the electrostatic repulsion within the metal d^n configuration.¹⁵ The impurity-host hybridization, as described by the local-impurity DOS, is often not easy to obtain. In the case of the Cu-Mn alloy containing Mn impurities a combination of photoemission and bremsstrahlung isochromat (BIS) measurements has been used to determine the partial density of states. The impurity-host interaction was described by a Clogston-Wolff model parametrized to the experimental valence-band DOS. The large hybridization of the majority-spin states with the host-metal d bands results in a substantial screening of the atomic Coulomb interactions at the Mn site. Moreover, for the lowest $d^3(^4F, ^4P)$ state, the average effective Coulomb interaction between the two holes is nearly zero.¹⁶ The holes act as independent particles and the Auger spectrum is given by the self-convolution of the local one-particle density of states.

In semiconductors crystal-field effects are usually larger than in metals and the strength of the electron coupling within a d^n subshell depends strongly upon the site symmetry. In $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ the tetrahedral crystalline environment splits the Mn $3d^5$ ground-state configuration 6A_1 into a doublet $e(\Gamma_2)$ and a triplet $t_2(\Gamma_5)$ representation (e_g and t_{2g} in the cubic symmetry). The e states are lower in energy than the t_2 states and are located at 3.4 eV below the top of the valence band.^{8,9} Although these states are well inside the band, their binding energy is insensitive to alloying.² This follows from symmetry considerations which prevent a significant hybridization with the Te $5p$ -like states of $t_2(\Gamma_{15})$ symmetry.⁹ On the other hand, the interaction between anion and cation states of the same t_2 symmetry is strong and gives rise to a lower bonding and a higher antibonding pair of filled bands. In the case of ferromagnetic CdMnTe_2 , detailed calculations of the bonding charge of d symmetry at the Mn site give at most 20% mixing for the hybridized t_2 component at the center of the Brillouin zone, whereas the e states are strictly atomiclike.

The removal of an electron from the e level, as done in photoemission, leaves the Mn ion in the $(t_2)^3e, ^5E$ final-state high-spin configuration. The partial DOS of the 5E

level can be obtained from the difference between the XPS spectra of CdTe and those of the $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ alloys. It is shown in Figs. 3(a) and 4(a) for two different concentrations of manganese. The narrow peak at 3.4 ± 0.2 eV below the top of the valence band corresponds to this component DOS. Since for a localized Mn ion containing a $3d$ hole the orbital energy should be ≈ 1.5 eV higher than that of the $3d^5$ ground state,⁹ this is precisely the amount of relaxation energy occurring in the solid phase. The 5E orbital is occupied by a single electron which suppresses many-body final-state effects accompanying the excitation.

The ionization of a t_2 electron leaves Mn mainly in its lowest $(t_2)^2(e)^2$, 5T_2 configuration, although higher multiplets could be excited as well. The broad structure between 4 and 8 eV binding energy shown in Figs. 3(a) and 4(a) could be therefore attributed in part to these t_2 states.² The comparison with Mn d -projected DOS calculations for the $\text{Cd}_{0.4}\text{Mn}_{0.6}\text{Te}$ (Ref. 8) and $\text{Cd}_{0.5}\text{Mn}_{0.5}\text{Te}$ (Ref. 9) alloys shown in Fig. 5 suggests, however, that higher crystal-field-split multiplets (3E , 5T_2) of d^4 are important as well. Their intensity is reduced by the hy-

bridization with the Te p -like valence states and by the lower site symmetry in comparison to the isolated ion, but it is still significant. Such an assignment is consistent with the revised interpretation of this part of the spectrum recently provided by Ley *et al.*¹⁷ on the basis of a configuration-interaction calculation on a MnTe_6^{6-} cluster.

The L_3VV Auger spectrum of Fig. 2 bears additional information on the correlation energy between the holes in the doubly ionized Mn d^3 final-state configuration. Since the $3d^5$ Γ_2 level does not hybridize with the valence states, the effective potential is predominantly spherical and the multiplet atomic states will not mix appreciably. We have then estimated the energy of the lowest d^4 term and that of the eight terms of d^3 using the Slater-Condon integrals $F^k(3d,3d)$ for equivalent electrons in the LS coupling and neglecting crystal-field corrections and spin-orbit splitting.¹⁸ The energy is referred to that of the d^5 ground state (6S) and the XPS value for the ionization energy of the d^4 (5E) term is

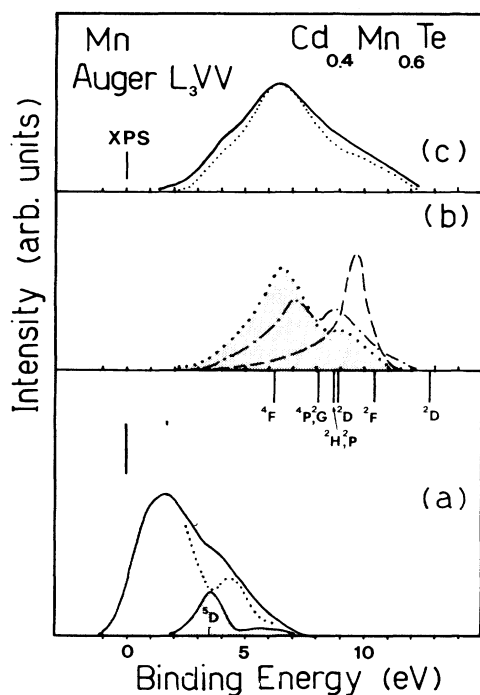


FIG. 3. (a) Partial Mn d -DOS (shaded) obtained from the difference between $\text{Cd}_{0.4}\text{Mn}_{0.6}\text{Te}$ and CdTe XPS spectra normalized at 1.5 eV. 5D is the ground state of the d^4 configuration. (b) Self-convolution of the DOS of (a) for $U=0$ eV (shaded), $U=1$ eV (dot-dashed), and $U=3$ eV (dashed). The energy positions of the multiplets of the d^3 configuration within the LS coupling are indicated. (c) Measured L_3VV Auger spectrum of Mn after background subtraction (solid line). Same spectrum (dotted line) deconvoluted with a Gaussian distribution (FWHM of 3.2 eV) which represents the broadening of the Mn $2p_{3/2}$ core line at 838.7 eV and the experimental resolution. The $2p_{3/2}$ XPS edge is shown.

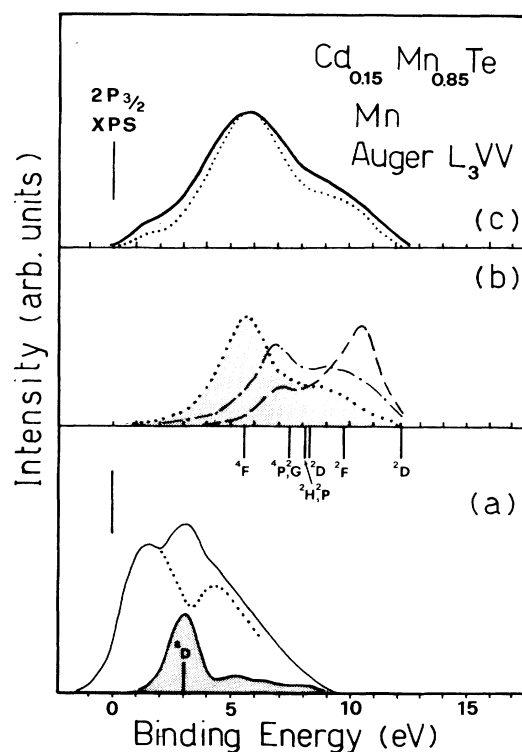


FIG. 4. (a) Partial Mn d -DOS (shaded) obtained from the difference between $\text{Cd}_{0.15}\text{Mn}_{0.85}\text{Te}$ and CdTe XPS spectra normalized at 1.5 eV. 5D is the ground state of the d^4 configuration. (b) Self-convolution of the DOS of (a) for $U=0$ eV (shaded), $U=1$ eV (dot-dashed), and $U=3$ eV (dashed). The energy positions of the multiplets of the d^3 configuration within the LS coupling are indicated. (c) Measured L_3VV Auger spectrum of Mn after background subtraction (solid line). Same spectrum (dotted line) deconvoluted with a Gaussian distribution (FWHM of 3.2 eV) which represents the broadening of the Mn $2p_{3/2}$ core line (at 838.7 eV) and the experimental resolution. The $2p_{3/2}$ edge is also shown.

used. The F^k values ($k=0,2,4$) are those adopted for Mn in metal alloys where the F^0 integral is strongly screened, whereas the higher-multipole terms are smaller and close (within 20%) to their free-atom values.¹⁵ The calculated positions of these multiplet components are compared with the Auger spectrum in Figs. 3 and 4 [panels (b) and (c)]. The Auger line shape has been deconvoluted with a Gaussian distribution of full width at half maximum (FWHM) 3.2 eV which represents the lifetime broadening of the Mn $2p_{3/2}$ core level and the resolution of the photoelectron experiment. It can be seen that the peak energy of the Auger L_3VV line agrees quite well with the position of the lowest 4F term of the d^3 multiplet. The other components are distributed over a 7-eV range and contribute to the shoulder between 8 and 12 eV binding energy. The relative intensities of these lines have not been calculated but it is expected that the lowest term will dominate, as is often found in other metals.¹⁹ It should be noted that the large change of the F^0 integral (≈ 21 eV) from its free-ion value is not entirely due to the intratomic contribution. Although most of the relaxation comes from the readjustment of the atomic charge on Mn, as suggested from the com-

parison with the metal alloys and the metallic Mn case, a consistent reduction of F^0 must be associated with extra-atomic relaxation or screening. In this case a dependence of the relaxation energy with changes in chemical environment is expected. In Fig. 2 a gradual shift of the Auger peak energy to lower binding energies with increasing Mn content can actually be observed for $x > 0.6$. This behavior could result from a tendency of Mn to cluster when the structural phase transition regime ($x=0.7$) is approached¹⁴ and demonstrates the great sensitivity of the Auger process to the local environment.

In the quasiatomic limit, the average atomic Coulomb energy U for the 4F and 4P terms of d^3 , written in terms of the Racach coefficients A and B , is¹⁸

$$U(^4F, ^4P) = A - \frac{35}{10}B = F^0 - \frac{1}{14}(F^2 + F^4). \quad (1)$$

Using the above-mentioned values of the Slater integrals, we see that the effective correlation energy of the two holes localized on the Mn site is zero. In the solid the L_3VV Auger line shape is therefore given by the self-convolution of the partial one-electron Mn $3d$ -like density of filled states $D^0(E)$. Figures 3(b) and 4(b) indicate clearly that $D^0(E)$ peaks exactly at the same energy of the Auger spectrum, in qualitative agreement with the atomic predictions. In presence of a finite correlation energy U , the Auger profile $D(E)$ deviates from the self-folding of $D^0(E)$. According to the Cini-Sawatzky theory,²⁰ $D(E)$ is given by

$$D(E) = \frac{D^0(E)}{[1 - F(E)U]^2 + \pi^2 U^2 [D^0(E)]^2}, \quad (2)$$

where $F(E)$ is the Hilbert transform of $D^0(E)$. The theory is valid if the band probed by the Auger transitions is full, a reasonable assumption for $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$. We have calculated $D(E)$ from Eq. (2) for $U=1$ eV and 3 eV. The resulting line shapes are strongly modified by the correlation and consist of a double-peaked structure shifted to high-binding energy with increasing U . A bound state starts growing when the Coulomb repulsion comes close to the one-electron bandwidth. The local two-hole DOS bears little resemblance to the measured L_3VV Auger spectrum. From this analysis we again conclude that the correlation energy of the Mn $3d$ states is close to zero, in agreement with the atomic analysis and with the Z dependence of the effective hole-hole interaction in the transition metals of the first row.²¹

A final point of major concern is the determination of the majority- and minority-spin splitting of the Mn $3d$ states. Using the Anderson or the linearized Hubbard Hamiltonian, such a splitting, expressed in terms of Slater integrals, reads¹⁵

$$E^\uparrow - E^\downarrow = F^0 + \frac{4}{14}(F^2 + F^4). \quad (3)$$

From our analysis of the Auger spectra we estimate a d -band exchange splitting $\Delta(d) \approx 5.2$ eV for $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$. Such a value is smaller than that (7.0 eV) reported by Ehrenreich *et al.*⁸ and closer to that (4.9 eV) given by Wei and Zunger.⁹ BIS measurements are therefore needed to set this point.

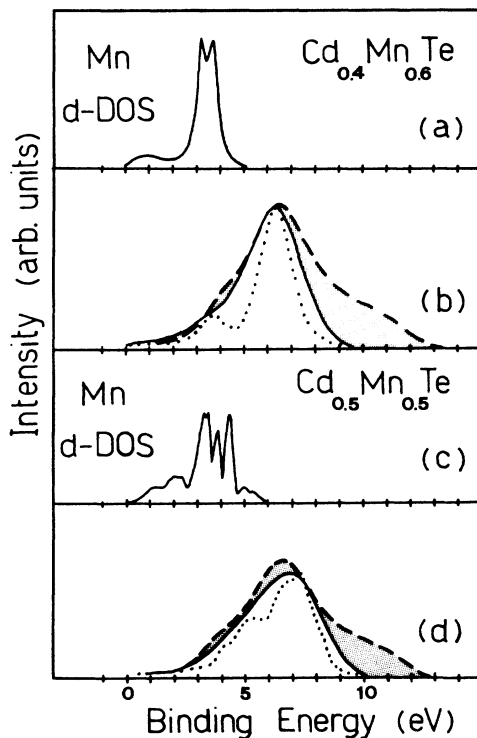


FIG. 5. (a) Partial Mn d density of states of ferromagnetic $\text{Cd}_{0.4}\text{Mn}_{0.6}\text{Te}$ after Ref. 8. (b) Self-convolution of (a) (dots). The solid line is the self-convoluted spectrum broadened with a Gaussian distribution (FWHM of 3.2 eV). The dashed curve is the experimental Auger L_3VV spectrum. (c) Partial Mn d density of states of ferromagnetic $\text{Cd}_{0.5}\text{Mn}_{0.5}\text{Te}$ after Ref. 9. (d) Self-convolution of (c) (dots). The solid line is the self-folded spectrum broadened with a Gaussian distribution (FWHM of 3.2 eV). The dashed curve is the experimental Auger L_3VV spectrum.

In conclusion, our analysis indicates that both crystal-field splitting and bond covalency tend to reduce many-body effects associated to the Mn *d*-hole states in the semimagnetic $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ alloy. Although the effective hole-hole repulsion is largely shielded, the electrostatic energies and the exchange splitting of the excited states are sizeable, particularly in the two-hole final states. The correlation between the localized holes is always negligible, as it happens in metallic manganese and in metal alloys doped with manganese.

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