

Resonant photoemission from surface states in GaP

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Enhanced electron-emission yield was observed in GaP(110)-cleaved crystals, by constant-final-state, constant-initial-state and energy-distribution-curve spectroscopies at photon energies which excite transitions from the Ga 3*d* levels to empty surface states. We prove that the resonance is mainly due to direct recombination involving filled surface states ≈ -2 eV below the top of the valence band. We observed an inversion of the intensity ratio between Ga 3*d*_{5/2} and 3*d*_{3/2} with respect to the statistical value due to the contribution of localized states to the optical transitions. In particular, different intensity ratios in constant-initial-state spectra at different initial-state energies have been interpreted as being due to different localization of the filled states participating to the resonant process.

The interpretation of photoemission results by a one-electron picture often fails near a core excitation edge. Resonant effects have been observed in metals,¹⁻³ semiconductors,⁴⁻⁷ and atoms⁸ when localized and highly correlated states participate to the excitation process. Valence-band resonant photoemission is easily identified in transition metals,¹ chemisorbed molecules on transition metals,⁹ and rare earths¹⁰ due to the presence of *d* or *f* localized states whose correlation energy is comparable with the bandwidth. In semiconductors, the highly dispersive valence bands are the major limiting factor in the detection of similar effects. But their observation could be favored by the presence of empty and filled localized surface states.¹¹ GaP is a good candidate because of the presence of localized empty surface states in the energy gap¹² [1.7 eV above valence-band maximum (VBM)] and filled surface states near the top of the valence band.

A resonant process is the enhancement of the primary electron yield when the photon energy is sufficient to excite transitions from a core level to empty localized states. Two possible recombination channels^{4,5} exist for the created core hole: the direct recombination (DR) mechanism, which leaves one hole in the valence band [Fig. 1(a)], and the Auger decay [Fig. 1(b)], indistinguishable from a shake-up process, which leaves two holes in the valence band. These two final configurations affect in a different way the core-hole lifetime. Discriminating between them may be very helpful in understanding the nature of the involved excitations, excitonic or core-conduction band. We shall see that the tunability of synchrotron radiation is necessary for the distinction of the two possible recombination processes.

We observed a resonant electron yield enhancement on cleaved GaP(110) at photon energies corresponding to transitions from Ga 3*d* levels to empty surface states in the energy gap. To discriminate between the two possible recombination channels we performed constant initial states (CIS), constant final states (CFS), and energy-distribution-curve (EDC) measurements.^{4,5} We used the synchrotron radiation from the Frascati storage ring and *n*-type GaP(110) samples ($n \approx 2.3 \times 10^{17} \text{ cm}^{-3}$) cleaved *in situ* in an ultrahigh vacuum chamber ($p \approx 1 \times 10^{-10}$ Torr) which

was described elsewhere.¹³ Synchrotron radiation was monochromatized by a toroidal grating monochromator in the energy range (10–100 eV).

The absorption from Ga 3*d* core levels is evident in the CFS spectrum of Fig. 2, taken with a final-state kinetic energy of 4 eV and for photon energies in the range 18–23 eV. The first two peaks separated by 0.5 eV correspond to transitions from the Ga 3*d* spin-orbit doublet to empty surface states in the gap.¹⁴ Structures at higher photon energy reflect transitions to conduction-band states. A best fit of the surface-state contribution was obtained with two Fano lines broadened by the instrumental response function. Their removal shows that the bottom of the conduction band is 20.6 eV above the Ga 3*d*_{5/2} level.

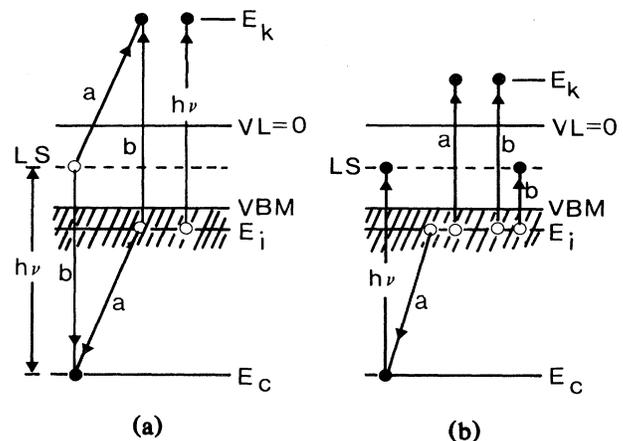


FIG. 1. Schematic illustration of possible deexcitation mechanisms of a core hole. (a) Configuration with one hole in the valence band is due to the strong interaction between the excited states (LS) and the localized states E_i in the valence band. The emitted electrons coming from processes *a* and *b* are indistinguishable, and these processes will be referred to as direct recombination (DR). The kinetic energy of the resonant electrons is the same as the primary emission. (b) Configuration with two holes in the valence band is due to an Auger decay, *a*. The emitted electrons have the same kinetic energy of shake-up electrons, *b*.

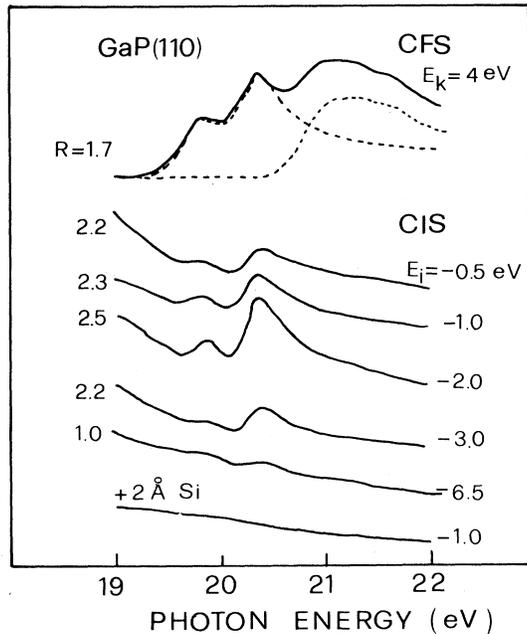


FIG. 2. CFS and CIS spectra of GaP(110) vs photon energy. Different initial states E_i and different intensity ratios R between Ga $3d_{3/2}$ and $3d_{5/2}$ are also reported.

CIS curves taken for different initial-state energies are also shown in Fig. 2. The normalized spectra exhibit a very narrow resonant enhancement at the photon energy corresponding to the above CFS surface transitions, 19.8 and 20.3 eV. The disappearance of the resonance after a deposition of 2 Å of silicon — as it is shown in the bottom curve of Fig. 2 — confirms the surface character of the observed features. The silicon coverage does not remove the bulk GaP emission as confirmed by Ga $3d$ and valence-band direct emission.¹⁵ Two main pieces of information can be extracted from the CIS data: (i) the energy position of the two resonant peaks does not change for different initial-state energies, and (ii) the peak width is nearly the same in all the spectra, and the strongest enhancement is observed for $E_i \approx -2$ eV. The first point rules out strong final-state effects. The second point demonstrates that the DR, involving empty localized surface states in the gap and filled surface states near the top of the valence band, is the dominant recombination process. In fact, the Auger process would have an onset at initial energies whose distance from the top of the valence band is equal to that of empty localized surface states (≈ 1 eV). Deeper initial states should give rise to enhanced yields of increasing width reproducing conduction-band features.

Further evidence that the DR is dominant is given by the EDC spectra of Fig. 3(a), taken for different photon energies through the resonance. The DR gives rise to enhanced electron emission in the same kinetic energy range of direct emission from states near the top of the valence band. The structure at $E_i \approx -2$ eV clearly evident at $h\nu = 19.8$ and 20.3 eV, whose intensity versus photon energy shows the same behavior as the CIS curves (Fig. 2), indicates that localized states with ≈ 2 -eV binding energy are the main contribution to the resonant process. The deeper part of the valence band is not appreciably modified by Auger

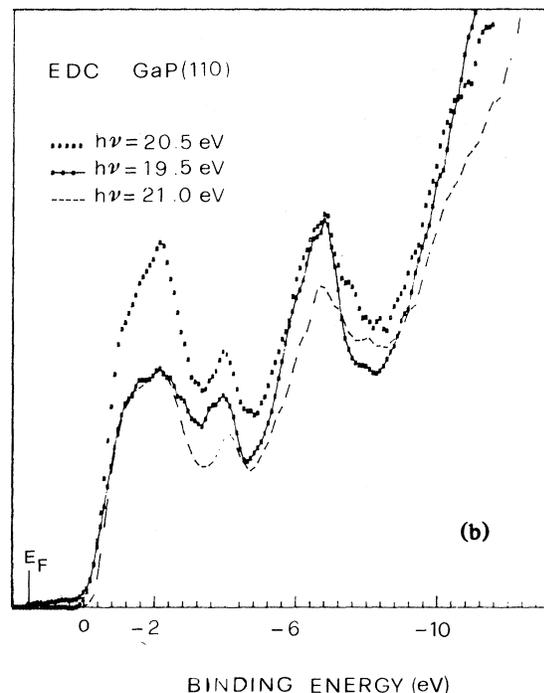
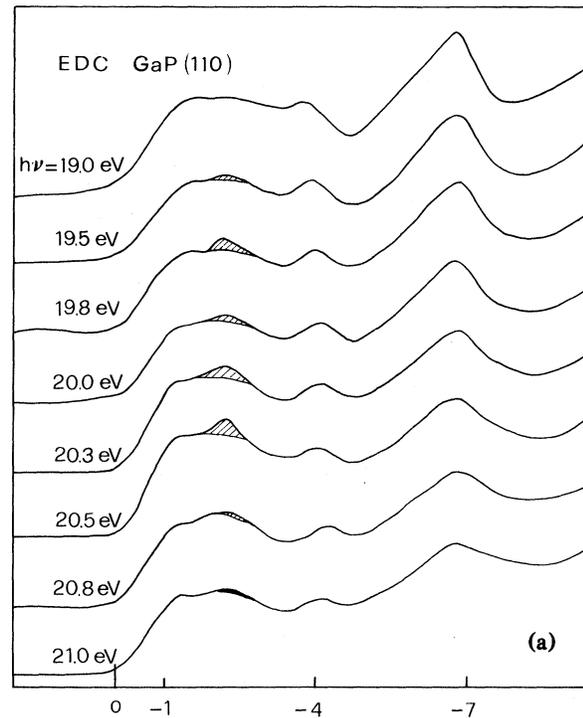


FIG. 3. (a) EDC's of GaP(110) for photon energies ranging through the values for the onset of the resonant processes. The major contribution to the resonance comes from states near -2 -eV binding energy and has been shaded in the figures. (b) Normalized EDC's for photon energies throughout the main resonance better evidencing the resonant process.

processes. The resonant enhancement is better evidenced by the normalized EDC's shown in Fig. 3(b) for photon energies throughout the main resonance. From Fig. 3(b) it is also clear that other states near the top of the valence band take part in the process. This is not surprising if we consider that different anion-derived (A_i) surface states have been theoretically predicted in GaP.¹⁶ In Ref. 16 the states A_5 , A_4 , and A_3 range between -0.7 and -3.2 eV from VBM. We attribute the major resonance contribution to the A_4 , P-derived $p_x p_y$ back-bond states between -1.7 and -1.1 eV,¹⁶ and to empty, Ga-derived surface states, 1.9 – 2.1 eV above the VBM.

The direct emission from Ga $3d$ levels for $h\nu = 30$ eV is reported in Fig. 4(a). Each $3d$ component was fitted with a Lorentzian convoluted with a Gaussian. The best fit gives the same full width at half maximum of 0.6 eV and the intensity ratio ($[Ga\ 3d_{3/2}]/[Ga\ 3d_{5/2}]$) is $R = 0.67$. The Gaussian line describing the broadening has a FWHM = 0.45 eV,¹⁷ and the Lorentzian intrinsic linewidth resulting from the fit is $2\Gamma = 0.30 \pm 0.05$ eV. The Ga $3d_{5/2}$ and $3d_{3/2}$ bulk binding energy are 18.4 and 18.9 eV. The surface $3d$ emission, not visible at these photon energies, has been found in an experiment more sensitive to the surface¹⁸ at 0.3 -eV higher binding energy. This places the final states for the surface transitions 1.1 eV above the VBM, and an excitonic shift of 0.8 – 1.0 eV is required to match this result with the theoretical energies of the final states.¹⁶ We attribute¹⁹ the pinning of E_F 1.5 eV above VBM (Fig. 3) to the lower edge of the empty surface band 1.53 eV above the VBM.¹⁶

In Fig. 4(b) we show the CIS spectrum for $E_i = -1$ eV (Fig. 2), after subtraction of the equivalent spectrum taken after deposition of 2 Å of silicon. We chose this initial state because no Auger emission is expected to contribute to the emitted electron intensity. Two differences are evident by a comparison of the Ga $3d$ direct emission and the valence resonant emission: a linewidth narrowing and an inversion

of the intensity ratio of the $3d_{5/2}$ and $3d_{3/2}$ components. This behavior indicates that we are observing a transition between localized states of excitonic character. While the direct emission linewidth is determined by the Auger decay of the valence electrons, the localized excitation of the electron core-hole pairs, observed in CIS, inhibits the Auger decay with an increase of the hole lifetime.²⁰ Moreover, the interaction between the core exciton states and the autoionizing continuum gives an asymmetric Fano line shape at the resonance.²¹ In fact, a best fit to the experimental data was obtained with the sum of two Fano line shapes convoluted with a Gaussian instrumental response function (FWHM = 0.25 eV),¹⁷ separated by 0.5 -eV spin-orbit splitting. The Fano line shape is

$$I(\epsilon) = \frac{(q + \epsilon)^2}{1 + \epsilon^2}, \quad (1)$$

where $\epsilon = (E - E_0)/\Gamma$. Γ is the spectral half-width of the autoionized state, E_0 is the energy of the Ga $3d$ absorption transition, and q is a fitting parameter whose meaning can be deduced from Ref. 21. The best fit gives $q = 1.9$, $2\Gamma = 0.17 \pm 0.05$ eV, $E_0(3d_{5/2}) = 19.8$ eV, $E_0(3d_{3/2}) = 20.3$ eV, and $R = 2.3$. The background subtraction is not critical to the values of 2Γ and E_0 . The value $2\Gamma = 0.17 \pm 0.05$ eV for the enhanced emission must be compared with $2\Gamma = 0.30 \pm 0.05$ eV obtained from the fit of the Ga $3d$ direct emission. This comparison shows, beyond the experimental uncertainties, that the core-hole lifetime is strongly changed when the additional recombination channel is present. A narrowing of the core-hole lifetime in an excitonic transition has been predicted theoretically by Strinati, because of a reduction of the Auger decay by dynamical screening effects.²⁰ In the case of GaP we have proved that the core-hole exciton lifetime is mainly determined by the direct recombination channel and that the Auger channel is practically suppressed. This should be taken into account in

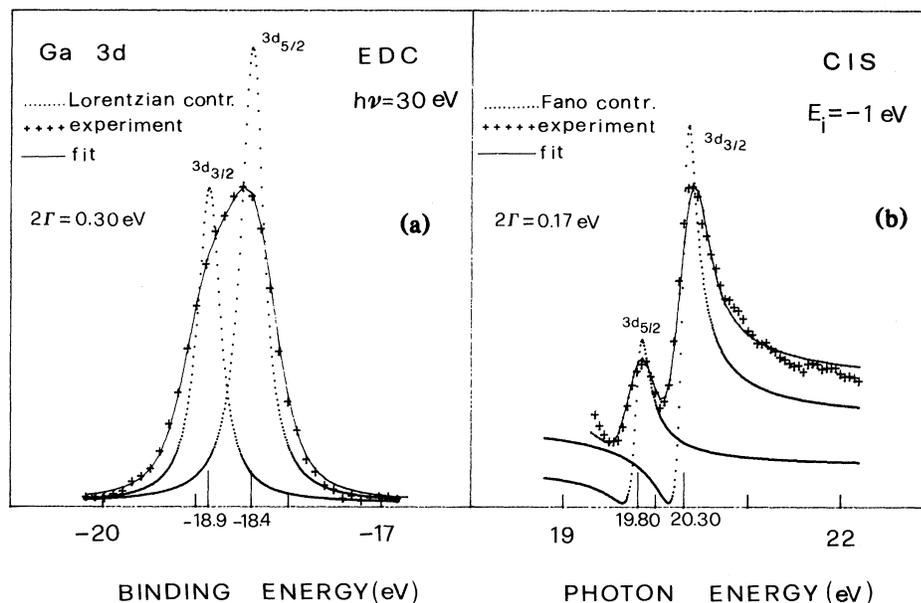


FIG. 4. (a) EDC of Ga $3d$ core levels for 30 -eV photon energy. The Lorentzian contribution ($2\Gamma = 0.30$ eV) to the best fit is shown. (b) CIS spectrum for initial binding energy $E_i = -1$ eV with the two-Fano-line contribution ($2\Gamma = 0.17$ eV) to the best fit.

theoretical calculations on materials like III-V compounds.

We shall now discuss the inversion of the intensity ratio between the $3d_{3/2}$ and the $3d_{5/2}$ components with respect to the direct emission value [$R = 0.67$, Fig. 4(a)] in CFS and CIS spectra of Fig. 2. The R inversion is due to the presence of the Coulomb exchange interaction between the localized states participating in the process, resulting in an intermediate coupling between LS and JJ .²² In the CFS spectrum the intensity ratio is equal to 1.7, while in the CIS data R ranges from 1.0 to 2.5 for different initial states as derived from the best fits of the curves of Fig. 2.²³ In a resonant process the observed statistical ratio is determined by the optical excitations and the direct recombination mechanism. The different R values observed for different initial states in CIS data is caused by the different localization of the valence orbitals involved in the deexcitation mechanism. The R value of the CFS spectrum is a weighted average value which derives from the contribution to the

secondary yield of all resonant valence states. The largest intensity ratio inversion occurs for $E_i = -2$ eV, confirming the high localized nature of the states which give the major contribution to the enhanced emission. This result also supports the interpretation of the only strong feature (at 3.5 eV) in the optical data,²⁴ which show transitions from the filled surface states at -2 eV to the first empty surface states.

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