Photoelectric Emission and Interband Transitions of GaP

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The photoelectric yield spectrum and energy distributions of the emitted electrons have been measured at photon energies between 3.0 and 6.0 eV on the (110) surface of GaP. Preparation of the emitting surfaces included cleavage in ultrahigh vacuum and deposition of various amounts of cesium. The results are interpreted in terms of direct optical transitions and compared with other optical properties. Photoelectric emission furnishes evidence supporting the interpretation of reflectivity data by Bergstresser *et al.*, and Woolley *et al.*, and the electro-reflectance studies of Cardona and co-workers. Good agreement is found with the band structure of GaP computed by Cohen and Bergstresser.

I. INTRODUCTION

PHOTOELECTRIC emission is the escape into vacuum of electrons excited by absorbed light to energies higher than the potential barrier at the surface of the emitter. It is thus related to other optical properties involving interband transitions[1] such as reflectivity or absorption coefficient and like them can be used for the determination of the band structure of crystals.[2,3] Photoelectric emission has the advantage that it distinguishes between optical transitions to states above and below the surface barrier (which can be changed by deposition of various amounts of cesium) and furthermore, allows measurement of the energy distribution of the emitted electrons. Thus, it not only determines the excitation energy $h\nu = E_f - E_i$ but in many cases yields the energy of the final (E_f) and initial (E_i) states of the transitions.

The two quantities measured in photoelectric emission experiments are the yield spectrum $Y(h\nu)$ or number of electrons emitted per absorbed photon, and the energy distributions dY/dE of the emitted electrons at various photon energies. Important transitions to states well above the potential *in vacuo* will increase the photoelectric yield and produce a peak in the energy distribution at the energy E_f; on the other hand, an accumulation of transitions to levels below the vacuum potential will cause a dip in the yield spectrum at the corresponding photon energy. Good agreement is generally obtained between the measured[3,4] and calculated values[5] of the spectral dependence of the photoelectric yield and of the imaginary part of the dielectric constant ϵ_2 assuming direct transitions. The agreement between the measured and the calculated energy distributions is in general poor. Kane[6] was able to improve this agreement by accounting for the effects of energy losses and group velocity of the excited electrons on their way towards the surface. These effects were found to exert considerable influence on the shape of energy distribution curves. Offsetting these complicating effects, the interpretation of measured energy distributions is aided by the fact that energy losses due to scattering of the excited electrons do not depend on the photon energy. Consequently, peaks in the distributions which appear only in a limited photon-energy range can be ascribed to optical transitions.

The present work reports on photoelectric emission measurements on two GaP crystals of different purity. The results are discussed in terms of the band structure computed by Cohen and Bergstresser[7] and compared with reflectivity data, in particular those obtained with the system Ga(As,P) by Bergstresser, Cohen, and Williams[8] and by Woolley, Thompson, and Rubenstein.[9]

II. EXPERIMENTAL METHOD

The measurements reported here were carried out with the equipment of Allen and Gobeli, described elsewhere.[10] In short, the experimental setup consists of a Pyrex vacuum tube with a quartz window through which uv radiation from a Bausch and Lomb 500-mm grating monochromator equipped with a mercury-arc or hydrogen-discharge source is admitted. The sample surface is prepared by cleavage in a vacuum of 1×10^{-10} Torr and subsequent coverage with the desired amount of cesium.[11] For the measurements of the total yield the current is measured at the sample while all other components of the tube are maintained at collecting potential. Total-energy distributions are measured with the retarding-field method. The electron-retarding electrode consists of a cylindrical mesh enclosure covered with an evaporated film of gold.

The GaP samples used in this work were epitaxially grown by Frosch.[12] The first crystal was *n*-type, with

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[4] F. G. Allen and G. W. Gobeli, Phys. Rev. **144**, 558 (1966).
[5] D. Brust, Phys. Rev. **134**, A1337 (1964).
[6] E. O. Kane (to be published).
[7] M. L. Cohen and T. K. Bergstresser, Phys. Rev. **141**, 789 (1966).
[8] T. K. Bergstresser, M. L. Cohen, and E. W. Williams, Phys. Rev. Letters **15**, 662 (1965); E. W. Williams and C. Jones, Solid State Commun. **3**, 195 (1965).
[9] J. C. Woolley, A. G. Thompson, and M. Rubenstein, Phys. Rev. Letters **15**, 670 (1965).
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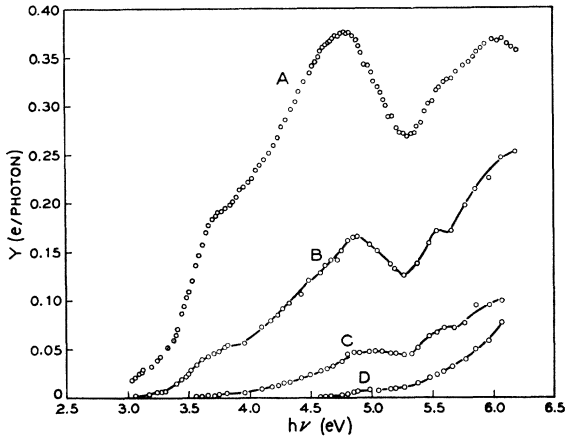

FIG. 1. Photoelectric yield of GaP covered with various fractions of a monolayer of cesium. Y is the number of electrons emitted per absorbed photon.

a resistivity of 100 Ω cm. It contained enough internal strain to prevent the exposure of a high-quality surface by cleavage. Observation with an optical microscope revealed the presence of many steps and evidence of concoidal fracture rather than cleavage on part of the surface. The second crystal was free of strain so that a cleavage face with a low density of steps could be obtained. The electrical resistivity of the second sample was too high to be measured with standard techniques ($\rho \gtrsim 10^{12}$ Ω cm). Special care had to be taken to avoid a potential difference along the sample due to the emitted current. Such a potential drop would prevent measurements of the energy distributions by the retarding potential method. Sufficient conductivity of the sample was achieved by diffusing in Zn at 800°C for 23 h. This procedure produced a highly conductive, p-type skin. Cleavage then resulted in a high-resistivity surface with a p-type border. Conductivity from the conductive layer to the emitting (uv-irradiated) part of the sample was ensured by flooding the surface with light whose photon energy ($h\nu = 3.0$ eV) is high enough for photoconductivity[13] and still below the threshold of photoelectric emission. This light produced a photo-emf between the doped and undoped parts of the crystal; the use of a stable dc power supply for the lamp avoided variations of this emf with time and a high intensity of the 3.0 eV light made the potential difference independent of the amount of emitted current. In addition, the energy distributions measured on the second sample were compared with the results from the first crystal ($\rho \approx 100$ Ω cm) where no such effects were expected. Reproducibility of the data from one sample to the other was good.

III. EXPERIMENTAL RESULTS

The photoelectric yield from the high-purity sample of GaP covered with various amounts of cesium is shown in Fig. 1. The yield is measured in electrons emitted per absorbed photon; correction for the reflected light was made using the reflectivity spectrum measured by Philipp and Ehrenreich.[14] Curve A was obtained from the surface with the lowest achievable work function, ($\varphi = 1.3 \pm 0.1$ eV). This yield curve was measured using the continuous light spectrum of a hydrogen lamp; curves B, C, and D were obtained with the more intense mercury arc. Figure 2 contains the energy distributions of the emitted electrons corresponding to yield curve A of Fig. 1. These distributions are normalized, i.e., the area under each curve is equal to the yield at the particular photon energy. The abscissa of Fig. 2 shows the energy of the electrons with respect to the Fermi level; this is the energy measured with the retarding-field method once the work function of the collector is known. The latter is determined by the well-defined low-energy limit of the distributions from a clean sample of known work function (in our case a Si crystal measured under the same conditions). Figure 3 shows the same energy distributions displaced towards lower energies by the amount of the photon energy $h\nu$. This representation emphasizes the initial states of the electrons. The results shown in Figs. 1 to 3 were chosen because more detailed measurements were performed on the high-purity sample. The photo-emission properties of the 100-Ω cm crystal are very similar and reproduce all the structure to be discussed in Sec. 4.

Direct information about the optical transitions and the band structure of the crystal is contained in the "internal energy distributions" $dN(E')/dE'$ which we define as number of electrons excited to the energy E' by the optical transition. The energy E' is measured relative to a fixed point in the band structure [e.g., the top of the valence band $E(\Gamma^v_{15})$]. Before we can interpret the measured distributions of Fig. 2, we must

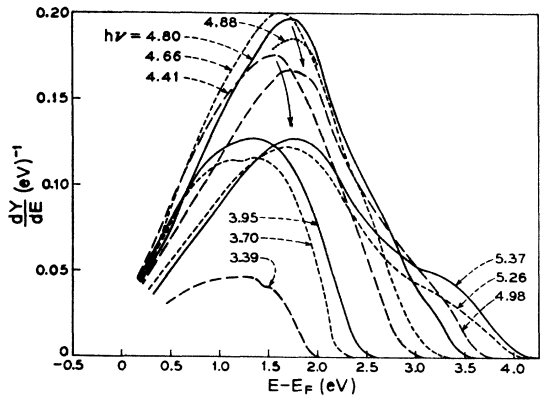

FIG. 2. Normalized energy distributions of the photoemitted electrons measured with curve A of Fig. 1. The abscissa represents the energy E of the electrons with respect to the Fermi level E_F. Each curve is labeled according to the photon energy producing it.

[13] H. Montgomery (private communication).

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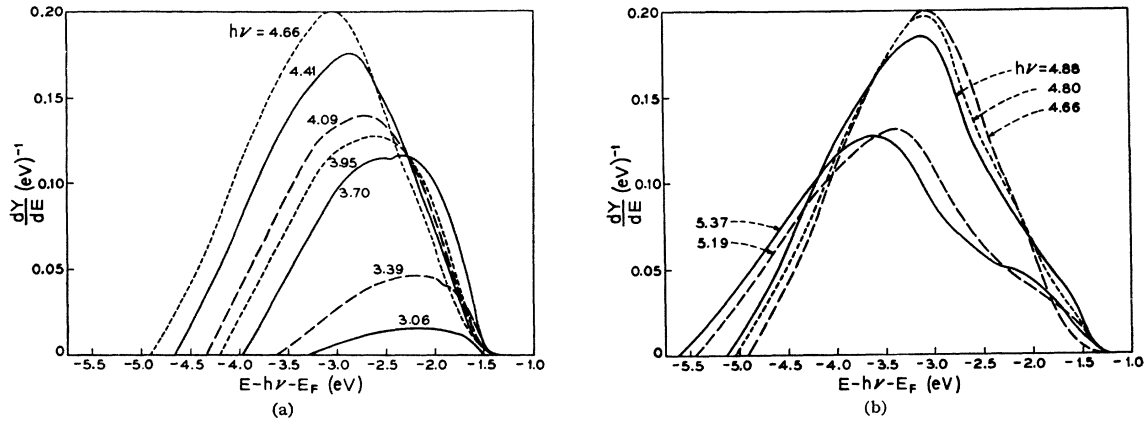

FIG. 3. Normalized energy distributions of photoemitted electrons from GaP. These are the same distributions as in Fig. 2 but displaced towards lower energies by $\Delta E = h\nu$. The abscissa $E - h\nu - E_F$ then represents the initial state with respect to the Fermi-level E_F. (a) Distributions for $h\nu \leq 4.66$ eV, (b) $h\nu \geq 4.66$ eV.

evaluate how these internal distributions are deformed during the migration of the electrons to the surface, the escape into vacuum, and the measuring procedure. We shall discuss briefly the effects of band bending, electron scattering, surface barrier, and fringe fields at the edge of the cleaved surface.

It is well known that surface and space charges can produce bending of the bands close to the surface. The final energy E' of a transition will be spread by the amount of the band bending which takes place over the depth from which most of the electrons originate; any structure in the "internal distribution" dN/dE' will be broadened by this amount in the measured distributions dY/dE. In the case of Si and Ge, deposition of a monolayer of Cs moves the bottom of the conduction band close to the Fermi level at the surface.[3,4,15] One might expect the same to hold true for GaP but we will present evidence that the Cs-covered surface of GaP is near intrinsic. In Fig. 3 the high-energy ends of all energy distributions coincide at approximately 1.40 eV below the Fermi level. The high value of the photoelectric yield indicates that the electrons excited to states near the high-energy limit originate from the top of the valence band rather than from impurity or surface states. Since the energy gap of GaP is $Eg = 2.24$ eV, the bottom of the conduction band E_c then lies $2.24 - 1.40 = 0.84$ above the Fermi level. The same result was obtained with the 100-Ω cm n-type sample, in which the bottom of the conduction band in the bulk is less than 0.3 eV above the Fermi level. Consequently the position of the bands with respect to the Fermi level as it is determined from Fig. 3 is characteristic of the cesium-covered GaP surface and not of the bulk (since the latter is more n-type than the former). The crystal on which the results in Figs. 1 to 3 were measured was compensated with a density of acceptors and donors of the order of 10^{15} cm^{-3}.[16] With the Fermi level as far as 0.84 eV from the nearest band at the surface and an impurity content of 10^{15} cm^{-3} no appreciable bending of the bands is expected over the penetration depth of the light (<100 Å for $h\nu \approx 5$ eV).[17]

Kane[6] has discussed how energy losses suffered by the electrons during their migration to the surface affect the energy distributions. In semiconductors the excited electrons lose energy mainly through collisions with phonons or with valence electrons (electron-hole pair production). Pair production decreases the photoelectric yield because the electron loses enough energy to prevent it from escaping into vacuum. We do not expect this scattering mechanism to be efficient in the present case ($h\nu \leq 6.2$ eV) because of the large value of the energy gap of GaP ($Eg = 2.24$ eV) In the absence of pair production the excited electrons can suffer many collisions with phonons before escaping. Kane has shown that in this case energy dependence of the scattering time and the group velocity exert considerable influence on the shape of the energy distributions. Another consequence of phonon scattering is an enhanced probability of escape because electrons reflected by the surface can be scattered back to it many times until they escape. In this connection it is worth pointing at the very high photoelectric yield of Cs-covered GaP (Fig. 1).

The most severe cause of error affecting the measurement of the energy distributions in our case is the electric field existing at the edges of the cleaved face because of the difference in the work functions between the cesium-covered cleavage plane ($\varphi \approx 1.3$ eV) and the oxide- covered side faces ($\varphi > 4.5$ eV). Such fringe fields result in a potential wall in the vacuum which the electrons must overcome before they can be collected. This potential wall will have no effect as long as it is lower than the potential just outside the analyzing collector. Distortions will appear when the analyzing potential of the collector is more positive than the potential due to

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[16] C. J. Frosch (private communication).
[17] G. Harbeke, in *Festkötperprobleme* (Vieweg und Sohn, Braunschweig, 1964), Vol. 3, p. 13.

fringe fields. In this case the actual energy of the electrons is higher than measured. In Fig. 2 the measured energies extend down to approximately $E-E_F=0$ while the true energy of the electrons cannot be lower than the work function $E-E_F \geq \varphi = 1.3$ eV. Usually the influence of the fringe fields is reduced by closely surrounding the sample with an electrode at collector potential. Typical errors at the low-energy extremity of energy distributions are less than 0.5 eV.[4,18] In the present work, however, the available GaP samples were less than 1 mm thick as compared to 2.5 mm for the other materials. Since these measurements were performed in the same vacuum run without transformation of the cage, the error at the low-energy end of the distributions is very large.

Band-bending, scattering, and fringe fields can introduce enough changes and errors so that great care must be used in extracting information about optical trantions from Figs. 2 and 3. The interpretation is helped by the following arguments: (1) All three mechanisms depend only on the final energy of the electrons; they are independent of the exciting light. If, therefore, a peak in dY/dE appears in a limited spectral range only it can be attributed to optical transitions. (2) Scattering and fringe fields result in a lowering of the real or apparent energy of the electrons with respect to the final state of a transition. Thus any structure visible in Figs. 2 and 3 represents a lower limit to the final state. Conclusions to be drawn from the structure at the high-energy ends of the distributions are little affected by the various distortions.

The most prominent peak in the energy distributions ($E-h\nu \approx 1.5$ eV in Fig. 2) should not be considered a real peak in the density of states. It merely reflects that the number of excited electrons increases but the probability of escape decreases with lower energies. However, we consider the wavelength-dependent structure appearing on top of this peak around $h\nu=4.9$ eV as real. Its coincidence with the peak is probably accidental.

IV. DISCUSSION

In this section we shall compare the experimental results presented above with other optical properties involving interband transitions; we shall restrict ourselves to the recent reflectivity measurements of Bergstresser *et al.*[8] and of Woolley *et al.*,[9] and the electro-reflectance data of Cardona and co-workers[19] which contain adequate reference to previous work. We shall see that the yield spectrum and energy distributions provide experimental evidence which supports the conclusions of these authors and agrees with the energy-band structure computed by Cohen and Bergstresser.[7] The reflectivity spectrum of GaP contains peaks at $h\nu=3.7$, 4.8, and 5.35 eV which are attributed to transitions at critical points along the [111] direction (Λ or L), at the center (Γ), and at the [100] boundary (X) of the Brillouin zone, respectively.

The peak in R at $h\nu=5.35$ eV is due to transitions from the valence band (X_5^v) into the minimum of the conduction band (X_1^c) at $\mathbf{k}=(2\pi/a)(1,0,0)$. Such a transition is expected to produce a dip in photoelectric yield because its final state lies below the vacuum potential even for the lowest work function. The X_5^v-X_1^c assignment is confirmed by the yield spectrum (Fig. 1) which has a sharp minimum at 5.28 ± 0.02 eV. The transition into the minimum of the next higher conduction band, X_3^c, is weaker than the former, (X_5^v-X_1^c), because the density of states at X_3^c is smaller than at X_1^c. It is usually not observable in the reflectivity spectrum. Since the theoretical value[7] of the X_1-X_3 splitting is 0.4 eV, we expect a weak dip in the yield spectra around $h\nu=5.70$ eV. Such a dip is observable on curves A, B, and C (Fig. 1) at 5.66 ± 0.01 eV; thus our experimental value for the X_1-X_3 splitting is 0.38 ± 0.03 eV. The dip is weaker on curve A (Fig. 1) than on curves B and C because the low work function allows a greater fraction of the electrons to be emitted.

A small peak in reflectivity[8,9] at 4.8 eV and a spin-orbit split doublet at approximately the same wavelength in electro-reflectance[19] suggest a critical point near the center of the Brillouin zone. We shall see that photoelectric emission, while it confirms this particular transition, displays a more complex behavior in this spectral range. We shall first discuss the critical point near Γ. A transition originating from the top of the valence band should produce an enhancement at the high-energy end of the energy distributions plotted in the way shown in Fig. 3(b). Indeed we observe a peak extending from $E-E_F-h\nu=-1.8$ eV to -1.4 eV which is strongest for $h\nu=4.88$ eV. (It is also observed, somewhat weaker, in the distributions for $h\nu=4.75$ eV and 4.98 eV not shown to avoid overloading the figure.) We estimate the threshold for the appearance of this peak at $h\nu=4.7\pm0.02$ eV. This high-energy peak presents direct experimental evidence for a transition at or near Γ. However, we see from the energy distributions that this transition contributes but a small fraction of the peak in photoelectric yield (Fig. 1) at $h\nu=4.8$ eV. The major part of this peak is made up of electrons excited to lower final states (see Figs. 2 and 3). The amplitude of the corresponding low-energy "peak" in Figs. 2 and 3 reaches its maximum at $h\nu=4.66$ eV. A similar behavior was observed with InP[18]: a weak shoulder in reflectivity coincided with the maximum of the low-energy-electron contribution to the yield and a transition at Γ. The broadness of this low-energy peak (even accounting for the broadening due to fringe fields) in Figs. 2 and 3 and the high value of the corresponding photoelectric yield ($Y \approx 37\%$ at $h\nu=4.8$ eV) suggest that the peak in Fig. 1 is not due to one critical point but to transitions to the lower conduction band in a large fraction of the Brillouin zone. However, there

[18] T. E. Fischer, Phys. Rev. **142**, 519 (1966).
[19] K. L. Shaklee, M. Cardona, and F. H. Pollak, Phys. Rev. Letters **16**, 48 (1966).

is evidence of the presence of a critical point with low final energy superimposed on the broad peak in Fig. 2. If we observe carefully the shape and position of the maxima in dY/dE for $h\nu=4.66-5.37$ eV occurring at $E-E_F\approx1.7$ eV in Fig. 2, we find that the energy distribution for $h\nu=4.98$ eV has the shape of a double peak. The maxima of the distributions (Fig. 2) for $h\nu<4.98$ eV, occurring at $E-E_F=1.6$ eV for $h\nu=4.66$ eV, at 1.75 for $h\nu=4.80$ eV, and at 1.80 eV for $h\nu=4.88$ eV, extrapolate naturally to the higher energy component (at $E-E_F\approx1.90$ eV) of the double peak for $h\nu=4.98$ eV (arrow in Fig. 2). The lower energy maximum which appears at $E-E_F=1.65$ eV on $h\nu=4.98$ eV is probably the one which becomes the peak for higher photon energies. In view of the distortions caused by fringe fields (Sec. 3) we cannot determine the initial or final states of this structure with precision. Following the discussion of Sec. 3, however, we can set a lower bound to the initial state of this transition at 1.8 eV below the top of the valence band [see Fig. 3(b)]. We discussed in Sec. 3 that the low-energy peak was brought about by the probability of escape and not a peak in optical transitions. It is probable that the coincidence of the structure just described, which we consider real because of its $h\nu$ dependence, with the peak is accidental. We cannot at present offer an interpretation of this structure in optical transitions but we thought it worth pointing out the simultaneous appearance of this structure, the broad low-energy peak and the Γ transition in the context of Kane's[20] theoretical result showing the simultaneous appearance of transitions in several regions of the Brillouin zone in approximately the same spectral region as we found here (i.e., close to the X-point transition).

We shall now turn our attention to the structure in yield and reflectivity at 3.7 eV. The interpretation of this peak in the $Ga(As_{1-x}P_x)$ system[8,9] presents some difficulties. While the position of other peaks changes linearly with phosphorus content in the mixed crystals, the position of this peak is best represented in the plot of $h\nu$ versus x by a broken line which is usually indicative of a shift from one type of transition to another. On the As-rich side of the alloys, the reflectivity has a double peak whose splitting makes it easy to attribute it to a critical point along the (111) direction (L or Λ). With increasing P content the high-energy component of this peak weakens rapidly but Woolley *et al.*,[9] find it to follow the broken line and to extrapolate to the correct spin-orbit splitting for GaP. This finding is corroborated by the electro-reflectance studies by H. Shaklee *et al.*,[19] who are able to observe the doublet for x values in $GaAs_{1-x}P_x$ as high as 0.9. This evidence suggests that the critical point responsible for this peak moves along the [111] axis in k space as the phosphorus content x in the alloy is changed. Both the photoelectric yield spectrum (Fig. 1) and the energy distributions (Figs. 2 and 3) show prominent structure around $h\nu=3.7$ eV. The photoelectric yield on curves A and B displays a shoulder with threshold at $h\nu=3.4$ eV and a peak at $h\nu=3.68\pm0.02$ eV. The energy distribution for $h\nu=3.7$ eV [Fig. 3(d)] shows a strong peak due to electrons excited from states near the top of the valance band. However, this peak is different in two ways from the one we attribute to a Γ transition at $h\nu=4.88$ eV [see below and Fig. 3(a)]. First the high-energy limit of the peak at 3.7 eV lies below $E-h\nu-E_F=1.5$ eV, energy at which the Γ peak of $h\nu=4.88$ [Fig. 3(a)] is already important. Second, the peak at 3.7 eV is broader, extending down to $E-E_F-h\nu=-2.45$ while the Γ peak in the distribution at $h\nu=4.88$ eV covers the range from $E-h\nu-E_F=-1.8$ eV to -1.4 eV only. Our experimental results thus show that the transition responsible for the structure around $h\nu=3.7$ eV originates from states lying between 0.9 and 0.1 eV below the top of the valence band. This is compatible with the conclusions drawn from reflectivity and electroreflectance that the structure around $h\nu=3.7$ eV in optical properties is due to transitions in an extended region along the [111] direction in k space (Λ) but rules out a position of the critical point at the center (Γ) and/or the border (L) of the Brillouin zone.

[20] E. O. Kane, Phys. Rev. **146**, 558 (1966).

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