

## Al $L_{2,3}$ core excitons in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ studied by soft-x-ray reflection and emission

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The Al  $L_{2,3}$  soft-x-ray reflection and emission spectra of  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  have been measured for  $x$  between 0.17 and 1.0. The valence-band maximum was monitored via the emission spectra using a fit based on band-structure parameters. The dominant features in the reflection spectra are produced by the  $L_{2,3}$  core excitons. Since both the reflection spectra and emission spectra were obtained using the same soft-x-ray spectrometer, the energies of the excitons above the valence-band maximum are accurately obtained. The known values of the optical band gap, as a function of  $x$ , are then used to determine the core exciton binding energy. The core excitons are found to follow and lie above the conduction-band minimum by 0.3 eV as the Al composition changes. Our results are compared to various core exciton theories and to previous experiments.

### INTRODUCTION

The  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  alloy system has attracted considerable attention primarily due to its applications in high-speed digital optoelectronics. Both electrical and optical properties have been investigated by a number of research groups over the past few decades.<sup>1-5</sup> As a result the band structure near the band gap is known for all concentrations ( $0.0 < x < 1.0$ ). In particular, the complex dependence of the conduction-band minima on concentration, which determines the band gap, is well understood.

In this paper we investigate the nature of the Al  $L_{2,3}$  core exciton in  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  ( $0.17 < x < 1.0$ ). This core exciton is the electronic state which is bound by a core hole on the  $2p$  core excited state of the Al atom. We use soft-x-ray reflectivity and emission measurements near the  $L_{2,3}$  x-ray threshold to precisely locate the exciton state with respect to the band edges for concentrations in the range  $0.17 < x < 1.0$ , and compare the results with other experiments and theory. We particularly wish to determine if the exciton is a localized state bound within the band gap, or a quasilocated state which resonates with the conduction-band states. The study has additional interest because, in a simple model, the Al  $L_{2,3}$  core exciton is similar to a silicon impurity on an Al site in the  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  lattice, in that the effect of a core hole is similar to that of the additional nuclear charge on the Si impurity. We are thus able to examine the validity of the so-called  $Z + 1$  approximation for the core exciton problem.

The features of the band structure which determine the band gap may be understood by reference to Fig. 1, which shows the energy bands which define the band gap for both AlAs and GaAs.<sup>6</sup> The valence bands of the two compounds are very similar and only those of AlAs are plotted. Minima occur in the conduction band at the

Brillouin-zone (BZ) center ( $\Gamma$ ) and along the (100) and (110) axes near the  $X$  and  $L$  points. In  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  alloys, the band structure changes continuously from that shown for GaAs to that shown for AlAs as  $x$  varies from 0 to 1. The variation of the energy gap between the valence-band maximum at  $\Gamma$  and the three conduction-band minima has been determined by Lee *et al.* as a function of  $x$ .<sup>2</sup> These values were obtained from measurements of the electrical conductivity and Hall coefficients and theoretical calculation involving a three-band model (at  $\Gamma$ ,  $L$ , and  $X$ ). The energy gap for these points is well described by a quadratic function of  $x$ . For  $x < 0.4$  the conduction-band minimum at  $\Gamma$  is below the conduction band at the  $L$  and  $X$  points and the gap is direct. For  $x > 0.4$  the conduction band at  $X$  is below  $\Gamma$  and  $L$  in the conduction band, and the gap is indirect. Near  $x = 0.4$ , the three minima very nearly coincide. The calculated variations of the band gaps with concentration will be used later (Fig. 7) in the discussion of the exciton data.

The valence-band maximum for  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  is located at  $\Gamma(\mathbf{k}=0)$ , and is derived primarily from the  $p_{3/2}$  and  $p_{1/2}$  states as As atoms.<sup>1</sup> These bands can be accurately

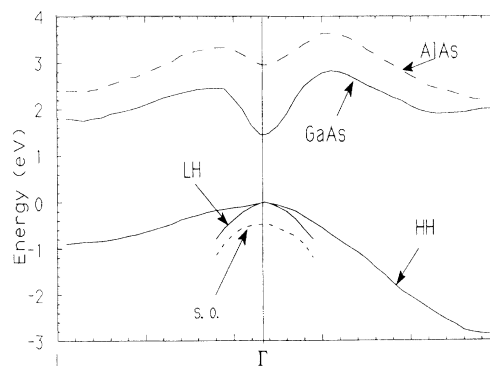


FIG. 1. Schematic band diagram of  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  near the band gap (from Ref. 6).

described in the effective-mass approximation. The  $p_{3/2}$  level is split into two bands, each doubly degenerate, and characterized by either a light or heavy effective mass. The  $p_{1/2}$  level is lower in energy by the spin-orbit energy, is doubly degenerate, and is characterized by its own effective mass. The three bands at the valence-band maximum are commonly referred to as the light- and heavy-hole bands, and the spin-orbit split band, respectively. We are not aware of any measurements of the effective masses or the spin-orbit splitting as a function of  $x$ . However, these values are known for AlAs and GaAs and Adachi<sup>1</sup> argues that a linear interpolation can be used to describe the three effective masses for the compound Al<sub>x</sub>Ga<sub>1-x</sub>As.

We are interested in determining where the core exciton fits into this band-structure picture. In other words, do the core excitons lie in the band gap or in the conduction band, and do they follow a point in the BZ as  $x$  changes? Hjalmanson, Buttner, and Dow<sup>7</sup> have developed a widely used theory of core excitons. In this theory both core and valence-band exciton states can be described. The valence-band exciton states are produced by the long-range screened Coulomb interaction of the electron-hole pair, while the core excitation is bound to a hole in a core level. In the so-called "optical alchemy approximation" a core excitation of an atom of atomic number  $Z$  may be regarded as an electronic state of a  $Z + 1$  impurity atom in the host at the  $Z$  atom site. Just as the impurity may generate either shallow or deep trap states, the core exciton may be of the extended Wannier type or it may be a localized Frenkel core exciton. According to Hjalmanson, Buttner, and Dow, core excitons lying very close to the conduction-band minima hybridize with the band-edge states, become delocalized, and may be described as Wannier excitons. Localized Frenkel states may have much larger positive or negative binding energies. The states with negative binding energies are resonant with conduction-band states and are referred to as Frenkel "resonances" by the author, though they are associated with experimental features identified as Frenkel excitons. For Al in AlAs, Hjalmanson, Buttner, and Dow<sup>7</sup> predict that the  $s$ -like core exciton states appear in the band gap (Fig. 2 in Ref. 7). In the one case where results for negative binding energies are cited,  $p$ -like Frenkel "resonances" are found near the  $X$ -minimum for Ga in GaAs and GaSb.

The theory of Hjalmanson, Buttner, and Dow<sup>7</sup> has been used to explain the anomalous broadening of the Si  $L_{23}$  core exciton in Si<sub>x</sub>Ge<sub>1-x</sub> alloys<sup>8,9</sup> at  $x = 0.15$ . This change in broadening was associated with a different final state in the exciton absorption. In Si<sub>x</sub>Ge<sub>1-x</sub> alloys at  $x = 0.15$ , there is a crossover in the conduction-band minimum from the  $L$  point of the Brillouin zone to the  $\Delta$  point. To ensure that the exciton appears in the band gap only for compounds with  $x = 0.15$  and thus explain their findings, Bunker *et al.* found that they needed to shift the predictions of the theory of Hjalmanson, Buttner, and Dow for the exciton energy upward by 0.13 eV, independent of composition. They argue that a shift of this magnitude is not surprising. An alternative explanation<sup>10</sup> suggests that this broadening is due to com-

petition between intrinsic broadening due to screening and extrinsic alloy broadening. Unfortunately, neither the theory of Hjalmanson, Buttner, and Dow nor the alloy broadening theory have been used to describe the Al  $L_{23}$  core exciton in Al<sub>x</sub>Ga<sub>(1-x)</sub>As.

In this paper we present new soft-x-ray emission and reflection data on the Al<sub>x</sub>Ga<sub>1-x</sub>As system. From these data we determine the binding energy of the core exciton using a model based on band-structure parameters. These results are discussed in terms of the theory of Hjalmanson, Buttner, and Dow and alloy broadening theories. Finally, we make a comparison with Si impurities in Al<sub>x</sub>Ga<sub>1-x</sub>As.

## EXPERIMENT

The Al<sub>x</sub>Ga<sub>1-x</sub>As samples were made at the Martin Marietta Laboratories-Baltimore by molecular-beam epitaxy with  $x = 0.17, 0.3, 0.4, 0.6,$  and  $1.0$ . The samples were grown as epitaxial layers of about  $2 \mu\text{m}$  thickness on single-crystal GaAs substrates. The epitaxial layers were doped with  $10^{18}/\text{cm}^3$  Si. Two of the samples,  $x = 0.17$  and  $1.0$ , were protected with a  $500\text{-\AA}$  GaAs cap which was removed with Chlorox immediately prior to vacuum insertion. The other samples were etched in a solution of  $4\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2/\text{H}_2\text{O}$  to remove any oxide layer immediately prior to vacuum insertion.

Measurements were performed on the soft-x-ray spectrometer, located on beamline U10A of the National Synchrotron Light Source, Brookhaven National Laboratory. This is a dedicated soft-x-ray emission (SXE) beamline employing both photon and electron excited SXE capabilities.<sup>11</sup> The spectrometer is a 5-m-radius toroidal grating instrument with Rowland optics. For these experiments a  $600 \text{ line/mm}$  grating was used. The input slit was set at  $40 \mu\text{m}$  corresponding to a resolution  $< 0.1 \text{ eV}$ . For the emission experiments  $2000\text{-eV}$  electrons were used to excite the spectra. For the reflectivity measurements a small fraction of the white light beam (power levels on the order of  $10 \text{ mW}$  were used) illuminated the samples at  $15^\circ$  off normal and the specularly reflected light was collected by the soft-x-ray spectrometer. For near normal incidence the reflectivity is governed by the following equation:

$$R = [(n - 1)^2 + k^2] / [(n + 1)^2 + k^2], \quad (1)$$

where  $n + ik$  is the complex index of refraction. For soft x rays we assume that  $(n + 1)^2 \gg k^2 \gg (n - 1)^2$ , so that the reflectivity is proportional to  $k^2$ . Within the same approximation,  $R$  follows  $\epsilon_2^2$ , where  $\epsilon_2$  is the imaginary part of the dielectric constant which is proportional to absorption. In this approximation the absorption is proportional to  $R^{1/2}$ . For a more complete discussion on the use of soft-x-ray reflectivity to determine  $\epsilon_2$  see Ref. 12.

Because the absorption coefficient is dependent on the unoccupied density of states, the electronic densities of states above and below the Fermi level could be determined with the same instrument. For comparison with the occupied density of states the soft-x-ray emission intensity as a function of wavelength,  $I(\lambda)$ , is converted to an energy scale [ $I(E) = I(\lambda)/E^2$ ] and further divided by

$E^3$  to account for the photon density of states. For the unoccupied density of states, the reflection intensity is converted from its measured wavelength dependence to an energy dependence and the square root is taken.

## RESULTS

Soft-x-ray emission and reflection spectra were taken for each of the samples  $x = 0.17, 0.3, 0.4, 0.5, 0.6,$  and  $1.0$ . A typical emission spectrum is shown in Fig. 2. In Fig. 3, the absorption spectrum is shown as a solid line along with the emission in the region of the exciton. These spectra have been converted into densities of states as described above. The absorption spectrum is for  $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$  and clearly shows the Al  $L_{2,3}$  spin-orbit splitting of  $0.43$  eV. We identify the doublet structure in the absorption spectrum as the core exciton. This is determined from a comparison of the absorption spectrum with the high-energy satellite appearing in the emission spectrum at  $75$  eV. This satellite has previously been identified as the Al  $L_{2,3}$  core exciton.<sup>5</sup> The absorption features have the same energy as the exciton emission. A core exciton would be expected to appear in both emission and absorption due to its localized nature. There may be a small shift in energy and some broadening in the emission due to phonon coupling, but it has been demonstrated that these effects are very small in semiconductors.<sup>13</sup> It should be noted, however, that the doublet is resolved in the absorption measurements but not in the emission.

The emission spectrum shown in Fig. 2 is for  $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$  and is similar to spectra previously published.<sup>4,5</sup> Hass has calculated the Al  $s$  local density of states (Al  $s$  LDOS) using a tight-binding, coherent-potential approximation calculation with an  $sp^3s^*$  basis.<sup>3</sup> The result is in excellent agreement with the measured Al  $L_{2,3}$  spectrum except that it underestimates the density of states near the top of the valence band. The low-energy ( $62$  eV) peak is due primarily to  $s$  orbitals located on As, the intense peak near  $67$  eV is due to hybrid combinations of  $s$  orbitals on the Al site with  $p$  orbitals on the As

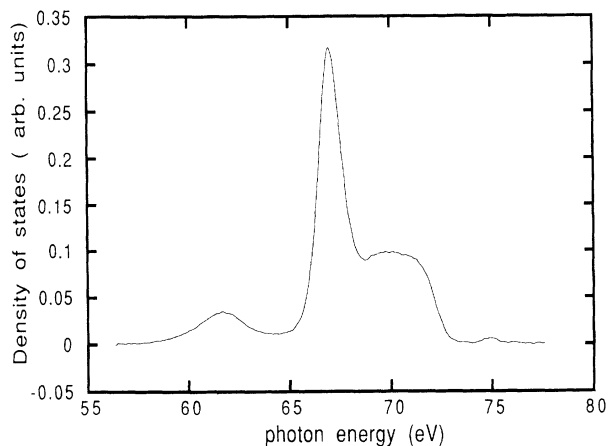


FIG. 2. Occupied density of states determined from soft-x-ray emission spectroscopy for  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ . The feature at  $75$  eV is the core exciton.

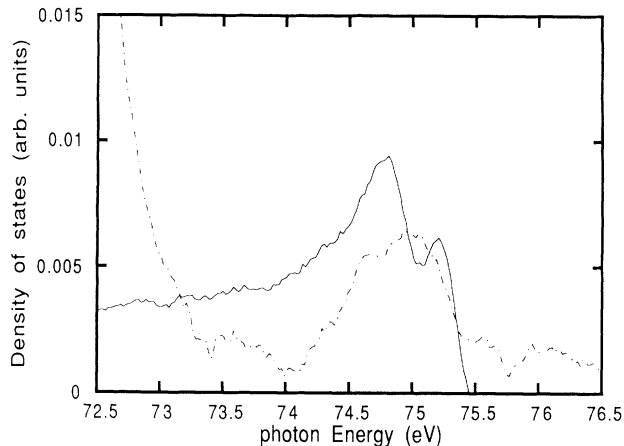


FIG. 3. Comparison of the core exciton as seen in absorption (—) and emission (---).

site and is thus the main feature in our dipole allowed  $L_{2,3}$  spectra. The region near the valence-band maximum ( $72$ – $73$  eV) is of particular interest in this paper because precise knowledge of the shape of the valence-band edge is required if the edge position is to be accurately determined. In the Hass calculation, the Al  $s$  LDOS is determined from the Al  $s$  orbitals of the  $sp^3s^*$  basis set and does not include contributions from the overlap of As orbitals onto the Al site. We believe that the Al  $s$  LDOS at the valence-band edge is due primarily to linear combinations of As  $p$  orbitals which have  $s$  or  $d$  symmetry about the Al site. Consequently the density of states near the valence-band edge should follow the total density of states which is determined at the band edge primarily by the As  $p$  orbitals.<sup>3,14</sup>

The emission spectra at the valence-band maximum were fit using the results of Adachi.<sup>1</sup> The densities of states were taken as proportional to  $m_{kk}^{3/2}(E_{\text{VBM}} - E)^{1/2}$  where for light holes  $kk = \text{LH}$ , for heavy holes  $kk = \text{HH}$ , and for spin-orbit holes  $kk = \text{s.o.}$  (see Fig. 1). The quantity  $E_{\text{VBM}}$  is the energy of the valence-band maximum. Adachi<sup>1</sup> gives the values for these effective masses as a function of  $x$  in  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  as

$$m_{\text{LH}} = 0.087 + 0.063x,$$

$$m_{\text{HH}} = 0.62 + 0.14x,$$

$$m_{\text{s.o.}} = 0.15 + 0.09x.$$

The same linear interpolation is used to determine the spin-orbit splitting,  $D_{\text{VB}}$ , in the valence band so that  $D_{\text{VB}}(\text{eV}) = 0.34 - 0.04x$ .

A value of  $0.43$  eV was used for the Al  $L_{2,3}$  spin-orbit splitting and statistical ratios were employed for the number of states in the two core levels. The data were fit to a model of the valence band by adjusting values of the valence-band maximum and the Gaussian broadening of the valence band until an optimum fit was obtained in the energy region between  $72$  and  $73.5$  eV. The accuracy of the fit was judged by eye. A typical fit to the data is presented in Fig. 4, for  $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ . The values of the

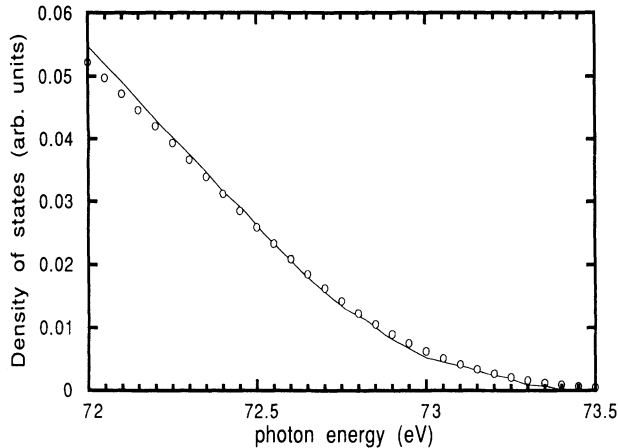


FIG. 4. Fit to the valence-band edge of  $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$  (circles). The fitting model and parameters used are described in the text. Measured emission data (solid line).

parameters used to fit a model curve to the data and our estimated probable error for the parameters are presented in Table I. In Fig. 5 we plot the energies of the valence-band maxima as determined by various fitting procedures. The solid triangles are based on the band-structure parameters in Table I; the solid circles are based on linear fits to our data; the open diamonds are taken from Ref. 5 and were obtained by linear fits to the data reported in that paper. The valence-band maxima are taken relative to the  $L_3$  core-hole transition energy. The trends in the value of the valence-band maximum are similar to those presented elsewhere.<sup>4,5</sup> It should be noted that the broadening is constant for the band-structure fits, but not for the linear fits. Thus the energy position of the band edge is the only variable that need be changed to fit all spectra in the region of the valence-band maximum.

The position of the  $L_3$  core exciton was determined from the position of the low-energy peak in the absorption spectra (solid line in Fig. 3). No model was employed to fit to the data due to the difficulty in interpreting the intensity at energies less than the exciton energy. The substantial signal below the exciton energy does not represent true absorption, but results from the contribution of the  $(n-1)^2$  term in Eq. (1). In this region, the absorption is reduced by an order of magnitude and  $(n-1)$

TABLE I. Values of valence-band maximum ( $E_{\text{VBM}}$ ) and Gaussian broadening (FWHM) found from fitting valence-band density of states as derived from soft-x-ray emission spectra of  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ . The energy of the core exciton is also shown.

$\text{Al}_x\text{Ga}_{1-x}\text{As}$	$E_{\text{VBM}}$ (eV)	FWHM (eV)	Core exciton (eV)
0.17	$72.67 \pm 0.02$	$0.7 \pm 0.1$	$74.54 \pm 0.03$
0.30	$72.56 \pm 0.02$	$0.7 \pm 0.1$	$74.69 \pm 0.03$
0.40	$72.47 \pm 0.02$	$0.7 \pm 0.1$	$74.71 \pm 0.03$
0.50	$72.45 \pm 0.02$	$0.7 \pm 0.1$	$74.73 \pm 0.03$
0.60	$72.40 \pm 0.02$	$0.7 \pm 0.1$	$74.73 \pm 0.03$
1.00	$72.36 \pm 0.02$	$0.8 \pm 0.1$	$74.73 \pm 0.03$

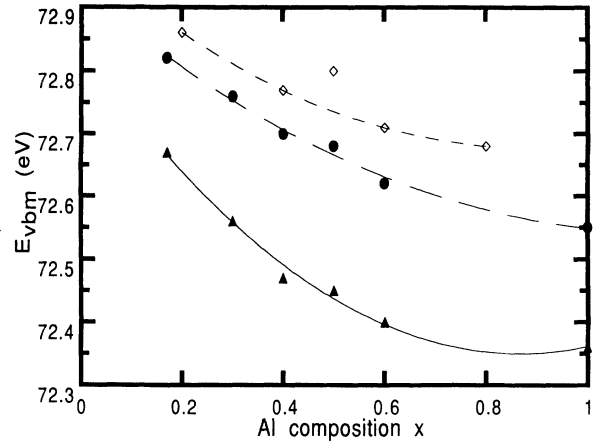


FIG. 5. Variation in the valence-band maximum vs  $x$  for fit based on band-structure parameters, solid triangles; based on linear fit to our data, solid circles; and from Ref. 5 using a linear fit, open diamonds. The lines are drawn as an aid to the eye.

is enhanced so that absorption no longer determines the reflectance spectrum. We have convinced ourselves, by employing different models to fit this spectral region, that this method of determining the exciton position is accurate within 0.03 eV for all reasonable assumptions. We did not obtain values for the broadening. The  $L_3$  core exciton energy as a function of the Al composition is presented in Table I and in Fig. 6.

The difference in energy between the valence-band maximum (obtained using a band-structure model) and the core exciton is plotted in Fig. 7 (circles) together with the energy gap for various high-symmetry points in the BZ. The energy gap data were taken from the work of Lee *et al.*<sup>2</sup> It is apparent that the core exciton follows the band gap, but lies above the conduction-band minimum by about 0.3 eV. This is in contrast to the behavior of the valence exciton, which also follows the band gap but lies within the gap.

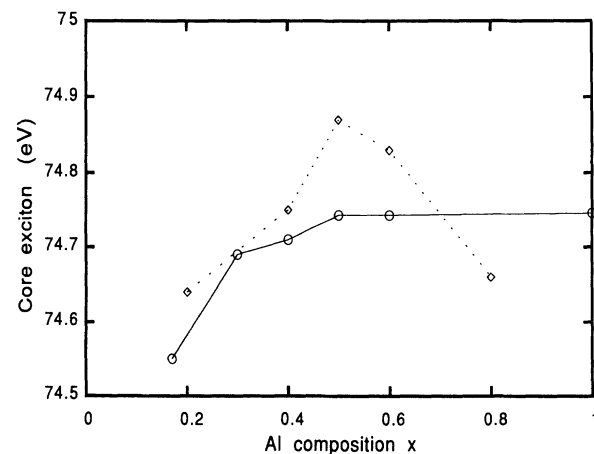


FIG. 6. Energy position of  $L_3$  exciton vs  $x$ : our results, circles, Ref. 5 results, diamonds. The lines are drawn as an aid to the eye.

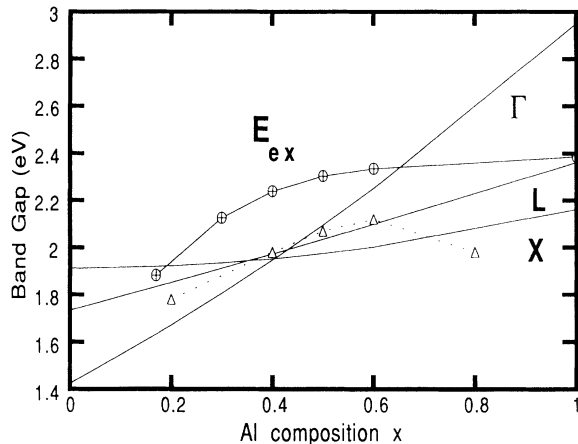


FIG. 7. Conduction-band energies at high-symmetry points in the BZ vs  $x$  compared with core exciton position relative to the VBM. The exciton follows the band gap but lies within the conduction band when using the band-structure model to fit the valence-band maximum, circles. The triangles represent the results from Ref. 5 which were determined from a linear fit to the valence-band maximum.

## DISCUSSION

Nithianandam and Schnatterly,<sup>5</sup> in a similar experiment, have measured the Al  $L_{2,3}$  soft-x-ray emission spectra of  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  as a function of  $x$ . They determined the position of the core exciton,  $L_3$ , by fitting the emission spectra near the band gap with a Voigt line shape using the statistical  $\text{Al } L_2:L_3$  ratio and a spin-orbit splitting of 0.4 eV. We compare their results (open diamonds) to ours (open circles) in Fig. 6. Nithianandam and Schnatterly<sup>5</sup> determined the valence-band maximum with a fit employing a linear function, the statistical ratio, and a spin-orbit splitting of 0.4 eV. The linear fit is justified as an approximation to a superposition of the  $(E_{\text{VBM}} - E)^{1/2}$  (allowed) and  $(E_{\text{VBM}} - E)^{3/2}$  (forbidden) shapes.<sup>5</sup> In Fig. 5 we compare the results from Ref. 5 for the energy of the valence-band maximum (open diamonds) to our results based on band-structure parameters (solid triangles) and a linear fit to our data (solid circles). The energies of the solid triangles are about 0.2 eV below those of the open diamonds, but the energies of the solid circles differ little from those of the diamonds. In Fig. 7 we compare the core exciton energy relative to the VBM obtained using a linear model in Ref. 5 (triangles) with our results obtained by using band-structure parameters (circles). The energies of the circles are all greater than those of the triangles. From Fig. 5 it is apparent that the difference between our results and those of Nithianandam and Schnatterly is due primarily to the method used to determine the position of the valence-band maximum.

The reason why the two models for obtaining the energy of the VBM yield different results is easily seen from Fig. 8. In this figure, the dots are experimental data for the valence-band edge of  $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ . Excellent fits to these data can be generated with either a linear fit or our band-structure parameters, plus Gaussian broadening terms. The solid line is the fit based on our band-

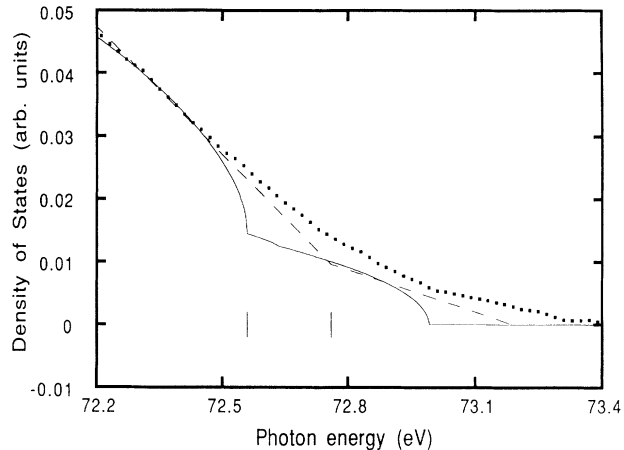


FIG. 8. Valence-band edge of  $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$  (solid squares), determined by two difference fitting procedures. The solid line is the fit obtained from a model based on band-structure parameters and gives the valence-band maximum at 72.56 eV. The dashed line is the linear fit and gives a valence-band maximum at 72.76 eV. Both procedures give excellent fits to the data when folded with Gaussian broadenings of 0.7 and 0.5 eV, respectively. They are presented here without the broadenings to illustrate the origin of the 0.2 eV difference in band threshold determined by the two methods.

structure parameters, plotted here without the Gaussian broadening of 0.7 eV. The dashed line is the linear fit plotted without a Gaussian broadening of 0.5 eV. The two models produce nearly indistinguishable fits to the data when the broadening terms are added, but lead to estimates of the position of the band edge that differ by 0.2 eV. This 0.2 eV is critical in determining the position of the core exciton relative to the conduction-band edge. It is also important to note that using the fit based on band-structure arguments we found a constant broadening of 0.7 eV full width at half maximum (FWHM). Using the linear fit we found a trend in the broadening versus  $x$  very similar to that found by Nithianandam and Schnatterly,<sup>5</sup> namely, larger broadenings (0.6–0.7 eV) for small and large  $x$  and smaller broadening (0.5 eV) for  $x$  near the crossover point,  $x = 0.4$ .

Information can be obtained from the broadening of the valence-band maximum and the exciton as a function of  $x$ . As mentioned above, Bunker *et al.*<sup>9</sup> have found an anomalously small broadening in the Si  $L_{2,3}$  exciton at the  $x = 0.15$  crossover point in  $\text{Si}_x\text{Ge}_{1-x}$ . This was explained by Bunker *et al.*<sup>9</sup> using the exciton theory of Hjalmarsen, Buttner, and Dow.<sup>7</sup> Another interpretation, based on competition between intrinsic broadening due to screening and alloy broadening, was given by Krishnamurthy, Sher, and Chen.<sup>10</sup> In this model the alloy broadening is greater for values of  $x$  near 0.5. The intrinsic broadening is dependent on the binding energy of the exciton, which in this model follows the  $X$  point. Above  $x = 0.15$ , the  $X$  point is the minimum and the binding energy is constant. Below the crossover point,  $x = 0.15$  where  $L$  becomes the minimum, the binding energy is reduced, and the broadening decreases. Thus for specific binding energies there can be a sharp decrease in the broadening at  $x = 0.15$ .

Unfortunately, we were unable to obtain sufficiently accurate values for the broadenings of the exciton in absorption for comparison to the ideas expressed in the preceding paragraphs. However, the broadenings at the valence-band maximum can be compared to the alloy broadenings predicted by Krishnamurthy, Sher, and Chen.<sup>10</sup> The alloy broadening, according to Krishnamurthy, Sher, and Chen, goes as  $x(1-x)$  and peaks at  $x=0.5$  with a value of 0.12 eV for  $\text{Si}_x\text{Ge}_{1-x}$ . With our fit based on band-structure parameters we found no change in the broadening as a function of  $x$ . Our sensitivity was on the order of 0.1 eV, suggesting that if the alloy broadening of  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  is of the same magnitude as that predicted for  $\text{Si}_x\text{Ge}_{1-x}$  we may not have been sensitive to the changes. On the other hand, the broadenings found by us and Nithianandam and Schnatterly for the *linear fit* varied by a few tenths of an eV but had the narrower widths at  $x=0.5$  with greater widths at smaller and larger  $x$ . This is in contradiction to the alloy broadening model and lends some support to the fit based on band-structure parameters.

In our soft-x-ray emission experiment we probe the local density of states at the Al atom site having *s*- or *d*-type symmetry. By employing the band-structure model, we assume that the  $\text{Al}(s+d)$  LDOS follows the total density of states near the top of the valence band. We are not aware of any calculations which compare the  $\text{Al}(s+d)$  LDOS with the total density of states near the valence-band maximum. A main component to the *Al s, d* LDOS is states which are linear combinations of As *p* orbitals with effective *s* or *d* symmetry about the Al.<sup>4</sup> As stated earlier, these states with effective *s* or *d* symmetry should have behavior near the valence-band maximum similar to that of the As *p* orbital from which they are derived. The behavior of the  $\text{Al}(s+d)$  LDOS near the valence-band maximum must be addressed theoretically before our interpretation can be established with complete confidence.

Our results, which show the Al  $L_{2,3}$  core exciton to have a negative binding energy, do not agree in detail with the calculations of Hjalmarson, Buttner, and Dow.<sup>7</sup> Their theory predicts that the *s*-like Al  $L_{2,3}$  core exciton is within the band gap for AlAs. This is not what we determine experimentally. It should be noted, however, that the theory of Hjalmarson, Buttner, and Dow is best suited to predict chemical trends and that the Al exciton position is predicted to be near the crossover point between being resonant with the conduction band and being in the gap in AlAs.<sup>7</sup> Thus we feel that the disagreement

between our results and the theory of Hjalmarson, Buttner, and Dow is not necessarily significant.

In a simple model, the Al core exciton can be approximated by a Si impurity in the  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  host. The energies of the Si impurity levels in  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  are well known.<sup>15</sup> They are found to follow the *L* point and lie below it by about 0.1 eV. Our results show the Al core exciton to lie in the conduction band but roughly follow the band gap. Clearly, this simple comparison of a core exciton with its neighbor on the periodic chart breaks down here. A major difference between the Al core exciton and the Si impurity is lattice relaxation around the impurity. In our measurements we assume that the core exciton decays before the lattice relaxes. In contrast, the binding energy of the silicon impurity is modified by lattice relaxation around the impurity. Li and Myles<sup>16</sup> calculated the effects of lattice relaxation on the binding energies of impurities in semiconductor hosts using a model based on Pauling radii. They found significant improvement over the theory of impurities of Hjalmarson *et al.*<sup>17</sup> when taking into account this relaxation. It is difficult to see, however, how lattice relaxation effects alone can account for the very different dependence of the binding energies of the Si impurity and the core exciton on the Al concentration.

In conclusion, we have presented soft-x-ray emission and reflection data from  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  compounds. The position of the core exciton relative to the band gap was found by fitting the edge of the valence band with a model based on band-structure parameters. The core exciton was found to lie in the conduction band, 0.3 eV above the conduction-band edge. The model used to fit the valence-band edge was found to be critical in obtaining these results. The broadening behavior of the different fits supported the use of the fit based on band-structure parameters. A comparison with silicon impurity information suggests that lattice relaxation alone cannot account for the differences between the Al core exciton and a Si impurity.

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