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# ENERGY BANDGAP AND LATTICE CONSTANT CONTOURS OF III-V QUATERNARY ALLOYS*

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Energy band gap and lattice constant contours are presented for the nine quaternary alloys formed from Al, Ga, In and P, As, Sb. The quaternary bandgaps were obtained using an interpolation formula proposed by Moon et al. The quaternary lattice constants were obtained by use of a linear interpolation technique using the binary lattice constants as boundary values.

Key words: quaternary alloys, bandgap, lattice constant.

## Introduction

There has been considerable interest in the quaternary III-V semiconductor materials for many applications, such as electro-optics and microwave devices [1-6]. One significant reason for this interest is the ability to synthesize materials with a fixed lattice constant and a variable range of energy bandgaps or, conversely, to synthesize materials with a constant energy bandgap and a variable lattice constant [7].

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In order to predict the energy bandgap or lattice constant for a quaternary material a two-step sequence is involved. Initially, it is necessary to have available experimental (or theoretical) values of these material parameters for the four possible binary III-V constituents of the quaternary compound. These values are readily available for most III-V materials in the literature [8]. There are also four possible ternary (pseudobinary) III-V systems in a given quaternary compound. In the first step, the energy bandgap and lattice constant as a function of alloy composition for each ternary system is computed from the known binary material parameters. This computation is on a good experimental and theoretical basis [9-13] involving the use of Vegard's law and the concept of the "bowing parameter" for the energy bandgap [14]. The final step involves the use of the compositional dependence of the energy bandgap and lattice constant for the four ternary combinations to interpolate to the desired quaternary energy bandgap and lattice constant. This final interpolation step is somewhat empirical in nature. There appear to be several such interpolation techniques used in the literature [6,7,15] and while these are similar, they also have non-trivial differences. This paper will discuss this critical interpolation procedure in view of the small amount of experimental quaternary data, and will present calculations for energy bandgaps and lattice constants for the nine quaternary alloys formed from Al, Ga, In and P, As, Sb using one of these interpolation techniques.

## Notation

There appears to be no generally-accepted scheme for symbolically describing the III-V quaternary alloys. In this paper the following convention has been adopted. Within both the group III and group V pairing, the first position is occupied by the element with lowest atomic number. The composition variables are associated with the four elements in the order 1-x, x, 1-y, y. For example, a quaternary alloy will be denoted as $A_{1-x}B_xC_{1-y}D_y$. Here A and B are group III elements with A having lower atomic number than B. Likewise, C and D are group V elements with C having lower atomic number than D. Following previous authors [6,7], a quaternary alloy parameter (e.g., bandgap or lattice constant) is described by a surface Q(x,y) over

the x,y composition plane ($0 \leq x \leq 1$, $0 \leq y \leq 1$). At the corners (x and y equal to zero and/or one) the values of the parameter for the four binary elements $Q(0,0) = B_1$, $Q(1,0) = B_2$, $Q(1,1) = B_3$ and $Q(0,1) = B_4$ are obtained. Along the boundaries of the plane the parameter for the four ternary elements $Q(x,0) = T_{12}(x)$, $Q(1,y) = T_{23}(y)$, $Q(x,1) = T_{43}(x)$ and $Q(0,y) = T_{14}(y)$ are obtained.

## Estimation of Alloy Parameters

Many ternary alloy parameters (e.g. lattice constant) are obtained by linear interpolation from those of the constituent binary compounds, i.e.,

$$T_{ij}(x) = xB_j + (1-x)B_i \tag{1}$$

For some parameters the theoretical variation with composition is nonlinear [14,16]. For the direct bandgap for example, Thompson and Woolley [9] have shown that

$$T_{ij}(x) = xB_j + (1-x)B_i - C_{ij}x(1-x) \tag{2}$$

where $C_{ij}$ is the bowing parameter for the ternary alloy bandgap $T_{ij}$.

In the absence of definitive theories for quaternary parameters, estimates of a quaternary alloy parameter Q(x,y) must be obtained by interpolation from the four ternary alloy parameters $T_{ij}$. Various interpolation schemes have been proposed. Onton and Chicotka [15] used the solution of Laplace's equation subject to the boundary conditions $Q(x,0) = T_{12}(x)$, etc. In Monte Carlo transport studies [6] the present authors have used the interpolation equation

$$Q(x,y) = \frac{x(1-x)[(1-y)T_{12}(x)+yT_{43}(x)]+y(1-y)[(1-x)T_{14}(y)+xT_{23}(y)]}{x(1-x)+y(1-y)} \tag{3}$$

This interpolation equation reduces to the ternary parameters on the quaternary plane boundaries and to the average

of the ternary parameters at the midpoint (x=0.5,y=0.5) of the compositional plane. This is incidentally the solution to Laplace's equation if the $T_{ij}$ are linear as in Eq. (1). Moon et al. [7] have proposed similar schemes for the estimation of lattice constant and bandgap. For the lattice constant, Moon gives (in the above notation)

$$Q(x,y) = B_1+(B_2-B_1)x + (B_4-B_1)y + (B_1-B_2+B_3-B_4)xy \quad (4)$$

For the lattice constant, the $T_{ij}$ are assumed to be linear in their arguments, so the solution to Laplace's equation is identical to Eq. (3), which in turn also reduces to Eq. (4).

For the bandgap, Moon et al. have used the equation

$$Q(x,y) = (1-x)T_{14}(y) + x\,T_{23}(y) - \Delta \quad (5)$$

where the $T_{ij}$ are determined from Eq. (1) and

$$\Delta = x(1-x)[(1-y)C_{12}+yC_{43}] + y(1-y)[(1-x)C_{14}+xC_{23}] \quad (6)$$

An important difference between this bandgap estimate and that obtained from Eq. (3) is in the manner in which the ternary bowing parameters $C_{ij}$ enter the calculation. In Eq. (3), the ternary bowing effects are included in the $T_{ij}$, whereas in Moon's method the bowing enters as a separate quaternary bowing parameter term given in Eq. (6). At the center of the composition plane, Eq. (3) yields (for the quaternary bowing) 1/16 ($C_{12} + C_{43} + C_{14} + C_{23}$) and Eq. (5) gives 1/8 ($C_{12} + C_{43} + C_{14} + C_{23}$), which is twice as large. Thus, at the center, Eq. (3) gives the average of the bowing contributions from the four ternaries, whereas Eq. (5) gives the average of the bowing contributions from the two sublattices. This is the principle difference between the interpolation schemes of Refs. 6 and 7.

## Comparison with Experiment

Onton and Chicotka compared their interpolation approach (solution to Laplace's equation) with measured values of the quaternary bandgap in $Ga_{1-x}In_xP_{1-y}As_y$ and found the interpolated values to be within ±30 meV of the measured values. We have repeated this comparison, using their measured data. The results are given in Table 1. The average error and standard deviation of the error are also shown, and it is seen that Eqs. (3) and (5) give comparable errors.

Table I. Comparison of Eqs (3) and (5) with Experimental Data for $Ga_{1-x}In_xP_{1-y}As_y$.

| Composition | | Bandgap (eV) | | |
|---|---|---|---|---|
| x | y | Eq (3) | Eq (5) | Measured [15] |
| 0.004 | 0.260 | 2.357 | 2.353 | 2.222 |
| 0.006 | 0.340 | 2.244 | 2.239 | 2.124 |
| 0.006 | 0.420 | 2.136 | 2.131 | 1.993 |
| 0.009 | 0.500 | 2.027 | 2.020 | 1.881 |
| 0.008 | 0.590 | 1.913 | 1.907 | 1.738 |
| 0.010 | 0.710 | 1.763 | 1.755 | 1.592 |
| 0.012 | 0.830 | 1.619 | 1.609 | 1.475 |
| 0.017 | 0.910 | 1.521 | 1.510 | 1.351 |
| 0.015 | 0.970 | 1.455 | 1.447 | 1.326 |
| 0.060 | 0.220 | 2.336 | 2.297 | 2.203 |
| 0.060 | 0.280 | 2.255 | 2.214 | 2.135 |
| 0.070 | 0.340 | 2.160 | 2.113 | 2.038 |
| 0.080 | 0.440 | 2.014 | 1.963 | 1.869 |
| 0.110 | 0.650 | 1.709 | 1.650 | 1.535 |
| 0.110 | 0.700 | 1.649 | 1.591 | 1.472 |
| 0.170 | 0.850 | 1.383 | 1.326 | 1.236 |
| 0.190 | 0.975 | 1.184 | 1.166 | 1.165 |
| 0.250 | 0.140 | 2.124 | 2.054 | 2.101 |
| 0.230 | 0.190 | 2.100 | 2.021 | 2.041 |
| 0.250 | 0.240 | 2.008 | 1.921 | 1.953 |
| 0.250 | 0.310 | 1.924 | 1.830 | 1.809 |
| 0.260 | 0.630 | 1.523 | 1.430 | 1.388 |
| 0.330 | 0.800 | 1.225 | 1.145 | 1.170 |
| 0.340 | 0.090 | 2.029 | 1.971 | 2.077 |

Table I continued.

| Composition | | Bandgap (eV) | | |
|---|---|---|---|---|
| x | y | Eq (3) | Eq (5) | Measured [15] |
| 0.370 | 0.120 | 1.954 | 1.883 | 1.978 |
| 0.410 | 0.170 | 1.843 | 1.757 | 1.850 |
| 0.400 | 0.030 | 1.983 | 1.957 | 2.086 |
| 0.460 | 0.040 | 1.887 | 1.854 | 2.019 |
| 0.500 | 0.040 | 1.830 | 1.797 | 1.953 |
| 0.570 | 0.060 | 1.723 | 1.678 | 1.854 |
| 0.650 | 0.060 | 1.625 | 1.580 | 1.750 |
| 0.710 | 0.060 | 1.558 | 1.513 | 1.686 |
| 0.830 | 0.100 | 1.401 | 1.346 | 1.470 |
| 0.870 | 0.130 | 1.333 | 1.276 | 1.389 |
| 0.920 | 0.190 | 1.216 | 1.166 | 1.268 |
| Average error (eV) | | -0.052 | -0.008 | |
| rms error (eV) | | 0.109 | 0.118 | |

## Calculation of Lattice Constant and Bandgap

For the calculation of the lattice constant, the three methods discussed above are identical, as given in Eq. (4). For the calculation of the bandgap, we have elected to use Moon's procedure, since it has some theoretical basis, whereas the other two are more or less ad hoc.

The quaternary lattice constant and energy bandgap contours are presented in Figure 1(a)-(i). These contours were obtained by numerical solutions of Eqs. (4) and (5), using the data given in Table 2. In all cases, the lowest quaternary bandgap is plotted in Figure 1. The shaded regions represent compositions for which the quaternary alloy is an indirect bandgap material.

Table II. Parameters Used in the Calculation of Quaternary Bandgaps and Lattice Constants

| Compound | Bandgaps (ev) Γ(000) | X(100) | L(111) | Lattice Constant (Å) |
|---|---|---|---|---|
| AlP | 3.6 | 2.42 | 4.0 | 5.462 |
| AlAs | 2.95 | 2.153 | 3.3 | 5.6611 |
| AlSb | 2.25 | 1.52 | 1.85 | 6.135 |
| GaP | 2.74 | 2.26 | 3.0 | 5.4495 |
| GaAs | 1.439 | 1.961 | 1.769 | 5.64191 |
| GaSb | 0.69 | 1.11 | 0.765 | 6.094 |
| InP | 1.34 | 2.04 | 1.87 | 5.86875 |
| InAs | 0.359 | 2.1 | 1.6 | 6.0584 |
| InSb | 0.175 | 1.0 | 0.63 | 6.47877 |

a) Binary bandgaps and lattice constants

| Alloy | Bowing Parameter Γ(000) | X(100) | L(111) |
|---|---|---|---|
| (Al,Ga)P | 0.0* | 0.0 | 0.0 |
| (Al,Ga)As | 0.26 | 0.02 | 0.45 |
| (Al,Ga)Sb | 0.0 | 0.0 | 0.0 |
| (Al,In)P | 0.0 | 0.0 | 0.0 |
| (Al,In)As | 0.52* | 0.0 | 0.0 |
| (Al,In)Sb | 0.42* | 0.0 | 0.0 |
| (Ga,In)P | 0.758 | 0.15 | 0.68 |
| (Ga,In)As | 0.6 | 0.15 | 0.5 |
| (Ga,In)Sb | 0.43 | 0.24 | 0.33 |
| Al(P,As) | 0.22* | 0.0 | 0.0 |
| Al(P,Sb) | 1.2* | 0.0 | 0.0 |
| Al(As,Sb) | 0.72* | 0.0 | 0.0 |
| Ga(P,As) | 0.21 | 0.21 | 0.25 |
| Ga(P,Sb) | 1.2* | 0.0 | 0.0 |
| Ga(As,Sb) | 0.65* | 0.0 | 0.0 |
| In(P,As) | 0.27 | 0.27 | 0.26 |
| In(P,Sb) | 1.2 | 0.0 | 0.0 |
| In(As,Sb) | 0.596 | 0.6 | 0.55 |

b) Ternary bowing parameters

*denotes estimate from Figure 2. In the X&L valleys unknown parameters are equated to zero.

## Estimation of Unknown Ternary Bowing Constants

Relatively few of the III-V ternary bowing constants are known with any certainty, especially for the X(100) and L(111) valleys. Figure 2 shows the reported bowing parameters for several ternary materials as a function of the lattice constant difference between the two end-point binary compounds. While there is some uncertainty in the experimental data there does appear to be a definite trend toward larger bowing parameters with larger lattice constant differences. The solid line relationship shown in Figure 2 has been used to estimate several unknown bowing constants, as identified by the asterisks in Table 2. Since bowing is known to occur, it was felt that this procedure is better than arbitrarily setting the unknown bowing constants to zero.

## Summary

Calculated bandgap and lattice constant contours have been presented for nine quaternary III-V material systems. The calculated values are based upon interpolation techniques which use known values of ternary III-V parameters to estimate the bandgap and lattice constant parameters for the quaternary systems. Since there is some uncertainty in both the ternary parameters and the best interpolation technique these calculated values must be considered as first order approximations until more experimental data is obtained for the quaternary systems. However, the curves should prove useful for many studies of the general properties of the increasingly important III-V quaternary materials.

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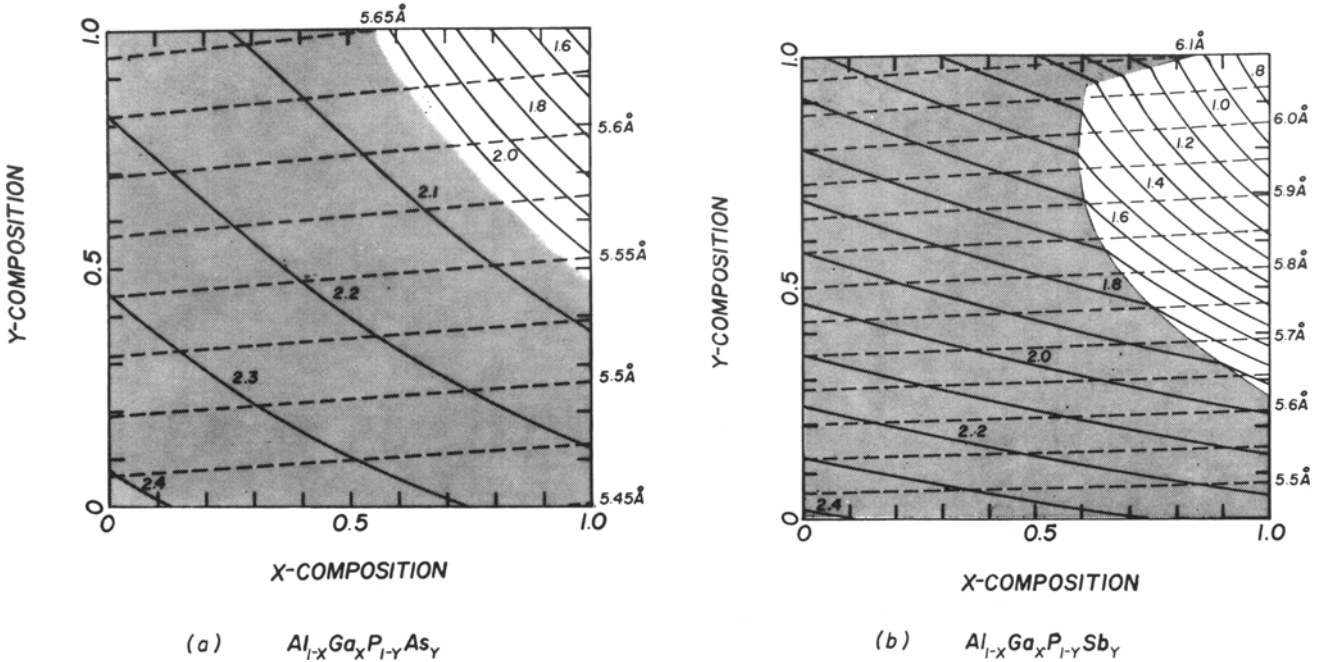
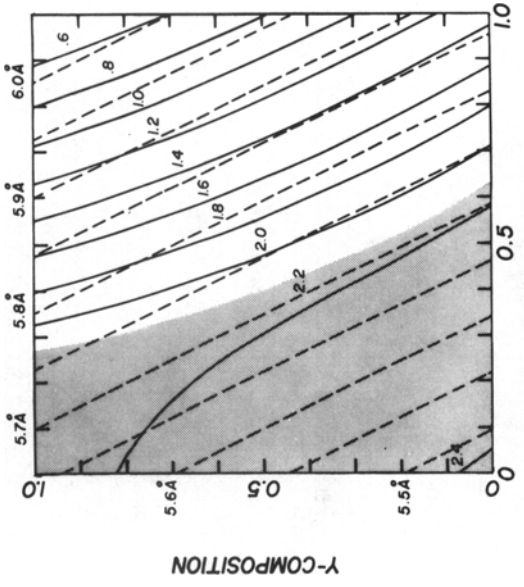
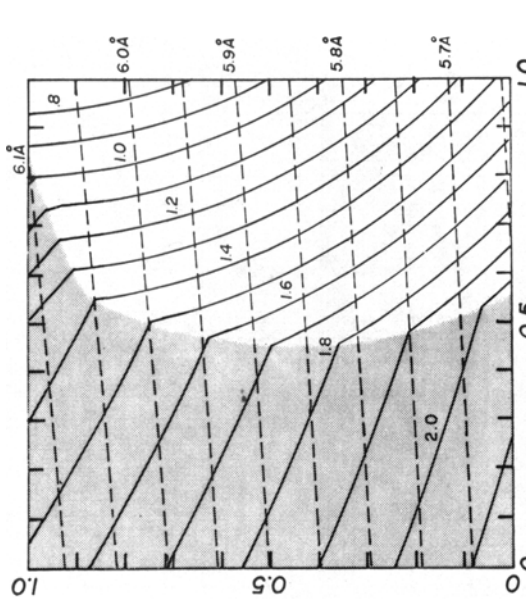



Figure 1. Energy bandgap and lattice constant contours for III-V quaternary alloys. The solid curves are the energy gap contours and the dashed curves are lattice constant contours. The shaded region shows the compositional range over which the material has an indirect bandgap.




(c) $Al_{1-X}Ga_XAs_{1-Y}Sb_Y$




(d) $Al_{1-X}In_XP_{1-Y}As_Y$

Figure 1 (continued)

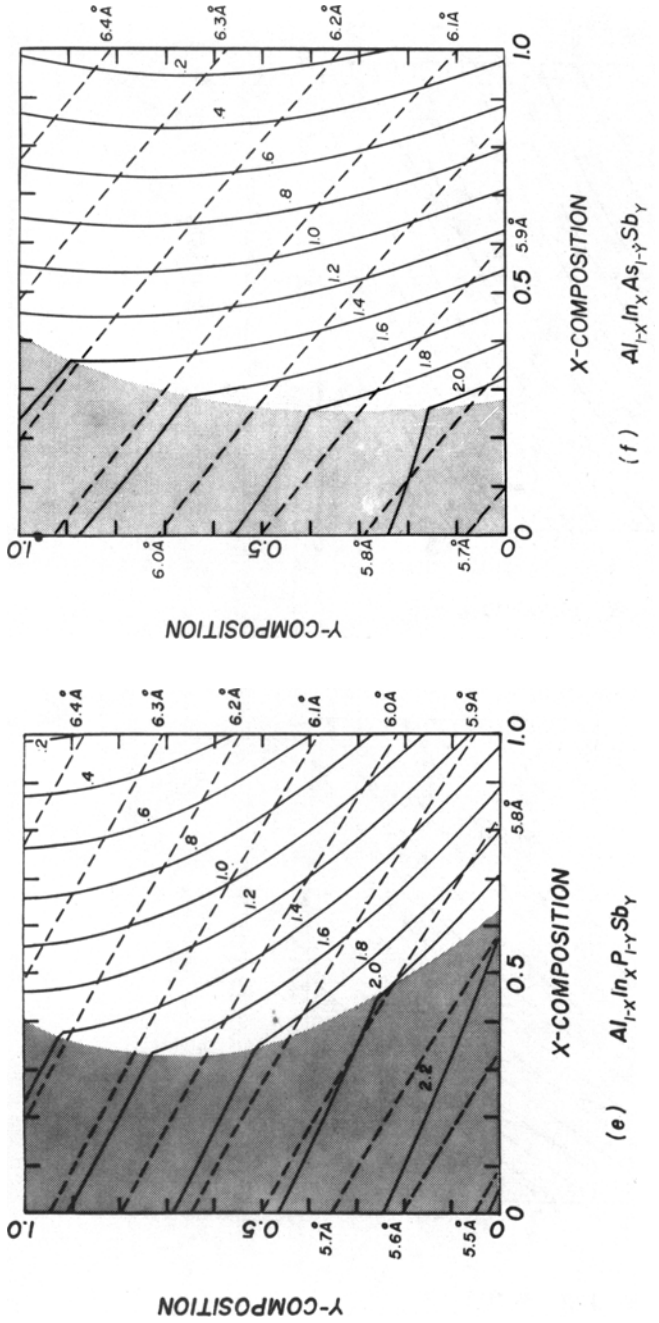
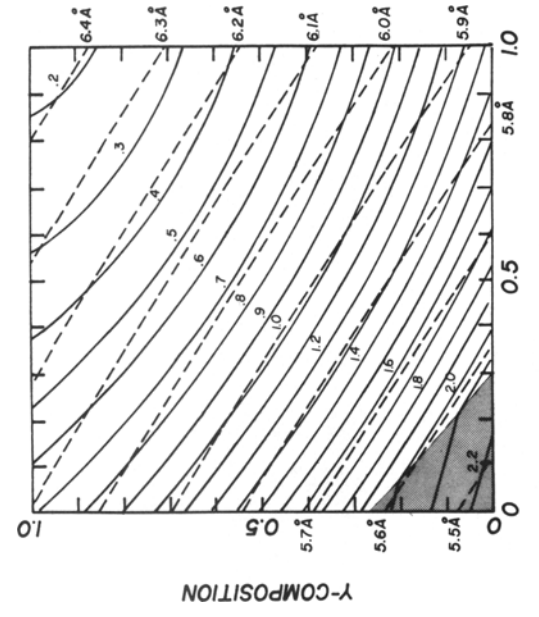
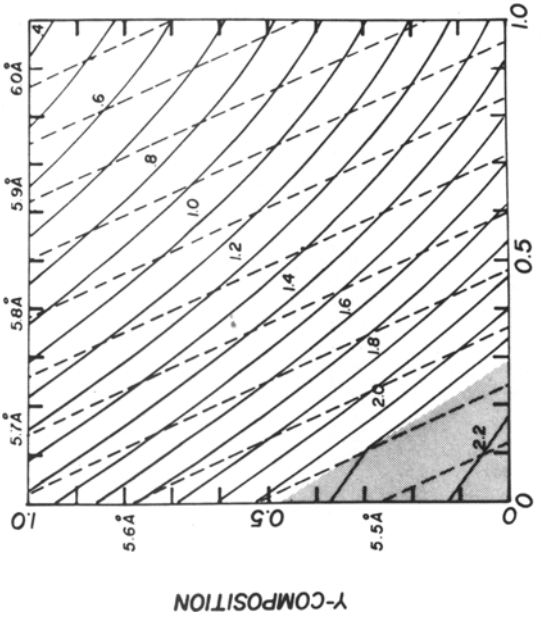



Figure 1 (continued)

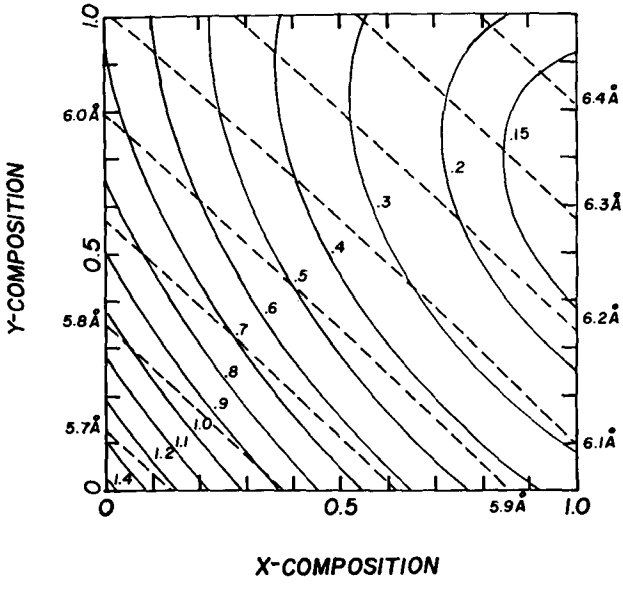



(h) $Ga_{1-X}In_XP_{1-Y}Sb_Y$




(g) $Ga_{1-X}In_XP_{1-Y}As_Y$

Figure 1 (continued)




(i) $Ga_{1-X}In_XAs_{1-Y}Sb_Y$

Figure 1 (continued)

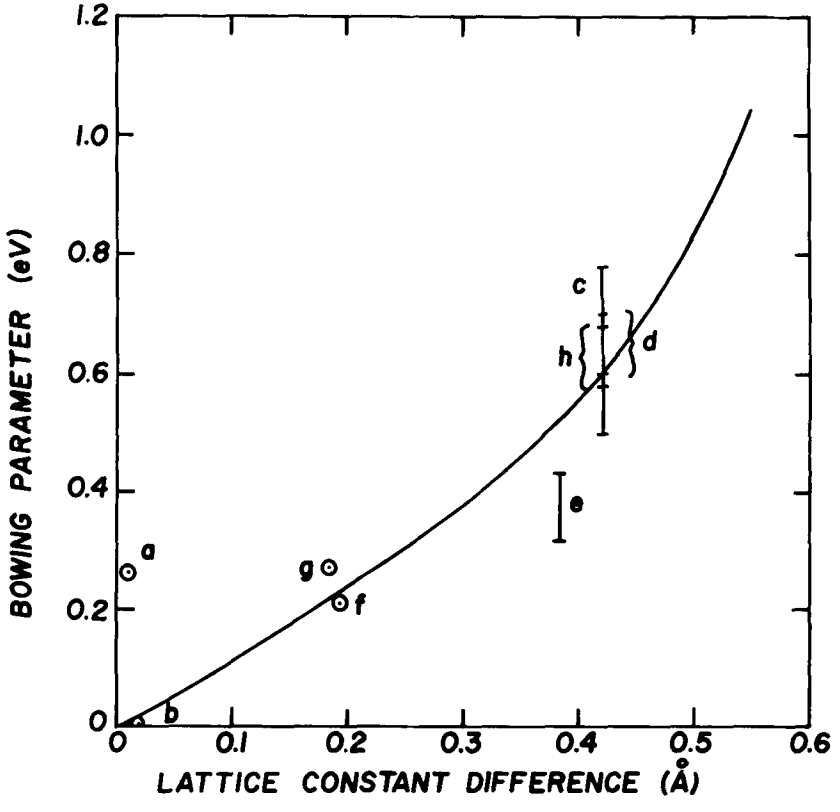



Figure 2. Experimental bowing parameters versus lattice constant difference for III-V ternary alloys. (a) $Al_{1-x}Ga_xAs$, (b) $Al_{1-x}Ga_xSb$, (c) $Ga_{1-x}In_xP$, (d) $Ga_{1-x}In_xAs$, (e) $Ga_{1-x}In_xSb$, (f) $GaP_{1-x}As_x$, (g) $InP_{1-x}As_x$, (h) $InAs_{1-x}Sb_x$.

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