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Structural Origin of Optical Bowing in Semiconductor Alloys

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The principle of conservation and transferability of chemical bonds explains the recent discovery by extended x-ray-absorption fine-structure measurements of two unequal anion-cation bond lengths P~c and &z~ in A„B~ „Czinc-blende semiconductor alloys de-spite the close adherence of the lattice constant to the average value (Vegard rule). This bond alternation, manifested as a structural distortion to a local chalcopyrite coordina-tion around the anions, explains also most of the observed optical bowing in semicon-ductor alloys.

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The lowest optical band gaps of semiconductor alloys are usual. ly sma1. 1.er than the concentration (x) weighted average of the band gaps of the con-
stituent binary semiconductors. ' This al1.oy
band-gap reduction AE, is often expressed phe-nomenologicaiiy by hE, = bx(x --1), where the bow-ing parameter b& 0, reflecting an upward concave non1.inearity, is found to be in the range of ~ 0.9 eV foV

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and provides predictions when it is not. (iv) The
first application of a self-consistent band-struc-
ture technique to the semiconductor alloy prob-
lem (equimolar InP-GaP in the InGaP, chalcopy-
rite arrangement) demonstrates that bond alter-
nation accounts for most of the observed optical
bowing, hence bz is smal. ler than hitherto accept-
ed in empirical, model. s of disorder. '
St~ctm. e model. —We suggest that, to zero or-
der, a tetrahedrally bonded AC-BC crystal will
attain values of anion displacement u, 71 Tf 61.68 9.86 Tf 90.03 578.26 Td (valu92Td ()Tj ET BT /Xi1 9.62 Tf 9 590.02226/Xi

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for band-struc-for

predictions orbi (will)Tj ET BT /X.62 1BT /X/Xi57.49/Xi1 8d (radiiem)Tj ET BT /Xi1 11.1 Tf 1499.49/Xi1 8d (Td (bond)Tj ET BT /9 4 ET BT /X93749/Xi1 8d (sca1((iv the ler ture whe(technique)Tj ET ET2753 Tf 1521 4 147 601.(8)Tj ET BT /Xi1f 604.1 Tf 14.59 48389.78 T~Tj ET BT /Xi1 9Xi1 11.2.f 1151474/89 8d (=alues)Tj ET BT .629.51 Tf 80553474/078 Td [u'+ure 1+ure St~ctm.

a (71 Tf 61.68 9..62962 Tf 38/89 47755578.26Racbond)Tj ET BT /9 49.48 258 82.474/89 8d (=alues)Tj ET BT 9T /Xi1 126/13.4 2X511 Td [(u(accept-)Tj ET BT /4 9.86 Tf 9463 25i1Td (We)Tj ET BT /Xi5 49.48 .18 Tf4Tf 69 8d (— (71 Tf 61.68 9..22389 Tf 4f 854Tf 1 8d ()'+ure)Tj ET BT /Xi2 10.52 90/Xi14611949.07 (1+g')/16](t(a (71 Tf 61.68 9.9i1 9.851T408814611i.16Td onuggest)Tj ET BT /Xi1 9.783X3814611i.16Td fi (sder,)Tj ET BT /Xi1 10.1710594611i.16Td fd (most)Tj ET BT /Xi /Xi1 127 Xi14Tf 078 Td 83.6tant"bonded)Tj ET BT8 9.47 T76 9.44 80.78 Td qbond)Tj ET BT /BT610.09.185534 Tf7 601.Td)Tj ET BT /Xi1 9/Xi.16 TT7 0784 Tf7 601.60.5libriu(equimolar)Tj ET 8 11.2.f2Xi.14 Tf7 601.6 Td (of)Tj ET BT /Xi1 9.53 T5/Xi1 3891949.07 d (first)Tj ET BT i1Tf 9 T81 9.390 078 Td 871 (ler)Tj ET BT /8i57.52 94/078390 1085 Td8ud (ler)Tj ET BT /ET BT /X0249.5390 1085 Tdat(in)Tj ET BT /Xi1 98 11.2. 14.59390 3578.26 Td (of)Tj ET BT /Xi1 9.53 Tf611759390 4285 Td (a)Tj ET BT /Xi1 0T /Xi1 78 T0.4390 4285 Td(tetrahedrally)T /062 Tf 14.85 390 3578.2d (provides)Tj ET 8.4 721710007 6390 77 601.u(accept-)Tj ET B1/X69 Tf20/X378391i1 11d (with'""bonded)Tj ET BT8 i1 9.9 46 T24388X99. Td galloy

=alues provides edictions=(provides)Tj ET /X74Xi1 172182. ler NUMBER

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t (s)Tj ET BT /Xi11 9 when disorder. 1 (The)Tj ET BT /Xi1 s

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separation in the A-

C and B-

C (as well as in
the A- A,

B -B and A-B) bonds. The second
contribution measures the bowing due to the re-laxation of the bond lengths to their equilibrium (unequal. bond) configuration characterized by u« (Table I)

~ We find for the fundamental I'»„-I;,
band gap bI =0.25 eV and b~ =0.17 eV, or

a tot-

al of b~ =0.42 eV, which together with the recently
calculated' CPA value for the disorder contribu-

tion b~~ =0.08 eV, produces a

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1Baler,echwiTj ET BT /Xi3 7.78 Tf 161049 T72.57Td (1nd)Tj ET BT /Xi3 8.7 Tf 117668 T72.51 Td (S.)Tj ET BT /Xi3 1868 Tf 158.796T72.526Td (CMachwke)Tj ET BT /Xi3 8.96 D.J.Chadi hys.D B

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