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alence of the various A sites can hence derive concomitant
fluctuations in the charge distribution on different A sites
and bond lengths. 2 '
The z = &

alloy is described through the SQS-2 su-
percell considered previously; this structure can be described as an AiB2AsB2 superlattice along the [113] direction. The z = 4

(or z = &) alloy is described by the
SQS-~~ supercell consisting of AsBq layers stacked along the [201] direction.

LARGE LATTICE-RELAXATION-INDUCED ELECTRONIC... 3389

a~ (A)
3.662
3.739
3.803
3.872

Cgq Q~
LAP&

1.046
0.988
0.947
0.903

Ceq Qg

Eq. (I)
1.044
0.992
0.949
0.905

error

0.2
0.4
0.2
0.2

TABLE I. Comparison of the tetragonal deformation

c,q(a~)/a~ for the Ilp structure of the CuPd as calculated
for a, range of perpendicular lattice constants a~ by the
LAPW method and from the continuum elasticity [Eq. (I),
1 Cu Pd ceq: g (cpq + ceq)j.

27

g 2.6
Z3

ccl 2.5—
Cu 0.2 0.4 0.6 0.8 Pd

Composition x

test it on CuPd in the Ilo structure (a [001] superlat-
tice), where accurate LAPW energy minimization is eas-ily performed. We compare the tetragonal deformation calculated from Eqs. (1) and (2) for a series of externally fixed a~ values, with those obtained from direct LAP W total-energy minimizations. Table I shows that the elas-tic model is remarkably accurate over a wide range of
deformations. We have next applied this elastic model to
the SQS, obtaining an initial guess for the relaxed atomic positions. This is then refined by minimizing the LAPW total energy with respect to all atomic positions. This is done by calculating the quantum-mechanical forces us-ing the method of Yu, Singh, and Krakauer, We find that the fully relaxed geometry is rather close to that predicted by the elastic model: the average bond lengths changed by less than 0.5% and the total energy was re-duced by less than 2 meV/atom. We find that the mixing

enthalpy of the disordered alloy EH;„(z) was reduced from the fully unrelaxed value of —45.0 meV/atom at z = 2

to the fully relaxed value of —62.5 meV/atom;

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of equal bond lengths in the two phases.
We fitted the calculated Cu—Pd bond lengths at z = 4,
2, and 4

to a parabolic function. By extrapolating the re-
sult to the dilute limit z = 0, we found that there is a lat-
tice expansion of 2.0% around a Pd impurity (open circle in Fig. 2), in good agreement with the extended x-ray ab-sorption fine-structure (EXAFS) experiment showing a 2% expansion.
The top part of Fig. 3 compares the Pd local DOS in the unrelaxed SQS for Cuo 7sPdp 25 with the unrelaxed KKR-CPA results of Ginatempo et a/.: There is an over-all agreement (except that the broad single structure cen-tered around e~ —5 eV is split in our calculation into a doublet).
The eA'ect of relaxation on the Pd local DOS is illus-

trated in the bottom part of I"ig. 3, displaying the dif-ference between our relaxed and unrelaxed results. The

increase in the Cu —Pd and Pd—Pd bond lengths over their common virtual lattice values (Fig. 2) removes intensity in the density of states from the bottom of the band at e~ —5.5 eV, result ing in much better agreement with experiment. Interestingly, the efFect of relaxation on the Cu LDOS is negligible; the more tightly bound (and narrower) Cu d states are less responsive to bond defor-

mations. This is also evidenced by the fact that DOS of pure fcc Cu shifts by less than 0.3 eV when the cu-bic lattice parameter is changed from the values of 3.646 A(approximate to the alloy at z = &) to 3.739 A (ap-proximate to the alloy at z = 2). The change in the DOS of pure Pd under the same deformation is much larger (0.7 eV).
We conclude that unlike the ordered Llg phase, the random alloy has a distribution of bond lengths and charges (neglected in current mean-field theories) and

that atomic relaxations expand the long bond (e.g., Pd-
Pd in CuPd). This results in a substantial shift of the bonding state to lower binding energies (

I eV in

Cup 7sPdp 2s) therefore removing

the c13.33 Td (7sPdp)Tj ET BT /Xi3 8.82 Tf 452.89 557.33

ej ET B54T /Xi3 57.33 T7cscre2 6

in10.56 Td (ccludET BT /Xi111.222 T Je P

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i32(approximate

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the MTj ET BT /Xi3 9.49 Tf 9245sear3g1 78 Td (iessa3 Td (eVTj ET BT .3562 T2 Tf.11 11 567.89PhyThe)Tj ET BT /Xi3/Xi3 9 T.743.89 11 67 Td (Wevhis)Tj ET BT /Xi3 8.62 T3.538.301 67 Td (Bttice)TT /Xi3 8.3 .82 T9.56 6301 78 Td (293 Td (eVTj ET BT9 Tf 114.7f 3 1 041.44 Td 171V)Tj ET BT /Xi3 8.3 9.11 2.22 63 Td (th(.4 4This)Tj ET BT /Xi3600.8 581352.22291 52fu4.4Je)Tj ET B4ET BT 9XTf 2969.56 6291 78 Td (Kudrnovsk.22 Td (())Tj ET 33.05 T46438.291 78 Td (the)Tj ET 6T BT /X0.84 Tf 1635 Tf 73.1Td (Je)Tj ET B4ET BT 9X3Xi3 9.6 9.34Tf 7 567.89Masekd)Tj ET BBT /Xi39Xi 203.4 4Tf 67.89PhyThe

Revhis642 ET BT /Xi3 9.75

W7 Tdrd

charges

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C9-105ET BT /Xi3 9.52 .9438 52267 56828 654.44 T(.4 7This

WEI,

chad (et)Tj ET BT

2761T BT /Xi3 9.

Papacon9 Td opoulosd

Gonisd

approximate f(.4 9(We)Tj ET BT /Xi3 9.B438.T .8207 Td (Ne)Tj ET B4ET BT 9Xi9.65631.56207 Td (Stefanou)Tj ET BT /Xi3 9 Tf7 doPoWEI, doS(to)Tj ET BT /Xi3 889 /Xi3 86.67 1B0.67 Td (Commuhe)Tj ET BBT /X99.18f 1061614.67220.67 Td (6nd)Tj ET BT /Xi3 6.3 9.21378 561631.56 Td 73V f(.4 7)he S(to)j ET BT /Xi3 889.6 Tf Td (i1648 Td Commuhe)Tj ET BBT /X99.1i3 9 T30Tf 50179 5.11 Td70splaying (.4 9Whe)Tj ET BT /Xi388.62 T1f 148142.78 Td (PhyThe)Tj ET BT /Xi3/X7 Tf 318 218 654.44 T/Xvhi4.490(We)Tj E B /Xi3 .93 10.182.78 149 557Td (739Tj ET BT /Xi383i9558 9183.119 557Td (Masek)Tj ET BBT /Xi3 91.79 Tf 01149 557Td (uhe)Tj ET BT /Xi

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charges

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f(.4 7This

(We(boumann)T BT /Xi3 3 /Xi4620063g1 78 Td (Je)Tj ET B4ET BT 9X.86 T4111 53g167.89PhyThe 7sTf 4413g1 78 Td (C)Tj ET BBT /X999.3 10.189.22 T3153.89 Td 17 ET BT /Xi3 8.9310.8 Tf 540538.311 78 Td (L101V)Tj ET BT /Xi3 9.1 Tf 560711 53g675 (eA'ct)j ET BT /Xi3 T359 3 1 04d (thmodehift)j ET BT /Xi3X3 9 3 1 04d (th2 dussTj ET BT /j E B611 Tf 489515.443Krakau72.6 (is)Tj ET BT 3 PhyThed)Tj ETBT /Xi3 04ic7 f 48733218.44 d (agreed)j ET /Xi3 di.9 Tf Tf 488..47 578.67 Trit((E BT /Xi33 8.65 Tf2 T79 78 2d (Je)T3T /Xi34 /Xi 8.330

bon3351