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## Effects of chemical and structural disorder in III–V semiconductors and their alloys

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**Abstract.** The cluster–Bethe-lattice (CBL) method is used to explore the effects of structural disorder in the electronic structure of a-GaAs, a-GaP and the alloy  $\text{GaAs}_{1-x}\text{P}_x$  for which recent EXAFS experiments show bond length disorder. The one-atom CBL approximation gives very accurate band gaps for the compounds and densities of states which agree well—except for the lower valence band (vB)—with the DOS of the crystalline compounds. The calculation for the alloy gives accurate bands but not band gaps. The five-atom CBL approximation retains the values of the band gaps for the compounds and produces DOS that show the features of the spectra of a-GaAs. For the alloy, a reasonable band-gap bowing is obtained while a substantial smoothing of both vB appears, which may compete with the effects of pure chemical disorder. The reasons for the difference between the results obtained using the two approximations are discussed.

### 1. Introduction

The high carrier mobilities of crystalline III–V semiconductors, such as GaAs, have made them an integral part of the microelectronics industry, especially in areas where fast circuits are needed. On the other hand, more effort has been made to investigate the electronic structure of amorphous III–V semiconductors, such as GaAs and GaP. The main problem lies in discovering the influence of defects.

‘Wrong bonds’ are one of the most frequently discussed defects in these semiconductors [1]. It is found experimentally that the main difference between the DOS of c-GaAs and a-GaAs is a filling with states of the region between the higher two peaks of the valence band (vB), thereby eliminating the dip between these peaks [2, 3]. Yndurain and Joannopoulos [4] made a study of the effects of homopolar bonds in GaAs using the simplified Weaire–Thorpe Hamiltonian [5] and came to the conclusion that this difference may be due to ‘wrong bonds’.

Experimentally, ‘wrong bonds’ are not found in GaAs [3, 6] although they have been detected in small quantities in GaP [7, 8]. Recent xps measurements [6] show that the elimination of the dip at around  $-5$  eV in the spectrum of GaAs is due to the amorphous network, i.e. to the loss of long-range order (LRO). O’Reilly and Robertson [9] have performed calculations for the Connell–Temkin [10] model using the recursion method and have found that As–As bonds introduce states in the gap while structural disorder causes very little movement of the band edges.

The alloys of the III–V compounds, such as  $\text{GaAs}_{1-x}\text{P}_x$ , have ‘tailorable’ band gaps and find wide application in microelectronics and optoelectronics [11]. These alloys were

originally studied in the virtual-crystal approximation (VCA), i.e. by considering them as crystals and neglecting the effects of disorder in the anion or cation sublattice. Studies using the CPA including chemical disorder in the form of diagonal disorder followed [12, 13]. Very recently Lempert and co-workers (LHE) have reported a study of such alloys including chemical and structural disorder, simulated as diagonal and off-diagonal disorder respectively, using the molecular coherent potential approximation (MCPA) [14]. Their results showed that the effects of disorder are manifested in the lower VB (for anion sublattice disorder) while their calculated band-gap bowing showed reasonable agreement with experiment but was not very different from the VCA or CPA results. The study by LHE was prompted by the experimental discovery by EXAFS that in these alloys the bond lengths deviate by only 2% from the corresponding values of their constituent compounds [15]. Such an effect destroys the translational periodicity of one of the sublattices (anion or cation) although LRO is preserved because the other sublattice (cation or anion) remains intact. In this study we examine the effects of chemical and structural disorder on the alloys of III-V compounds, without assuming that a Bravais lattice exists. Whereas LHE have retained a Bravais lattice and have modelled the variation in bond length as disorder in the off-diagonal matrix elements, we examine structural disorder from a different point of view: we simulate the environment of any given atom, or an atom with its nearest neighbours, by a Bethe lattice. Although this is an appropriate model for amorphous III-V semiconductors but not entirely for their alloys we expect to find out by comparison with the work of LHE which features of the electronic structure of these alloys are affected by pure chemical disorder and which by actual structural disorder. We choose  $\text{GaAs}_{1-x}\text{P}_x$  as a test case because there is a lot of experimental information available on a-GaAs and a-GaP and because the bond lengths of c-GaAs and c-GaP differ considerably (2.45 Å and 2.36 Å respectively).

## 2. Method

We have performed calculations for GaAs, GaP and the alloy  $\text{GaAs}_{1-x}\text{P}_x$  using the cluster-Bethe-lattice (CBL) method [16, 17]. The method treats short-range order (SRO) correctly, i.e. according to the size of the cluster, while the environment is treated via an effective-medium approach using transfer matrices. It is a direct-space method, in contrast to the CPA which is a  $k$ -space method. However, for the Bethe lattice the two methods treat disorder equivalently if off-diagonal disorder is ignored. This was established in [18, 19].

In the Kittler-Falicov (KF) method [17], which we are using, there are four transfer matrices  $\mathbf{t}_{AB}$ , one for each type of bond. If however the  $\mathbf{V}_{AB}$  of KF reduce to a single  $\mathbf{V}$  then the four equations (2.21) for the  $\mathbf{t}$  matrices in [17] reduce to two, which are identical to equations (9a) and (9b) of [18] which have been shown to be, in turn, equivalent to the CPA results of [20]. When off-diagonal disorder is included one has to use a set of four coupled matrix equations for the  $\mathbf{t}$  matrices. These are difficult to solve analytically and no direct comparison can be made with the MCPA. We expect, however, that any similarities or differences we find should be correlated to the absence of a perfect (Bravais) lattice in the effective medium surrounding the cluster. For the end points our calculations will be applicable to a-GaAs and a-GaP.

Since the alloy we are considering is of the form  $\text{AB}_{1-x}\text{C}_x$ , with anion sublattice disorder only, the transfer matrices we need are different from those of KF. In particular, we define the following transfer matrices:  $\mathbf{T}_1 = \mathbf{T}_{\text{GaP}}$ ,  $\mathbf{T}_2 = \mathbf{T}_{\text{GaAs}}$ ,  $\mathbf{T}_3 = \mathbf{T}_{\text{AsGa}}$ ,

$\mathbf{T}_4 = \mathbf{T}_{\text{PGa}}$ , where in  $\mathbf{T}_{\text{AB}}$  the atom A is on the outer shell and B is on the inner. These are easily shown to obey the following set of equations:

$$\mathbf{T}_1 = \left( z\mathbf{I} - \mathbf{U}_{\text{Ga}} - x \sum_{i=2}^4 \mathbf{R}_i^+ \mathbf{W} \mathbf{T}_4 \mathbf{R}_i - (1-x) \sum_{i=2}^4 \mathbf{R}_i^+ \mathbf{V} \mathbf{T}_3 \mathbf{R}_i \right)^{-1} \mathbf{W}$$

$$\mathbf{T}_2 = \left( z\mathbf{I} - \mathbf{U}_{\text{Ga}} - x \sum_{i=2}^4 \mathbf{R}_i^+ \mathbf{W} \mathbf{T}_4 \mathbf{R}_i - (1-x) \sum_{i=2}^4 \mathbf{R}_i^+ \mathbf{V} \mathbf{T}_3 \mathbf{R}_i \right)^{-1} \mathbf{V}$$

$$\mathbf{T}_3 = \left( z\mathbf{I} - \mathbf{U}_{\text{As}} - \sum_{i=2}^4 \mathbf{R}_i^+ \mathbf{V} \mathbf{T}_2 \mathbf{R}_i \right)^{-1} \mathbf{V},$$

$$\mathbf{T}_4 = \left( z\mathbf{I} - \mathbf{U}_{\text{P}} - \sum_{i=2}^4 \mathbf{R}_i^+ \mathbf{W} \mathbf{T}_1 \mathbf{R}_i \right) \mathbf{W}'.$$

The  $\mathbf{U}$  matrices are  $4 \times 4$  and contain the on-site diagonal matrix elements of the  $sp^3$  orbitals of each atom;  $\mathbf{V}$  and  $\mathbf{W}$  are  $4 \times 4$  matrices containing the off-diagonal hopping integrals between (i) Ga and As and (ii) Ga and P  $sp^3$  orbitals in a bond direction arbitrarily labelled one; and  $\mathbf{R}_i$ ,  $i = 2, 4$ , are the symmetry operations that transform the orbitals to the other three. The parameters for  $\mathbf{V}$  and  $\mathbf{W}$  have been obtained from the work of Talwar and Ting ( $\tau\tau$ ) [21]. They are values that give very accurate valence bands and band gaps and reasonable conduction bands for the crystalline materials. ( $\tau\tau$  have included second-nearest-neighbour interactions which we omit here.) See table 1.

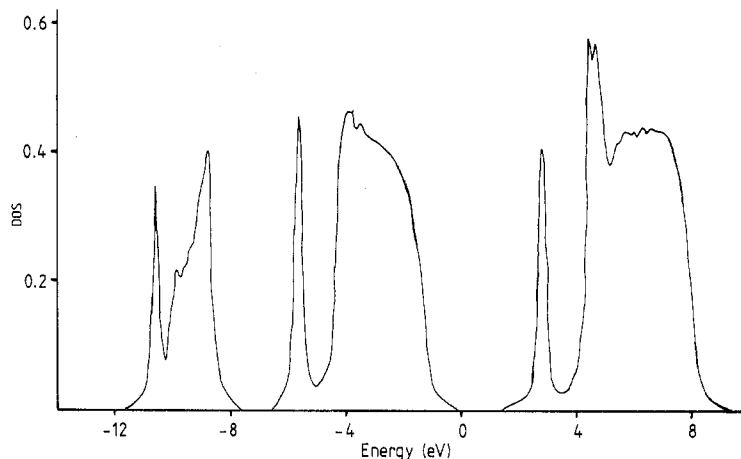
The equations for the  $\mathbf{T}$  matrices are solved numerically by an iterative procedure starting well outside the bands. A small imaginary part has been added to the energy (0.1 eV) to attain convergence.

**Table 1.** Hamiltonian parameters for the compounds and the alloy  $\text{GaAs}_{0.5}\text{P}_{0.5}$  (in eV). The diagonal elements referring to a Ga atom have been varied linearly between  $x = 0.0$  and  $x = 1.0$ . For the  $sp$  hopping integral the first letter indicates an orbital on an anion.

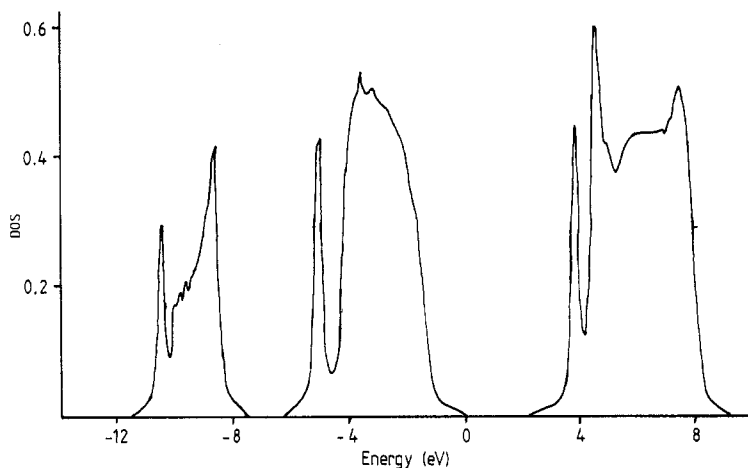
As-Ga bond		P-Ga bond	
$E_s^{\text{As}} = -6.72$	$E_s^{\text{Ga}} = -3.99$	$E_s^{\text{P}} = -6.28$	$E_s^{\text{Ga}} = -2.79$
$E_p^{\text{As}} = 0.64$	$E_p^{\text{Ga}} = 2.87$	$E_p^{\text{P}} = 1.09$	$E_p^{\text{Ga}} = 2.38$
$ss\sigma = -1.73$	$pp\sigma = 3.25$	$ss\sigma = -1.94$	$pp\sigma = 3.39$
$sp\sigma = 2.27$	$pp\pi = -0.89$	$sp\sigma = 2.28$	$pp\pi = -0.78$
$ps\sigma = 1.87$		$ps\sigma = 2.11$	

### 3. Results and discussion

Our calculated DOS for GaAs and GaP in the one-atom CBL approximation are shown in figures 1 and 2, respectively. Our results still contain the dip at around  $-5$  eV but agree, surprisingly, quite well with the DOS of crystalline GaAs and GaP of  $\tau\tau$ , whose values we are using for Hamiltonian parameters. The only large discrepancy is for the gap of GaAs between the lower and upper  $\text{vB}$ —usually called the ionic gap. This is too small (1 eV compared with 3 eV of  $\tau\tau$ ). Also, the double peak of the lower  $\text{vB}$  is more pronounced for GaAs, but not for GaP, than in the DOS of  $\tau\tau$ . However, the band gaps are very well reproduced. They are 1.6 and 2.3 eV for GaAs and GaP respectively, compared with 1.51 and 2.16 of  $\tau\tau$ . Furthermore, very little movement of the band edges is observed. These points require some further discussion.



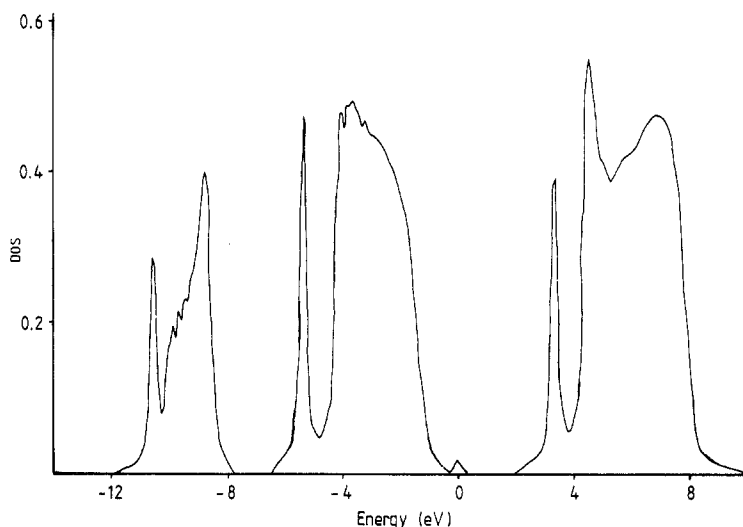
**Figure 1.** The DOS of GaAs in the one-atom CBL approximation. The number of states is normalised to four.



**Figure 2.** The DOS of GaP in the one-atom CBL approximation. The number of states is normalised to four.

It has been demonstrated that in calculations with the CBL method and with the one-orbital Hamiltonian the band widths are smaller and are determined exclusively by the Bethe lattice, irrespective of the size of the cluster [4]. As the size of the cluster increases more  $\delta$ -functions appear and the spectrum approaches that of a crystalline material and shows structure related to rings of like-atom bonds [22]. If SRO that favours unlike-atom bonds is built into the method the  $\delta$ -functions move into the continuous spectrum [23]. Furthermore, if one uses a four-orbital Hamiltonian with non-zero  $pp\pi$  interactions the  $\delta$ -functions split into a band [17]. It is not surprising therefore that we get such accurate band gaps—considering that we have a binary compound and we have used a full Hamiltonian. In fact, the agreement is better with experimental values.

Our DOS for GaAs show remarkable agreement—other than for the lower VB—with those of O'Reilly and Robertson, who used the recursion method. Both sets of results show little movement of the upper VB. There is also available a CBL calculation performed by Agrawal and Agrawal [24] which produced similar results but with a band gap of



**Figure 3.** The DOS of the alloy  $\text{GaAs}_{0.5}\text{P}_{0.5}$  in the one-atom CBL approximation. The number of states is normalised to four.

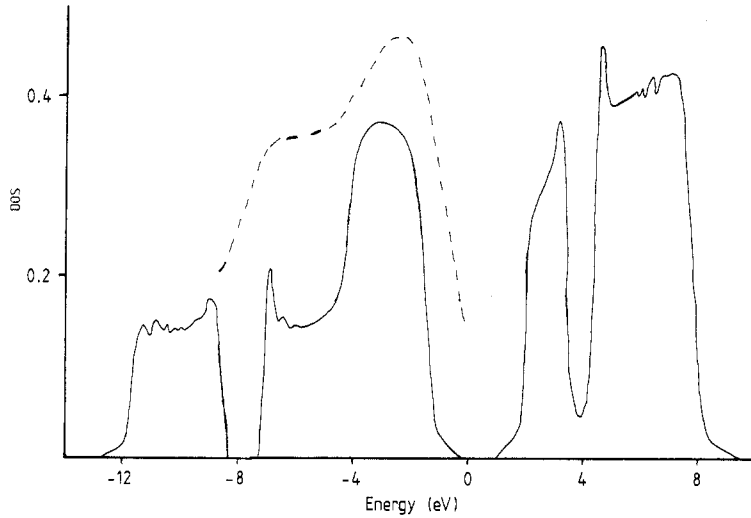
2.0 eV. They used empirical parameters, however, with large deviations from a set that gives an accurate crystalline band structure.

Figure 3 shows our computed DOS for the alloy  $\text{GaAs}_{0.5}\text{P}_{0.5}$  in the one-atom CBL approximation. For anion sublattice disorder Lempert and co-workers performed a calculation for the alloy  $\text{ZnSe}_{0.5}\text{Te}_{0.5}$ , but since they claim that their results are valid for most III–V and II–VI semiconducting alloys we attempt a comparison. The overall features of the bands are the same (we discuss the behaviour of the band gap immediately below). In particular, the double peak of the lower VB, which is present in the CPA and the MCPA results of LHE but not in their VCA results, is also present in ours. However, we were sure to find it because it was a feature of both the GaAs and GaP DOS.

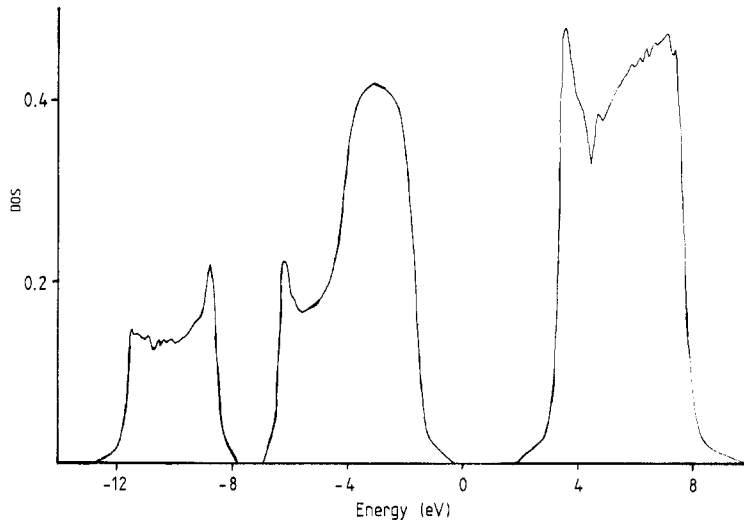
It can be seen from figure 3 that a very small yet detectable peak appears in the gap of the alloy. This is clearly incorrect—it is due to the use of the one-atom CBL approximation and, in particular, to the linear dependence of the effective potential—which a Ga atom ‘sees’—on  $x$  and  $1 - x$ , the partial DOS of which is solely responsible for this peak. We then proceed to calculations in the five-atom CBL approximation. All possible clusters have been taken into account, i.e. the five centred on a Ga atom and the remaining two.

Our results for the DOS of GaAs, GaP and the alloy  $\text{GaAs}_{0.5}\text{P}_{0.5}$  are shown in figures 4, 5 and 6, respectively. We have also performed calculations for  $x = 0.25$  and  $x = 0.75$ , but these are not shown here, for economy of space, since they exhibit the same characteristics. It can be seen that the bands are smoother and the band gaps remain the same but, more importantly, states are added in the region between the two peaks of the upper VB. The dip is not eliminated, but is drastically reduced. This occurs also in the lower VB and for both the compounds and the alloy.

It must be emphasised that for GaAs there is strong experimental evidence that this filling with states in the energy region around  $-5$  eV is due to the loss of LRO. In particular, in the experiments described in [6], when the samples giving a typical a-GaAs XPS spectrum were annealed at  $230$  °C, the dip was just beginning to emerge again. As far as we know no XPS spectra are available in the literature for a-GaP. The fact, however,



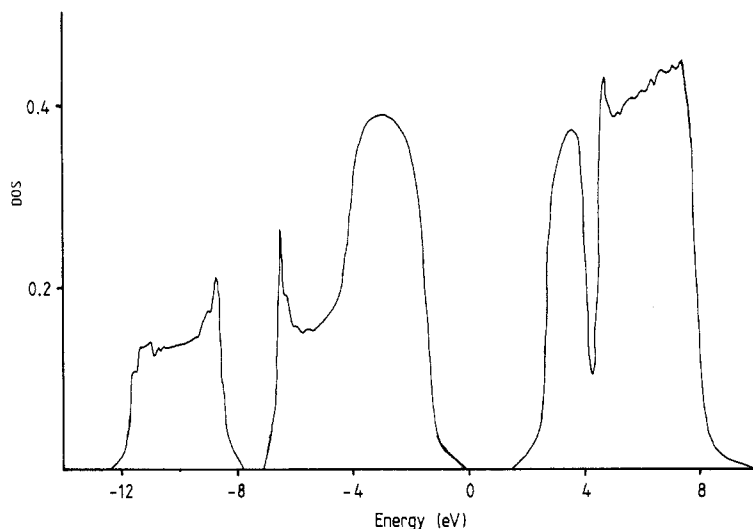
**Figure 4.** Full trace: DOS of GaAs in the five-atom CBL approximation. The number of states is normalised to four. Broken trace: the XPS spectrum of a-GaAs.



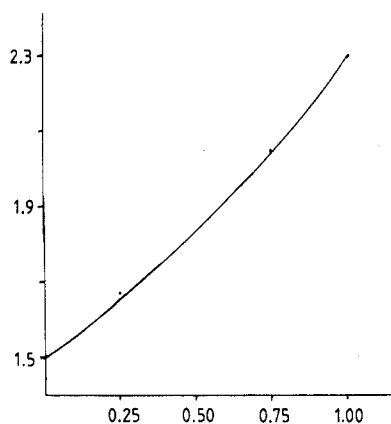
**Figure 5.** The DOS of GaP in the five-atom CBL approximation. The number of states is normalised to four.

that this effect is present for both compounds, together with the experiments described, should distance it from the subject of 'wrong bonds'.

An explanation must be given as to why the five-atom CBL approximation gives a better DOS for amorphous GaAs than that of the one-atom CBL. Mathematically, extra  $\delta$ -functions are introduced, which are split by the  $pp\pi$  interaction, and the bands become smoother, but—physically—we tentatively put forward the following explanation: it seems that the five-atom CBL approximation is more representative of the amorphous compound in that it retains the atoms with their nearest neighbours and treats the remaining atoms (i.e. the loss of LRO) as a Bethe lattice. On the other hand the one-atom CBL is closer to a crystalline compound since the effective medium covers the whole of space with no partitioning into a cluster and an effective medium.



**Figure 6.** The DOS of the alloy  $\text{GaAs}_{0.5}\text{P}_{0.5}$  in the five-atom CBL approximation. The number of states is normalised to four.



**Figure 7.** The variation of the band gap of the alloy  $\text{GaAs}_{0.5}\text{P}_{0.5}$  with respect to  $x$ . Calculations have been performed for  $x = 0.0, 0.25, 0.50, 0.75, 1.0$ .

For the alloy  $\text{GaAs}_{0.5}\text{P}_{0.5}$  the effects of structural disorder due to bond length variations are more pronounced in the region of the lower VB and around  $-5$  eV in the upper VB, with a smoothing of these bands and a corresponding filling of states. The effect in the lower VB is in contrast to the near halving of this band which LHE have obtained and attributed to chemical disorder. It seems therefore that the effects of pure chemical disorder and structural disorder produce competing processes. We did not find in the literature any experiments (e.g. photoelectron spectroscopy studies) that could render untenable one or the other of the processes in alloys with a substantial lattice mismatch.

Figure 7 gives our calculated band-gap variation with respect to  $x$ . The band-gap bowing, i.e. the deviation from linearity, shows reasonable agreement with experiment. For  $x = 0.50$  the calculated band-gap bowing is approximately 100 meV. There is, however, an uncertainty of 20–40 meV for the following reason. The computations can only be performed above or below the real energy axis by a small amount. This has the effect of making the energy levels Lorentzians instead of  $\delta$ -functions, so there is always



a tail when the DOS goes to zero. When energy differences of the order of a few meV are involved the CBL method is not very reliable.

#### 4. Conclusions

We have used the CBL method to simulate the structure of a-GaAs and a-GaP and the alloy  $\text{GaAs}_{1-x}\text{P}_x$ . For the compounds the method gives very accurate band gaps and in the five-atom CBL it shows the experimentally observed filling with states in the energy region between the two peaks of the upper vB. This also holds for the alloy in the five-atom CBL for which the effects of structural disorder due to a bimodal bond length distribution may compete with those of chemical disorder. Finally the band gap of the compounds seems to be determined only by topology and SRO to within 0.1–0.15 eV.

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