

## Tight-binding coherent-potential approximation including off-diagonal disorder

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We present a generalization of the tight-binding coherent-potential approximation (TB-CPA) to substitutionally disordered alloys with both diagonal and off-diagonal disorder (ODD), taking into account all relevant  $s$ ,  $p$ , and  $d$ , orbitals. This generalization is based on the work of Blackman, Esterling, and Berk [Phys. Rev. B **4**, 2412 (1971)] which treated ODD within a single-band model of a disordered alloy. The method is illustrated with calculations of the density of states of disordered  $\text{Cu}_{0.75}\text{Pd}_{0.25}$  alloys. We find that inclusion of ODD improves the agreement with specific-heat data, but it does not resolve a discrepancy with the results of first-principles, muffin-tin CPA calculations regarding the Pd component of the density of states.

### I. INTRODUCTION

It is now rather broadly accepted that the Soven-Taylor coherent-potential approximation<sup>1-5</sup> (CPA) provides an overall satisfactory description of the electronic structure of substitutionally disordered metal and semiconductor alloys. In fact, the CPA allows the most accurate treatment of substitutionally disordered systems within a single-site approximation. The state of development of the computational aspects of this method has progressed sufficiently far that calculations based on tight-binding (TB) and more realistic muffin-tin (MT) Hamiltonians can be carried out and compared with one another. The latter type of calculations are performed within the Green-function or multiple-scattering formalism of Korringa, Kohn, and Rostoker (KKR-CPA),<sup>4-5</sup> and provide an *ab initio* description of the electronic structure of substitutional alloys. In particular, such calculations take into account fully both diagonal and off-diagonal disorder (ODD) referring, respectively, to the dependence of the diagonal and off-diagonal elements of the Hamiltonian on the configuration of an alloy.

Although the use of a TB Hamiltonian requires fitting to the band structure at the stoichiometric end points, in order to determine various physical parameters, such as the site-off-diagonal elements describing electron hopping in the alloy, it has the advantage of allowing the decoupling and the separate study of specific effects, for example ODD, on the alloy band structure. In addition, the TB-CPA is much easier to program and apply than its first-principles counterpart, the KKR-CPA. Applications of TB-CPA can be used to readily obtain estimates of the effects of various physical features, such as diagonal and off-diagonal disorder on the electronic structure of an alloy. Off-diagonal disorder in particular can be the

dominant feature in so-called<sup>6</sup> common-band alloys such as  $\text{Cu}_x\text{Pd}_{1-x}$ . Here the  $d$  resonances characterizing the pure materials essentially overlap, and the disorder is primarily a manifestation of the different bandwidths of the pure systems.

A proper treatment of ODD within the TB-CPA has been presented by Blackman, Esterling, and Berk (BEB)<sup>7</sup> in connection with single-band alloys. For the same model Hamiltonian, the method has been rederived by Gonis and Garland.<sup>8</sup> In this paper, we present the first application of the TB-CPA to multiband alloys, which treats properly the effects of so-called general ODD, defined as the dependence of the hopping integrals  $\underline{W}_{ij}$  on the species of atoms at sites  $i$  and  $j$ . We use under-tildes to denote matrices in orbital space, and for a binary alloy,  $A_cB_{1-c}$ , we assume that the  $\underline{W}_{ij}$  can take three values,  $\underline{W}_{ij}^{AA}$ ,  $\underline{W}_{ij}^{AB}$ , and  $\underline{W}_{ij}^{BB}$ , corresponding to a pair of  $A$  atoms, an  $A$  and a  $B$  atom, and a pair of  $B$  atoms, respectively. Given these alloy parameters, one can then examine accurately the separate effects of diagonal and of off-diagonal disorder in substitutionally disordered alloys.

In a recent paper,<sup>9</sup> Laufer and Papaconstantopoulos showed that TB-CPA calculations for Pd-Ag alloys in which ODD plays only a minor role are in excellent agreement with both experiment and the results of KKR-CPA calculations.<sup>10</sup> These authors used an improved version of the TB-CPA which includes  $s$ ,  $p$ ,  $t_{2g}$ , and  $e_g$  electron self-energies avoiding the previously used simplification of a one-level TB Hamiltonian. In addition, they used TB parameters<sup>11</sup> which are of much greater accuracy than those used in previous studies. By contrast, calculations by the same authors for Cu-Pd alloys yielded substantial discrepancies from the results of KKR-CPA calculations,<sup>6</sup> particularly at the low end of the spectrum for Cu-rich systems.

It is, therefore, of interest to examine the effects of ODD in Cu-Pd alloys using a TB formulation. Such a study might also shed some light on the interpretation of experimentally obtained soft-x-ray emission (SXE) spectra.<sup>12</sup> These experiments indicate the presence of a much larger Pd density of states (DOS) just below the Fermi level, and a correspondingly much lower DOS near the bottom of the band in Cu-rich systems, than is obtained by the KKR-CPA<sup>10</sup> calculations. Although it is not expected that a TB-CPA, even with ODD properly treated, will yield results more reliable than those of the KKR-CPA, it would be instructive to compare the two methods for a nontrivial case such as CuPd. It is also instructive to compare the present approach for the treatment of ODD to more simplified treatments.<sup>13,14</sup> The results of our calculations will be discussed in Sec. IV, after they are presented in Sec. III. A brief summary of the formalism used in carrying out these calculations is given in the following section.

## II. FORMALISM

In the tight-binding approximation, the electronic Hamiltonian of a material is given by the expression

$$\underline{H} = \sum_i |i\rangle \underline{\varepsilon}_i \langle i| + \sum_{i,j} |i\rangle \underline{W}_{ij} \langle j|, \quad (2.1)$$

where  $|i\rangle$  denotes a state vector associated with site  $i$ . The site-diagonal energies  $\underline{\varepsilon}_i$  and the off-diagonal transfer term  $\underline{W}_{ij}$  in general depend on the occupancy of sites  $i$  and  $j$  and the local environment of those sites. In the usual treatments of disordered materials, the environmental dependence is neglected. For example, in a binary alloy  $A_c B_{1-c}$ , the  $\varepsilon_i$  can assume the "values"  $\underline{\varepsilon}^A$  or  $\underline{\varepsilon}^B$ , while the  $\underline{W}_{ij}$  can take on the values  $\underline{W}_{ij}^A$ ,  $\underline{W}_{ij}^{AB} = \underline{W}_{ij}^{BA}$ , and  $\underline{W}_{ij}^B$ . The variation of the diagonal elements  $\underline{\varepsilon}_i$  with composition is commonly referred to as diagonal disorder, whereas the similar variation of the transfer terms gives rise to off-diagonal disorder (ODD). The formalism of this section is specifically concerned with the treatment of general ODD, i.e., when no special relations are assumed between the values of the transfer terms  $\underline{W}_{ij}$ .

As mentioned in the Introduction, general ODD can be treated in a straightforward way within the reformulation of the CPA proposed<sup>7</sup> by BEB. As this reformulation has been presented in a previous publication,<sup>8</sup> we shall confine ourselves to a brief summary.

Given the tight-binding Hamiltonian Eq. (2.1), we seek methods for evaluating the associated Green function

$$\underline{G}(z) = (z - \underline{H})^{-1} \quad (2.2)$$

at any (complex) energy parameter  $z$  and in the presence of both diagonal and off-diagonal disorder. In a site representation the matrix elements of  $\underline{G}(z)$  satisfy the equation of motion

$$\underline{G}_{ij} = g_i \left[ \delta_{ij} + \sum_{k(\neq i)} \underline{W}_{ik} \underline{G}_{kj} \right], \quad (2.3)$$

where

$$g_i = (z - \underline{\varepsilon}_i)^{-1} \quad (2.4)$$

is the "bare" locator associated with site  $i$ . For the sake of concreteness we specialize to the treatment of binary alloys; the extension of the formalism to multicomponent materials is straightforward. We note that both  $g_i$  and  $\underline{W}_{ij}$  are in general correlated functions of the species of atoms at sites  $i$  and  $j$ , and Eq. (2.3) must be treated with special care. In order to account for the effects of ODD, Blackman *et al.*<sup>7</sup> rewrote Eq. (2.3) in a matrix form in which the hopping terms become composition independent.

To accomplish this transformation, we introduce indices  $x_i$  and  $y_i = 1 - x_i$ ,

$$x_i = \begin{cases} 1, & \text{if site } i \text{ is occupied by an } A \text{ atom} \\ 0, & \text{otherwise,} \end{cases} \quad (2.5)$$

multiply Eq. (2.3) from the left and right with all possible combinations of  $x$ 's and  $y$ 's, insert the identity  $x_k + y_k = 1$  into the product of  $\underline{W}_{ik} \underline{G}_{kj}$  and collect the resulting expressions in the single matrix form

$$\hat{\underline{G}}_{ij} = \hat{\underline{g}}_i \left[ \delta_{ij} + \sum_{k(\neq i)} \hat{\underline{W}}_{ik} \hat{\underline{G}}_{kj} \right]. \quad (2.6)$$

Here, the various matrices are defined by the expressions

$$\hat{\underline{G}}_{ij} = \begin{bmatrix} x_i \underline{G}_{ij}^{AA} x_j & x_i \underline{G}_{ij}^{AB} y_j \\ y_i \underline{G}_{ij}^{BA} x_j & y_i \underline{G}_{ij}^{BB} y_j \end{bmatrix}, \quad (2.7a)$$

$$\hat{\underline{g}}_i = \begin{bmatrix} x_i g_i^A & 0 \\ 0 & y_i g_i^B \end{bmatrix}, \quad (2.7b)$$

with

$$g_i^\alpha = (z - \underline{\varepsilon}_i^\alpha)^{-1}, \quad \alpha = A \text{ or } B, \quad (2.7c)$$

and

$$\hat{\underline{W}}_{ij} = \begin{bmatrix} \underline{W}_{ij}^{AA} & \underline{W}_{ij}^{AB} \\ \underline{W}_{ij}^{BA} & \underline{W}_{ij}^{BB} \end{bmatrix}. \quad (2.7d)$$

We note that the matrix  $\hat{\underline{W}}_{ij}$  is translationally invariant, depending only on the distance between sites  $i$  and  $j$ .

The matrix Eq. (2.6) can be treated along lines analogous to those of the original, scalar applications of the CPA.<sup>1-3</sup> The true disordered material is replaced<sup>8</sup> by a translationally invariant effective medium characterized by a site-diagonal matrix self-energy

$$\hat{\underline{\sigma}} = \begin{bmatrix} \underline{\sigma}^{AA} & \underline{\sigma}^{AB} \\ \underline{\sigma}^{BA} & \underline{\sigma}^{BB} \end{bmatrix}. \quad (2.8)$$

This self-energy is determined through the CPA self-consistency condition that the site-diagonal element of the effective medium Green function be equal to the single-site average of the corresponding element of the disordered material,

$$\langle \hat{\underline{G}}_{00} \rangle = \hat{\underline{G}}_{00}, \quad (2.9)$$

where  $\langle \dots \rangle$  denotes an average over the occupation of a single site. The Green functions in Eq. (2.9) are given explicitly<sup>7,8</sup> by the expressions

$$\langle \hat{G}_{00} \rangle = \begin{pmatrix} c\hat{G}_{00}^A & 0 \\ 0 & (1-c)\hat{G}_{00}^B \end{pmatrix}, \quad (2.10)$$

with

$$G_{00}^\alpha = \{ [1 - \hat{g}_0 (\hat{g}_0^{-1} - \hat{G}_{00}^{-1})]^{-1} \hat{g}_0 \}^{\alpha\alpha}, \quad \alpha = A \text{ or } B \quad (2.11)$$

$$\hat{g}_0 = (z - \hat{\epsilon})^{-1}, \quad (2.12)$$

and  $z = z\mathbb{1}$ , where  $\mathbb{1}$  denotes the  $2 \times 2$  unit matrix in site and orbital space. The effective medium Green function  $\hat{G}_{00}$  takes the usual form,

$$\hat{G}_{00} = \frac{1}{\Omega_{\text{BZ}}} \int_{\text{BZ}} [z - \hat{\epsilon} - \hat{W}(\mathbf{k})]^{-1} d^3\mathbf{k}, \quad (2.13)$$

where

$$\hat{W}(\mathbf{k}) = \sum_j \hat{W}_{0j} e^{i\mathbf{k} \cdot \mathbf{R}_{0j}}, \quad (2.14)$$

and the integration extends over the first Brillouin zone (BZ) of the reciprocal lattice with  $\Omega_{\text{BZ}}$  the volume of the zone. Alternative expressions for the CPA equations can be derived,<sup>8</sup> and these considerations can be extended in a conceptually simple way to multicomponent alloys.

Once  $\langle \hat{G}_{00} \rangle$  or, equivalently,  $\hat{G}_{00}$ , has been determined, a number of physical quantities can be obtained. For example, the species-resolved local density of states (DOS) corresponding to component  $\alpha$  in the alloy is given by the relation

$$n^\alpha(E) = -\frac{1}{\pi} \text{Im Tr} \hat{G}_{00}^{\alpha\alpha}, \quad (2.15)$$

whereas the total DOS is obtained in the form

$$n(E) = -\frac{1}{\pi} \text{Im Tr} \langle \hat{G}_{00} \rangle = -\frac{1}{\pi} \text{Im Tr} \hat{G}_{00}. \quad (2.16)$$

The designation Tr in these expressions is taken to include any possible summations of diagonal elements in a given basis such as that of angular momentum.

### III. NUMERICAL RESULTS

The parameters entering the TB description of the alloy were determined through a Slater-Koster<sup>15</sup> parametrization procedure of the electronic structure of elemental Cu and Pd obtained through an application of the Slater augmented-plane-wave (APW) method. This procedure involved an orthogonal TB Hamiltonian with 32 three-center parameters, the values of which are given in Ref. 11. We are particularly interested in studying the effects of ODD, which can now be delineated from those of diagonal disorder using the method of BEB.<sup>7</sup>

The hopping matrix elements between different alloy species were obtained as the concentration weighted average  $\ln W^{AB} = c \ln W^{AA} + (1-c) \ln W^{BB}$ . This yields a more general type of ODD than the commonly used<sup>13</sup> geometric model  $W^{AB} = (W^{AA} W^{BB})$ , requiring the use of the general formulation of the previous section.

In order to check the reliability of the scheme for determining the hopping matrix elements  $W^{AB}$ , we calculated the DOS for an ordered  $\text{Cu}_3\text{Pd}$  alloy using these values and compared them with a self-consistent APW calculation that we performed for the same system. The results are shown in Fig. 1. We see here that although the TB results shown in panel (a) are not in *exact* agreement with those of the APW method, they agree much better than those obtained in Ref. 14 for *pure* Cu, and agree with pure Cu in which Harrison's parameters were used to estimate  $W$ . The TB results shown in panel (a) of Fig. 1 are slightly "narrower" than the APW DOS's, but are fairly well structured, as one expects from an ordered material, and the main peaks are generally in the positions indicated by the APW results. This structure is nearly washed away in the Harrison scheme used in Ref. 14.

The CPA effective Hamiltonian, resulting from the formalism described in the previous section, is an  $18 \times 18$  matrix that consists of four  $9 \times 9$  blocks, which for CuPd alloys involve Cu-Cu, Pd-Pd, Cu-Pd, and Pd-Cu interactions. The calculations were performed on a uniform mesh of 505  $k$  points in the  $1/48$ th of the Brillouin zone.

The following figures depict DOS's for the  $\text{Cu}_{0.75}\text{Pd}_{0.25}$  alloy obtained through applications of the TB-CPA without ODD (Fig. 2), with ODD (Fig. 3), and of the KKR-CPA (Fig. 4). A comparison between the two TB calculations reveals a similar structure in the DOS's with the following important differences:

(i) The overall width of the total DOS increases with the introduction of ODD to  $\sim 0.37$  Ry, from  $\sim 0.34$  Ry in the absence of ODD. This increase is in keeping with the wider bands,  $\sim 0.38$  Ry, obtained in the KKR-CPA (Fig. 4).

(ii) The DOS at the Fermi level decreases in the presence of ODD to  $N(E_F) = 4.4$  states/Ry spin from  $N(E_F) = 7.7$  states/Ry spin in the absence of ODD, which agrees better with the low value of  $N(E_F)$  obtained

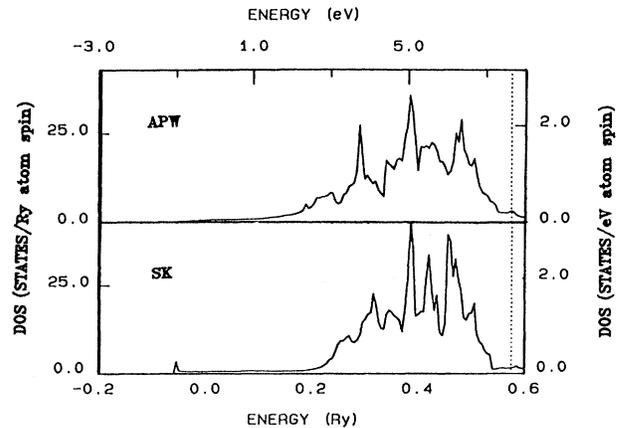


FIG. 1. Comparison of density of states resulting from a self-consistent APW calculation for ordered  $\text{Cu}_3\text{Pd}$  (top panel) with density of states from a TB calculation using the Slater-Koster parameters of Cu and Pd (bottom panel).

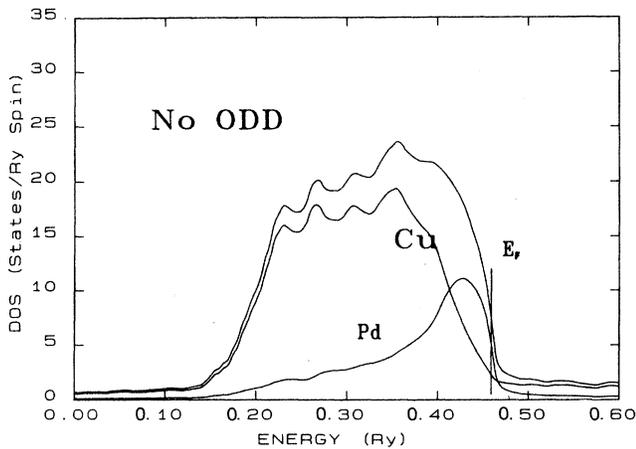


FIG. 2. Densities of states (total and Cu,Pd sites composition weighted) for  $\text{Cu}_{0.75}\text{Pd}_{0.25}$  using the TB-CPA without ODD.

in the KKR-CPA calculation, and is in good agreement with the measured specific-heat<sup>16</sup> coefficient  $\gamma$ .

(iii) The effects of ODD appear to be smaller than the differences in the densities of states obtained within the TB-CPA and the KKR-CPA.

(iv) In the calculation that includes ODD, the Pd-site DOS has a much broader and lower peak near  $E_F$  than that obtained if ODD is neglected.

Comparing the results of the TB and KKR versions of the CPA we note that the latter yields a much more structured DOS inside the band than the former. But the most striking difference between these two sets of calculations is that in the TB results, with and without ODD, the Pd-site DOS has practically no weight at energies far below  $E_F$ . This is in sharp disagreement with the results of the KKR-CPA shown in fig. 4, which reveal the presence of a secondary broad peak near the bottom of the band. Consequently, and rather inexplicably at present,

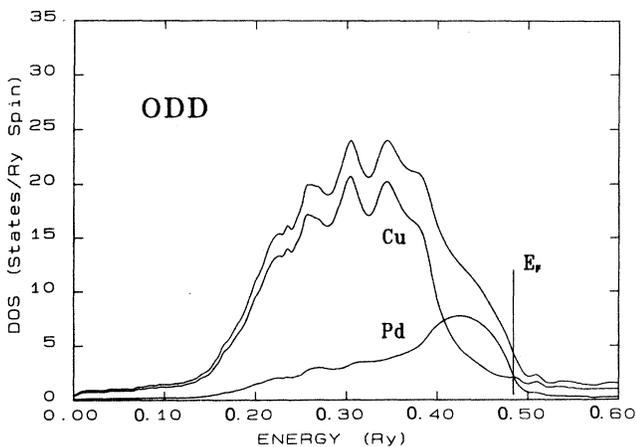


FIG. 3. Densities of states (total and Cu,Pd sites composition weighted) for  $\text{Cu}_{0.75}\text{Pd}_{0.25}$  using the TB-CPA with ODD.

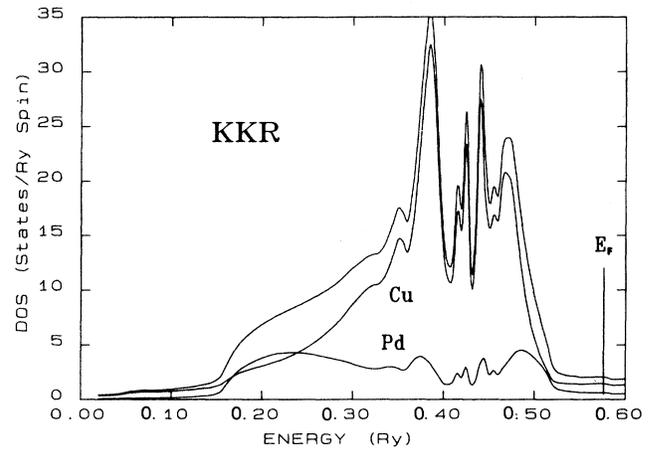


FIG. 4. Densities of states for  $\text{Cu}_{0.75}\text{Pd}_{0.25}$  from the KKR-CPA calculations of Ref. 6.

the TB-CPA results appear to be in better agreement with measured XSE spectra.<sup>12</sup>

Recently Stefanou *et al.*<sup>17</sup> argued that the intensity of the low-energy peak in the Pd DOS is sensitive to charge transfer, relativistic effects, and lattice relaxation which are not included in the KKR-CPA calculations. They performed cluster calculations that incorporate these effects and show a trend of reducing the Pd peak at low energies. Our calculations include relativistic effects (unlike the KKR-CPA) but ignore both charge transfer and lattice relaxation. So it is presently unclear why we obtain a better agreement with experiment than results from applications of the KKR-CPA.

#### IV. CONCLUSIONS

In this paper, we presented for the first time a proper treatment of ODD within a TB formalism applicable to multiband, substitutionally disordered alloys. We find that such a treatment results in DOS curves which are in better agreement with those obtained within the KKR-CPA, than those resulting when ODD is neglected, or treated in the virtual crystal limit. However, even with the incorporation of ODD there are serious discrepancies with the KKR-CPA. Our calculations indicate that the differences between the TB-CPA density of states curves with and without ODD are smaller than the differences between these curves and the DOS obtained in the KKR-CPA. At the same time, the low weight of the Pd subband at low energies obtained in both TB-CPA calculations is indeed puzzling. We can say with some certainty that ODD, per se, which is treated properly within the KKR-CPA, does not seem to cause the presence of the high Pd DOS in the KKR-CPA results. Neither does it appear to be the case that the interpolation scheme used to obtain  $\overline{W}^{AB}$  is less accurate than the admittedly simplified approximation of geometrical average.<sup>14</sup> The parameters given in Ref. 11 fit the first-principles energy bands with an rms deviation of approximately 3 mRy. As we discussed in Sec. III, alternative schemes such as

the Harrison parameters used in Ref. 14 can only yield rather crude representations of the energy bands. This has also been demonstrated for the case of Nb in a recent publication.<sup>18</sup> In the same publication,<sup>18</sup> a calculation on the CsCl-structure compound TiFe generated from the Slater-Koster parameters of pure bcc Ti and Fe and their averages reproduces reasonably well the APW results of this compound, as is the case for Cu<sub>3</sub>Pd in the present work.

Presently, matters with respect to the low-energy *d* band of disordered Cu<sub>0.75</sub>Pd<sub>0.25</sub> alloys appear to stand as follows: The KKR-CPA, which admittedly treats ODD exactly, and a TB calculation<sup>14</sup> on the basis of rather crude parameters and a simplified treatment of ODD, yield DOS's which agree with one another but disagree with experiment. The present TB calculation, carried out on the basis of more accurate TB parameters and a proper treatment of ODD, yields results which agree better with experiment, but not with these of the KKR-CPA or

simplified TB methods. Given that TB parameters are the results of fitting and/or parametrization schemes, we can only conclude that the present fitting of the TB parameters happens to reflect more accurately the underlying physics of Cu<sub>0.75</sub>Pd<sub>0.25</sub> alloys. At the same time, it should be pointed out that it is unclear if the discrepancies between SXE and "band-structure calculations" is due to inadequacies in the one-electron calculation of the partial DOS or deviations from a one-electron description. It is a challenge to understand why this is so, and if it is possible to obtain agreement with experiment by using an extended version of the KKR-CPA.

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