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Electronic structure of ordered and disordered Cu_xPd_{1-x} alloys via the linear-muffin-tin-orbitals method

S. K. Bose
Department of Physics, Brock University, St. Catharines, Ontario, Canada L2S 3A1
and Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, Postfach 80 06 65, D-7000 Stuttgart 80, Germany

J. Kudrnovský
Institute of Physics, Czechoslovak Academy of Sciences, Na Slovance 2, CZ-180 40 Prague 8, Czechoslovakia
and Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, Postfach 80 06 65, D-7000 Stuttgart 80, Germany

O. Jepsen and O. K. Andersen
Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, Postfach 80 06 65, D-7000 Stuttgart 80, Germany

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We present the electronic density of states (DOS) in ordered and disordered $Cu_{50}Pd_{50}$ and $Cu_{75}Pd_{25}$ alloys calculated by using the linear-muffin-tin-orbitals (LMTO) method. For ordered alloys the results are obtained via a self-consistent standard LMTO method. We then show how the LMTO potential parameters for pure Cu and pure Pd (in the fcc phases) can be appropriately transferred to the ordered-alloy calculation to produce results that are in excellent agreement with the self-consistent calculation. For disordered alloys we present the electronic DOS calculated via LMTO-recursion and LMTO-CPA (coherent-potential-approximation) methods, and study the effect of the relaxation of the lattice, i.e., the deviation from the ideal lattice structure, due to different sizes of the Cu and the Pd atoms, on the electronic structure of these alloys. We also discuss how the above scheme of transferring parameters from the pure components to the alloy can be used in the calculation for the disordered phase to obtain nearly-self-consistent results.

I. INTRODUCTION

The electronic structure of the (substitutionally) disordered Cu_xPd_{1-x} alloy system has been the subject of considerable theoretical[1-7] and experimental[8-15] investigation in recent years. From a theoretical viewpoint the disordered Cu-Pd alloys are interesting on several grounds. (i) Off-diagonal disorder is much stronger than the diagonal disorder in these alloys, rendering the split-band picture of alloy theory totaly invalid. (ii) There is an appreciable size difference between the Cu and the Pd atoms, the radius of the Pd Wigner-Seitz (WS) sphere being about 7% larger than that of Cu. This nonisochoricity poses some problems in the calculation of the electronic structure. (iii) They can be prepared in the ordered as well as the disordered phase over a wide composition range, and thus provide an important test case for theoretical studies of alloy phase stability.

Considerable interest was generated recently about this alloy system when the results of charge-self-consistent Korringa-Kohn-Rostoker coherent-potential-approximation (KKR-CPA) calculations predicted features in the electronic density of states (DOS) which disagreed with experimental results.[1,2] The case for this disagreement has been investigated by several authors.[1,2,16] Among the techniques applicable to random (substitutionally disordered) alloys, the one that yields results in best agreement with experiments for nonisochoric alloys such as Cu-Pd seems to be the CPA version[1,17,18] of the linear-muffin-tin-orbitals[19-21] (LMTO) method. Nonisochoricity, i.e., the size difference between the component atoms, gives rise to deviations from the ideal lattice structure. This relaxation of the ideal lattice, which has been verified by extended x-ray-absorption fine-structure (EXAFS) experiments for the Cu-Pd alloy system,[16] can be treated in a simple and physically transparent way within the LMTO-CPA method. Because of the simplicity of the scheme, only an approximate treatment of the lattice-relaxation effect has been possible so far. However, results based on this approximate treatment have been found particularly encouraging.[1,17,18,22,23] In this paper we present and discuss some results for the electronic structure of ordered and disordered $Cu_{75}Pd_{25}$ and $Cu_{50}Pd_{50}$ alloys obtained by using the standard LMTO (for the ordered state) and LMTO-CPA (Refs. 1, 17, and 18) and LMTO-recursion (Refs. 24 and 25) (for the disordered state) methods. Suffice it to say that the results we present are in good agreement with available experimental results.[14,16] However, the primary object of the present paper is not a comparison between theory and experiments, but to illustrate some important aspects of the LMTO method. We have chosen the Cu-Pd alloy system as a test case to illustrate these aspects because it provides a nontrivial and interesting example from a theoretical standpoint, as discussed above.

It is generally believed that a charge-self-consistent calculation is necessary for an accurate description of the electronic structure of alloys. Although charge self-consistency within a given method offers the best possible result for that method, it is usually expensive and time

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consuming. So the issue as to how we can avoid a charge-self-consistent calculation and yet obtain reasonably accurate results is of interest. In particular, we may want to know how the knowledge of the pure components can help us in the calculation for the alloy. We explore this issue within the framework of the LMTO method using the example of Cu-Pd alloys. The LMTO Hamiltonian depends on the structure (arrangement of atoms in space) of the system via the structure constants and the chemical properties of the atoms via the potential parameters.[20,21] It is interesting to study to what extent the structure-independent quantities, i.e., the potential parameters, are transferable from the pure-component systems to the alloy. We illustrate simple and physically transparent schemes of transferring parameters from the pure components to ordered and disordered alloys. Apart from enabling us to perform reasonably accurate electronic-structure calculations using less resources, such a study also clarifies some important physics underlying the method. In Sec. II we discuss the ordered-alloy (Cu_3Pd and CuPd) calculation, where results of self-consistent LMTO calculations are compared with those obtained with transferred parameters. In Sec. III we discuss various aspects of the disordered-alloy calculation. In Sec. III A we show the effect of relaxation of the lattice, due to the size difference of the Cu and Pd atoms, on the electronic structure of disordered $Cu_{75}Pd_{25}$ and $Cu_{50}Pd_{50}$ alloys by applying the recursion method[24] to a tight-binding form of the LMTO Hamiltonian.[25] In Sec. III B we present a comparison of the LMTO-CPA and LMTO-recursion results, and in Sec. III C we discuss the best way to use the potential parameters of the pure components in the calculation for the disordered alloy.

II. ELECTRONIC STRUCTURE OF ORDERED Cu_3Pd AND CuPd ALLOYS

The object of the present section is to discuss and test the transferability of the LMTO potential parameters from the pure components to the alloy as prescribed by Andersen *et al.*[20] In effect, we want to obtain the potential parameters for an intermetallic compound from those of its constituents, without any self-consistent calculation. For structures that can be packed closely with atomic (atom-centered) spheres, without the introduction of empty spheres (spheres centered about interstitial sites), the prescription of Andersen *et al.*[20] for estimating the potential in the compound is simply to use the atomic-sphere potentials of the elements. These frozen atomic-sphere potentials correspond to neutral spheres, and the lineup of the internal energy zeros is consistent as long as the spheres remain neutral in the compound. Experience shows that this charge neutrality, defined with respect to the atomic spheres of the elements, is maintained within a few tenths of an electron in most cases. This means that for alloys obeying Vegard's law, where the volume per atom in the alloy is simply the concentration-weighted average of the normal-pressure atomic volumes of the constituents, the use of normal-pressure values of the constituents' potential parameters should yield a sufficiently accurate potential and charge density. When the binding in the compound is different from that in the constituents, there is no reason why the atomic volumes of the elements should be taken at normal pressure, i.e., the same pressure as the volume of the compound. For such alloys (showing deviation from Vegard's law) the potentials of the elements should be calculated at such a pressure that the concentration-weighted sum of the atomic volumes equals the actual volume per atom in the alloy. Thus for binary A_xB_{1-x} alloys with volume V^{alloy} per atom, the atomic volumes of the constituents, V^Q $(Q=A,B)$, should satisfy the volume constraint

$$xV^A+(1-x)V^B=V^{\text{alloy}} . \tag{1}$$

The assumption of a linear pressure-volume relation yields

$$(V^A-V_0^A)/V_0^A:(V^B-V_0^B)/V_0^B=B_0^B:B_0^A , \tag{2}$$

where V_0^Q $(Q=A,B)$ are the normal-pressure atomic volumes of the components and B_0^Q $(Q=A,B)$ are the bulk moduli. The solution to Eqs. (1) and (2) is

$$\begin{aligned} V^A&=\frac{B_0^BV^{\text{alloy}}+(1-x)V_0^B(B_0^A-B_0^B)}{xV_0^AB_0^B+(1-x)V_0^BB_0^A}V_0^A ,\\ V^B&=\frac{B_0^AV^{\text{alloy}}+xV_0^A(B_0^B-B_0^A)}{xV_0^AB_0^B+(1-x)V_0^BB_0^A}V_0^B . \end{aligned} \tag{3}$$

The potential parameters in the alloy for the component Q $(Q=A,B)$ should be calculated at new radius $s^Q=(3V^Q/4\pi)^{1/3}$.

Using the atomic-sphere approximation (ASA),[20,21] the matrix elements of the one-electron Hamiltonian in a nearly orthogonal LMTO representation can be written as

$$\begin{aligned} H_{\mathbf{R}L,\mathbf{R}'L'}&=C_{\mathbf{R}L}\delta_{\mathbf{R}\mathbf{R}'}\delta'_{LL}\\ &\quad+\Delta_{\mathbf{R}L}^{1/2}[S^0(1-\gamma S^0)^{-1}]_{\mathbf{R}L,\mathbf{R}'L'}\Delta_{\mathbf{R}'L'}^{1/2} . \end{aligned} \tag{4}$$

Here, $\mathbf{R}$ and $L(l,m)$ are the site- and the orbital-angular-momentum indices, respectively. S^0 is the canonical structure constant matrix, which depends on the relative positions of the sites, but is independent of the type of atoms that occupy the sites. The properties of the atoms are completely described by the matrices $\mathbf{X}$ $(\mathbf{X}=C,\Delta,\gamma)$, which are diagonal in the indices $\mathbf{R}$ and L and are independent of m, i.e.,

$$(\mathbf{X})_{\mathbf{R}L,\mathbf{R}'L'}=X_{\mathbf{R}L}\delta_{\mathbf{R}\mathbf{R}'}\delta_{LL'}=X_{\mathbf{R}l}\delta_{\mathbf{R}\mathbf{R}'}\delta_{LL'} .$$

Also, $X_{\mathbf{R}l}=X_l^Q$, where Q is the type of the atom occupying the site $\mathbf{R}$. The matrix elements $X_{\mathbf{R}L}$ are called the potential parameters. The Löwdin-orthogonalized Hamiltonian in the ASA, $O^{-1/2}\text{H}O^{-1/2}$, can be obtained from the knowledge of an additional (small) potential parameter, $p_{\mathbf{R}L}=p_{\mathbf{R}l}$,[20,21] which determines the overlap matrix O:

$$O=I+hph,\quad h=H-E_\nu ,$$

where E_ν is the matrix of the reference energies, diagonal in the **R**L representation with $E_{\nu,\mathbf{R}L}=E_{\nu,\mathbf{R}l}=E_{\nu l}^{Q}$. The potential parameters are derived from the solution of the radial Schrödinger equation or the scalar-relativistic wave equation at the sphere boundary and its energy derivative at the reference energies $E_{\nu l}^{Q}$ of the linear method. The values of the potential parameters at the radii appropriate in the alloy phase s^{Q} $(Q=A,B)$ can be obtained from the normal-pressure radii s_0^Q and the volume derivatives of the potential parameters.[17,20] As pointed out in Ref. 20, for large differences between s^Q and s_0^Q it is important not to interpolate linearly in s^Q. In general, it is safe to use the following equations using logarithmic interpolation:

$$
\begin{aligned}
C_L^Q&=C_{0L}^Q+\frac{dC_L^Q}{d\ \ln s^Q}\ln(s^Q/s_0^Q)\ ,\\
\gamma_L^Q&=\gamma_{0L}^Q+\frac{d\gamma_L^Q}{d\ \ln s^Q}\ln(s^Q/s_0^Q)\ ,\\
\Delta_L^Q&=\Delta_{0L}^Q(s^Q/s_0^Q)^{d\ \ln\Delta_L^Q/d\ \ln s^Q}\ ,\\
(p_L^Q)^{-1/2}&=(p_{0L}^Q)^{-1/2}(s^Q/s_0^Q)^{d\ \ln(p_L^Q)^{-1/2}/d\ \ln s}\ .
\end{aligned}
\tag{5}
$$

The potential parameters of 33 elemental metals for normal pressure, as well as their radial derivatives obtained via self-consistent s,p,d,f-basis LMTO-ASA calculations (including combined corrections), are tabulated in Ref. 21. Thus, for most intermetallic alloys the component potential parameters appropriate to the alloy phase can be obtained "by hand," i.e., without a computer. After extrapolation of the potential parameters to new radii, one must take into account the fact that the alloy WS radius is different from that of the pure components, where the WS radii are the same as the sphere radii. This affects only two of the parameters, viz., Δ and γ, which should be multiplied by $(s^Q/W)^{2l+1}$, where $W=(3V^{\text{alloy}}/4\pi)^{1/3}$ is the alloy WS radius, i.e.,

$$
(G_L^Q)_{\text{alloy}}=(s^Q/W)^{2l+1}(G_L^Q)_{\text{pure component}}\ , \tag{6}
$$

where $G=\Delta,\gamma$. Prescription (3) for obtaining the sphere radii for the components in the alloy usually leads to only a small charge transfer (within a few tenths of an electron) between the spheres, and hence the potential parameters obtained by using Eqs. (5) and (6), appropriate for neutral spheres, yield a reasonably accurate electronic structure for the alloy. The charge transfer gives rise to a Madelung term in the one-electron potential. The potential in a given sphere undergoes a constant shift depending on the charge transfer for that sphere. The effect of this Madelung shift is present in the potential parameters obtained in a self-consistent calculation. The potential parameters obtained by using Eqs. (5) and (6) are for neutral spheres, and therefore do not show this Madelung shift, resulting in slightly inaccurate positioning of the bands. A small charge transfer, and consequently a small Madelung shift, is the key to the success of the above transferability scheme.

We calculate the electronic structure of the ordered Cu_3Pd and CuPd alloys using the above transferability scheme as well as via the self-consistent standard LMTO scheme. We consider Cu_3Pd in the Cu_3Au (fcc) structure with its experimental WS radius of 2.712 a.u. (Ref. 26) and CuPd in the CsCl (bcc) structure with its experimental WS radius of 2.771 a.u.[26] The Vegard's-law values of the WS radii for Cu_3Pd and CuPd are 2.723 and 2.775 a.u., respectively. Since these alloys obey Vegard's law extremely well, it is not necessary to strictly adhere to the compressibility criterion [Eq. (3)] in determining V^A and V_B, which are extremely close to the pure element values V_0^C $(C=A,B)$ in this case. Suppose we keep the radius of the Cu sphere, s^{Cu}, the same as in pure Cu [2.669 a.u. (Ref. 21)]. Then the sphere radii for Pd, s^{Pd}, as obtained from the volume preservation based on the experimental WS radii of the alloys, are 2.865 and 2.833 a.u. in CuPd and Cu_3Pd, respectively, while $s_0^{\text{Pd}}=2.873$ a.u. (Ref. 21). In Table I we present the potential parameters for the alloys obtained by using the above transferability scheme [Eqs. (5) and (6)]. These potential parameters were obtained from those of pure Cu and pure Pd based on an s,p,d-basis LMTO calculation. The latter vary only slightly from the parameters based on s,p,d,f-basis calculation reported in Ref. 21. The numbers within the parentheses in Table I are the potential parameters obtained in a charge-self-consistent scalar-relativistic LMTO-ASA (s,p,d-basis) calculation including combined corrections[20,21] for the alloys using the sphere radii quoted above. The agreement between the numbers testifies to the validity of the prescription used. If we transfer the tabulated parameters from Ref. 21, based on an s,p,d,f-basis calculation, the agreement with the results of the s,p,d-basis calculation becomes only slightly worse and is perfectly understandable. As shown in Figs. 1–4, the DOS's calculated via the self-consistent LMTO method for the two alloys are indistinguishable from those obtained by using the transferred parameters.

III. ELECTRONIC STRUCTURE OF DISORDERED $Cu_{75}Pd_{25}$ AND $Cu_{50}Pd_{50}$ ALLOYS

In this section we discuss the electronic structure of substitutionally disordered fcc phase (α phase) of the $Cu_{75}Pd_{25}$ alloy, which can be prepared by the rapid quenching technique. Since these alloys show negligible deviation from Vegard's law, we use the radii of the Cu and Pd atomic spheres for the pure crystalline phases in the alloy calculation. Although the lattice parameters for the ordered CuPd and Cu_3Pd are known, it is not clear whether the ordered and the disordered alloys have the same lattice parameters. In view of the possible lattice relaxation in the disordered phase, a small difference between the lattice parameters in the ordered and disordered states is not unlikely. Since the exact lattice parameters for the disordered phase is not known, we have assumed that Vegard's law is obeyed fully in the disordered phase. This is a reasonable assumption since the ordered alloy is known to satisfy Vegard's law very closely. For the purpose of comparing the electronic structure of the ordered and disordered states, this (the use of slightly different radii for the ordered and disordered alloys) does not pose a serious problem. The potential parameters obtained by using the pure-component radii

($s^{\mathrm{Cu}}=2.669$ a.u. and $s^{\mathrm{Pd}}=2.873$ a.u.) in a self-consistent ordered structure calculation for CuPd and $\mathrm{Cu_3Pd}$ are presented in Table II. They differ very little from the parameters in Table I. This is not surprising since the differences in the radii used are very small. The ordered-structure DOS's obtained (not presented in this paper) by using the potential parameters from Table II are almost indistinguishable from those presented in Figs. 1–4. This indicates that the use of pure-component radii for the disordered alloy should not result in DOS's any different from those that would be obtained for the slightly different radii actually used in the ordered-structure calculation.

A. Effect of lattice relaxation on the electronic structure

Because of the appreciable difference in the sizes of the Pd and Cu atoms, the fcc structure of the alloy is perturbed in the disordered phase. Such deformations are missing in the ordered phase. The effect of such deformations should enter the electronic-structure calculation via the structure constants $S_{RL,R'L'}$ appearing in the Hamiltonian given by Eq. (4). These can be calculated if the exact arrangement of the atoms in the disordered phase is known. In the absence of this knowledge, one can resort

TABLE I. LMTO potential parameters for ordered $\mathrm{Cu_3Pd}$ ($\mathrm{Cu_3Au}$ structure) and CuPd (CsCl structure) alloys obtained from the pure-Cu and pure-Pd potential parameters, with $s^{\mathrm{Cu}}=2.669$ a.u. and $s^{\mathrm{Pd}}=2.833$ a.u. in $\mathrm{Cu_3Pd}$ and 2.865 a.u. in CuPd. The numbers in parentheses are the potential parameters obtained using the self-consistent LMTO calculation for the alloys for the same sphere radii.

	C (Ry)	Δ (Ry)	γ	$p^{-1/2}$ (Ry)
		$\mathrm{Cu_3Pd}$		
s (Cu)	−0.4286	0.1641	0.4161	4.2209
	(−0.4255)	(0.1642)	(0.4162)	(4.2287)
p (Cu)	0.5682	0.1508	0.1066	5.9135
	(0.5719)	(0.1511)	(0.1067)	(5.9298)
d (Cu)	−0.3069	0.0083	−0.0032	0.6184
	(−0.2951)	(0.0084)	(−0.0035)	(0.6197)
s (Pd)	−0.3264	0.1762	0.4515	4.7522
	(−0.3265)	(0.1763)	(0.4519)	(4.7772)
p (Pd)	0.6960	0.1876	0.1353	6.2781
	(0.6986)	(0.1883)	(0.1356)	(6.5331)
d (Pd)	−0.3003	0.0232	0.0081	0.9832
	(−0.3048)	(0.0231)	(0.0088)	(0.9849)
		CuPd		
s (Cu)	−0.4287	0.1605	0.4073	4.2203
	(−0.4265)	(0.1606)	(0.4073)	(4.2224)
p (Cu)	0.5681	0.1414	0.0999	5.9135
	(0.5726)	(0.1421)	(0.1003)	(5.9707)
d (Cu)	−0.3070	0.0075	−0.0029	0.6184
	(−0.2957)	(0.0076)	(−0.0032)	(0.6193)
s (Pd)	−0.3423	0.1686	0.4463	4.5663
	(−0.3387)	(0.1690)	(0.4469)	(4.6077)
p (Pd)	0.6548	0.1765	0.1309	6.2781
	(0.6594)	(0.1770)	(0.1311)	(6.3389)
d (Pd)	−0.3155	0.0208	0.0075	0.9414
	(−0.3077)	(0.0210)	(0.0078)	(0.9456)

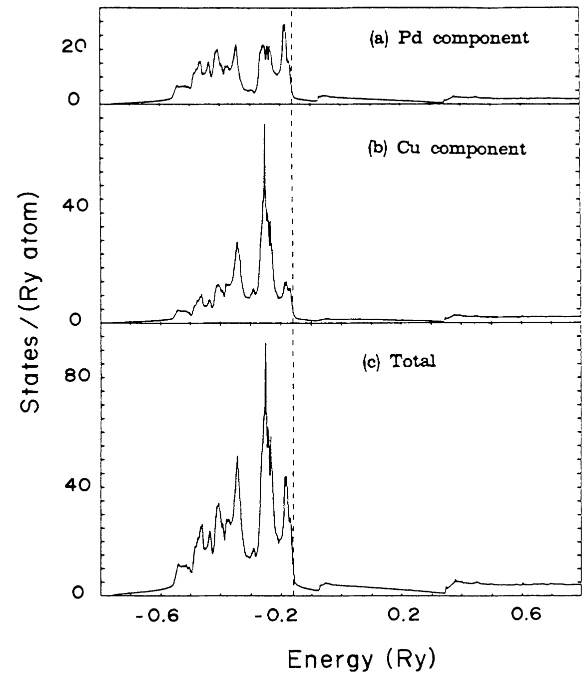

FIG. 1. Density of states (DOS) in the ordered CuPd (CsCl structure) alloy obtained using the self-consistent standard LMTO method. Panels (a) and (b) show the Pd and Cu components (concentration weighted), respectively. The total DOS in panel (c) is the sum of the DOS's in panels (a) and (b). The dashed vertical line shows the position of the Fermi levels.

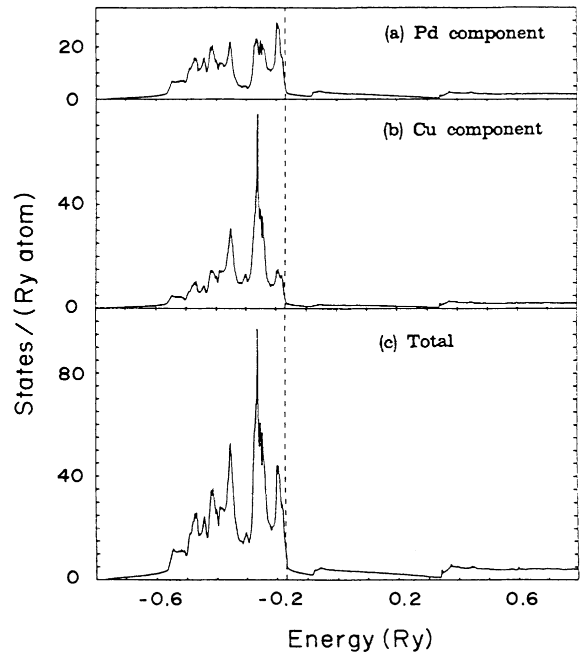

FIG. 2. DOS in the ordered CuPd (CsCl structure) alloy obtained using potential parameters transferred from pure components. Panels (a)–(c): same as Fig. 1.

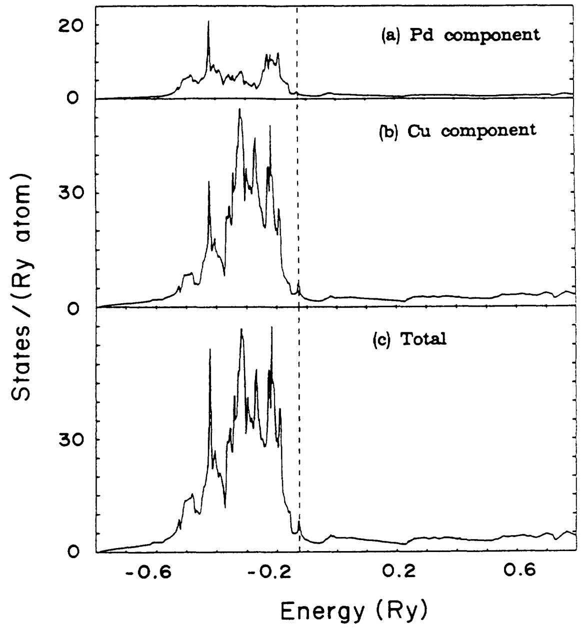

FIG. 3. DOS in the ordered Cu_3Pd (Cu_3Au structure) alloy obtained using the self-consistent standard LMTO method. Panels (a)–(c): same as Fig. 1.

TABLE II. Potential parameters for ordered Cu_3Pd (Cu_3Au structure) and CuPd (CsCl structure) alloys obtained in using a self-consistent LMTO calculation using pure-component radii $s^{\mathrm{Cu}}=2.669$ a.u. and $s^{\mathrm{Pd}}=2.873$ a.u.

	C (Ry)	Δ (Ry)	γ	$p^{-1/2}$ (Ry)
		Cu_3Pd		
s (Cu)	−0.4308	0.1632	0.4140	4.1972
p (Cu)	0.5668	0.1491	0.1054	5.9271
d (Cu)	−0.3089	0.0082	−0.0031	0.6192
s (Pd)	−0.3429	0.1709	0.4549	4.5093
p (Pd)	0.6474	0.1862	0.1387	6.2686
d (Pd)	−0.3166	0.0227	0.0089	0.9363
		CuPd		
s (Cu)	−0.4289	0.1601	0.4062	4.1930
p (Cu)	0.5692	0.1410	0.0997	5.9395
d (Cu)	−0.3058	0.0075	−0.0029	0.6190
s (Pd)	−0.3446	0.1676	0.4468	4.5325
p (Pd)	0.6469	0.1761	0.1313	6.2840
d (Pd)	−0.3165	0.0207	0.0080	0.9367

to an approximate but effective treatment of the lattice relaxation suggested by Kudrnovský and Drchal.[1,17] The prescription is simply to use the structure constants for the ordered phase, while absorbing some of the effect of structural relaxation in the potential parameters. Kudrnovský and Drchal[1,17] argue that if the multiplication by the factor $(s^{Q}/W)^{2l+1}$ in Eq. (6), which must be performed for an ordered-lattice calculation, is omitted, then the structural relaxation between nearest neighbors in the disordered phase is taken care of. The arguments holds if the distance between nearest neighbors, which is the arithmetic average $(s^{Q}+s^{Q'})/2$, can be approximated by the geometric average $(s^{Q}s^{Q'})^{1/2}$. This procedure, fairly accurate for the nearest neighbors, leaves the treatment of the relaxation involving more distant neighbors uncertain and somewhat unsatisfactory. However, in transition-metal alloys, the electronic structure is mostly determined by the rapidly decaying d-d matrix elements, and thus a reasonably accurate treatment of the nearest neighbors results in a reasonably accurate description of the electron states. We have used the above prescription to calculate the electronic structure for the lattice-relaxed disordered phase. For the sake of comparison, we also calculate the electronic structure of the disordered alloy using the factor $(s^{Q}/W)^{2l+1}$ in Eqs. (6), which corresponds to an unrelaxed-lattice calculation. We have used the recursion method of Haydock[24] to calculate the DOS for the disordered phase. The continued-fraction expansion of the diagonal matrix elements of the Green's function is terminated using the prescription of Allan.[27] Since the recursion method operates in a tight-binding (TB) basis (i.e., with short-ranged Hamiltonian matrix elements), we convert the potential parameters corresponding to the standard (long-ranged) LMTO orbitals into the TB-LMTO parameters using the prescription of Refs. 19–21. The relation between the LMTO Hamiltonian H given by Eq. (4), in a nearly orthogonal long-ranged basis, and the TB-LMTO Hamiltonian, $H^{\alpha}(=E_{\nu}+h^{\alpha})$, is given by

$$\begin{aligned} H &= E_{\nu}+h^{\alpha}(1+o^{\alpha}h^{\alpha})^{-1} \\ &= H^{\alpha}-h^{\alpha}o^{\alpha}h^{\alpha}+h^{\alpha}o^{\alpha}h^{\alpha}o^{\alpha}h^{\alpha}-\cdots\ . \end{aligned} \tag{7}$$

The superscript α refers to quantities in the TB-LMTO basis. The TB-LMTO Hamiltonian H^{α} has a form similar to H:

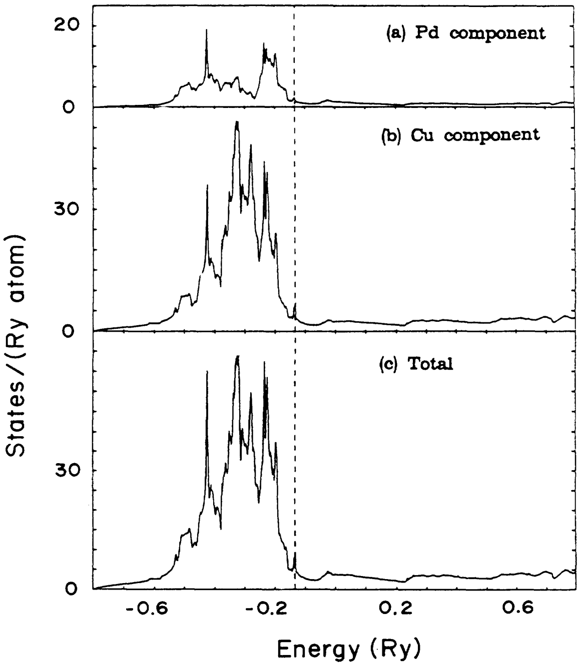

FIG. 4. DOS in the ordered Cu_3Pd (Cu_3Au structure) alloy obtained using potential parameters transferred from pure components. Panels (a)–(c): same as Fig. 1.

$$H^{\alpha}=C^{\alpha}+(\Delta^{\alpha})^{1/2}S^{\alpha}(\Delta^{\alpha})^{1/2}\ . \tag{8}$$

The TB-LMTO potential parameters, with superscript α, are related to the standard LMTO potential parameters via

$$\begin{aligned}&(\Delta^{\alpha})^{1/2}=\Delta^{1/2}+(\alpha-\gamma)(C-E_{v})\Delta^{-1/2}\ ,\\&C^{\alpha}=E_{v}+(\Delta^{\alpha})^{1/2}(C-E_{v})\Delta^{-1/2}\ ,\\&o^{\alpha}=(\alpha-\gamma)/(\Delta\Delta^{\alpha})^{1/2}\ .\end{aligned} \tag{9}$$

α is the screening matrix (l-dependent and site-independent), diagonal in the **R** representation, used to construct the TB-LMTO orbitals from the standard LMTO orbitals:

$$\alpha=0.3485,\ 0.053\,03,\ 0.010\,714\quad \text{for } l=0,1,2\ ,$$

and

$$\alpha=0\quad \text{for } l>2\ .$$

The TB structure-constant matrix S is related to the structure constants S^0 via

$$S^{\alpha}=S^{0}+S^{\alpha}\alpha S^{0}=S^{0}(1-\alpha S^{0})^{-1}\ . \tag{10}$$

The recursion-method calculations for the disordered phase are performed with the first two terms ($H^{\alpha}-h^{\alpha}o^{\alpha}h^{\alpha}$) in the matrix series (7) for an 864-atom cluster under periodic boundary conditions, using potential parameters that correspond to relaxed and unrelaxed lattices according to the prescription of Kudrnovský and Drchal.[1,17] In Fig. 5 we show the DOS for the disordered $Cu_{75}Pd_{25}$ alloy. In Figs. 6 and 7 we compare the Pd- and Cu-projected DOS's with their crystalline counterparts, respectively. The solid and dashed curves correspond to the relaxed and unrelaxed (ideal fcc) lattices, respectively. The deviation from the ideal fcc structure gives rise to non-negligible changes in the electronic structure. The narrowing of the Pd band as a result of the relaxation is easily understandable in light of increased Pd-Pd and Pd-Cu nearest-neighbor distances. The center of gravity of the Pd LDOS (local DOS) shifts slightly towards higher energy, and the low-energy peak is broadened. Both effects are in agreement with experimental data[16] and also appear in the LMTO-CPA calculation of Kudrnovský and Drchal.[1] In the LMTO-CPA calculation, which uses the full infinite series of Eq. (7) instead of the first two terms as in the recursion-method calculation, the low-energy peak in the Pd LDOS is almost suppressed, in closer agreement with the experimental Pd Auger profile[16] in the alloy. The increased Pd-Cu distance also gives rise to additional structure in the Cu LDOS, making the latter more Cu-like in ordered fcc Cu_3Pd.

B. Comparison between LMTO-CPA and LMTO-recursion results

In Figs. 8 and 9 we compare the DOS calculated via the recursion and CPA methods for disordered $Cu_{75}Pd_{25}$ and $Cu_{50}Pd_{50}$ alloys. Both calculations are for relaxed lattices. The ideal (unrelaxed) lattice is supposed to be fcc for both alloys. The recursion-method calculations are for 864-atom clusters considered with periodic boundary conditions. The Cu and Pd LDOS's, as well as the total DOS, agree qualitatively for the two calculations. Some features of the DOS as obtained in the two calculations are presented in Table III. The differences in the results due to the two methods can be summarized as follows. The recursion-method results are based on a less accurate Hamiltonian, $H^{\alpha}-h^{\alpha}o^{\alpha}h^{\alpha}$, than the Hamiltonian H used in the CPA calculation, the former being given by only the first two terms in an infinite-matrix series representation of the other. The recursion-method results carry errors dependent on the finite cluster size and the nature of the terminator used, both of which cause the electrons to experience a medium that deviates from the intended structure away from the central sites. The recursion method uses the LDOS calculated at a finite number of sites (in our case, 50) and hence cannot efficiently sample all the possible environments in which the constituent atoms can be found. The CPA method uses a **k**-space calculation and hence is more accurate. It is suitable for substitutionally disordered alloys, where

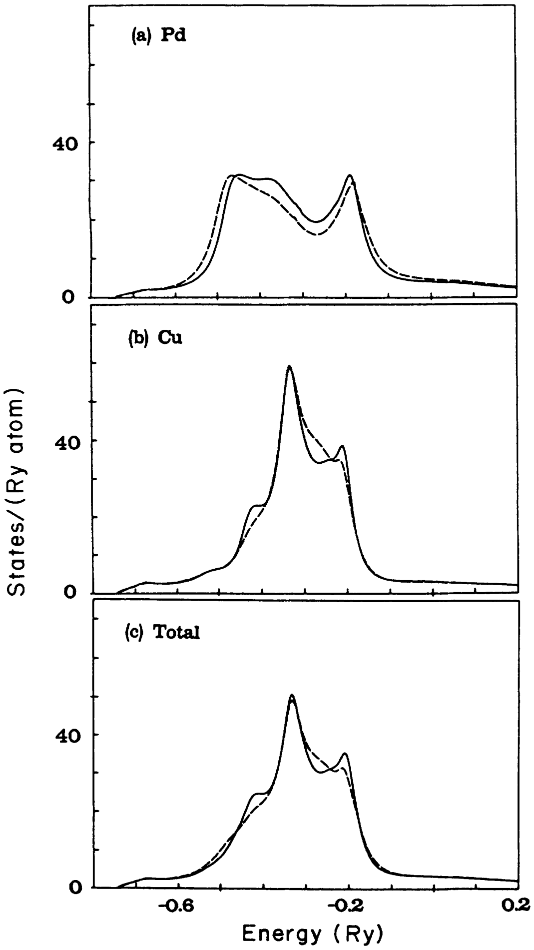

FIG. 5. Total, Pd-, and Cu-projected DOS's (not concentration weighted) for the disordered $Cu_{75}Pd_{25}$ alloy obtained using the LMTO recursion method; solid and dashed lines represent results of relaxed- and unrelaxed-lattice calculations, respectively.

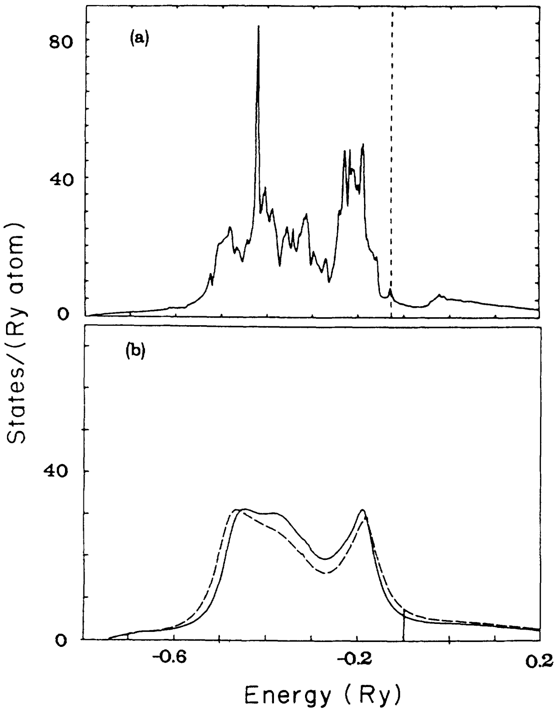

FIG. 6. Pd LDOS in ordered and disordered Cu_3Pd alloys: panel (a) is for the ordered alloy, and panel (b) is for the disordered alloy. The solid and dashed lines in panel (b) show results of relaxed- and unrelaxed-lattice calculations, respectively. Vertical lines show the positions of the Fermi levels.

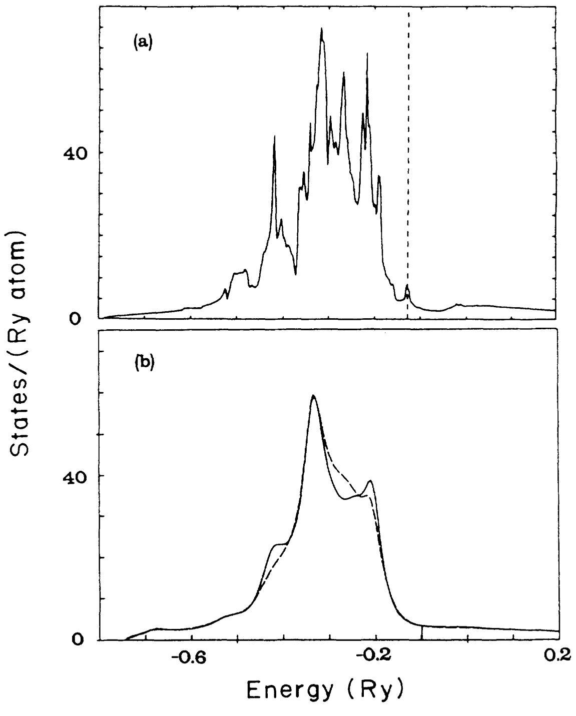

FIG. 7. Cu LDOS in ordered and disordered Cu_3Pd alloys. See caption of Fig. 6 for details.

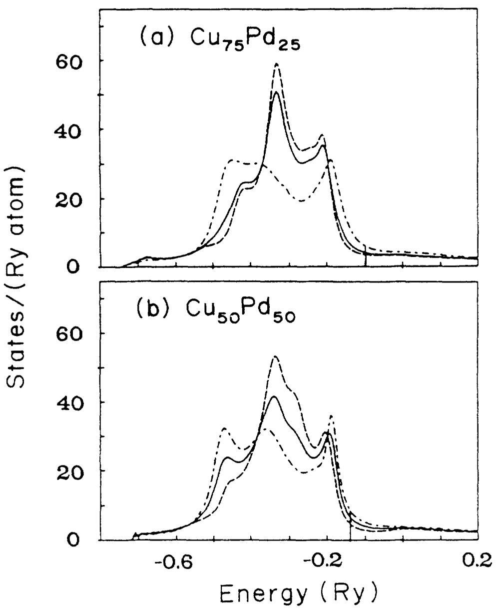

FIG. 8. DOS's obtained using the LMTO-recursion method for disordered $Cu_{75}Pd_{25}$ and $Cu_{50}Pd_{50}$ (relaxed-lattice) alloys. Solid line, total DOS; dashed line, Cu LDOS; dotted-dashed line, Pd LDOS. Vertical lines show the positions of the Fermi levels.

the underlying crystal structure is (more or less) preserved. The strength of the recursion method lies, on the other hand, in being able to handle positionally disordered systems and explore truly local environment effects not amendable to CPA.

As mentioned in the Introduction, we do not intend to

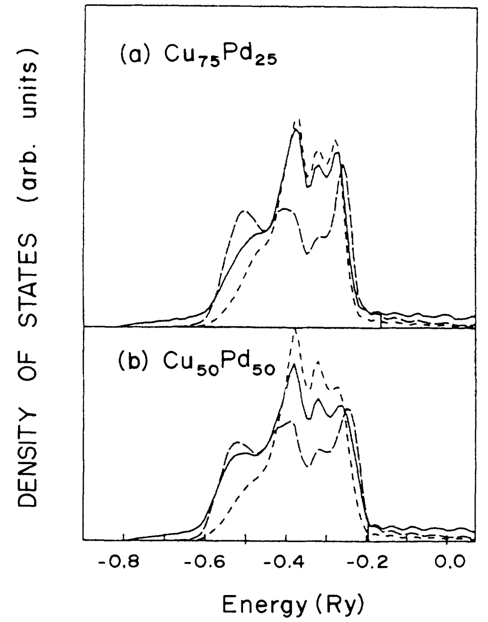

FIG. 9. DOS's obtained using the LMTO-CPA method for disordered $Cu_{75}Pd_{25}$ and $Cu_{50}Pd_{50}$ (relaxed-lattice) alloys. Solid line, total DOS; short-dashed line, Cu LDOS, long-dashed line, Pd LDOS. The vertical axis of this figure is in arbitrary units. Vertical lines show the positions of the Fermi levels.

TABLE III. Comparison of LMTO-CPA and LMTO recursion results, with the Pd- and Cu-sphere radii the same as in pure Pd and pure Cu ($s^{\mathrm{Cu}}=2.669$ a.u., $s^{\mathrm{Pd}}=2.873$ a.u.). $N(E_F)$, $N^{\mathrm{Pd}}(E_F)$, and $N^{\mathrm{Cu}}(E_F)$ denote the total DOS, and the Pd- and Cu-projected DOS's at the Fermi energy E_F.

	CPA	Recursion
$\mathrm{Cu_{75}Pd_{25}}$ (relaxed fcc)		
E_F (Ry)	−0.16	−0.10
$N(E_F)$ (states/Ry atom)	4.05	4.14
$N^{\mathrm{Pd}}(E_F)$ (states/Ry atom)	5.17	5.98
$N^{\mathrm{Cu}}(E_F)$ (states/Ry atom)	3.68	3.53
Charge in Cu sphere (electrons)	10.88	10.92
Charge in Pd sphere (electrons)	10.36	10.24
$\mathrm{Cu_{50}Pd_{50}}$ (relaxed fcc)		
E_F (Ry)	−0.19	−0.14
$N(E_F)$ (states/Ry atom)	7.69	6.38
$N^{\mathrm{Pd}}(E_F)$ (states/Ry atom)	10.86	8.29
$N^{\mathrm{Cu}}(E_F)$ (states/Ry atom)	4.53	4.48
Charge in Cu sphere (electrons)	10.76	10.85
Charge in Pd sphere (electrons)	10.24	10.15

present a detailed comparison between the calculated and experimentally obtained DOS in this paper. Our primary object here is to illustrate some important recent developments within the LMTO method. However, for the benefit of our readers, we reproduce in Fig. 10 the Cu- and Pd-projected DOS's in disordered $\mathrm{Cu_{75}Pd_{25}}$ as obtained using valence-band photoemission measurements by Wright *et al.*[14] Figure 10 is essentially Fig. 3 of Ref. 14, where the details about how the DOS curves were obtained from the valence-band photoelectron spectra are discussed. A comparison of Fig. 10 with Figs. 8 and 9 shows that the CPA result is better agreement with the experimental curves (in terms of the relative heights of the peaks). As mentioned in the preceding paragraph, the CPA result, based on the **k** space, is more reliable for substitutionally disordered systems.

From the viewpoint of computational efforts, the CPA method is more efficient. In the LMTO-CPA method the computation time depends linearly on the number of energy points and on the number of **k** points used in the irreducible wedge of the Brillouin zone (IBZ). For lower symmetry the volume of the IBZ is larger and the effort increases. The computation time also depends on the disorder present, because the number of CPA situations is greater for a more disordered system. The computation time roughly varies as N^3, where $N=nL$, n being the number of atoms per unit cell, and L the number of orbitals on each atom. For a binary disordered alloy such as CuPd, with nine orbitals per atom, 240 **k** points in the IBZ, and 100 energy points, the time for one concentration, on a Cray-XMP/24 computer, is 150–170 sec. In the recursion method the time depends linearly on the cluster size (number of atoms), the number of orbitals per atom, the number of neighbors for each atom, the number of orbitals for which the local DOS is calculated, and the number of energy points. It also depends on the nature of the "terminator" used, the "linear predictor terminator" of Allan[27] being the most time consuming and the quadratic terminator[28] the least. For an 864-atom cluster, with two cells of neighbors (14), and nine orbitals on each atom, it takes about 165 sec, on a Cray-XMP/24, to construct the Hamiltonian $H^\alpha - h^\alpha o^\alpha h^\alpha$, about 150 sec to compute the recursion coefficients (20 each) for the local Green's function for 81 states (nine orbitals each on 9 atoms), and 25 sec to compute the DOS from these 81 orbitals, on 250 energy points using 200 extrapolated coefficients for each local Green's function using the "linear predictor terminator" of Allan.[27] Less-time-consuming choices for the terminator, though less accurate, are those due to Beer and Pettifor,[29] to Haydock and Nex,[30] and to Luchini and Nex.[31]

C. Approximate treatment of charge self-consistency

Charge-self-consistent calculations can be performed for a disordered alloy in a manner in which the self-consistency is achieved for the "average"-component atoms. The "average" may mean a CPA average or an average over a finite number of representative atoms as in the recursion method. From the average-component atom-projected DOS, one calculates the charge density in the average-component spheres, which gives a new set of potential parameters, and the calculation is repeated until

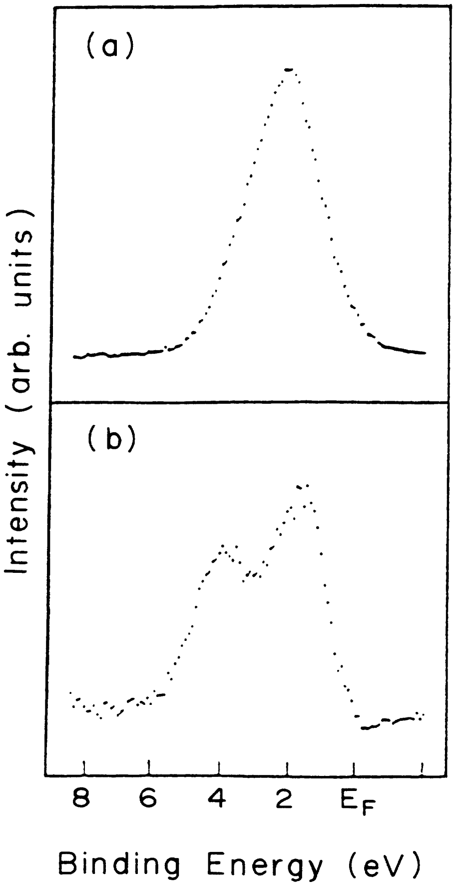

FIG. 10. (a) Cu and (b) Pd LDOS's obtained from the valence-band photoelectron spectra in $\mathrm{Cu_{75}Pd_{25}}$ of Wright *et al.* (Ref. 14) (reproduced from Ref. 14).

the input and output charge densities (or potentials) are identical within a preassigned limit. The problem one faces is in the calculation of the Madelung potential due to the transfer of charge between various spheres. Unlike the ordered alloys, there is no well-defined procedure to calculate this for disordered systems. To avoid this problem, one could try to vary the sphere radii to render them neutral, so the Madelung potentials for these "average" spheres disappear. Towards this end we start with the potential parameters for the component atoms, A and B, in the alloy as obtained from the pure-state potential parameters, discussed in Sec. II. Since the compressibility prescription of Eq. (3) leads to only a small charge transfer between the atoms, the Madelung potential is small to start with. From the alloy Fermi level and the local DOS, we compute the deviations δq^{Q} $(Q=A,B)$ from charge neutrality for the A and B spheres $[x\delta q^{A}+(1-x)\delta q^{B}=0]$. To make, for example, the A spheres charge neutral, we set $\delta q^{A}=-4\pi(s^{A})^{2}n^{A}\delta s^{A}$, where n^{A} is the electron density at the sphere radius s^{A}, which is tabulated for 33 elemental metals in Ref. 21. The corresponding value of δs^{B} is obtained from alloy volume preservation. The potential parameters for the new radii can be calculated using the prescription of Sec. II, and the electronic-structure calculation can be repeated until the spheres become neutral. With the sphere radii determined by Eq. (3), the spheres are approximately neutral to start with. Hence, one or two iterations are sufficient to achieve the exact charge neutrality for the "average"-component atoms. The result obtained via such approximate treatment of charge self-consistency within the LMTO-CPA method is shown in Fig. 11. Panel (b) shows results for non-neutral spheres, with Cu and Pd radii the same as in pure solids [as in panel (a) of Fig. 9]. The charges in the Cu sphere ($s^{\mathrm{Cu}}=2.669$ a.u.) and the Pd sphere ($s^{\mathrm{Pd}}=2.873$ a.u.) are, respectively, 10.880 electrons and 10.360 electrons. Panel (a) shows the results for neutral spheres ($s^{\mathrm{Cu}}=2.690$ a.u., $s^{\mathrm{Pd}}=2.817$ a.u.). Both calculations are for relaxed lattices. The features of the neutral-sphere DOS are summarized in Table IV. The disappearance of the Madelung potential for neutral spheres results essentially in the repositioning of the centers of the Pd and Cu bands. This is reflected mainly in the potential parameters C_{d}^{Pd} and C_{d}^{Cu}. There is a slight upward shift of C_{d}^{Pd} with respect to C_{d}^{Cu}. This makes the weight of the lower part (well below E_F) smaller, and that of the peak close to E_F, greater in the Pd LDOS curve. Because $s^{\mathrm{Pd}}<s_{0}^{\mathrm{Pd}}$, the full width at half maximum (FWHM) of the Pd LDOS is slightly greater in the neutral-sphere case.

Such neutral-sphere calculations, in the way of obtaining approximate charge self consistency, can also be carried out using the recursion method. We have not performed the recursion-method calculations using neutral spheres. However, such calculations would most definitely show the same type of changes with respect to the pure-component-radii results as revealed by the CPA calculations. This is because the charge transfers obtained in the CPA and the recursion calculations are similar for the pure-component radii. In both calculations the Cu spheres lose charge to the Pd spheres. Therefore, the corrections in the sphere radii to achieve charge neutrality should be in the same direction for the two calculations. The magnitude of change in the DOS in going from the pure-component radii to the neutral-sphere radii should be a bit smaller for the recursion method than for the CPA, simply because the charge transfer is a little smaller for the recursion-method calculation (see Table III).

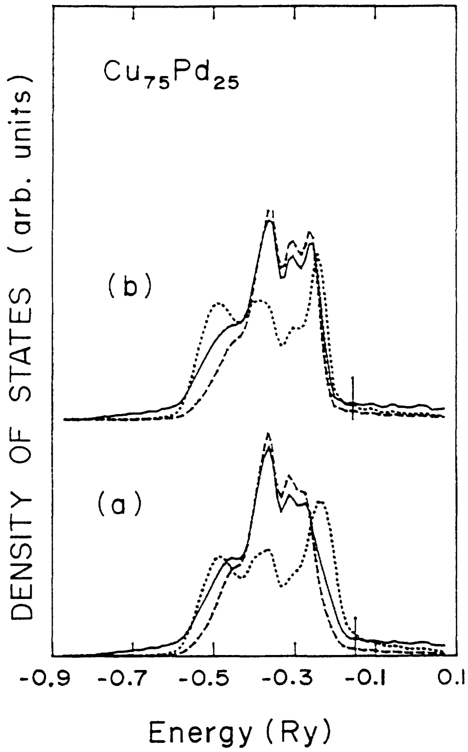

FIG. 11. DOS for the disordered $Cu_{75}Pd_{25}$ alloy (relaxed lattice) obtained using the LMTO-CPA method. Panel (b) shows results for non-neutral spheres, with Cu and Pd radii the same as in pure solids [as in panel (a) of Fig. 9], and panel (a) shows results for neutral spheres. Solid line, total DOS; dotted line, Pd LDOS; dashed line, Cu LDOS. Vertical lines show the positions of the Fermi levels.

IV. SUMMARY

We have shown how, for the purpose of electronic-structure calculations, the potential parameters of the

TABLE IV. Comparison of LMTO-CPA results for the disordered $Cu_{75}Pd_{25}$ alloy (relaxed fcc structure) obtained using non-neutral spheres ($s^{\mathrm{Cu}}=2.669$ a.u., $s^{\mathrm{Pd}}=2.873$ a.u.) and neutral spheres ($s^{\mathrm{Cu}}=2.690$ a.u., $s^{\mathrm{Pd}}=2.817$ a.u.). $N(E_F)$, $N^{\mathrm{Pd}}(E_F)$, and $N^{\mathrm{Cu}}(E_F)$ denote the total DOS, and the Pd- and Cu-projected DOS's at the Fermi energy, E_F.

	Non-neutral spheres	Neutral spheres
E_F (Ry)	-0.165	-0.158
$N(E_F)$ (states/Ry atom)	4.05	4.21
$N^{\mathrm{Cu}}(E_F)$ (states/Ry atom)	3.68	3.39
$N^{\mathrm{Pd}}(E_F)$ (states/Ry atom)	5.17	6.69
Charge in Cu sphere (electrons)	10.880	10.976
Charge in Pd sphere (electrons)	10.360	10.072

component atoms A and B can be transferred to the ordered and disordered binary ($A_xB_{(1-x)}$) alloys using the tabulated values[21] of their volume derivatives and the electron density at the sphere radii.[21] We have illustrated the transferability scheme with the example of $Cu_{50}Pd_{50}$ and $Cu_{75}Pd_{25}$ alloys. Because these alloys exhibit negligible deviation from Vegard's law, the transferability scheme for the potential parameters works extremely well. The larger the deviation from Vegard's law, the larger the difference in the electronic structure obtained with transferred parameters and the charge-self-consistent procedure.[32] However, even for alloys such as CsAu, which show a large deviation from Vegard's law, important features of the electronic structure are reproduced reasonably well via transferred parameters.[20] So the transferability criterion discussed in Sec. II is better than any *a priori* expectation. For the disordered alloy, we have shown how an approximate self consistency can be achieved without any appreciable increase in computational efforts. The neutral-sphere calculation, presented for the disordered alloy, can be performed with the help of tabulated quantities. Such a calculation can also be performed for ordered alloys. However, since self-consistent calculations for ordered structures are being performed routinely, we have not performed neutral-sphere calculations for the ordered alloys. The strength of the neutral-sphere approach lies in the electronic-structure calculation for disordered systems, where the Madelung potential is difficult to compute.

For the disordered alloy we have shown and discussed the effect, on the electronic DOS, of the deviation from the ideal lattice structure (lattice relaxation) due to the size difference of the component atoms. The relaxed-lattice calculation produces results in closer agreement with experiments.[14,16] We have also presented a comparison of the electronic structure of the disordered $Cu_{50}Pd_{50}$ and $Cu_{75}Pd_{25}$ alloys calculated via LMTO recursion and LMTO-CPA methods.

Note added in proof. After the submission of the final version of this manuscript the authors have become aware of a recent study by Lu, Wei, and Zunger [Phys. Rev. B **44**, 3387 (1991)] on the lattice-relaxation effects in $Cu_{1-x}Pd_x$ alloys using the "special quasirandom structure" method.

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