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Calculation of electronic density of states for an amorphous Zr-Cu alloy

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The recursion method has been used to calculate the *d*-band density of states for a cluster simulating amorphous $Zr_{41}Cu_{59}$. Normally these calculations are performed using energies and overlap parameters obtained by detailed fitting of a linear combination of atomic orbitals scheme to existing crystalline calculations. Here an alternative approach is illustrated, where the relative position of the *d* resonances for the alloy is determined by self-consistently adjusting the diagonal elements of the Hamiltonian to ensure that a given amount of charge transfer takes place. For transition-metal—transition-metal alloys, the assumption of zero charge transfer is usually a good approximation. The overlap integrals tabulated by Harrison are used for the off-diagonal elements. The energy spread among atoms of the same kind due to different local environments is obtained and shown to be small. The results of the calculations are in good agreement with x-ray photoelectron spectroscopy data and we find the density of states at the Fermi level to be consistent with measured values.

I. INTRODUCTION

In the last few years much progress has been made in the fabrication and characterization of amorphous alloys. Among these systems the transition-metal glassy alloys have received considerable attention, due to their interesting magnetic and superconducting properties. Central to understanding the behavior of these systems is a knowledge of the electronic density of states. Lately, the measurement of ultraviolet photoelectron spectroscopy (UPS) and x-ray photoelectron spectroscopy (XPS) spectra in this class of material has generated a great deal of information about binding energies and *d*-band widths.[1–4] Experimental access to the density of states at the Fermi level is also provided, usually by measurements of specific-heat measurements. In superconductors this information is even more readily available via measurements of the upper critical field H_{c2} versus temperature.[5]

It has been suggested[2,6] that several features of the XPS spectra of these amorphous materials, such as binding energy and *d*-line widths, can be explained in terms of the density of states for crystalline compounds of similar composition. A series of calculations of the density of states in crystalline close-packed binary systems for various compositions was performed to that effect.[7] (Here these calculations will serve as a guide to the amount of charge transfer we should expect for a determined alloy at a certain composition range.) Although rough features of the density of states, such as binding energies and average linewidth, are similar for amorphous and relatively close-packed crystalline structures, the line shape can be very different because the density of states for amorphous materials lacks the sharp peaks generally associated with van Hove singularities. Thus the density of states at the Fermi level for an amorphous sample can be extremely different from that of its crystalline counterpart. Therefore, if one is, for example, interested in superconducting properties, where the density of states at the Fermi level is the relevant quantity, a calculation allowing for amorphous structure cannot be avoided.

Here we are interested in using the simplest possible method of calculation which will give us a meaningful description of the density of states for the amorphous transition-metal alloys of interest. This will enable us to perform calculations for a greater number of systems and have a general view of the behavior of these materials. The major difficulty involved in finding the density of states for amorphous systems is due to the lack of periodicity. The powerful and well-established *k*-space methods cannot be applied, and therefore, we have to rely on real-space methods, usually based on a linear combination of "atomic" orbitals (LCAO). A great deal of effort has been channeled into perfecting these real-space techniques, which are well suited to treat *d* bands. Since a first-principles solution is conceptually difficult and computationally costly, some of the most successful approaches for[8,9] simulating realistic systems are based on using information about the atom in a crystalline environment (available from usual *k*-space methods) to establish the behavior of the same unit in an amorphous environment.

The recursion method[8] which will be used here is based on the above approach. To keep it simple (and low in cost) we will neglect *s*-*d* hybridization when calculating the *d*-band density of states and require our LCAO basis set to be orthogonal.[10] The *s* band will be included in the free-electron approximation, making use of an effective mass to simulate hybridization effects.[11] Under these circumstances the input necessary to perform the calculations will be the Hamiltonian matrix elements H_{mn}, m and n describing localized "atomic" basis functions, five for each site. The off-diagonal elements are related to overlap integrals and the diagonal terms are effective atomic energies. The standard way of obtaining this information is by fitting a LCAO scheme to a crystalline *k*-space calculation for a similar compound, in the way described by Slater and Koster.[12]

In practice, however, we rarely have the necessary detailed information about the crystalline bands. Even when the information is available, in several instances the empty orbitals above the Fermi level are not presented,[13] making fitting procedures difficult and unreliable. Even in the ideal case where all information is available, we are presented with a complex set of hybridized bands which, to be consistent, must be fitted to a nonorthogonal LCAO set. With so many parameters, the fit is rarely unique, and the accuracy of the parameters suffers. Finally, the d-band matrix elements obtained in this way will certainly be representative, but if the aim is to use an orthogonal set of orbitals and not to include hybridization, it is not clear that these parameters, obtained for a hybridized nonorthogonal set, will be the best for this purpose.

In this paper we illustrate an alternative approach which avoids the difficulties mentioned above. To find the off-diagonal elements of the Hamiltonian we use the overlap integrals tabulated by Harrison[11] for each of the elements. These parameters were obtained by a less rigorous fitting procedure than described in Ref. 11, but are readily available and certainly representative. Of course, if better parameters are known, they can be used.

Now we must establish values for the diagonal terms in the Hamiltonian which fix the relative position of the bands in the compound. When different species are brought together to form a compound, there is always the possibility of charge transfer as electrons find unoccupied levels of lower energy available. As this transfer takes place, a potential difference is developed between the atomic sites for the different species, shifting the energy levels of different sites relative to each other. Equilibrium is reached when the Fermi level is the same throughout the material. Given the amount of charge transfer (generally small) we can calculate the diagonal matrix elements through a rapidly converging self-consistent calculation as described below. A similar procedure has been used to treat the surface density of states of a monoatomic crystalline system.[14]

A first estimate for the diagonal energy term for each species of atom is given. The local density of states at each site is then found using the recursion method. A given amount of charge is assigned to each site to give the expected charge transfer and the Fermi level is determined. The diagonal values of energy for each atom are then redefined to make the Fermi level coincide for all sites. The calculation is then done using these new values and the procedure is repeated until self-consistency is achieved. Corrections to the off-diagonal terms are expected to be less important. Since they are very difficult to include, they are neglected here.

In Sec. II we give a more detailed description of the procedure and results are presented. In Sec. III we discuss the results and compare with available experimental data. Finally, conclusions and further discussion are presented in Sec. IV.

II. PROCEDURE

We calculate the density of states using a tight-binding Hamiltonian

$$H=\sum_{i,m} |i\rangle_m \epsilon_{i,m}\, {}_m\langle i| + \sum_{\substack{i,j\\ i\neq j}} |i\rangle_m t_{ij,mm'}\, {}_{m'}\langle j| \ ,$$

where we take the basis orbitals $\{|i\rangle_m\}$ to be orthonormal such that

$${}_m\langle i|j\rangle_{m'}=\delta_{ij}\delta_{mm'} \ .$$

Here i,j indicate the site and m, m' the "atomic" orbital in the given site. We proceed to express H in terms of a matrix with diagonal matrix elements given by "atomic" energy levels ϵ_{im} and off-diagonal matrix elements $t_{ij,mm'}$ given in terms of a set of three parameters $dd\sigma$, $dd\pi$, and $dd\delta$, according to Slater and Koster's atomic-orbital scheme. To find $t_{ij,mm'}$ using this scheme[12] the position of every atom has to be supplied.

Given the Hamiltonian we can use the recursion method to find the local density of states at a given site. This method, thoroughly described in Ref. 12, is given here only in outline. The procedure is to define a new orthonormal basis set $\{|u_n\rangle\}$, using the recursion relation

$$b_{n+1}|u_{n+1}\rangle=(H-a_n)|u_n\rangle-b_n|u_{n-1}\rangle$$

and the orthonormal requirement to find $\{a_n,b_n\}$. The starting orbital $|u_0\rangle$ is chosen to be equal to the $|i\rangle_m$ (the mth orbital at the site i), whose local density of states we desire to find. This density of states is then expressed in terms of the diagonal element of the Green's function

$$n_{im}(E)=\pi^{-1}\mathrm{Im}\langle u_0|(E-H)^{-1}|u_0\rangle \ ,$$

which can then be written in terms of the parameters a_n and b_n as a continued fraction

$$n(E)=-\pi^{-1}\mathrm{Im}\frac{1}{E-a_0-\cfrac{b_1^2}{E-a_1-b_2^2/E-a_2-\cdots}} \ .$$

In the above equations, E has an infinitesimal imaginary part. By construction, the recursion relation generates orbitals $|u_n\rangle$ which are spread out further and further away from the chosen site as n gets larger, leading to corresponding parameters a_n and b_n which contribute less and less to the local density of states at the desired site. This allows us to truncate the recursion after a number of levels LL, neglecting contributions from $|u_n\rangle$ for $n>LL$. Because of truncation the levels are discrete and a rounding-off procedure[15] is used to obtain a continuous density of states at the site. The total density of states at site i is then found by summing $n_{im}(E)$ over m. Finally, the total density of states in the compound is given by averaging over all sites.

To simulate the amorphous $Zr_{41}Cu_{59}$ compound we have used the 39-atom cluster ($Cu_{23}Zr_{16}$) with periodic boundary conditions described by Jaswal *et al.*[16] In their procedure the atoms were packed so that the two constituents were evenly distributed in a cube. A Lennard-Jones–type potential was used to relax the periodic unit and the density was adjusted to simulate the density in real systems. Given this periodic system, our cluster was then built as a superposition of all points whose distance to any one atom of the 39-atom unit was less than a given R_0. We chose $R_0\cong 9$ Å corresponding to a sphere diameter of 7 times the nearest-neighbor distance of Cu in a regular fcc structure. Using the procedure outlined above, we obtained the 640-atom cluster, on which our calculations were performed. As we stressed before the recursion method does not require periodicity. But, since the overlap integral of each atom with every close neighbor has to be computed, the amount of information to be stored is substantially reduced by taking large enough periodic clusters. Also, to characterize the density of states, we have to average over the local density of states for a representative set of atoms. In a nonperiodic cluster this set is not well defined and, being finite, it restricts the generality of the procedure. Here, if we average over the 39-atom unit, we automatically get the best value for the cluster. Having a set of atoms which represent the whole cluster is also essential, if one wants to do an atom-by-atom self-consistent procedure as we do here, without unreasonable cost. On the other hand, since our cluster is of irregular shape and includes only 640 atoms, it is very unlikely that any features due to periodicity will be present in our results.

In the spirit of the Slater-Koster[12] scheme, the calculation of the density of d states requires the knowledge of the overlap integrals $dd\sigma$, $dd\pi$, and $dd\delta$ for each combination of neighbors. We use for these values those suggested by Harrison, who allows the parameters to vary inversely with the fifth power of the distance r between the two atoms being considered.[11] We only retain the "first-neighbor interaction," in the sense that only interactions between atoms a distance $r < r_c$ apart are considered. The actual values for the cutoff distances r_c and the overlap integrals used in the calculations are summarized in Table I.

We tested different values for the level cutoff LL, using different cluster geometries and sizes (for example, a cubic cluster of size $2R_0$ with a given atom at the center) to maximize LL while avoiding significant contribution from the boundaries. A value of $LL = 12$ was chosen and used in all calculations presented here. To treat the s bands we follow Harrison[11] and fix the bottom of the s band at an energy E_d lower than the "atomic" d energy of the corresponding element. An effective mass m_s^* was also used to simulate hybridization. The values used for E_d and m_s^* for Cu and Zr s bands[11] are shown in Table I.

Finally, to find the diagonal elements of the Hamiltonian we must know the amount of charge transfer in this alloy. We can rely on the crystalline close-packed band calculation for a compound of similar composition for this purpose. Band calculations for Zr-Cu in both CuAu and CsCl structures are available[7] and show that charge can be transferred either way (from Cu to Zr or vice versa) but in very small amounts (of order 0.03 electrons). Based on this information we assume approximate charge neutrality when treating the Zr-Cu alloy around this composition.

In our calculations the "atomic" level of Zr is taken as our zero of energy. The Cu "atomic" energy is then given by E_0 and adjusted self-consistently to achieve charge neutrality. Our first guess was taken to be $E_0 = -0.355$ Ry, given by the renormalized atom approximation.[17]

III. RESULTS AND DISCUSSIONS

The total density of states (averaged over all 39 atoms) for $E_0 = -0.355$ Ry is shown in Fig. 1(a). The Fermi energy shown in the figure was found by filling the band with available electrons without any restrictions regarding charge transfer. We find as a result of this procedure that for $E_0 = -0.355$ Ry, an average charge transfer of 0.23 electrons from Zr to Cu sites is required. However, as discussed before approximate charge neutrality would better represent the Zr-Cu system.

In Fig. 2(a) we show the results for the d density of states for Cu (average over 23 atoms) and Zr (averaged over 16 atoms) calculated for $E_0 = -0.355$ Ry. The indicated individual Fermi energies for Cu and Zr sites are determined by imposing approximate charge neutrality. They were calculated by choosing the average number of electrons per spin around individual sites (including s and d contributions) to be 5.5 for Cu and 2 for Zr. It is clear that, in first approximation, we can make the two values of E_F coincide by shifting the "atomic" level E_0 of the Cu atoms by the approximate amount ΔE_0 as illustrated in Fig. 2(a).[18]

We can now use the new value $E_0 = -0.303$ to recalculate the density of states for the alloy. At this point, however, it is interesting to show the effect of local environment and illustrate how the d local density of states behaves at different sites. In Figs. 3(a) and 3(b) we show the local density of states for Cu and Zr atoms in two different environments. The question of how many such environments have to be considered to have a significant average density of states comes immediately to mind. In Fig. 4 we try to answer this question by calculating the averaged density of states for two different sets of Cu atoms, one containing 12 atoms and the other 11. From our results it is clear that an average over 10 sites of the same kind should already be representative of the density of states of the chosen species in the alloy. The linewidth, the general shape, the binding energy and the Fermi level for the two sets of atoms shown in Fig. 4 are identical within our resolution. On the other hand, we see that no significance can be attached to the small oscillations on the top of the d resonance. Actually they depend not only on the local environment, but also in the value of LL.

Finally, calculations of the total density of states (average over all 39 atoms) and those of Zr and Cu for $E_0 = -0.303$ Ry are shown in Figs. 1(b) and 2(b), respectively. The correction ΔE_0 shown in Fig. 1(b) is now small, indicating fast convergence toward self-consistency. Actually the difference in Fermi energy between Zr and Cu atoms is of the same order as the spread in Fermi energy,

TABLE I. Numerical values of parameters used in the calculations. See text for explanation of symbols. Energies are given in Ry and distances in Å.

	$dd\sigma$	$dd\pi$	$dd\delta$	r_c (Å)	Ed	m_s^*/m
Cu-Cu	$-2.73/d^5$	$1.78/d^5$	0	3.24	0.434	0.854
Zr-Zr	$-25.4/d^5$	$13.7/d^5$	0	3.70	0.527	0.554
Cu-Zr	$-8.33/d^5$	$4.50/d^5$	0	3.46		

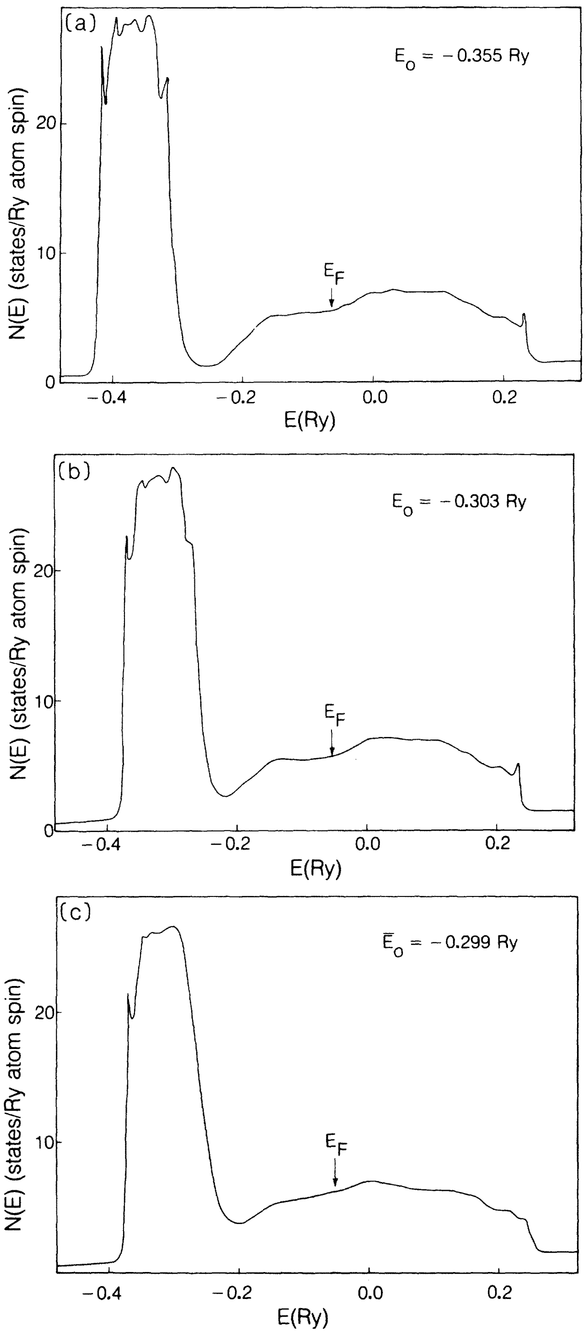

FIG. 1. Total density of states for the $Zr_{41}Cu_{59}$ cluster for the three steps toward achieving self-consistency. The zero of energy is taken to coincide with the d "atomic" energy level of Zr. The energy E_0 of the "atomic" level of Cu atoms and the Fermi level are also shown for (a) $E_0 = -0.355$ Ry, (b) $E_0 = -0.303$ Ry and (c) $\bar{E}_0 = -0.299$ Ry. In part (c), the "atomic" levels for the Cu and Zr atoms were allowed to vary around their respective mean values of −0.299 Ry and zero.

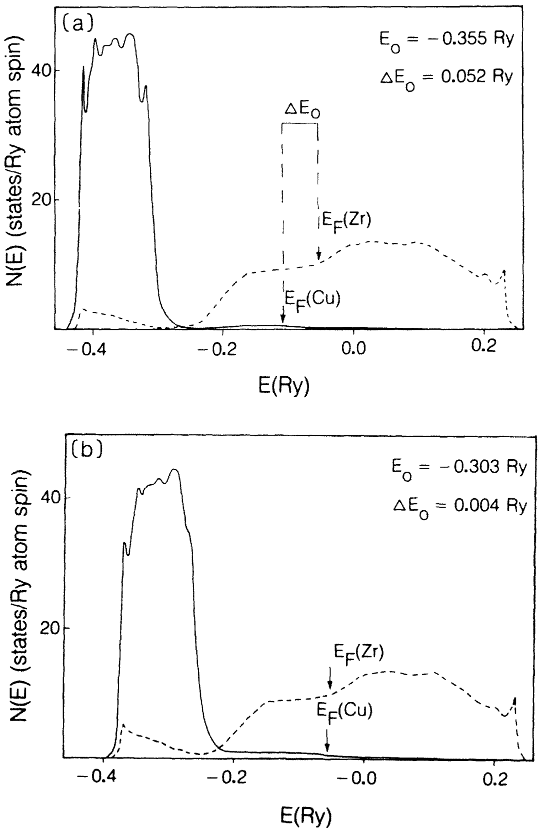

FIG. 2. Calculated density of states for Cu (solid line) and Zr (dotted line) in the Zr-Cu alloy for (a) $E_0 = -0.355$ Ry and (b) $E_0 = -0.303$ Ry. The Fermi energies for Cu and Zr were calculated under the assumption of negligible charge transfer. A shift ΔE_0 of the "atomic" Cu energy level is required to make the two Fermi levels coincide.

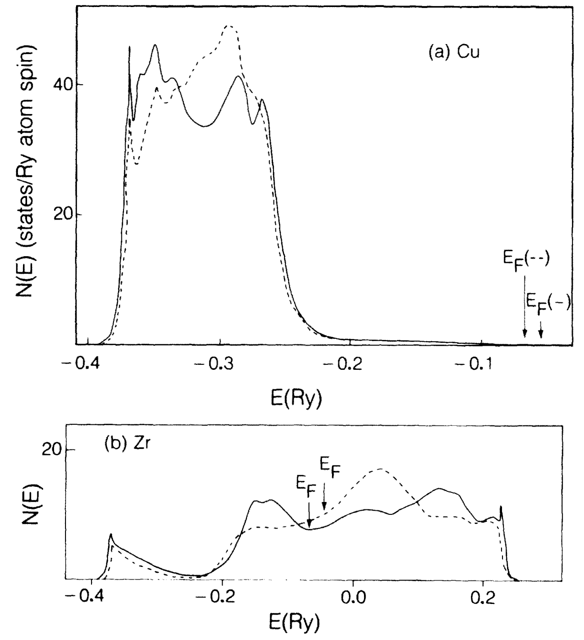

FIG. 3. Local density of states for (a) Cu and (b) Zr atoms in two different local environments, calculated with $E_0 = -0.303$. The respective Fermi levels, calculated under the assumption of negligible charge transfer, are also shown.

due to different local environments as illustrated in Fig. 3. To proceed further toward self-consistency we must shift the diagonal elements of the Hamiltonian in order to make the values of E_F coincide for every atom throughout the system. It is clear from Fig. 3 that we have to allow each of the 39 atoms in the amorphous unit to contribute to the Hamiltonian with a different diagonal energy term,

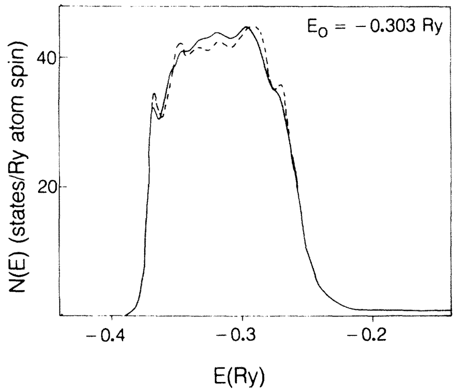

FIG. 4. Density of states for Cu atoms in the cluster averaging over 12 Cu atoms (solid line) and averaging over 11 Cu atoms (dotted line), distinct from those used in the previous average.

reflecting the influence of local environment on the *d*-level energy of the atoms. Since the difference in Fermi energies is small, we could almost stop at this point. Nonetheless, we will proceed under the assumption of approximate charge neutrality to illustrate qualitatively the effect of different local environments on individual atoms energies, and how these effects can be reflected on the final line shape.

In Fig. 1(c) we show the final result. The Fermi levels for local densities of states at all 23 sites are made to coincide within 0.008 Ry (~0.1 eV). The Fermi level is located at an energy $E_F = -0.053$ Ry relative to the reference energy (now given by the average "atomic" energy for Zr sites). The spread in atomic energies around an average energy as measured by the mean-square value is 0.016 Ry (~0.22 eV) for Zr and 0.013 Ry (~0.18 eV) for Cu. This spread is small compared to the width of the respective *d*-band resonances but, in the case of Cu, it does change the line shape considerably, as shown in Fig. 1(c).

In Fig. 5 we compare our density of states to XPS measurements for an amorphous sample of $Zr_{40}Cu_{60}$.[3,4] The agreement is quite good in general terms. The binding energy is correctly given and a thinning of the Cu *d* resonance occurs relative to the pure fcc Cu. Calculations for fcc Cu with the same parameters give a width (at a height of 10 states/Ry atom spin) of approximately 2.2 eV while the linewidth for the Cu density of states in the alloy is ~1.6 eV.

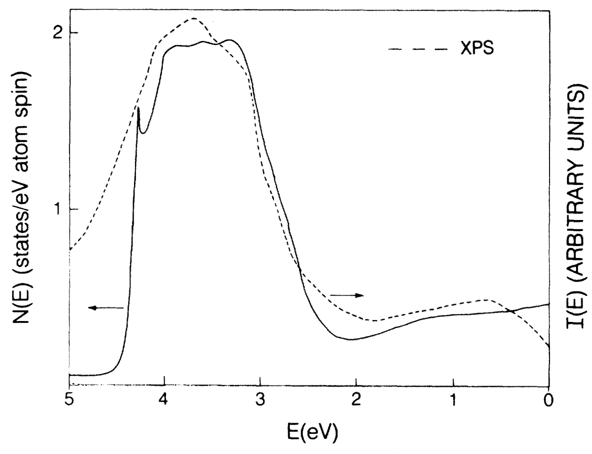

FIG. 5. Calculated density of states for the $Sr_{41}Cu_{59}$ cluster (solid line) is compared with the XPS results (arbitrary units) of Ref. 4 (dotted line). The energy scale was chosen to make the Fermi energy zero.

Finally, in Fig. 6 we compare our results with those obtained by Moruzzi *et al.* for $Zr_{50}Cu_{50}$ in a CuAu structure using the self-consistent augmented spherical wave method.[19] It is suggested that the density of states of an amorphous alloy can be well represented by that of a close-packed crystalline compound of similar composition.[6,7] The advantage of this approach is that well-established, extremely reliable *k*-space methods can be used to calculate the density of states for simple crystalline compounds. We note that our results were calculated using Harrison's parameters taken from band calculations for the pure metals. The results of Moruzzi *et al.* enter our calculations only to support our procedure of neglecting charge transfer between the atoms. Therefore, the agreement between the two results shown in Fig. 6 regarding the general features, binding energy, and linewidth of the density of states supports the claim that UPS and XPS data for amorphous alloys can be understood in terms of their crystalline counterparts. On the other hand, as is to be expected due to the variety of local environments, our results for the density of states show much less structure than those obtained for the crystalline compound. It is clear that the single environment present in the crystalline compound cannot reproduce the smooth density of states of the amorphous alloy. As a consequence it is clear that our simple procedure should give better values for the density of states at the Fermi level for the alloy. We find the density of states at the Fermi level to be given by $N(E_F) = 0.46$ states/eV atom spin. This value can be compared with $N(E_F) = 0.39$ states/eV atom spin obtained by Jaswal *et al.*[16] In a previous paper[20] we have used a simple dilution model to find $N(E_F)$ for split-band Zr compounds with high concentrations of Zr. This model fails when Zr is the minority compound, as thinning of the Zr resonance gets to be important. Our calculated density of states is higher than the one the simple model would predict, and agrees with the trend shown by experimental

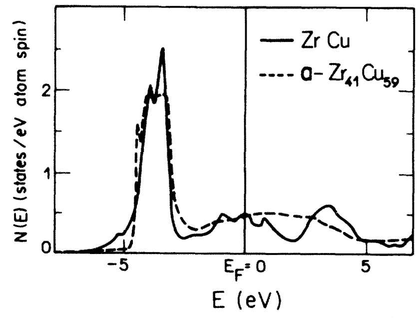

FIG. 6. Results of Moruzzi *et al.* (Ref. 7) for ZrCu (solid line) are compared to our results for amorphous $Zr_{41}Cu_{59}$ (*a*-$Zr_{41}Cu_{59}$, dotted line). In both cases the zero for the energy scale is taken at the Fermi level.

results.[20] No experimental results on the density of states are available for amorphous $Cu_{40}Zr_{60}$, but for $Cu_{50}Zr_{50}$ a bare density of states $N(E_F) \sim 0.47$ states/eV atom spin was inferred from experimental results.[21] The crystalline close-packed CuAu structure for ZrCu shown in Fig. 6 gives $N(E_F) \sim 0.50$ states/eV atom spin, in agreement with our results and experiment. But we note that for ZrCu in the (crystalline) CsCl structure, $N(E_F) \sim 0.68$ states/eV atom spin,[17] indicating the sensitivity of $N(E_F)$ to changes in the local atomic environment.

IV. CONCLUSION

We have used the recursion method to calculate the *d* density of states for a cluster of 640 atoms, simulating an amorphous $Zr_{41}Cu_{59}$ alloy. To avoid detailed fitting procedures, we have used for the overlap integrals the parameters tabulated by Harrison. Of course, if available, parameters from other sources can be used. The "atomic" energies were then found by a self-consistent procedure where approximate charge neutrality (the amount of charge transfer is expected to be negligible for this alloy) was imposed. We find that the Cu *d*-resonance line is thinner than that of pure Cu, in agreement with XPS results. Also, due to interaction with Zr, some of the Cu states are spread over the energy range of the Zr band. With some of the states shifted to higher energies the number of states available in the *d*-resonance line is smaller. Therefore, to maintain the same electronic occupation the Fermi level has to be further from the center of the Cu *d* resonance, explaining the higher binding energy of the alloy relative to that of pure Cu. Actually, the same behavior, a thinner *d*-resonance band with fewer states available, can qualitatively explain why Zr-Rh and Zr-Pd show a split band for a wide range of compositions[12] and very little charge transfer.[7]

Despite the greater variety of environments allowed in a binary alloy leading to very different local densities of states, we find that an average over 10 sites is already quite representative of the behavior of the density of states of a given species in the compound. The local environment can cause a spread in the "atomic" energy of individual sites of the same kind, but from our results these "atomic" energy differences are expected to be smaller than those found by Jaswal *et al.*[22] Finally, if we compare our results with those of a close-packed crystalline compound ($Zr_{50}Cu_{50}$),[7] we see that the main features are very similar (especially for the Cu density of states). However, the crystalline calculation shows much more structure, and may fail to represent the density of states at the Fermi level for amorphous materials of similar composition. Our results indicate that the recursion method is a powerful tool to obtain the density of states at the Fermi level for binary transition compounds. Further work is needed to evaluate the full potential of our procedure. Its application to other materials is currently underway.

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