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Linear-muffin-tin-orbital (LMTO) supercell and LMTO recursion calculations for the electronic structure of metallic glasses: Ca_7Al_3

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The electronic structure of an 800-atom realistic model of a Ca_7Al_3 glass is calculated with use of the tight-binding linear muffin-tin-orbitals (TB LMTO) scheme in conjunction with the recursion method. Results are compared with those obtained in a self-consistent standard LMTO calculation for 60-atom supercells of this glass. The total and partial densities of states (DOS's) obtained in the two calculations show quantitative agreement and the results at the Fermi level agree with the experimentally available information. The recursion results for the 800-atom model show less structure, but retain all the essential features in the DOS obtained via the supercell calculation, indicating that a tight-binding description of (s,p)-bonded metallic systems is indeed possible. Minor differences in the DOS's are believed to be primarily due to the difference between the standard LMTO Hamiltonian and the Hamiltonian used in the recursion calculation, the latter being less accurate than the former at energies away from the reference energies E_ν's. Computational efforts needed for the supercell (**k**-space) and the recursion (real-space) calculations are compared.

I. INTRODUCTION

The interplay between the atomic and the electronic structure is of fundamental importance in the study of metallic glasses. The (s,p)-bonded metallic glasses play a key role in such a study for two reasons. The first is that the generalization of the Hume-Rothery rules (which correlate phase stability and valence-electron concentration) to amorphous alloys is based on nearly-free-electron arguments[1] and hence is expected to hold best for the (s,p)-bonded alloys. In analogy to the crystalline phase, the stability of the glass is thought to be associated with the existence of a structure-induced minimum in the electronic density of states near the Fermi level. The second reason is that a discussion of the interplay between the atomic structure and the electronic structure requires, in principle, a self-consistent calculation of both. For the moment, this is an impossible task due to the lack of a method for deducing the interatomic forces from the electronic structure of a glass. However, since the ions scatter the electrons only weakly in (s,p)-bonded metals, the effective interatomic potentials can be deduced from the response of the conduction electrons to the perturbing electron-ion potentials. These effective interatomic interactions can then be used for the construction of realistic structural models using computer-simulation techniques. The Ca-Al system has been chosen for the present study because of its outstanding structural, thermodynamic, and electron-transport properties.[2]

Electronic-structure calculations for amorphous systems are performed mainly in two different ways. One of these involves calculations in **k** space for clusters of atoms as large as the available computer can handle. Typically less than a hundred atoms can be considered in such calculations. These "supercell" calculations are undoubtedly accurate for the given clusters of atoms but may suffer from the drawback of small size. Spurious (i.e., not pertaining to the bulk material) features in the density of states (DOS) may result from the assumed periodicity of the structure. In practice, one has to consider supercells of various sizes in order to discover the features in the DOS originating from this periodicity. Averaging over several supercells reduces the error. The alternatives to the supercell calculations are the real-space techniques, such as the recursion[3] and moment[4] methods. These offer a complementary scheme where the emphasis is on the local electronic structure. The average DOS for the bulk amorphous material is obtained by summing the densities of states projected on to various atoms in the model cluster. Using these techniques it is possible to carry out calculations involving large clusters of atoms (from a few hundred to one or two thousand). However, there are errors due to the finite cluster size and the various possible ways of extrapolating the results for a finite cluster to that of an infinite system.

The choice between the supercell and the real-space calculation is dictated by factors such as the available cluster size, the spatial extent of the basis orbitals, and the quantities to be calculated. Supercell calculations can operate with long-ranged basis functions since for small periodic structures one can use the Ewald procedure to calculate the Bloch sums. Real-space calculations involving large clusters, however, rely on having well-localized basis functions. The matrix elements of the Hamiltonian or, more precisely, of $O^{-1}H$ or $O^{-1/2}HO^{-1/2}$ (where H is the Hamiltonian and O the overlap) must decay rapidly in space in order that the real-space schemes may be applied efficiently and without appreciable error.

Because of a lack of first-principles tight-binding methods, most real-space calculations for large amorphous clusters have so far relied on empirical or semiempirical tight-binding schemes. Often in such schemes the transferability of the parameters entering the Hamiltonian matrix elements is assumed without proper justification. The chemical pseudopotential scheme of Anderson and co-workers[5] has indeed provided an important advancement in the theory. Apart from providing a set of atomiclike orbitals suitable for a tight-binding description of the solid, this scheme was able to show why some empirical tight-binding schemes seemed to work so well. However, in practice, this scheme is difficult to use in its full form,[6,7] and the approximate forms used for the matrix elements may lead to significant loss of accuracy in the calculated results. Also, although the scheme yields the matrix elements of $O^{-1}H$ directly, these are not necessarily short ranged. In recursion calculations involving this scheme, the matrix elements beyond a certain number of near neighbors are simply ignored.

The tight-binding linear-muffin-tin-orbital (TB LMTO) scheme[8-11] developed during the past few years seems to have overcome most of the problems related to accurate electronic-structure calculations for large amorphous clusters. It provides a procedure for self-consistent[9,12] *ab initio* electronic-structure calculations, but can also be used, under suitable circumstances, as a semiempirical tight-binding scheme. The one-electron Hamiltonian is expressed in terms of some "potential parameters" and a "hopping matrix" that depends only on the structure, i.e., the arrangement of the atoms.[13] The potential parameters are local quantities, obtained from the solution of the one-electron wave equation inside the atomic or the Wigner-Seitz spheres surrounding the atoms. The environment dependence of the Hamiltonian matrix elements enters primarily through the hopping matrix (also called the structure matrix), which can be calculated explicitly without any approximation. The potential parameters can be calculated exactly for the system under study. However, they can also be borrowed from some reference system that has already been studied (e.g., from a pure system to an alloy). In this case the scheme becomes similar to an empirical tight-binding scheme. If need be, changes in the potential parameters due to the change in the environment relative to the reference system can be estimated and these estimates turn out to be fairly accurate.[14,15]

In this paper we calculate the electronic structure of a realistic model of a Ca_7Al_3 glass by the TB LMTO recursion scheme using potential parameters derived from self-consistent LMTO-supercell calculations. It will be shown that the TB LMTO method can be used with the ease and efficiency of any other tight-binding scheme, and produce accurate results. The system we have chosen is nontrivial both from the tight-binding and recursion points of view. Recursion will actually be carried out with the Löwdin-orthonormalized Hamiltonian $O^{-1/2}HO^{-1/2}$, truncating a series representation in terms of a two-center tight-binding Hamiltonian. Within the LMTO formalism the effect of such a truncation is well understood, with precise error estimates.

The remainder of this paper is divided into sections as follows. In Sec. II we discuss the construction of the 800-atom model of the Ca_7Al_3 glass. In Sec. III we briefly describe the supercell calculation and the TB LMTO method. Results of the two calculations are compared in Sec. IV and summarized in Sec. V.

II. ATOMIC-STRUCTURE CALCULATIONS

Since the details of these calculations are already given elsewhere, only a brief outline of the procedure is given here.[16-18] The construction of the structural model is based on pseudopotential-derived interatomic forces, molecular dynamics, and potential-energy–mapping techniques. The pseudopotentials are based on an orthogonalized-plane-wave expansion of the conduction-electron states in the alloy. The pseudopotential is optimized to achieve an optimal convergence of the perturbation expansion, a procedure equivalent to folding down higher-order contributions.[16] The resulting interatomic potentials are strongly composition dependent. The most relevant chemical binding effects reflected in the interatomic potentials are a strong compression of the Ca—Ca bonds and the nonadditivity of the potentials upon alloying with Al. The compression of the Ca pseudoatoms is due to the intraatomic charge redistribution primarily from the extended *s* to the localized *d* states.[19] The nonadditivity of the potentials is manifest in a pronounced preference for the formation of Ca-Al pairs at the composition of the Laves-phase $CaAl_2$ compared to that at the Ca-rich glass-forming composition.

A difficult step in any modeling algorithm of a glass is the equilibration with respect to the local chemical composition. Since the approach to equilibrium is controlled by the interdiffusion process, it is extremely slow at low temperatures. We follow a two-step procedure in our model construction. First, we perform a molecular-dynamics simulation for the high-temperature liquid phase. Here the local chemical equilibrium is easily achieved on the time scale of a computer experiment. Parallel to the molecular-dynamics run, the instantaneous configurations of the liquid are periodically mapped onto the local minima of the potential energy via a steepest-gradient descent on the potential-energy hypersurface. This potential-energy mapping results in a substantial image enhancement of the local order.[20] A configuration average over a large number of "mapped" configurations is found to be independent of the thermodynamic conditions before the quench.[20,21] The mapping is essentially equivalent to an infinitely rapid quench with no subsequent relaxation. It has been shown that this procedure yields realistic models for the structure of amorphous metals[21,22] and semiconductors.[23]

The computer simulations have been performed for samples of 800 atoms in a periodically repeated box with the shape of a rhombic dodecahedron, and our structural model is in very good agreement with the available diffraction data.[24] Small cubes containing about 60 atoms were cut out of the large models for the supercell electronic-structure calculations. The smaller models

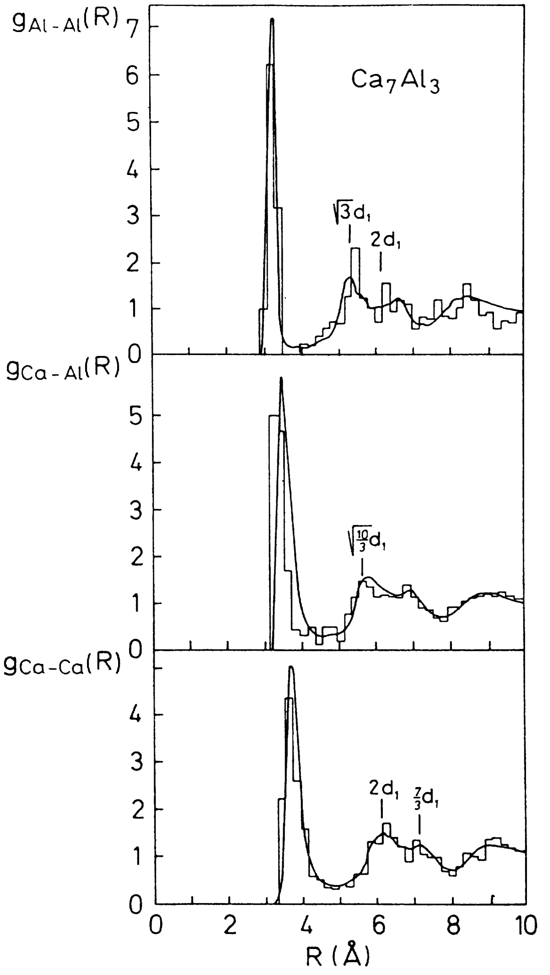

FIG. 1. Partial pair-correlation functions $g_{ij}(R)$ for amorphous Ca_7Al_3. The smooth lines show the computer-simulation result obtained by the potential-energy mapping of 20 independent configurations of the 800-atom sample. The histograms represent the correlation functions of a single 60-atom model prepared out of one of these configurations.

were relaxed to eliminate stresses across the surfaces of the cube after periodic repetition. The partial pair-correlation functions of a single 60-atom model compare well with those based on a configuration average over 20 independent 800-atom models, as shown in Fig. 1.

III. ELECTRONIC-STRUCTURE CALCULATIONS

Since the supercell-LMTO (Refs. 19 and 22) and TB LMTO (Refs. 8 and 12) methods have been discussed extensively in some recent publications, a brief discussion is given here for the sake of completeness.

In the LMTO method space is divided into muffin-tin spheres centered at various atomic sites **R**. In open structures with a large interstitial region, additional spheres in the interstitial region may also be needed. The potential inside the spheres is assumed to be spherically symmetric, while outside the spheres it is assumed to be constant. The potential is calculated using the density-functional theory of Hohenberg, Kohn, and Sham,[25] and the local-density approximation to the exchange-correlation potential is made.

Usually, supercell calculations are done for the zone center of the Brillouin zone only and a continuous DOS is derived from the discrete spectrum by an appropriate Gaussian broadening (we use a Gaussian of width 0.2 eV).[26] Because of the rather large dispersion of the free-electron-like bands in the (s,p)-bonded metals, the four corners of the irreducible wedge of the Brillouin zone are used as well in the DOS calculations. The statistical representation of the electronic structure of the glass is further improved by taking the average over two different 60-atom models taken from independently mapped configurations. Only two models were considered in the averaging here because the changes produced by the second model were quite small.

A TB LMTO basis orbital of (collective) angular-momentum index $L=(l,m)$, centered at site **R**, can be expressed as

$$\chi^{\alpha}_{RL}(\mathbf{r}-\mathbf{R})=K^{\alpha}_{RL}(\mathbf{r}-\mathbf{R})+\phi_{RL}(\mathbf{r}-\mathbf{R}) + \sum_{R',L'}\dot{\phi}^{\alpha}_{R'L'}(\mathbf{r}-\mathbf{R}')h^{\alpha}_{R'L'RL} \;, \tag{1}$$

where K^{α}, the envelope function of χ^{α}, is truncated inside all the muffin-tin spheres and the ϕ and the $\dot{\phi}$ functions are truncated outside the sphere at **R** and **R**′, respectively. The envelope function represents the solution of the one-electron wave equation in the interstitial region. ϕ_{RL} is the solution inside the sphere of radius s_R at **R** for some reference energy $E_{\nu Rl}$ and is normalized within the sphere,

$$\phi_{RL}(E,\mathbf{r}-\mathbf{R})=\phi_{Rl}(E,r_R)Y_{lm}(\mathbf{r}-\mathbf{R})/|\mathbf{r}-\mathbf{R}| \;, \quad r_R=|\mathbf{r}-\mathbf{R}| \tag{2}$$

$$\int_0^{s_R}\phi^2_{Rl}(E,r)r^2\,dr=1 \;, \tag{3}$$

$$\phi_{RL}(\mathbf{r}-\mathbf{R})\equiv\phi_{RL}(E_{\nu Rl},\mathbf{r}-\mathbf{R}) \;. \tag{4}$$

The function $\dot{\phi}^{\alpha}$ is given by

$$\dot{\phi}^{\alpha}_{RL}(\mathbf{r}-\mathbf{R})=\dot{\phi}^{\alpha}_{Rl}(r_R)Y_{lm}((\mathbf{r}-\mathbf{R})/|\mathbf{r}-\mathbf{R}|) \;, \tag{5}$$

$$\dot{\phi}^{\alpha}_{Rl}(r_R)=\dot{\phi}^{\gamma}_{Rl}(r_R)+\phi_{Rl}(r_R)o^{\alpha}_{Rl} \;, \tag{6}$$

where

$$\dot{\phi}^{\gamma}_{Rl}(r_R)\equiv\left.\frac{\partial\phi_{Rl}(E,r_R)}{\partial E}\right|_{E=E_{\nu Rl}} \;. \tag{7}$$

The constants o^{α} are chosen to give ϕ^{α} the same radial logarithmic derivative at the sphere radius s_R as the tail of the envelope function K^{α}. The multiplication by h^{α} in Eq. (1) makes the augmentation of the envelope function K^{α} continuous at the sphere boundary.

The envelope $K^{\alpha}_{RL}(\mathbf{r}-\mathbf{R})$, before augmentation by the ϕ functions, can be expanded in a spherical-harmonics series about a neighboring site **R**′, and the expansion coefficients $S^{\alpha}_{R'L'RL}$ are the so-called screened structure constants. These depend only on the sphere positions and not their type or radii. Unlike the bare canonical structure constants $S^{0}_{R'L'RL}$ that are long ranged, the screened structure constants can be made short ranged with a suitable choice of a "screening matrix" α. The structure constants S^0 and S^α are related via the Dyson equation

$$S^\alpha_{RLR'L'}=S^0_{RLR'L'}+\sum_{R'',L''}S^\alpha_{RLR''L''}\alpha_{R''l''}S^0_{R''L''R'L'} \ . \tag{8}$$

In matrix notation,

$$\begin{aligned}S^\alpha&=S^0+S^\alpha\alpha S^0=S^0(1-\alpha S^0)^{-1}\\&=\alpha^{-1}[(\alpha^{-1}-S^0)^{-1}-\alpha]\alpha^{-1} \ ,\end{aligned} \tag{9}$$

where α is a diagonal matrix with elements α_{Rl}. Different choices of the screening matrix α are discussed in Ref. 10. The augmentation of the envelope function K^α at the sphere boundary relates the coefficients h^α in (1) to the screened structure matrix elements S^α and the relation can be expressed as[9–12]

$$\begin{aligned}h^\alpha_{RLR'L'}&=(c^\alpha_{Rl}-E_{\nu Rl})\delta_{RR'}\delta_{LL'}\\&\quad+(d^\alpha_{RL})^{1/2}S^\alpha_{RLR'L'}(d^\alpha_{R'L'})^{1/2} \ ,\end{aligned} \tag{10}$$

where c^α_{Rl} and d^α_{RL} are potential parameters to be obtained from the ϕ and $\dot{\phi}$ functions at the sphere boundary.

In the present work we will use the atomic-sphere approximation (ASA), in which one replaces the muffin-tin spheres by space-filling atomic spheres and neglects the remaining interstitial region. In this approximation the first term on the right-hand side (rhs) of (1) drops out. The Hamiltonian and the overlap matrices receive no contribution from the interstitial region and are given by[9–12]

$$H=h+hoh+(1+ho)E_\nu(1+oh) \ , \tag{11}$$

$$0=\langle\chi\,|\,\chi\rangle=(1+ho)(1+oh) \ , \tag{12}$$

In (12) we have neglected terms involving a small parameter, which is the integral of the function $\dot{\phi}^{\gamma^2}$ within the atomic sphere. In (11) and (12), 1 is the unit matrix and we have consistently dropped the subscripts R and l as well as the superscript α. The Löwdin-orthonormalized Hamiltonian in the ASA assumes the form

$$H=O^{-1/2}HO^{-1/2}=E_\nu+h(1+oh)^{-1} \tag{13}$$

$$\begin{aligned}&=E_\nu+h-hoh+\cdots\\&=H^{(1)}-hoh+\cdots \ ,\end{aligned} \tag{14}$$

where

$$H^{(1)}\equiv E_\nu+h \ . \tag{15}$$

Thus the Löwdin-orthonormalized Hamiltonian can be expressed as a power series of a matrix $h\equiv H^{(1)}-E_\nu$, which is an effective, two-center tight-binding [see Eq. (10)] Hamiltonian, $H^{(1)}$, minus an energy E_ν, chosen at the center of interest. If the power series is truncated after the first-order term, the Hamiltonian in the orthonormal representation is approximated by the two-center tight-binding Hamiltonian $H^{(1)}$ and the resulting energy positions of the features in the densities of states are correct to first order in the deviations from the energies E_ν. If, on the other hand, the truncation is performed after the second-order term, the range of the Hamiltonian in the orthonormal representation is approximately twice that of the two-center tight-binding Hamiltonian and the resulting DOS features will have positions correct to second order in their distance from E_ν. Thus, within the LMTO formalism the effect of truncating the range of the Hamiltonian is well defined and can be controlled. From the relation (10) and the fact that the S^α are short ranged, we see that the first-order Hamiltonian itself is short ranged. With proper choice of the screening matrix α, the matrix elements of $H^{(1)}$ connecting atoms beyond the second shell of neighbors in all close-packed structures can be made to vanish.

Equations (10), (14), and (15) define the Hamiltonians that will be used in conjunction with the recursion method for the electronic-structure calculation. Calculation of the Hamiltonian matrices involves two steps: (i) calculating the potential parameters c^α, d^α, and o^α, and (ii) calculating the screened structure matrix S^α. Relations that can be used to obtain the potential parameters are discussed in the Appendix. The screened structure matrix S^α can be calculated from the unscreened structure matrix S^0, available in analytic forms, by iterating the Dyson equation (8) to self-consistency or by matrix inversion using the last expression on the rhs of (9).

The screening matrix α used in this work is a site-independent but l-dependent set with only three distinct nonzero elements:

$$\begin{aligned}&0.3485,\ 0.05303,\ 0.010714\ \text{ for } l=0,1,2\\&\text{and}\\&0\ \text{ for } l\geq 3 \ .\end{aligned} \tag{16}$$

It has been found that, with nonzero screening on all sites in the solid for $l=0$, 1, and 2, these α values give rise to the most localized LMTO basis orbitals and short-ranged structure matrix elements for all reasonably homogeneous and close-packed structures. The structure constants S^α involve a length parameter w, which is determined by the density of the screening multipoles. Thus we can calculate w from the volume per atom V_0 using

$$V_0=(4\pi/3)w^3 \ . \tag{17}$$

The off-site elements of the structure matrix S^α can also be obtained from an interpolation formula for the "Slater-Koster" terms $\bar{S}_{ll'}(d)$, where the intersite separation $\mathbf{d}=\mathbf{R}-\mathbf{R}'$ is along the z axis. The interpolation formula[10,11] that has been found suitable for arbitrary homogeneous structures is of the form

$$\bar{S}_{ll'm}(d)=A_{ll'm}e^{-z}, \quad z=\beta_{ll'm}d/w \ . \tag{18}$$

The values of the constants A and β for the various Slater-Koster terms $ss\sigma$, $sp\sigma$, . . . depend on the screening matrix α. For the set (16) these values are available in Table II of Ref. 10 and Table I of Ref. 11.

The on-site elements of the screened structure matrix depend sensitively on the local arrangement of atoms. There is no simple interpolation formula for these, but they can be calculated using the off-site elements of S in the Dyson equation

$$S^{\alpha}_{RLRL'}=\sum_{\substack{R'',L''\\(R''\neq R)}} S^{\alpha}_{RLR''L''}\alpha_{R''l''}S^{0}_{R''L''RL'} \; . \tag{19}$$

The importance of evaluating these on-site elements correctly has been discussed in Ref. 12.

In an amorphous system every atom sits in an environment that is different from the environment of any other atom. Thus the potential in each sphere is different and, in principle, one is required to calculate as many sets of potential parameters as there are spheres. Since this is computationally cumbersome, one can resort to an approximate treatment. For example, potential parameters for a small number of spheres can be calculated exactly and for the rest some average potential parameters can be used.[12]

Usually, all spheres of a given type are assumed to have a fixed radius. The ratio of the radii of the two types of spheres in a binary system can be determined by considering small variations about the ratio of the Goldschmidt radii of the corresponding atoms. The ratio for which the overlap of the spheres is minimized should finally be chosen. The actual values of the radii are to be determined by conserving the total volume. Instead of the Goldschmidt radii, one can consider the positions of the first peaks in the partial pair distribution functions for the alloy. A detailed polyhedron analysis may also be carried out in order to determine the optimum sphere radii. However, the electronic-structure results are not sensitive to the sphere radii as long as the overlap is within 20%, i.e., $s_1+s_2<1.20d$, where s_1 and s_2 are the radii of the two spheres whose centers are separated by distance d.

The potential parameters c^{α}, d^{α}, and o^{α}, and the structure constants S^{α}, are all that is needed for a calculation of the DOS. In a self-consistent calculation[12] one further calculates the charge density in the various spheres. From an admixture of the old and the new charge densities, a new potential is calculated, and, from this, a new set of potential parameters, which is used in the subsequent DOS calculation. The cycle is iterated until self-consistency in the charge distribution is achieved. The reference energies E_{ν} are chosen to lie at the centers of gravities of the occupied parts of the respective l bands, and are updated in each cycle of the iteration.

Our object here is to perform the simplest possible TB LMTO calculation that would yield accurate results for the DOS. Since we want a calculation that is comparable in speed to any other tight-binding scheme, we will resort to some approximations in calculating the structure matrix and the potential parameters. Our results will indicate that these approximations are indeed reasonable.

IV. RESULTS FOR THE Ca_7Al_3 GLASS

The atomic-sphere radii for Ca and Al in our calculation were taken to be the same as in the LMTO supercell calculation of Hafner and Jaswal,[22] where these were derived from the minima in the pair potentials. Since we are interested in the simple TB LMTO recursion calculation, we consider just one set of potential parameters for all the Ca spheres and one set for all the Al spheres. From the final self-consistent result of the standard LMTO (Ref. 22) supercell calculation, we choose the potential parameters for one representative set of Ca and Al spheres. These standard LMTO parameters are then converted to TB LMTO parameters c^{α}, d^{α}, and o^{α}, which are listed in Table I. The relations used for this conversion are given in the Appendix.

For calculations involving a binary (AB) alloy, the potentials in the A and B spheres are usually not available *a priori*. In this case one can start from the parameters for the pure A and the pure B solids without performing a self-consistent (supercell) calculation for a representative cell. Standard LMTO parameters for pure Ca (solid) are available in Table III of Ref. 9, where the results for 33 elemental metals are listed. The procedure to estimate the parameters for the alloy from those for the pure solid by performing appropriate corrections due to the change in the atomic- and the average Wigner-Seitz sphere radii is described in Ref. 10.[14] We found that the parameters for the Ca sphere in the Ca_7Al_3 alloy estimated from the pure calcium parameters are reasonably close to the values obtained in the standard LMTO alloy calculation. This indicates transferability of these quantities from the pure crystalline system to an amorphous alloy. Since the parameters for pure crystalline Al are not included in Ref. 10, a transferability test for aluminum was not performed.

Sob *et al.*[27] have developed a technique to calculate the screened structure constants using the inversion of the matrix $(\alpha^{-1}-S^{0})$ as indicated in Eq. (9). However, for reasonably accurate results for the DOS one can also use the interpolation formula (18). The advantage of this interpolation scheme is that it can generate the screened structure constants in an order of magnitude (~ 10 times) less time than is needed by the matrix-inversion technique. Quantitative accuracy of the results obtained by using the interpolation scheme is discussed in Ref. 10. We have thus used Eqs. (18) and (19) to obtain the on-site elements of the structure matrix. With given values for the potential parameters and the interpolation formula for the hopping integrals, the TB LMTO scheme acquires the speed of an empirical tight-binding scheme. An important point is that in most tight-binding schemes the on-site elements are held fixed, whereas in the TB LMTO scheme these are determined by the environment of the atom.

Recursion calculations for the 800-atom cluster (in the

TABLE I. Potential parameters for the Ca_7Al_3 glass (in units of rydbergs).

	c^{α}	d^{α}	$(o^{\alpha})^{-1}$	E_{ν}
	Calcium (Wigner-Seitz	radius 3.9789 a.u.)		
s	-0.2889	0.0763	-0.8382	-0.3318
p	-0.0145	0.0278	-0.6336	-0.2949
d	-0.0300	0.0124	-0.6833	-0.2756
	Aluminum (Wigner-Seitz	radius 3.3720 a.u.)		
s	-0.6163	0.0668	18.7606	-0.4933
p	-0.4211	0.0419	-3.5520	-0.2844
d	-0.3643	0.0135	-1.3537	-0.2633

shape of a truncated dodecahedron) were carried out using periodic boundary conditions and the "linear predictor terminator" due to Allan.[28] 500 recursion coefficients were extracted, typically from 10 *s*, 15 *p*, and 20 *d* calculated coefficients, following the scheme of Allan. The calculated and the extracted coefficients were used, together with the constant chain terminator,[3] to compute the diagonal matrix elements of the Green's function, from which local densities of states were obtained. The number of calculated coefficients used to extract the subsequent part of the chain was lowered from the figures quoted above, whenever it was necessary to do so. We found that the calcium local densities of states were rather insensitive to the number of extrapolated coefficients used prior to introducing the constant chain terminator. In other words the oscillations in the calcium coefficients were quite damped and, most often, 30 extrapolated coefficients, together with the constant chain terminator, were sufficient to yield convergence in the corresponding partial local DOS. The aluminum coefficients showed pronounced oscillatory behavior and at least 100 coefficients needed to be extrapolated before using the constant chain terminator. Since increasing the number of extrapolated coefficients in the Allan scheme does not significantly increase the time needed to compute the local DOS, we used 500 extrapolated coefficients for all the aluminum as well as calcium local densities of states.

The local densities of states obtained by using the first-order TB LMTO Hamiltonian $H^{(1)}$, with the E_ν's chosen at the centers of the occupied part of the bands, showed considerable difference from the standard LMTO results. The bottom of the band was 3–4 eV too low and the maximum in the density of states following the Fermi level (for the calcium projected DOS) too high. The standard LMTO Hamiltonian is accurate to third order in deviations from the reference energies (the E_ν's). The results for the first-order Hamiltonian $H^{(1)}$ thus differ increasingly from the standard LMTO results as the deviations from the reference energies increase. This difference is even more pronounced in case of calcium, for which the overlap parameters o^α are rather high (see Table I), or the parameters $(o^\alpha)^{-1}$ too low. The $(o^\alpha)^{-1}$ parameters, with dimensions of energy, provide a measure of the energy window about the reference energies E_ν for which the DOS results obtained from $H^{(1)}$ are reliable. These parameters are large for aluminum, but too small for calcium to yield accurate results for the occupied part of the valence band. Another way of looking at this problem is that since the o^α parameters for calcium are all larger than unity, higher-order terms such as *hoh* in the formal series expansion (14) are not negligible. Thus to obtain an accurate DOS such terms must be included in the Hamiltonian used in the recursion calculation.

Successive terms in the series expansion (14) connect more and more distant neighbors. However, the recursion method can operate efficiently and without appreciable error (due to finite cluster size) only as long as the Hamiltonian matrix elements connect an atom to a modest number of neighbors. We therefore include only the "*hoh*" term in the series expansion for *H*. Furthermore, only the nonzero terms of $H^{(1)}$ are updated due to the inclusion of this correction. Atoms that were unconnected via $H^{(1)}$ are still left unconnected. Our results indicate that even this approximate treatment of the "*hoh*" term yields substantial improvement in the calculated DOS. Since all of the calcium and two of the aluminum *o* parameters are negative, the effect of adding the "*hoh*" term is to add a positive shift to almost all the eigenvalues. This shifts the bottom of the band to a higher energy, bringing the results in reasonable agreement with the standard LMTO results. Since almost all eigenvalues away from the reference energies E_ν are shifted upwards in energy, the DOS at energies above the E_ν's is decreased. The maximum in the DOS following the Fermi level is brought down to a value in close agreement with the standard LMTO result.

It is clear that the inclusion of the higher-order terms in the Hamiltonian would further improve the results. However, because of their long range, such terms are difficult to include in the recursion calculation. Also, calculating these higher-order terms for large clusters such as the one used here would require either enormous computation time or huge storage and the corresponding gain in accuracy is perhaps not worth the cost involved.

In Fig. 2 we compare the result of the recursion calculation [Fig. 2(b)] with the self-consistent LMTO supercell calculation [Fig. 2(a)]. The two DOS's in Fig. 2 show remarkable similarity. The DOS at the Fermi level and the maximum in the DOS are almost identical. In the recursion calculation the position of the maximum is a little higher and the bottom of the band is 0.5 eV lower than in the supercell calculation. This difference is similar to, but much smaller than, that due to $H^{(1)}$ alone. Thus the inclusion of the higher-order terms in Eq. (14) should further improve the agreement between the two methods.

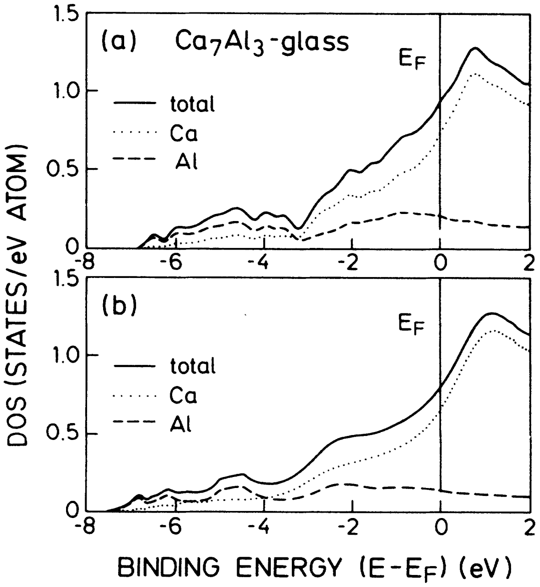

FIG. 2. Calculated density of states for Ca_7Al_3 glass using (a) the LMTO supercell method and (b) the TB LMTO recursion method. ($E_F = -2.3936$ eV.)

The DOS in Fig. 2(b) is calculated by considering 36 calcium and 12 aluminum local densities of states. This DOS, calculated via the recursion method and for a cluster much larger than that used to obtain the result of Fig. 2(a), shows less structure than the latter, but contains all the essential features.

In Figs. 3 and 4 we show the partial calcium and aluminum contributions to the total DOS shown in Fig. 2 for the two calculations. The average *d* partial DOS for calcium is almost identical for the supercell and the recursion calculations. This demonstrates the effectiveness of the recursion method in being able to treat the *d* band, or, in general, narrow bands, accurately. The *s* and *p* bands are usually harder to deal with via the recursion method. But our calculations show significant difference (between the recursion and **k**-space results) only for the aluminum *s* states. Even this difference is likely to diminish if an average over larger number of atoms in the recursion calculation is considered. On the whole, we found the aluminum *s* local DOS to be the most sensitive to the particulars of the termination. Also, these local DOS's showed the most pronounced variation from one atom to another. This is expected on the basis of the large magnitude of the *s* matrix elements in aluminum, and the error can perhaps be reduced by increasing the size of the cluster. Another reason for large fluctuations in the local aluminum *s* DOS might be the lack of self-consistency in the potentials in the various spheres. Though this should affect all states, it is conceivable that the aluminum *s* states are the ones most affected by this non-self-consistency. Integrated properties are less sensitive to the details of termination and the finite size of the cluster used in recursion. Both the supercell and the recursion calculations indicate negligible charge transfer, on the average, from calcium to aluminum.

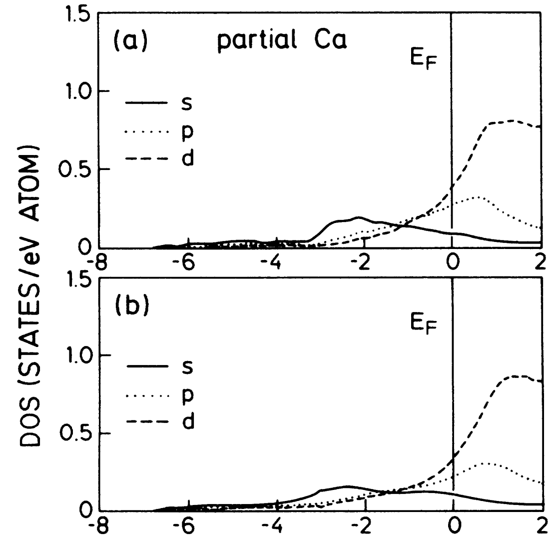

FIG. 3. Partial density of states for Ca in Ca_7Al_3 glass using (a) the LMTO supercell method and (b) the TB LMTO recursion method.

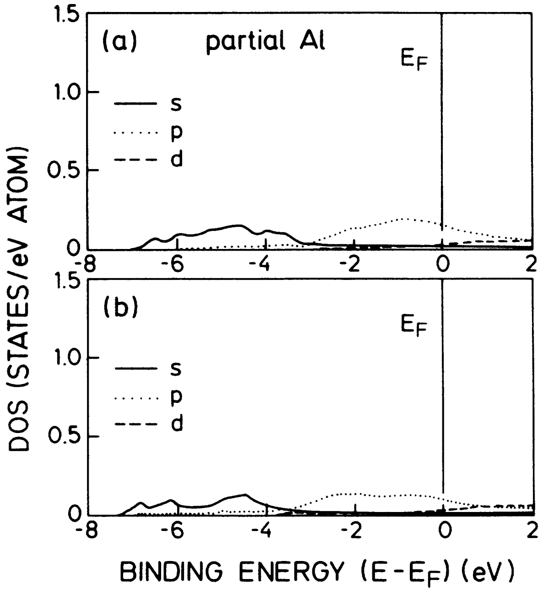

FIG. 4. Partial density of states for Al in Ca_7Al_3 glass using (a) the LMTO supercell method and (b) the TB LMTO recursion method.

It is worth comparing the computational efforts involved in the two calculations. On a Cray machine the DOS calculation for the 60-atom cell required 4 min for each **k** point. Hence a total of 32 min was required to produce the result of Fig. 2(a). For the recursion calculation computation time mainly depends on the size of the cluster and the number of recursion coefficients calculated. We computed 20 recursion coefficients for each orbital (initial recursion vector) considered. For a single atom, i.e., nine orbitals, this used 1 min on the Cray. The DOS calculation for each set of recursion coefficients, using the "linear predictor terminator" with 500 extrapolated coefficients, takes less than a second. Hence the calculation involving the average of 48 atoms to produce the result in Fig. 2(b) used approximately 50 min. Of course, this last figure depends on the number of atoms considered to obtain the average DOS and, if one were interested only in integrated properties, then a much smaller computation time would suffice. On a normal IBM machine the computation would be approximately 10 times slower, but certainly the relative time requirement for the two methods would remain unchanged.

V. CONCLUSIONS

We have shown that within the LMTO formalism it is possible to provide a tight-binding description of an (s,p)-bonded metallic glass such as Ca_xAl_{1-x}. The LMTO recursion calculation performed on an 800-atom model of Ca_7Al_3 is in good agreement with a standard LMTO 60-atom supercell (**k**-space) calculation. Minor differences between the two results can be explained within the LMTO theory. In carrying out the LMTO recursion calculation, we have resorted to approximations that make this scheme comparable, in terms of computational ease, to other (semi)empirical tight-binding schemes. However, while the accuracy of these latter tight-binding schemes is usually doubtful, the TB LMTO scheme, with some modification, is shown to possess an accuracy comparable to that of the standard LMTO method.

The TB LMTO results confirm the conclusions drawn on the basis of the LMTO supercell calculations. There is no indication of a structure-induced minimum in the electronic DOS close to the Fermi level. The DOS at the Fermi level is considerably enhanced over the free-electron value due to a substantial contribution from the Ca 3*d* states. However, this Ca 3*d* contribution is not strong enough to support an interpretation of the unusual electron-transport properties in terms of strong *d*-state scattering.[2] The most relevant feature of the electronic structure of Ca-Al glasses seems to be the incipient dehybridization of the conduction band: a pronounced DOS minimum separates an Al 3*s* band (which shows only very small admixture of other states) from an Al 3*p* band (which strongly interacts with the Ca *spd* states). The deviation of the Hall constant[2] from the free-electron value can be explained if we assume that the electrons in the band below the minimum in DOS do not contribute to the transport process. The recently established correlation between the electrical resistivity and the deviation of the Hall constant from its free-electron value support the assumption that the incipient localization of the electrons plays a key role in the electron-transport processes. In this respect, Ca-Al glasses are similar to other strong-scattering disordered systems like the liquid alloys of alkali metals with the heavy polyvalent metals.

APPENDIX

The parameters c^α and d^α can be obtained from the solutions ϕ^α alone. Thus a calculation involving the first-order, two-center, tight-binding Hamiltonian $H^{(1)}$ can be performed without calculating the energy derivative functions $\dot{\phi}^\alpha$. However, these are needed to calculate the parameter o^α. Calculation of these parameters is discussed in detail in Refs. 9–12. In the following we provide the relations that can be used to convert the standard LMTO parameters, as discussed in the monograph by Skriver[25] and tabulated for the elemental metals in Ref. 9, into the parameters used in the LMTO recursion calculation. These are

$$C=E_\nu+\omega(-)\ , \tag{A1}$$

$$\Delta=\tfrac{1}{2}(s/w)^{2l+1}s\Phi^2(-)\ , \tag{A2}$$

$$\gamma=[\tfrac{1}{2}(2l+1)](s/w)^{2l+1}\Phi(-)/\Phi(+)\ , \tag{A3}$$

$$\Phi(+)=\phi+\omega(+)\dot{\phi}^\gamma\ , \tag{A4}$$

$$\Phi(-)=\phi+\omega(-)\dot{\phi}^\gamma\ , \tag{A5}$$

$$\omega(+)=-\frac{\phi}{\dot{\phi}^\gamma}\frac{l-D\{\phi\}}{l-D\{\dot{\phi}^\gamma\}}\ , \tag{A6}$$

$$\omega(-)=-\frac{\phi}{\dot{\phi}^\gamma}\frac{-l-1-D\{\phi\}}{-l-1-D\{\dot{\phi}^\gamma\}}\ , \tag{A7}$$

$$D\{\phi\}=s\phi'(s)/\phi(s),\quad D\{\dot{\phi}^\gamma\}=s\dot{\phi}^\gamma(s)'/\dot{\phi}^\gamma(s)\ , \tag{A8}$$

$$\phi'(s)\equiv\left.\frac{\partial\phi(r)}{\partial r}\right|_{r=s}\ ,\quad \dot{\phi}^\gamma(s)'\equiv\left.\frac{\partial\dot{\phi}^\gamma(r)}{\partial r}\right|_{r=s}\ , \tag{A9}$$

$$(o^\alpha)^{-1}=\omega(-)\frac{\Delta}{(\gamma-\alpha)}\ , \tag{A10}$$

$$\frac{(d^\alpha)^{1/2}}{(\Delta)^{1/2}}=\frac{c^\alpha-E_\nu}{C-E_\nu}=\frac{\alpha-\gamma}{\Delta}\frac{1}{o^\alpha}\ . \tag{A11}$$

Here, *s* and *w* are the atomic- and the average Wigner-Seitz–sphere radii, respectively. ϕ and $\dot{\phi}^\gamma$ are defined in Sec. III [Eqs. (2)–(6)]. Note that, in Skriver's notation,[25]

$$\phi\equiv\Phi_\nu,\quad \dot{\phi}^\gamma\equiv\dot{\Phi}_\nu,\quad D\{\phi\}\equiv D_\nu,\quad D\{\dot{\phi}^\gamma\}\equiv D_{\dot{\nu}}\ .$$

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