Calculation of electronic properties of amorphous alloys

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Abstract

We describe the application of the locally-self-consistent-multiple-scattering (LSMS)[1] method to amorphous alloys. The LSMS algorithm is optimized for the Intel XP/S-150, a multiple-instruction-multiple-data parallel computer with 1024 nodes and 2 compute processors per node. The electron density at each site is determined by solving the multiple scattering equation for atoms within a specified distance of the atom under consideration. Because this method is carried out in real space it is ideal for treating amorphous alloys. We have adapted the code to the calculation of the electronic properties of amorphous alloys. In these calculations we determine the potentials in the atomic sphere approximation self consistently at each site, unlike previous calculations[2] where we determined the potentials self consistently at an average site. With these self-consistent potentials, we then calculate electronic properties of various amorphous alloy systems. We present calculated total electronic densities of states for amorphous Ni\textsubscript{80}P\textsubscript{20} and Ni\textsubscript{40}Pd\textsubscript{40}P\textsubscript{20} with 300 atoms in a supercell.

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1. Introduction

In the past[2] we have carried out calculations of the electronic properties of various concentrations of NiP amorphous alloys in the Local Density Approximation (LDA) in which the atoms were arranged in a supercell and relaxed using Weber-Stillinger potentials. The electronic wave functions were determined by a linearized Korringa-Kohn-Rostocker (KKR) band-structure calculation within the LDA. Spherical muffin-tin potentials were used which, for a particular concentration, were determined self consistently from a separate KKR Coherent-Potential-Approximation (CPA) calculation on a random alloy in which the atoms were placed at random on an fcc lattice. Thus the potentials were not determined self consistently for the particular arrangement of the atoms in the supercell for the amorphous alloy.

The results of these calculations produced densities of states and electrical resistivities due to disorder scattering in quite good agreement with experimental results, although the variation of the resistivities with concentration appeared to be somewhat less than experiment. We also calculated the thermopower, and we found a variation with concentration which was in reasonable agreement with experiment. However, we did not find a change in sign of the thermopower with concentration that was found experimentally.

The LSMS is a real-space, multiple-scattering method for solving the Kohn-Sham equations that is well-suited for massively parallel computers. We have made the relatively minor changes in the code needed to apply this method to supercell models of amorphous alloys. The advantages of using this method over our earlier procedures are several. First of all, with LSMS we can now determine the potential self consistently at each site in the supercell. Secondly, we can go to a larger number of atoms in the supercell. In our previous serial calculations on a Cray YMP, we were limited to about 340 atoms in the cell. With our LSMS calculations on the Intel Paragon XP/S-150 on which we assign one atom to a node, we can have as many as 1024 atoms in the cell. Finally, with our previous
serial calculations on the YMP with 340 atoms, because of memory limitations, we had to confine our angular momentum decomposition sums to an $l_{max} = 2$. With LSMS on the XPS150 we can handle up to $l_{max} = 3$ or 4.

In the next section we discuss briefly the LSMS method. In Sect. 3, we discuss our calculational procedures. In Sect. 4, we present our results for the calculated density of states of amorphous NiP and amorphous NiPdP alloys. In Sect. 5 we discuss our results, and in Sect. 6 we give our conclusions.

2. Locally-self-consistent-multiple-scattering method

The LSMS method[1] is a single-electron, real-space, multiple-scattering approach based on LDA. This method is ideally suited for calculating the electronic properties of a large number $N$ of atoms ($N$ up to the number of nodes which is currently 1024 on the XP/S-150) in a supercell by massively parallel supercomputers because it exhibits linear (O($N$)) scaling. At the heart of the LSMS method is the observation that a good approximation to the electron density $\rho^i(\mathbf{r})$ on atom site $i$ can be obtained by considering only the electronic multiple-scattering processes in a limited spatial region about the site $i$. The cluster of $M$ atoms inside this region is referred to as the Local Interaction Zone (LIZ) for atom $i$. Each atom is at the center of its own unique LIZ. In solving the Schrödinger equation to obtain $\rho^i(\mathbf{r})$ based at site $i$, one replaces the effect of all of the atoms outside the LIZ of atom $i$ by a constant potential. The potential that is to be used in the next Self-Consistent Field (SCF) iteration is calculated by solving Poisson’s equation for an electron density made up of all of the single-site densities $\rho^i$. A real-space multiple scattering approach is also being used by Arnold and Solberg[3]

In our calculations, we assigned each atom in the supercell to its own node on the Intel Paragon XPS150 parallel computer at Oak Ridge National Laboratory. Starting with an initial assumed potential we calculate the scattering path matrix $\tau_{jk}^i(\epsilon)$ at site $i$ with $j, k = 1, 2, ..., M$. The scattering path matrix is the inverse of the real space KKR
matrix $t^{-1}(-\varepsilon) - g(\varepsilon)$ where $t$ is the single-site t-matrix, $g$ is the real space structure constant matrix, and $\varepsilon$ is the electron energy. With a maximum angular momentum of $l_{\text{max}} = 3$, the KKR matrix that must be inverted on each node is of dimension 16 times $M$. The Green’s function, and from this the charge density at site $i$, can be determined from the scattering path matrix. With this we then obtain a new potential for the next iteration. These iterations are carried to convergence at which point we have a self-consistent electron potential at each site.

3. Calculational procedures

For our preliminary calculations using LSMS to determine electronic properties of amorphous alloys, we have examined amorphous Ni$_{80}$P$_{20}$ and Ni$_{40}$Pd$_{40}$P$_{20}$. These are interesting systems to compare because, although both can be produced as amorphous systems, the NiPdP system can be made in the amorphous form with slow cooling from the melt[4] whereas NiP alloys become amorphous only with very rapid cooling from the melt. The NiPdP alloys can thus be produced as amorphous materials in bulk three-dimensional samples. Such alloy systems could have important potential applications. Thus it is of interest to determine on a microscopic scale the differences between these two systems.

We have used the atomic sphere approximation (ASA) with overlapping spheres to represent our potential. The ASA sphere volume at a site is taken to be equal to that of the Voronii polyhedron surrounding it. Thus each site has a different ASA sphere radius.

We report here on results for the electronic density of states determined using one sample of 300 atoms for the supercell for each of the two alloys. The sample was constructed by relaxing with pair potentials a dense random packing of hard spheres as described in reference[2]. The sample was shown to agree with experimental partial pair distribution functions of Ni$_{80}$P$_{20}$. Unfortunately partial pair distribution functions are not available for Ni$_{40}$Pd$_{40}$P$_{20}$. Furthermore, the density has not been published. We therefore took the
sample for Ni$_{40}$Pd$_{40}$P$_{20}$ to be identical to that for Ni$_{80}$P$_{20}$ except that half the Ni atoms were replaced at random with Pd.

The LIZ was taken to have a radius of 5.1AU which includes the nearest neighbor shell of atoms. Other calculations indicate that this size LIZ is sufficient to give electron densities and potentials such that evaluation of the LDA energy using these electron densities and potentials and evaluating the eigenvalue sum using a large LIZ radius (approximately 10.0AU) will give total energies accurate to tenths or hundredths of a mRy. The fact that the energy can be accurately determined using electron densities calculated with a small LIZ radius is related to the stationarity of the energy with respect to the electron density. Unfortunately there is no stationarity principle to insure the accuracy of the density of states. We anticipate that the density of states shown here will be very close to densities of states calculated with a LIZ radius taken to convergence.

4. Results for NiP and NiPdP amorphous alloys

After iterating the calculations for the self-consistent potential to convergence for the Ni$_{80}$P$_{20}$ sample of 300 atoms, we can examine the charge transfer at each Ni and at each P site. In terms of the number of electrons transferred to a particular site (a positive number means that electrons, or negative charge, has been transferred to that site while a negative number means just the opposite), we find that the maximum transfer to the 240 Ni sites is 0.574, the minimum is -.096, and the average transfer is 0.169. For the 60 P sites, the maximum is -0.269, the minimum is -0.997, and the average is -.675.

For both the Ni$_{80}$P$_{20}$ and the N$_{40}$Pd$_{40}$P$_{20}$ samples, we calculated the total electronic density of states for the converged potentials. Fig. 1 shows the calculated density of states for Ni$_{80}$P$_{20}$. The solid curve is the result of the present calculation in which the potential is determined self consistently at each site, while the dotted curve is for a previous calculation [2] in which the potential was not determined self consistently.
Fig. 2 gives the result of our calculation of the electronic density of states for our 300 atom sample of Ni$_{40}$Pd$_{40}$P$_{20}$ with the potential determined self consistently at each site.

5. Discussion

The amount of charge transferred at each atomic site compared to the neutral atom depends very much on the particular volume taken around the atom. Thus the actual value for the charge transfer has limited significance. However, a comparison of the charge transfer values among all the Ni atoms or among all the P atoms gives an indication of the variation of local environments among all of the atoms of a given species in the sample. The point is that the large variation that we find for our samples of amorphous Ni$_{80}$P$_{20}$ and Ni$_{40}$Pd$_{40}$P$_{20}$ after the potentials have been determined self consistently indicate that there are large variations in the potentials among the atoms of a given species in the sample.

On comparing the electronic density of states of Ni$_{80}$P$_{20}$ calculated here with self-consistent potentials (Fig. 1, solid line) and an earlier calculation[2] in which there was one Ni potential used for all the Ni sites and one P potential used for all the P sites (Fig. 1, dotted line), we note several points of qualitative agreement. Both calculations exhibit a large d-band peak of roughly the same width, and the position of the peak is at about the same energy with respect to the Fermi level. Also the density of states at the Fermi level is approximately the same in the two cases. This last value has important consequences in determining the specific heat and the transport properties. Our earlier calculation produced quite good agreement with experiment for these properties. Serious calculation of the specific heat and transport properties would entail greatly extending the LIZ. It is likely that such an extension of the LIZ would broaden the density of states and move the Fermi level up slightly. Therefore at this point we are not concerned about the difference between the LSMS density of states at E$_F$ and our earlier work.

There are also quantitative differences between the two calculations. The d-band den-
sity of states is broader, and its peak occurs closer to the Fermi level for the earlier calculation compared to the present one. The density of states at the Fermi level is about 15% lower in the present calculation than in the earlier one. Also the present calculation produced a second smaller peak at about 0.2 Ry below the Fermi level while the earlier calculation has only a shoulder in this energy region.

The calculated electronic density of states that we found for Ni\textsubscript{40}Pd\textsubscript{40}P, Fig. 2, differs considerably from that of Ni\textsubscript{80}P, Fig. 1. As one would expect, because Pd is a much larger atom than Ni, the overlap between Pd d-orbitals and the d-orbitals on neighboring Ni and Pd atoms results in a density of states with a much wider d-band peak as shown in Fig. 2. Recall that we have fixed the atomic positions at the values appropriate for Ni\textsubscript{80}P\textsubscript{20}, with no scaling to larger volume to accommodate the larger Pd atoms. However the pressure calculated at this volume is only slightly positive indicating that the equilibrium volume is not much larger for Ni\textsubscript{40}Pd\textsubscript{40}P\textsubscript{20} than for Ni\textsubscript{80}P\textsubscript{20}. Relaxations other than simple scaling will tend to increase the Pd-Pd and Pd-Ni bond lengths and narrow the density of states. The density of states at the Fermi level is approximately 25% smaller for the Ni\textsubscript{40}Pd\textsubscript{40}P\textsubscript{20} compared to the Ni\textsubscript{80}P\textsubscript{20}.

6. Conclusions

We have demonstrated that we can apply the LSMS method to amorphous alloys represented by a supercell of 300 atoms and can determine the potential at each atomic site self consistently on a massively parallel supercomputer. We have found that the charge transfer varies appreciably from site to site for the same species in a given sample indicating that the use of potentials made self consistent only at an average site is of limited validity. We have also demonstrated that we can use the the fully self-consistent potentials to calculate electronic properties of these alloys. We have found the electronic density of states for one sample with 300 atoms representing amorphous Ni\textsubscript{80}P\textsubscript{20} and one sample with 300 atoms representing amorphous Ni\textsubscript{40}Pd\textsubscript{40}P\textsubscript{20}.
For future work, we plan to go to larger samples and to explore more fully the dependence of our results on both sample size and the size of the local interaction zone. We also plan to extend the calculations to determining transport properties and the free energy.
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Figure Captions

Fig. 1. Calculated electronic density of states (in Ry$^{-1}$ atom$^{-1}$ for both spins) for amorphous Ni$_{80}$P$_{20}$. The solid line is for our present calculation with 300 atoms in a supercell and using LSMS converged to self-consistent potentials at each site. The dotted curve is from a previous calculation[1] and represents an average over several supercells with 160 atoms in each cell. For the dotted curve, the potentials were self consistent only for an average site.

Fig. 2. Calculated electronic density of states (in Ry$^{-1}$ atom$^{-1}$ for both spins) for amorphous Ni$_{40}$Pd$_{40}$P$_{20}$ with 300 atoms in a supercell. For the calculation we used LSMS converged to self-consistent potentials at each site.