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Microscopic Real-Space Approach to the Theory of Metallic Glasses

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The electronic and transport properties of three metallic glass systems, a-$Cu_{60}Zr_{40}$, a-$Mg_{75}Zn_{25}$, and a-Ni, are studied by means of realistic microscopic real-space calculations. At low temperature, the transport properties are controlled by the magnitude and the shape of the conductivity function σ_E near the Fermi energy. It is shown that for a stable metallic glass the Fermi energy is quite close to a local minimum in σ_E and this causes the negative temperature coefficient of resistivity which is purely due to the elastic scattering of the conduction electrons from the disordered atoms.

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The theory of electronic transport in noncrystalline solids has been a subject of intense research for many years.[1,2] In metallic glasses (MG), many interesting phenomena such as a negative temperature coefficient (NTC) of resistivity, the Mooij correlation for resistivity and/or thermoelectric power, the sign of the Hall coefficient, the resistivity anomaly, etc., have stimulated the development of many theoretical models for their explanation. These include the generalized Ziman theory,[3] the Mott *s-d* scattering theory,[4] the two-level tunneling (Kondo-type effect),[5] interactions involving localized states,[6] and ones based on weak localization or quantum coherence,[7] as well as many others.[8] Each of these models usually can explain a particular phenomenon or the results for a particular type of system but fails in other instances. In recent years, the theory of weak localization appears to be quite successful in explaining the transport properties of many MG,[7] especially the Mooij correlation.[7-9] Yet, the theory is sufficiently general that in applying it to a specific system one has to estimate parameters, such as elastic-scattering time, τ_{el}, density of states (DOS) at the Fermi level (E_F), and number of free charge carriers per atom, etc., in order to be able to compare with measurement. It is not uncommon that the choice of these parameters, in some case, is influenced by the anticipated outcome. It is therefore highly desirable that a large-scale quantum-mechanical calculation based on first principles be performed on specific amorphous MG. Such a calculation will provide deep insight into the scattering processes at the microscopic level and serve as a possible criterion to check the validity or the invalidity of a particular theoretical model. There have been many electronic structure calculations on MG using different computational schemes.[2] Most of these calculations aim at obtaining the DOS functions and inferring from them other properties. Some attempts to calculate the transport properties directly were hampered by approximations or the use of adjustable parameters that were inherent to the method.[10] The transport properties of randomly substituted alloys on a regular lattice have been successfully treated by the first-principles Korringa-Kohn-Rostoker coherent-potential-approximation (KKR-CPA) method.[11] However, the extension to the toplogically disordered systems such as MG has not yet been realized.

In this Letter, we present the results of a realistic local-density calculation of the transport properties of MG using the orthogonalized linear combination of atomic orbitals (OLCAO) method. This method has been applied to study the electronic structures of a variety of noncrystalline solids in the past with great success.[12,13] The method employs a direct-space approach which is particularly suitable for studying amorphous solids, because the short- and intermediate-range orders can be accurately incorporated. Since all the multicenter integrals of the Hamiltonian are accurately evaluated with the use of a nonorthogonal basis set, all the effects of multiple scattering and quantum interference are implicitly taken into account irrespective of whether the system under study is a strong-scattering system or a weak-scattering one. The static disorder of the system is treated exactly while the dynamic disorder, i.e., the electron-phonon (e^--ph) interaction, is totally ignored. In addition to DOS, explicit wave functions in the entire energy range are obtained which are then used to calculate transport properties. Each state can also be characterized by a localization index. Thus, the localized or delocalized nature of all the states across the entire energy spectrum can be quantitatively displayed.[13] The potential of the system is obtained from a superposition of atomiclike potentials centered at each site in the amorphous solid, which are obtained by the accurate self-consistent local-density calculation[14] on a smaller system. (For a binary MG, an idealized Cu_3Au structure is usually employed.) This procedure is justified because in the direct-space OLCAO method, both the basis and the potential functions are atom centered with no geometry-dependent parameters. So we expect the results thus obtained to be almost the same as if the self-consistent calculation were actually carried out with the large model.

We chose three very different MG for our study: (1) The free-electron-like a-$Mg_{75}Zn_{25}$; (2) a-$Cu_{60}Zr_{40}$, a system with high resistivity and strong scattering of the conduction electrons; and (3) a-Ni, a metastable single-component transition-metal glass. The first two are nonmagnetic while a-Ni is weakly ferromagnetic, but here we have ignored any magnetic interactions. We feel that a successful theory must be able to treat the different systems on an equal footing and be able to predict results in good agreement with experiments for all of them. By studying these very different MG systems in great detail, we are able to obtain additional insights which are often ignored or neglected in the study of a single system.

The calculation starts with the construction of a large atomic model with periodic boundary conditions, using a Monte Carlo computer relaxation method. The details of the model construction will be presented elsewhere,[15] and it suffices to say that these models were carefully checked by calculating the radial distribution functions and comparing them with experimental data, and are found to be satisfactory. The computed and measured[16] pair correlation functions for a-$Cu_{60}Zr_{40}$ are shown in the inset of Fig. 1 as an illustration. The size of the model is determined by the total number of atoms in the cell and the mass density. For a-$Mg_{75}Zn_{25}$, a-$Cu_{60}Zr_{40}$, and a-Ni glasses, the mass densities are 3.02, 7.37, and 8.07 g/cm^3, respectively. We have used 200-atom models for the first two MG and a 100-atom model for a-Ni with corresponding cell dimensions of 15.9685, 14.9809, and 10.650 Å, respectively, much larger than the electron mean free paths in any of these glasses. These models do not have the usual drawback of excessive porosity and global inhomogeneity encountered by many cluster-type models and do not give rise to the contaminating surface states which are always present in a cluster-type calculation.

The OLCAO method is applied to calculate the electronic structure of each MG, utilizing the atomic model. Some other computational details are outlined in Ref. 17. From the resulting eigenvalues and eigenfunctions, the temperature (T) dependent dc conductivity due to pure elastic scattering is evaluated directly from the Kubo-Greenwood formula,[18]

$$\sigma(T)=\int_{-\infty}^{\infty}\langle\sigma_E\rangle\left(-\frac{\partial f}{\partial E}\right)dE\,, \tag{1}$$

where f is the Fermi distribution function and $\langle\sigma_E\rangle$ is the configurational average of the conductivity function defined as

$$\sigma_E=\frac{2\pi e^2}{3m^2\Omega}\sum_{nm}\left|\langle n|p|m\rangle\right|^2\delta(E_n-E)\delta(E_m-E)\,. \tag{2}$$

Here Ω is the cell volume and $\langle n|p|m\rangle$ is the MME between the states $|n\rangle$ and $|m\rangle$ with energies E_n and E_m. In the actual evaluation of Eq. (2), the δ function is approximated by a Gaussian function with a width of 0.03 eV. This is necessary because our calculation is for a finite system with discrete values of energy distribution. To increase the statistical sampling of energy states near E_F, σ_E is averaged over two configurations obtained by diagonalization of secular equations at the center and the corner "k points" of the quasi-Brillouin zone. To check the size dependence, σ_E's are calculated for 100-, 150-, and 200-atom models for a-$Cu_{60}Zr_{40}$. We found that the $\sigma_E(E_F)$ for the 100- and 150-atom models differ from that of the 200-atom model by +10% and +6%. An average over more configurations may further improve the results. From the eigenfunction ψ_n and the overlap integrals, a localization index (LI) for the state n may be defined using Mulliken analysis.[13] For a completely delocalized state, LI approaches $1/N$, where N is the dimension of the secular matrix.[13]

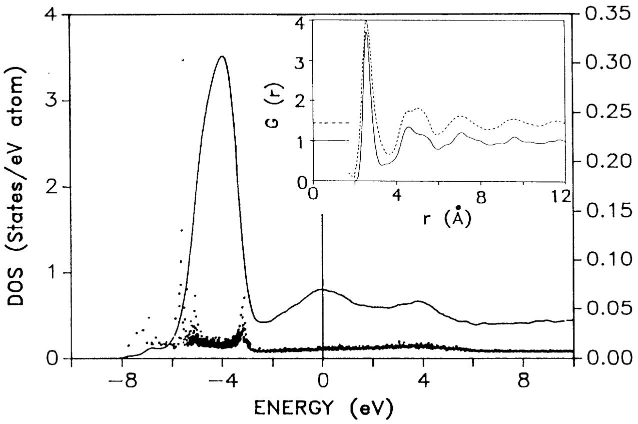

FIG. 1. Density of states (solid line, left-side scale) and localization index (dots, right-side scale) for a-$Cu_{60}Zr_{40}$. Inset: Pair correlation function $G(r)$: Solid line, calculated from the model; dashed line, data from Ref. 16.

Figure 1 displays the DOS and LI calculated for a-$Cu_{60}Zr_{40}$ as an illustration. It is clear that E_F is located at a local maximum in the DOS curve in a region consisting mainly of Zr-4d states. The states near E_F are relatively delocalized. The highly localized states are at the edges of the Cu-3d band centered at about −4.5 eV. This is contrary to the conventional wisdom that the d electrons in transition-metal glasses are localized and the scattering process involves only the delocalized s electrons. The fact that the Zr-4d states near E_F are relatively delocalized is due to the large d-band width of Zr in CuZr glass. DOS curves and similar LI plots have also been obtained for a-$Mg_{75}Zn_{25}$ and a-Ni.[15] The former has a DOS which is very flat, with low values of LI, typical of a free-electron-like system; while in a-Ni, E_F cuts at the edge of the Ni d band and there are localized states at about 0.15 eV above E_F.

The calculated zero-temperature resistivity $\rho(0)$ and other transport properties for three MG are listed in Table I together with relevant experimental values.[19-26] It is gratifying to see that the calculated $\rho(0)$ values are in very close agreement with the experimental data for the three very different MG. All three MG have a NTC α of ρ so the measured ρ at room temperature are lower than the calculated $\rho(0)$ values. In Fig. 2, we plot $\rho(T)/\rho(2\text{ K})$ for a-$Cu_{60}Zr_{40}$ as calculated from Eq. (1) together with experimental data.[22] This curve shows the T dependence of $\rho(T)$ as purely due to the elastic scattering of the e^- in a topologically disordered system.

TABLE I. Calculated transport properties of metallic glasses.

System	$N(E_F)$ $\left(\frac{\text{states}}{\text{eV atom}}\right)$	$\frac{1}{\rho}\frac{d\rho}{dT}$ (200 K)	$\rho(T)$ ($\mu\Omega$ cm) Calc.	Expt. (300 K)	$S(T)$ (μV/K) Calc. (160 K)	Expt. (160 K)
a-$Cu_{60}Zr_{40}$	0.80	-4.12×10^{-4}	197(2 K) 185(200 K)	195^a 182^b 179 ± 3^c	2.01	1.4^d
a-$Mg_{75}Zn_{25}$	0.39	-2.00×10^{-5}	68(2 K) 67(200 K)	55 ± 5^e 75^f	−0.95	-0.8^g
a-Ni	2.97	-3.97×10^{-4}	120(2 K) 111(200 K)	100^h	−7.79 (120 K)	...

[a] Reference 19.
[b] Reference 20.
[c] Reference 21.
[d] Reference 22.
[e] Reference 23.
[f] Reference 24.
[g] Reference 25.
[h] Reference 26.

For a-$Cu_{60}Zr_{40}$, $\rho(T)$ is a decreasing function of T with a negative α. It is clear that for $T < 80$ K, the resistivity is purely due to the elastic scattering. As T is increased beyond about 80 K, the phonon scattering starts to set in, raising the resistivity, but it is not enough to offset the effect of the elastic scattering so as to change the sign of α. If this interpretation is true, the Mooij correlation[27] can be naturally explained: e^--ph scattering does make a positive contribution to resistivity in MG, but it is the competition between phonon scattering and the elastic disorder scattering that determines the sign of α. For a high-resistivity system, such as a-$Cu_{60}Zr_{40}$, the electron mean free path is short and the phonon contribution is generally not enough to overcome the negative-α effect due to the elastic disorder scattering. But for a low-resistivity alloy, a similar degree of e^--ph scattering may be sufficient to overcome the elastic part so as to give a positive α. The Mooij correlation should not be strictly universal as pointed out by Tsuei,[9] since the actual T dependence of $\rho(T)$ and the strength of the e^--ph interaction depend on the details of the electronic structure of the system.

From Eq. (1), it is obvious that the transport properties of the MG are controlled by σ_E in the vicinity of the E_F. In Fig. 3, we plot σ_E near E_F for the three MG. As can be clearly seen, the E_F are located at or near local minima in the σ_E curves and this is the source of the negative α which is purely due to the elastic disorder scattering. As T is raised above zero, $f(E)$ changes from a step function into an exponential form both above and below E_F where the conductivity increases and ρ becomes smaller.

The thermopower $S(T)$ is also greatly influenced by the structure of σ_E above and below E_F. The calculated values of $S(T)$ at 160 K for the three MG are listed in Table I. The signs of the calculated $S(T)$ agree with measurements at room temperature. However, it is difficult to make a more quantitative comparison because the experimental data include the effects of e^--ph scattering which are not included in the calculation. The small diffusion thermopowers are consistent with the fact

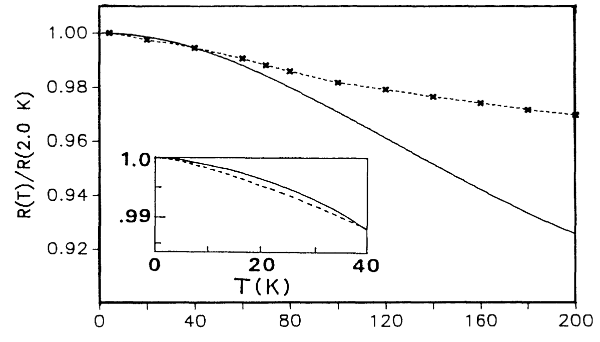

FIG. 2. Calculated $\rho(T)/\rho(2\text{ K})$ for a-$Cu_{60}Zr_{40}$; crosses, experimental data from Ref. 22. Inset: A blowup for the region T=0–40 K.

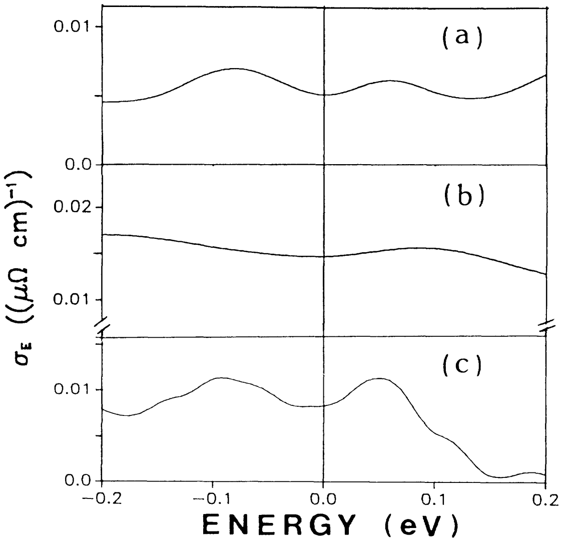

FIG. 3. σ_E near E_F: (a) a-$Cu_{60}Zr_{40}$; (b) a-$Mg_{75}Zn_{25}$; (c) a-Ni.

that E_F is located near a local minimum in σ_E. The calculation can also be extended to the study of the Hall coefficient in MG.

Based on a free-electron model, Nagel and Tauc have argued[28] that the stability of a glass is related to the fact that E_F happens to be at a local minimum in the DOS. Such is not the case for all three MG studied here although a photoemission experiment appeared to suggest that there is a structure-induced minimum in the DOS near E_F in glassy Au-Sn films.[29] In fact, what we find is that E_F is located at a local minimum in the σ_E curve. This result can be tentatively interpreted as indicating that the electronic states at the Fermi surface are more strongly affected by the disorder than the states immediately above or below E_F. We speculate that in a total-energy calculation, one would find that the equilibrium configuration was also the one where the conductivity was a minimum. Departure from the equilibrium point in configuration space would be associated with more "crystallinelike" configurations which have correspondingly higher conductivity. The conjecture that the stable equilibrium point is also one where the intrinsic (i.e., arising from static disorder) conductivity is a minimum is consistent with experimental observations. For example, in the a-Cu$_x$Zr$_{1-x}$ series, experimental results[21,30] indicate that a-Cu$_{60}$Zr$_{40}$ has a higher resistivity while being the easiest to form.

In conclusion, we have obtained a microscopic understanding of the electronic transport properties of MG by means of realistic real-space calculations on three different systems. The good agreement between the calculated and measured values of the resistivity bears testimony to the general success of a local-density theory as applied to amorphous solids. This may also indicate that e^--e^- scattering and other many-body interactions may not be too important in MG. It is shown that at low temperature the elastic disorder scattering alone is sufficient to account for the NTC of resistivity. The Mooij correlation can be explained in terms of the competition between this effect and the positive contribution to α from the e^--ph scattering. The origin of NTC is traced to the fact that E_F is located at or near a local minimum in the conductivity function, and this fact may also be linked to the relative stability of a MG against local configurational fluctuations.

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