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Electronic structure of $Cu_{60}Zr_{40}$ glass

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The $Cu_{60}Zr_{40}$ glass is simulated by a 39-atom cluster ($Cu_{23}Zr_{16}$) with periodic boundary conditions. The orthogonalized linear combination of atomic orbitals method is used to calculate the electronic structure of the glass after it is relaxed with Lennard-Jones potentials. A structural model that gives the pair distribution function and the electron density of states in good agreement with the experimental x-ray and photoemission data is obtained. The model suggests a slight chemical short-range order in the glass.

In a very active field of amorphous metals, the Cu-Zr system is one of the most widely studied glasses. X-ray,[1–3] neutron,[4] ultraviolet, photoelectron spectroscopy,[5] and x-ray photoemission spectroscopy[6] studies of $Cu_{60}Zr_{40}$ glass have been reported. We apply here our recently developed method[7] to calculate the electronic structure of $Cu_{60}Zr_{40}$ glass. The calculated results are compared with the experimental data.

A brief outline of the method is as follows. The glass is simulated by a 39-atom cluster ($Cu_{23}Zr_{16}$) with periodic boundary conditions. The mass density of amorphous $Cu_{57}Zr_{43}$ is about 7% lower than the average density of Cu and Zr as determined by their concentrations.[8] The same scaling factor gives a density of 7.43 g/cm^3 used in the present calculations. The atoms are packed such that the two constituents are somewhat evenly distributed in a cube. The Lennard-Jones potentials used to relax the periodic cluster are of the form[8]

$$V(r)=\frac{A}{r^6}+\frac{B}{r^{12}}+Cr+D \quad .$$

The Cu-Cu and Zr-Zr interatomic potentials parameters are determined from the lattice parameters and cohesive energies of the respective crystals and the truncation distances (r_t) where the potentials and their respective derivatives vanish. The values of r_t for Cu-Cu and Zr-Zr potentials are 7 and 8 Å, respectively. The input data for the Cu-Zr potential are the averages of those of Cu and Zr crystals. The minima for the Cu-Cu, Cu-Zr, and Zr-Zr potentials are at 2.8, 3.0, and 3.2 Å, respectively. The orthogonalized linear combination of atomic orbitals method is used to calculate the electronic states.[9] The glass potential is derived from the superposition of the atomic potentials. The atomic potentials are determined from the wave functions given by Clementi and Roetti.[10] The exchange and correlation effects are treated in the spirit of $X\alpha$ method, with the α parameters being the same as in Ref. 7 ($\alpha_{Cu}=0.82$ and $\alpha_{Zr}=0.73$). The potential for each atom is fitted to a screened Coulomb term and a set of Gaussians. The basis functions are expanded in terms of 13 Gaussians with exponents ranging from 0.12 to 18 000. The Gaussian expansions of the potential and the basis functions enable us to calculate the multicenter integrals in the Hamiltonian matrix analytically. We use 18 orbitals for Cu (4 *s*'s, 3 *p*'s, and 1 *d*) and 24 orbitals (5 *s*'s, 3 *p*'s, and 2 *d* 's) for Zr. The outermost *s*, *p*, and *d* orbitals (9) for each atom are treated as valence states and the remaining as core states. It is assumed that the core states remain unchanged as one goes from the atom to the solid and that there is no overlap between the core states on different atoms in the solid. The final valence state basis functions are obtained by orthogonalizing valence Bloch states to the core Bloch states. The size of the Hamiltonian matrix to be diagonalized is equal to the number of valence states times the number of atoms in the cluster. Thus the Hamiltonian and overlap matrices in the present calculations are 351×351.

The structural information available from x-ray scattering in amorphous materials is the pair distribution function $G(r)$. Since $G(r)$ is the normalized number density of the neighbors averaged over all the atoms, it does not lead to a unique structural model for the glass. We use the x-ray and photoemission data as a guide in deciding on a suitable structural model in the present calculations. The calculations were carried out for five structural models with the short-range order coefficient defined below ranging from -0.1 to $+0.2$. The electronic density of states of Cu-Zr glasses is dominated by the Cu d band. As pointed out in Ref. 7, the position of the Cu d band below the Fermi level is quite sensitive to the details of the surroundings of the Cu atoms. From the calculations on various structural models we find that, as the Cu-to-Zr ratio near a Cu atom increases or the near-neighbor Cu-Cu distance decreases, the Cu d band shifts to higher binding energy and vice versa. The $G(r)$ for the structural model giving the most reasonable agreement with the experimental data is shown in Fig. 1. Except for the reversal in intensity of the subpeaks of second peak, our results are in fairly good agreement with the x-ray data of Waseda and Masumoto.[1] The calculated density of states is compared with the photoemission data[6] in Fig. 2. The structure near the Fermi energy is due to Zr and the broad peak around 4 eV below the Fermi level is due to Cu. Except for the shoulder between 5 and 6 eV below the Fermi level, the theoretical results are in very good agreement with the experimental data. The cause of this shoulder is pointed out below.

According to Cargill and Spaepan,[11] the partial coordination numbers in the limit of complete chemical disorder of a binary amorphous alloy AB is given by

$$Z_{AB}^{*} = x_B Z_A Z_B / \langle Z \rangle \ ,$$

where x_B is the concentration of B, Z_i is the average number of atoms in the nearest-neighbor coordination shells of i-type atoms, and

$$\langle Z \rangle = x_A Z_A + x_B Z_B \ .$$

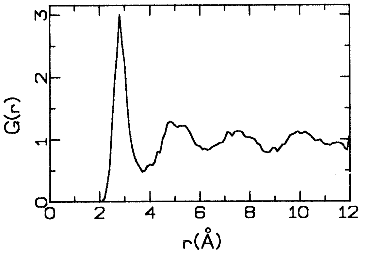

FIG. 1. Total pair distribution function $G(r)$ for the present model of $Cu_{60}Zr_{40}$ glass without the atomic scattering factors.

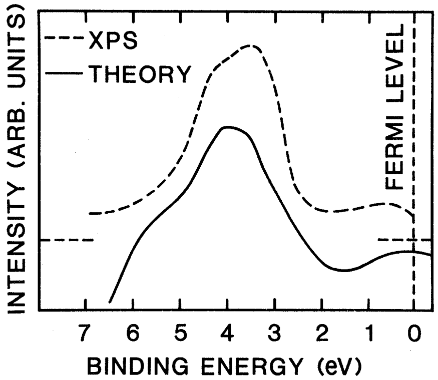

FIG. 2. Calculated electronic density of states and the XPS data from Ref. 5. For clarity, the zero of the experimental curve is shifted as indicated by the horizontal dashed lines on the right and left sides of the figure.

They define the short-range order coefficient as

$$\eta_{AB} = \eta_{BA} = \frac{Z_{AB}}{Z_{AB}^{*}} - 1 \ ,$$

where Z_{AB} is the actual coordination number for a given structural model. $Z_{AB} < Z_{AB}^{*}$ corresponds to clustering of similar atoms. The shoulder between 5 and 6 eV in our calculated density of states is due to clustering of a few of the Cu atoms. However, because of the good overall agreement between the present calculations and the experimental data, we feel that our structural model is quite reasonable.

The various coordination numbers up to 3.5 Å required to calculate η_{AB} for our model are

$$Z_{\mathrm{Cu}} = 11.3, \quad Z_{\mathrm{Zr}} = 12.3 \ ,$$

$$Z_{\mathrm{CuZr}}^{*} = 4.83, \quad Z_{\mathrm{CuZr}} = 5.35 \ .$$

The value of η_{AB} for our model is 0.1, implying a slight chemical short-range order. The values of η_{AB} from various sources are compared in Table I and the present value is in agreement with that from the x-ray data of Chen and Waseda.[3] According to our model, a given atom on the average has slight preference for the atoms of opposite kind for its neighbors.

TABLE I. Short-range-order coefficient η_{AB} for $Cu_{60}Zr_{40}$ glass.

Source	η_{AB}
Our model ($Cu_{59}Zr_{41}$)	0.1
X rays[a] ($Cu_{65}Zr_{35}$)	0.1
X rays[b] ($Cu_{60}Zr_{40}$)	0.31
Neutrons[b] ($Cu_{57}Zr_{43}$)	0.01

[a] Reference 3. [b] Reference 11.

The negative heat of mixing for amorphous Cu-Zr alloys also favors bonding of the unlike atom pairs.[3]

Finally, the density of states at the Fermi level for $Cu_{60}Zr_{40}$ glass (0.39 states/eV spin atom) is lower than that for $Cu_{33}Zr_{67}$ glass (0.45 states/eV spin atom),[7] which is in agreement with the trend suggested by photoemission data.[5]

In summary, we have simulated $Cu_{60}Zr_{40}$ glass with a model whose radial distribution function and electronic density of states are in good agreement with the x-ray and photoemission data, respectively. Our model suggests a slight chemical short-range order.

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