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Structure-Induced Minimum in the Average Spectrum of a Liquid or Amorphous Metal

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Nonperturbative multiple-scattering theory is used to study the influence of the first peak in the density correlation function, $s(k)$, on the electronic properties of a structurally disordered metal. The present calculations yield a well-defined minimum in the average density of states and a corresponding peak in the electrical resistivity. The position of these structures is directly related to that of the principal peak in $s(k)$.

In a previous paper[1] we discussed the application of the effective-medium approximation[2] (EMA) to the muffin-tin model of a structurally disordered metal. Our results indicated that the EMA provides a satisfactory description of the average electronic spectrum in the energy range associated with the $l=2$ scattering resonance characteristic of noble- and transition-metal systems. In the present paper we consider strong-scattering effects that are *structural* rather than *atomic* in orgin. In particular, we are concerned with the influence of the first peak in the structure function on the average spectrum. If this peak is centered at K_p, then estimates based on second-order perturbation theory indicate that nearly-free-electron states with wave vectors $k \approx K_p/2$ should be strongly coupled.[3,4] In a rough sense, this coupling is analogous to the band gap that appears in a perfect crystal as $\vec{k}$ approaches the boundary of the Brillouin zone. (Here, of course, $\vec{k} = \vec{K}_n/2$, where $\vec{K}_n$ is a reciprocal-lattice vector.) Since liquid and amorphous systems do not exhibit any long-range order, we cannot reasonably expect a true band gap. However, because the structure function is isotropic, the scattering associated with the first peak in $s(k)$ will not depend on the direction of the electron wave vector and the effects of this scattering will add coherently when the contributions from dif-

ferent wave vectors are summed to produce the total spectrum. The issue then is whether or not this scattering leads to any characteristic structure in the average density of states $\rho(E)$. We emphasize that the calculations described in this paper are nonperturbative and address this issue within a framework that is already known to work well in the strong-scattering regime.

In the following section we describe the effects of the principal peak in $s(k)$ on the density of states, the spectral density function, and the electrical resistivity. In the final section we discuss briefly some physical consequences of these effects. It is to be understood, however, that the purpose of this paper is to clarify a *qualitative* feature of the electronic spectrum in structurally disordered systems, rather than to present results relating to a particular system or experiment.

As described in Ref. 1, muffin-tin EMA calculations are based on a system of coupled nonlinear integral equations. The complexity of these equations implies that there is no explicit relationship between the electronic density of states and the pair distribution function. The character of this relationship can only be studied by examining the results of detailed numerical calculations, and in Fig. 1 we compare the results of three such calculations. Curve 2 is based on the same atom-

ic potential, atomic density, and radial distribution function used in Ref. 1 to describe molten Cu. (The d states of Cu, which were of principal interest in Ref. 1, are centered at $E = 0.4$ Ry and only the upper edge of the d band is shown in curve 2.) Note that the density of states shows a distinct minimum at $E = 0.82$ Ry. As indicated in Fig. 1, the first peak in the structure function for molten Cu is centered at $K_p = 1.56$ a.u. To establish more clearly the connection between this peak and the minimum in $\rho(E)$, we have carried out two additional calculations in which the atomic potential is unchanged, while the atomic density and radial distribution function are rescaled as follows:

$$n' = c^3 n \tag{1a}$$

and

$$g'(R) = g(cR). \tag{1b}$$

The corresponding structure function is

$$s'(k) = s(k/c). \tag{2}$$

This transformation allows us to shift the peak in $s(k)$ without changing the effective number of nearest neighbors or violating the constraint $s(k) > 0$.[5] [Equation (2) also leaves unchanged the value of $s(k=0)$, which is related to the isothermal compressibility.[6]] From curve 1 of Fig. 1 it is evident that the case $c < 1$, which corresponds to an $s(k)$ with a principal peak that is sharper and shifted down to $K_p = 1.52$ a.u., leads to a minimum in $\rho(E)$ that is slightly more pronounced and is shifted to low-

er energies. Similarly, the case $c > 1$ (curve 3) shows a more diffuse minimum shifted toward higher energies. We note that in all three cases the minima in $\rho(E)$ are well above the free-electron value $E = (K_p/2)^2$. This is a consequence of the hybridization between the d states and the conduction states which serves to shift the conduction states to higher energies. [We emphasize, however, that the energies of interest here are high enough so that the d contribution to the spectrum is essentially exhausted and the magnitude of $\rho(E)$ is roughly equal to that given by perturbation-theory estimates.]

In Fig. 2 we see that the minimum in $\rho(E)$ is associated with a decrease in amplitude and an increase in width of the underlying spectral density function $A(k, E)$. The enhanced width of $A(k, E)$ is, of course, consistent with the minimum in $\rho(E)$ being due to an increase in the effective scattering of the electrons. This increased scattering, together with the decrease in $\rho(E)$, leads to a maximum in the electrical resistivity. Indeed, if vertex corrections are neglected, the Kubo formula is[7]

$$\sigma = (8\pi/3)\int_0^\infty [k^2 A(k, E_F)]^2 dk \tag{3}$$

and results (based on the spectral functions shown in Fig. 2) are presented in Fig. 3. It should be noted that the most widely used description of transport processes in liquid and amorphous metals is based on the Faber-Ziman theory.[8] However, various authors[9] have questioned this
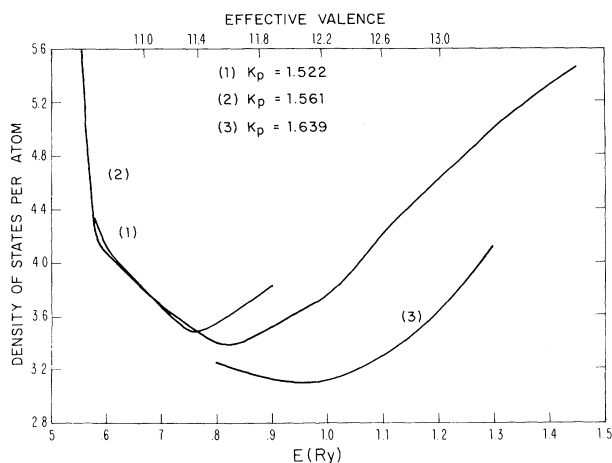

FIG. 1. Densities of states for three different choices of n and $g(R)$. The three cases are related via Eqs. (1) and the values of K_p are given in atomic units. The upper horizontal scale gives the integrated density of states $N(E_F)$ corresponding to curve 2.
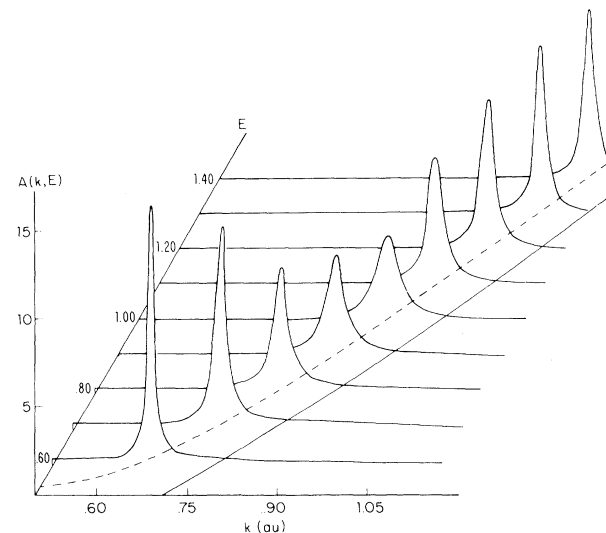

FIG. 2. Spectral density functions corresponding to curve 2 of Fig. 1. Dashed and solid lines in the E-k plane are the locus of peak positions and the curve $E = k^2$, respectively.
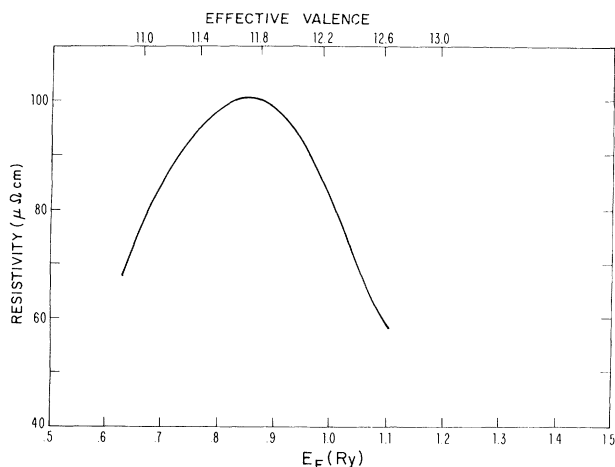
FIG. 3. Electrical resistivity (α^{-1}) as a function of E_F. The upper horizontal scale gives the integrated density of states $N(E_F)$.

analysis because (1) the Faber-Ziman equations are based on second-order perturbation theory and (2) they require an *a priori* knowledge of the Fermi wave vector k_F. The results shown in Fig. 3 indicate that the present calculations yield results that are quite similar to those obtained via the Faber-Ziman theory without invoking either of these assumptions. Finally we note that these results suggest that negative temperature coefficients of the electrical resistivity can be understood within the present framework. Systems exhibiting this effect are believed to have effective Fermi wave vectors $k_F \approx K_p/2$. In this case, raising the temperature will lead to (1) a broader peak in $s(k)$, (2) a less pronounced minimum in the density of states, and (3) a decrease in the height of the peak in the resistivity. Here again, the conventional analysis of this effect is based on the Faber-Ziman theory and has recently been questioned.[10]

From an experimental viewpoint, the effects described above are primarily of interest in connection with multivalent systems.[11] In these systems the Fermi energy may be located either within or just above the structure-induced minimum in $\rho(E)$. For example, we note that photoemission data on liquid Hg are consistent with a dip in $\rho(E)$ just below E_F,[12] and that in liquid $Cu_{1-x}Sn_x$ alloys, the concentration (x) dependence of the magnetic susceptibility is quite nonlinear and a large diamagnetic contribution appears at values of x for which $k_F \approx K_p/2$.[13] In addition, a variety of multivalent alloys (like $Cu_{1-x}Sn_x$) are known to exhibit maxima

in their electrical resistivities and a negative temperature coefficient of the resistivity (at fixed x) for concentrations corresponding to $k_F \approx K_p/2$.[14] As we have seen in connection with Fig. 3, these effects can be understood within the muffin-tin EMA framework.

Our results are also of interest in connection with the Nagel-Tauc[15] description of transition-metal–metalloid glass formation. These glasses tend to form over a relatively narrow range of concentrations (typically, 20% metalloid). Adopting a nearly-free-electron picture of the host material and a rigid-band approach to the alloying process, Nagel and Tauc argue (1) that there should be a structure-induced minimum in $\rho(E)$, and (2) that at roughly 20% metalloid concentration E_F should be located at the position of the minimum.[16] If this were the case, then states whose energy had been lowered (in forming the minimum) would be occupied, while those whose energy had been raised would be unoccupied, and this concentration would correspond to a metastable minimum of the total energy. In a sense, this argument is analogous to the Hume-Rothery arguments on the limits of α-phase stability in noble-metal–based substitutional alloys.[17] [It should also be noted that Moruzzi, Oelhafen, and Williams[18] have recently emphasized the relation between a minimum in the density of states (at E_F) and glass formation in early-late transition-metal alloys. In these systems, however, there does not appear to be a direct relation between the minimum in $\rho(E)$ and the principal peak in $s(k)$.] The results described in Figs. 1 and 2 certainly lend support to the Nagel-Tauc picture in that a minimum in $\rho(E)$ is shown to exist in precisely the kind of system that forms the host in their rigid-band model. Indeed, we find that the minimum in $\rho(E)$ is centered at an energy that corresponds to an effective valence of 11.6 (again using curve 2 of Fig. 1) which is in good agreement with the Nagel-Tauc estimate of 11.7.[19] Also consistent with their arguments is the fact that the minimum in $\rho(E)$ becomes less pronounced as the peak in $s(k)$ is broadened.

The calculations described here are clearly not specific enough to justify a serious estimate of the electronic contribution to the free energy of a transition-metal–metalloid glass.[20] A proper description of these systems requires calculations based on two atomic potentials and three pair distribution functions. Calculations of this kind are now feasible and our belief is that they will again yield a structure-induced minimum in $\rho(E)$. The

point to be made in the present paper is that the characteristics of such minima can be understood within the muffin-tin EMA framework and that their influence should be taken into account in describing the properties of a variety of structurally disordered metallic systems.

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[5]It should be emphasized that one cannot simply shift the first peak in $s(k)$ in an arbitrary way. Such a procedure almost always leads to unphysical behavior in $g(R)$ [which is related to $s(k)$ by Fourier transformation].

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[20]It is clear, however, that a minimum in $\rho(E)$ must lead to nonlinear terms in the concentration dependence of the total electronic energy. In a comparison of the free energy of the liquid or amorphous case with that of the phase-separated crystal, these nonlinear terms will almost certainly favor structural disorder.