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Electrical transport in transition-metal liquids and metallic glasses

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The extended Ziman-Faber theory is developed in terms of a consistent single-site approximation to the density of states that permits a simple interpretation and evaluation of the effective valence Z^* and other relevant parameters without reference to crystalline-band calculations. Results for four transition-metal liquids (Fe, Co, Ni, Cu) and two amorphous alloys (*Ni*P and *Co*P) yield $Z^* \gtrsim 1$ for the former and $Z^* \simeq 2$ for the latter. In contrast with previous calculations, the electrical resistivity is greatly overestimated when the theory is applied consistently to strong-scattering liquids such as Fe and Co, while better results are found for Cu and Ni, in which the scattering is weaker. It is concluded that for the former type of system the Ziman formula should not be used to compute the magnitude of the resistivity. Similar results are obtained for α-*Co*P and α-*Ni*P. The effect of the metalloid on the resistivity of the glass and its relationship to the corresponding transition-metal liquid is explained within the context of the model.

I. INTRODUCTION AND CONCLUSIONS

The recent experimental demonstrations[1,2] that the electrical properties of an amorphous metal at room temperature are very similar to those of the corresponding liquid near the melting point have led to renewed interest[3-5] in the Ziman-Faber transport theory as extended to transition-metal systems.[6,7] The present paper develops the ingredients of this theory from a consistent application of the single-site approximation underlying the extended Ziman formula for the resistivity. In contrast with previous calculations, the effective valence Z^* and Fermi energy E_F are obtained without the use of crystalline band calculations. This procedure is the only one consistent with the theory's original formulation.[8-10] The present calculations, using the *same* set of assumptions, provide for the first time a valid systematic comparison with experiment for transition-metal liquids, and thus help to develop empirical criteria for the applicability of the theory. They also permit an unambiguous identification of the effect on the resistivity of adding a metalloid to a disordered transition-metal host. Previously published calculations[3] for amorphous *Ni*P made no connection with the properties of pure liquid Ni. The present results also include the first to be reported for amorphous *Co*P.

The calculations reported in Sec. II for liquid Fe, Co, Ni, and Cu yield $Z^* \gtrsim 1$ in all cases, a value that has been suggested empirically[11] but not explained. The electrical resistivity so obtained, however, is much too large for the strong-scattering systems Fe and Co, while semiquantitative agreement with experiment is found for the weaker-scattering liquids Cu and Ni. It is possible to conclude that in the former case coherent multiple-scattering effects, explicitly neglected by the Ziman formula, that might serve to increase the mean free path and decrease the resistivity, are important. Proper inclusion of these effects would require more detailed information about the short-range order in the liquid or glass than is contained in the ordinary structure function $a(q)$. Since this information is not available from experiment, and since realistic yet tractable multiple-scattering transport theories have not yet been perfected, it is difficult to do much better at present. In this respect, however, the recent increased activity[12] in electronic structure calculations for liquid transition metals is encouraging and may soon lead to improved transport calculations.

Similar results are obtained in Sec. III for the amorphous alloys *Co*P and *Ni*P, for which $Z^* \simeq 2$. The resistivity is dominated by the term involving the intertransition-metal part of the structure function, while the presence of the metalloid serves mainly to lower the muffin-tin zero of energy. This effect is shown to increase the resistivity of the alloy relative to that of the pure transition-metal liquid.

The present calculations also underline the fact that the computed resistivity is extremely sensitive to small changes in the parameters, and therefore emphasize the need to choose these in a systematic, consistent fashion. When this is done the results may be semiquantitative for relatively weak scatterers. Although the fact that the theory is essentially qualitative for strong-scattering systems was suggested in some of the earlier work,[7,13] this point seems to have been lost sight of in more recent applications. The present results are thus intended to provide a word of caution in the use of the extended Ziman formula as well as a guide to the limits of its validity.

II. TRANSITION-METAL LIQUIDS

The Ziman theory,[14] originally formulated to describe electrical transport in simple-metal liquids, was later extended by Evans *et al.*[6] to apply to liquid transition metals. They simply replaced the weak ion pseudopotential $u(q)$ in the original theory by the single-site, on-shell t matrix $t(q,E)$ defined using the muffin-tin approximation. This reasoning led to the so-called extended Ziman formula for the resistivity

$$\rho=\left(\frac{3\pi\Omega_0}{\hbar e^2 v_F^2}\right)(4k_F^4)^{-1}\int_0^{2k_F} dq\, q^3 a(q)\,|t(q,E_F)|^2\,, \quad (1)$$

where $a(q)$ is the liquid structure function, Ω_0 is the average atomic volume, and v_F is the Fermi velocity. This expression neglects all multiple-scattering corrections and in effect describes the scattering by the phase shifts of the muffin-tin potential. Calculations based on this formula[6,7,15] were in remarkably good agreement (~10%–20%) with experiment not only for monatomic transition-metal liquids but also for their alloys. This fact raises the following questions: (i) Why should a single-site formula apply to systems in which conduction electrons are strongly scattered by d-band resonances and in which persistent short-range atomic ordering, that might lead to significant coherent multiple-scattering effects, is present? (ii) How precisely are the conduction-electron parameters entering Eq. (1) to be defined in systems characterized by strong s-d hybridization? In particular, why does the effective valence Z^*, needed to compute k_F, lie in the range $1<Z^*<2$?[11]

The present paper answers these questions by providing an interpretation of the Ziman-Faber theory, firmly rooted in a consistent application of the single-site t-matrix approximation, which permits systematic calculations based on appropriate potentials and structure functions. As in previous calculations, the single-site, on-energy-shell t matrix is expressed in terms of the phase shifts $\eta_l(E)$:

$$t(q,E_F)=-\left(\frac{4\pi}{\Omega_0 E_F^{1/2}}\right)\sum_l (2l+1)e^{i\eta_l(E_F)} \times \sin\eta_l(E_F)P_l(\cos\theta)\,, \quad (2)$$

in atomic units, where $\vec{q}=\vec{k}_F-\vec{k}_F'$, θ is the angle between $\vec{k}_F$ and $\vec{k}_F'$, and $E_F=k_F^2=k_F'^2$. The last equality characterizes the "free-electron gas" containing the scatterers: k_F labels "the unperturbed state...present before the potential was switched on,"[7] and is defined in terms of an effective valence Z^*:

$$k_F^3=3\pi^2 Z^*/\Omega_0\,. \quad (3)$$

Z^*/Ω_0 corresponds to the density of conduction electrons having a Fermi velocity $v_F=\hbar k_F/m$. Previous calculations have always assumed a value for Z^* and then computed k_F for Eq. (3) (using the experimental Ω_0), while E_F was computed by a separate technique,[16] usually involving the results of crystalline band calculations.

The present interpretation is based on Lloyd's expression for the integrated density of states per atom,[17]

$$N(E)=N_0(E)+\left(\frac{2}{\pi}\right)\sum_l (2l+1)\eta_l(E)+N_m(E)\,, \quad (4)$$

appropriate to a system of nonoverlapping muffin-tin potentials. Here $N_0(E)\propto E^{3/2}$ is the integrated free-electron density of states (with E referred to muffin-tin zero); the second term depends only on the phase shifts η_l of the single-site scattering and thus is structure independent; the third term $N_m(E)$ describes the effects of multiple scattering.

A prescription for obtaining E_F and other "free-electron" parameters that is consistent with the Ziman-Faber formula must involve only single-site scattering in a system of ions having the average density of the liquid. This implies that the liquid E_F is to be determined from the condition for the *total* number of valence (d and conduction) electrons per atom

$$Z=N(E_F)\approx N_0(E_F)+\left(\frac{2}{\pi}\right)\sum_l (2l+1)\eta_l(E_F)\,, \quad (5)$$

which neglects the multiple-scattering terms $N_m(E_F)$. This approximation is, in fact, reasonably accurate (~0.05–0.1 Ry) even in crystalline transition metals,[18] but (as will be shown) yields results for ρ that differ appreciably from those obtained previously using crystalline values. Equation (5) clarifies the meaning of the "free-electron" gas and the effective valence Z^* in a precise way: Z^* is to be associated with the integrated free-electron component of the density of states, i.e.,

$$Z^*\equiv N_0(E_F) \quad (6)$$

with E_F determined by Eq. (5). k_F is then computed from Eq. (3), which, from the above definition of Z^*, yields simply $k_F=\sqrt{E_F}$. This procedure is thus consistent with the use of the on-shell t-matrix element [Eq. (2)]. Finally, ρ is computed from Eq. (1) using experimentally determined structure functions.[19]

This prescription has been used to calculate ρ for liquid Fe, Co, Ni, and Cu. The results, discussed in detail below, are in poor agreement with experiment for Fe and Co. Furthermore, the mean free paths are smaller than an interatomic distance. However, the calculated ρ's are sufficiently sensitive to k_F and E_F that a relatively small adjustment (within the range of differences among various crystalline band calculations, for example) can produce the sort of agreement found by previous groups. Indeed, since earlier calculations used input arising from different sources, usually based on band results and empirical data for *solids*, and made somewhat arbitrary choices for the values of Z^*, the Ziman-Faber theory was not applied consistently.[20]

The present results are viewed as a reflection of the fact that atomic positional correlations are seriously underestimated in the spherical-averaged $a(q)$. As a result, coherence of the electron wave function within atomic clusters, which arises from the short-range order and which would be accounted for in a true multiple-scattering theory, is suppressed. Thus the mean free path is shorter than that observed in the liquid. This point has also been made by Greig and Morgan[21] on the basis of a tight-binding model of d-band conduction, in which higher-order correlation functions [beyond $a(q)$] are essential in computing the scattering matrix elements.

Details of the present calculation are summarized in Table I. Muffin-tin potentials appropriate to the liquid were constructed using the renormalized-atom method.[22] The resulting Z^* is seen to be nearly unity for Co and Ni, and somewhat larger for Fe and Cu. By contrast, previous calculations have assumed $Z^*=1$ for noble metals and either $Z^*=1$ or $Z^*=2$ for transition metals without theoretical justification. Except in the case of Ni, the computed ρ's overestimate the experimental values by a factor of two or more. For Fe and Co the mean free paths Λ are appreciably smaller than an interatomic distance (defined as twice the muffin-tin radius R_{MT}).

Table II summarizes the results of Dreirach *et al.*[7] $Z^*=1$ in all cases. For Ni and Cu, E_F was computed semiempirically utilizing band-structure results and optical data for the solid. For Fe, previously computed phase shifts and E_F for the solid were used. In all cases k_F was computed using Eq. (3). Except for Ni, their results agree far better with experiment than those obtained here.

In order to understand the discrepancy between the two sets of calculations, consider first the case of Cu. Tables I and II show E_F to be the same in the two cases. However, Z^* and hence k_F differ, the latter by about 7%. The fact that ρ is so sensitive to such a small change in k_F is due, of course, to the fact that for nearly monovalent metals the upper limit of the resistivity integral at $q=2k_F$ lies in the middle of the steeply rising slope of $a(q)$. Figure 1 shows the variation of ρ with k_F for fixed $t(q,E_F)$ for Cu and Fe. ρ increases rapidly at first, reaching a maximum near $2k_F=q_p$, the location of the first peak in $a(q)$. For $k_F>\frac{1}{2}q_p$, ρ decreases because in this region the integral in Eq. (1) increases only slowly while the prefactor $v_F^{-2}k_F^{-4}\propto k_F^{-6}$ decreases rapidly. For Cu, the choice $Z^*=1$ leads to $\rho=22$ μΩ cm in agreement with Table II. This value is about half that obtained using $Z^*=1.21$ as in Table I. The same effect occurs for Fe: for $Z^*=1$, $\rho=730$ μΩ cm. The remaining discrepancy with the value listed in Table II is probably associated with the overestimate of E_F in Ref. 7, since the E_F value for the denser solid was used there. Thus the separation between E_F and the resonant d level is too large and $\eta_2(E_F)$, and hence ρ obtained from the input of Table II, too small.

The calculated resistivity can also vary rapidly with E_F, particularly near the d resonance, because of the parametric dependence of $t(q,E_F)$ on E_F. The single-site values of E_F [cf. Eq. (5)] when computed for the *solid* density differ from those obtained from crystalline band calculations,[18] using *the same input parameters* (potentials, phase shifts, radii, etc.) by about -0.07, -0.07, 0.00, and 0.06 Ry for Fe, Co, Ni, and Cu, respectively. The Fermi energies for the true liquids having short-range order and the appropriate density are expected to fall somewhere in these respective intervals for each of the four elements, except possibly when E_F lies too near a d resonance,

TABLE I. Details of the present resistivity calculations for liquid transition metals. Values of ρ_{exp} are from Ref. 34 (Fe, Co, Ni) and Ref. 1 (Cu).

Metal	Ω_0 (au^3)	R_{WS} (au)	R_{MT} (au)	Z	E_F (Ry)	$\eta_2(E_F)$	Z^*	k_F (au^{-1})	$\Lambda/2R_{\mathrm{MT}}$	ρ_{calc} (μΩ cm)	ρ_{exp}
Fe	88.4	2.76	2.50	8	.549	2.25	1.21	0.741	0.2	1130	136
Co	87.7	2.76	2.49	9	.482	2.56	0.99	0.694	0.6	329	115
Ni	84.6	2.72	2.46	10	.480	2.87	0.95	0.693	2.5	74	83
Cu	90.4	2.78	2.52	11	.539	3.04	1.21	0.734	4.9	41	21

TABLE II. Details of the previous calculation of Dreirach *et al*. (Ref. 7). The values of k_F, not specified in their paper, were obtained using their Table I and Eq. (13).

Metal	Z^*	E_F (Ry)	k_F (au^{-1})	ρ_{calc} ($\mu\Omega$ cm)
Fe	1	0.77	0.69	196
Ni	1	0.62	0.70	78
Cu	1	0.54	0.69	24

since the single-site approximation severely underestimates the d-band width.[18]

The variation of ρ within the range of E_F defined above should be indicative of what a single-site transport theory can achieve with reasonable adjustment of the parameters. Figure 2 shows the variation of ρ with E_F [with Z^* and k_F varied according to Eqs. (6) and (3)] for Fe and Co. The single-site Fermi energy, E_F^{ss}, in Fe lies just above the d resonance (indicated by the arrow) and thus ρ decreases rapidly with increasing E_F. A shift of E_F by + .07 Ry to the value E_F^{corr} (assuming the *shift* to be the same as for the solid) reduces ρ to about 550 $\mu\Omega$ cm, a value about four times ρ_{exp}. Agreement can be obtained by choosing $E_F = 0.77$ Ry, as was done in Ref. 7 (cf. Table II), a value almost certainly too high for the liquid. However, the corresponding mean free path is greater than the interatomic distance, which is not the case for the values of ρ computed using either E_F^{ss} or E_F^{corr}.

In Co, E_F^{ss} lies slightly farther above the d resonance. E_F^{corr} falls into a broad plateau where $\rho \sim 2\rho_{\mathrm{exp}}$ and the mean free path barely equals an interatomic spacing. A further increase of E_F by as much as 0.1 Ry would change ρ very little.

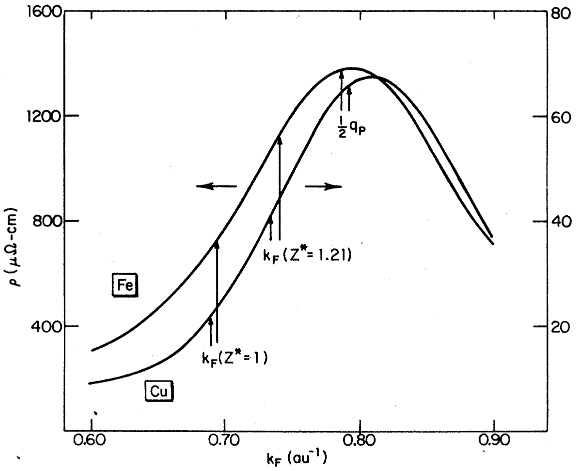

FIG. 1. Calculated resistivity ρ as a function of k_F with $t(q, E_F)$ fixed, for Fe and Cu. Vertical arrows indicate the position of k_F for two different values of the valence Z^* (see text). ρ is largest near the point where $2k_F = q_p$ (also indicated), the location of the first peak in the structure function $a(q)$.

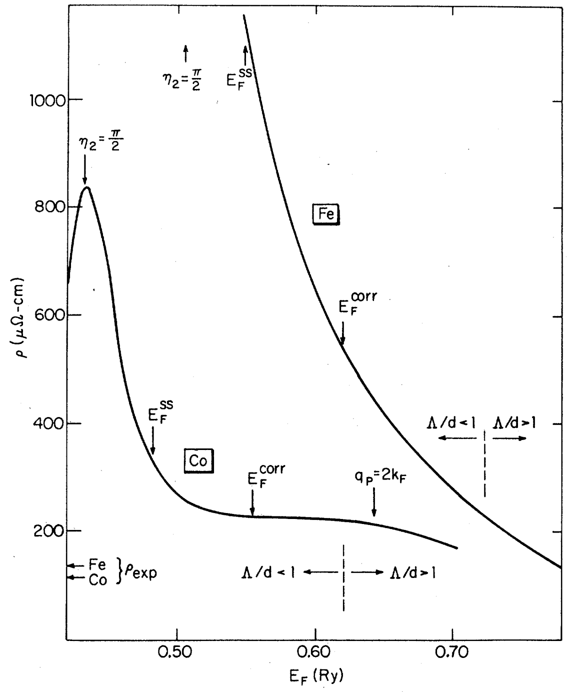

FIG. 2. Calculated resistivity ρ as a function of E_F (referred to muffin-tin zero) with Z^* and k_F varied according to Eqs. (3) and (6), for Fe and Co. Location of the d resonance ($\eta_2 = \frac{1}{2}\pi$) is indicated. E_F^{ss} is the Fermi energy computed from the single-site formula, Eq. (5); E_F^{corr} is obtained by adding to E_F^{ss} an approximate correction to compensate for the shortcomings of the single-site approximation. Λ/d is the ratio of the computed mean free path to a nearest-neighbor distance. Experimental resistivities ρ_{exp} are from Ref. 34.

These results indicate that at least for Fe and Co a single-site transport theory, when applied in a systematic and consistent fashion, cannot be made to yield agreement with experiment for any reasonable estimate of E_F.[23]

The results for Cu and Ni are more encouraging. Figure 3 shows that in Cu, E_F lies far enough above the d resonance that decreasing E_F lowers ρ, largely because of the concomitant decrease in k_F. A change from E_F^{ss} to E_F^{corr} reduces ρ to a value in agreement with experiment. In Ni, E_F also falls above the region where $\eta_2(E_F)$ is large and rapidly varying. Since $E_F^{\mathrm{ss}} \simeq E_F^{\mathrm{corr}}$, the former is presumably nearly the same as the true liquid E_F. The computed value of 74 $\mu\Omega$ cm, again, is in reasonable accord with experiment.

The weaker electron scattering in Cu and Ni (as compared with Fe and Co), associated largely with the smaller values of $\eta_2(E_F)$, may well ac-

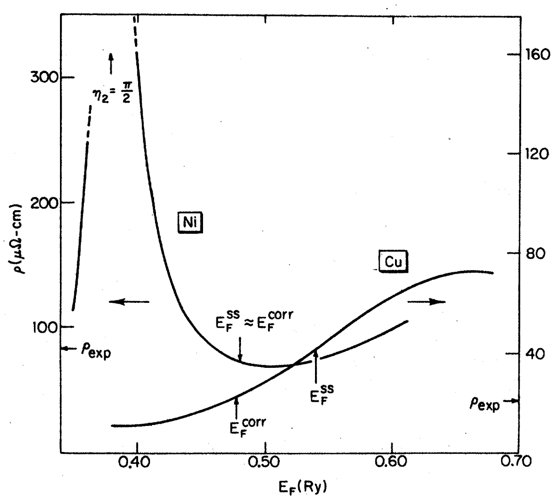

FIG. 3. ρ calculated as a function of E_F for Ni and Cu. For Cu, the d resonance lies far to the left of the figure. In Ni, E_F^{ss} and E_F^{corr} approximately coincide.

count for the semiquantitative results of the Ziman-Faber theory: coherent multiple-scattering effects would be expected to be relatively less important in this case. A recent argument by Ballentine[24] supports this conclusion. He suggests that the Ziman formula should apply to transition metal liquids satisfying $\Gamma/E_F < 1$, where Γ is the width of the electron spectral density function. On the basis of this criterion, which amounts essentially to the requirement that the mean free path be larger than a few interatomic spacings, he concludes that the single-site theory should be valid for a liquid metal such as Ni but not for one such as Fe.

Since Z^* was the basic parameter in previous work, it is also of interest to examine the dependence of ρ on E_F with Z^*, and hence k_F, fixed. Such a calculation would best indicate the sensitivity of previous results to the choice of E_F. For Cu, ρ is found to be virtually independent of E_F between 0.4 and 0.7 Ry, changing by less than 10% over this range for either value of Z^*. Hence the precise choice of E_F in Table II is unimportant. For Fe, however, ρ is found to decrease rapidly with E_F (as expected) from 0.5 to 0.8 Ry. This accounts for the good agreement with experiment found in Table II.

The computed resistivity is therefore seen to be quite sensitive to the choice of input parameters, and with only small adjustments in the latter (for Cu and Ni) can be made to agree well with experiment. Nevertheless, the theory remains a useful interpolation scheme for understanding the qualitative concentration dependence of the resistivity and its temperature coefficient in some liquid transition-metal alloys.[7,15] If the computed ρ's are adjusted to agree with experiment at the pure metal limits, then the theory would appear to do quite well at intermediate compositions for systems in which the scattering properties of the two constituents are very similar, such as Cu-Au.[7] When this is not the case and when, moreover, the precise concentration dependence of E_F is difficult to estimate, as in[7] Fe-Ge and[15] Co-Sn, the theory does not do so well.

III. METALLIC GLASSES

It has been suggested[1,2] that metallic glasses (amorphous metallic alloys) can be regarded structurally as "frozen liquids" and their electronic transport properties computed using the modified Ziman-Faber theory. A recent calculation[3] of the resistivity of amorphous Ni-P supports this general view but contains certain inconsistencies common to earlier liquid alloy calculations (cf. Sec. II). In the present section the procedure already developed is extended to the binary alloy case and applied to amorphous (α-) $Co_{81}P_{19}$ and $Ni_{81}P_{19}$. The effect of the presence of P on the energy dependence of the resistivity is examined. As in the pure liquid case, the results for both systems are sensitive to the choice of parameters, but are better for the alloy containing the weaker-scattering transition metal, Ni-P.

For a binary alloy, the resistivity is again given by Eq. (1), but with $a|t|^2$ replaced by[25]

$$\begin{aligned} |\langle t\rangle|^2 = {} & c_1|t_1|^2[1-c_1+c_1a_{11}(q)] \\ & + c_2|t_2|^2[1-c_2+c_2a_{22}(q)] \\ & + c_1c_2(t_1^*t_2+t_1t_2^*)[a_{12}(q)-1]\,, \end{aligned} \tag{7}$$

where c_i and t_i are the concentrations and single-site t matrices of the two constituents, and the $a_{ij}(q)$ are the partial structure factors. $t_l(q, E_F)$ is still given by Eq. (2) (with Ω_0 now the *average* volume per atom in the system) and E_F is determined from

$$\begin{aligned} c_1Z_1 + c_2Z_2 &= N(E_F) \\ &\simeq N_0(E_F) + \frac{2}{\pi}\sum_l (2l+1)[c_1\eta_l^1(E_F) + c_2\eta_l^2(E_F)]\,. \end{aligned} \tag{8}$$

Z^* and k_F for the alloy are then given by Eqs. (3) and (6).

For α-$Co_{81}P_{19}$ the experimentally determined[26,27] $a_{ij}(q)$ and "hard-sphere" diameters (identified with twice the respective muffin-tin radii) were used. In the construction of alloy potentials by the renormalized-atom method,[22] it is necessary to assign an atomic volume Ω_i to each constituent.

TABLE III. Details of the present calculation for amorphous $Co_{81}P_{19}$ and $Ni_{81}P_{19}$. The value of Ω_0 (for $Co_{81}P_{19}$) is from Ref. 29. Values of $\rho_{exp.}$ are estimates (see text).

Metal	Ω_i (au^3)	R_{WS} (au)	R_{MT} (au)	Z	E_F (Ry)	$\eta_2^{Co(Ni)}$	Z^*	k_F (au^{-1})	Λ/d	ρ_{calc} ($\mu\Omega$ cm)	ρ_{exp}
Co	74.6	2.61	2.40	9	0.858	2.46	2.02	0.926	0.7	349	~160
P	79.0	2.66	1.98	3							
Ni	Same as above			10	0.874	2.72	2.08	0.935	1.5	168	~132
P				3							

It was assumed here that the Co atom retains the same volume Ω_{Co} as in the pure crystalline (*not* the liquid) state, an assumption that is consistent with a wealth of volumetric data on metallic glasses.[28] The P atom then has volume Ω_P determined from

$$\Omega_0 = 0.81\Omega_{Co} + 0.19\Omega_P ,$$

using the experimental Ω_0.[29] Results and various ingredients of the calculation are shown in Table III. An analysis of the logarithmic derivatives of the renormalized-atom wave functions indicates that the P 3*s* level exists as a bound state below the muffin-tin zero[30] and is therefore to be treated as a core state. Thus the P valence Z_P [cf. Eq. (8)] is set equal to three. ρ_{exp} is an estimate based on measurements in related systems[31] and is probably fairly accurate. The computed ρ is seen to overestimate this value by a factor of 2, and the mean free path is less than one interatomic (Co-P) distance d.

The term containing $|t_{Co}|^2$ in Eq. (7) is the dominant one by far and accounts for between 90% and 98% of the computed resistivity in the relevant energy range. Furthermore, $a_{CoCo}(q)$ is very similar to $a(q)$ in liquid Co. Thus, the results for the amorphous alloy are most appropriately compared with those for the pure liquid. Figure 4 shows the behavior of ρ for the glass as a function of E_F (referred to V_{MT}). It is seen to differ appreciably from that of the liquid shown in Fig. 2. The principal effect of adding P to Co is a lowering of V_{MT} by about 0.23 Ry, since the P potential is more strongly attractive in the interstitial region. The Co d resonance, and hence the main component of $N(E)$, however, is more or less fixed relative to the atomic zero: the smaller Co Wigner-Seitz radius in the glass in fact raises the d resonance by about 0.08 Ry with respect to that in the liquid. The separation between the resonance and V_{MT} thus increases (by 0.31 Ry) as the latter shifts downward. Hence E_F, k_F, and Z^* in Table III are appreciably larger than in Table I. Also the value of E_F (~0.65 Ry) for which $2k_F = q_p$ [the first-peak location in $a_{CoCo}(q)$], which was ~0.2 Ry above the resonance in the liquid, is now just below the resonance in the alloy. Hence ρ is larger at its peak than in the liquid, and falls off steadily with increasing E_F. In the liquid ρ decreases more rapidly initially, but then levels off as $2k_F$ sweeps through q_p. In both systems the scattering is strong ($\Lambda \lesssim d$) for the appropriate values of E_F.

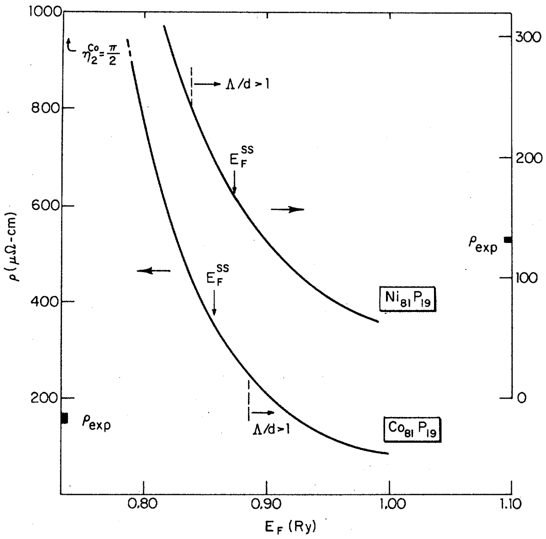

FIG. 4. ρ calculated as a function of E_F for two amorphous alloys (note shifted scale on right). The Ni d resonance lies to the left of the figure.

In view of the strong short-range structural order characteristic of metallic glasses, it is essential to include the information contained in the partial structure factors in the calculation of the resistivity. Since this information is not available from experiment for the Ni-P system, the $a_{ij}(q)$ appropriate to $Co_{81}P_{19}$ were used to compute ρ for $Ni_{81}P_{19}$. A number of arguments can be given to show that this procedure is reasonable. A detailed comparison of the *total* structure factors in these two systems,[27,29] for example, shows the essential features of both to be virtually identical (as is true also for liquid Ni and Co). Results of the calculation are shown in Table III and Fig. 4. ρ_{exp} was obtained by interpolating measured values[3] for alloys with 15- and 25-at.% P ($\rho_{exp} = 104$ and 175 $\mu\Omega$ cm, respectively). ρ_{calc} overestimates this value by less than 30%. The variation of ρ with E_F is qualitatively similar to that in Co-P, except that the d resonance (~0.67 Ry) lies farther below the E_F values of interest. Hence the scattering is weaker, the mean free path is longer, and the Ziman-Faber formula is in better accord with experiment. In addition, the P-P term in Eq. (7) is relatively more important, contributing almost 20% to ρ.

The recent calculation by Meisel and Cote[3] for $Ni_{85}P_{15}$ and $Ni_{75}P_{25}$ was performed in the same spirit as earlier liquid calculations already discussed, using Percus-Yevick (PY) hard-sphere structure functions fitted to the first-peak height in the total Ni-P $a(q)$. Since the PY model[32] neglects important short-range order by permitting two P spheres to touch, which occurs only with low probability in such glasses,[29] the resulting $a_{PP}(q)$, and perhaps also $a_{NiP}(q)$, is inappropriate.[33] Their choice of conduction-electron valences, 0.5 for Ni and 5 for P, leads to $Z^* \gtrsim 1$, in contrast to $Z^* \gtrsim 2$ found here. The resulting values of E_F and k_F, computed in the usual way (cf. Sec. II), are correspondingly smaller than the present ones. The final results, however, agree well with experiment, as was the case with previous calculations for liquid Ni (Sec. II).

The present calculations indicate that the limits of applicability of the extended Ziman-Faber theory when carefully and consistently applied to metallic glasses are the same as for the case of liquid transition metals. For glasses containing a strong-scattering transition metal, the theory overestimates the resistivity, giving mean free paths smaller than an interatomic distance. For weaker-scattering systems the results are semiquantitative, though still sensitive to the choice of effective free-electron parameters.

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[20] A possible exception is the recent calculation by Lopez-Escobar and Brown [Philos. Mag. 35, 1609 (1977)] for liquid Pd, in which E_F is computed from a single-site formalism previously employed by Evans, Gaspari, and Gyorffy [J. Phys. F 3, 39 (1973)]. It is not possible to make a detailed comparison with the present work, however, since the authors do not give explicit details of their calculation; in particular, they do not state how k_F is computed. It is interesting to note, however, that their calculated resistivity is sensitive to the choice of exchange-correlation potential as well as to the various parameters of the Ziman formula.

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3953 (1972)]. The only essential ingredients of the method are the Wigner-Seitz radius R_{WS} (computed from the experimental Ω_0 for the liquid) and the starting neutral-atom configuration (taken as $d^{n-1}s$). The muffin-tin radius R_{MT} is determined as for an fcc crystal at the liquid density. V_{MT} is computed as the volume average of the resulting potential between R_{MT} and R_{WS}, and ranges from -0.77 to -0.80 Ry for the four metals considered here.

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[30] V_{MT} for the alloy is computed by taking an appropriate volume- and concentration-weighted average of the constituent potentials in the region between R_{MT} and R_{WS}, and equals approximately -1.01 Ry for both Co-P and Ni-P.

[31] It is an unfortunate fact that the partial structure functions, but not the experimental resistivity, are known for Co-P. (The converse is true for Ni-P.) The value of ρ_{exp} for $Co_{81}P_{19}$ was estimated by assuming that the ratio of the resistivity of the glass to that of the pure transition-metal liquid is the same as for the Ni-P system (at the same composition). Approximately this same value has been estimated independently by R. Hasegawa (private communication).

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[33] In addition, the P hard-sphere diameter that results from the PY model is 25% smaller than that of Ni, yet the authors choose a P muffin-tin radius 5% larger than that for Ni.

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