Application of the extended Ziman theory to amorphous nickel-phosphorus alloys

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The extended Ziman model, which has proven useful in the description of electrical transport in liquid transition metals, is applied to solid amorphous nickel-phosphorus alloys. Muffin-tin potentials, constructed from atomic wave functions, were used to compute the required scattering phase shifts. Partial structure factors were computed in the Percus-Yevick hard-sphere model. Computed resistivities are in accord with the experimentally observed values over the realizable range of compositions. The composition at which the temperature coefficient of resistivity changes sign is correctly given. Measurements on related alloys indicate that the NiP thermopower is correctly predicted as well. The results suggest that electron transport in metallic glasses can be described in terms of liquid-metal theory.

I. INTRODUCTION

The behavior of the electrical resistivity of amorphous NiP has been explained qualitatively[1] in terms of the extended Ziman theory for liquid transition metals.[2] Support for this interpretation was obtained from measurements of the temperature dependence of the NiP structure factor[3] which is seen to parallel that of liquid metals. In this paper, we present detailed results based on the application of the full muffin-tin model of Drierach et al.[2] to amorphous NiP which support the earlier conclusions. Good accord with experiment is found including the correct magnitude and composition dependence for the resistivity, and the transition from positive to negative temperature coefficients of resistivity. Based on data from related alloys, the thermopower also appears to be correctly predicted.

Although amorphous NiP exists in a relatively narrow composition range (15- to 26-at.% P) it is nevertheless a convenient system for study because of the availability of information relating to its electronic structure from specific-heat,[4] x-ray diffraction,[5] and magnetic-susceptibility[6] measurements (also Ref. 3).

The expression used by Drierach et al.[2] for calculating the resistivity is given by

$$\rho = \frac{3\pi\Omega_0}{e^2\hbar v_F^2}\int_0^1 d\left(\frac{q}{2k_F}\right)4\left(\frac{q}{2k_F}\right)^3 |T(\vec{k},\vec{k}')|^2, \quad (1)$$

with

$$|T(\vec{k},\vec{k}')|^2 = c_1|t_1|^2(1-c_1+c_1 I_{11})$$
$$+c_2|t_2|^2(1-c_2+c_2 I_{22})$$
$$+c_1c_2(t_1^* t_2 + t_1 t_2^*)(I_{12}-1), \quad (2)$$

where $q = |\vec{k}-\vec{k}'|$, the c_i's are the concentrations, and the I_{ij}'s are the partial structure factors for the elements of the binary alloy. The t matrix for

the ith element is given by

$$t_i(\vec{k},\vec{k}') = \frac{2\pi\hbar^3}{m(2mE)^{1/2}}\left(\frac{1}{\Omega_0}\right)\sum_l (2l+1)\sin\eta_l^i(E)$$
$$\times \exp[i\eta_l^i(E)]P_l(\cos\theta), \quad (3)$$

with the phase shifts $\eta_l^i(E)$ evaluated from a muffin-tin potential for the ith atom. A more-complete discussion of the formalism is given by Evans et al.[7]

Using the Ashcroft and Langreth[8] definition of the partial structure factors, S_{ij}, Eq. (2) reduces to

$$T(\vec{k},\vec{k}') = c_1|t_1|^2 S_{11} + c_2|t_2|^2 S_{22}$$
$$+(c_1 c_2)^{1/2}|t_1 t_2^* + t_1^* t_2|S_{12}. \quad (4)$$

This t-matrix modification of the Ziman theory has proven to be a successful technique for calculating the resistivity of liquid transition metals and alloys.[2] The original Ziman theory[9] was formulated only for simple metals. The strong scattering effects of d levels at or near the Fermi level are reflected in large $l=2$ phase-shift contributions to the resistivity. Unfilled d levels are indicated over most of the amorphous NiP composition range[3] so that the extended Ziman theory should also be appropriate for this system.

Following Ashcroft and Langreth,[8] the Percus-Yevick[10] hard-sphere model was used with parameters selected to fit the total NiP structure factors measured by Cargill.[5] The main peak in the structure factor is most important in determining the resistivity and is well represented by this model. The temperature dependence of the resistivity was estimated by varying the packing fraction in the Percus-Yevick model to simulate the measured temperature dependence of the NiP structure factor.[3]

II. CALCULATION OF PHASE SHIFTS

The muffin-tin potentials were constructed using the Matheiss prescription[11] with full Slater exchange and Herman and Skillman neutral atom wave functions.[12] The $3d^9 4s^1$ configuration was selected for nickel.

The radius of the Fermi sphere k_F is taken from the free-electron expression $k_F^3 = 3\pi^2 \bar{z}/\Omega_0$ where $\bar{z}$ is the effective valence (or average conduction electron per atom ratio) for the alloy. It is usually assumed that there are 0.5 holes/atom in the pure nickel d band which leaves 0.5 conduction electrons per nickel atom, consistent with the conclusion of Guntherodt et al.[13] that the conduction electron per atom ratio for liquid transition metals is less than one. Five valence electrons are assumed for phosphorus. Thus, one expects a strong composition dependence of the Fermi sphere radius in NiP alloys. We used the above simple procedure as a guide for determining $\bar{z}$ in our computations and accounted for the d-band filling reflected in magnetization[6] and specific-heat data.[4] This indicated that $\bar{z}$ should be about 1.10 for the 15-at.% P case and about 1.28 for the 25-at.% P case. Since these $\bar{z}$ determinations were not rigorous we actually computed at $\bar{z}$ = 1.03, 1.10, and 1.21 for 15-at.% P and at $\bar{z}$ = 1.28 and 1.33 for 25-at.% P.

The Fermi energy in the alloys was computed from

$$E_F = E_F \text{ (pure Ni)} - k_F^2 \text{ (pure Ni)} + k_F^2 = 0.128 + k_F^2,$$

as suggested by Drierach et al.[2] The muffin-tin radii were chosen to be 1.24 and 1.30 Å for nickel and phosphorus, respectively, these values are consistent with the density measurements of Cargill.[5]

The phase shifts were evaluated from modified versions of computer routines given by Loucks.[14] The results are presented in Table I.

III. PARTIAL STRUCTURE FACTORS

Ashcroft and Langreth[8] found that the Percus-Yevick hard-sphere model provides a suitable approximation to the partial structure factors needed for Ziman theory resistivity calculations in liquid alloys. We used the same approach since the partial structure factors for NiP have not been measured. The two parameters characterizing hard-sphere binary alloys are α the ratio of sphere diameters and η the packing fraction of the mixture. These parameters were selected to give the best fit to the composition dependence of the first peak height in the total structure factor for NiP.[5] The resulting hard-sphere diameters are 2.46 Å for nickel and 1.85 Å for phosphorus which gives $\eta \approx 0.55$ and $\alpha = 0.75$ for the alloys studied. The deduced nickel hard-sphere diameter is identical to that obtained by Cargill[15] using Finney's "dense-random-packing" model results.[16] The packing fraction may also be compared with $\eta \approx 0.63$ obtained from a number of hard-sphere models.[15] The ratio of hard-sphere diameters

TABLE I. Phase shifts. Nickel concentration c_{Ni}, effective valence z, $I = 1$ and 2 corresponds to atomic volume 75.35 and 76.60 a.u., respectively, and the Fermi momentum k_F and Fermi energy E_F are in atomic units. The η_l are the computed phase shifts for angular momentum l.

c_{Ni}	z	I	k_F	E_F		η_0	η_1	η_2	η_3
0.85	1.03	1	0.739	0.674	Ni	−0.302	0.008	2.877	0.001
					P	0.925	0.795	0.076	0.005
		2	0.734	0.668	Ni	−0.300	0.008	2.872	0.001
					P	0.931	0.785	0.075	0.005
	1.10	1	0.756	0.700	Ni	−0.312	0.008	2.897	0.001
					P	0.912	0.830	0.081	0.006
		2	0.752	0.693	Ni	−0.309	0.008	2.891	0.001
					P	0.916	0.820	0.080	0.006
	1.21	1	0.781	0.738	Ni	−0.323	0.008	2.910	0.002
					P	0.887	0.850	0.084	0.006
		2	0.777	0.731	Ni	−0.323	0.011	2.915	0.004
					P	0.887	0.850	0.084	0.006
0.75	1.28	1	0.796	0.761	Ni	−0.332	0.008	2.917	0.002
					P	0.873	0.879	0.089	0.006
		2	0.791	0.754	Ni	−0.332	0.008	2.917	0.002
					P	0.873	0.879	0.089	0.006
	1.33	1	0.806	0.778	Ni	−0.341	0.007	2.924	0.002
					P	0.865	0.923	0.095	0.006
		2	0.802	0.771	Ni	−0.338	0.007	2.922	0.002
					P	0.868	0.914	0.095	0.006

may be compared with $\alpha = 0.81$ deduced for CoP,[17] or $\alpha = 0.67$ deduced for NiPdP,[18] from metal to metal and metal to phosphorus interatomic distances. In what may be fortuitous agreement, these parameters give the observed first peak position 3.11 Å^{-1} in the NiP structure factor.[15]

The partial structure factors I_{NiNi}, I_{NiP}, and I_{PP} have their main peaks at 3.09, 3.21, and 3.38 Å^{-1}, respectively. The corresponding measured[17] CoP partial structure factors have their peaks at approximately 3.04, 3.27, and 2.26 Å^{-1}. If the phosphorus distribution in NiP and CoP is assumed to be similar, there is a large discrepancy in the I_{PP} positions. This is not considered serious for our resistivity calculations since the contribution from I_{PP} in Eq. (2) is small due to the c_P^2 factor. In general, the S_{ij}'s, which enter directly into the resistivity calculations [Eq. (4)], are less sensitive to errors in the model parameters than are the I_{ij}'s.

In order to estimate the temperature dependence of the resistivity, the peak height reduction and broadening was approximated in the Percus-Yevick model by allowing for a change in packing fraction with temperature. This was computed by assuming that the hard-sphere radii are temperature independent so that

$$\frac{d\eta}{dT} = -\frac{\eta}{\Omega}\frac{d\Omega}{dT} = -\frac{3\alpha\eta}{\Omega},$$

where α is the linear thermal-expansion coefficient, which gives

$$\frac{d\rho}{dT} \cong \left(\frac{\rho(\eta_A,\Omega_A) - \rho(\eta_B,\Omega_B)}{\eta_A - \eta_B}\right)\frac{d\eta}{dt}$$

$$= \frac{-3\alpha\eta}{\Omega}\frac{\rho(\eta_A,\Omega_A) - \rho(\eta_B,\Omega_B)}{\eta_A - \eta_B},$$

where the arguments of the resistivities explicitly include Ω to emphasize that k_F, E_F, etc. are functions of Ω (e.g., $k_F^3 = 3\pi^2\overline{z}/\Omega$). We note that the hard-sphere radii are expected to decrease with increasing temperature so that the magnitude of $d\eta/dt$ is underestimated by this technique. The results for resistivity, temperature coefficient of resistivity, and thermopower are given in Table II. The results are in reasonable agreement with experiment. In particular, the composition at which the transition from positive to negative temperature coefficient of resistivity occurs is correctly given.

Thermopower data are presently unavailable for amorphous NiP. However, thermopower measurements[19] in amorphous $(\text{Ni}_x\text{Pt}_{1-x})_{75}\text{P}_{25}$ exhibit only small nonsystematic variations for x ranging between 0.2 and 0.6. Therefore, we expect the NiP thermopower to be close to that for these ternary alloys or about 2.2 $\mu\text{V K}^{-1}$ at 300 K which is indeed close to the value calculated here for $\text{Ni}_{75}\text{P}_{25}$ (Table II).

Nickel is the major contributor to ρ (~65%) over the composition range studied due in large part to its d-wave phase shift. Thus, the approximation

$$\rho = \frac{30\pi^3\hbar^3 c_{\text{Ni}}^2}{Me^2\Omega_0 k_F^2 E_F}\sin^2[\eta_2^{\text{Ni}}(E_F)]I_{\text{Ni}}(2k_F)$$

provides a qualitative description of the behavior of the resistivity in amorphous NiP. The dominant feature is the position of $2k_F$ with respect to the first peak in the Ni-Ni partial structure factor. The next largest contribution to ρ (~30%) comes from the $c_P(1-c_P)|t_P|^2$ term in Eq. (2). The cross terms contribute less than 5%.

TABLE II. Transport properties. Nickel concentration c_{Ni}, resistivity ρ, temperature coefficient of resistivity (TCR), effective valence z, and VI is defined in Table I. The thermopower S is computed from

$$S = \frac{\pi^2 k^2 T}{3|e|\rho}\frac{\partial\rho}{\partial E}\bigg|_{E_F}$$

c_{Ni}	ρ_{expt} ($\mu\Omega\,\text{cm}$)	$10^5(\text{TCR})_{\text{expt}}$ ($^\circ\text{K}^{-1}$)	z	VI	ρ ($\mu\Omega\,\text{cm}$)	S ($\mu\text{V}/^\circ\text{K}$)	$10^5(\text{TCR})$ ($^\circ\text{K}^{-1}$)
0.85	104	+18.0	1.03	1	96.1		11.7
				2	100.4	+3.20	
			1.10	1	100.1		11.9
				2	108.9		
			1.21	1	128.0		5.5
				2	130.7		
0.75	175	−4.0	1.28	1	167.5		−1.83
				2	166.4		
			1.33	1	174.5	+2.51	−2.84
				2	172.7		

In summary, calculations based on the extended Ziman theory are in good agreement with the magnitude and composition dependence of the resistivity and exhibit the transition from positive to negative temperature coefficient of resistivity in amorphous NiP. Measurements on glassy NiPtP alloys suggest that the calculated thermopower in amorphous NiP has the correct magnitude and sign. These results strongly support the view that electronic transport in glassy metals should be treated in the same way as in liquid metals. That is, our results support the use of the extended Ziman theory to describe electron transport in amorphous metals.

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