

Hall-effect measurements and the electronic structure of amorphous Pd-Si-(Cu) alloys

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Measurements of the Hall-effect coefficient (R_H) have been performed at room temperature on the same set of amorphous alloy ribbons in the systems Pd-Si and Pd-Si-Cu for which electronic specific-heat measurements have been reported earlier. The behavior of the Hall coefficient shows a marked change in the range of 18–20 at. % Si, coinciding with the previously observed maximum in the electronic density of states in the same range. The diameter of the Fermi sphere, $2k_F$, calculated from the Hall data, appears to be smaller for all alloys investigated than the wave number q_p corresponding to the occurrence of the first peak in the structure factor. Hence the condition $2k_F = q_p$ is never reached in the amorphous alloys. The corresponding effective electron concentration $(e/a)_{\text{eff}}$ in the conduction band, derived from the Hall coefficient and appropriate densities, varies between 0.8 and 1.3 electrons per atom. The increasing trend of $(e/a)_{\text{eff}}$ with silicon content is approximately linear above 19 at. % Si, and in that range the effective valences of Pd and Si are approximately 0.38 and 4, respectively. Below 19 at. % Si, the effective valence of Si decreases markedly, suggesting that the silicon atoms are no longer fully ionized in the dilute Pd-Si alloys. Under these conditions, the 3s and 3p electrons are likely to exist in the form of bound states near the Fermi level, and their presence is most likely the reason for the occurrence of a maximum in the corresponding density of states observed previously.

I. INTRODUCTION

Several years ago, Nagel and Tauc¹ proposed that the stability of certain glassy alloys is likely to be enhanced by the reduction in their electronic energy through the occurrence of a minimum in the density-of-states curve near the Fermi level. The minimum in the density of states was assumed to occur when $q_p = 2k_F$; here q_p represents the wave number of the first peak in the structure factor $S(q)$ and k_F is the Fermi radius for the conduction electrons. The condition $q_p = 2k_F$ is, therefore, somewhat analogous to the interaction of the Fermi surface with a Brillouin-zone plane, as in crystalline metals. However, in an amorphous alloy both k_F and q_p will be diffused and will correspond to a spherical Fermi surface and a spherically symmetrical structure factor shell, respectively. The present authors and their collaborators recently carried out several low-temperature specific-heat measurements on a series of binary Pd-Si, and ternary Pd-Si-Cu alloys, to investigate the variation in the density of states at the Fermi level on alloying.^{2,3} The linearly-temperature-dependent coefficient γ clearly showed a pronounced maximum, instead of a minimum, at about 19 at. % Si in the binary-alloy system. This was taken to indicate a contradiction to the Nagel and Tauc hypothesis, assuming that the measured γ coefficient directly reflects the density-of-states trend at the Fermi level.

It is of interest, therefore, to study further the origin of the maximum observed in the γ trend and, particularly, whether or not this feature is related to the $2k_F = q_p$ condition.

In the present work, we report on the measurement of the Hall coefficient R_H measured at room temperature on the specimens identical to those employed in the previous low-temperature specific-heat measurements.^{2,3} The important electronic parameters such as the Fermi radius k_F and the electron concentration e/a , deduced from the Hall coefficient, are then considered in combination with the previously reported electronic specific-heat data to discuss further the electronic structure of the Pd-Si glassy alloys.

II. EXPERIMENTAL DETAILS AND RESULTS

The amorphous alloy ribbons were prepared initially for the specific-heat experiments by a rapid quench from the melt, utilizing a single-roller-type spinning-wheel apparatus.³ A ribbon was generally about 1.5–2 mm wide and 30 μm thick. For the Hall-effect measurement each ribbon was cut to a length of approximately 40 mm. The dc method was employed. In this a direct current of approximately 600 mA was fed through a specimen, and the magnetic field was applied perpendicular to its surface. Three thin Cu lead wires, of 0.1-mm diameter, were spot-welded to the extreme edges of the ribbon speci-

TABLE I. Hall-effect coefficients in Pd-Si-(Cu) glasses.

at. % Si	R_H (10^{-11} m ³ /A s)	$2k_F$ (\AA^{-1})
16.5	-11.6 ± 1.0	2.34
17.5	-11.5 ± 1.0	2.34
18.0	-10.5 ± 1.0	2.41
19.0	-7.9 ± 1.2	2.59
20.0	-7.2 ± 1.0	2.70
21.0	-7.6 ± 1.0	2.75
22.0	-6.8 ± 1.0	2.79
Si _{17.0} Cu _{3.0}	-10.0 ± 1.1	2.45
Si _{16.8} Cu _{3.2}	-9.7 ± 1.0	2.48
Si _{16.0} Cu _{4.0}	-9.8 ± 1.0	2.47

men, and were used to measure the Hall voltage. The Hall voltage was of the order of 1 μ V, which was amplified by a nanovoltmeter (Keithley Model 147) and recorded on an *xy* recorder. The Hall voltage measured under different constant magnetic fields shows a linear dependence upon the applied field, with the resulting straight line extrapolating through zero for zero field. The Hall coefficient R_H was determined from the slope of the V_H -vs- H curve.

Hall-coefficient measurements were limited to room temperature, since the temperature dependence of R_H was reported to be fairly small in an amorphous Pd-Si alloy studied by Güntherodt *et al.*⁴ The experimental error involved in the determination of R_H largely results from the reduction in the effective width, across which the Hall voltage is measured, due to an unavoidable overlap of the Cu-lead wires with the edge of the specimen. In order to minimize this effect an approximate correction was made, based on the relation

established between the Hall voltage and the degree of lead wire overlap, using a gold foil with the same geometry as that of the amorphous specimens. The R_H value of -7.2×10^{-11} m³/A s for the pure Au was available in the literature,⁵ and was assumed to correspond to a limiting value, as the overlap region is reduced to zero. The present results are shown in Table I, and are plotted in Figs. 1 and 2 for the binary- and ternary-alloy systems, respectively. The data obtained by others^{4,6,7} are also included in these figures. Specimens covering the glassy Pd-Si range were also subjected to x-ray diffraction in order to determine the position of the first diffraction peak, and the corresponding q_p values. For the alloy Pd_{0.80}Si_{0.20}, q_p was determined to be 2.83 \AA^{-1} , as was also found by Suzuki *et al.*⁸ Little change from this value occurs in alloys covering the stable glassy range.

III. DISCUSSION

The R_H coefficient in the binary Pd-Si glassy alloys shows a rapid change in the range 18–20 at. % Si. This corresponds to the composition at which the electronic specific-heat coefficient γ shows a pronounced maximum.^{2,3} Hence, we believe that the same feature is likely to be responsible for the observed effects in both cases. It has been suggested earlier³ from the magnitude of the γ coefficient in the stable glassy region of the Pd-Si alloys (16–22 at. % Si) that the Pd 4d band is completely filled by electrons donated by the Si atoms. In fact, the x-ray-photoemission XPS spectrum observed by Nagel *et al.*⁹ clearly showed the Fermi level to be at about 0.5 eV above the Pd 4d band in the Pd_{0.775}Si_{0.165}Cu_{0.06}

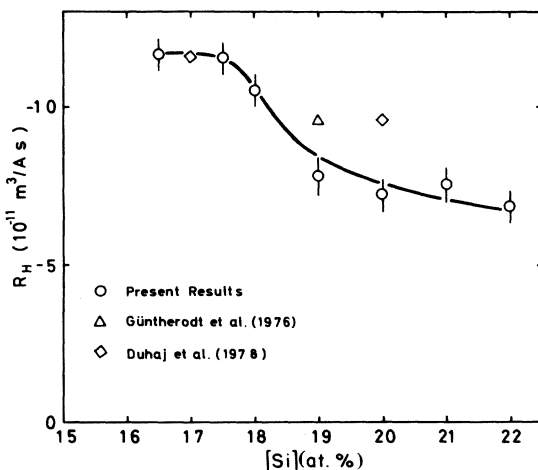


FIG. 1. The Hall-effect coefficients for the Pd-Si glassy alloys at room temperature.

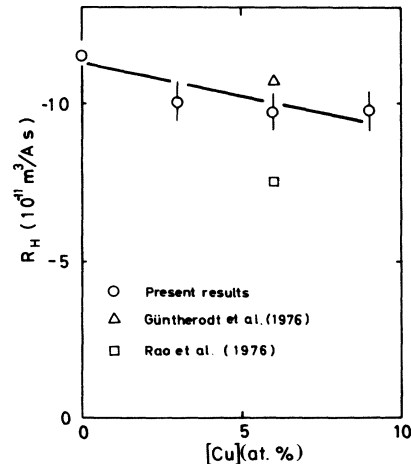


FIG. 2. The Hall-effect coefficients in the Pd-Si-Cu glassy alloys at room temperature.

glassy alloy. Although a small tail of the Pd 4d band is likely to spread out to the Fermi level,² only the conduction electrons are likely to be mainly responsible for the observed Hall effect.

The Hall coefficient R_H based on the free-electron model can be expressed in a simple form⁵

$$R_H = -1/ne = -A/eN_0d(e/a)_{\text{eff}}, \quad (1)$$

where n is the number of conduction electrons per unit volume, e is the electronic charge, N_0 is Avogadro's number, A is the atomic weight, d is the density, and $(e/a)_{\text{eff}}$ is the effective electron concentration per atom. Hence, in order to determine $(e/a)_{\text{eff}}$ from Eq. (1) the density d must be known in addition to R_H . On the other hand, the Fermi radius k_F can be calculated directly from R_H and is given by

$$k_F = (3\pi^2 n)^{1/3} = (-3\pi^2/eR_H)^{1/3}. \quad (2)$$

The $2k_F$ values thus obtained vary between 2.34 and 2.79 \AA^{-1} and are given in Table I. It is seen that the Fermi diameter $2k_F$ increases as the Si content increases in the binary system, but its value is only slightly affected by the change in the Cu content in the ternary system. The $2k_F$ value can now be compared with the wave number $q_p = 2.83 \text{ \AA}^{-1}$, at which the structure factor $S(q)$ shows the first maximum, corresponding to the inverse of the average nearest-neighbor distance in the glassy alloys. For all the alloys investigated, the present results can be taken to mean that the $2k_F$ is always smaller than the corresponding q_p and that the condition $2k_F = q_p$ is never reached over the stable glass region of the Pd-Si system.

It is well known that a negative temperature coefficient of the resistivity $d\rho/dT$ has been observed at certain compositions in various normal liquid metals and alloys.¹⁰ Ziman¹¹ could successfully account for its occurrence in terms of the $2k_F = q_p$ condition. An extension of the Ziman theory to the glassy alloys has been attempted by various investigators.¹²⁻¹⁴ The results in the relatively high-temperature region ($T > \theta_D$, θ_D is the Debye temperature) are essentially identical to the Ziman liquid-metal theory. It is significant that a positive $d\rho/dT$ has been observed over the entire composition range of the currently used stable Pd-Si glassy samples,⁽³⁾ being again indicative of the absence of the $2k_F = q_p$ interaction. Therefore, the pronounced downward change in R_H as well as the presence of a maximum is the γ coefficient at about 19 at. % Si must be due to some effect other than the near coincidence of the Fermi surface and structure factor in k space.

In order to gain further insight into the electron-

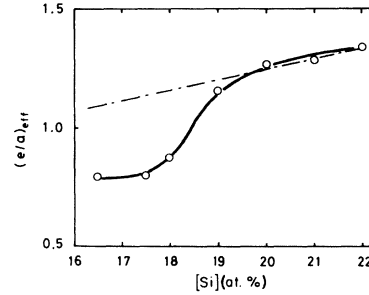


FIG. 3. The effective electron concentration deduced from the measured Hall-effect coefficients in the Pd-Si glassy alloys. The dash-dot line is given as $(e/a)_{\text{eff}} = 0.38 + 4.3x$ for $\text{Pd}_{1-x}\text{Si}_x$, leading to $n_{\text{Pd}} = 0.38$ and $n_{\text{Si}} = 4$.

ic structure of the Pd-Si glassy alloys, the effective electron concentration $(e/a)_{\text{eff}}$ was estimated from the measured Hall coefficient by inserting appropriate values of densities into Eq. (1). Since the densities were not measured in the present experiment, their values were estimated from extrapolation of the Chen and Park¹⁵ data on the pseudobinary alloys $(\text{Pd}_{0.928}\text{Cu}_{0.072})_{1-x}\text{Si}_x$ and $(\text{Pd}_{0.824}\text{Si}_{0.176})_{1-y}\text{Cu}_y$, with $0.155 \leq x \leq 0.205$ and $0 \leq y \leq 0.14$ to the concentration range of the present specimens. The $(e/a)_{\text{eff}}$ thus obtained is plotted in Fig. 3 as a function of the Si content. Under the assumption that Pd and Si atoms contribute, respectively, n_{Pd} and n_{Si} electrons per atom as their effective valences to the conduction band, and that only these conduction electrons contribute to the Hall effect, the $(e/a)_{\text{eff}}$ for a $\text{Pd}_{1-x}\text{Si}_x$ alloy can be written in linear form

$$(e/a)_{\text{eff}} = n_{\text{Pd}}(1-x) + n_{\text{Si}}x. \quad (3)$$

The data points above 19 at. % Si fall nearly on a straight line having the slope and intercept of 0.38 and 4.3, respectively. Hence, in this range the effective valences of Pd and Si may be taken, respectively, as $n_{\text{Pd}} \approx 0.38$ and $n_{\text{Si}} \approx 4$. The derived value of n_{Pd} may be considered as that of the hypothetical "pure Pd glass" or perhaps liquid Pd. Müller *et al.*¹⁶ recently reported that the magnetic susceptibility of pure Pd changes only 7% on melting and, hence the n_{Pd} value for the liquid state should not be too far from the well-established value of 0.36 for the solid state.¹⁷ However, below 19 at. % Si, the $(e/a)_{\text{eff}}$ values fall short of the straight-line extrapolation in Fig. 3 and this suggests that the Si atoms no longer act as fully ionized four-valent atoms, but rather that they release only a part of their valence. In this case, the 3s and 3p electrons are likely to form bound states. If such bound states are formed near the Fermi level, their growth with increasing Si content will cause the γ coefficient to increase. A

subsequent decrease in the γ coefficient above 19 at. % Si may be simply due to a rapid delocalization of the bound states, associated with the change in the valence of the Si atoms. This would also increase the electron concentration and raise the Fermi level past the peak of the bound states. In fact, photoemission and Auger spectra involving both core and valence electrons have recently been measured for the glassy $\text{Pd}_{0.81}\text{Si}_{0.19}$ alloy.¹⁸ The results indicate that the Si 3*p* partial density of states forms a local maximum at the Fermi level as a result of the Pd 4*d*-Si 3*p* hybridization. This is quite consistent with the present interpretation. Consequently, the change in the electronic structure of the amorphous Pd-Si alloys with varying Si content is most likely the result of a marked change in the electronic states of the Si

atoms occurring over a relatively narrow composition region, as reflected in the trends of the Hall coefficient and the electronic specific-heat coefficient.

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