Transport and magnetic properties of icosahedral and glassy Pd-U-Si alloys

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The glassy phase of $Pd_{58.8}U_{20.6}Si_{20.6}$ alloys can be transformed into an icosahedral quasicrystalline phase by thermal annealing. Electrical transport properties of samples undergoing different degrees of glassy-to-icosahedral phase transformation have been measured. The icosahedral phase has an electrical resistivity of $\sim 220\ \mu\Omega$ cm at room temperature and a negative temperature coefficient of resistivity. The short electronic mean free path is discussed. At low temperature, the negative magnetoresistivity is attributed to magnetic scattering effects. The low-field ac susceptibility as a function of temperature exhibits a spin-glass-type transition which is not suppressed by a dc magnetic field.

The recently discovered icosahedral solid has added a new ordered atomic structure to the solid state.[1] This new class of materials, known as icosahedral quasicrystals[2] or six-dimensional crystals,[3–5] may also provide a wealth of new electronic and vibrational properties. In the past, comparison has frequently been made between the crystalline and glassy structures. As the number of icosahedral alloy systems increases, it becomes possible to carry out a detailed investigation of the physical properties of this novel class of materials and to compare them with those of the other two known structures.

In this paper, we present a comparative study of the transport and magnetic properties of glassy and icosahedral alloy ribbons of composition $Pd_{58.8}U_{20.6}Si_{20.6}$ which have been found to undergo a glassy-to-icosahedral phase transformation upon annealing.[6]

Glassy ribbons of $Pd_{58.8}U_{20.6}Si_{20.6}$ were prepared by melt spinning. Sections of ribbons were then annealed at 495 °C for various intervals of time to produce different volume fractions of icosahedral phase in the samples. The structures were studied by x-ray and electron diffraction. Details of synthesis and processing of samples were described in Ref. 6. The microstructure of these samples will be discussed elsewhere.[7] Electrical resistivity measurements were made from 0.35 K to room temperature using a four-point probe. The magnetoresistivity was measured in fields up to 85 kOe. Magnetic susceptibility data were taken in 100-Hz ac fields of 0.5 and 1.0 Oe. Measurements were also carried out in the presence of a dc applied field of 100 Oe.

Room-temperature resistivity values ρ_{RT} and resistivity ratios $\rho(4.2\ \text{K})/\rho_{RT}$ where $\rho(4.2\ \text{K})$ is the value at 4.2 K are plotted in Fig. 1 against the volume fraction of the icosahedral phase. It can be seen that all samples have negative temperature coefficients of resistivity. Moreover, ρ_{RT} and $\rho(4.2\ \text{K})/\rho_{RT}$ show a decreasing trend from the fully glassy structure to the fully icosahedral structure. These values differ by less than approximately 5%. Negative temperature coefficients occur ubiquitously in metallic glasses with high electrical resistivities ($> 150\ \mu\Omega$ cm, Ref. 8). Recently, this behavior has been attributed to the localization and interaction effects of electrons in metallic glasses.[9–13] A detailed analysis of the temperature dependence of resistivity $\rho(T)$ by including spin-orbit scattering effects was given in Ref. 11. In general, $\rho(T)$ is not a simple function of temperature. However, at high and very low temperatures (with respect to some characteristic phonon energy), it can be shown that $\rho(T)$ varies as $\sqrt{T}$ (Ref. 12). This is because the inelastic scattering time τ_ϵ is then either long (low T) or short (high T) compared to the spin-orbit scattering time. One also has to assume that τ_ϵ varies as $1/T$ at high temperature. For the high-T regime, we have plotted ρ as a function of $\sqrt{T}$ (Fig. 2). It is seen that for $T > 70$ K, ρ follows $\sqrt{T}$ quite well for both structures. The behavior in the low-T regime ($0.35 < T < 10$ K) will be discussed later.

Electron-microscopy studies reveal that the fully transformed samples are packed with grains of icosahedral crystal of approximately 1000 to 2000 Å in size.[7] It is thus important to question if the resistivity behavior observed in the fully crystallized state is intrinsic to the icosahedral structure. On the other hand, an overaged Pd-U-Si sample containing approximately 10% volume fraction of Pd_3U grains of 1000 to 2000 Å in size has lower resistivity ($\sim 170\ \mu\Omega$ cm) and a positive tem-

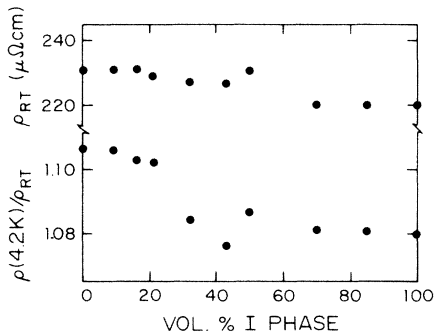

FIG. 1. Resistivity at room temperature ρ_{RT} and resistivity ratio $\rho(4.2\ \text{K})/\rho_{RT}$ versus volume fraction of icosahedral (I) phase. All $Pd_{58.8}U_{20.6}Si_{20.6}$ samples contain only the glassy and icosahedral phases.

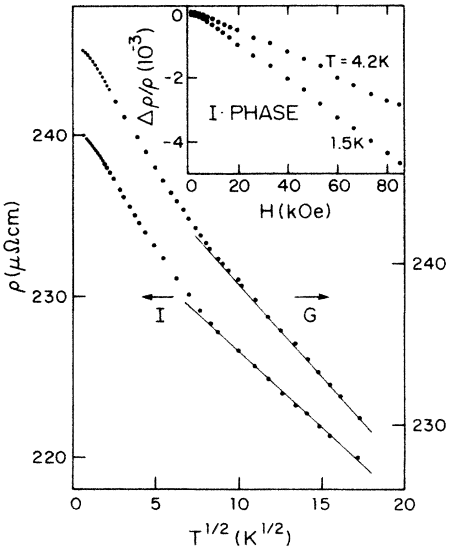

FIG. 2. Resistivity as a function of $\sqrt{T}$ for glassy (G) and icosahedral (I) $Pd_{58.8}U_{20.6}Si_{20.6}$ alloys. Inset shows magnetoresistivity data $\Delta\rho/\rho$ (see the text) of icosahedral phase.

perature coefficient. In fact, crystalline Pd_3U was found to have a much lower resistivity value[14] than glassy and icosahedral Pd-U-Si. This suggests that the transport properties are largely determined by the intrinsic conductivity of the grains. Large resistivity values and negative temperature coefficients of resistivity have also been observed in icosahedral alloys based on aluminum.[15–18] The short electron mean free paths in quasicrystals have recently been attributed to large scattering of electrons due to structural defects in the Penrose tilting, *s-d* hybridization,[19] and virtual bound states.[18] To address the importance of these effects, additional alloys which do not contain *d* states at or near the Fermi level need to be investigated.

Magnetoresistivity data expressed as

$$\Delta\rho/\rho=[\rho(H,T)-\rho(0,T)]/\rho(0,T)$$

for the icosahedral phase are shown in the inset of Fig. 2. Negative $\Delta\rho/\rho$ values are observed. The glassy samples give almost identical results. For metallic glasses of the $4d$ and $5d$ series, the low-temperature $\Delta\rho/\rho$ is positive, and it only becomes negative at very high magnetic fields ($H > 100$ kOe, Refs. 10–12). This is because spin-orbit scattering is important in alloys containing heavy elements. If magnetic components are introduced (e.g., a few percent of Gd in glassy Zr-Cu alloys, Ref. 11), $\Delta\rho/\rho$ is negative at low T. The scattering of electrons due to the formation of spin clusters at decreasing temperature is reduced when the localized spins are aligned in a magnetic field. Since the present alloys possess localized moments ($\sim 2.3\mu_B$ per U atom, Ref. 6), magnetic effects give rise to negative magnetoresistivity and also a fraction of the resistivity upturn at low T (< 10 K), despite the fact that spin-orbit scattering is important.

The Curie-Weiss temperatures for the icosahedral and glassy phases equal -13.5 and -11.3 K, respectively, indicating that the mean-field interaction is antiferromagnetic. The magnetic ac susceptibility $\chi_{ac}(T)$ in zero dc applied field exhibits maxima in both samples (Fig. 3). Susceptibility maxima were also observed in icosahedral and amorphous Al-Mn-Si alloys.[20] We have also carried out measurements in the presence of a dc field of 100 Oe. Samples were warmed to approximately 20 K and then a magnetic field of 100 Oe was applied. Results are shown in Fig. 3. One can see that both cases produce the same susceptibility curves. For most crystalline and amorphous spin glasses, $\chi_{ac}(T)$ is usually reduced in the presence of a dc field.[21] The results here are similar to some of the more concentrated spin glasses. However, the high concentration of magnetic U atoms in our samples and the rather uniform structural units formed by them[22] suggest that the magnetic transition is not simple in nature. Additional experiments are needed to unravel this magnetic state.

In summary, there are apparent similarities in the intrinsic transport properties and magnetic state of icosahedral and glassy Pd-U-Si alloys. They can be qualitatively explained in terms of similar building units (short-range order) in the two structures. However, any fundamental understanding of these properties cannot be achieved until one can unravel the atomic positions in the icosahedral crystal. Specifically, questions pertinent to electron transport and frustration of spins in a quasilattice remain to be answered. At present, the magnetic transition in these materials is to be studied by other experiments.

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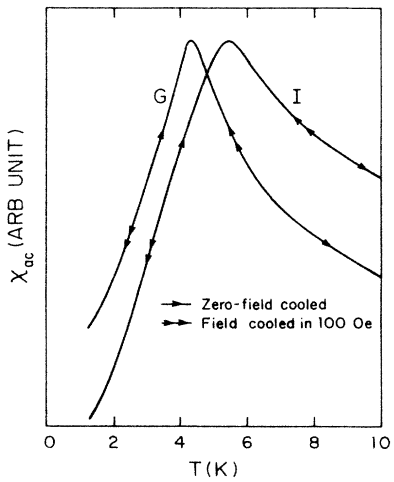

FIG. 3. ac susceptibility as a function of temperature for glassy and icosahedral $Pd_{58.8}U_{20.6}Si_{20.6}$ alloys measured in both zero dc field and 100 Oe dc field.

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