Glassy to Icosahedral Phase Transformation in Pd-U-Si Alloys

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We observe for the first time the transformation of glassy alloys ($Pd_{100-x-y}U_xSi_y$, $x \simeq y \simeq 20$ at.%) into a metastable icosahedral phase with quasicrystalline order upon annealing. The icosahedral symmetry of the latter phase is confirmed by x-ray and electron diffraction. This phase can be formed only within a very narrow compositional range (< 2 at.%) of U and Si, suggestive of a strong chemical ordering in it. The icosahedral and glassy phases have similar electrical transport properties. However, magnetic-susceptibility results indicate that the electronic structure of the icosahedral phase is very different from its glassy and crystalline (UPd_3) counterparts.

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Recently, Schechtman and co-workers observed icosahedral point symmetry in the electron-diffraction pattern of aluminum-manganese alloys.[1] Since then, theoretical studies have been made to elucidate the structure and stability of the icosahedral (I) phase.[2–8] In particular, calculations of diffraction patterns and intensity from structures based on the three-dimensional Penrose tiling (projection of a twelve- or six-dimensional hypercubic lattice) show reasonable agreement between theories and experiments.[2–4]

Steinhardt, Nelson, and Ronchetti observed icosahedral bond-orientational order in a molecular-dynamics simulation of an undercooled Lennard-Jones liquid.[9] A correlation between the structure factors of metallic glasses and the icosahedral solid was also noted.[10] It is because of the similarity in their structural properties that one may expect the temporal evolution of a glassy phase into an icosahedral phase under the right thermodynamical conditions. However, the occurrence of the icosahedral phase is still rare (previously only in Al-based alloys) in comparison with the glassy phase.

In this Letter we report the first observation of the transformation of a glassy phase into an icosahedral phase in the ternary alloy system containing palladium, uranium, and silicon. The small compositional range over which the I phase can be formed resembles that of a stoichiometric intermetallic compound. Samples prepared at the "stoichiometric" compositions contain only a very small trace (minimized to less than ~1%) of a second phase. Thus, these alloys provide model systems for studying the structural, electronic, transport, and magnetic properties of an icosahedral solid. Comparison can be made with the glassy counterpart.

Alloy ingots of $Pd_{100-x-y}U_xSi_y$ with x and y near 20 at.% were prepared in an arc furnace. Portions of the ingots were used in melt spinning which produced ribbon samples. Heat treatments were carried out on as-quenched ribbons sealed in evacuated Pyrex tubes which also contained zirconium chips as oxygen getters. X-ray diffraction studies were performed by use of Cu $K\alpha$ radiation. Transmission-electron-microscopy measurements were made on samples thinned by ion milling in a cold stage. Thermal studies were carried out by use of a differential scanning calorimeter. A four-point probe was employed to measure resistivity as a function of temperature. Magnetic susceptibility was measured with a SQUID susceptometer.

Melt-spun samples of compositions $23 \geqslant x \geqslant 17$, $21 \geqslant y \geqslant 16$ were found to be glassy. The x-ray diffraction pattern of a sample at the composition $Pd_{60}U_{20}Si_{20}$ is shown in Fig. 1 (inset). Thermal differential-scanning-calorimetric measurements on this sample show a two-peak (at ~480 °C and 540 °C) pattern. Structural studies show that these peaks correspond to the transformations from the glassy phase to the I phase (480 °C) and from the I phase to the equilibrium phases (540 °C). The change in enthalpy for the glassy → I transformation is ~3 kJ/mole which can be compared with the enthalpy of crystallization (~4 kJ/mole) for glassy $Pd_{80}Si_{20}$. Figure 1 shows the diffraction pattern of a glassy sample of $Pd_{60}U_{20}Si_{20}$ after being annealed at 440 °C for 200 min.

The x-ray peaks in Fig. 1 can be indexed by use of the twelve vectors pointing from the center to the vertices of an icosahedron.[11] The peak at $2\theta = 37°$ is taken as the diffraction based on the fundamental

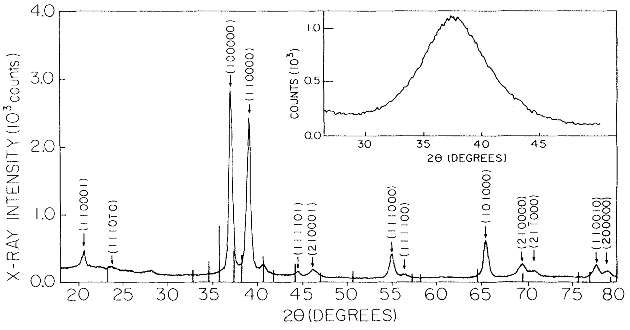

FIG. 1. X-ray diffraction pattern of $Pd_{60}U_{20}Si_{20}$ (annealed at 440 °C for 200 min). Labels are the icosahedral Miller indices as discussed in the text. Vertical lines represent positions and relative peaks intensities from the equilibrium phases. The inset shows the pattern of an as-quenched sample at the same composition.

(100000) reciprocal-lattice vector, yielding an interplanar spacing of 2.424 Å. Positions of all other lines are then calculated (indicated by vertical arrows). The second strongest (110000) line is at 39°. Also shown in this figure are vertical lines representing the positions and relative scattering intensities from the equilibrium phases obtained by annealing of the sample at 630 °C for 30 min. These phases are those of hexagonal UPd_3, an orthorhombic, and an unindexed (*X*) phase. The strongest line from the *X* phase is at 40.6°, corresponding to the small "hump" in the diffraction pattern. There is only one equilibrium line (69.3°) which matches an I-phase line. The small hump at ~28° belongs to that of a uranium oxide. The intensity of this line is significantly reduced simply by sanding of the surface of the sample. No detectable trace of the other two equilibrium phases (strongest lines at 34.6°, 35.8°, 37.8°, and 38.3°) is present. In addition to the ten peaks whose indices are the same as those observed in the Al-Mn alloys,[11] we are able to index five other peaks (at increasing 2θ) as the (111101), (210000), $(21\bar{1}000)$, (220000), and (211000) lines (the last two are not shown in the figure). The maximum deviation of the observed line positions from those calculated with use of a perfect icosahedron is about 0.1°, similar to the Al-Mn system.[11] Since there is only a small trace of the *X* phase in the sample, the composition of the I phase is therefore well defined. This is also confirmed by energy-dispersive x-ray analysis. It is interesting to note that the relative intensities of the I-phase peaks in Pd-U-Si and Al-Mn are quite similar. Two facts are pertinent to this result. In both systems, the atomic-number ratios of the constituents (Mn/Al, U/Pd) are equal to ~2. Moreover, the optimal Al/Mn composition for the I phase was found to be ~$Al_{3.9}Mn$ (see Guyot and Audier[12]).

Convergent-beam electron-diffraction patterns taken with the beam along twofold, threefold, and fivefold axes (I phase, $Pd_{60}U_{20}Si_{20}$) are shown in Fig. 2. These patterns, taken with a 40-nm spot size, correspond almost exactly to patterns obtained from the icosahedral Al-Mn phase, and the angles of rotation between the different axes are similar to those reported for this system.[1,11] Grains of the I phase ranged in size from 20–140 nm. No evidence of microtwinning was found in any of the I-phase crystallites. Very small amounts of an unidentified, heavily faulted phase were also present in this particular sample.[13]

If a criterion for an almost single-phase sample is chosen on the basis of the relative line intensities of the I phase and *X* phase (or other equilibrium phases) shown in Fig. 1, then both Δx and Δy are about 2 at.%. The quantity of equilibrium phases present increases rather rapidly as one moves away from the "ideal" compositions. For example, by keeping the relative Pd/U composition the same while decreasing the Si content to 18 at.%, we obtained no I phase by annealing the glassy phase. A detailed mapping of the stoichiometric composition would require structural studies on samples made at small compositional intervals (~0.2 at.%) near $x \simeq y \simeq 20$ at.%. Preliminary

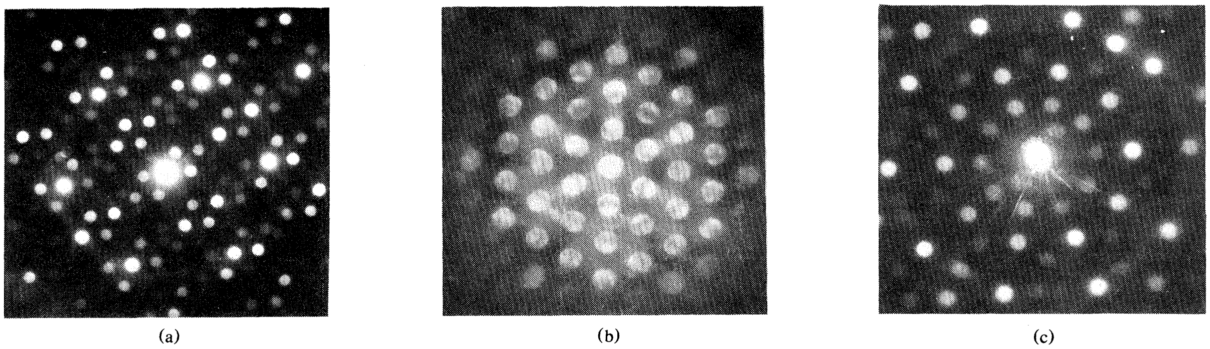
(a) (b) (c)

FIG. 2. Electron-diffraction patterns for $Pd_{60}U_{20}Si_{20}$ (same heat treatment as for the sample shown in Fig. 1. (a) Twofold axis, (b) threefold axis, (c) fivefold axis.

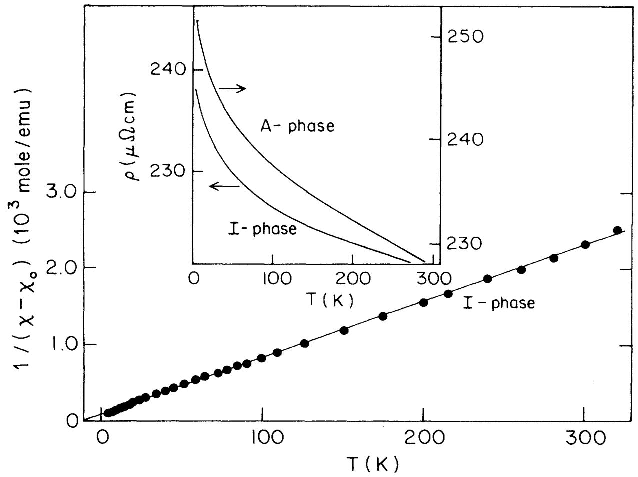

FIG. 3. Inverse Curie-Weiss magnetic susceptibility as a function of temperature for the I phase. The inset shows the temperature-dependent resistivity of both the A phase and the I phase.

results indicate that the quantity of the X phase can indeed be reduced to below the ~1% level. The very restricted compositional variation (a compositional cross section of ~2 at.% × 2 at.%) for the I phase can be compared to that for the glassy phase (~5 at.% × 6 at.%). Short-range order (chemical and geometrical) has been shown to exist in glassy ternary alloys.[14] On the basis of the present results, it is probable that chemical ordering is important in the formation of the quasicrystalline phase.

Since our samples are composed almost entirely of one phase, a comparison of the physical properties of the I phase with its glassy and crystalline (UPd_3 intermetallic) counterparts is possible. In Fig. 3 (inset) is shown the temperature dependence of the resistivity ρ for the I phase ($Pd_{60}U_{20}Si_{20}$) and the glassy (A) phase. The resistivity values are comparable in both cases. The resistivity ratios $\rho(293\ K)/\rho(1.4\ K)$ for the I phase and the A phase are 0.93 and 0.91, respectively. On the other hand, a partially crystallized sample containing ~10% of the equilibrium phases shows lower resistivity (~170 $\mu\Omega$ cm) and a resistivity ratio of ~1.1. Thus, it can be said that the I phase and the A phase have similar transport properties. At present, we are not able to explain the high resistivity value in the I phase in relation to aperiodicity or chemical ordering. The scattering of quasi Bloch states[2] by "impurity" sites (deviation from "ideal" chemical ordering), defects, and grain boundaries deserves further investigation. It is interesting to note that the electron mean free path is comparable to the average interatomic spacing in a well-ordered system.

Since uranium has $5f$ electrons, the magnetic-susceptibility data are analyzed by use of the relation $\chi = \chi_0 + C/(T - \Theta)$, where C and Θ are constants. That is, a temperature-independent term is added to the Curie-Weiss term. The value of χ_0 is obtained from a plot of χT vs T above 100 K. We do not observe a magnetic transition in either the I or the A phase down to 4.2 K. Figure 3 shows the inverse Curie-Weiss susceptibility from 4.2 to 320 K for the I phase ($Pd_{60}U_{20}Si_{20}$). A straight line can be drawn through the data points in the temperatre range 20–320 K. From this plot, the Curie-Weiss constant C which yields the effective moment μ_{eff} (in units of Bohr magneton μ_B) per U atom and the Curie-Weiss temperature Θ are obtained. A similar plot is obtained for the glassy phase. In Table I are listed the values of μ_{eff}, Θ, and χ_0 for the I phase, the A phase, and crystalline UPd_3 (Wernick *et al.*[15]) Except for the presence of crystal-field effects in UPd_3, the values of μ_{eff} and Θ are similar for all three structures. A somewhat striking difference is noted in the χ_0 values. The one for the icosahedral phase is significantly lower (~4 times) than those for the glassy and crystalline phases. The paramagnetic susceptibility χ_0 contains the Pauli term χ_P, the core term (small), and the Van Vleck term χ_{VV}. χ_P gives the band density of states at the Fermi energy. If the values of χ_{VV} are positive and similar for the three structural phases, then the small χ_0 for the I phase leads to a much lower density of states than in the other two phases. In any case, the present result indicates that the electronic structure of the I phase is very different from its glassy and crystalline counterparts.

TABLE I. Magnetic parameters for the three structures discussed in text. Crystalline data are taken from Ref. 15.

Phase	μ_{eff} (μ_B)	θ (K)	χ_0 (10^{-3} emu/mole)
I	2.31	−10	0.22
A	2.29	−7	0.96
UPd_3	~2.63	. . .	~0.88

We have also investigated other ternary Z-U-Si (Z = Pt,Rh,Ru) systems. No icosahedral phase is observed. Topics such as the growth of I phase from the glassy phase and the effect of metalloids on the formation of this novel phase will be studied.

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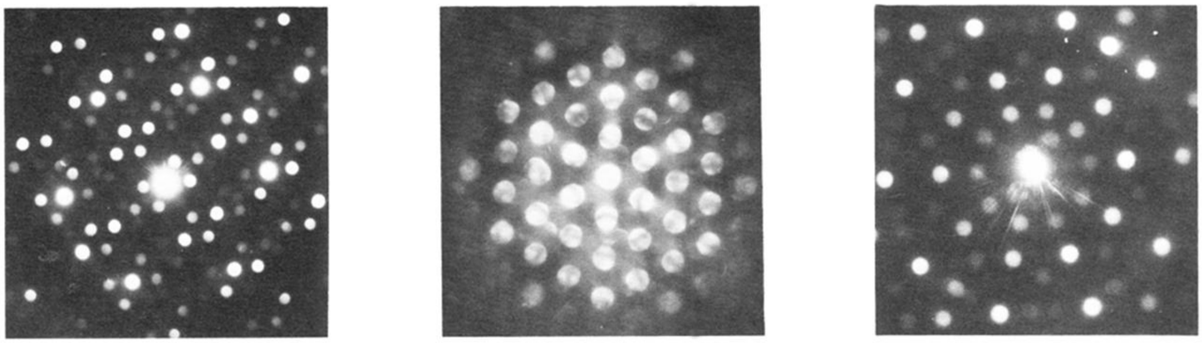

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