

Impurity diffusion in icosahedral Al-Mn

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The platinum-impurity diffusion in icosahedral $\text{Al}_{86}\text{Mn}_{14}$ produced by melt spinning has been measured for the first time. Platinum was introduced into the metastable Al alloy by ion implantation, and depth profiles were measured by Rutherford-backscattering spectrometry. The activation energy for diffusion is found to be 1.1 eV. The preexponential factor is evaluated to be $3 \times 10^{-11} \text{ m}^2/\text{s}$, a value which is about six orders of magnitude smaller than that observed for normal diffusion in Al.

The fundamental incompatibility of icosahedral symmetry with crystallographic translational symmetry is well known.¹ However, recently the existence of materials with long-range icosahedral angular correlation have been demonstrated in melt-spun Al alloys.^{2,3} Also, more recently, a new ordered state with a 12-fold-symmetry axis inconsistent with the existence of a Bravais lattice has been reported.⁴

Most of the present work has been focused on theoretical⁵ and experimental^{2,3,6} determination of the diffraction patterns. The immediate challenge for experimentalists is to gain further insight into the formation and stability of the quasicrystals, the unique specification of the unit cells, and the actual atomic sites that decorate the cells, and further information for quantitative tests of various theories of icosahedral order. In this paper, we report the first diffusion measurements in melt-spun quasicrystalline $\text{Al}_{86}\text{Mn}_{14}$. Specifically, Pt-impurity diffusion has been measured. The Pt atoms were introduced by ion implantation, and the diffusion profiles were measured at room temperature by Rutherford-backscattering spectrometry (RBS).⁷ Our studies indicate that in these quasicrystals, the activation energy is rather low ($\sim 1.1 \text{ eV}$), and the preexponential factor D_0 is about six orders of magnitude smaller than that observed for normal diffusion in Al.

The quasicrystalline $\text{Al}_{86}\text{Mn}_{14}$ alloys were made by melt spinning in a well-controlled Ar atmosphere. The ribbons were 12 μm thick, with a width of approximately 1 mm. Transmission-electron-microscopy measurements revealed the icosahedral diffraction patterns, with the grain sizes 1000 \AA or larger, up to one micrometer (note that in this case, a typical diffusion length $\sqrt{2Dt}$ is $\sim 100 \text{ \AA}$). While microprobe analyses on these samples revealed small amounts of fcc Al between the grains, no detectable oxygen was found. For the diffusion studies, the Pt ions (in some cases Au) were implanted by use of a heavy-ion accelerator at 100 keV to a fluence of $1 \times 10^{15} \text{ ions/cm}^2$, giving a maximum impurity content of 0.6 at.%. The heat treatments were carried out in a vacuum of $\sim 3 \times 10^{-5} \text{ Pa}$, with the temperature controlled to within 1 K.

Before and after diffusion, the Pt depth profile was measured by RBS, carried out at a 2-MV HVEC Van de Graaff. Typical spectra are shown in Fig. 1, together with spectra fit-

ted by computer. The fitted spectra are obtained from the depth-profile formula,

$$f(x) = (A/\sqrt{2\pi}\Omega) [e^{-(1/2)[(x-x_m)/\Omega]^2} + e^{-(1/2)[(x+x_m)/\Omega]^2}], \quad x > 0, \quad (1)$$

$$f(x) = 0, \quad x < 0,$$

where x is the depth and Ω and x_m are fitting parameters. For $\Omega \ll x_m$, x_m is the mean position of the peak, and Ω^2 is the variance. Equation (1) is based on the assumption that the surface is reflecting the diffusing atoms. The function was folded with the experimental depth resolution. The diffusion coefficient is derived from the formula

$$D = (\Omega_2^2 - \Omega_1^2)/2t, \quad (2)$$

where t is the diffusion time, and Ω_1 and Ω_2 are the Ω values before and after diffusion, respectively. For our case, this fitting procedure essentially consists of fitting a Gaussian function to the measured profile, the second

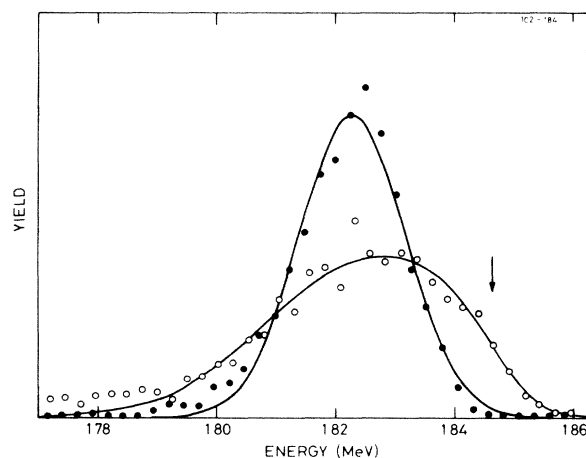


FIG. 1. RBS spectra for nonannealed sample (●) and a sample annealed at 300°C for 8 h (○) together with fitted curves (solid lines). The arrow indicates the surface.

Gaussian function of Eq. (1) making a correction only close to the surface. It should be mentioned that the fitting function [Eq. (1)] yields the correct diffusion constant only if the Pt depth profile before annealing is well described by a Gaussian which does not extend significantly out to the surface, or if a large amount of diffusion has occurred. In all the cases we are dealing with here, we chose the experimental conditions such that the above procedure was accurate. We can exclude contributions due to grain-boundary diffusion in the analyses of our data for the following reasons: (i) The diffusion lengths are an order of magnitude shorter than the smallest grain size, (ii) the measured profiles can be well fitted by Eq. (1), and (iii) negligible tails are observed.

In Fig. 2, typical results of diffusion measurements are displayed. Measured values $\Omega_2^2 - \Omega_1^2$ (in keV, the depth scale is 16 Å/keV) as a function of annealing time are shown for annealings carried out at 275 °C and 325 °C, respectively. In the case of normal diffusion behavior, $\Omega_2^2 - \Omega_1^2$ versus time should yield a straight line, from the slope of which the diffusion constant can be derived [Eq. (2)]. As clearly seen from the figure, initially the diffusion constant is larger, leveling off to a constant value at longer annealing times.

From the initial and final slopes of the $\Omega_2^2 - \Omega_1^2$ versus time curves, initial and final diffusion constants are derived for the various annealing temperatures, as shown in Fig. 3. Here, the diffusion constants are plotted as a function of the reciprocal annealing temperature (in degrees Kelvin). The two straight lines through the data points indicate that diffusion-activation energies can be assigned to the initial and final diffusion constants, being 1.6 ± 0.1 and 1.1 ± 0.1 eV, respectively. The corresponding preexponential factors are 9×10^{-6} m²/s and 3×10^{-11} m²/s. For comparison, normal impurity diffusion in Al gives⁸ activation energies of about 1.3 eV and preexponential factors of 2×10^{-5} m²/s.

By ion-beam mixing, thin evaporated films of alternating layers of Al and Mn can be turned into amorphous structures. A subsequent heat treatment produces quasicrystalline Al₈₆Mn₁₄.^{9,10} Based on these findings and the fact that

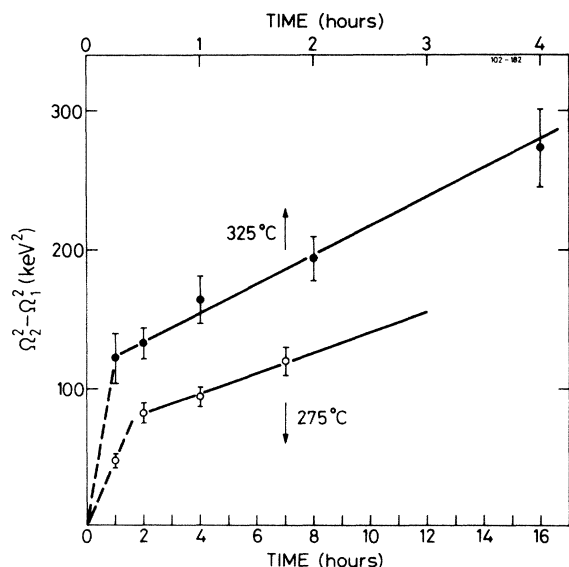


FIG. 2. The increase in variance, $\Omega_2^2 - \Omega_1^2$, as a function of annealing time for annealing at 275 °C and 325 °C, respectively.

even an implantation dose as low as 10^{15} atoms/cm² of Pt gives rise to ~ 1 displacement per atom in the implanted region, we suggest that the initial diffusion reflects diffusion in strongly damaged (perhaps amorphous regions) quasicrystalline Al₈₆Mn₁₄. At longer annealing times, we suggest that the defects are annealed out so that the diffusion constants derived from the long-time anneals correspond to diffusion in defect-free quasicrystalline material.

Preliminary measurements of the Au-impurity diffusion in quasicrystalline Al₈₆Mn₁₄ have also been carried out. However, here the results are very ambiguous. Several measurements have been carried out, but the data show a large scatter. Only three data points for the Au diffusion constant are shown in Fig. 3. Diffusion two orders of magnitude faster is observed for Au diffusion as compared with Pt diffusion. Since typical annealing times in the case of Au diffusion are much shorter than those of Pt diffusion, the Au diffusion may correspond to the initial Pt diffusion. At higher annealing temperatures, it was not possible to fit the diffusion profile with the function of Eq. (1), the profile indicating that phase changes occur. This phenomenon is connected with the Au implantation itself since preannealing before implantations has no influence on the diffusion, and the profile anomalies scale with the ion ranges. The higher-temperature Au-diffusion behavior probably reflects that the Au destabilizes the quasicrystalline Al₈₆Mn₁₄ structure.

In summary, we have studied the diffusion of Pt implanted into quasicrystalline Al₈₆Mn₁₄. We suggest that the initial fast diffusion is due to implantation damage in the Al₈₆Mn₁₄ quasicrystalline structure, while longer annealing times yield diffusion constants for quasicrystalline Al₈₆Mn₁₄, with the activation energy for diffusion equal to 1.1 eV.

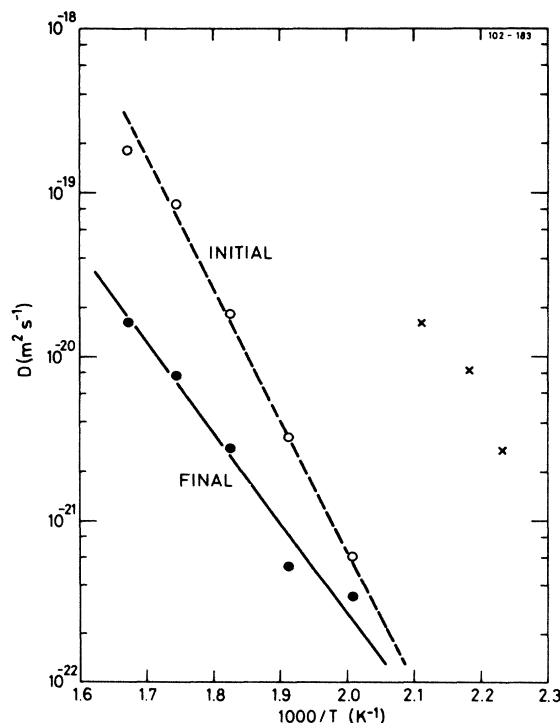


FIG. 3. The initial and final Pt-diffusion constant as a function of reciprocal temperature and three data points for Au-impurity diffusion (x). For details, see text.

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