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Abstract

The self-diffusivity of ⁵⁴Mn in single grain icosahedral Al₇₀Pd_{21.5}Mn_{8.5} quasicrystals has been determined by a precision grinding technique. In the range from 870 to 1093 K the temperature dependence of the Mn self-diffusivity D follows the Arrhenius equation with an activation energy $Q = (180.8 \pm 4.6) \text{ kJ mol}^{-1}$ and a pre-exponential factor $D_0 = 3.4 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$. The experimental results are discussed together with diffusion mechanisms proposed for quasicrystals from theoretical considerations.

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Mn Self-Diffusion in Single Grain Icosahedral Al₇₀Pd_{21.5}Mn_{8.5} Quasicrystals

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The self-diffusivity of ⁵⁴Mn in single grain icosahedral Al₇₀Pd_{21.5}Mn_{8.5} quasicrystals has been determined by a precision grinding technique. In the range from 870 to 1093 K the temperature dependence of the Mn self-diffusivity D follows the Arrhenius equation with an activation energy $Q = (180.8 \pm 4.6)$ kJ mol⁻¹ and a pre-exponential factor $D_0 = 3.4 \times 10^{-4}$ m² s⁻¹. The experimental results are discussed together with diffusion mechanisms proposed for quasicrystals from theoretical considerations. [S0031-9007(96)01898-4]

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Since the discovery of the icosahedral structure in Al₈₆Mn₁₄ by Shechtman *et al.* [1], alloys with aperiodic crystal structure, also called quasicrystals, have become foci of research in solid state physics. Structural, electronic, and mechanical properties have been investigated intensively. Various new compounds have been found to exhibit quasicrystalline structure and the growth technique for large grains of quasicrystals has been improved remarkably, especially for quasicrystals of the Al-Pd-Mn system. However, diffusion data for these structures are still scarce; only a few diffusion data on quasicrystals have been reported previously [2,3]. Accumulation of precise diffusion data is necessary to reveal atomic diffusion mechanisms in quasicrystals. Furthermore, as aluminides are very reactive and brittle materials, special effort has to be made to obtain reliable data. Recently high quality samples of perfectly icosahedral quasicrystals of the Al-Pd-Mn system can be grown in cm³ size [4], which are stable up to the melting temperature, and diffusion measurements over several hundreds of micrometers in depth are possible. The present Letter reports diffusion measurements performed on samples of perfectly icosahedral Al₇₀Pd_{21.5}Mn_{8.5} quasicrystals in order to elucidate the diffusion mechanism.

The Al₇₀Pd_{21.5}Mn_{8.5} quasicrystal was grown by the Bridgman technique at the Ames Laboratory/Iowa State University (for details, see [4]). The rod with approximate length of 60 mm and 16 mm in diameter contained several large grains of icosahedral phase, in the following denoted as *i*-AlPdMn. The icosahedral structure has been determined by x-ray diffraction. Square shaped samples, single icosahedral grains with 4 to 5 mm length and 2 to 3 mm thickness, were cut by the spark erosion technique from the original rod. Composition, homogeneity, and single-phase character of the samples were confirmed by electron probe microanalysis. Sample surfaces were prepared by standard metallographical procedures on lapping tape and diamond paste down to 1 μm.

The radioactive isotope ⁵⁴Mn in 0.5 M HCl was purchased from E. I. DuPont de Nemours & Co. The spe-

cific activity was 1.5 GBq/mg. The solution diluted with ethanol was deposited on the surface and dried by an infrared lamp. The sample was attached to an *i*-AlPdMn dummy sample, wrapped in Ta foil, and encapsulated together with a piece of pure Mn in quartz ampoules which were evacuated to a pressure less than 2×10^{-4} Pa. The attachment of the dummy together with the pure Mn prevented evaporation from the sample as well as of the Mn tracer. Diffusion annealing was carried out in an electric resistivity furnace; the temperature control was within ± 0.5 K. After annealing the side surfaces of the samples were reduced by grinding off about $10\sqrt{Dt}$ to avoid effects from lateral diffusion on the profile analysis.

Sequential sectioning of the sample was carried out with a precision grinding device specially designed for diffusion profile measurements of brittle materials. Deep penetration profiles extending into the bulk of more than a hundred micrometers are measurable by this method. The deep penetration is necessary to circumvent any influence of surface artifacts which are very likely to occur for these highly reactive aluminides. For each section about 300 to 500 μg were removed from the sample. The weight loss after each sectioning was determined by a microbalance (Mettler AT20) with a precision of ± 2 μg. The weight loss of the sample was then converted to penetration depth using the known sample geometry and density. The density $\rho = (5.05 \pm 0.05)$ g/cm³ of the quasicrystalline phase was determined with a buoyancy method. The average section thickness was between 5 and 20 μm. The activity of each removed section was measured in a well-type NaI gamma counter (Aloka ARC-300). At least 10⁴ counts were collected for each section.

The thin film solution of the diffusion equation for semi-infinite diffusion geometry is

$$c(x, t) = \frac{M}{\sqrt{\pi Dt}} \exp\left(\frac{-x^2}{4Dt}\right). \quad (1)$$

Here c is the concentration at penetration depth x after annealing time t and M is the initial amount of tracer at the surface. The diffusion coefficient D can be determined

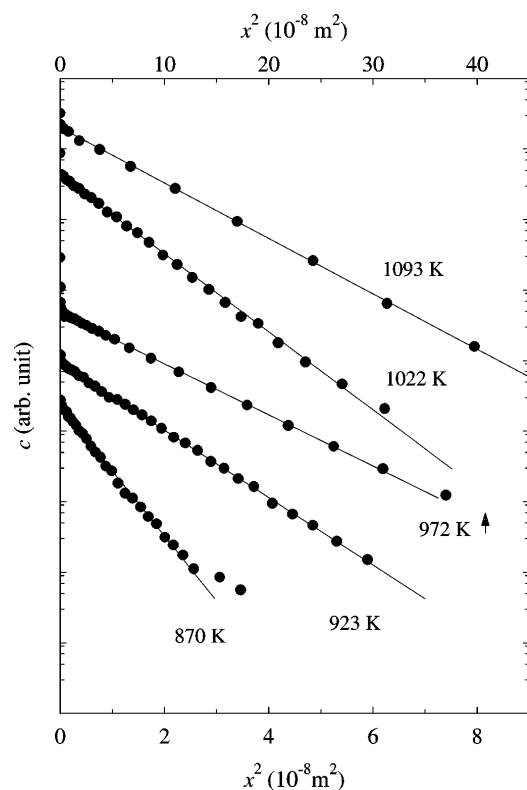


FIG. 1. Diffusion-penetration profiles for ^{54}Mn diffusion in icosahedral $\text{Al}_{70}\text{Pd}_{21.5}\text{Mn}_{8.5}$ quasicrystals. (The upper horizontal axis corresponds to the profile for 972 K.)

from fits of the concentration profiles $c(x)$ to this equation. The concentration profiles for all temperatures are shown in Fig. 1 in a logarithmic scale. The solid lines are fits to Eq. (1). The first section of all diffusion profiles contained a large amount of tracer. This tracer hold up may be due to surface reaction of the deposited tracer with the sample. The profiles extended over a specific activity range of three or more decades until for the final section background activity was reached. No deviation from the Gaussian fit described by Eq. (1) was observed. The measured diffusion coefficients D are summarized in Table I.

The diffusivities were determined in a temperature range from 870 to 1093 K which reaches close to the melting temperature of $T_m = 1150$ K for $i\text{-AlPdMn}$ [5,6]. In this range the temperature dependence of the Mn self-diffusivity $D(T)$ in $i\text{-AlPdMn}$ can be described by the

TABLE I. Diffusivity of Mn in icosahedral $\text{Al}_{70}\text{Pd}_{21.5}\text{Mn}_{8.5}$.

Temperature (K)	Annealing time (s)	Diffusivity ($\text{m}^2 \text{s}^{-1}$)	\sqrt{Dt} (μm)
1093	3600	7.71×10^{-13}	52.7
1022	10800	1.77×10^{-13}	43.7
972	219600	6.81×10^{-14}	122.3
923	108000	2.10×10^{-14}	47.6
870	273960	4.31×10^{-15}	34.4

Arrhenius equation

$$D(T) = 3.4 \times 10^{-4} \times \exp\left(\frac{-(180.8 \pm 4.6) \text{ kJ mol}^{-1}}{RT}\right) \text{ m}^2 \text{ s}^{-1}, \quad (2)$$

as shown in Fig. 2.

Figure 3 shows the temperature dependence of the diffusivity together with diffusion data for quasicrystals and crystalline Al from the literature. The Mn self-diffusivity of the present work is about 3 orders of magnitude higher than previously published data on Mn self-diffusivity in $i\text{-AlPdMn}$ [3]. The difference can be mainly attributed to the difference in sample quality and experimental method. Several years ago the technique for growing large single grain and perfect $i\text{-AlPdMn}$ crystals was not established yet. At that time it was impossible to get high quality samples of several mm in size as usually required for an optimum in self-diffusion measurements. Therefore, the earlier diffusion measurements were restricted to much smaller samples and very short diffusion profiles (less than $1 \mu\text{m}$). The ion beam sectioning technique which was used by Nakajima *et al.* [3] was originally developed to analyze short diffusion profiles. However, it does not seem to be suitable for diffusion measurements on Al based quasicrystals. As already mentioned these compounds are very reactive and surface reactions can hardly be avoided during diffusion annealing. Influence of oxidation and/or evaporation on diffusion behavior in the near surface

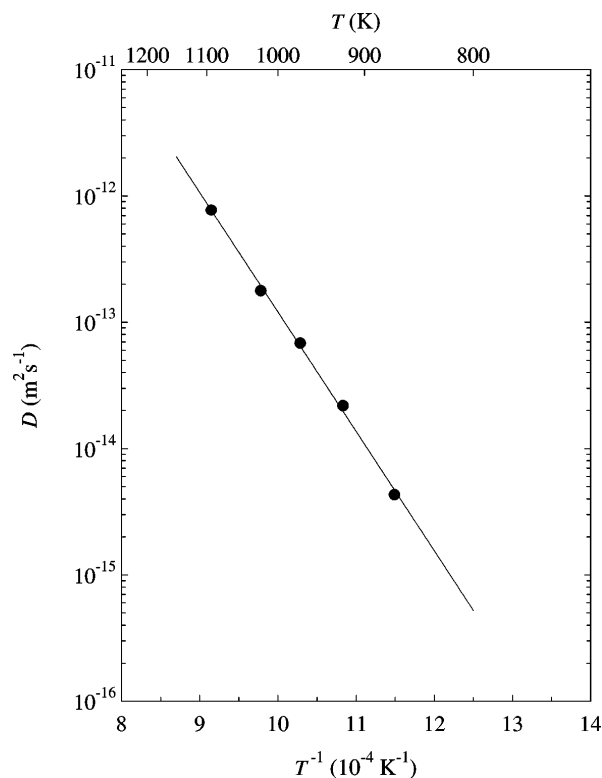


FIG. 2. Temperature dependence of ^{54}Mn self-diffusivity D in icosahedral $\text{Al}_{70}\text{Pd}_{21.5}\text{Mn}_{8.5}$ quasicrystals.

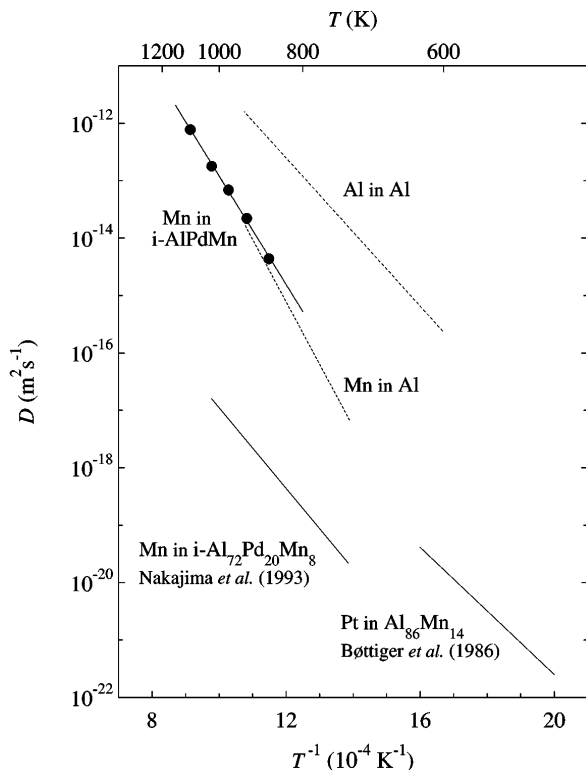


FIG. 3. Temperature dependence of diffusivity D in quasicrystals [2,3] (●: present work) and crystalline Al [16,17].

region is likely to give ambiguous data. Diffusion profile measurement of deeper penetration in i -AlPdMn is desirable in order to make surface effects negligible. Thus, a precision grinding method was used in the present work to analyze deep diffusion penetration of more than one hundred micrometers. These diffusion profiles then unambiguously represent pure volume diffusion in the i -AlPdMn phase. Similar arguments hold for the first diffusion data for quasicrystals published by Böttiger *et al.* [2] in 1986. They used the Rutherford backscattering (RBS) technique to analyze Pt diffusion in $\text{Al}_{86}\text{Mn}_{14}$ quasicrystals. RBS is a rather indirect method to determine diffusivities and is limited to diffusion ranges of far less than $1 \mu\text{m}$ below the surface. In this context it is also noteworthy to mention that first generation quasicrystals of the Al-Mn system were far from having ideally quasicrystalline structure as turned out later [7]. A comparison of the Mn self-diffusivity in i -AlPdMn with data for intermetallic compounds of similar composition is not possible, because no such experiments have been reported.

It is well known that self-diffusion in pure metals and intermetallic compounds takes place by a vacancy mechanism, which requires the presence of vacancies. The diffusivity is strongly affected by the vacancy concentration which is temperature dependent. In quasicrystals with aperiodic crystal structure a new type of defect, the so called phason, exists besides vacancies. Kalugin *et al.* [8] suggested that atom movements can occur only via

these phasons; local atomic rearrangements can take place without involvement of vacancies. The temperature dependence of the diffusivity by the pure phason diffusion mechanism should then exhibit a curvature in the Arrhenius plot which is usually a straight line for a pure vacancy mechanism. Joseph *et al.* [9] adopted the phason flipping model and carried out computer simulations of sequences of phason flips. Their result showed that this process yields to long range diffusion. Additionally they determined the temperature dependence of the diffusion data obtained from the simulation and also found a deviation from Arrhenius behavior. As both approaches are more or less qualitative ones the authors give neither values for the diffusion coefficients nor the temperature range for which the deviation occurs. On the other hand, the experimental results on self-diffusion of Mn in i -AlPdMn show Arrhenius behavior. No deviation was observed in the present work. Thus, it is concluded that at least in the investigated temperature range from 870 to 1093 K diffusion via phasons cannot be the dominant diffusion mechanism. Furthermore, values for the preexponential factor D_0 and the activation energy Q are of the same order as corresponding values for self- and impurity diffusion in various pure metals for which vacancy diffusion mechanisms are established [10].

To explain a possible vacancy diffusion mechanism for Mn diffusion in i -AlPdMn we have to consider the structure of i -AlPdMn in more detail. Boudard *et al.* [11–13] proposed a spherical model for local atomic arrangements in i -AlPdMn quasicrystals resulting from structural analysis by x-ray and neutron diffraction. According to the authors, three distinct sites can be distinguished: (a) sites with an inner core of Mn atoms surrounded by an intermediate shell of Pd atoms and an outer shell of Al atoms, (b) sites with an inner core of Mn atoms entirely surrounded by Al atoms, and (c) sites exclusively occupied by Pd atoms. Thus, long range diffusion of Mn can take place only if Mn atoms temporarily occupy Al or Pd sites.

Tsai *et al.* [14] investigated the change of the lattice parameter for i -AlPdMn with varying Pd concentration of $\text{Al}_{90-x}\text{Pd}_x\text{Mn}_{10}$. They found a strong correlation, suggesting that Pd atoms do not randomly substitute Al atoms in i -AlPdMn but form a highly ordered Pd superstructure. This is in agreement with the results of Boudard (c) of the preceding paragraph. In conclusion a change of Mn atoms to Al sites is more favorable than to a Pd site.

To the authors' knowledge no data on thermal or structural vacancy concentrations in i -AlPdMn are available at present. However, there exists a positron annihilation study by Lawther and Dunlap [15] on vacancy concentrations in icosahedral Al-Cu-Fe quasicrystals, which are also known to be perfectly icosahedral. Their results show that thermal and structural vacancies are present on Al sites in icosahedral Al-Cu-Fe quasicrystals. If such structural vacancies are also present on Al sites in icosahedral Al-Pd-Mn quasicrystals besides thermal vacancies,

Mn self-diffusion may preferentially occur by a vacancy mechanism on the Al-site network. In this respect it is interesting to mention that the Mn diffusion in *i*-AlPdMn can be seen as an extension of the Mn impurity diffusion in Al [16] to higher temperatures (see Fig. 3) with similar activation energy. Of course one should be aware of the differences as well in structure as in composition of the two host matrices.

In summarizing, it is concluded that a vacancy mechanism for Mn diffusion in *i*-AlPdMn is very likely. No evidence for a quasicrystal specific phason diffusion mechanism was found.

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