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Diffusion of ^{54}Mn and ^{59}Fe in icosahedral Al-Pd-Mn single quasicrystals

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Self-diffusion of ^{54}Mn and diffusion of ^{59}Fe was studied in icosahedral single quasicrystals of $\mathrm{Al}_{70.4}\mathrm{Pd}_{21.2}\mathrm{Mn}_{8.4}$. The radiotracer method in combination with serial sectioning of the diffusion samples was used to determine concentration depth profiles. The temperature dependences of diffusion are expressed by Arrhenius equations with the following activation enthalpies (Q) and pre-exponential factors (D_0): Mn: $Q=1.99$ eV; $D_0=8.91\times10^{-4}$ m^{2}s^{-1}, Fe: $Q=2.61$ eV; $D_0=1.63\times10^{-2}$ m^{2}s^{-1}. The results are compared with the scarce literature data on quasicrystals and with data on diffusion in fcc aluminium and in iron aluminide. The quasicrystal data are not significantly different from those in related crystalline materials, for which a vacancy-mediated mechanism is generally accepted for diffusion. Deviation from an Arrhenius behavior as predicted for phason-assisted diffusion could not be detected. [S0163-1829(96)51834-5]

I. INTRODUCTION

Since the discovery of quasicrystalline intermetallic alloys by Shechtman *et al.*[1] these materials have attracted much attention. Diffusion is fundamental and ubiquitous in the art and science dealing with solid matter at elevated temperatures. A knowledge of diffusion properties of quasicrystals is of practical interest for the production of these materials and also for their potential use in technological applications. Kalugin and Katz[2] proposed the possibility of a mechanism of self-diffusion in quasicrystals. This mechanism is based on the specific geometric properties of the quasicrystalline structure and the necessity that matching rules have to be obeyed to build up a perfect quasilattice. Matching-rule violations are called phason defects. It is conceivable that atom jumps in connection with phasons occur at very low activation energies. The authors discuss the possibility that the ''phason mechanism'' could dominate over the vacancy mechanism which is known to be the mechanism of self-diffusion in crystalline metallic elements (see, e.g., Refs. 4–6) and in ordered intermetallic compounds.[7] Katz and Kalugin[2] expect a strongly nonlinear Arrhenius plot for diffusion in quasicrystals but they did not specify the temperature region in which this behavior should be observed.

Up to now experimental studies of diffusion in quasicrystals are extremely scarce. The only literature data have been obtained on polycrystalline samples.[8–10] Studies on single-quasicrystals are not available. Nakajima *et al.*[8] in their study of Mn diffusion in icosahedral $\mathrm{Al}_{72}\mathrm{Pd}_{20}\mathrm{Mn}_{8}$ polyquasicrystalline material observed a very small activation enthalpy and a small pre-exponential factor. Diffusion of Mn was very slow and seemed to indicate unusual features. On the other hand, significant deviations from Arrhenius behavior were neither observed in Ref. 8 nor in any other reported data mentioned above. After the discovery of thermodynamically stable ternary quasicrystalline phases[3] it is now possible to grow large single quasicrystals appropriate for diffusion studies. In this paper we present data for self-diffusion of Mn and for diffusion of the foreign element Fe in icosahedral single quasicrystals of composition $\mathrm{Al}_{70.4}\mathrm{Pd}_{21.2}\mathrm{Mn}_{8.4}$. The radiotracer technique, which is a well-established technique for diffusion studies in metals and intermetallic compounds, has been employed.

II. EXPERIMENTAL PROCEDURE

A. Preparation of single quasicrystals

The icosahedral Al-Pd-Mn single quasicrystals (*i*-Al-Pd-Mn) were prepared by first induction melting the 99.99% pure elements under Ar atmosphere. Cylindrical single quasicrystals of 7 cm in length and 1 cm in diameter were grown from the melt by the Czochralski technique with an orientation along a twofold axis. As indicated by scanning electron microscopy, by imaging and by selected area electron diffraction in the transmission electron microscope the quasicrystals exhibited a very high degree of structural perfection. They consist of a single icosahedral phase of $F1$-type homogeneous in composition with only few voids. The composition of the as-pulled sample $\mathrm{Al}_{70.4}\mathrm{Pd}_{21.2}\mathrm{Mn}_{8.4}$ as determined by chemical analysis and by electron microprobe analysis.

B. Diffusion experiments

The radio-tracer method in conjunction with serial sectioning techniques—grinder and sputter sectioning—was employed. Cylindrical diffusion samples, about 3 mm high, were cut from the single quasicrystals by spark erosion. One front surface of each sample was polished on a precision grinding machine with various grinding films down to 3 μm grade. To avoid oxide hold-up effects, the oxide layer

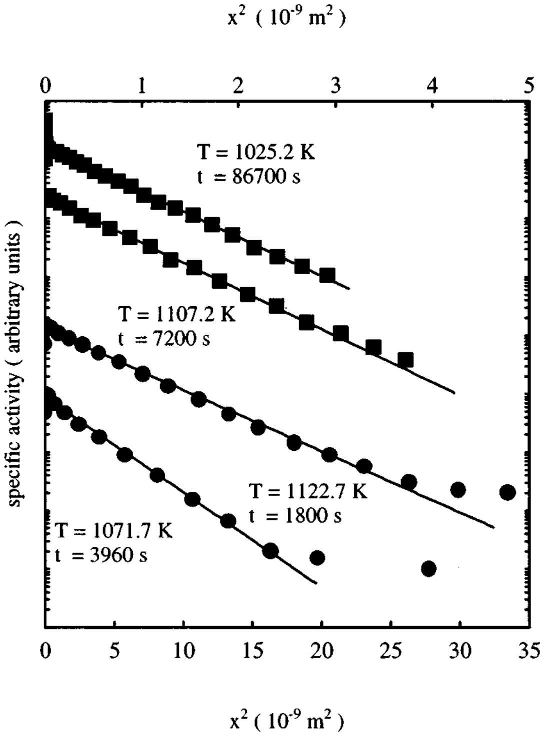

FIG. 1. Diffusion penetration profiles of ^{54}Mn and of ^{59}Fe in single quasicrystals of Al-Pd-Mn obtained by grinder sectioning. The data points with square symbols belong to ^{59}Fe and to the upper x axis. The solid lines represent fits by Eq. (3.1).

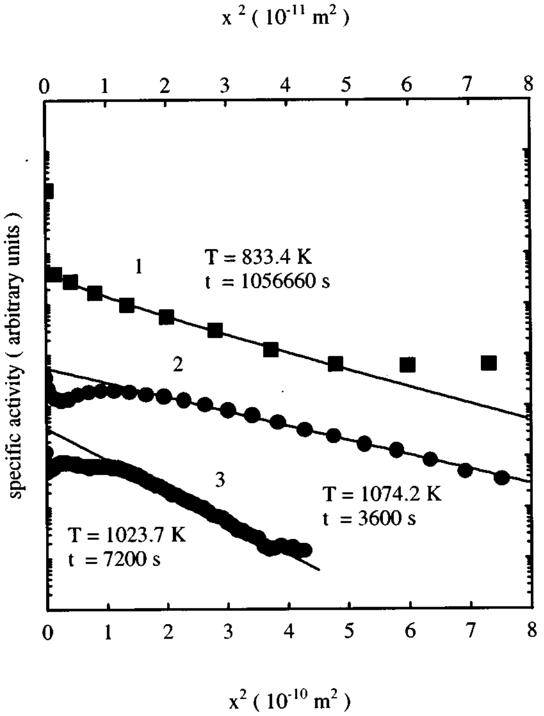

FIG. 2. Diffusion penetration profiles of ^{59}Fe in single quasicrystals of Al-Pd-Mn obtained by sputter sectioning. The solid lines 2 and 3 represent fits by Eq. (3.1). The data points with square symbols belong to the upper x axis and the solid line 1. They were obtained by a fit with an error function.

was removed by ion sputtering prior to deposition of the radioisotopes. ^{54}Mn (half life: 312d) and ^{59}Fe (half life: 45d)—both in chlorine solution were evaporated from a tungsten boat onto the sample surface. In a few cases ^{59}Fe was ion implanted at the Bonn isotope separator using an acceleration voltage of 60 kV. Radioisotope deposition by ion implantation is another way to avoid oxide hold-up and solubility problems.[11,13]

In diffusion anneals with a free surface of the diffusion sample intolerable evaporation losses and degradation of the surface were observed. With the following procedure this degradation could be largely avoided. During the diffusion anneal two samples with the flat surfaces facing a tantalum foil between each other were loaded in a welding clamp machined from stainless steel. The loaded clamp was sealed in quartz ampoules evacuated to a pressure of better than 10^{-5} Pa and annealed for periods of several hours to several weeks under argon atmosphere in a resistance furnace. The temperature during the diffusion anneal was controlled within ±1 K. Heating up corrections were performed for annealing times less than 5 h. After the diffusion anneals the samples were reduced in diameter by about $6\sqrt{Dt}$ to eliminate lateral diffusion effects.

Usually mechanical sectioning was applied and performed by slowly grinding on a precision grinding machine which was designed and constructed in the laboratory in Münster. This device permits serial sectioning of brittle materials. The thickness of each section was determined from the sample diameter, the section weight and the density of the specimen. The density of the quasicrystal, determined by the Archimedes method, was 5.08 g cm^{-3}. The grinding films from the sections were collected into counting vials. The activity of each section was determined for both isotopes by γ counting in a well-type NaI(Tl) scintillation counter and normalized with the section weight to obtain the specific activity which is proportional to the isotope concentration per section. Some penetration profiles were measured employing sputter sectioning techniques using a powerful sputtering device. For details of the device and the experimental procedure, we refer to Ref. 12.

III. RESULTS AND DISCUSSION

If the deposited and/or implanted tracer layer is thin compared with the mean diffusion length, $\sqrt{Dt}$, the distribution after a diffusion anneal is described by the thin-film solution of Fick's second law

$$c(x,t)=\frac{N}{\sqrt{\pi Dt}}\exp\left(-\frac{x^2}{4Dt}\right). \tag{3.1}$$

Here $c(x,t)$ denotes the tracer concentration at a distance x from the surface after diffusion time t, and N is the number of tracer atoms deposited per unit area. D is the tracer diffusion coefficient at temperature T.

Figure 1 shows diffusion penetration profiles for ^{54}Mn and ^{59}Fe in plots of the logarithm of the specific activity versus penetration distance squared. We note that diffusion profiles were followed over several 10 μm and several orders of magnitude in activity decrease by grinder sectioning techniques. To the data we fitted straight lines representing

TABLE I. Diffusion data of ^{54}Mn and ^{59}Fe in *i*-Al-Pd-Mn. D_{Gauss} (D_{erfc}) are D values obtained by fitting the thin film solution of Eq. (3.1) (a complementary error function) to the diffusion profiles.

	T/K	t/s	$D_{\mathrm{Gauss}}/\mathrm{m}^2\ \mathrm{s}^{-1}$	$D_{\mathrm{erfc}}/\mathrm{m}^2\ \mathrm{s}^{-1}$
^{54}Mn	833.4[c]	221 700	(5.35×10^{-16})	6.92×10^{-16}
	875.2[c]	104 400	(3.25×10^{-15})	3.30×10^{-15}
	930.2[c]	62 400	(1.16×10^{-14})	1.43×10^{-14}
	976.2[c]	317 400	4.81×10^{-14}	
	1071.7[c]	3 690	3.50×10^{-13}	
	1122.7[c]	1 800	9.98×10^{-13}	
^{59}Fe	833.3[c]	1 210 020	(2.04×10^{-18})	2.39×10^{-18}
	833.3[b]	1 056 660	(2.59×10^{-18})	3.19×10^{-18}
	920.2[c]	718 440	(5.52×10^{-17})	6.65×10^{-17}
	1023.7[a]	7 200	2.60×10^{-15}	
	1025.2[c]	86 700	2.07×10^{-15}	
	1073.2[c]	7 200	8.95×10^{-15}	
	1074.2[a]	3 600	1.15×10^{-14}	
	1107.2[c]	7 200	1.98×10^{-14}	
	1132.2[c]	7 200	3.64×10^{-14}	

[a] Implantation and sputtering.
[b] Evaporation and sputtering.
[c] Evaporation and grinding.

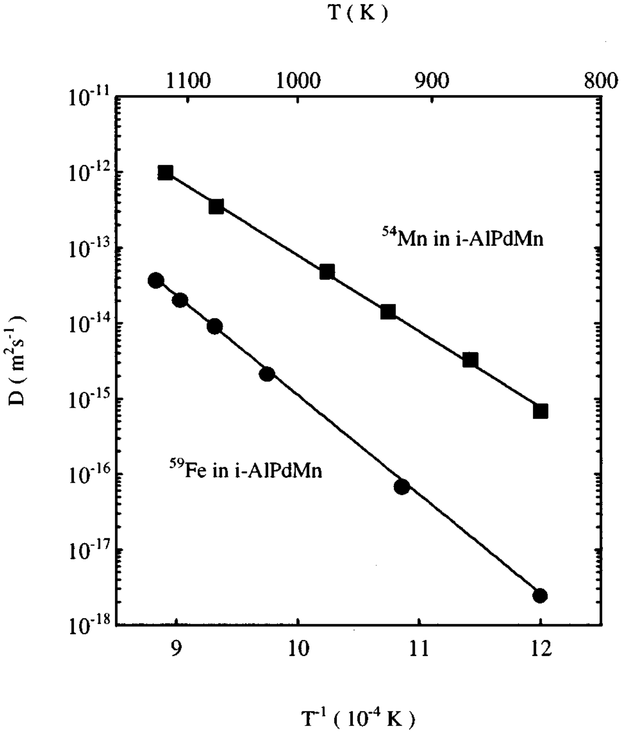

FIG. 3. Temperature dependence of the diffusion coefficient of ^{54}Mn and ^{59}Fe in single quasicrystalline Al-Pd-Mn samples. For activation enthalpies and pre-exponential factors see Eqs. (3.2) and (3.3).

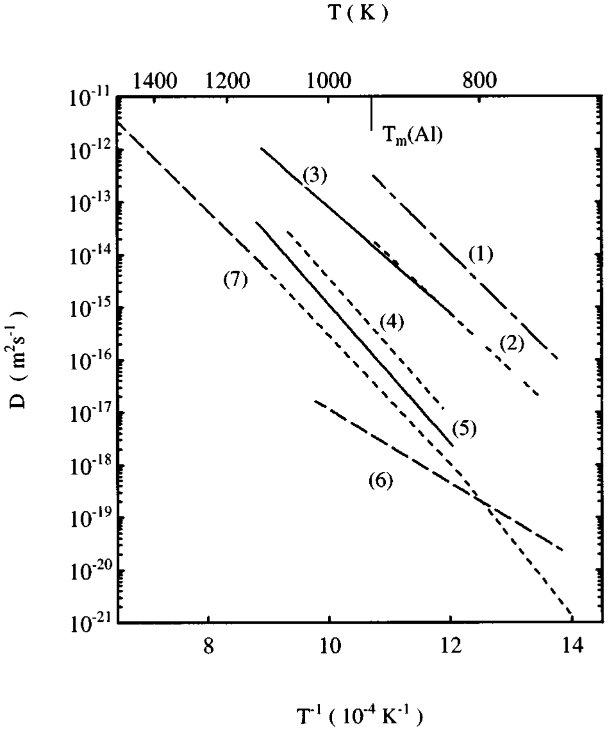

FIG. 4. Temperature dependence of the diffusion coefficient of various materials in comparison with the present data on ^{54}Mn (3) and ^{59}Fe (5) diffusion in quasicrystalline Al-Pd-Mn samples. The following data are included: ^{54}Mn (6) diffusion in polycrystalline icosahedral quasicrystals of an $Al_{72}Pd_{20}Mn_8$ alloy[8]; ^{59}Fe (4) diffusion in $Al_{62}Cu_{25.5}Fe_{12.5}$ polycrystalline icosahedral quasicrystals.[9] In addition data of ^{54}Mn (2) and ^{59}Fe (1) diffusion in aluminium single crystals[13] and of ^{59}Fe (7) in the intermetallic compound Fe_3Al[7] are shown which were obtained in the laboratory at Münster.

Gaussian behavior in accordance with Eq. (3.1) which is characteristic of volume diffusion. Penetration profiles obtained by sputter sectioning are shown in Fig. 2. These profiles indicate some near-surface effects. However, in the deeper penetrating region of the profiles fits by Eq. (3.1) are possible which are displayed as solid lines. The diffusion coefficients obtained thereof are in good agreement with values obtained from deeper penetrating profiles measured by grinder sectioning. In each case at the three lowest temperatures ($\leqslant$ 930.2 K) a slightly better fit could be achieved by using a complementary error function instead of Eq. (3.1). The diffusion coefficients obtained at various temperatures are listed in Table I and plotted in the Arrhenius diagram of Fig. 3. The temperature dependences are described by

$$D=8.91\times10^{-4}\exp\left(-\frac{192.4\ \mathrm{kJ\ mol}^{-1}}{RT}\right)\mathrm{m}^2\mathrm{s}^{-1}. \quad (3.2)$$

for ^{54}Mn self-diffusion and by

$$D=1.63\times10^{-2}\exp\left(-\frac{251.9\ \mathrm{kJ\ mol}^{-1}}{RT}\right)\mathrm{m}^2\mathrm{s}^{-1}. \quad (3.3)$$

for ^{59}Fe diffusion. R is the universal gas constant. These relations correspond to the solid lines displayed in Fig. 3. In Eq. (3.2) and in Eq. (3.3) D values from Table I without brackets were used. If for all temperatures the D values from Gaussian fits (D_{Gauss}) are used we get only slighly different pre-exponential factors (D_0) and activation enthalpies (Q):

^{54}Mn: $D_0 = 1.63\times10^{-3}$ $\mathrm{m^2 s^{-1}}$, $Q = 198.0$ kJ mol^{-1}; ^{59}Fe: $D_0 = 3.09\times10^{-2}$ $\mathrm{m^2 s^{-1}}$, $Q = 257.7$ kJ mol^{-1}.

A comparison of our results with various diffusion data is displayed in Fig. 4. The salient features of this comparison are the following:

(1) According to our results Mn diffusion in Al and in the *i*-Al-Pd-Mn quasicrystal proceed at similar rates.

(2) By contrast, the data reported by Nakajima *et al.*[8] for Mn diffusion in polycrystalline quasicrystals of an $\mathrm{Al_{72}Pd_{20}Mn_8}$ alloy are by orders of magnitude lower. This discrepancy can neither be attributed to the alloy composition, which is almost the same as in our study, nor to the presence of grain boundaries. Grain boundaries are known to act as diffusion short circuits,[5,6] which would enhance and not decrease the overall diffusivity over the volume diffusion value. The diffusion profiles of Nakajima *et al.*[8] have been obtained by sputter sectioning. The studied penetration is typically 300 nm only, which is very shallow even compared to our sputter sectioned profiles. The penetration profiles follow less than one order of magnitude activity decrease and the profiles indicate surface hold-up effects which are often encountered in Al or in Al-based alloys (see, e.g., Ref. 13 for a further discussion). We presume that the data by Nakajima *et al.*[8] are influenced by near-surface effects and not representative for the diffusion behavior in the volume of the quasicrystal. Near-surface effects are also visible in our diffusion profiles, especially in the sputtered ones.[14]

(3) Our results show that diffusion of ^{59}Fe in *i*-Al-Pd-Mn is considerably slower than self-diffusion of Mn; ^{59}Fe diffusion is even much slower in *i*-Al-Pd-Mn than in aluminium single crystals.

(4) Fe diffusion in *i*-Al-Pd-Mn (our results) and in *i*-Al-Cu-Fe[9] proceeds with similar diffusivities.

(5) Fe diffusion in *i*-Al-Pd-Mn and in the intermetallic phase $\mathrm{Fe_3Al}$[7] also proceeds with similar diffusivities.

It is well established that self-diffusion and substitutional solute diffusion in pure metals or solid solution alloys occurs by nearly random motion of vacancies.[5,6] In intermetallics with long-range crystalline order, random vacancy motion would disrupt the equilibrium ordered arrangement of atoms. The present status of diffusion studies and our understanding of diffusion mechanisms in binary intermetallics has recently be reviewed.[7] An atomistic interpretation of diffusion in intermetallics replaces the concept of random vacancy motion by more sophisticated jump sequences of vacancies. Nevertheless, self-diffusion and diffusion of substitutional solute atoms is believed to be mediated by vacant lattice sites. Very little is known about diffusion mechanisms in quasicrystals. Quasicrystals may be considered as intermetallic compounds where translational symmetry is missing. The fact that the diffusion data for quasicrystals presented in Fig. 4 do not show a qualitatively different behavior compared to cases for which vacancy-mediated diffusion is well established also supports the view of vacancy-mediated diffusion in quasicrystals. In addition the activation enthalpies and pre-exponential factors determined in our experiments are not unusual. Significant deviations from the Arrhenius behavior which could be attributed to a phason contribution to diffusion as suggested in Ref. 2 could not be detected within the fairly wide temperature range investigated.

IV. CONCLUSIONS

The present study demonstrates the following:

(1) Reproducible diffusion data for quasicrystals can be obtained with the radiotracer method.

(2) The ''spectrum of diffusivities'' in quasicrystals is not significantly different from that of related crystalline systems in which vacancy-mediated diffusion is generally accepted as the basic mechanism of diffusion.

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[14] W. Sprengel, T. A. Lograsso, and H. Nakajima (unpublished). Very recently Sprengel and Nakajima have repeated experiments on Mn diffusion in *i*-Al-Pd-Mn single quasicrystals. In the investigated temperature range between 870 and 1093 K Mn diffusion is described by an activation enthalpy of 180.8 kJ mol^{-1} and a pre-exponential factor of 3.4×10^{-4} $\mathrm{m^2 s^{-1}}$. The diffusivities are in good agreement with our values.