

## First Low-Temperature Radiotracer Studies of Diffusion in Icosahedral Quasicrystals

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The diffusivities of implanted, radioactive  $^{103}\text{Pd}$  and  $^{195}\text{Au}$  in icosahedral  $\text{Al}_{70.4}\text{Pd}_{20.8}\text{Mn}_{8.8}$  quasicrystals were measured between 810 and 270 °C by a radiotracer technique, where serial sectioning was done by high-precision grinding or ion-beam sputtering. Both diffusion coefficients obey different Arrhenius laws above and below 450 °C. Whereas diffusion above this temperature is explained in terms of a vacancy mechanism that reflects the heterogeneity of the icosahedral structure, diffusion below 450 °C is proposed to occur via a phason-assisted direct mechanism. [S0031-9007(97)05243-5]

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Among the large body of investigations performed on quasicrystals since their discovery [1] in 1984, surprisingly little work has been devoted to the atomic transport [2–10] in these materials, though an understanding of diffusion is of great interest for both their production and technological applications. Sudden interest in the diffusion in quasicrystals has been triggered by the theoretical prediction of Kalugin and Katz [11] that, in these structures, diffusive motion may be mediated by so-called phasons, which are defects that occur where the quasicrystalline matching rules are violated [12]. More specifically, these authors proposed that, in quasicrystals, phason-controlled diffusion may be superimposed on or even predominate over diffusion via vacancies (which normally controls self- and substitutional-solute diffusion in crystalline metals) and should show up by a non-Arrhenius-type temperature dependence of the diffusion coefficients. In the wake of Kalugin and Katz, further theoretical work on phason-related diffusion in quasicrystals has been published (see, e.g., Refs. [13–15]).

The first experimental diffusion study on a quasicrystalline material (Pt diffusion in icosahedral  $\text{Al}_{86}\text{Mn}_{14}$ ) was done by Bøttiger *et al.* [2] by means of Rutherford-backscattering spectrometry. It was followed by a series of investigations on icosahedral Al-Pd-Mn alloys, in which the diffusivities of the radiotracer atoms  $^{54}\text{Mn}$  [3–8],  $^{59}\text{Fe}$  [5,7], and  $^{68}\text{Ge}$  [6,8] were measured, respectively. In a French collaboration [10], the bulk and the grain-boundary contributions to the self-diffusion of  $^{59}\text{Fe}$  in  $\text{Al}_{62}\text{Cu}_{25.5}\text{Fe}_{12.5}$  were separately determined. Finally, also on an icosahedral Al-Cu-Fe alloy, Franchouk and Larikov [9] investigated the diffusion of  $^{24}\text{Na}$  and  $^{59}\text{Co}$  by secondary-ion mass spectroscopy (SIMS). In all cases, the temperature dependences of the diffusivities  $D$  were Arrhenius-type,

$$D = D_0 \exp(-H/kT)$$

( $D_0$  is the preexponential factor,  $H$  is the diffusion enthalpy,  $k$  is Boltzmann's constant, and  $T$  is the absolute temperature), in contrast to the prediction of Kalugin and Katz [11].

Since this Letter aims at contributing to the clarification of *bulk*-diffusion mechanisms in quasicrystals, it has to be taken into account that, in the precedingly mentioned experiments, both polyquasicrystalline specimens [2,3,9,10] and specimens consisting of one or a few grains only (hereafter called "large-grain specimens") [4–8] were used. Whereas for large-grain specimens the preexponential factors  $D_0$  are  $10^{-4} \text{ m}^2 \text{ s}^{-1}$  or larger, for polyquasicrystalline samples much smaller  $D_0$  values ( $\leq 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ) have been reported. (Some early data [2,3] with  $D_0 \leq 10^{-10} \text{ m}^2 \text{ s}^{-1}$  have turned out to be erroneous [6,7].) In the only case in which, in the analysis of diffusion data on polyquasicrystals, bulk and grain-boundary diffusion effects have been separated [10],  $D_0$  for bulk diffusion was found to be larger than  $10^{-4} \text{ m}^2 \text{ s}^{-1}$ . From these findings, we conclude that the preexponential factors of all bulk-diffusion coefficients measured yet on quasicrystals are  $10^{-4} \text{ m}^2 \text{ s}^{-1}$  or somewhat larger. It will be demonstrated below that, taken together with the magnitude of the diffusion enthalpies ( $1.5 \leq H \leq 2.6 \text{ eV}$ ), this may be rationalized in a straightforward way in terms of diffusion via vacancies in the inhomogeneous icosahedral structures.

In the following, we report on novel measurements of the diffusivities of  $^{103}\text{Pd}$  and  $^{195}\text{Au}$  in large-grain icosahedral  $\text{Al}_{70.4}\text{Pd}_{20.8}\text{Mn}_{8.8}$  between 810 and 270 °C, the results of which are compiled in Table I and displayed in Fig. 1.

TABLE I. Bulk diffusion in Al-Pd-Mn alloys and  $\text{Al}_{62}\text{Cu}_{25.5}\text{Fe}_{12.5}$  (last line).

Radiotracer	$D_0$ ( $\text{m}^2 \text{ s}^{-1}$ )	$H$ (eV)
$^{103}\text{Pd}$ (>450 °C)	$(1.2_{-1.0}^{+9.7}) \times 10^{-2}$	$2.32 \pm 0.17$
$^{103}\text{Pd}$ (<450 °C)	$(1.4_{-1.2}^{+11}) \times 10^{-10}$	$1.20 \pm 0.12$
$^{195}\text{Au}$ (>450 °C)	$(8.2_{-2.9}^{+4.5}) \times 10^{-1}$	$2.57 \pm 0.04$
$^{195}\text{Au}$ (<450 °C)	$(4.6_{-4.4}^{+137}) \times 10^{-12}$	$0.90 \pm 0.20$
$^{59}\text{Fe}$ [5,7]	$1.63 \times 10^{-2}$	2.61
$^{68}\text{Ge}$ [6,8]	$1.4 \times 10^{-4}$	1.54
$^{54}\text{Mn}$ [4–8]	$(3.4\text{--}8.91) \times 10^{-4}$	1.88–1.99
$^{59}\text{Fe}$ [10]	$4.5 \times 10^{-2}$	2.55

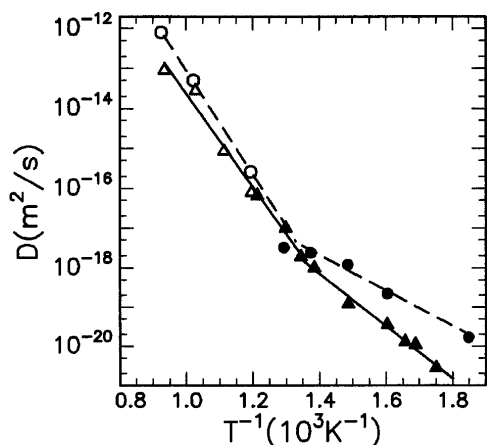


FIG. 1. Arrhenius plots of the diffusion coefficients of  $^{103}\text{Pd}$  (triangles) and  $^{195}\text{Au}$  (circles) in  $\text{Al}_{70.4}\text{Pd}_{20.8}\text{Mn}_{8.8}$ . The underlying diffusion profiles were determined by grinding (empty symbols) or ion-beam sputtering (filled symbols).

Above  $450^\circ\text{C}$ , both diffusion coefficients obey Arrhenius laws with  $D_0 > 10^{-4} \text{ m}^2 \text{ s}^{-1}$  and  $H = 2.3$  and  $2.6 \text{ eV}$ , respectively. This will be shown to be in accordance with a modified vacancy mechanism, as just announced for previous data of this kind. Below  $450^\circ\text{C}$ , both  $D(^{103}\text{Pd})$  and  $D(^{195}\text{Au})$  behave Arrhenius-like, too, but, in this low-temperature regime, the values of  $D_0$  and  $H$  are  $\leq 10^{-10} \text{ m}^2 \text{ s}^{-1}$  and  $\approx 1 \text{ eV}$ , respectively. It is noteworthy that, to our knowledge, this is the first time that radiotracer diffusion measurements on quasicrystals have been extended to diffusion temperatures below  $450^\circ\text{C}$ . Though the small  $D_0$  values below  $450^\circ\text{C}$  resemble those previously observed in inadequate studies on polyquasicrystalline samples, in the present case, deficiencies masking bulk diffusion may be safely excluded. This will become amply clear in the subsequent description of the conduction of our experiments and of the preparation of our diffusion samples. Here, we only mention that our specimens were virtually monoquasicrystalline, that at intermediate temperatures, where precision grinding as well as ion-beam sputtering are applicable for specimen sectioning, both techniques led to the same results, and that the  $D_0$  values ( $> 10^{-4} \text{ m}^2 \text{ s}^{-1}$ ) found above  $450^\circ\text{C}$  indicate conventional bulk-diffusion features.

The starting material for our diffusion specimens was a Czochralski-grown, 75 mm long, and 15 mm thick rod of  $\text{Al}_{70.4}\text{Pd}_{20.8}\text{Mn}_{8.8}$  (chemical analysis) that consisted of four grains whose orientations deviated from each other by less than  $3^\circ$  ( $\gamma$  diffractometry) and which were single-phase face-centered icosahedral (Laue, Debye-Scherrer, and electron diffraction). From this rod, 1 mm thick and otherwise irregularly shaped, large-grain or even monoquasicrystalline specimens were sawn. Since, in the lower part of the diffusion-temperature regime covered in the present investigations, the penetration depths of the radiotracer atoms only amounted to 300 nm or less,

it was important that the specimen surfaces possessed an average roughness  $\leq 3 \text{ nm}$  (image-processing-assisted interferometry), which was maintained during diffusion annealing. This was achieved by a special five-step polishing procedure in which mechanical polishing (in the final step on a soft cloth) with an  $\text{Al}_2\text{O}_3$  suspension (final grain size  $0.3 \mu\text{m}$ ) and chemical polishing with aqueous colloidal silicic acid alternated.

The conventional procedures for the deposition of radiotracer atoms on the specimen surfaces, radiotracer evaporation or dripping on of a solution of radiotracers, were not applicable. Evaporation had to be excluded since the surfaces of the Al-rich specimens are always covered by an oxide layer, whereas the application of acidic solution leads to surface damaging by etching. Therefore, at the mass separator of Bonn University, neutron-activated  $^{103}\text{Pd}$  tracers and, at the on-line isotope separator (ISOLDE) of the European Nuclear Research Center (CERN) in Geneva, radioactive ions, which decay via nuclear reactions into the desired  $^{195}\text{Au}$  radiotracer atoms, were implanted with 60 keV to depths of about 30 nm, i.e., at least in part, beyond an  $\sim 20 \text{ nm}$  thin oxide layer (SIMS and nuclear reaction analysis) inevitably formed on the specimen surfaces during subsequent diffusion annealing.  $^{103}\text{Pd}$  and  $^{195}\text{Au}$  possess half-lives of 17 and 183 days, respectively, which are suitable for diffusion studies.

The specimens were diffusion annealed in a conventional furnace under high-vacuum conditions ( $10^{-8} \text{ mbar}$ ) in the temperature regime  $810\text{--}270^\circ\text{C}$ . The annealing durations ranged from 8 min to 144 h.

The penetration profiles of the radiotracer atoms were determined by serial specimen sectioning and subsequent measuring of the  $\beta$  activity of the sections, which is proportional to the tracer concentrations  $C$  at the corresponding depths  $x$ . Between  $810$  and  $550^\circ\text{C}$  (mean penetration depths  $\approx 10^2\text{--}10^1 \mu\text{m}$ ), the sectioning was

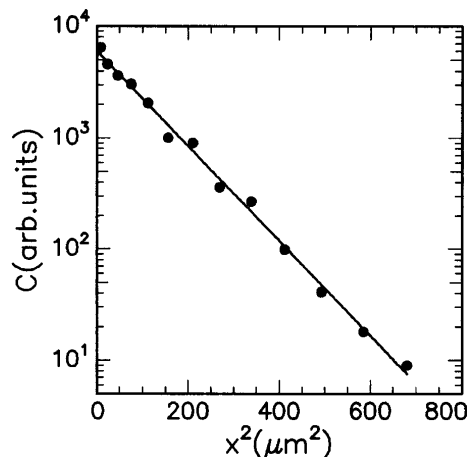


FIG. 2. Diffusion profile of  $^{103}\text{Pd}$  in  $\text{Al}_{70.4}\text{Pd}_{20.8}\text{Mn}_{8.8}$  after annealing for 90 h at  $563^\circ\text{C}$ . Specimen sectioning was done by grinding.

done by high-precision grinding (Fig. 2); between 550 and 270 °C (mean penetration depths  $\approx 10^2$  nm), Ar<sup>+</sup>-beam sputtering was used (Fig. 3). It should be noted that for the diffusivity of <sup>103</sup>Pd at about 550 °C which was determined by grinding and ion-beam sputtering as well the same value was obtained by means of both sectioning techniques (Fig. 1). From this, we conclude that the bends in the  $D-T^{-1}$  Arrhenius lines at 450 °C (Fig. 1) are not an artifact arising from the change of the sectioning technique, as it might seem from exclusive inspection of the <sup>195</sup>Au data.

The extraction of diffusion coefficients from penetration profiles was done in different ways for profiles determined by grinding and sputtering. As indicated by the fact that, in plots of the kind of Fig. 2, grinding-produced diffusion profiles appear as straight lines, these profiles obey the thin-film solution of the diffusion equation, and, thus, the slopes of the lines are equal to  $(4Dt)^{-1}$ , where  $t$  is the duration of diffusion annealing. From sputtering-produced profiles (Fig. 3), one realizes that tracer atoms implanted inside the surface oxide layer ( $x < 0$ ) do not diffuse at all. Therefore, from such diffusion profiles, the diffusion coefficients were determined by exclusively evaluating the penetration-depth regime  $x > 0$ . For this purpose, diffusion-equation solutions were numerically adjusted which fulfil the boundary condition of perfect tracer-atom reflection at  $x = 0$  and reproduce the implantation profiles for  $t = 0$ . Since, for the diffusivity of <sup>103</sup>Pd at about 550 °C, the same value was obtained from both the sputtering-produced profile ( $t = 8$  min) and the grinding-produced profile ( $t = 70$  h) though these refer to totally different diffusion depths ( $20 \lesssim x \lesssim 300$  nm and  $3 \lesssim x \lesssim 26$   $\mu$ m, respectively), it is very unlikely that the bends of the Arrhenius lines in Fig. 1 are due to a structural modification of the specimen surfaces.

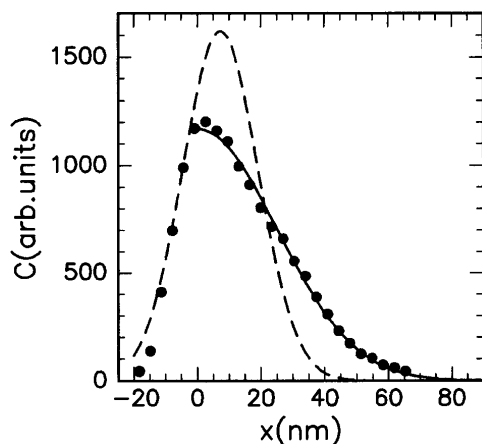


FIG. 3. Diffusion profile of <sup>103</sup>Pd in Al<sub>70.4</sub>Pd<sub>20.8</sub>Mn<sub>8.8</sub> measured with the aid of Ar<sup>+</sup>-beam sputtering after annealing for 20 h at 298 °C (filled circles). The dashed curve shows the shape and location of the implantation profile measured prior to annealing.

A good starting point for the interpretation of the data presented in this Letter (Fig. 1) is Table I, which summarizes the Arrhenius parameters of this work and of those quasicrystal-diffusion data yet reported in the literature which, with a great likelihood, refer to bulk diffusion. It is obvious that, irrespective of the compositions of the quasicrystals and of the chemical nature of the diffusing atoms, all high-temperature data ( $>450$  °C) may be understood in terms of basically the same mechanism, whereas the mechanism that controls <sup>103</sup>Pd and <sup>195</sup>Au diffusion in Al<sub>70.4</sub>Pd<sub>20.8</sub>Mn<sub>8.8</sub> at low temperatures ( $<450$  °C) must be radically different.

We propose that, in the *high-temperature regime*, diffusion in icosahedral alloys is mediated by vacancies. This is supported by the magnitude and sign of the activation volume, +0.67 atomic volumes, deduced by Zumkley *et al.* [7] from the dependence of the diffusivity of <sup>54</sup>Mn in Al<sub>70.4</sub>Pd<sub>21.2</sub>Mn<sub>8.4</sub> on hydrostatic pressure as well as by the  $H$  and  $D_0$  values concerned (Table I). As for the diffusion in Al-Pd-Mn alloys, a closer inspection of the Arrhenius parameters leads us to distinguish between <sup>68</sup>Ge and <sup>54</sup>Mn diffusion on the one hand and <sup>103</sup>Pd, <sup>195</sup>Au, and <sup>59</sup>Fe diffusion on the other hand. The  $D_0$  values for <sup>68</sup>Ge and <sup>54</sup>Mn are in accordance with a normal vacancy mechanism, and the corresponding activation enthalpies, particularly that of <sup>68</sup>Ge, appear to indicate a preference for diffusion in the Al network (cf. the self-diffusion enthalpy of 1.28 eV for Al [16]). By contrast, the  $H$  values for <sup>103</sup>Pd, <sup>195</sup>Au, and <sup>59</sup>Fe are very close to the self-diffusion enthalpy of Pd, 2.7 eV [17], and the corresponding  $D_0$  values distinctly exceed the regime acceptable for a conventional vacancy mechanism. However, these findings may be understood within the framework of a vacancy mechanism that accounts for the heterogeneity of the icosahedral structure. More specifically, one has to assume that <sup>103</sup>Pd, <sup>195</sup>Au, and <sup>59</sup>Fe can undergo vacancy-mediated diffusion in both the Al and the Pd substructure, that the diffusivity is slow in the Pd regions and, thus, Pd-site controlled, and that the Al regions are traversed extremely rapidly. Quantitative modeling of this scenario yields

$$D \approx (D_{0,\text{Pd}}/8) [7 + (A/a)^2] \exp(-H_{\text{Pd}}/kT).$$

Here,  $D_{0,\text{Pd}}$  is the preexponential factor of the diffusion coefficient for vacancy-mediated diffusion in the Pd network,  $H_{\text{Pd}}$  is the sum of the enthalpies of formation and migration for vacancies in these regions, and  $A/a$  is the average distance (in units of the mean nearest-neighbor-atom separation  $a$ ) covered by vacancies in the Al regions. Using a typical value of  $D_{0,\text{Pd}}$  ( $10^{-4}$  m<sup>2</sup> s<sup>-1</sup>), for the diffusion of <sup>103</sup>Pd in Al<sub>70.4</sub>Pd<sub>20.8</sub>Mn<sub>8.8</sub>, for instance, one finds  $A/a \approx 30$ , which is very reasonable in view of the local arrangement of atoms in icosahedral Al-Pd-Mn proposed by Janot [12].

In the *low-temperature regime*, the  $D_0$  values for the diffusion of <sup>103</sup>Pd and <sup>195</sup>Au in Al<sub>70.4</sub>Pd<sub>20.8</sub>Mn<sub>8.8</sub> are extraordinarily small (Fig. 1) and, under no circumstances,

reconcilable with conventional diffusion mechanisms previously invoked for diffusion in crystalline solids. Therefore, we propose that this kind of diffusion is phason related, thus reflecting the specific nature of the icosahedral structure. At first sight, it might seem that our low-temperature data are in accordance with the Kalugin-Katz-type long-range transport of matter mediated by sophisticated sequences of phason flips [11] and that the non-Arrhenius-type behavior expected for this mechanism at higher temperatures is buried under the vacancy contribution. However, this is quite unlikely since the diffusion enthalpies of about 1 eV found for  $^{103}\text{Pd}$  and  $^{195}\text{Au}$  in  $\text{Al}_{70.4}\text{Pd}_{20.8}\text{Mn}_{8.8}$  below 450 °C appear to be too high in view of the smallness of the atomic displacements generated by phason flips [11]. Therefore, we prefer the admittedly speculative interpretation that the low-temperature diffusion of  $^{103}\text{Pd}$  and  $^{195}\text{Au}$  is not phason mediated but phason assisted in the following sense. In the icosahedral  $\text{Al}_{70.4}\text{Pd}_{20.8}\text{Mn}_{8.8}$ , the diffusion of these elements is locked, but it may be temporarily unlocked by collective phason flips. These represent excitations that, within small regions comprising some atomic volumes, increase the atomic order and, thus, provide enough open space for direct (i.e., not defect-mediated) diffusional jumps of the tracer atoms. This picture is a long-range-diffusion modification of one of several alternative interpretations recently offered by Coddens [18] to account for unusual features of localized atomic jumps detected in icosahedral Al-Cu-Fe by means of quasielastic neutron scattering. It implies that, in the expression for the equilibrium fraction  $F^{\text{eq}}$  of unlocked volume

$$F^{\text{eq}} = \exp(\Delta S/k) \exp(-\Delta H/kT),$$

the activation entropy  $\Delta S$  is distinctly negative and the corresponding activation enthalpy  $\Delta H$  is smaller than 1 eV (see above). The occurrence of such entropy-decreasing local fluctuations appears particularly plausible for quasicrystals which are entropy stabilized by random tiling, though this is not a prerequisite. If the diffusivity in the unlocked regions is denoted by

$$d = d_0 \exp(-h/kT),$$

the effective diffusion coefficients of  $^{103}\text{Pd}$  and  $^{195}\text{Au}$  in  $\text{Al}_{70.4}\text{Pd}_{20.8}\text{Mn}_{8.8}$  below 450 °C may be written as

$$D = F^{\text{eq}} d = \exp(\Delta S/k) d_0 \exp[-(\Delta H + h)/kT].$$

Using  $d_0 = 10^{-5} \text{ m}^2 \text{ s}^{-1}$ , which is a typical preexponential factor of  $d$  for direct diffusion, one finds  $-10k \approx$

$\Delta S \approx -15k$ , suggesting that the collective phason flips and, thus, the unlocked regions, comprise 20 to 30 atoms. This, as well as the resulting activation enthalpies  $h \approx 1$  eV for the direct tracer migration in these regions, appears highly reasonable. It is noteworthy that the preceding diffusion mechanism may operate in quasicrystals and approximants, but not in normal crystals with small unit cells, in which phason-flip-like small atomic displacements are not possible.

In summary, it is concluded that above 450 °C the diffusion of  $^{103}\text{Pd}$  and  $^{195}\text{Au}$  in icosahedral  $\text{Al}_{70.4}\text{Pd}_{20.8}\text{Mn}_{8.8}$  is vacancy mediated in an unusual way, whereas the anomalous diffusion behavior at lower temperatures, which has been observed for the first time, is tentatively explained in terms of a direct mechanism that is assisted by collective phason flips.

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