

Low-Temperature Magnetic Aftereffects of Hydrogen Isotopes in Diluted PdFe Alloys

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In diluted PdFe alloys the motion of hydrogen isotopes in the vicinity of substitutional iron atoms has been investigated in the temperature range $40\text{ K} < T < 150\text{ K}$ by means of magnetic-aftereffect and complex-susceptibility measurements. In the temperature ranges $100\text{ K} < T < \infty$ and $60\text{ K} < T < 100\text{ K}$ the relaxation rates of all three isotopes obey Arrhenius laws with an inverse isotope effect of the activation enthalpies in the high-temperature range, and a mixed isotope effect at low temperatures with 0.13 eV for H, 0.12 eV for D, and 0.16 eV for T.

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The motion of hydrogen isotopes in fcc and bcc metals in the whole temperature ranges investigated so far cannot be described by conventional thermally activated processes.^{1,2} This is most clearly demonstrated by the fact that the diffusion coefficients of H isotopes show distinct isotope effects in the preexponential factors and in the activation energies.³⁻⁵ Previous investigations are mainly concerned with bcc metals because these are characterized by large diffusion coefficients (small activation energies), and therefore the contribution of tunneling processes to the H diffusion becomes dominant at higher temperatures than in fcc metals where the activation energies for H diffusion are a factor of 2-3 larger than in bcc metals.

For a study of isotope effects on the motion of H isotopes in fcc metals, therefore, measurements at rather low temperatures should be performed. Palladium seems to be especially suitable for investigations of this kind because this metal is characterized by the lowest activation energy for H diffusion measured so far for fcc metals. Just recently it was shown^{6,7} that in the high-temperature range the diffusion coefficients of the H isotopes show the so-called *inverse* isotope effect with the smallest activation enthalpy of $H^M = 0.19$ eV for tritium and $H^M = 0.23$ eV for hydrogen. Measurements of the activation parameters of H isotopes below room temperature therefore are highly desirable in order to study the transition from the high-temperature range to the low-temperature range where tunneling processes dominate.

Measurements of hydrogen motion at low temperatures in general are impeded as a result of small

H solubilities and the precipitation of the β phase.⁸ Furthermore, only those measuring techniques are useful which allow the measurement of jump frequencies far below 1 s^{-1} . As a result of these restrictions, many of the classical methods applied for the study of H diffusion are excluded.

A rather powerful technique for low-temperature investigations of the hydrogen mobility has been shown to be the method of *magnetic aftereffects* (MAE)⁹⁻¹² For an application of this technique the material investigated should be ferromagnetic and the H atoms should occupy interstitial positions of a lower point-group symmetry than that of the host lattice. Under these conditions the H atoms are characterized by an anisotropic magnetic-interaction energy⁹ depending on the orientation of the symmetry axes of the H interstitial with respect to the direction of the spontaneous magnetization \vec{M}_s . Within domain walls, where \vec{M}_s rotates from one magnetic easy direction to another one, the H isotopes therefore rearrange by reorienting their symmetry axes into positions with the smallest magnetic interaction energy. This process in general is possible by one atomic jump. The thermodynamics of this process and the resulting formation of a stabilization potential of the domain wall has been treated in detail elsewhere.^{9,10,13}

According to the above-mentioned conditions palladium is absolutely inadequate to apply the method of MAE. However, by alloying small amounts of iron this material becomes ferromagnetic. A Curie temperature of $T_C = 150\text{ K}$ is observed for Pd₉₅Fe₅. According to Fig. 1 the alloying element Fe introduces in its neighborhood intersti-

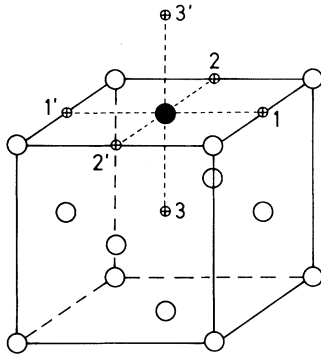


FIG. 1. Model of a tetragonal Fe-H complex in an fcc lattice.

tial sites for H atoms of lower symmetry than in the host lattice. As a further advantage it should be noted that H atoms precipitated in the β phase do not contribute to the MAE because the β phase is nonferromagnetic. Thus the application of the method of MAE becomes possible. Here it should be noted that the present measurements are not comparable to the studies of the diatomic complexes of the type N-H or O-H in bcc metals¹⁴ because in this case both impurities occupy interstitial sites and are bound by an appreciable binding energy.

The MAE in general is measured as a decrease of the initial susceptibility, χ , as a function of time, t , at constant temperature T . Figure 2 shows a series of isothermal relaxation curves of the reciprocal susceptibility (reluctivity) $r(t, T) = 1/\chi(t, T)$ for $\text{Pd}_{95}\text{Fe}_5\text{T}_x$ ($x = 0.013$) after charging with tritium. By these MAE measurements we were able to determine relaxation times as large as $\tau = 20\,000$ s. Smaller relaxation times, in the millisecond range, were determined by resonance measurements of the complex susceptibility in the high-frequency region from the resonance condition $\omega\tau = 1$.

The isothermal relaxation curves were analyzed under the assumption that we deal with a superposition of exponential Debye processes, each being characterized by a relaxation time τ_i which obeys an Arrhenius equation $\tau_i = \tau_0 \exp[Q_i/k_B T]$. It turned out that the $r(t, T)$ isotherms may be fully fitted by a box-type distribution function of activation enthalpies Q_i with limits $Q_1 \leq Q \leq Q_2$ where the preexponential factor τ_0 is held constant, giving

$$r(t, T) = r_0 + \Delta r_s \left[1 + \frac{E_1(t/\tau_1) - E_1(t/\tau_2)}{\ln(\tau_2/\tau_1)} \right]. \quad (1)$$

Here $E_1(x) = \int_x^\infty (e^{-x}/x) dx$, and r_0 and Δr_s corre-

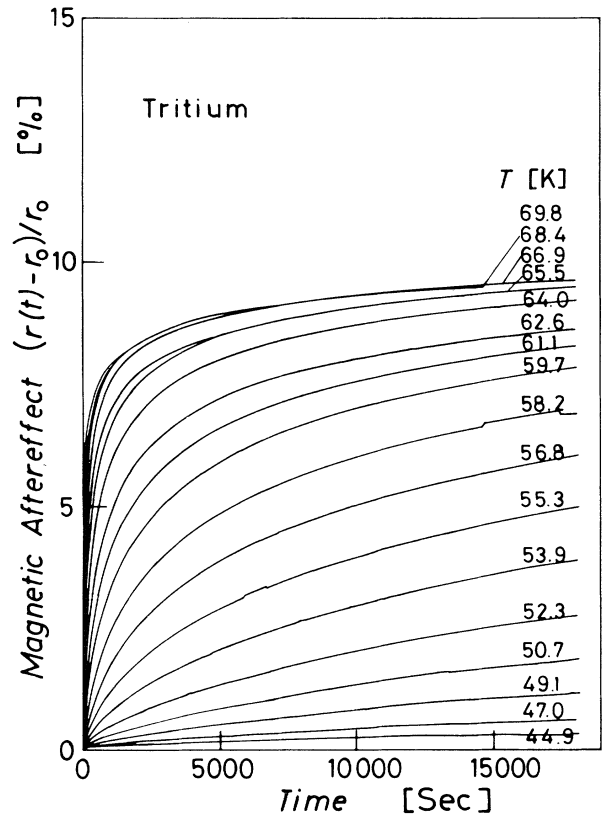


FIG. 2. Isothermal magnetic aftereffect curves of $\text{Pd}_{95}\text{Fe}_5\text{T}_x$ ($x = 0.013$).

spond to the initial reluctivity at $t = 0$, and to the relaxation amplitude, respectively. τ_1 and τ_2 are the lower and upper bounds of the relaxation time spectrum ($\tau_{1,2} = \tau_0 \exp[Q_{1,2}/k_B T]$). From the computer fits of Eq. (1) to the isotherms, the parameters Δr_s , τ_1 , and τ_2 may be determined as a function of temperature. From the numerical results we find for the width of the spectrum $\Delta Q = Q_2 - Q_1 = k_B T \ln(\tau_2/\tau_1) \sim 3kT$.

Furthermore, we have measured the annealing behavior of the relaxation amplitude, Δr_s , for $\text{Pd}_{95}\text{Fe}_5$ and $\text{Pd}_{92.5}\text{Fe}_{7.5}$ by isothermal and isochronal annealing runs in the temperature range of 300–400 K. It turned out that for both alloys the annealing is governed by an activation energy of 0.23 ± 0.015 eV in agreement with previous results.¹⁵ This activation energy is in good agreement with the migration energy of H in pure Pd. It is therefore justified to assume that the trapping energy of H at substitutional Fe in Pd is smaller than 0.01 eV. Consequently we may compare the relaxation time, $\bar{\tau}_{\text{rel}} = (\tau_1 \tau_2)^{1/2}$, as determined by MAE, with the mean time of residence, $\bar{\tau}$, of a H atom on an octahedral site, where $\bar{\tau}$ is derived from the dif-

fusion coefficient according to $D = a^2/(12\bar{\tau})$ (a is the lattice parameter). As a result of the small binding energies of H to Fe atoms the measured MAE is mainly due to statistically formed Fe-H pairs.

From a solution of the rate equations for the hopping processes of the H atoms around the Fe atom, taking into account transitions between nearest-neighbor interstitial sites and between nearest-neighbor and next-nearest-neighbor interstitial sites, under the assumption of zero binding energy, it is found that the relaxation time of the MAE, $\bar{\tau}_{rel}$, is related to $\bar{\tau}$ by $\bar{\tau} = (13/12)\bar{\tau}_{rel}$. Inserting this result into the equation for D we obtain $D = a^2/(13\bar{\tau}_{rel})$. For a comparison of the experimental results we have represented in Fig. 3 the jump frequencies $\bar{\nu} = 1/\bar{\tau}$ as obtained by other authors from NMR, permeation, and mechanical-relaxation experiments in the Pd-H system, together with the jump frequencies $\bar{\nu}_{rel} = 12/(13\bar{\tau}_{rel})$ derived from the MAE of diluted PdFe-H alloys.

From the temperature dependence of $\bar{\nu}$ and $\bar{\nu}_{rel}$ shown in Fig. 3 it is tempting to distinguish three temperature ranges which may be attributed to characteristic diffusion mechanisms, developed previously for the diffusion of light particles.¹⁶⁻¹⁹

Region I. ($T > 100$ K)—In this temperature range, now expanded down to 120 K as a result of our complex-susceptibility measurements, an Arrhenius law

$$\nu = \nu_0^I \exp(-H^I/kT), \quad (2)$$

holds for the jump frequency of H atoms. The activation enthalpy reveals a significant isotope effect with activation enthalpy $H_H^I = 0.23$ eV, $H_D^I = 0.21$ eV, $H_T^I = 0.19$ eV for the isotopes, hydrogen, deuterium, tritium. This inverse isotope effect is attributed to the different energy levels of the isotopes in the ground-state and the saddle-point configurations. As a result of their small atomic mass the H atoms respond adiabatically to the vibrations of the host lattice.

For $T \rightarrow \infty$ all three isotopes seem to extrapolate to the same value of D or ν , leading to a preexponential factor of $\nu_0^I = \tau_0^{-1} \approx 1.9 \times 10^{12} \text{ s}^{-1}$ which is comparable to the Debye frequency, $\nu_D = 6 \times 10^{12} \text{ s}^{-1}$. This value ν_D has been determined from $\nu_D = k_B \Theta_D/h$ with the Debye temperature $\Theta_D = 275$ K.

Region II. ($60 \text{ K} < T < 100 \text{ K}$)—In this temperature range the hopping of the H isotopes occurs predominantly by incoherent, phonon-assisted tunneling processes. The activation energy of this process corresponds to a lattice activation enthalpy, H_a , which is required to produce coincident energy lev-

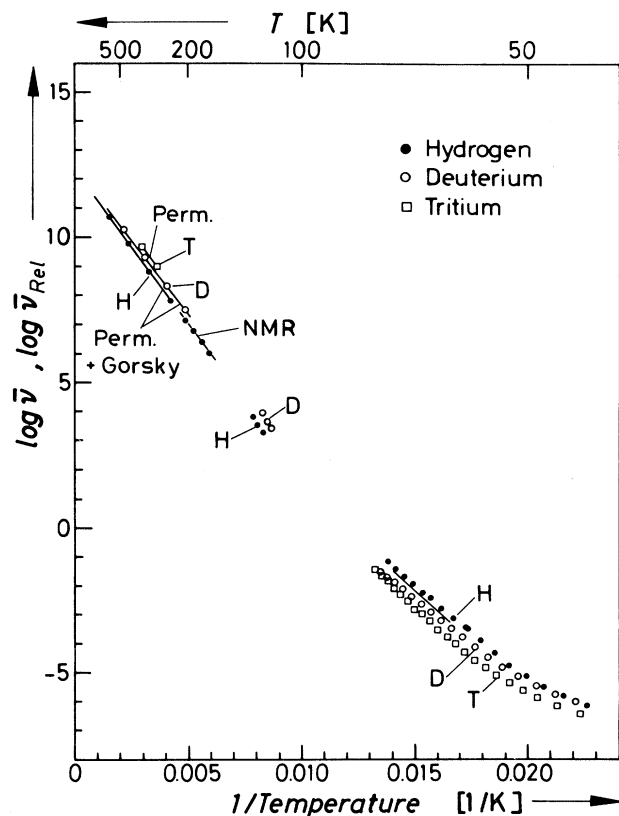


FIG. 3. Arrhenius plot of jump frequencies, $\bar{\nu}_{rel}$, of H isotopes in Pd₉₅Fe₅ and of $\bar{\nu}$ in Pd as obtained by different measuring techniques. Full circles represent hydrogen; open circles, deuterium; open squares, tritium. The present results below 80 K and around 130 K were obtained by MAE and complex-susceptibility measurements, respectively. The full line between 50 and 60 K results from elastic aftereffect measurements (Ref. 22). The results above 130 K are due to NMR measurements of the longitudinal spin-lattice relaxation time in PdH_x ($x = 0.74$) (Ref. 22), as well as to permeation and Gorsky-effect measurements for H and D (Ref. 6), and to permeation measurements of tritium (Ref. 7).

els in neighboring potential wells of the originally self-trapped interstitial atom. In the multiphonon regime of this temperature range according to Flynn and Stoneham¹⁶ the jump frequency for ground-state transitions is given by

$$\nu = (2\hbar)^{-1} (\pi/H_a^I k_B T)^{1/2} |J_{inc}^0|^2 \times \exp[-H_a^I/k_B T], \quad (3)$$

where J_{inc}^0 corresponds to the tunneling matrix element in the Condon approximation. The lattice activation enthalpy H_a for the three isotopes are given

by

$$H_{a,H}^{II} = 0.13 \text{ eV}, \quad H_{a,D}^{II} = 0.12 \text{ eV},$$

$$H_{a,T}^{II} = 0.16 \text{ eV},$$

with average preexponential factors of

$$\nu_{0,H}^{II} = 8.3 \times 10^7 \text{ s}^{-1}, \quad \nu_{0,D}^{II} = 6.25 \times 10^6 \text{ s}^{-1},$$

$$\nu_{0,T}^{II} = 1.0 \times 10^9 \text{ s}^{-1}.$$

If we determine the transition temperature between the Arrhenius regions I and II we find for hydrogen $T_H^{II} = 100 \text{ K}$; for deuterium $T_D^{II} = 75 \text{ K}$, and for tritium $T_T^{II} = 65 \text{ K}$. In fact such a behavior is expected because a larger isotope mass shifts the dominance of tunneling processes to lower temperatures. Here it should be noted that the activation enthalpy H_a^{II} in the Flynn-Stoneham approximation¹⁶ should be approximately independent of the isotope mass. In contrast to this, the experimental results indicate a significant isotope effect pointing to the fact that tunneling processes between ground states and excited states are of importance.

Region III. ($T < 60 \text{ K}$)—In this temperature range the falloff of the jump frequencies is further reduced. According to current theories of light-particle diffusion¹⁷⁻²⁰ we may suggest that we are dealing with a transition from the multiphonon processes to the few-phonon ground-state-to-ground-state tunneling regime. As shown by Teichler and Seeger²¹ under certain conditions one-phonon processes may become dominant in this low-temperature region.

According to the present results the isotope effects of the preexponential factors neither in the high-temperature nor in the low-temperature range obey a $\sqrt{m_H}:\sqrt{m_D}:\sqrt{m_T}$ law as suggested for a classical impurity diffusion mechanism.² Instead, the preexponential factor in the high-temperature range seems to be related more likely to the Debye frequency of the matrix atoms than to the local vibration frequencies of H isotopes. At low temperatures the observed small preexponential factors of 10^7 – 10^9 s^{-1} are proposed to be determined by the

tunneling matrix elements between coincident energy levels in neighboring potential wells.

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