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Determination of Interstitial Sites for Localized Diffusion from Interference of Mössbauer γ Radiation

W. Petry and G. Vogl
Freie Universität Berlin, D-1000 Berlin 33, Germany, and Hahn-Meitner-Institut, D-1000 Berlin 39, Germany

and

W. Mansel
Physik Department, Technische Universität München, D-8046 Garching, Germany

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By Mössbauer spectroscopy, the anisotropy of recoilless γ radiation emitted from a jumping atom is observed. The set of interstitial sites is determined for localized diffusion of Fe in an interstitial cage in Al. From the temperature dependence of the broadening of the Mössbauer resonance 18 (± 1) meV is obtained for the activation energy of this process.

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Mössbauer spectroscopy has been used to study the microscopic environment of an ^{57}Fe (mother isotope ^{57}Co) impurity in electron-irradiated aluminum.[1] Interstitial atoms trapped at these probe impurities give rise to a separate resonance line. Particularly interesting is the dynamics of the iron atom after trapping of an interstitial: First measurements on polycrystalline samples[2] showed that the recoilless fraction is strongly temperature dependent and decreases by more than a factor of 4 in a narrow temperature range around 17 K. This strong decrease in the recoilless fraction has been attributed to the thermal activation of a localized diffusional motion in a so-called interstitial cage. As a consequence of the jumps of the Mössbauer atom in the cage, in measurements on a *single crystal* one expects an anisotropy of the recoilless γ radiation caused by the interference of parts of the wave train of one chopped Mössbauer γ quantum. In the present paper we report about the first observation of this anisotropy of recoilless γ radiation emitted by a jumping atom. We can thus determine the arrangement of sites occupied alternatively by a diffusing Mössbauer atom. In addition, we are able to follow the temperature dependence of the broadening of a fraction of the Mössbauer spectrum and can thus clearly prove the existence of the cage diffusion process.

An aluminum single crystal was doped with about 0.5 at. ppm ^{57}Co by diffusion at about 925 K. γ diffractometry, autoradiography, and Mössbauer spectroscopy proved low mosaic spread (14 min) of the single crystal and homogeneous distribution as well as substitutional sites for the ^{57}Co atoms. Interstitials were then produced by irradiations with 3-MeV electrons with fluences of the order of $10^{18}/\mathrm{cm}^2$. The irradiations were performed at 100 K; at this temperature the interstitials were mobile and could be trapped by the ^{57}Co impurities. After each irradiation Mössbauer spectra were measured in different crystal directions at temperatures varying from 4.2 to 200 K.

As mentioned above the recoilless fraction for ^{57}Fe, after trapping of an interstitial, decreases strongly in a narrow temperature range around 17 K. At 4.2 K, the recoilless fraction f is isotropic ($f = 0.89$), whereas at temperatures sufficiently above 17 K, f becomes anisotropic. Figure 1 (top panel) shows the anisotropy of that part of the recoilless fraction $f(k)$ which is due to trapped single interstitials (after correction for multiple interstitial trapping[3]). The measurements were performed at 25.5 K, the angular resolution was ±6°. The experimentally determined decay of $f(k)$ is largest and equal in the directions $\langle 111\rangle$ and $\langle 110\rangle$ and smaller in the $\langle 100\rangle$ direction.

The anisotropy is caused by the set of sites occupied alternatively by the jumping atom. In order to get information about the arrangement of the jump sites one has to compare the experimental anisotropy with the results of model calculations of the emission probability. The probability $w_e(\omega, k)$ for the emission of a γ quantum with an energy $E_0 + \hbar\omega$ (with E_0 the energy difference between the excited and ground states of the nucleus) and a momentum $\hbar\vec{k}$ (with $k = E_0/\hbar c$) for a discrete-jump model is given by

$$w_e(\omega, \vec{k}) = (\tfrac{1}{2}\pi\hbar) f_0 \int_{-\infty}^{\infty} dt \exp[-i\omega t - (\Gamma |t|/2\hbar)] \sum_{m,n}^{N} \exp[i\vec{k}\cdot(\vec{R}_m - \vec{R}_n)]\, G_s(\vec{R}_m, t\,|\,\vec{R}_n, 0). \tag{1}$$

Here f_0 is the Debye-Waller factor due to thermal vibrations, Γ is the natural line width of the excited nuclear state, $\vec{R}_m, \vec{R}_n$ are the N corner positions of the interstitial cage, and $G_s(\vec{R}_m, t|\vec{R}_n, 0)$ is the self-correlation function of the jump process. In the limit of many jumps during the lifetime of the excited Mössbauer state the probability to find the ^{57}Fe atom at one of the N sites of the cage is $1/N$. Thus the Fourier transform of the self-correlation function reduces to

$$\sum_{m,n}^{N} \exp[i\vec{k}\cdot(\vec{R}_m - \vec{R}_n)]\, G_s(\vec{R}_m, t|\vec{R}_n, 0) = |N^{-1} \sum_{n=1}^{N} \exp[i\vec{k}\cdot\vec{R}_n]|^2. \tag{2}$$

Therefore, the emission probability $w_e(\omega, \vec{k})$ reduces to a Lorentzian function with natural width Γ and intensity

$$f(\vec{k}) = f_0 |N^{-1} \sum_{n=1}^{N} \exp(i\vec{k}\cdot\vec{R}_n)|^2. \tag{3}$$

Equation (3) corresponds to the conditions for x-ray diffraction leading to Bragg reflexes; thus a measurement of $f(k)$ allows us to determine the geometry of the cage in an analogous way as by x-ray scattering by static crystal lattices. Since only very few sites, namely the corners of one cage, contribute to the interference, we do not get sharp Bragg peaks but only an anisotropic distribution of intensity. It is important to note that the cage sites do not form a static lattice since only *one* ^{57}Fe atom jumps between these possible sites.

A cage must consist of equivalent sites in the fcc cell. We specify a cage by the direction from its center to one of the corner positions. The simplest arrangement is a ⟨111⟩ tetrahedron (number of corners $N = 4$), others are the ⟨100⟩ octahedron ($N = 6$), the ⟨111⟩ cube ($N = 8$), and further on polyhedrons with N equal to or larger than 12. Figure 1 (bottom) shows, as examples, the results of calculations from two possible cages, the ⟨111⟩ cube cage and the ⟨100⟩ octahedron cage. A comparison of measured and calculated anisotropy for all possible cages shows the following: (i) Cages with more than twenty-four positions give negligible anisotropy not in agreement with our experimental results. (ii) Only the ⟨111⟩ cube cage is consistent with the measured anisotropy between ⟨100⟩ and ⟨110⟩ as well as with the flat region between ⟨110⟩ and ⟨111⟩. (iii) The magnitude of the anisotropy is very sensitive to the distance b between the center and the corners of the cage; therefore, b can be determined within rath-

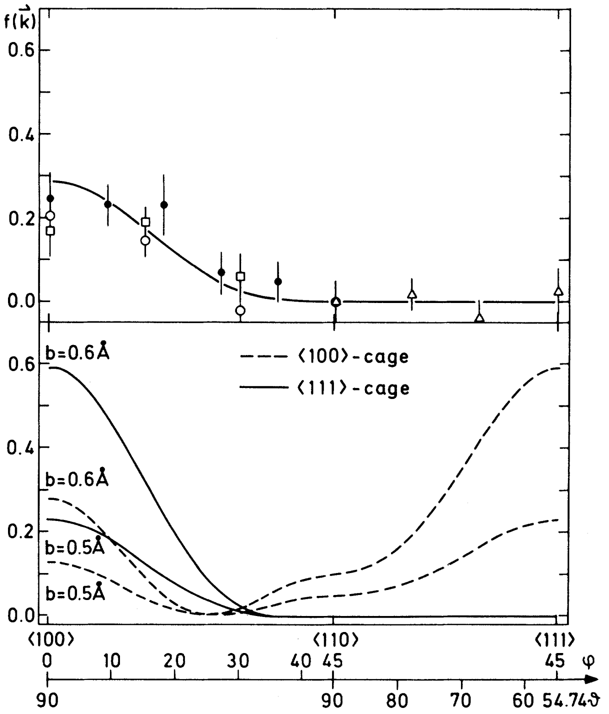

FIG. 1. Anisotropy of the recoilless fraction $f(\vec{k})$ of ^{57}Fe atoms with trapped single interstitials. Top: experimental results (measuring temperature 25.5 K, angular resolution ± 6°). Different runs are designated by different symbols. Bottom: calculations for ⟨111⟩ cube cage and ⟨100⟩ octahedron cage. b is the distance from the cage center to one of the sites. The solid line in the top figure is obtained by fitting the data with the convolution of Eq. (3) for the ⟨111⟩ cube cage (with $b = 0.52$ Å) and the resolution function of the spectrometers.

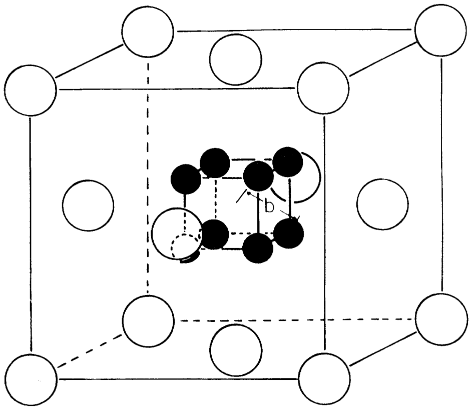

FIG. 2. The eight possible interstitial sites for an Fe atom (closed dots) in the ⟨111⟩ cube cage in Al (open dots).

er close limits: $b = 0.52\ (\pm 0.02)$ Å. Thus we have the following result: Interstitial trapping leads to squeezing the iron atom out of its originally substitutional position into one of the interstitial positions shown in Fig. 2. The configuration of iron after trapping an interstitial is different from the ⟨100⟩ mixed dumbbell tentatively proposed in Ref. 2 in analogy to the self-interstitial dumbbell configuration[5] and channeling results from Al containing Mn, Cu, Ag, or Zn[6] impurities. More recently also Rehn, Robrock, and Jacques have interpreted their internal-friction results on *Al*Fe as noncompatible with the ⟨100⟩ mixed dumbbell.[7]

Equation (3) applies to the limit of many jumps of the ^{57}Fe atom during the lifetime of the Mössbauer excited state. However, in the case of only one or a few jumps of the ^{57}Fe atom during the lifetime one must expect an additional contribution to the recoilless resonance whose width increases with rising temperature. The line broadening $\Delta\Gamma$ is principally due to the Heisenberg relation $\Delta\Gamma \propto \hbar/\tau_j$ where τ_j is the mean time between jumps. This line broadening $\Delta\Gamma$ has already been observed for long-range diffusion processes in polycrystals.[8] For localized diffusion among a limited number of sites the complete solution of Eq. (1) shows[9] that the Mössbauer spectrum decomposes into two (or even more) lines, their relative intensities depending on the direction of observation. One line remains narrow even during fast jumping; this corresponds to the intensity as given by Eq. (3). The broadening $\Delta\Gamma$ of the rest must be proportional to the jump frequency $1/\tau_j$, where $\tau_j = \tau_0 e^{U/kT}$. Here $1/\tau_0$ is the attempt frequency and U the activation energy to overcome the barrier for a jump into a neighbor position. The line broadening can be most clearly detected in the directions where $f(\vec{k})$ approaches zero during fast jumping (e.g., ⟨110⟩ or ⟨111⟩ according to Fig. 1). In these directions the full intensity must show the broadening. Mössbauer spectra in ⟨110⟩ direction of ^{57}Fe atoms with trapped single interstitials at various temperatures (Fig. 3) show that in the region of the fast decay of $f(\vec{k})$ the line width indeed increases drastically. Plotting the increasing line width on a logarithmic scale versus $1/T$ (Fig. 4) yields a straight line proving the thermal activation of the jumps. From the slope of the Arrhenius plot we determine the activation energy $U = 18\ (\pm 1)$ meV and from the y-axial section we get the attempt frequency $1/\tau_0 = 10^{12(\pm 1)}$/s.

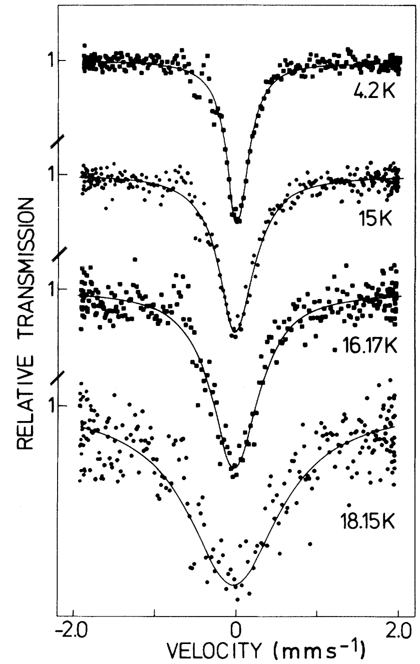

FIG. 3. Mössbauer spectra due to ^{57}Fe in Al at various temperatures in ⟨110⟩ direction after trapping single interstitials (absorber: *Pd* 1 at.% ^{57}Fe at room temperature). Mössbauer fractions due to substitutional ^{57}Fe atoms and ^{57}Fe atoms with trapped multiple interstitials are only weakly temperature dependent and have been subtracted from the measured spectra. The maximum resonance depths are 1.5% at 4.2 K, 1.0% at 15 K, 0.8% at 16.17 K, and 0.3% at 18.15 K.

The defect line has a small quadrupole splitting which due to relaxation will approach zero when the jump rate increases.[10] Because of the low magnitude of the quadrupole interaction in the

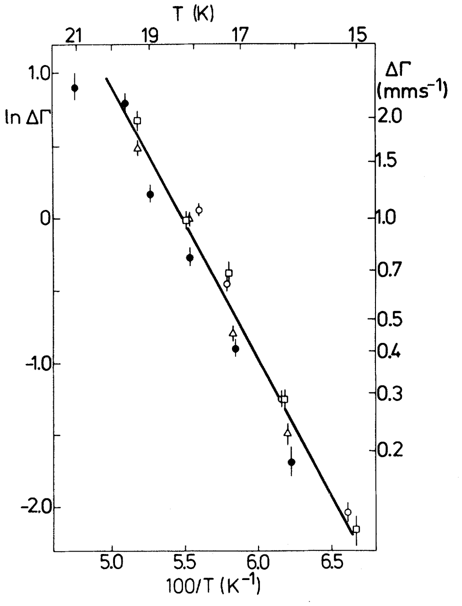

FIG. 4. Temperature dependence of line broadening in the ⟨110⟩ direction. The values correspond to the spectra of Fig. 3. The different symbols correspond to different runs (same as in Fig. 1).

present system, this effect is small and will not be discussed.

The experiment reported here is the base for an application of more general interest: The geometry and activation energy of long-range diffusion mechanisms (diffusion via vacancies, via interstitials, etc.) can be determined from similar experiments performed on a single crystal close to the melting point. Such experiments are in progress.[11]

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