

### Local Atomic-Jump Process of Iron in $\alpha$ -Zr

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After recoil implantation of Coulomb-excited  $^{57}\text{Fe}$  into  $\alpha$ -Zr at 24 K, 30% of the implanted atoms end up on interstitial positions where they experience large electric field gradients. Between 40 and 100 K the quadrupole splitting shrinks by a factor of 2 accompanied by a sharp decrease of the line intensity. This effect is interpreted as a localized diffusion of the Fe atoms jumping in the octahedral cage of the hcp Zr lattice.

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A setup for in-beam Mössbauer spectroscopy combining Coulomb excitation and recoil implantation has been developed allowing high-precision experiments for the study of atomic-jump and diffusion processes.<sup>1,2</sup> This technique opens the way for the study of systems with small or even vanishing solubility of the Fe Mössbauer atoms.

Solid solutions of Fe in Zr are particularly attractive for diffusion studies because in both phases of Zr, hexagonal  $\alpha$ -Zr stable up to 860°C and bcc  $\beta$ -Zr, Fe diffusion is very fast. From tracer diffusion studies it has been deduced<sup>3</sup> that Fe diffusion in  $\alpha$ -Zr is 6 orders of magnitude faster than self-diffusion. It is supposed that fast impurity diffusion is—at least partially—due to impurities on interstitial sites, but no definite experimental proof exists. In this study we have therefore implanted Fe atoms into  $\alpha$ -Zr in the expectation of finding part of the implanted atoms on interstitial sites.

We use Mössbauer spectroscopy to study diffusion in a microscopic way. With Mössbauer spectroscopy, atomic jumps can be investigated via quasielastic line broadening and/or relaxation of monopole and quadrupole interactions.<sup>4</sup> The in-beam Mössbauer technique has been briefly described before.<sup>1</sup> It consists of the following three steps: (1) excitation of the 14.4-keV  $^{57}\text{Fe}$  nuclear level (Mössbauer level) in the target ( $^{57}\text{Fe}$  foil) via Coulomb interaction with a pulsed heavy-ion beam ( $^{40}\text{Ar}$ , 110 MeV); (2) ejection of  $^{57}\text{Fe}$  atoms and recoil implantation into specimens; (3) measurement of a Mössbauer spectrum within 30 to 400 ns after implantation with use of parallel-plate avalanche detector, repeated after every beam burst.

Zirconium foils with a thickness of 10  $\mu\text{m}$  were prepared from the same material as had been used for the study on anomalously fast diffusion of Fe in bcc  $\beta$ -Zr.<sup>5</sup> The foils were annealed at 700°C for 2 h under UHV ( $5 \times 10^{-7}$  Pa) and attached to a specimen holder.

A typical Mössbauer spectrum measured at 24 K after the recoil implantation of  $^{57}\text{Fe}$  into  $\alpha$ -Zr is shown in Fig.

1(a). The fitting parameters for the spectrum are summarized in Table I. The main line has a large relative intensity (65% of all components) and an unresolved quadrupole splitting ( $\approx 0.1$  mm/s) much smaller than that of the other components. The doublet 1 at the right side of the main line in Fig. 1(a) has the relative intensi-

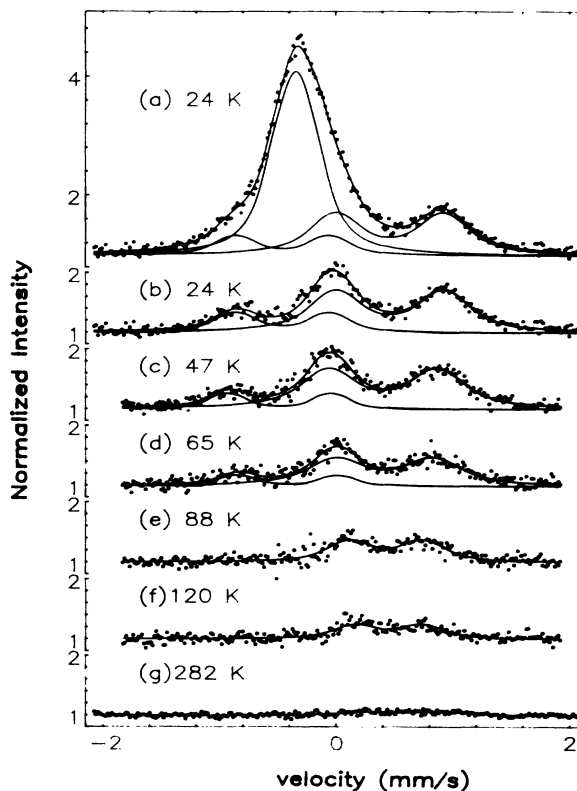


FIG. 1. (a) Mössbauer spectrum of  $^{57}\text{Fe}$  implanted into  $\alpha$ -Zr at 24 K. Note that the implantation and measuring temperatures are identical. (b)–(g) Satellite doublets in the Mössbauer spectra measured at various temperatures. Each spectrum was obtained by subtraction of the main line.

TABLE I. Fit parameters of the Mössbauer spectrum obtained at 24 K. Center shift relative to iron at room temperature.

	Relative intensity (%)	Quadrupole splitting $\Delta E_q$ (mm/s)	Center shift $\delta$ (mm/s)
Main line	65(5)	0.10(5)	-0.34(1)
Doublet (1)	30(3)	0.95(5)	+0.40(5)
Doublet (2)	5(2)	0.80(10)	-0.45(10)

ty of 30%, a large quadrupole splitting of 0.95 mm/s, and a more positive center shift (sum of isomer shift and second-order Doppler shift) than the main line. The doublet 2 at the left side of the main line (relative intensity only about 5%) also has a large quadrupole splitting but a more negative center shift.

In order to show the satellite doublets and their behavior with increasing temperature, the main line was subtracted from each of the spectra. The results are shown in Figs. 1(b)–1(g). The temperature dependences of the relative intensities (resonance areas) of the components differ strongly [Fig. 2(a)]: Whereas the intensity of the main line varies with temperature in a Debye-Waller-factor-like way ( $\Theta_D=200$  K), the intensity of doublet 1 decreases strongly with increasing temperature in the range from about 40 to 100 K. Simultaneously the quadrupole splitting of the doublet strongly decreases between 40 and 100 K from 0.95 to 0.5 mm/s. At higher temperatures it decreases only weakly up to 360 K. The unresolved splitting of the main line nearly stays constant [Fig. 2(b)]. The temperature dependence of both the center position of the main line and the center of doublet 1 follows the usual second-order Doppler shift [Fig. 2(c)]. Because of its small intensity, no definite temperature behavior can be measured for doublet 2.

The main line can be interpreted as due to Fe atoms on substitutional sites of the Zr lattice: As mentioned before, the line intensity follows a usual Debye model with a temperature  $\Theta_D=200(20)$  K. The small quadrupole splitting is similar to values found in other hcp transition metals with similar  $c/a$  ratios.<sup>6</sup> In earlier work<sup>7,8</sup> on <sup>57</sup>Fe atoms in Zr, conventional source and/or absorber preparation (including low-energy implantation at 70 keV) has led to unsatisfactory linewidth and/or hyperfine parameters which appear to represent special phases of the Fe-Zr system like Zr<sub>2</sub>Fe.<sup>9</sup> Evidently the solubility of Fe in  $\alpha$ -Zr is so low that we suppose that formerly published values are not attributable to isolated Fe atoms in Zr. On the other hand, our in-beam technique is free from these problems because of an extremely small dose of Fe (less than  $10^{10}$  ions/cm<sup>2</sup>) and the deep implantation covering several micrometers.

Doublet 1 is of central importance in our work. We assign it to Fe atoms directly implanted into interstitial

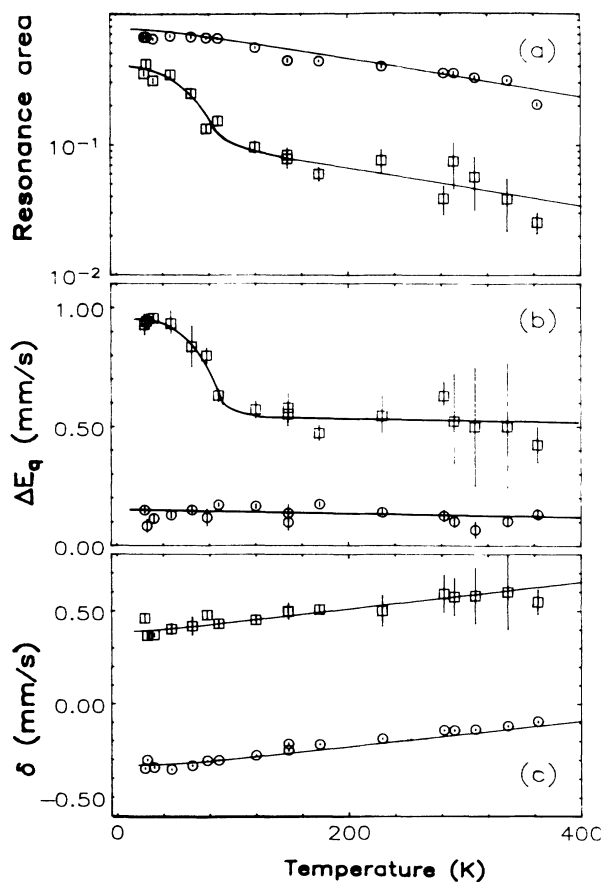


FIG. 2. Temperature dependences of (a) normalized resonance areas, (b) quadrupole splittings, and (c) center shifts for the main line (circles) and doublet 1 (squares).

sites for the following reasons: (i) the strongly positive center shift, reflecting a higher electron density at this lattice position relative to the substitutional site; (ii) the very large quadrupole splitting, indicating the accompanying charge perturbation in very close distance to the probe atom; and (iii) the strong decay of the apparent line intensity with temperature, which will be discussed below in conjunction with the temperature dependence of the quadrupole splitting.

The very small doublet 2 to the left of the main line will not be discussed here because details are difficult to ascertain because of its very small intensity. It is, however, interesting to note that this doublet completely disappears around 70 K.

In what follows we concentrate on doublet 1 which henceforth we shall call just "doublet." The simultaneous decay of the line intensity and the quadrupole splitting can be understood if one assumes that the Fe atoms perform fast jumps in a localized region of the Zr lattice. Very little is known on geometrical configurations of isolated interstitials in hcp metals. Since the largest available space in the hcp structure is the octahedral position,

we propose the following model: At low temperature the Fe atoms sit at "off-center" (asymmetrical) positions around the octahedral interstitial site (see Fig. 3). At high temperature the Fe interstitials can jump between these equivalent positions (in a "cage") in an analogous way as known for Fe atoms on interstitial sites in fcc Al.<sup>1,10</sup>

The model has the following consequences:

With Mössbauer spectroscopy the cage jumps become observable at about 40 K when the jump frequency  $\nu$  reaches values of the order of the reciprocal lifetime of the 14.4-keV nuclear level ( $1/100 \text{ ns} = 10^7/\text{s}$ ). From the temperature at which the intensity decay is strongest with  $\nu = \nu_0 \exp(-E/k_B T)$  (where  $\nu_0$  is an attempt frequency assumed  $10^{12}/\text{s}$ ), the activation energy  $E$  of the cage jumps can be roughly estimated as  $E = 0.07(1) \text{ eV}$ .

At high temperatures where the cage jumps of the interstitials are much faster than the reciprocal lifetime, the apparent intensity of the doublet is reduced to the component which remains narrow,<sup>11</sup>

$$f_0(\mathbf{k}) = |Z^{-1} \sum_n \exp(i\mathbf{k} \cdot \mathbf{R}_n)|^2,$$

the other components becoming so broad that they disappear in the background. Here  $Z$  is the number of equivalent cage sites ( $Z=6$  in our model),  $\mathbf{k}$  is the  $\gamma$  wave vector, and  $\mathbf{R}_n$  are the position vectors of the different cage sites. For a polycrystalline specimen, as we have here,  $f_0(\mathbf{k})$  has to be averaged over all possible orientations of  $\mathbf{k}$  relative to the crystal axes. The high-temperature limit is reached around 100 K.

Since the size of the cage determines the high-temperature limit of the apparent intensity of the doublet, an exact measurement of the intensity can, in principle, yield the jump distance between the equivalent positions of the cage. From the present data we can estimate the jump distance as  $0.35(5) \text{ \AA}$ . Two simplifications have been made, however, to arrive at this value: (i) Because of the hexagonal symmetry of Zr the cage may contain two different jump lengths between nearest neighbors (parallel to the basal plane and out of

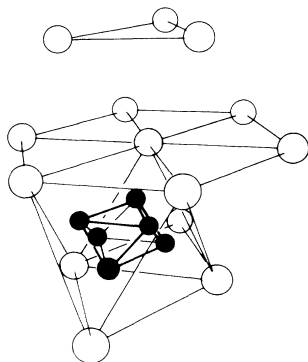


FIG. 3. Octahedral interstitial sites in  $\alpha$ -Zr. The cage is enlarged for the sake of better representation.

this plane). In our model the same  $c/a$  ratio for the jump cage as for the Zr lattice is assumed, leading to nearly identical jump lengths. (ii) The most general cage of equivalent sites around the octahedral position comprises twelve sites instead of six in our model. If we considered this more complicated case, several jump lengths with rather different values would appear for the Fe atom jumping between equivalent sites which cannot be inferred from the present experiment. However, the value of  $0.35(5) \text{ \AA}$  estimated for the jump distance of the six-site cage would remain meaningful, in the sense that this value gives the overall dimension of the volume occupied by the jumping Fe atom.

Simultaneously with the apparent decrease of the Debye-Waller factor, we observe the striking effect that the quadrupole splitting  $\Delta E_q$  shrinks by almost a factor of 2 in the same small temperature interval. Caging leads to motional narrowing as soon as the jump frequency becomes comparable to the quadrupole splitting of the 14.4-keV nuclear level. At about 100 K a "saturation" value of  $0.5 \text{ mm/s}$  is reached: The fact that line intensity and electric field gradient both have their rapid decay in the same temperature region proves that the intensity decay cannot be due to an annealing out of interstitial sites (which, in addition, must be accompanied by an increase of the intensity of the main line) but that it is indeed due to caging.

The electric field gradient (EFG) at a cage site does not, in general, have axial symmetry. Two principal axes of the EFG tensor lie in the plane containing the  $c$  axis of the hcp lattice and the cage site. The largest principal axis, in general, is not parallel to the lattice  $c$  axis. In the high-temperature limit the EFG is an average of the EFG's at the cage sites touched during the jump process. Because of the threefold symmetry of the hcp lattice the averaged EFG is axially symmetric, the largest component pointing in the  $c$ -axis direction. The reduced magnitude indicates that the EFG at the cage site is tilted with respect to the  $c$  axis.

Although the slowing-down process of implanted  $^{57}\text{Fe}$  produces cascade damage, the final positions of  $^{57}\text{Fe}$  atoms are evidently well separated from the defects in the sense that the cage motion of Fe atoms ending up at interstitial sites is not suppressed by the lattice distortion around the defects and can be observed in the spectra.<sup>1</sup>

In summary, two important atomistic details can be inferred: Firstly, the Fe interstitial is not residing on a symmetric site in the hcp lattice (octahedral or tetrahedral) but assumes an asymmetrical position at low temperatures. Secondly, the clear-cut observation of motional narrowing of quadrupole interaction accompanied by the apparent decrease of the Debye-Waller factor shows that a localized motion of interstitially solved Fe is not restricted to fcc lattice<sup>1,10,11</sup> but appears to be a more general phenomenon.

An apparent decrease of the Debye-Waller factor accompanied by motional narrowing of the quadrupole in-

teraction has been predicted by theory in the past<sup>12,13</sup> to be a consequence of fast jumps in a localized region. Experimentally, Kemerink *et al.* have studied the Mössbauer effect of <sup>129</sup>I (daughter of <sup>129</sup>Te)<sup>14</sup> in Te-implanted single-crystalline silicon after subsequent laser annealing. A particularly interesting result in the spectra is the remarkable anisotropy of the intensity of one Mössbauer component at high temperatures. In an extensive discussion<sup>15</sup> Kemerink *et al.* were able to assign this effect and other more complex changes in the Mössbauer spectra with increasing temperature to quadrupole relaxation and an anisotropic decrease of a "jump Debye-Waller factor."

The Mössbauer spectra of the present work are simpler than those of Kemerink *et al.*,<sup>15</sup> which is why the interpretation is easier. This is because the in-beam Mössbauer technique enables us to study tiny concentrations of completely isolated Mössbauer probe atoms implanted one by one directly into interstitial sites. This makes our method and results different from classical implantation.

Our model presented here is consistent with all experimental data. Nevertheless, it cannot be regarded as a final proof that the interstitial sites are indeed off-center octahedral. Measurements of the directional dependence of  $f_0(\mathbf{k})$  after recoil implantation into a single crystal could help to ascertain the symmetry and size of the cage, as has been possible for iron interstitials in Al.<sup>11</sup>

For the future it would be highly interesting to search at higher temperatures for long-range diffusion which would manifest itself in an increase of the doublet's linewidth with increasing temperature. Results might show the connection between jumps in an interstitial cage (diffusion in a restricted region) and long-range interstitial diffusion.

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