

Time Domain Study of ^{57}Fe Diffusion using Nuclear Forward Scattering of Synchrotron Radiation

B. Sepiol,¹ A. Meyer,^{2,3} G. Vogl,¹ R. Ruffer,³ A. I. Chumakov,³ and A. Q. R. Baron³

¹*Institut für Festkörperphysik der Universität Wien, Strudlhofgasse 4, A-1090 Wien, Austria*

²*Physik-Departement, Technische Universität München, D-85747 Garching, Germany*

³*European Synchrotron Radiation Facility, F-38043 Grenoble, France*

(Received 27 November 1995)

Diffusion of ^{57}Fe in the intermetallic alloy Fe_3Si was investigated using nuclear forward scattering of synchrotron radiation parallel to the [113] crystal direction with the aim to demonstrate the feasibility of a diffusion study in a crystalline solid. The jumps between different sites on a lattice, corresponding to a finite residence time on one and the same lattice site, cause a loss of coherence of scattered synchrotron radiation. This gives rise to a decay of the forward scattered intensity which is faster than under static conditions. From the time dependence of the decay diffusivities of iron are derived. [S0031-9007(96)00019-1]

PACS numbers: 76.80.+y, 66.30.Fq

In the past, two methods have been applied for studying the diffusion mechanism in solids on an atomistic scale and in space and time. These are quasielastic Mössbauer spectroscopy (QMS) and quasielastic neutron scattering (QNS) [1]. In the case of QMS the diffusion manifests itself through the broadening and change in shape of the resonance line(s). For free long-range diffusion on a Bravais lattice it is a simple broadening of one Lorentzian shaped line. In the case of a non-Bravais lattice it can be a superposition of Lorentzians, their number corresponding to the number of sublattices [2].

Here we present the first measurement of solid state diffusion using nuclear resonance scattering of synchrotron radiation (SR) [3,4]. This technique permits studies directly in the time domain, whereas QMS and QNS studies are performed in the energy domain.

The choice of the investigated material is most important for such a feasibility study. It should be a material well known and already thoroughly investigated with QMS and tracer diffusion. The diffusion mechanism should be easy from the Mössbauer point of view. All these requirements are well fulfilled by the intermetallic alloy Fe_3Si as argued in the following.

(a) Fe_3Si crystallizes in a simple structure (cubic, D_{03} consisting of three iron sites and one silicon site in a primitive cell) and is perfectly ordered up to the melting point ($T_m = 1500$ K). (b) Single crystals of Fe_3Si are stable during the high-temperature measurement. They can be grown, oriented, cut, and polished up to the required final thickness. (c) Fe_3Si shows extremely fast diffusion of the iron atoms, the fastest of all iron intermetallics with high iron content found up to now. Thus diffusion phenomena can be observed at low temperature (about 900 K) which reduces technical problems, as has been demonstrated by QMS [5] and confirmed by tracer diffusion studies [6].

An essential advantage of Fe_3Si for a feasibility test is that the diffusion mechanism of iron in this structure

is well known from QMS studies [5,7]. These studies have proven that Fe atoms which occupy sites on three sublattices (Fig. 1) jump between nearest neighbor iron sites remaining at each sublattice site for different residence times. In the Mössbauer spectrum this leads to a sum of three different Lorentzians with different broadenings, weights of Lorentzians, and broadenings depending on crystal orientation. In the [113] direction the spectrum is composed of two lines only: one unbroadened and one diffusively broadened line.

A single crystal of the Fe-Si alloy was grown by the Bridgman technique with a composition 75.5 at. % Fe (natural ^{57}Fe abundance), 24.5 at. % Si. Slices of about 10 mm diameter were cut by a wire saw with the surface parallel to the (113) plane. Two samples of about 24 and 15 μm final thickness were prepared.

In order to compare most directly we measured both conventional Mössbauer spectroscopy and nuclear forward scattering of SR. Conventional Mössbauer absorption spectra were registered with the 15 μm sample and ^{57}Co in Rh as a source (Fig. 2) and in the same furnace which was afterwards used for the synchrotron experiment. Column 2 of Table I gives the line broadening of the broad line Γ_d which yields directly the residence time on a particular lattice site with respect to the natural

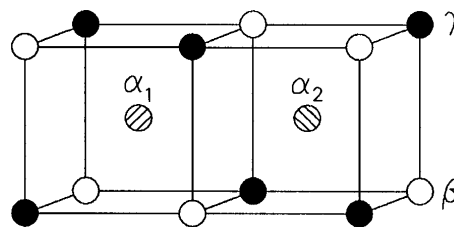


FIG. 1. D_{03} structure of Fe_3Si (2/8 of elementary cell). The iron atoms occupy the sublattices α_1 , α_2 , and γ , the silicon atoms the sublattice β .

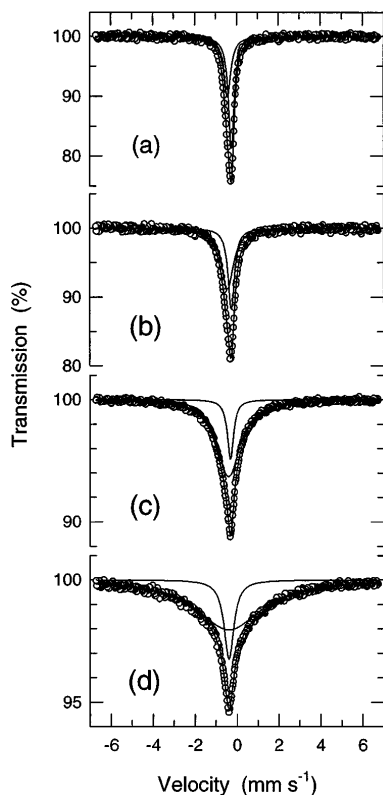


FIG. 2. Conventional Mössbauer absorption spectra of Fe_3Si measured in the [113] direction at (a) 876 K, (b) 916 K, (c) 959 K, and (d) 1013 K. At and above 916 K two Lorentzian lines are observable, one of which is strongly broadened.

linewidth Γ_0 of the 14.4 keV Mössbauer level. From the residence time the diffusivity (column 3 of Table I) follows directly via the Einstein-Smoluchowski equation [8].

The experiments with nuclear resonance scattering of SR were carried out at the nuclear resonance beam line of the ESRF (for details see [9]). The storage ring operated in 16-bunch mode providing short pulses of x rays every 176 ns. The radiation from the undulator source, optimized for the 14.4 keV transition in iron, was filtered by a double Si(111) reflection followed by a high resolution nested monochromator [9,10]. The delayed events, resulting from the nuclear forward scattering [11],

TABLE I. Line broadening of the broad line Γ_d/Γ_0 from the Mössbauer (QMS) data (Fig. 2), q from forward scattering of synchrotron radiation (SR) (Fig. 3) and the corresponding diffusivities D_{QMS} and D_{SR} . Only statistical errors are given.

T (K)	Γ_d/Γ_0	D_{QMS} ($\text{m}^2 \text{s}^{-1}$)	q	D_{SR} ($\text{m}^2 \text{s}^{-1}$)
876	1.2(4)	$2.0(6) \times 10^{-14}$	2.2(3)	$2.1(5) \times 10^{-14}$
916	4.1(4)	$6.8(7) \times 10^{-14}$	4.8(3)	$6.1(5) \times 10^{-14}$
959	10.6(9)	$1.7(2) \times 10^{-13}$	8.0(8)	$1.1(2) \times 10^{-13}$
1013	35(2)	$5.8(3) \times 10^{-13}$	10.2(8)	$1.5(2) \times 10^{-13}$

were counted by a fast avalanche photodiode (APD) detector [12,13].

In the present work because of limited experimental time, low count rate from the unenriched sample, and overload of the detector caused by the prompt pulse, measurements are reliable from 30 ns after the pulse is on. In principle the short-time limit is determined by the synchrotron radiation pulse length (~ 100 ps) and the detector resolution (~ 100 ps FWHM). The detector tail after the prompt pulse [14], from available APD's, indicates that with measurements beginning about 2 ns after the pulse, at the cost of seriously reduced count rate, the signal of delayed forward scattering will be above the noise.

Forward scattered SR was registered with two different sample thicknesses, one with the $24 \mu\text{m}$ sample and another one with both samples packed together (total thickness $39 \mu\text{m}$) which leads to an increase in the delayed count rate. Depending on the synchrotron ring current, sample thickness, and temperature, the count rates were between 2 and 30 delayed counts/s. This resulted in a measuring time of 1 h at the highest temperature. The constant background of the APD diode was 0.05 counts/s.

Figure 3 shows time spectra—forward scattered intensity as a function of time after the SR pulse—for four different temperatures and two sample thicknesses: $24 \mu\text{m}$ [Figs. 3(a) and 3(d)] and $39 \mu\text{m}$ [Fig. 3(b) and 3(c)]. At 876 K an exponential decay of the intensity appears which becomes steeper with increasing temperature. As will be shown the increase in the slope is an effect of faster diffusion at higher temperatures. A second decay shows up at longer times.

In the following we propose an interpretation. Without diffusion the time dependence of forward scattered intensity as a function of sample thickness z and time t is described by the following relation [15–17]:

$$I_{\text{FS}}(z, \tau) \propto \exp(-q\tau) \frac{L}{\tau} J_1^2(\sqrt{L\tau}), \quad (1)$$

with $q = 1$. Here $\tau = t/\tau_0$ with τ_0 the natural lifetime of the excited state (141 ns), $L = \sigma_0 f_{\text{LM}} n \chi z$ the effective thickness where σ_0 is the nuclear absorption cross section ($2.56 \times 10^{-22} \text{m}^2$), f_{LM} the Lamb-Mössbauer factor derived from Ref. [18] ($f_{\text{LM}} = 0.42$ at 876 K), n the number of iron atoms per unit volume ($5.66 \times 10^{22} \text{cm}^{-3}$ at 700 K), χ the isotope abundance of ^{57}Fe (0.021), z the thickness of the sample, and J_1 the first order Bessel function.

Diffusive jumps between different sites lead to a loss of coherence of the radiation and therefore an accelerated decay; as a consequence q will be greater than 1 [17,19]. q is connected to the diffusional line broadening of one resonance line in conventional QMS in the following way:

$$q = 1 + \frac{\Gamma_d}{\Gamma_0}. \quad (2)$$

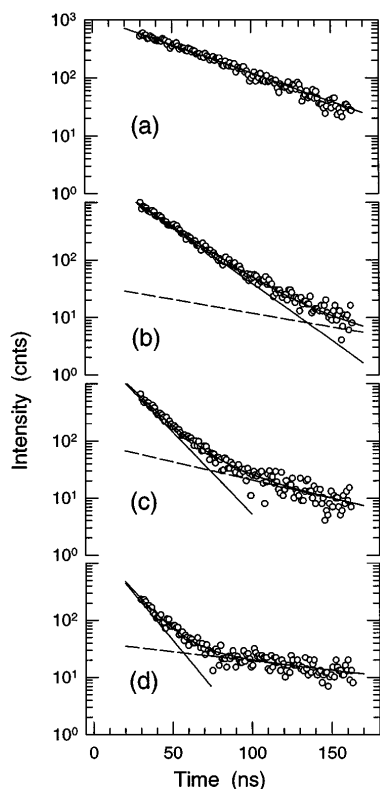


FIG. 3. Nuclear forward scattering of synchrotron radiation at the same sample as in Fig. 2 at (a) 876 K, (b) 916 K, (c) 959 K, and (d) 1013 K. The line through the data is a fit according to Eq. (1). Above 916 K a two-step exponential decay is clearly visible. The two straight lines indicate the asymptotic behavior of the decay at short and long times.

For diffusion on a non-Bravais lattice as in the present case of Fe_3Si and in the [113] direction we find *two Lorentzians* in the conventional QMS spectra; therefore, we expect *two different q values* corresponding to a *two-step exponential decay* in Eq. (1). Equation (1) contains time dependence in a twofold way: via the exponential connected with diffusion, $\exp(-q\tau)$, and via a part connected with the effective thickness L . In a first approximation we split the exponential part into a sum of two exponentials, one in the limit of short-time decay corresponding to the broad QMS line and one for long times. We fitted the spectra of Fig. 3 with the effective thickness L due to the change of the sample thickness z and to the temperature dependence of the f_{LM} factor. The fitting procedure took account of the constant background of the APD diode and of delayed quanta from the previous pulse. The values of q for the short-time decay are given in column 4 of Table I.

At temperatures where both the diffusional line broadening in Fig. 2 and the short-time behavior in Fig. 3 can be determined with sufficient reliability (between 876 and 959 K) and at identical temperatures the ratio Γ_d/Γ_0 is nearly the same whether determined from conventional QMS (Fig. 2) or derived via Eq. (2) from the diffu-

sionally accelerated decay of forward scattered intensity (Fig. 3).

Column 5 of Table I gives the diffusivities D deduced from the forward scattered intensity of SR. Up to $T = 959$ K the diffusivities agree sufficiently well with the values deduced from conventional QMS and mean times confirmed by tracer measurements of samples with similar Fe-Si composition [6]. Indeed the diffusivity is extremely high compared to other alloys at comparable temperatures, e.g., $1.1 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ at 959 K. Notice that at 876 K diffusion is too slow to lead to a two-step exponential decay in the accessible time window, whereas at 1013 K the short-time decay is so fast that its reliable determination is problematic, the tabulated value of $1.5 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ being definitely too low. The reason is certainly the lack of data below 30 ns. Opening the time window down to 2 ns would extend the range of diffusivities up to $10^{-12} \text{ m}^2 \text{ s}^{-1}$ (about $50\Gamma_0$ in conventional ^{57}Fe QMS). We regard this as the upper limit of diffusivities accessible to SR.

The exponential decay in forward scattered intensity dominating at longer times (e.g., above about 80 ns at 959 K) corresponds to the narrow line in Fig. 2 which is not broadened through diffusion. We used samples with two different thicknesses; therefore, the difference in the slopes of Figs. 3(c) and 3(d) is due to the different effective thicknesses L .

We finally note that a more exact fit of the diffusional decay of the forward scattered intensity can be accomplished with an ^{57}Fe enriched sample. In that case one leaves the asymptotic region and, for longer times, registers the first minimum of the Bessel function. Then both values, q and the effective thickness L , can be fitted independently, whereas for our nonenriched sample the effective thickness L had to be fixed. A detailed theory of nuclear forward scattering of SR in the case of diffusion in crystalline lattices going beyond the asymptotic approach of the present paper and accounting for different crystal directions will be the subject of a more extensive paper [20].

In conclusion, we state that it is possible to follow diffusion by nuclear resonance scattering of SR, i.e., Mössbauer spectroscopy in the time domain, in complete analogy to conventional quasielastic Mössbauer spectroscopy (QMS) or quasielastic neutron scattering (QNS), both in the energy domain. The method and its results appear even more straightforward since the decay of coherence is caused in a direct and appealing way by the stochastic motion of the jumping atom, whereas conventional QMS and QNS register diffusion by following the time-energy Fourier transform of the diffusion process. Compared to the problematic standard task in QMS and QNS of separating various differently broadened lines, the separation of different exponential decay rates of the intensity of scattered synchrotron radiation is more direct. This advantage of the SR method compared to QMS and

to QNS can be exploited in the case of diffusion investigations of complicated non-Bravais lattices.

Further advantages are as follows: with a SR beam size of less than 1 mm^2 at the sample position diffusion investigations in tiny crystals and recrystallized foils should be possible. Furthermore, a divergence of the x-ray beam in the μrad range will enable measurements of diffusional line broadening with considerably reduced "smearing" of the crystal orientation.

The authors appreciate valuable discussions with V.G. Kohn. This work was supported by grants from the Austrian FWF (Project No. S5601) and from the German BMBWF (Project No. 05 643WOB).

-
- [1] G. Vogl, *Hyperfine Interact.* **53**, 197 (1990); K. Ruebenbauer, J. G. Mullen, G. U. Nienhaus, and G. Schupp, *Phys. Rev. B* **49**, 15 607 (1994); B. Sepiol, *Defect Diffus. Forum* **125–126**, 1 (1995).
- [2] O.G. Randl, B. Sepiol, G. Vogl, R. Feldwisch, and K. Schroeder, *Phys. Rev. B* **49**, 8768 (1994).
- [3] E. Gerdau, R. Ruffer, H. Winkler, W. Tolksdorf, C.P. Klages, and J.P. Hannon, *Phys. Rev. Lett.* **54**, 835 (1985).
- [4] See, e.g., E. Gerdau and U. van Bürck, in *Resonant Anomalous X-Ray Scattering. Theory and Applications*, edited by G. Materlik, C.J. Sparks, and K. Fischer (Elsevier, New York, 1994), p. 589.
- [5] B. Sepiol and G. Vogl, *Phys. Rev. Lett.* **71**, 731 (1993).
- [6] A. Gude, *Doktorarbeit*, Universität Münster, 1995.
- [7] B. Sepiol and G. Vogl, *Hyperfine Interact.* **95**, 149 (1995).
- [8] For a $D0_3$ structure $D = \frac{1}{24}a^2/\tau$, with the Fe_3Si lattice constant $a = 5.72 \text{ \AA}$ at 770 K and the residence time $\tau = 6\hbar/\Gamma_d$.
- [9] R. Ruffer and A. I. Chumakov, *Hyperfine Interact.* **97–98**, 509 (1996).
- [10] T. Ishikawa, Y. Yoda, K. Izumi, C.K. Suzuku, X.W. Zhang, M. Ando, and S. Kikuta, *Rev. Sci. Instrum.* **63**, 1015 (1992).
- [11] J.B. Hastings, D.P. Siddons, U. van Bürck, R. Holland, and U. Bergmann, *Phys. Rev. Lett.* **66**, 770 (1991).
- [12] S. Kishimoto, *Rev. Sci. Instrum.* **63**, 824 (1992).
- [13] A.Q.R. Baron and S.L. Ruby, *Nucl. Instrum. Methods Phys. Res., Sect. A* **343**, 517 (1994); A.Q.R. Baron, *Nucl. Instrum. Methods Phys. Res., Sect. A* **352**, 665 (1995).
- [14] S. Kishimoto, *Nucl. Instrum. Methods Phys. Res., Sect. A* **351**, 554 (1994).
- [15] F.J. Lynch, R.E. Holland, and M. Hamermesh, *Phys. Rev.* **120**, 513 (1960).
- [16] Yu. Kagan, A.M. Afanasev, and V.G. Kohn, *J. Phys. C* **12**, 615 (1979).
- [17] G.V. Smirnov and V.G. Kohn, *Phys. Rev. B* **52**, 3356 (1995); G.V. Smirnov, Kurchatov Institute, Moscow, Report No. IAE-5907/9, 1995.
- [18] O.G. Randl, G. Vogl, W. Petry, B. Hennion, B. Sepiol, and K. Nembach, *J. Phys. Condens. Matter* **7**, 5983 (1995).
- [19] In the paper by G.V. Smirnov and V.G. Kohn [17] the case of free diffusion in a dispersive medium was calculated. For diffusional broadening of *one* Lorentzian line it was shown that relation (1) holds. In our case we may regard this as the asymptotic limit of diffusion in a crystal lattice for short jump lengths.
- [20] A. Meyer *et al.* (to be published).