

First Study of a Diffusion Mechanism with Synchrotron Radiation

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Abstract. Nuclear resonant scattering of synchrotron radiation is used for the first time to study the atomic diffusion process in the solid state. The feasibility of a diffusion study was demonstrated on the intermetallic phase Fe₃Si. It is shown that this new method is capable to distinguish between different diffusion mechanisms. A theory of resonant forward scattering in the case of diffusion is discussed. The potential of nuclear resonant scattering is compared to that of conventional Mössbauer spectroscopy.

Introduction

The aim of this paper is to present a new and promising method in diffusion-mechanism studies - nuclear resonant scattering of synchrotron radiation (NRSSR). This technique combines the properties of a small and intense synchrotron beam with the spatial and energy resolution of conventional Mössbauer spectroscopy. The first experiment showing the applicability of synchrotron radiation (SR) to diffusion studies was performed recently at the ESRF [1]. We will show that NRSSR allows to determine the diffusion mechanism on an atomic scale in space and time.

Theoretical principles of nuclear resonant scattering of Mössbauer radiation were worked out just after the discovery of the Mössbauer effect (for a review see [2]). First experiments in the time domain were performed still with Mössbauer sources [3]. The theory of Mössbauer optics was developed by Hanon et al [4]. Ruby [5] suggested in 1974 that SR could be used for a resonant excitation of nuclei. In the following years the theory of NRSSR was developed by Kagan et al [6]. Only 11 years later Gerda et al. [7] observed for the first time the resonant effect with SR by resonant Bragg-scattering on single crystals. Recently Smirnov and Kohn [8] proposed a theory of nuclear resonant scattering in the presence of diffusive motion of nuclei.

The experimental observation of the time structure of the scattered SR radiation in the *forward* direction was introduced by Hastings et al. [9]. In this paper we will focuss on the resonant forward scattering of a single crystal Fe₃Si foil.

Principles

Tracer or macroscopic methods of diffusion investigation deduce atomic events from macroscopical effects as for instance the concentration gradient of diffusing atoms. If one wants to have insight into the elementary diffusion jump, then photons or particles with wave lengths of the order of the atomic distances have to be used. This is offered by quasielastic Mössbauer spectroscopy QMS (for reviews see [10,11]) and quasielastic neutron scattering QNS (see [12]).

The phenomenon of emission or absorption of a γ -ray photon without loss of energy due to a recoil of the nucleus is known as the Mössbauer effect. On the other hand the low-lying nuclear levels, as for instance the 14.41 keV level in ^{57}Fe , can be directly excited by SR. The nucleus exhibiting the Mössbauer effect is characterized by its excited-level life time resulting via the Heisenberg uncertainty principle in the natural line width of the Mössbauer resonance. The experimental procedure is simple. The sample containing resonant ^{57}Fe nuclei is mounted in between the monochromatic X-ray source and the fast avalanche photo diode (APD) detector [13, 14]. The detector, which is synchronized with the electron-beam phase of the synchrotron, and measures the intensity as a function of elapsed time after each prompt pulse. The resonantly scattered photons are delayed with a characteristic time of 141 ns and can in this way be distinguished from the very short SR pulse. To avoid an detector overload from the incoming radiation the synchrotron beam is monochromatized with a sophisticated arrangement of silicon single crystals (for more details see [15]). Measurement is possible inbetween the tail in the time spectra after the prompt pulse and the next SR pulse (at ESRF in 16 bunch mode the time between the pulses is 176 ns). In the scattering of the Mössbauer/X-ray radiation coherence plays a crucial role. The very short SR pulse excites most of the ^{57}Fe nuclei. Due to the coherence in time one can observe the following effects during the decay of nuclear excitation:

- In conventional Mössbauer spectroscopy the resonance line(s) can be broadened due to the diffusive motion of the nuclei, provided the nuclei jump at least once during the lifetime of the excited state. In NRSSR this effect manifests itself in an *accelerated decay* of the forward scattered intensity.
- Multiple scattering of radiation propagating through the target results in *dynamical beats*, i.e., a *speed up* in the decay rate in comparison to the natural decay which is best visible at short times. To longer times oscillations in intensity are observed. Both the speed up and the position of the minima in intensity depend on the effective thickness of the sample.

The effect of diffusion on the Mössbauer spectrum was investigated theoretically by Singwi and Sjölander [16] and soon applied in experiments (for a review see [10]). To describe the influence of diffusion on the time decay of the scattered intensity, we should consider first the simplest situation: the scattering of a target with only one hyperfine position of iron atoms i.e. with only one Lorentzian line in the Mössbauer spectrum and gas-like (uncorrelated) diffusion. In this situation the time dependence of the forward scattered intensity can be described analytically [8] as a function of effective sample thickness, L , and time by

$$I_{\text{FS}}(L, t) \propto \exp\left(-q \frac{t}{\tau_0}\right) \frac{L\tau_0}{t} J_1^2\left(\sqrt{L \frac{t}{\tau_0}}\right), \quad (1)$$

where τ_0 is the natural lifetime of the excited state of iron (141 ns). $L = \sigma_0 f_{\text{LM}} n \chi z$ is the effective sample thickness where σ_0 is the nuclear absorption cross section, f_{LM} the Lamb-Mössbauer factor, n the number of iron atoms per unit volume, χ the isotope abundance of ^{57}Fe and z the thickness of the sample. J_1 is the first order Bessel function responsible for the *dynamical beats*. Diffusion enters through the factor q in the exponential decrease [8]. Without any motion of nuclei (neglecting the vibrational motion, which is already incorporated in the Lamb-Mössbauer factor) $q = 1$ [17]. In case of diffusive motion which is from its nature a random process, the dephasing of radiation-field components from different atomic sites proceeds faster. The coherent signal is additionally destroyed, i.e. the diffusional broadening of the nuclear resonance leads to a faster intensity decay as compared to the static situation. q is connected to the diffusional line broadening of one resonance line in conventional QMS in the following way :

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

where Γ_0 is the natural line width of the Mössbauer level $\Gamma_0 = \hbar/\tau_0$ and Γ_d is the diffusional line broadening. One can see that the effective sample thickness of L in Eq. (1) is not affected by diffusion. Therefore the initial intensity of the forward scattering and - in this simple case - the *dynamical beats* described by the Bessel function J_1 are not changed [8]. The time-integrated intensity of the forward scattering, however, will strongly decrease with increasing the jump frequency of diffusion, i.e. growing q in the exponent in Eq. (1). The simulated Mössbauer spectra and corresponding I_{FS} for different q values are shown in Fig. 1. From this “diffusional acceleration”, i.e. from the q parameter, the jump rate of iron atoms and the diffusivity can be derived [1]. This is, however, not the most important application of SR in diffusion studies. Tracer methods are considerably superior to atomistic methods like NRSSR, QMS or QNS in respect of accuracy and versatility. Atomistic methods are specially appropriate for recognizing the diffusion mechanism

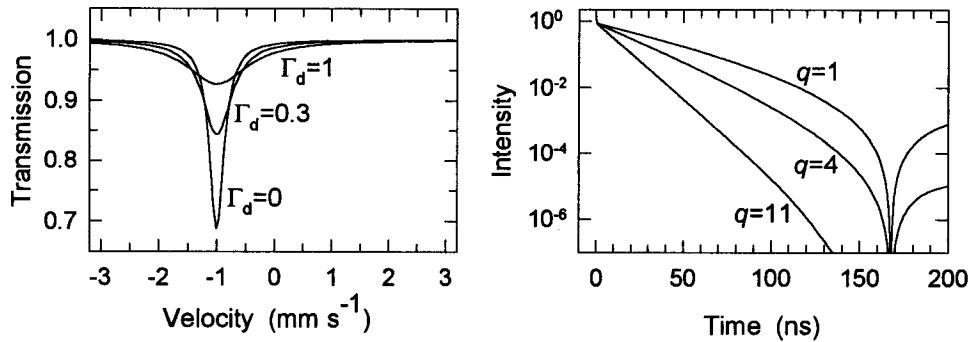


Fig. 1. Simulated Mössbauer spectra with diffusional broadening Γ_d (mm s^{-1}) in the energy (Doppler shift) domain (left); intensities of NRSSR in the time domain with corresponding q values (right) and an effective thickness $L=12$.

in selected model systems. This is a simple consequence of the *microscopic view* onto the dynamics of diffusion. The resonant line width, or in NRSSR the intensity decay depends not only on the frequency of the ^{57}Fe jumps, but also on the angle between the beam direction and the jump vector \mathbf{R} connecting the adjacent lattice sites. This is caused by the different phase-shifts of the resonant X-ray waves between lattice sites connected by \mathbf{R} . The aim of a SR scattering experiment performed on an ordered sample is to find what kind of elementary jump process is responsible for diffusion in this sample. We should notice that the answer can be obtained only if we perform measurements on single crystals, otherwise all the space information about diffusion is lost due to the polycrystalline averaging. In the experimental part we will show that NRSSR spectra depend really on the angle if one performs a measurement on a single crystal, indicating that we are able to distinguish a diffusion mechanism with SR.

We should be aware of the single line approximation considered up to now, because only in this approximation the time spectrum of SR can be solved analytically as Eq. (1). If the sample has a complicated structure with a couple of inequivalent iron sites (non-Bravais lattice), one can expect that the time domain spectrum will be more complicated. In the general case the intensity of the forward scattering of SR is calculated as a Fourier integral of the standard resonant factor $\varphi(\mathbf{Q}, \omega)$

$$I_{\text{FS}}(L, t) \propto \left| \int_{-\infty}^{\infty} d\omega \exp(i\omega t) \exp\left(i \frac{L}{2} \varphi(\mathbf{Q}, \omega)\right) \right|^2, \quad (3)$$

where the form of $\varphi(\mathbf{Q}, \omega)$ depends on the investigated lattice. \mathbf{Q} is a wave vector of X-ray 14.4 keV radiation. It will be just one resonance in Bravais lattices (Eq. (1)), or a sum of three resonant components in the stoichiometric D0_3 lattice with different weighting factors and line broadenings [18]. In this case the transformation in Eq. (3) must be performed numerically.

Experimental

We demonstrate the potential of the method by a study on diffusion of ^{57}Fe in a well-investigated intermetallic alloy, Fe_3Si [18]. We regard the Fe_3Si system as the best one for a feasibility test of NRSSR diffusion because of the following arguments: (a) Fe_3Si crystallizes in a simple structure (cubic, D0_3) and is perfectly ordered up to the melting point ($T_m = 1500\text{K}$). (b) The diffusion mechanism is well known and already investigated by Mössbauer spectroscopy [18] and tracer techniques [19, 20]. These studies have proven that Fe atoms, which occupy three sublattices, jump between nearest-neighbor iron sites, remaining at each sublattice for a different residence time (for more details about the diffusion mechanism, see [20]). (c) The iron diffusion in the intermetallic phase of Fe_3Si is probably the fastest of all systems with high iron content, and the diffusional line broadening measured by Mössbauer spectroscopy shows a clear angular dependence [18].

A single crystal of $\text{Fe}_{74.5}\text{Si}_{25.5}$ was prepared as a thin foil (about $20 \mu\text{m}$) transparent for 14.41 keV X-rays and oriented with the normal to its surface lying between the [111] and the [113] crystal direction. The oriented foil which was placed in a standard Mössbauer furnace, rotated on a goniometer-head, allowing measurements in [111] and [113] direction and as function of temperature. Fig. 2 shows the time dependence of forward scattered intensity at two different temperatures and directions.

At lower temperatures diffusion is slow and the effect on the measured intensity is rather weak. The decay is described mainly by the effective sample thickness ($L=8$) due to Eq. (1) and the curvature caused by the Bessel function is well visible. In [111] direction the Mössbauer spectrum consists of only one resonance line whereas in [113] direction two resonance lines contribute to the signal. The lower temperature of $T=827\text{K}$ is only slightly higher than the Curie temperature of Fe_3Si , but even at this temperature the difference between the scattering in the [111] and in the [113] direction is observable. At higher temperature a decay with two different rates is clearly visible in the [113] direction. These rates correspond to the narrow and the broad line in the Mössbauer spectrum of the same sample [1, 18]. The solid lines were fitted using Eq. (3) and the microscopic diffusion model allowing jumps of iron atoms between nearest neighbor lattice sites [18].

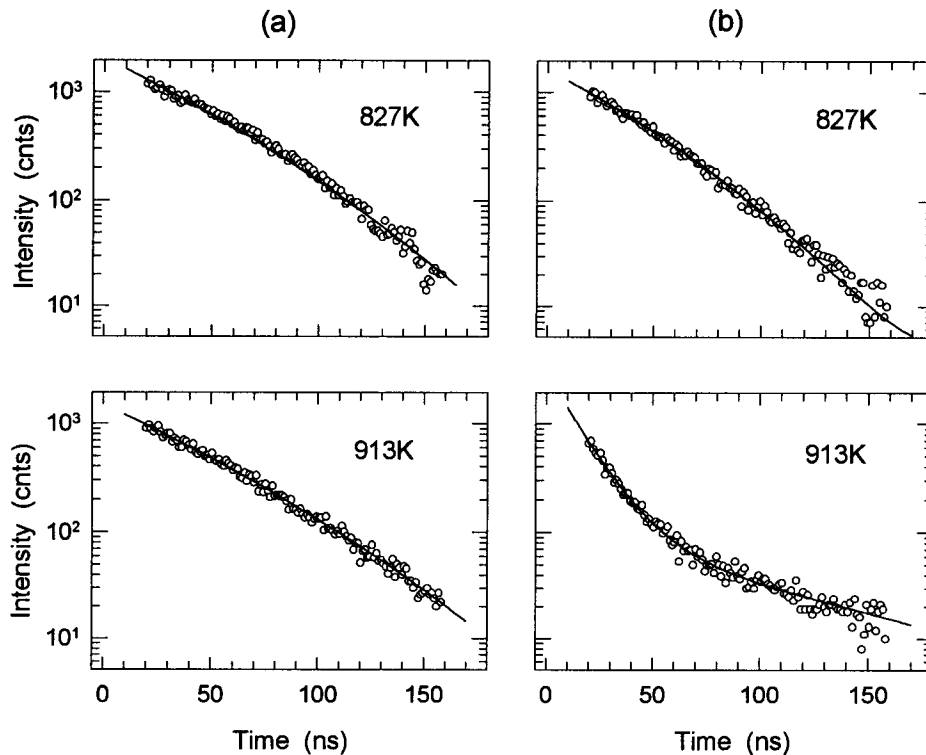


Fig. 2. Nuclear forward scattering of synchrotron radiation measured in (a) [111] and (b) [113] direction at 827 K and 913 K. Fits by Eq. (3). Due to the thickness of $L \approx 8$, the first minimum in the intensity is outside the time window of the experiment.

Converting a possible diffusion model into a mathematical model one can obtain the theoretical resonant scattering factor which, after transformation using Eq. (3), can be compared with the experimental forward scattering intensity shown in Fig. 2. One should note that angle dependent SR measurement is preferable in forward direction, because in this direction the constructive interference of X-rays is retained. Another possibility is the measurement in Bragg directions, but this results only in a limited choice of strictly selected angles due to the Bragg condition.

Summary

Among the nuclear techniques like quasielastic Mössbauer spectroscopy (QMS) and quasielastic neutron scattering (QNS) nuclear forward scattering of synchrotron radiation (NRSSR) can be an efficient tool for the investigation of the atomic diffusion mechanism.

We showed in the previous paper [1] that this new technique is capable of measuring diffusion coefficients like other macroscopic methods. In this paper we presented different NRSSR spectra measured at constant temperature but variously oriented versus X-ray beam. The correct fit of the spectra set is possible only if we use a proper atomistic diffusion model in complete analogy to QMS and QNS. In conclusion we find, that the diffusion mechanism can be also investigated by the new method.

Due to the very small beam dimensions ($\sim 1 \text{ mm}^2$) one can investigate tiny crystals, not measurable with QMS and QNS. An extremely small beam divergence makes superfluous the angle correction typical for old techniques, demanding wide solid angles due to low intensity sources used. Therefore, the measurement of different exponential decay rates or, in non-Bravais lattices, the differentiation one exponential decay rate from more complicated decays is more exact than in QMS and QNS.

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