Probing single jumps of surface atoms

G. Vogl* and M. Sladecek†
Fakultät für Physik, Universität Wien,
Strudlhofgasse 4, A-1090 Wien, Austria

S. Dattagupta
Indian Institute of Science Education and Research,
Salt Lake, 700106 Kolkata, India
(Dated: May 5, 2007)

Jumps of single atoms at surfaces can be followed on their time and space scale (nanoseconds and nanometers) by applying nuclear resonant scattering of synchrotron radiation. Here we develop the theory for jump diffusion in two-dimensional systems. Two types of phenomena are noteworthy: apparent acceleration of the nuclear decay and relaxation of hyperfine interactions, in particular electric quadrupole interactions. The latter effect becomes for the first time one of significance and well measurable due to the inherent anisotropy of the surface. We compare with a first experiment and deduce jump frequencies and activation energy Q. We show how by way of motional narrowing to distinguish between the motion of the probe atom itself and the motion of ad-atoms.

PACS numbers: 61.72.Ji, 66.30.-h, 68.35.Fx, 76.80.+y
Keywords: Diffusion jumps, quadrupole interaction, surface, synchrotron radiation, Mössbauer

Interference of highly brilliant, polarized and pulsed synchrotron x-radiation can probe jumps of single atoms directly in time domain in the range of nanoseconds and on the space scale of nanometers. For grazing incidence of x-rays even the jumps in a monolayer or less can be investigated within a reasonable experimental time. We consider nuclear resonance at the nuclear ground level of the probe atom ^{57}Fe leading to excitation of the 14.4 keV level which decays within a lifetime of 141 nanoseconds and re-emits (scatters) the radiation. The method is therefore called nuclear resonant scattering of synchrotron radiation (NRS), and corresponds in energy domain to the Mössbauer effect. NRS has first been achieved by Gerdau et al. [1], and shortly later Hastings et al. [2] developed coherent nuclear forward scattering.

The nuclear transition matrix for the M1 transition of ^{57}Fe yields the angular dependence of the intensity of the outgoing NRS beam and the ratio of the intensities of the emission lines of the Mössbauer effect. Due to its polarization the incoming photon (electric field vector in the surface plane and vertical to its k vector) selects just $M = 0$ transitions from the ground to the excited state of ^{57}Fe. Since the excited state of ^{57}Fe is a 3/2 state and the ground state is 1/2, only $M_e = \pm 1/2$ sublevels of the excited state are relevant. The result is different for different directions of the scattered beam, but here we focus on scattering in forward direction.

Following a proposal by Smirnov and Kohn [3], Sepiol et al. [4, 5] have for the first time exploited the capability of NRS to observe interactions of the radiation with the nucleus and its environment for studying diffusion in bulk solids. The essential result was an apparent acceleration of the intensity decay of coherent nuclear resonant forward scattering, corresponding to a loss of coherency, from which details of the diffusion process were deduced: The slope and the angular dependence of the decay yielded the jump frequency and the jump vector. Recently Kmiec et al. [6] have applied NRS for determining the depth dependence of the diffusivity close to a metallic surface.

In this Letter we develop the theory of diffusion in a two-dimensional system like a surface considering not only the apparent accelerated decay of NRS intensity, i.e. the loss of coherency, but in addition and in detail the relaxation of hyperfine interactions. Since an Fe monolayer is paramagnetic at room temperature [7], we do not expect magnetic hyperfine interaction but rather quadrupole interaction. The latter is proportional to the product of the electric field gradient caused by the surrounding atoms and the quadrupole moment of the probe nucleus.

This is to our knowledge the first time that jumps of single atoms at surfaces can be followed on the time and space scale of the jumps and opens the way for detailed studies of the atomistics of diffusion on and at surfaces. We think that this is also the first time that the predicted effect of hyperfine relaxations on diffusion on a crystalline lattice becomes of significance and has in fact been seen (see Dattagupta-Schroeder prediction [8] for bulk without relevant experiment). For studying the rotational dynamics of a glass Sergueev et al. [9] have recently successfully exploited nuclear resonant scattering of synchrotron radiation applying a method related to the method discussed here. The difference is that they studied *incoherent* scattering by way of angular correlation, whereas here advantage is taken of the *coherency* of the reemitted radiation in forward direction. This again as in the earlier bulk studies opens the way for studying the details of the diffusion jump vector [5].

The simplest system is a monolayer with a limited number of vacancies into which atoms can jump when thermally excited. In Fig. 1(a) we show schematically a (110) plane of a body-centered cubic lattice with the ^{57}Fe probe atom surrounded by nearest neighbor (NN) atoms and one vacancy. For practical and physically plausible reasons we consider only nearest-neighbor interactions and confine the calculations to self-diffusion. Alternatively we consider ad-atom diffusion (Fig. 1(b)).

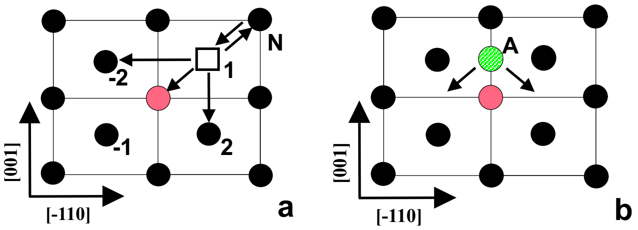

FIG. 1: (a) Diffusion of atoms in iron monolayer on (110) surface of tungsten. 1, -1, 2, -2 designate possible vacancy positions at NN sites of the probe atom, N a site outside the NN shell to which a NN atom can jump.
(b) Diffusion of ad-atom A on top of an iron surface.

The theoretical treatment has to describe the time development of the nuclear decay in the presence of diffusion. The central quantity of interest is the average over defect sites of the time and space transformed time-development operator as developed by Dattagupta [10] incorporating diffusion effects into the Blume [11] approach

$$\left(\tilde{U}(s,k)\right)_{\mathrm{av}} = \sum_{\alpha,\beta}\left(\alpha\middle|\left[(i\omega+\frac{\Gamma_0}{2\hbar})\mathbb{1}-W_k-\frac{i}{\hbar}\sum_{\mu}V_\mu F_\mu\right]^{-1}\middle|\beta\right)p_\beta. \tag{1}$$

For diffusion via vacancies (Fig. 1(a)) this is a 20x20 matrix because there are four nuclear sublevels in the excited state ($\pm 3/2, \pm 1/2$) and five defect sites with running indices α, β and μ. $i\omega + \Gamma_0/2\hbar$ describes the nuclear decay in absence of diffusion (Lorentz line in energy $\hbar\omega$ with linewidth Γ_0), $\mathbb{1}$ is a unit matrix and p_β is the occupational probability of vacancy site β.

The effect of the atoms changing sites in absence of fluctuating hyperfine interactions is described by the second term in the square bracket of equ. (1), W_k, and in the general case is a 5x5 "jump frequency matrix". The matrix elements are the jump rates for leaving a site (diagonal elements) or changing from one site to another site. For self-diffusion all frequencies are identical and the same pertains to jumps of ad-atoms. The diffusion jumps via vacancies produce the accelerated decay of the NRS intensity. This has been seen earlier for bulk diffusion [4]. Acceleration of the NRS decay corresponds to line broadening in Mössbauer effect. Note however that Mössbauer measurements of diffusion are hardly possible for monolayers, as they do not yield sufficient statistics even after very long measuring times.

For diffusion via vacancies most interesting is the jump vector of the ^{57}Fe atom with respect to the wave vector of the incoming radiation. In the present case the incoming beam is chosen parallel to the [001] direction of the monolayer, as in the experiment compared below.

The effect of fluctuating quadrupole interactions is described by the third term $V_\mu F_\mu$ in the square bracket of equ. (1). The Hamiltonians corresponding to the interaction V_μ are given by

$$V_{\pm 1} = V_N + (V_0 + V_m), V_{\pm 2} = V_N + (V_0 - V_m) \text{ and } V_N \tag{2}$$

where ± 1, ± 2 and N refer to vacancies on sites as indicated in Fig. 1. For the excited state of ^{57}Fe (nuclear spin 3/2) and the (110) plane [12]

$$\begin{aligned} V_N &= Q_N(3{I_z}^2 - 15/4), \\ V_0 &= Q_D({I_x}^2 + 2{I_y}^2 - 15/4), \\ V_m &= \sqrt{2}Q_D(I_x I_y + I_y I_x). \end{aligned} \tag{3}$$

Q_N the pure surface quadrupole interaction of the undisturbed (i.e. defect-free) sample and Q_D is the defect contribution to the quadrupole interaction. I_x, I_y and I_z are the spin component operators of the excited 3/2 state. F_μ is a projection operator that ensures that the defect's quadrupole interaction acts on the probe atom only when the defect is on one of the probe atom's NN sites. What is new here compared to the theory of combined jump diffusion and quadrupole relaxation in the bulk [8] is the clear anisotropy of the electric field exerted on the nucleus by the neighboring atoms due to the two-dimensional structure of the system.

One has to numerically invert the 20x20 matrix under the square brackets in equ. (1) and take its average as implied by the summation over α and β. The emission spectrum of the Mössbauer effect can now be computed and by its Fourier-transform into the time domain the time spectrum of NRS is received.

In Fig. 2 we show the expected NRS spectra in time domain resulting from a simulation based on the theory. We compare to the corresponding spectra in energy domain as expected from conventional Mössbauer effect taking into account quadrupole interactions through the anisotropy of the surface and through interaction with defects.

Ad-atom diffusion, i.e. diffusion of atoms on top of the surface, follows similar logics as vacancy diffusion with one marked difference: *the nuclear probe atom itself is not moving.* Therefore at large jump frequencies there will be no accelerated decay but rather "motional narrowing" of the Mössbauer line and therefore a return to a slow decay of NRS (in the ideal case with natural life time). The reason is the averaging out of the fluctuating field gradient.

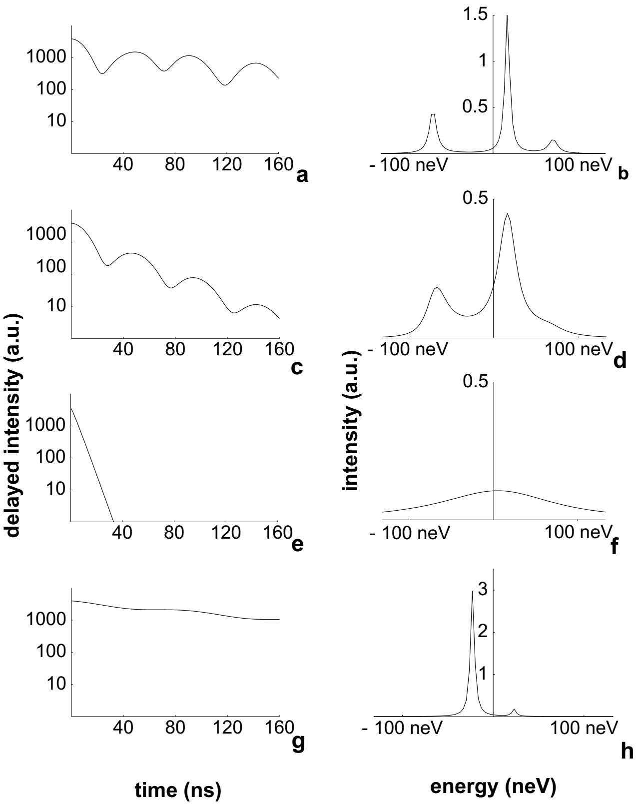

FIG. 2: Simulations according to theory. Left column: NRS spectra (intensity decay vs time), right column: corresponding Mössbauer emission spectra (intensity vs energy). Jump frequency of atoms: (a) and (b) 0.1 MHz corresponding to very slow diffusion, (c) and (d) 1.5 MHz, (e) through (h) 22.5 MHz. In (g) and (h), however, the probe atom is kept immobile, and as a consequence the decay of the NRS intensity flattens and motional narrowing occurs in the Mössbauer spectrum. Following Przybylski [7] the quadrupole interaction of pure Fe on a W surface is 32 neV , i.e. about 7 times natural linewidth (4.7 neV). The defect concentration was assumed to be 10 percent, the additional quadrupole interaction from the defects 140 neV because these will be the best values to match the experimental spectra. Note in (b): The outer quadrupole doublet is due to the defect component. Because of the polarization of the synchrotron beam only the surface component at positive energy remains.

For NRS the quadrupole interaction from neighboring vacancies or ad-atoms leads to beats in the decay as is demonstrated in the simulation based on the theory in Fig. 2, left column, whereas for Mössbauer emission additional lines appear (Fig. 2, right column). The NRS beat frequency is larger the higher the quadrupole interaction acting on the nucleus. Fluctuation of the quadrupole interaction due to diffusion causes a more pronounced smearing of the beats the faster the atoms in the neighborhood and the ^{57}Fe atom itself move. Most remarkable is the difference in the spectra for mobile and immobile probe atoms: whereas for mobile probe atoms the decay of the NRS intensity in time continues to steepen with increasing jump frequency and the Mössbauer line continues to broaden, in case of immobile probe atom from a certain jump frequency on the decay becomes flatter and the Mössbauer line becomes narrower. The marked difference of the scenarios for vacancy diffusion and adatom diffusion is a criterion permitting a decision which of the two cases persists.

In the following we compare with the results of the first published NRS experiment [13] on surface monolayer diffusion. For studying experimentally the diffusion in a monolayer or even a sub-monolayer or of the ad-atoms in an incomplete surface layer two conditions had to be fulfilled: a very brilliant x-ray source (highly collimated, strong flux) as realised by a synchrotron of third generation and grazing incidence of synchrotron radiation in order to achieve high scattering intensity. The experiment reported in Ref. 13 was performed under these stringent conditions: An ^{57}Fe sub-monolayer on a near (110) vicinal W surface was measured at UHV conditions at grazing incidence of x-rays with the direction of the incident beam parallel to the [001] direction of the W substrate.

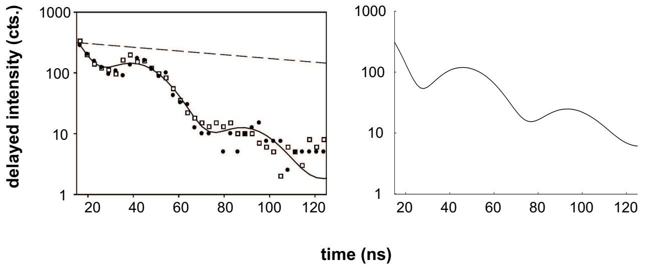

FIG. 3: Left: Measured NRS spectrum [13] of ^{57}Fe submonolayer on (110) tungsten at room temperature before (open squares) and after (full circles) an NRS measurement at 670 K which led to complete disappearance of the beats. Please note: In NRS experiments data collection starts not earlier than 20 ns after the nuclear excitation. The dashed line corresponds to NRS in the absence of diffusion. Right: ^{57}Fe NRS spectrum according to theory with probe atom immobile, jump frequencies of surrounding atoms 3 MHz. Quadrupole interaction and defect concentration same as in Fig. 2.

Fig. 3 shows the results of the NRS experiment at room temperature together with a simulation based on the theory.

A comparison of the simulated spectrum with the experimental spectrum implies that a defect induced quadrupole interaction energy of (140 ± 20) neV, corresponding to a splitting of the Mössbauer doublet of (3.0 ± 0.5) mm/s matches the experiments.

The most interesting effect in the experiment [13] is the decrease of the beat frequency between room temperature (300 K) and 470 K and the complete disappearance of the beats at 670 K. This is in agreement with a jump frequency of the surface atoms of (3 ± 0.5) MHz at 300 K, increasing to (6 ± 1) MHz at 470 K and to (20 ± 3) MHz at 670 K where the beats disappear. Very striking is that the increase in the beat period is *not* accompanied by an accelerated intensity decay as would be expected if the probe atom itself was jumping, compare Fig. 2 (e). This implies that we can exclude vacancy diffusion which would lead to an identical jump frequency of the ^{57}Fe probe atom and the other Fe atoms. We rather conclude that *impurity ad-atoms are jumping*, by this way producing quadrupole relaxation which becomes so fast that the *decay of the NRS intensity flattens* (compare Fig. 2 (g)) and *motional narrowing* appears in the Mössbauer spectrum (Fig. 2 (h)). To the best of our knowledge this is the first time that such a phenomenon has been observed on surfaces. The nature of the ad-atoms remains unknown, experiments with controlled charging with gas atoms are proposed.

From the temperature dependence of the beat frequency we can estimate the activation energy for atomic jumps of the impurity atoms on top of the Fe surface:

$$Q = (0.08 \pm 0.02)\,\mathrm{eV}.$$

This value is considerably lower than for vacancy diffusion in an Fe/W film which has been investigated by means of DFT ab-initio calculations by Spisak and Hafner [14]. These authors predict activation energies of vacancy diffusion between 0.7 and 1.6 eV.

In conclusion we state that nuclear resonance scattering of synchrotron radiation permits the determination of the diffusional jump frequency of single atoms in very thin layers. We have developed a simplified theory which allows to distinguish vacancy from ad-atom diffusion. Future experiments will draw profit from the information contained in the angular dependence of the spectra, i.e. determine also the jump vector and thus distinguish details as e.g. diffusion directions. By this way the elementary diffusion jump in and on surfaces will be determined.

We are grateful to Bogdan Sepiol, Vienna and Binayak Dutta-Roy, Kolkata for many enlightening discussions. Manfred Smolik, Vienna provided essential assistance with the computer graphics and Michael Leitner helped bringing the manuscript to its final form. One of us would like to thank the Indian Institute of Science Education and Research (IISER), Kolkata for its hospitality. The work was financially supported by the Austrian Federal Ministry for Education, Science and Culture (Project No. GZ 45.529/2-VI/B/7a/2002).

---

[*] to whom correspondence should be addressed: `gero.vogl@univie.ac.at`

[†] Now at Philips Austria GmbH / CoC Klagenfurt Koningsbergerstr. 11, A-9020 Klagenfurt, Austria

[1] E. Gerdau, R. Rüffer, H. Winkler, W. Tolksdorf, C. P. Klages, and J. P. Hannon, Phys. Rev. Lett. **54**, 835 (1985).

[2] J. B. Hastings, D. P. Siddons, U. van Bürck, R. Hollatz, and U. Bergmann, Phys. Rev. Lett. **66**, 770 (1991).

[3] G. V. Smirnov and V. G. Kohn, Phys. Rev. B **52**, 3356 (1995).

[4] B. Sepiol, A. Meyer, G. Vogl, R. Rüffer, A. Chumakov, and A. Q. R. Baron, Phys. Rev. Lett. **76**, 3220 (1996).

[5] G. Vogl and B. Sepiol, in *Diffusion in Condensed Matter - Methods, Materials, Models*, edited by P. Heitjans and J. Kärger (Springer, Berlin/Heidelberg, 2005), pp. 65–91.

[6] D. Kmiec, B. Sepiol, M. Sladecek, M. Rennhofer, S. Stankov, G. Vogl, B. Laenens, J. Meersschaut, T. Slezak, and M. Zajac, Phys. Rev. B **75**, 054306 (2007).

[7] M. Przybylski, Hyperfine Interact. **113**, 135 (1998).

[8] S. Dattagupta and K. Schroeder, Phys. Rev. B **35**, 1525 (1987).

[9] I. Sergueev, U. van Bürck, A. I. Chumakov, T. Asthalter, G. V. Smirnov, H. Franz, R. Rüffer, and W. Petry, Phys. Rev. B **73**, 024203 (2006).

[10] S. Dattagupta, *Relaxation Phenomena in Condensed Matter Physics* (Academic Press, Orlando, 1987).

[11] M. Blume, Phys. Rev. **174**, 351 (1968).

[12] J. J. Sakurai, *Modern Quantum Mechanics* (Pearson Education, Singapore, 1994).

[13] M. Sladecek, B. Sepiol, J. Korecki, T. Slezak, R. Rüffer, D. Kmiec, and G. Vogl, Hyperfine Interact. **566-568**, 372 (2004).

[14] D. Spisak and J. Hafner, Phys. Rev. B **70**, 195426 (2004).