



	<b>Experiment title:</b> X-ray photon correlation spectroscopy investigations of diffusion in hard-condensed matter	<b>Experiment number:</b> HS-2541
<b>Beamline:</b> ID10A	<b>Date of experiment:</b> from: 23/02/05 to: 03/03/05	<b>Date of report:</b> 20/03/06
<b>Shifts:</b> 21	<b>Local contact(s):</b> Dr. Federico ZONTONE	<i>Received at ESRF:</i>

**Names and affiliations of applicants** (\* indicates experimentalists):

Lorenz-Mathias Stadler<sup>1,\*</sup>, Bogdan Sepiol<sup>1,\*</sup>, Rüdiger Reitinger<sup>1,\*</sup>, Nika Spiridis<sup>2,\*</sup>, Svetoslav Stankov<sup>1,4,\*</sup>, Gerhard Grübel<sup>3</sup>, Anders Madsen<sup>4</sup>, Gero Vogl<sup>1</sup>

<sup>1</sup> Institut für Materialphysik, Fakultät für Physik, Universität Wien, Strudlhofg. 4, 1090 Wien, Austria

<sup>2</sup> Institute of Catalysis and Surface Chemistry Polish Academy of Sciences, ul. Niezapominajek 8, 30-239, Krakow, Poland

<sup>3</sup> DESY (HASYLAB), Notkestr. 85, 22607 Hamburg, Germany

<sup>4</sup> ESRF, BP220, 38043 Grenoble Cedex, France

**Report:**

Diffusion in crystalline solids is of utmost importance in daily life, e.g., rusting of metals, doping of semi-conductors, nitrogen hardening of steels, etc. Only very few methods, however, are capable of determining the microscopic fundamental diffusion mechanism, which is in crystalline solids a jump process of atoms, typically mediated by vacancies. So far these methods are resonant techniques like quasielastic Mössbauer spectroscopy (QMS) [1] or nuclear resonant scattering of synchrotron radiation (NRS) [2]. Apart from the fact that only certain isotopes can be probed by these methods, one is limited to systems showing very fast diffusion with  $D \geq 10^{-14} \text{ m}^2 \text{ s}^{-1}$ . Hence, a non-resonant method, which can detect slow diffusion, is extremely desirable. X-ray photon correlation spectroscopy (XPCS) is the most promising candidate to fill this gap. Though, it is not clear whether the coherent intensity available today is sufficient for measurements with large momentum transfers in the diffuse scattering regime, which is necessary for resolving dynamics on atomic scale. Furthermore, crystalline systems are usually well ordered, which additionally reduces the diffuse scattered intensity, where such high momentum transfers occur. Up to now XPCS experiments predominantly dealt with measurements of soft-condensed matter in small-angle X-ray scattering (SAXS) or grazing incidence SAXS (GISAXS) geometry, e.g., [3], and only a few with dynamics in crystalline solid systems [4].

Facing the refurbishment of the undulators of the TROIKA beamline there is a realistic chance to measure diffusion in crystalline solids in the continuum limit. After consultation of the scientific staff at TROIKA we wanted to take this chance and find out what is possible and where are the limits for diffusion investigations in hard-condensed matter. For that

purpose several systems, ranging from bulk glass ( $\text{Zr}_{65}\text{Ni}_{10}\text{Cu}_{17.5}\text{Al}_{7.5}$ ) [5] to single-crystalline intermetallic phases ( $\text{Fe}_{65}\text{Al}_{35}$ ) and even to clusters on surfaces ( $\text{Au}/\text{Fe}_3\text{O}_4$ ), were investigated with respect to their diffuse scattering strength.

The outcome of our measurements is somewhat deflating. Figure 1 shows a  $2\Theta$  scan (in transmission geometry) of a  $13\ \mu\text{m}$  thin  $\text{Zr}_{65}\text{Ni}_{10}\text{Cu}_{17.5}\text{Al}_{7.5}$  foil with the  $100\ \mu\text{m}$  pinhole. Even at the structure function maximum, which corresponds to the mean next-neighbour distance, the intensity is just about 100 counts per second. For a coherent set-up, however, the beam has to be restricted to about  $10\ \mu\text{m}$ , i.e. the intensity is then expected to be two orders of magnitude weaker. Reasonable measurements of dynamics taking place on time scales of seconds (ideally milliseconds) is thus not possible. For single-crystalline samples the situation becomes even worse. When doing diffuse scattering measurements ( $2\Theta=20^\circ$ ) with an (001)-oriented  $\text{Fe}_{65}\text{Al}_{35}$  single crystal (B2 phase), the Fe-K fluorescence dominated the scattering pattern, which was taken with a directly illuminated CCD camera. Analysing the ADU spectrum by means of a droplet algorithm (by courtesy of F. Livet) yielded a maximum frequency for iron-fluorescence photons, having lower energy (6.4 keV) and thus lower ADU values ( $\approx 230$ ) than the 8 keV photons ( $\approx 290$  ADU) from the monochromator. Figure 2 shows such a frequency spectrum (red points) in comparison with an analysis of a coherent SAXS pattern of a NiAlMo sample containing  $\text{Ni}_3\text{Al}$  precipitates (black points). All in all, it seems still a long way to go for realising diffusion measurements in crystalline solids on an atomic scale by means of XPCS.

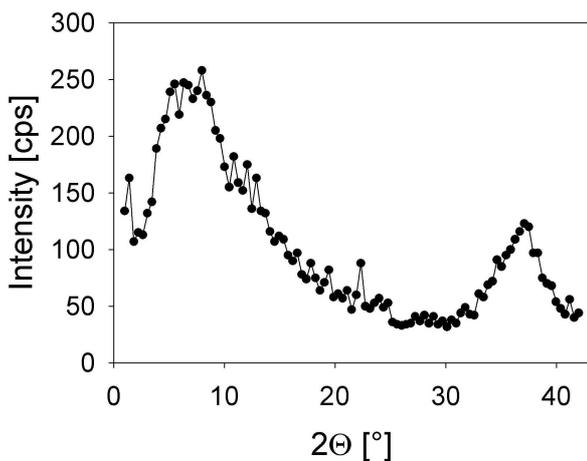


Fig. 1:  $2\Theta$  scan of a  $13\ \mu\text{m}$  thin  $\text{Zr}_{65}\text{Ni}_{10}\text{Cu}_{17.5}\text{Al}_{7.5}$  foil with  $100\ \mu\text{m}$  pinhole, i.e. in an incoherent set-up. The structure function maximum is at about  $38^\circ$ . The broad “halo” at  $8^\circ$  belongs to the same amorphous phase [6].

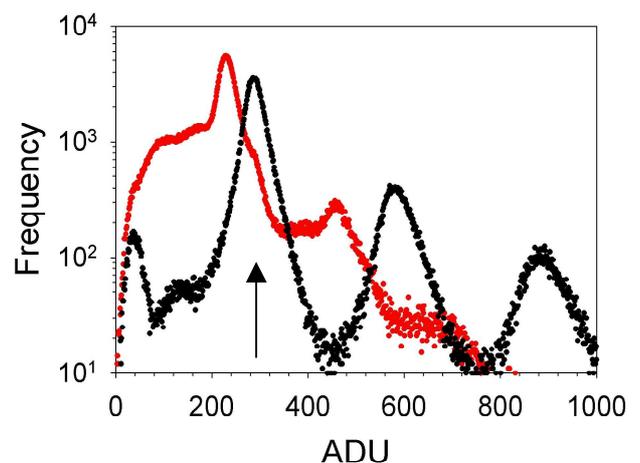


Fig. 2: Droplet analysis (courtesy of F. Livet) of diffuse scattering intensity of a  $\text{Fe}_{65}\text{Al}_{35}$  single crystal ( $2\Theta=20^\circ$ ) with a fluorescence peak at  $\approx 230$  ADU, red points. The analysis of a SAXS pattern of NiAlMo containing  $\text{Ni}_3\text{Al}$  precipitates, black points yields the one-photon peak for 8 keV photons correctly at  $\approx 290$  ADU (arrow).

[1] B. Sepiol and G. Vogl, Phys. Rev. Lett. **71**, 731 (1993).

[2] B. Sepiol *et al.*, Phys. Rev. Lett. **76**, 3220 (1996).

[3] T. Thurn-Albrecht *et al.*, Phys. Rev. Lett. **77**, 5437 (1996); S.G.J. Mochrie *et al.*, Phys. Rev. Lett. **78**, 1275 (1997); D.O. Riese *et al.*, Phys. Rev. E **61**, 1676 (2000); D. Lumma *et al.*, Phys. Rev. Lett. **86**, 2042 (2001); A. Madsen, J. Als-Nielsen and G. Grübel, Phys. Rev. Lett. **90**, 085701 (2003).

[4] S. Brauer *et al.*, Phys. Rev. Lett. **74**, 2010 (1995); A. Malik *et al.*, Phys. Rev. Lett. **81**, 5832 (1998); F. Livet *et al.*, Phys. Rev. E **63**, 036108 (2001); S. Francoual *et al.*, Phys. Rev. Lett. **91**, 225501 (2003); L.-M. Stadler *et al.*, Phys. Rev. B **68**, 180101(R) (2003); L.-M. Stadler *et al.*, Phys. Rev. B **69**, 224301 (2004).

[5] A. Meyer *et al.*, Phys. Rev. B **53**, 12107 (1996).

[6] P.S. Frankwicz, S. Ram, and H.-J. Fecht, Appl. Phys. Lett. **68**, 2825 (1996).