	Experiment title: Mechanism of diffusion in NiAl measured by XPCS	**Experiment number:** HS-4082
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Report:

Scattering coherent X-rays at a sample displaying disorder leads to a so-called speckle pattern in the scattered intensity, which is nothing but the absolute square of the Fourier transform of the (disordered) electron density in the sample. Recording the temporal fluctuations of the speckle pattern is the principle of X-ray Photon Correlation Spectroscopy (XPCS). This technique therefore measures the lifetime of fluctuations in the sample corresponding to a given scattering vector $\vec{q}$. We have recently demonstrated that it is possible to apply this technique for studying the dynamics at atomic scales: by using a single crystal and varying $\vec{q}$ both in length and orientation relative to the crystal lattice one can elucidate the diffusion mechanism of single atoms [1].

Here we report on our measurements at a single crystal of $Ni_{48}Al_{52}$, which has the cubic B2-phase. Measurements were done with a photon energy of 8 keV, the Si(111)-monochromator gave a temporal coherence of $\Delta E/E = 1.42 \times 10^{-4}$ and the beam-defining slits were set to $8 \times 8\,\mu m^2$. The beam was focussed with the compound refractive lenses-system. The sample was mounted in a custom-built vacuum furnace. The entrance and exit windows of both furnace and flight tube were made from Kapton foil. Frames were taken with ID10A's 1024×1024 CCD camera with $13 \times 13\,\mu m^2$ pixel size, the exposure was 10 s per frame with about one second read-out. The distance sample–detector was 0.5 m. With this set-up, the count rate was below 0.01 photons per pixel and frame, and the coherence factor varied from 0.09 at scattering angles $2\theta = 6°$ to 0.02 at $2\theta = 20°$.

The resulting correlation times for a fixed detector position, i.e., a given scattering vector $\vec{q}$, but different sample temperatures are given in Fig. 1, the variation of the correlation time with the orientation of $\vec{q}$ with respect to the crystalline lattice, but with fixed scattering angle, i.e., length of $\vec{q}$, at a fixed temperature of 417 °C is given in Fig. 2.

The fit in Fig. 1 gives a value for the activation enthalphy of 1.24 ± 0.14 eV. This value is much smaller than the values obtained from tracer measurements for both constituents in this system [2]. On the other hand, the pronounced maximum in the orientational dependence of the correlation times at $\varphi = 90°$ (which corresponds to the [001]-direction) means that the effective displacement vectors that drive the temporal evolution of the disorder in the system are $\langle 100 \rangle$, i.e., the edges of the cubes or the nearest-neighbour-vectors in either sublattice.

To understand these observations it is necessary to consider the B2-NiAl-system on the atomic scale: It is well established that for Al-rich samples (which is here the case) the off-stoichiometry is accommodated
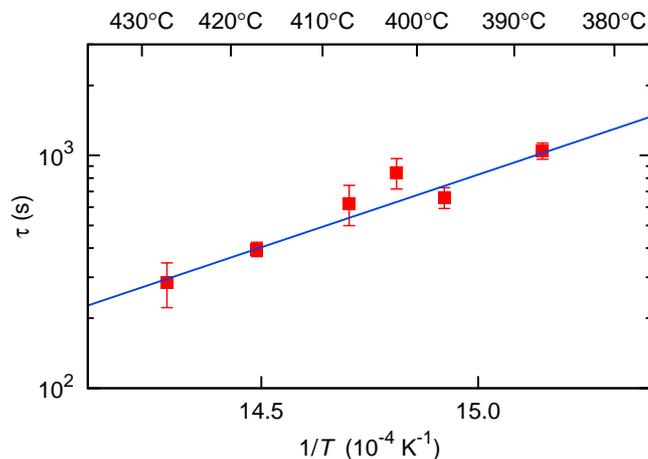
Figure 1: Arrhenius plot of correlation times.
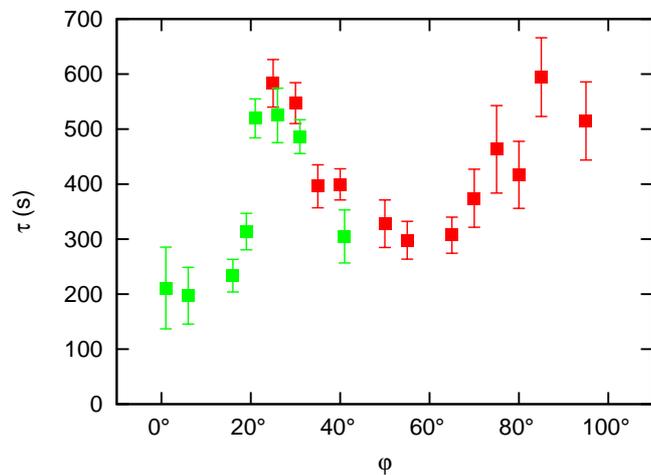
Figure 2: Variation of correlation time in $(1\bar{1}0)$-plane as function of azimuthal angle. [110] is at $\varphi = 0°$, [001] at $\varphi = 90°$. Data are taken from two sample setups.

by constitutional vacancies on the Ni-sublattice, whereas the Al-sublattice is (apart from thermal defects) exclusively populated by Al-atoms [3, 4]. The disorder that gives rise to the diffuse scattering is therefore the disorder on the Ni-sublattice, i.e., the configuration of the constitutional vacancies, and the above quoted $\langle 100 \rangle$-vectors are the effective displacement vectors of these vacancies.

The phenomenon of constitutional Ni-vacancies explains the low activation enthalpy: in contrast to most other systems, and also the stoichiometric case of NiAl, where the activation enthalpy of diffusion is the sum of the vacancy formation enthalpy and the migration enthalpy, here the vacancy concentration is (nearly) independent of temperature, corresponding to a vacancy formation enthalpy of zero.

Our picture of diffusion on the atomic scale is therefore as follows: the elementary event is a next-nearest-neighbour jump of a Ni atom into a constitutional Ni vacancy. The highest state along this transition path corresponds to the Ni atom passing through a square window of four Al atoms. Due to the abundance of Ni vacancies it is probable that at least one of these Al atoms, but probably even more, has an additional vacant nearest-neighbour site and can move out of the way, thereby lowering the migration enthalpy significantly compared to the one-vacancy case considered up to now [4].

In conclusion, we have elucidated here the diffusive dynamics on the Ni-sublattice in Al-rich NiAl, which is probably the first example that the motion of vacancies in the bulk has been directly followed.

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