# Electronic Supplementary Information (ESI) for Order-disorder phase transition of the subsurface cation vacancy reconstruction on $Fe_3O_4$(001)

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## 1. Temperature calibration for FastSTM measurements

In order to ensure that the temperature reading during our FastSTM experiments is comparable to that from the SXRD experiments, we performed temperature-dependent LEED on the sample used for STM measurements. The sample is kept on the same sample holder and the same heater and thermocouple (both included in the holder) are used to control and read the temperature in the two experiments. Figure 1 shows the amplitude of the (1/2, 3/2) diffraction spot of the $(\sqrt{2} \times \sqrt{2})$R45°reconstruction while heating the sample up through the phase transition and cooling back down, measured with an electron energy of 25 eV. To account for the hysteresis behavior in the heating and cooling curves, we take the mean value of the two curves at the point where the intensity drop is half of its maximum. This approach is justified since the sample is equilibrated at one temperature for a significantly longer time in the STM than during the LEED measurement. We obtain a transition temperature of 725±20 K, in excellent agreement with Ref. [**?** ].

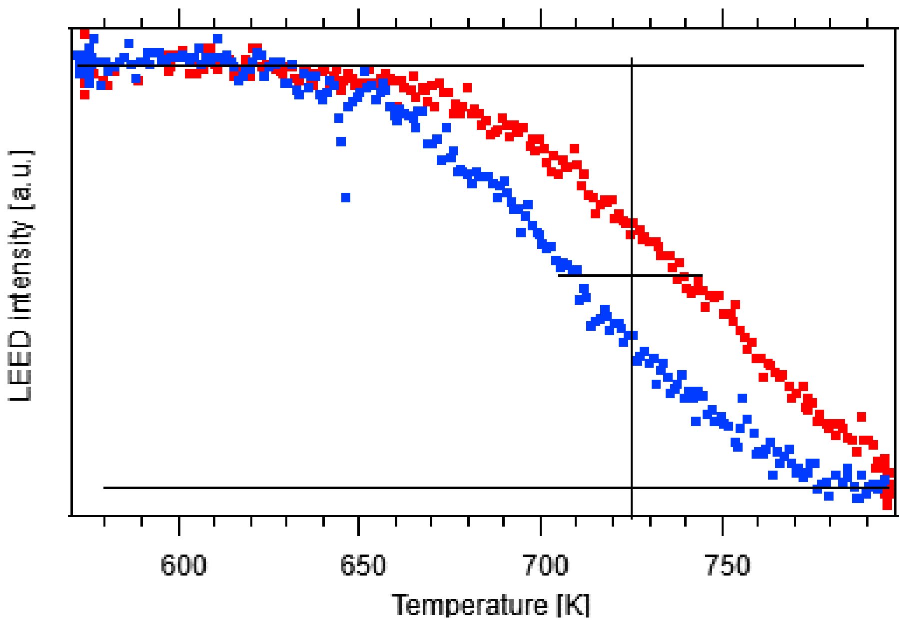


Figure 1: Intensity of the $(\sqrt{2} \times \sqrt{2})$R45°(1/2, 3/2) LEED spot while heating (red) and cooling (blue) the sample through the phase transition. The horizontal lines mark the minimum and maximum intensity levels and the cross is used to identify the transition temperature as the mean value of the heating and cooling curves where the intensity has dropped by half of the total drop.

## 2. Surface dynamics in FastSTM movies

Three supplementary movies are available which were recorded with the following settings:

Supplementary Movie S1: 701 K, $V_b = 1.5$ V, $I_t = 0.9$ nA, 4 fps.

Supplementary Movie S2: 745 K, $V_b = 1.3$ V, $I_t = 1.0$ nA, 11.7 fps.

Supplementary Movie S3: 784 K, $V_b = 1.5$ V, $I_t = 1.0$ nA, 11.7 fps.

For better visualization, Movie S1 has been accelerated by a factor of 7.5 and Movie S2 has been slightly filtered to remove streaks and every other frame has been omitted to avoid slight vertical phase shifts between upward and downward measurements. In line with the rearrangement of the iron atoms, we have further information for possible vertical mass transport in the measurements obtained at 784 K: In rare events, we see the formation of depressions extending across two iron rows with a well-defined rim that disappear after some frames and occasionally reappear at the same position. The frequency of occurrence of these depressions depends on the sample preparation. When cooling down the sample to room temperature, some of these defects can still be observed as static features. In view of the magnetite lattice dynamics governed by Fe transport and not by O transport [**?** ], we assign these depressions either to Fe transport processes or to contaminants in the cation lattice that occasionally reach the surface on their diffusion path.

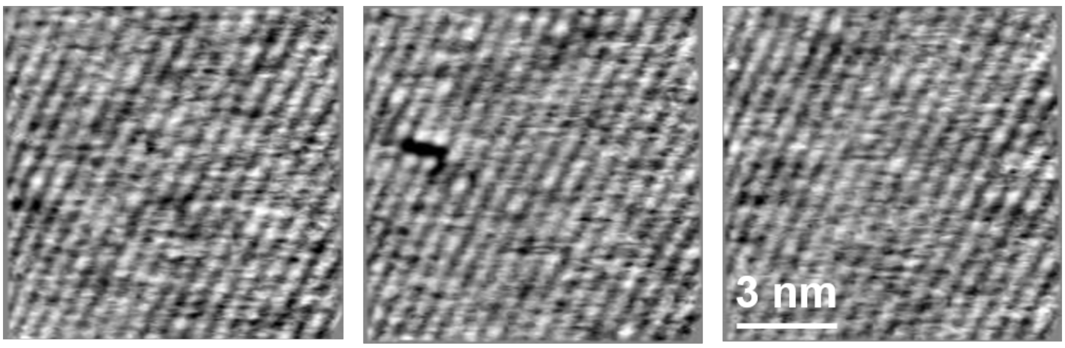


Figure 2: Frames from a FastSTM movie at 784 K which are separated in time by approx. 0.3 s show that a depression appears in a location where previously the pristine surface was visible, and disappears again.

## 3. Temperature calibration for XPS, UPS and LEIS measurements

On the crystal used for XPS, UPS and LEIS, the phase transition was also investigated by low energy electron diffraction (LEED), as shown in Fig. 3. We could thus confirm that the phase transition occurs in a similar temperature range in this crystal as in the ones used for SXRD and STM experiments, respectively.

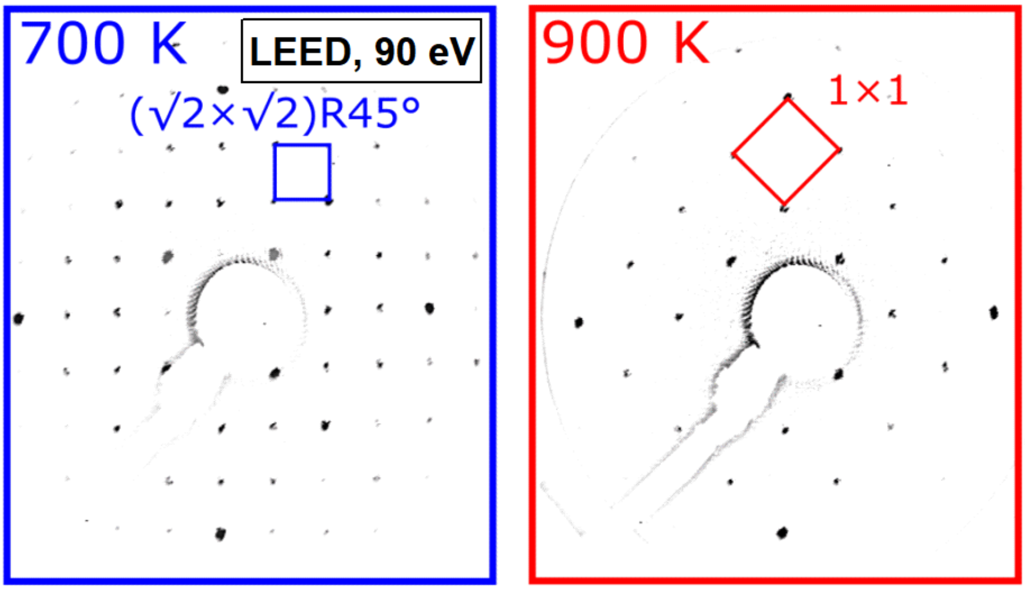


Figure 3: LEED pattern below (700 K) and above the phase transition (900 K)