The dipole moment of the spin density as a local indicator for phase transitions: Supplementary Information

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Supplementary Methods

Vibrating sample magnetometry. In order to determine the Verwey transition (VT) temperature of the present film sample, field cooled (FC) and zero field cooled (ZFC) measurements have been performed with a vibrating sample magnetometer (VSM) for different magnetic fields. The FC-ZFC measurements are shown for a magnetic field of 20 mT as an example in Fig. **S1** (top panel) together with the difference between the FC and ZFC measurements (middle panel). The corresponding blocking temperature distribution (BTD), calculated as the negative derivative of the FC-ZFC difference divided by the temperature [1] and the magnetic field, is shown in the bottom panel (solid line) together with the BTDs for 50 mT (dashed line) and 100 mT (short-dashed line). The VT already appears as a small bump in the FC curve (top panel) and more clearly as a peak in the BTD which does not shift in temperature with the magnetic field (bottom panel). This result demonstrates that the magnetite film exhibits the VT at a temperature of about 120 K. In order to find out whether the VT is also observed for the nanoparticles (NPs), the FC-ZFC measurements have also been performed for them. The resulting BTDs shown in Fig. **S2** do not bear an indication for the VT because they are dominated by blocking effects as will be discussed in the following.

The BTDs obtained for the NPs clearly exhibit each two different peaks, i.e. one very sharp at low temperatures and a broad distribution with a peak at higher temperatures. Each of the two contributions could be fitted with a log-normal distribution (not shown here) leading to a reasonable simulation of te experimental data. We found that the temperature at which these distributions are maximum ($T_{max}^{1,2}$) clearly depends on the magnetic field applied for the measurement: The higher the field, the lower the values of $T_{max}^{1,2}$. This type of magnetic field dependence is typical for magnetic blocking behavior and shows that none of the peaks can be assigned to the VT. For noninteracting NPs which were spatially separated by a matrix the peaks at lower and higher temperatures are known to be due to surface spin glass and individual NPs [2], respectively. For systems like in the present case where the NPs are not spatially separated, the peak at higher temperatures is known to be due to clusters of interacting NPs which were described by a correlation volume [3, 4]. Moreover, the VT would not be observed with VSM if it appeared at temperatures below the minimal measured temperature of 4.5 K or above the maximal blocking temperature. The latter increases with decreasing external field and for the minimal applied magnetic field of 10 mT it was roughly about 100 K for the NPs. The VT temperatures of magnetite NPs presented in the literature are contradictory. According to Ref. [5] the VT temperature of magnetite NPs with a diameter of about 50 nm was already reduced to 16 K whereas in Ref. [6] the VT temperature of magnetite NPs with a diameter of 5.5 nm was determined to be 96 K. Therefore we conclude regarding this point that our magnetometry data showed no indication for the VT in the present NPs, but that the presence of the VT cannot be excluded.

Magnetometry compared with XMCD. The magnetic dipole moment that is measured with x-ray magnetic circular dichroism (XMCD) is known to be negligibly small for cubic symmetry [7] and to be non-negligible for non-cubic symmetries and at surfaces where the cubic symmetry is broken [8], in systems with low dimension like monolayers and monatomic wires [9] and clusters [10]. It is difficult to verify experimentally that the dipole moment is not observable with macroscopic magnetometry. The reason for this is that usually the dipole moment is large in systems with reduced dimensions which cannot be detected with sufficient sensitivity with macroscopic magnetometry and sufficient accuracy with XMCD [11]. Contrary, in magnetite the average Fe dipole moment in the low-temperature phase according to our electronic structure calculations is sufficiently large to be both, reliably quantified with XMCD and measurable (if in principle observable) with macroscopic magnetometry. Therefore, magnetite is an exception and very suitable to experimentally verify at the Verwey transition that the dipole moment is not observable with macroscopic magnetometry. In this sense, the present comparison of the magnetic moments measured with XMCD and VSM proofs experimentally that the dipole moment is not observable with VSM.

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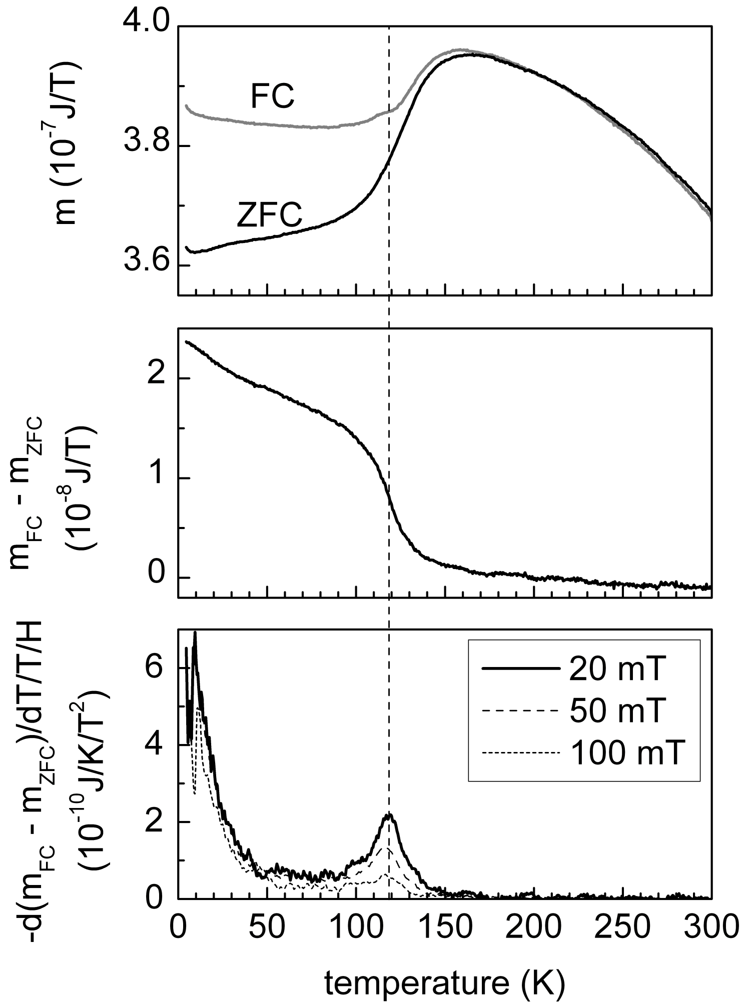
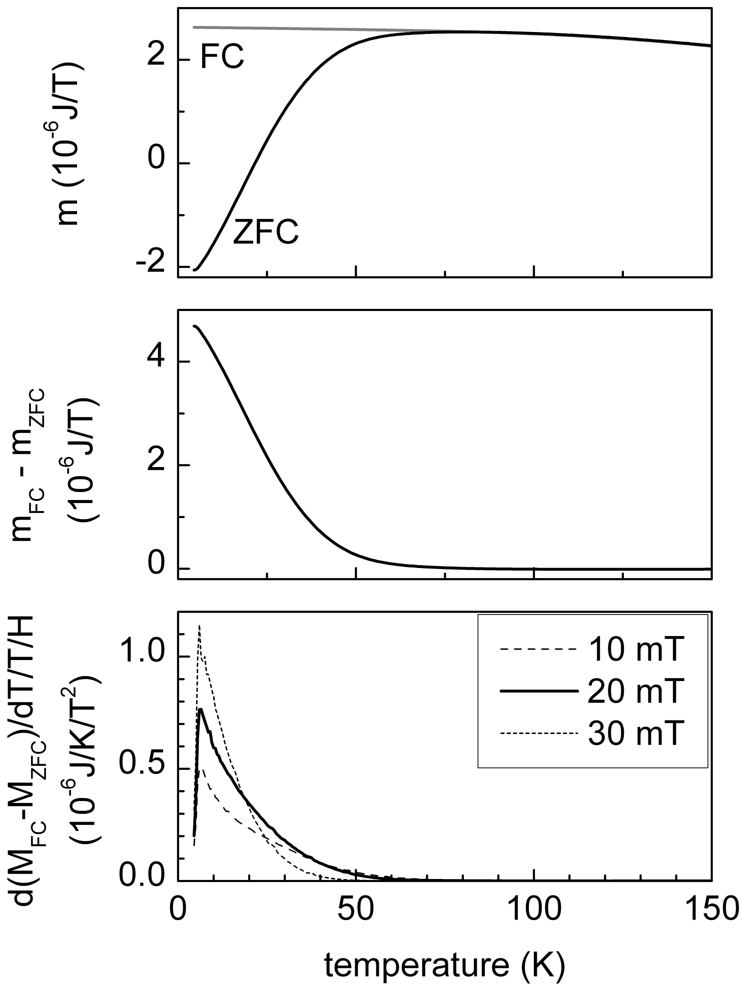


Supplementary Figure S1: Top panel: Magnetic moment measurements of a 200 nm thick magnetite film performed with a vibrating sample magnetometer in a magnetic field of 20 mT during heating after field cooling (FC) in 20 mT and zero-field cooling (ZFC). Middle panel: Difference of the FC and ZFC curves shown in the top panel. Bottom panel: Blocking temperature distributions for different magnetic fields. The 20 mT curve (solid line) has been determined from the difference in the medium panel. For comparison, blocking temperature distributions for 50 mT (dashed line) and 100 mT (short dashed line) are also shown.



Supplementary Figure S2: Top panel: Magnetic moment measurements of an ensemble of nanoparticles performed with a vibrating sample magnetometer in a magnetic field of 20 mT during heating after field cooling (FC) in 20 mT and zero-field cooling (ZFC). Middle panel: Difference of the FC and ZFC curves shown in the top panel. Bottom panel: Blocking temperature distributions for different magnetic fields. The 20 mT curve (solid line) has been determined from the difference in the medium panel. For comparison, blocking temperature distributions for 10 mT (dashed line) and 30 mT (short dashed line) are also shown.