Revealing a masked Verwey transition in nanoparticles of coexisting Fe-oxide phases

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The attractive electronic and magnetic properties together with their biocompatibility make iron-oxide nanoparticles appear as functional materials. In Fe-oxide nanoparticle (IONP) ensembles, it is crucial to enhance their performance thanks to controlled size, shape, and stoichiometry ensembles. In light of this, we conduct a comprehensive investigation in an ensemble of ca. 28 nm cuboid-shaped IONPs in which all the analyses concur with the coexistence of magnetite/maghemite phases in their cores. Here, we are disclosing the Verwey transition by temperature dependent (4–210 K) Raman spectroscopy.

Considered as the oldest known magnetic material, magnetite (Fe₃O₄) has been revealed as a prototypical multifunctional material in the last decades. The renewed interest is especially connected to applications associated with the reduction of such a compound to the nanoscale. Some of its fascinating applications are related to electronics and magnetism, catalysis and especially connected to applications associated with the reduction of magnetite/maghemite phases in their cores. Here, we are disclosing the Verwey transition by temperature dependent (4–210 K) Raman spectroscopy.

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Additionally, other magnetite counterparts are included here to draw a complete comparison.

The IONPs were synthesized by an oxidative precipitation process described elsewhere, followed by a dextran coating procedure under high-pressure homogenization conditions. Finally, the IONPs were magnetically fractionated using a commercial magnetophoresis setup SEPMAG-Q100 system to refine size inhomogeneities. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were performed, respectively, in a FEI Tecnai G2 T20 (equipped with LaB6 electron gun) and a FEI Titan 80-300. In both cases the sample was prepared by depositing droplets of water-dispersed IONPs on a carbon-coated copper grid. The transmission high-energy X-ray diffraction (XRD) study was conducted in Debye–Scherrer geometry at HEMS beamline P07b located at PETRAIII (DESY), Hamburg (Germany). A Si (220) monochromator was used to select a wavelength of $\lambda = 0.1424$ Å. The diffraction pattern was collected with a Perkin Elmer image plate detector, characteristic of a resolution of 2048 × 2048 pixels and a pixel size of 200 μm, at a sample to detector distance of 1254 mm. The experimental setup was calibrated using a standard Al2O3 powder. The transmission Mössbauer spectrum was recorded at room-temperature (RT) with a built-inhouse Mössbauer spectrometer equipped with a $^{57}$Co source in Rh foil and operating in constant acceleration mode. Specific heat $C_p$ was measured within the temperature range 5 K $\leq T \leq$ 300 K. A standard two-τ relaxation method was used to obtain the absolute value of $C_p$ in a Quantum Design PPMS-system. Prior to the $C_p(T)$ measurement, the IONPs powder was compressed into a pellet of 5 mm diameter and a thickness of ca. 1 mm. To guarantee a good thermal contact, apiezon N grease was used to stick the sample to the sample holder. Instrumental (and adhesive grease) contributions to the $C_p(T)$ signal have been subtracted. Magnetic AC-susceptibility was performed in a Quantum Design MPMS-system at a frequency of 0.5 Hz using a field amplitude of $\mu_0 H_{ac} \approx 0.3$ mT. Unpolarized micro-Raman scattering measurements were carried out with a triple monochromator Horiba-Jobin-Yvon T64000 spectrometer in subtractive mode backscattering configuration, equipped with a Horiba Symphony liquid-nitrogen-cooled CCD detector. The 647 nm line of a Coherent Innova 70Ar+-Kr+ laser was focused on the sample with a 20× objective for micro-Raman, and the laser powder was kept below 2 mW to avoid heating effects. The laser spot was 20 μm in diameter and the spectral resolution was better than 0.6 cm$^{-1}$. An Oxford Microstat He optical cryostat attached to the Raman microscope

![Figure 1](image_url)

**Fig. 1** (a) TEM images of single-core IONPs with cuboid shaped. At the top inset it is shown an HRTEM image of the IONPs. The black circle delimits the crystal-size used to evaluate the TEM size. The size-distribution is displayed at the bottom inset. (b) RT Rietveld refinement of the synchrotron powder diffraction pattern. * designates a small glitch during the measurement. (c) RT Mössbauer spectrum to determine the isomer-shift variation. Red line indicates the global fit, whereas black dots are the experimental data.

| Parameters | RT-values |
|------------|-----------|
| Oxygen coordinate $u$ | 0.2528(1) |
| Lattice parameter, $a$ (Å) | 8.3741(1) |
| Crystal size, $D$ (nm) | 20(1) |
| Strain, $\epsilon$ (1000) | 24(3) |
was used for temperature-dependent measurements between 4 and 210 K.

Fig. 1(a) shows a representative TEM image of an ensemble of single-core IONPs displaying a variety of aggregates ranging from 4 units up to several dozens. The synthesis method produces cuboid-shaped IONPs with nearly monodispersed single-cores as it is illustrated in Fig. 1(a). The size-distribution was examined with TEM by counting 250 particles (see bottom

Fig. 2  (a) Specific heat of bulk magnetite and IONPs. (b) Temperature evolution of the real $\chi'(T)$ and complex $\chi''(T)$ contributions to the AC-susceptibility at the frequency of 0.5 Hz. The inset shows the position of the weak hump in $\chi''(T)$ after subtracting the solid line, for clarity.

Fig. 3  (a) Raman spectra of the $A_{1g}$ mode. Arrows indicate the shift in the frequency. Solid red lines are the Lorentzian fits. (b) Thermal evolution of both Raman-shift (black circles) and linewidth (red squares) of the $A_{1g}$ mode around $T_V$. (c) $A_{1g}$ Raman-shift of different samples are displayed for comparison and summarized in Table 2. Raman spectra have been vertically displaced for clarity. Solid red curves are the fits of the anharmonic contribution. (d) Relative frequency change $\Delta \omega(T)/\Delta \omega_{\text{anh}}(T_V)$ (left axis) and frequency change $\Delta \omega$ (right axis) of the $A_{1g}$ mode after subtracting the harmonic term $\omega_0$ and the anharmonic contributions. Dashed lines are guides to the eye.
left inset of Fig. 1(a)). A number-weighted mean value of 28 nm with a standard deviation of 4 nm was obtained using a log-normal distribution.

In Fig. 1(b) we show the Rietveld refinement of the synchrotron XRD pattern using the FULLPROF program.\textsuperscript{31} It should be noted that magnetite crystallizes at RT in an inverse-spinel with a cubic \textit{Fd3m} space group,\textsuperscript{33} whereas maghemite can present different crystal structures depending on the vacancy ordering.\textsuperscript{34} Bearing this in mind, the analysis satisfactorily accounts for all the reflections with a lattice parameter of \(a = 8.3741(1) \text{ Å}\). This value suggests the presence of a mixture of maghemite (\(γ-\text{Fe}_2\text{O}_3, a = 8.34 \text{ Å (ref. 35)}\)) and magnetite phases (\(\text{Fe}_2\text{O}_4, a = 8.40 \text{ Å (ref. 36)}\)) in the core of the IONPs. The main structural parameters refined at RT, together with the agreement factors, are compiled in Table 1. The average crystal-size obtained from the Rietveld refinement is slightly deviated from the size estimated with TEM by a factor of \(ca. 0.7\). We can properly explain this mismatch by applying the correction factor proposed for cuboid-shaped NPs,\textsuperscript{37} \(D_{\text{Rietveld}} = \frac{<D_{\text{TEM}}⋅\text{cos}(π/4)}>}{4}\), as depicted in the top-right inset of Fig. 1(a). Therefore, the average size obtained with TEM and XRD (synchrotron) is \(ca. 28\) nm.

Fig. 1(c) displays the Mössbauer spectrum conducted at RT. Provided the \(\delta_{\text{RT}}\) isomer-shift variation obtained from the analysis of the RT Mössbauer data, Fock and Bogart \textit{et al.}\textsuperscript{19} showed that a quantitative evaluation of the amount of magnetite is feasible in solid-solutions of mixed maghemite-magnetite phases.\textsuperscript{19} The evaluation of the amount of magnetite is estimated through the expressions \(\alpha = \frac{<\delta_{\text{RT}} - \delta_0>}{m}\) and \(w = \frac{28.94\alpha}{29.94 - \alpha}\). The quantity \(\alpha\) designates the atomic percentage of \(\text{Fe}^{2+}\) ions in the sample, whereas \(w\) indicates the weight percentage of magnetite. The parameters \(\delta_0\) and \(m\) are evaluated to be \(0.321 \pm 0.002 \text{ mm s}^{-1}\) and \(0.21 \pm 0.01 \text{ mm s}^{-1}\), respectively, by the calibration-curve described in.\textsuperscript{31} In this ensemble of IONPs, the corresponding \(\delta_{\text{RT}}\) is \(0.38 \pm 0.02 \text{ mm s}^{-1}\), and consequently a weight percentage of \(28 \pm 10\) (wt%) in magnetite is estimated. Therefore, the structural analysis conveys that our ensemble of IONPs constitutes a good example of coexisting \(\text{Fe}_2\text{O}_4/γ-\text{Fe}_2\text{O}_3\) phases.

Fig. 2(a) shows the temperature dependence of specific heat for the ensemble of IONPs (red circles) and for a bulk polycrystalline magnetite sample (black squares) for comparison. It is worth noting that no distinctive peak is observed for the IONPs, whereas the bulk magnetite exhibits the characteristic peak identifying the Verwey transition at \(\text{ca. } 114 \text{ K}\).\textsuperscript{33,43} Fig. 2(b) depicts the temperature evolution of the real \(\chi'(T)\) and the complex \(\chi''(T)\) components of the AC-susceptibility.\textsuperscript{46} No trace of the Verwey transition is observed neither in \(\chi'(T)\) nor in zero-field-cooled DC-magnetization (not shown here). However, a low-temperature kink (below 50 K) is perceived in Fig. 2(b). This is usually associated with magnetic clustering (spin-glass-like transition) of IONPs,\textsuperscript{46} but it has also been related to spin polarization effects.\textsuperscript{41,42} Additionally, \(\chi''(T)\) exhibits an absorption peak at \(T \approx 27 \text{ K}\) that is surely connected with the mentioned magnetic clustering of IONPs. For the work presented here, it is relevant to ascertain the presence of magnetite as a very weak hump appearing centered around 120 K and illustrated in the inset of Fig. 2(b). In view of this result, we surmise that this feature provides a feeble indication of the Verwey transition in the ensemble of IONPs.\textsuperscript{45,46}

Unpolarized Raman spectra recorded at temperatures well below and above the Verwey transition temperature \(T_v\) are represented in Fig. 3(a). In the spectra, a clear peak around \(670 \text{ cm}^{-1}\) is visible for all temperatures between 4-210 K. This peak must be related to an active Raman mode. To understand the origin of such a peak it is necessary to briefly review the theoretical expectations governing the Raman modes. According to group theory and considering that magnetite crystallizes in a cubic inverse-spinel structure, the irreducible modes in the cubic phase at the zone center are the following:\textsuperscript{34,49}

\[
\Gamma = A_{1g}(R) + E_g(R) + 3T_{2g}(R) + 2A_{2u}(S) + 2E_u(S) + 5T_{1u}(IR) + 2T_{2u}(S) \tag{1}
\]

where \(R, \text{IR and S designate Raman, infrared and silent modes, respectively. As a result, five Raman-active modes are expected at temperatures above } T_v, \text{ i.e., } A_{1g} \text{ at } 669 \text{ cm}^{-1}, E_g \text{ at } 410 \text{ cm}^{-1} \text{ and } 3T_{2g} \text{ modes at } 193 \text{ (T}_{1u}\text{), } 540 \text{ (T}_{2u}\text{) and } 300 \text{ cm}^{-1} \text{ (T}_{2g}\text{). However, we note that the temperature is reduced below } T_v, \text{ the symmetry of the magnetite crystal lowers to a monoclinic structure.}^{33,47}\] This complicates the low-temperature analysis because of the increasing number of Raman active modes resulting from the symmetry reduction.\textsuperscript{48} However, Gasparov \textit{et al.} observed that the \(A_{1g}\) mode of the parent phase persisted over the transition in the low-temperature phase.\textsuperscript{33} They noticed a simultaneous change in both frequency and linewidth through \(T_v\). Moreover, the broadening of the \(A_{1g}\) mode is consistent with neutron and synchrotron diffraction experiments in the vicinity of the Verwey transition.\textsuperscript{33,47,49} The small lattice distortions (~0.24 Å) observed between the parent and the low-temperature phases must be closely connected with the softening of this phonon. In view of this, the softening of the \(A_{1g}\) mode not only does confirm the first-order phase transition undergoing at \(T_v\)\textsuperscript{37} but also evinces the sensitivity of this mode with respect to the Verwey transition. Therefore, following the work of Gasparov \textit{et al.},\textsuperscript{45} we have kept track of the thermal evolution of the \(A_{1g}\) mode across

| & \(\Delta \omega_0\) & \(\Delta \omega/\omega_0\) & \(T_v\) & \(\Delta T\) & \(A\) \text{ (cm}^{-1}\) & \(B\) \text{ (cm}^{-1}\) | \(\text{Fe}_2\text{O}_4\) samples |
|---|---|---|---|---|---|---|
| ~10 & ~1.5 & ~120 & ~11 & 1.39 & ~0.92 & IONPs |
| ~7 & ~1.0 & ~120 & ~14 & 2.58 & ~1.59 & Single-crystal \textsuperscript{45} |
| ~6 & ~0.9 & ~114 & ~30 & 1.37 & ~0.71 & Bulk magnetite \textsuperscript{19} |
| ~3.4 & ~0.5 & ~121 & ~48 & 0.012 & ~0.11 & Single-crystal \textsuperscript{48} |
| ~0.5 & ~0.1 & ~119 & ~9 & 1.1 & ~2.2 & Thin-film \textsuperscript{30} |

\(a\) \(T_v\) appears to coincide with the temperature at which the frequency starts to vary upon cooling.
I

\[ T_V \]

since it presents the strongest signal to monitor the Verwey transition.

In light of the above considerations, in Fig. 3(a) the arrows are indicative of the \( A_{1g} \) Raman-shift across \( T_V \). Solid red lines represent the fitting to a Lorentzian function,

\[
(w) = \frac{I_0 \Gamma_0^2}{4(w - \omega_0)^2 + \Gamma_0^2},
\]

where \( \Gamma_0, \omega_0, \) and \( I_0 \) are the phonon linewidth (full width at half maximum), frequency, and intensity of the Raman scattering, respectively. The frequency and linewidth of the \( A_{1g} \) mode hallmarking the Verwey transition are clearly depicted in Fig. 3(b). The thermal evolution of the frequency shows a clear increase of ca. 10 cm\(^{-1}\) across \( T_V \) upon cooling. Moreover, the linewidth draws a monotonous reduction down to a temperature around 110 K from which it experiences a sudden variation nearby \( T_V \). All these phenomena confirm the transition around \( T_V \).

In Fig. 3(c) we compare the \( A_{1g} \) Raman-shift of the ensemble of IONPs with respect to other investigated magnetite samples (bulk, single-crystals, and thin-film) close to \( T_V \). There, all samples show a jump in the Raman-shift at a similar temperature, however in the thin-film case, the frequency variation is extremely small in comparison. To account for the temperature dependence of the Raman-shift of a phonon, one can write:

\[
w(T) = w_0 + \Delta w_{\text{latt}}(T) + \Delta w_{\text{anh}}(T) = \Delta w_{\text{latt}}(T) + \Delta w_{\text{anh}}^*(T) \tag{2}\]

where \( w_0 \) is the harmonic frequency of the mode, and \( \Delta w_{\text{latt}} \) is ascribed to lattice distortions. The latter contribution is usually approximated by the Grüneisen law as

\[
\left( \frac{\Delta w}{w_0} \right)_{\text{latt}} = -\gamma_{A_{1g}} \left( \frac{\Delta V}{V} \right).
\]

Regarding the reported Grüneisen parameter of this mode \( \gamma_{A_{1g}} = 0.96 \), and the small relative volume change \( \Delta V/V_{Fe_3O_4} \) across \( T_V \) that varies from ca. 0.2% (ref. 53) to 0.004%, this term does not explain alone the change in the frequency displayed in Fig. 3(c).

Below we perform the subtraction of the anharmonic contribution and the harmonic frequency to highlight the intrinsic change across \( T_V \). For this, we evaluate the \( \Delta w_{\text{anh}}^*(T) \) term. This term represents the anharmonic effects of phonon-phonon interactions at a constant volume, along with the harmonic frequency \( w_0 \), and can be described by the following equation:

\[
\Delta w_{\text{anh}}^* = \Delta w_{\text{anh}} + A \left( 1 + \frac{2}{\epsilon^2 - 1} \right) + B \left( 1 + \frac{3}{\epsilon^2 - 1} + \frac{3}{(\epsilon^2 - 1)^2} \right), \tag{3}\]

where \( x = \hbar w_0/2k_B T \) and \( y = \hbar w_0/3k_B T \) correspond to three- and four-phonon interaction, respectively; and \( A \) and \( B \) are constants that are indicative of the strengths of the interaction (listed in Table 2). For the thin-film and for the single-crystal, the three-phonon interaction is predominant in all samples. For comparison, we show in Fig. 3(c) the Raman-shift of the mentioned magnetite samples. The fits to eqn (3) of the anharmonic contribution \( \Delta w_{\text{anh}}^*(T) \) are represented by solid red lines, and their main parameters are compiled in Table 2.

The fit adequately describes the behavior above the transition. However, other contributions are needed to explain the variation of the frequency below \( T_V \), e.g., electron-phonon interactions. The fine interpretation of these interactions is restricted to highly stoichiometric single-crystal magnetite, and is consequently beyond the scope of this work.

In Fig. 3(d) we show the frequency change of the \( A_{1g} \) mode and the relative frequency change that are respectively defined as, \( \Delta w(T) \equiv w(T) - w_{\text{anh}}^*(T) \), and \( \Delta w(T)/\Delta w_{\text{anh}}^*(T_V) \). Although it is difficult to draw a comparison among samples of different stoichiometry and shape, our ensemble of IONPs with coexisting Fe-phases exhibits a sharp phase transition at ca. 120 K with a small \( \Delta T \) temperature span (see Table 2). Such a small \( \Delta T \) in the IONPs is similar to the magnitudes provided in. By comparison with the magnetite samples in Table 2, the ensemble of IONPs shows the largest frequency change (ca. 10 cm\(^{-1}\)) and relative frequency change (1.5%). Hereby, it needs to be considered that the spectral resolution is 0.6 cm\(^{-1}\) in the Raman-shift (see Fig. 3(b)). Hence, we surmise that the magnetite nanocrystals within the ensemble of IONPs are highly stoichiometric. We suggest that the main cause for the variety of \( \Delta T \) values listed in Table 2 is caused by texture effects. This fact may merit future investigations.

In conclusion, we have performed a thorough investigation and have proven that the ensemble of IONPs are constituted of coexisting Fe\(_3\)O\(_4\)/\( \gamma \)-Fe\(_2\)O\(_3\) phases with an average size of ca. 28 nm. No sign of the Verwey transition was noticed either by specific heat or within the real component of the AC-susceptibility. However, an extremely feeble hump appears centered at around 120 K in \( \gamma''(T) \). A temperature-dependent analysis of Raman scattering on the \( A_{1g} \) mode has been carried out. The outcome is a conspicuous change in the frequency at around 120 K. This has allowed us to reveal the masked Verwey transition in the ensemble of IONPs. This finding highlights Raman spectroscopy as a powerful tool for the evaluation of Fe\(_3\)O\(_4\) existence in iron-oxide compounds and towards the improvement of synthesis routes in ensembles of IONPs.

**Conflicts of interest**

There are no conflicts to declare.

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