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Evidence for the Verwey transition in highly nonstoichiometric nanometric Fe-based ferrites

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The nanometric scale allows an investigation of the Verwey transition: the impact of varying degree of oxidation of Fe cations on this transition was studied by means of zero-field-cooled superconducting quantum interference device measurements in nanometric highly nonstoichiometric particles of pure and Ti-substituted magnetite synthesized using soft chemistry route. It is clearly shown that (i) there is a shift of the transition towards higher temperatures for nanometer scaled compounds and (ii) the amplitude, the temperature, and the order of the transition are only depending on the number of Fe^{2+}/Fe^{3+} pairs in octahedral coordination.

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INTRODUCTION

In 1939, Verwey evidenced a sharp anomaly around $T_v = 120\,\mathrm{K}$ in the temperature dependence of the electrical conductivity of magnetite Fe_3O_4.[1] This metal-insulator transition is explained by a change from a dynamic disorder of electrons resonating on octahedral (*B*) sites above T_v (Fe_3O_4 offers spin polarized transport) to a long-range order of the *B* sites cations in alternate planes of Fe^{2+} and Fe^{3+} below T_v.[2] Although further neutron-diffraction experiments at the end of 1960s were reported in contradiction with this description,[3,4] the simple ordering Verwey picture is still successfully used to explain the variations of several physical properties at T_v such as the cubic magnetic anisotropy constant[5] and the lattice symmetry.[6–8] Until now, the Verwey transition has been mainly observed on monocrystals or large grain polycrystalline samples with a composition very close to that of magnetite. First, in doped magnetite the Verwey transition has been detected by heat capacity and electrical measurements for only small substitution contents $x \leqslant 0.04$, 0.04, 0.03, 0.04, 0.05, and 0.05 in, respectively, $Fe_{3-x}Zr_xO_4$,[9] $Fe_{3-x}Ti_xO_4$,[9,10] $Fe_{3-x}Al_xO_4$,[11] $Fe_{3-x}Mg_xO_4$,[12] $Fe_{3-x}Ni_xO_4$, and $Fe_{3-x}Co_xO_4$.[12,13] However, the Verwey transition has been evidenced from the temperature dependence of the permeability for *x* as high as 0.5 in the case of $Fe_{3-x}Mg_xO_4$ and 0.2 in the case of $Fe_{3-x}Li_xO_4$.[14] It has been also observed in Mössbauer experiments in the case of $Fe_{3-x}Ga_xO_4$ for $0.5 < x < 0.8$.[15] Second, in nonstoichiometric magnetite $Fe_{3(1-\delta)}O_4$ the transition has been only detected for small deviations from oxygen stoichiometry $\delta \leqslant 3\delta_c$: further investigations are limited by the boundaries of the stability field of magnetite which undergoes a transformation to a rhomboedric phase for higher δ (Ref. 16) ($\delta_c = 0.0039$ is the limit of a first-order phase transition, for $\delta > \delta_c$ a higher-order transition occurs[9]). The Verwey transition is claimed to disappear if samples with $\delta > 3\delta_c$ could be stabilized.[9] More recently, a temperature shift of this transition has also been observed in thin layers of Fe_3O_4 via conductivity and superconducting quantum interference device (SQUID) magnetometry.[17–20]

Despite these extensive studies, there is still some dispute remaining about the origin of the Verwey transition. It is either considered to be a structural[21] or magnetic[22] transition. In the first hypothesis proposing a structural transition, the pertinent parameter involved in the transition is the number of Fe^{2+}/Fe^{3+} pairs on octahedral sites as inferred by Rosencwaig from Mössbauer measurements.[21] In the second scheme, it is the difference in population of Fe^{3+} cations on the tetrahedral (*A*) and octahedral (*B*) sites, $\Delta[Fe^{3+}]_{A-B}$, which is considered as the driving force of the transition, since the stronger magnetic interaction arises between the two sublattices, *A* and *B*. This interpretation recently received very sound justifications: the temperature evolution of the anisotropy constants below T_v has been found to depend significantly on the order of the Verwey transition.[23] Also, both the Verwey (T_v) and the Curie (T_C) temperatures could be deduced from the J_{ab} exchange integral between *A* and *B* sites in $Fe_{3_{(1-\delta)}}O_4$.[18] Finally, an experimentally relation in magnetite, Zn and Ti ferrites, has been observed between T_v and $\Delta[Fe^{3+}]_{A-B}$.[9] However, this relation is not observed for Al-doped magnetite[9] so that no definitive conclusion can be drawn.

In the present paper, a possible approach opening a different way to determine the nature of the Verwey transition is proposed. It consists in studying the transition in materials at a nanometric scale. The first advantage obtained by studying nanometric powders with a grain size of 30–50 nm is that the relative contributions of the structural and magnetic interactions may be modified. Therefore an observation of a shift of T_v or a modification of the transition order will indicate the nature of the transition driving force. Strong modifications of the sample structures are expected to be induced by surface energy effects in the nanometric range as observed for $BaTiO_3$,[24] ZrO_2,[25] and Fe_2O_3.[26] Concerning the evolution of the magnetic properties with grain size in the 30–50 nm range, only a small influence of spin canting upon the saturation magnetization[27] and a negligible surface anisotropy contribution[28] to the magnetocrystalline anisotropy are expected. Therefore eventual large changes of T_v may be clearly attributed to structural effects rising from a significant contribution of the surface chemical potentials. The second advantage expected by considering nanoscaled compounds consists in the possibility of studying the Verwey transition in samples with compositions which cannot be obtained in monocrystals or large grains polycrystals. As mentioned previously the stability field of the spinel structure is largely increased in nanoscaled compounds so that in many Fe-based spinels [M=Mn, V, Mo, Zn, Al, Cr, Ti in the formula $Fe_{3-x}M_xO_4$ where $0 \leqslant x \leqslant 1$ (Ref. 29)] δ could be varied without formation of a new phase from slightly negative values to the maximum one corresponding to the highest valence of each cation.

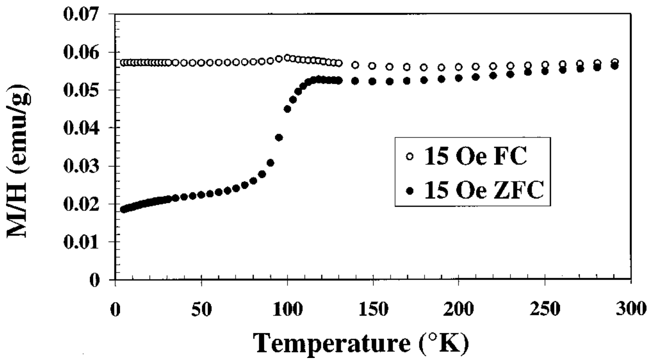

FIG. 1. Zero-field-cooled and Field-cooled curves of $Fe_{3(1\text{-}0.039)}O_4$ powder with a grain size of 120 nm for applied fields of 15 Oe.

RESULTS AND DISCUSSION

Among the numerous techniques for investigation of the Verwey transition, only those sensitive to nearest neighbors are convenient in highly nonstoichiometric magnetite. Indeed, neutron investigations have shown that for $\delta > \delta_c$ the iron cations ordering below the Verwey transition occur in clusters of ≈ 28 unit cells.[30] In this paper the Verwey transition has been characterized by magnetization measurements using a commercial Quantum Design SQUID magnetometer. Samples have been zero-field cooled (ZFC) or field cooled (FC) from ambient temperature to 4 K. Then, with an increase in temperature, the anomaly in the magnetization was studied in low applied fields (between 10 and 50 Oe). This method seems to be preferred to measurements of the magnetization under large magnetic fields since contrary to the anisotropy the saturation magnetization does not present a sharp anomaly at T_v. The method has first been validated in the case of nonstoichiometric magnetite with $\delta = 0.039$ and a grain size of 120 nm. This powder has been prepared by the soft chemistry route based on a precipitation step followed by a thermal reducing treatment at 460 °C under appropriate $N_2/H_2/H_2O$ atmosphere.[31] Powder was then oxidized under air atmosphere. δ was deduced from x-ray-diffraction (XRD) results using the Rietveldt refinement, thermogravimetric measurements, and qualitatively from saturation magnetization measurements at 5 K. Powder reactivity to oxidation decreases when δ increases.[32] Since SQUID experiments cannot be performed in a chamber with strictly controlled $H_2/N_2/H_2O$ atmosphere, only powders with sufficiently high $\delta > 0$ were then investigated. In the case of magnetite with $\delta = 0.039$, Mössbauer experiments and lattice parameter investigations demonstrated that the particles were constituted of a core with uniform composition of $\delta = 0.039$ and a γ-Fe_2O_3 surface shell with a thickness less than 1 nm. γ-Fe_2O_3 does not present any Verwey transition. Such transition arises then only from the uniform core of the particles ($\delta = 0.039$). In Fig. 1 are shown the FC and ZFC curves for an applied field of 15 Oe. A discontinuity appears in the magnetization at about 94 K. This result is in total discordance with those obtained for monocrystals with the same δ in which the extrapolated Verwey transition according to the Honig model[9] occur at 16 K. Such a strong difference (more than 70 K) between Verwey transition temperature in nano- and monocrystalline compounds may be ascribed to a grain-size effect similar to that evidenced in the 10–100-nm range for the $BaTiO_3$ quadratic/cubic[24] and ZrO_2 monoclinic/tetragonal[25] transitions. Nevertheless, no conclusion can be drawn: the shift of transition temperature is toward low temperature in the case of $BaTiO_3$ and ZrO_2 and toward high temperature for ferrites.

In order to obtain magnetite with grain size in the 30–50-nm range and with δ varying in its full range, Ti ($x = 0.25$) was introduced in substitution to stabilize the spinel structure and to avoid grain growth. Titanium ferrites powders were synthesized by the same soft chemistry route as magnetite. Powders were then oxidized under air atmosphere for different temperatures varying from 25 to 350 °C, leading to δ varying from 0.024 to 0.135 (Table I). Care was taken to ensure that problems arising from segregation phenomenon occurring during the oxidation were eliminated: further annealings under N_2 gas at higher temperature lead to oxygen

TABLE I. For $(Fe_{2.75}Ti_{0.25})_{(1-\delta)}O_4$ given are δ, $[Fe^{2+}/Fe^{3+}]_B$ the absolute difference of Fe^{2+} and Fe^{3+} cations in octahedral coordination, $[Fe^{2+} \times Fe^{3+}]_B$ their multiplication, the difference $\Delta[Fe^{3+}]_{A-B}$ in population of the Fe^{3+} cations of the A and B sublattices, as well as the saturation magnetization (M_s) determined at 4 K in a field of 20 kOe the Verwey transition temperature T_v, the transition width ΔT_v, and the magnetization jump ΔM at the transition.

δ	$[Fe^{2+}/Fe^{3+}]_B$	$[Fe^{2+} \times Fe^{3+}]_B$	$\Delta[Fe^{3+}]_{A-B}$	M_s (emu/g)	T_v (K)	ΔT_v	ΔM (emu/g)
0.024	0.66	0.67	0.34	67.8	112±2	22±2	0.28±0.01
0.061	0.69	0.61	0.10	63.0	112±2	22±2	0.28±0.01
0.089	0.43	0.46	0.08	60.9	87±2	29±2	0.13±
0.135	0.00	0	0.38	57.7	—	—	—

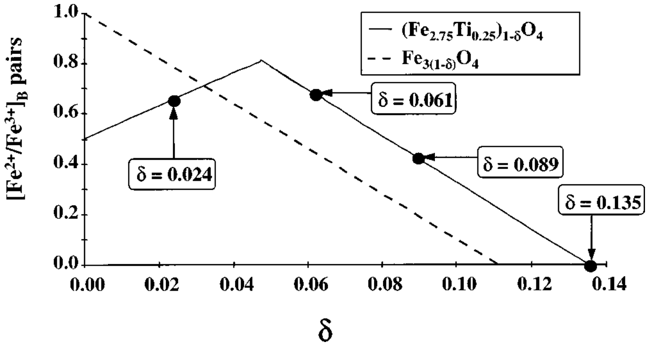

FIG. 2. Represented is the number of Fe^{2+}/Fe^{3+} pairs in octahedral coordination as a function of δ calculated for $(Fe_{2.75}Ti_{0.25})_{(1-\delta)}O_4$ (solid line) and $Fe_{3(1-\delta)}O_4$ powders (dot line).

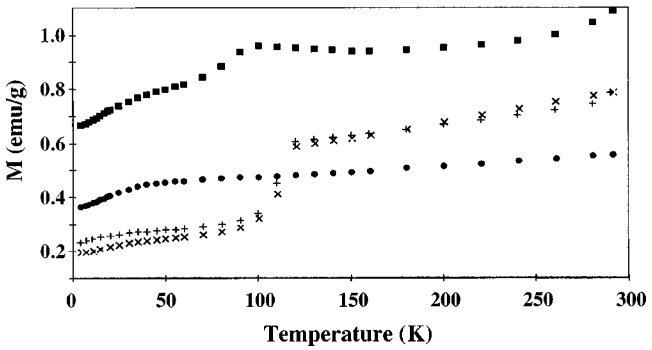

FIG. 3. The Zero-field-cooled magnetization curves of $(Fe_{2.75}Ti_{0.25})_{(1-\delta)}O_4$ samples are shown with the number of Fe^{2+}/Fe^{3+} pairs, $[Fe^{2+}/Fe^{3+}]_B$, equal to 0.66 (×), 0.69 (+), 0.43 (■), and 0 (●). The Verwey transition temperature depends strongly on this number and not on δ or on the difference $\Delta[Fe^{3+}]_{A\text{-}B}$ in the population of the Fe^{3+} cations of the A and B sublattices.

stoichiometry homogenization inside the particles.[29] Powders, which remain in the spinel structure, are very well dispersed and homogeneous with grains size of about 45 nm (scanning electron microscopy, surface specific measurements, and x-ray diffraction analyses). Using anomalous powder x-ray diffraction, these titanomagnetites have been found to contain the Fe^{2+} cations only in octahedral sites[33]

$$(Fe^{3+})_A(Fe^{2+}_{(5-8\delta)/(4+\delta)}Fe^{3+}_{(2+7\delta)/(4+\delta)}$$
$$\Box_{3\delta/(4+\delta)}Ti^{4+}_{1/(4+\delta)})_B O_4^{2-}.$$

The use of nanometric grains synthesized by a soft chemistry method allows us to control in a large range the number of Fe^{2+}/Fe^{3+} pairs in the octahedral coordination and δ (see Fig. 2 and Table I). Hence we have the unique possibility to investigate directly the driving mechanism of the Verwey transition by preparing two samples with the same cationic distribution Fe^{2+}/Fe^{3+} on the octahedral site and a difference in population of Fe^{3+} cations on the A and B sublattices. Two parameters, quite similar (Table I), can characterize the Fe^{2+}/Fe^{3+} pairs number in octahedral coordination: their absolute difference $[Fe^{2+}/Fe^{3+}]_B$ and their multiplication $[Fe^{2+}\times Fe^{3+}]_B$ which is linked to the probability of the two cations Fe^{2+} and Fe^{3+} to be in two adjacent sites. Again, no change in saturation magnetization with the temperature has been observed around the Verwey transition, nevertheless the Verwey transition appears clearly in ZFC measurements (Fig. 3). Short-range order similar to those reported in literature for nonstoichiometric magnetite[34] appears here above the transition (no long-range-order structural change have been observed by cryogenic XRD analyses). The Verwey transition temperature has been identified as the inflection point of the magnetization jump (Fig. 3) and deduced from a ZFC plot derivative. Two major conclusions can be drawn from these experiments: one related to the characteristics of the transition as a function of the sample composition and the second to the nanometric effect upon T_v. First, it is obvious that the Verwey transition does not disappear when increasing δ. Moreover, since $\delta=0.024$ and $\delta=0.061$ lead to the same ZFC behavior ($T_v=112\,\mathrm{K}$ and $\Delta M_{tv}=0.28\,\mathrm{emu/g}$ for $\Delta T=22\,\mathrm{K}$), the Verwey transition appears to be only affected by the Fe^{2+}/Fe^{3+} cations pairs number in octahedral sites: $[Fe^{2+}/Fe^{3+}]_B\approx 0.66$ for $\delta=0.024$ and $[Fe^{2+}/Fe^{3+}]_B\approx 0.69$ for $\delta=0.061$. Then the pertinent parameter of the transition should neither be directly δ nor $\Delta[Fe^{3+}]_{A-B}$ (clearly different: 0.34 and 0.1, respectively). In particular, the order of the transition, characterized by the temperature range of the magnetization jump, is found to depend only on the Fe^{2+}/Fe^{3+} cations pairs number in octahedral sites. As proposed by Rosencwaig, this fact may suggest that the origin of the Verwey transition should rise from structural rather than from magnetic interactions. Second, it is also of interest to notice that the Verwey transition temperatures of our samples do not fit with the relation which exists in literature for single crystals.[9] By extrapolation of this curve the Verwey transition temperature should be lower than 50 K for $\delta=0.024$ (value for magnetite) while the experimental temperatures are near 112 K. As explained by a grain size effect, the change in T_v is more important in Ti ferrites with a particle size of 45 nm than in a 150-nm scaled magnetite. In view of this strong shift of T_v, the Verwey transition which is significantly affected by surface properties may be probably from structural rather than magnetical origin.

CONCLUSION

In conclusion, since it is possible to stabilize iron based spinels with large δ in the nanometric range, the impact of varying the degree of oxidation of Fe cations on the Verwey transition can be investigated. First, the Verwey transition shifts towards higher temperatures for nanometer scaled compounds. Second, the amplitude, the temperature and the order of the transition are only depending on the number of Fe^{2+}/Fe^{3+} pairs in octahedral coordination in the case of titanium ferrites. We demonstrated by ZFC measurements that the nanometric scale of the samples in combination with the control of the deviation from oxygen stoichiometry opens interesting insights into the nature of the Verwey transition.

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