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Large Room Temperature Magneto-Resistance in Magnetically Disordered $Fe_{1.5}Ti_{0.5}O_{3-\delta}$ Thin Films

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Abstract

Electronic transport properties of magnetically disordered R(-3)c phase $Fe_{1.5}Ti_{0.5}O_{3-\delta}$ thin films epitaxially grown on Al_2O_3(0001) substrates have been studied. The measured magnetization in configurations with the magnetic field perpendicular and parallel to the film plane shows weak values of $0.1\mu_B$/formula compared to the theoretical value of $2\mu_B$/formula and a strong anisotropy with no saturation in perpendicular configuration. These properties are associated with the atomic scale disorder of Ti/Fe ions along c-axis. At zero-magnetic field and within the temperature range of 80 K to 400 K, the conduction mechanism appears to be Efros-Shklovskii variable range hopping with a carrier localization length of $\xi_0 = 0.86\,\text{nm}$. Magneto-resistance (MR) is positive in perpendicular configuration, while it is negative in parallel configuration, with significant values of $|MR| = 27\% - 37\%$ at room temperature at 9 Tesla. Electron localization lengths were deduced from experiment for different external magnetic fields. The origin of magneto-resistance observed in experiment, is discussed.

Keywords

PACS Numbers: 73.50.-h. Transport Processes in Thin Films, 72.20.Ee Hopping Transport, 75.47.Lx Magnetic Oxides, 75.70.Ak Magnetic Properties of Monolayers and Thin Films

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1. Introduction

$Fe_{1.5}Ti_{0.5}O_{3-\delta}$ (FTO) is a mixed valence transition metal oxide based on the solid solution of hematite (Fe_2O_3) and ilmenite ($FeTiO_3$). The electrical and magnetic properties of this wide band gap material in bulk form were already investigated half a century ago [1] [2]. Recently, new interest occurred for this material in thin films due to its potentiality for spintronics applications, which require a combination of room temperature ferromagnetic properties and spin polarized conductivity [3]-[7].

FTO thin films can be obtained in two crystallographic phases depending on the preparation conditions: the ordered R(-3) or the disordered R(-3)c phase. In the R(-3) phase, the cations in FTO are ordered perpendicular to the c-direction in the hexagonal basis of the rhombohedral symmetry. Every consecutive dense cations layer are pure iron atoms (α planes) with respect to iron/titanium cation ones (β planes). While in the case of R(-3)c disordered symmetry, titanium atoms are randomly distributed on the cation sites. This atomic scaled Ti/Fe order along the c-direction strongly influences the macroscopic magnetization of FTO thin films as it demonstrates the significantly larger macroscopic magnetization in ordered phase then in disordered one [4] [5]. The influence of this atomic scaled "order-disorder" on the electrical properties (conductivity, magneto-resistance) of FTO was not studied in detail. Only one report is claiming that conductivity in zero magnetic field does not depend on cation order [4].

In the present work, we aim to investigate the conductivity mechanism in FTO in a wide temperature range. The influence of external magnetic field on the longitudinal resistance in both configurations of the magnetic field perpendicular and parallel with respect to the film plane are investigated and the electrical transport and magnetic properties are subsequently correlated. We focused on FTO with a composition $x = 0.5$ $\left(Fe_{1.5}Ti_{0.5}O_{3-\delta}\right)$ in the disordered phase R(-3)c. The choice of the composition $x = 0.5$ is motivated by the high value of Curie temperature (>400 K) necessary for room temperature spintronics applications [2].

2. Samples and Experimental Details

The $Fe_{1.5}Ti_{0.5}O_{3-\delta}$ thin films were epitaxially grown by pulsed laser deposition (PLD) technique from targets prepared from high purity Fe_2O_3 (99.999%) and TiO_2 (99.99%) powders by standard ceramic processing method. The Fe/Ti ratio was checked by chemical titration to be 3.02 ± 0.01. It corresponds to the target composition $Fe_{1.503}Ti_{0.497}O_{3\pm\delta}$.

The ilmenite thin films were deposited onto α-Al_2O_3(0001) substrates [8] [9]. The mismatch between the lattice parameters of $Fe_{1.5}Ti_{0.5}O_{3-\delta}$ and α-Al_2O_3 in (0001) plane is about 7% and initial layers of the film undergo a large compressive stress.

The ilmenite-hematite thin film deposition was performed in an ultra-high vacuum chamber with a base pressure of 5×10^{-9} Torr. The target was ablated using a KrF laser with a wavelength of 248 nm and pulse duration of 20 ns. The laser fluency was maintained at about 1.6 J/cm^2 for all depositions. The repetition frequency was set to 2 Hz. The target to substrate distance was kept at 5 cm. The samples were grown without additional oxygen injection, *i.e.* in residual chamber pressure of about 10^{-7} Torr at high temperature and during target ablation. The substrate temperature was set to 970 K. After the growth, the sample was cooled down in the growth atmosphere. The cooling procedure started immediately after the termination of target ablation. No post-deposition annealing was performed. Film thickness was measured *in situ* using spectroscopic ellipsometry. The final thickness was checked *ex situ* by step-meter profiling and was found to be consistent with the results of ellipsometry measurements. The studied samples are of 70 nm thickness.

The film structure and crystallinity have been verified using reflection high-energy electron diffraction (RHEED) and X-ray diffraction measurements (not shown here, for details see for example [7] [8]). All the samples are single phase FTO epitaxially grown on sapphire substrates. No diffraction peaks (0, 0, 0, 2n + 1) corresponding to cationic order along [0001] film axis were observed. FTO films are R(-3)c phase with a c-axis parameter of 1.37 nm.

A high-resolution transmission electron microscopy (TEM) study, using a Tecnai F20 fitted with a spherical aberration corrector (point resolution = 0.12 nm), has been performed, allowing a description of the structure of the films. The cross-sectional specimens for TEM studies were cut along the $(1\bar{2}10)$ alumina planes before thinning by tripod grinding and ion milling (using a precision ion polishing system) to achieve the electron transparency.

Figure 1(a) shows TEM image taken at low magnification. The film is continuous and has low roughness. The film growth is columnar with two crystalline domains. The average column (domain) size is about 20 - 40 nm. The high-resolution image at the film/substrate interface is presented in **Figure 1(b)**. The film/substrate interface is sharp. The crystallographic domain boundary is also visible in the image. It is clear that the column boundary is about one atomic plane thick and the two domains are epitaxial. The film/substrate epitaxial relations can be written as $(0001)\left[10\bar{1}0\right]_{Al_2O_3} \| (0001)\left[10\bar{1}0\right]_{FTO}$ and $(0001)\left[10\bar{1}0\right]_{Al_2O_3} \| (0001)\left[01\bar{1}0\right]_{FTO}$, corresponding to two crystallographic domains rotated by $\pi/3$ in the (0001) plane.

The magnetic properties were measured by a Quantum Design PPMS-9 Tesla vibrating sample magnetometer, both parallel and perpendicular to the film plane orientation.

Electrical contacts on thin films were deposited in "aligned 4 points" and "Van der Pauw" configurations by using a conductive silver paint. Contact ohmicity was systematically verified by I - V characteristics. DC-resistivity and Hall effect measurements were performed in a Van der Pauw configuration in the temperature range of 90 K to 400 K and for magnetic fields perpendicular to the film plane varying from 0 T to 1.6 T using a custom designed high impedance measurement set-up.

High magnetic field longitudinal DC-magneto-resistance was studied using a Quantum Design PPMS-9 Tesla environment in 150 K to 400 K temperature range and for magnetic fields parallel and perpendicular to the current plane up to 9 T. The lowest measurement temperature (150 K) was determined by the minimum value 5 nA of possible applicable current and consequently the maximum ~4 MΩ measurable resistance for PPMS. Measurements have been performed in "aligned 4 points" configuration with current inversion to eliminate voltage off-sets.

3. Results

3.1. Magnetic Properties

Before analysing the electrical transport and magneto-transport properties of FTO, macroscopic magnetization measurements of the films have been performed in two magnetic field directions: perpendicular and parallel to the film plane. Currie temperature T_c was determined as 500 K. **Figure 2** presents the magnetic field dependence of magnetization $M(\mu_0 H)$ for R(-3)c phase $Fe_{1.5}Ti_{0.5}O_{3-\delta}/Al_2O_3(0001)$ thin films. At 300 K (**Figure 2(a)**), the saturation magnetization is low $\left(M_s \sim 30\ \mathrm{kA/m}\right)$, *i.e.* only 16.7% of the maximum observed value at 300 K either for sintered bulk material [2] or thin films [9] [10] for this titanium content ($x = 0.5$).

This value corresponds to $0.1\mu_B$ per chemical formula of $Fe_{1.5}Ti_{0.5}O_{3-\delta}$; while the maximum theoretical value for a macroscopically ordered R(-3) phase of $Fe_{1.5}Ti_{0.5}O_{3-\delta}$ is 2 μ_B/formula. This is coherent with the disordered R(-3)c phase observed by X-ray diffraction. Applied magnetic field values of the irreversible $M(\mu_0 H)$ behaviour and saturation are respectively of 1 Tesla and 1.5 Tesla. Very surprising is the strong magnetic anisotropy observed when the magnetic field is applied perpendicularly to the film. This effect has been reported in thin films by Rode *et al.* for $x = 0.6$ and $x = 0.8$ [11]. At best, the sample shape can contribute to the anisotropy field for a value of $\mu_0 M_S < 0.1$ Tesla (at 80 K). The origin of this magneto-crystalline anisotropy may be connected to the single-ion anisotropy of the ferrous Fe^{2+} ion in the trigonal crystal field at octahedral sites in the structure. This phenomenon also governs the metamagnetic transition in the pure ilmenite [12]. In the present films, for perpendicular applied magnetic field, no saturation of the magnetization is observed up to 9 Tesla even at low temperatures ($T = 5$ K). For this applied magnetic field direction and above 0.2 T, magnetization increases linearly with the increasing magnetic field and no magnetic hysteretic is observed. The high slope variation of the magnetization $M(\mu_0 H)$ at low applied fields of $\mu_0 H < 0.2$ T originates from an instrumental artefact of the VSM technique ($\sim 5 \times 10^{-9}$ A·m^2). At 80 K (**Figure 2(b)**), the situation is similar with a reversibility field of 2 T in in-plane configuration and a saturation field of 2.5 T; while in perpendicular configuration there is no saturation up to 9 T. To summarize, $Fe_{1.5}Ti_{0.5}O_{3\pm\delta}/Al_2O_3\left(0001\right)$ in the R(-3)c phase has a low magnetization and a low internal magnetic field, strongly aligned in the film plane. This strong and unusual magnetic anisotropy, as we will see below, influences the electrical magneto-transport properties.

3.2. Electrical Conductivity

Stoichiometric ilmenite $FeTiO_3$ and α-Hematite Fe_2O_3 are insulators as most other oxides. The electrical proper-

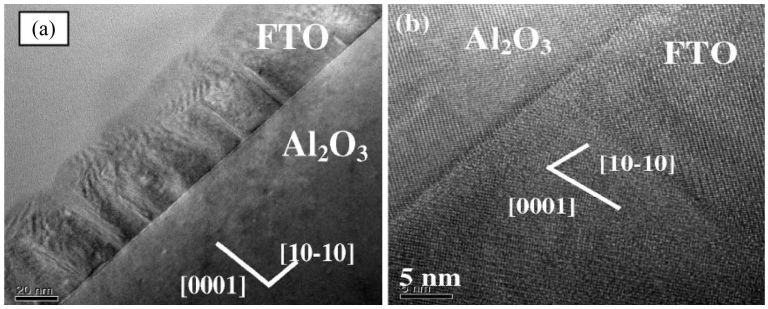

Figure 1. TEM measurements: (a) Lower magnification view; (b) HRTEM of film/substrate interface.

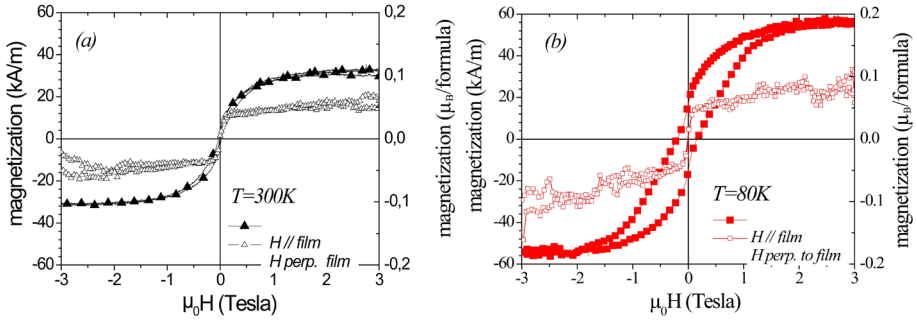

Figure 2. Magnetic field dependence of the magnetization at 300 K (a) and 80 K (b) in parallel and perpendicular magnetic fields for the R(-3)c phase of $Fe_{1.5}Ti_{0.5}O_{3-\delta}/Al_2O_3(0001)$ thin films.

ties of $(1-x)FeTiO_3 \cdot xFe_2O_3$ solid solution in bulk form for different concentrations x have been studied by Ishikawa. $Fe_{1+x}Ti_{1-x}O_3$ is known to be n type when $x > 0.73$, *i.e.* when conduction by (Fe^{3+}, Fe^{2+}) predominates over Ti^{3+}, Ti^{4+} conduction and p type when $x > 0.73$, this composition approaching limonite. Since the n type conductivity is caused by the existence of (Fe^{3+}, Fe^{2+}) pairs, the degree of the deviation from stoichiometry in oxygen will play a decisive role in the change of the material resistively. Indeed, the influence on the conductivity of the oxygen partial pressure during the PLD process of $Fe_{1.5}Ti_{0.5}O_{3-\delta}$ has been previously demonstrated [13]. The increase of conductivity with decreasing oxygen partial pressure should be related to the formation of oxygen vacancies and consequently to the change of the iron valence state from Fe^{3+} to Fe^{2+}. Indeed, our recent study revealed that existing charge ordering and Fe^{2+}/Fe^{3+} mix-valence state is an origin of electrical conductivity in this material [14].

Resistively and Hall Effect measurements were carried out in Van der Pauw configuration, with four electrical contacts in the corner of the samples, on home built set-up. At room temperature and zero magnetic field the resistively of $Fe_{1.5}Ti_{0.5}O_{3-\delta}$ films equals 0.4 Ohm·cm.

This high conductivity indicates that samples are oxygen non-stoichiometric, as resistively for stoichiometric $Fe_{1.5}Ti_{0.5}O_3$ was reported to be $\rho \approx 10^3$ Ohm·cm [15]. The measurement was performed in the temperature range from 80 K up to 400 K, in order to avoid phase transformation through oxidation of the material at higher temperatures. The resistively presents a semi conducting behaviour, gradually increasing with lowering of the temperature of the sample. A similar thermal variation of the resistively was previously observed by other groups for different compositions of $Fe_{2-x}Ti_xO_3$ [5] [16]-[18]. Hall Effect measurements have been performed for magnetic fields up to 1.6 Tesla and at various temperatures. In all cases the unambiguous determination of the Hall voltage (V_H) was impossible, which can be understood for charge carrier motion occurring by hopping in an extremely narrow band (polaron) or in specially localized levels. This problem has a long history of investigation and was very actively discussed half-century ago by Friedman, Holstein, Miller and Abrahams [19]. In iron oxides, usually a strong localization of conduction electrons is observed. Indeed, in Fe_2O_3, it is very difficult to measure the Hall effect due to localization of charges [20]. A strong localization of carriers was observed in insulating stoichiometric $Fe_{2-x}Ti_xO_3$. Indeed, as shown in a previous study, the stoichiometric films are highly

resistive [15]. The questions we aim to answer in this work are the nature of the carriers in oxygen non-stoichiometric $Fe_{2-x}Ti_xO_{3-d}$ thin films and the related conduction mechanism.

To study in details electrical conductivity and magneto resistance up to 9 T, we used PPMS. Four electrical contacts were aligned in the sample. Assuming that carriers are localized in the material, a hopping nature of the conductivity might be expected. A variable range hopping regime (VRH) usually is described by Mott's or/and by Efros-Shklovskii laws. The conductivity in VRH by Mott is given by:

$$\sigma(T) = \sigma_0 \exp -(T_0/T)^{1/n+1} \tag{1}$$

where n is the dimension of the system (n = 3 for 3D and n = 2 for 2D), $T_0 = \left(18.1/k_B N(E_f) x^3\right)$, ξ is a carrier localization length. T_0 is Mott's activation energy and $N(E_f)$ is the density of the states at Fermi level [21]. In the Mott model, the density of states near Fermi level is constant. Contrary to this statement, Efros and Shklovskii proposed that the density of the states near the Fermi level is not constant. They introduced so called "Coulomb gap", which is the result of the long range Coulomb interaction between localized carriers [22] [23]. Their theory requires the quantum localization length to be much smaller than the distance between the impurity centres and the overlap between the wave functions to be negligible. In other words, the Efros/Shklovskii theory applies when the concentration of impurity centres is not large enough for an impurity band creation. Efros-Shklovskii variable range hopping (ES-VRH) is expressed by the following equation:

$$\sigma(T) = \sigma_a \exp -(T_1/T)^{\frac{1}{2}} \tag{2}$$

where $T_1 = \dfrac{\beta_1 e^2}{\varepsilon_0 \varepsilon_r \xi k_B}$, β_1 is a constant with a value of 2.8, ε_r the relative dielectric constant, ξ the carrier localization length, ε_0 is the vacuum dielectric permittivity and k_B the Boltzmann constant.

To discriminate between these two behaviours, we have used the data analysis method introduced by Hill [24]. This method is based on the fact that laws (1) or (2) have the general dependence: $\sigma(T) = \sigma^* \exp -\left(T^*/T\right)^{\alpha}$, with α a real number. One has to note that $\alpha = 1$ corresponds to the general Arr-henius case. This case also includes Nearest Neighbor Hopping (NNH) when one can neglect the prefactor in the $\sigma(T)$ dependence. Tracing the functional dependence of $\dfrac{\mathrm{d}[\log(\sigma)]}{\mathrm{d}[\log(T)]}$ versus $\log(T)$ allows for the discrimination of the exponent. The best fit yields the ES-VRH coefficient 0.5. **Figure 3** The same conduction mechanism and coefficient has been determined in the case of magnetically ordered sample [14].

The Mott's VRH model is usually valid when there is a high concentration of impurity centres, very close to insulator-metal transition, while ES-VRH model applies for slightly doped and intermediate compensated crystalline semiconductors [22].

The oxygen off-stoichiometric FTO is expected to have n-type conduction, on the one hand due to the natural presence of Fe^{2+} in the stoichiometric structure and on the other hand related to the fact that each oxygen vacancy gives two electrons. Nevertheless the value of conductivity of the samples and their temperature dependence indicate that the system is far from an insulator to metallic transition. Consequently, all results are compatible with the usual Efross-Shklovskii approach. As a significant difference to usual semiconductors (except of diamond) where any hopping mechanism is observed only at quite low temperatures, VRH hopping exists in FTO even above room temperatures. That is a specificity of many transition metal oxides with very strong electronegativity in the crystalline matrix (see for example [22]). With the value of $T_1 = 1.8 \times 10^4$ K, determined from the fit of the conductivity as represented in **Figure 4**, one can estimate the coherence length ξ_0 in zero magnetic field. This requires the knowledge of the relative dielectric constant value. Existing data from capacity measurements at low frequencies in $FeTiO_3$ on sintered powders are $(\varepsilon_r \sim 100 - 200)$ [25] and in α-Fe_2O_3 $(\varepsilon_r \sim 20 - 120)$ [26]. We take $\varepsilon_r \sim 40$. The calculated value of the electron localization length equates to $\xi_0 = 0.86$ nm. Taking in account this value of ξ_0 one can estimate [27] an average hopping energy of $W_{opt} = 0.5 k_B (T_1 T)^{1/2} \sim 32$ meV at 300 K and a hopping distance $R_{hop} = 0.86 \xi_0 (T_1/T) \approx 12.9$ nm. In coherence with the theory, the average hopping energy exceeds the thermal energy at ambient temperature $\left(W_{opt} > k_B T = 25 \text{ meV}\right)$

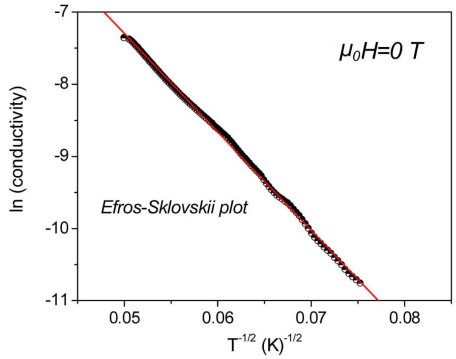

Figure 3. Temperature dependence of DC electrical conductivity plotted for Efros-Shklovskii laws. The solid line is a fit to Equation (2).

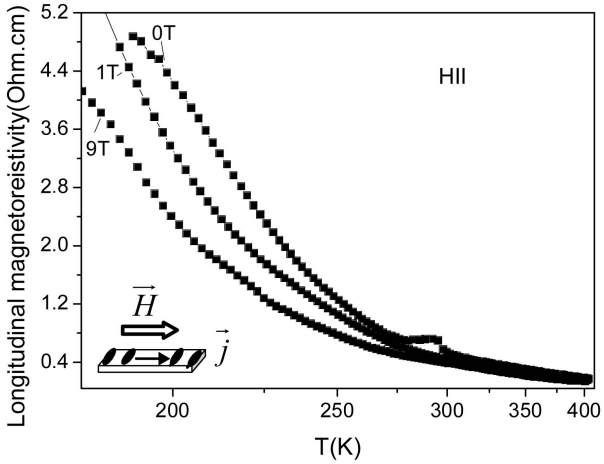

Figure 4. Longitudinal magneto-resistivity for $\mu_0 H$ = 0 T; 1 T; 9 T, in fields parallel to the current plane.

and the hopping distance exceeds the correlation length $\left(R_{hop} > \xi_0\right)$. The hopping distance has to be compared with the nearest neighbor distances between irons ions in the FTO structures: 0.289 nm [28] and 0.300 nm in α-Fe_2O_3 and $FeTiO_3$ respectively [29].

Is important to underline that the value of $\xi = 0.86$ nm for the electron localization length is very small if compared for example with 350 nm localization length for vanadium oxide [30] and 1400 nm for Indium oxide [31].

To summarize: chemical disorder in non-stoichiometric *n*-type $Fe_{2-x}T_xO_{3-\delta}$ causes a strong localization of charge carriers, determining the hopping nature of conduction mechanism. As the conductivity is attributed to the mixed valences of Fe^{3+}/Fe^{2+}, the observed microscopic mechanism is a variable range hopping of electrons from Fe^{2+} to Fe^{3+}, mostly in dense irons planes perpendicular to c-axis, as the shortest iron-iron distance within the plane $\left(\sim 0.29 - 0.30 \text{ nm}\right)$ is shorter than the out of plane nearest neighbour distance $\left(\sim 0.40 \text{ nm}\right)$. The localised nature of charge carriers, as will be discussed further in this report, plays an important role in magneto-transport features of this material.

3.3. Magneto-Transport

The influence of magnetic field on the electrical transport properties (magneto-resistance, spin polarization) might strongly depend on the type of the conduction mechanism in material; *i.e.* weather conductivity occurs by "free" or localized carriers. Our interest was to understand the effect of an external magnetic field applied per-

pendicular or parallel with respect to the plane of the sample on the magneto-resistance. Magneto-resistance is studied not in "classical" AMR configuration were the angle between magnetic field and current direction is in film plane. In our study, magnetic field is oriented parallel to current and film plane, or put perpendicular to film plane. The geometry of the contacts is "four aligned probes"; see schemes in **Figure 4** and **Figure 5**. At room temperature the measured resistance in zero magnetic field is $R(0) = 1.68 \times 10^4$ Ohm for a resistivity value of $\rho = 0.4$ Ohm·cm. The magneto-resistance is defined as $MR(H) = R(H) - R(0)/R(0)$, with $R(H)$ the resistance value for a magnetic field H and $R(0)$ the value at zero field.

For MR measurements we applied two protocol: The first: from $T = 400$ K ($T_c \approx 500$ K) we cooled down in zero filed, at 130 K applied magnetic field and warmed up the sample, so called ZFC/FW procedure. The secondly, at $T = 400$ K we applied a magnetic field and cooled sample down (FC).

3.3.1. Magneto-Resistance in Parallel Magnetic Field

We measured magento-resistance of the sample in two configuration of magnetic fields: parallel and perpendicular to current plan. After applying external parallel magnetic filed (0.1 - 9 T) resistance decreases, negative magneto-resistance has been observed (**Figure 4**). At room temperature $MR_{200\,\mathrm{K}}(9\,\mathrm{T}) = 43\%$ and $MR_{300\,\mathrm{K}}(9\,\mathrm{T}) = 27\%$.

Plotting as we have done for zero field, magneto-resistivity versus temperature, we found that after applying magnetic field hopping conductivity mechanism still obeys Efros-Shklovskii law (**Figure 5**).

The negative magneto-resistance in case of VRH mechanism has been reported for Fe_2O_3 where similar to FTO conductivity is by Fe^{3+}, Fe^{2+} pairs and also in number of magnetic semiconductors and oxide materials [32]-[37].

3.3.2. Magneto-Resistance in Perpendicular Magnetic Field

Secondly, the case of external magnetic field applied perpendicularly to the current plane will be discussed ("field perpendicular"). As we can see from **Figure 6**, the sample behaves like a non-degenerate semiconductor for all measured magnetic field values, as the resistance increases with the decrease of temperature.

An external perpendicular magnetic field increases the sample resistance with respect to zero field value, inducing a positive magneto-resistance.

Magneto-resistance has been studied for magnetic fields varying between 0 T and 9 T. Magneto-resistance values are positive with high magnitudes: $MR_{200\,\mathrm{K}}(0.3\,\mathrm{T}) = 60\%$, $MR_{200\,\mathrm{K}}(9\,\mathrm{T}) = 89\%$ and $MR_{300\,\mathrm{K}}(9\,\mathrm{T}) = 37\%$. The observed linear dependence (**Figure 7**) is a confirmation of the ES-VRH conduction mechanism in this material. From the slope, one can again determine the values of T_1 and deduce the values for the localization lengths ξ_H in magnetic field, supposing again an average value for $\varepsilon \approx 40$ (**Table 1**). As we see from **Figure 4**, magneto-resistance tends to be saturated with external perpendicular magnetic field. This behaviour is different from what usually is observed in non magnetic semiconductors with hopping conductivity, when positive large magneto-reistance (caused by wavefunction shrinking) increases linearly with external magnetic field.

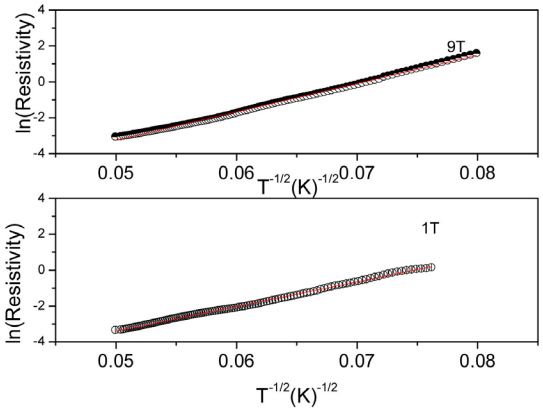

Figure 5. $\ln\rho(H)$ versus $T^{-1/2}$ plots for external magnetic fields of 1 T and 9 T in in fields parallel to the current plane.

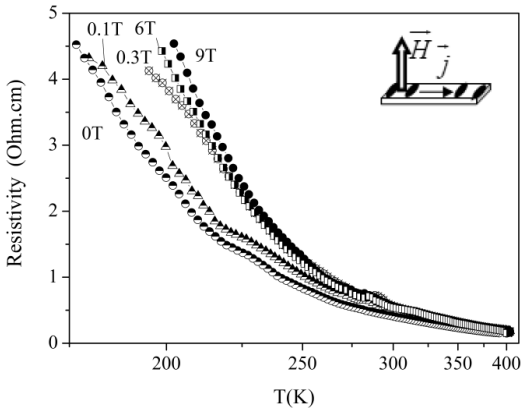

Figure 6. Longitudinal resistance versus temperature for H = 0 T; 0.1 T 0.3 T; 6 T and 9 T in four aligned points probe configuration.

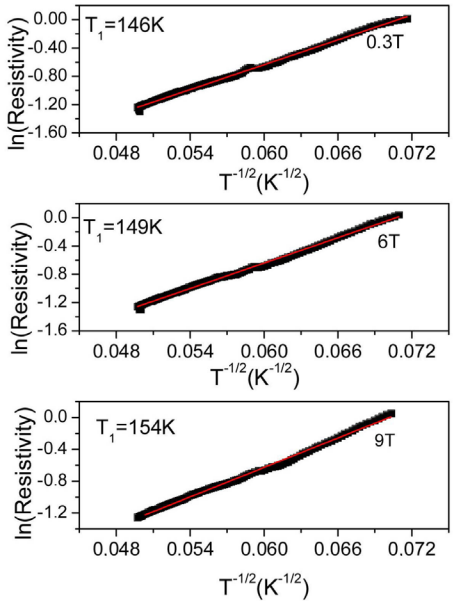

Figure 7. ln$\rho(H)$ versus $T^{-1/2}$ plots for external magnetic fields of 0.3 T, 6 T and 9 T in perpendicular configuration.

Table 1. Values of T_1 and of ξ_H as a function of the applied perpendicular magnetic field.

External magnetic field (T)	T_1 (K)	Experimental ξ_H (nm)
0	$1.85 \times 10^4 \pm 1$ K	0.86
0.3	$2.13 \times 10^4 \pm 1$ K	0.80
6	$2.22 \times 10^4 \pm 1$ K	0.78
9	$2.31 \times 10^4 \pm 1$ K	0.75

Positive magneto-resistance at low temperature is usually observed in deluted magnetic semiconductors at low field which is related with the splitting of band state caused by *s-d* exchange interaction [38] [39]. In magnetic semiconductors, with positive magneto-resistance, differently to FTO with strong carrier localization, carriers are free and spin polarization between free carriers and the spin of magnetic impurity occurs. Except of deluted magnetic semiconductors, such an important value of positive magneto-resistance even at room temperatures are

characteristic for hopping mechanism of conduction, as observed in many weakly doped nonmagnetic semiconductors [40]-[42]. For weak magnetic fields, the effect of magnetic potential on the wavefunctions is small, while in a strong field electrons are much stronger localized by the magnetic potential then by the Coulomb potential [19]. In the VRH regime and for a transverse external magnetic field, according to Shklovskii and Spivak, an additional interference phenomenon occurs between many paths of tunnelling electron during scattering process [43]. This interference phenomenon gives a negative magneto-resistance, that can be evidenced in weak magnetic fields, when the shrinking of wave functions can be neglected.

Interestingly, large positive magnetio-resistance was reported for Co doped ZnO, where conductivity was by variable range hopping [44]. In reported work magneto-resistance was not saturated even at the field when macroscopic magnetization was in saturation state. Authors explain this fact that due to long range hopping distance variable range hopping has no spin dependant character, *i.e.* there was not spin-spin interaction leading decrease of resistance and finely the positive sign of magneto-resistance was attributed to the shrinking effect of wave-functions. It is important to underline that wave function shrinking effect was proposed as an explanation even though applied magnetic filed was parallel to current plane.

For our case, the magnetic length at field at about 1 T is of the order of 30 nm that is much larger then localization length and hopping distance. So one should compare the magneto-resistance with the expression for wave-shrinkage mechanism at low fields.

This expression is [45]:

$$\frac{\Delta R}{R} = t_1 \frac{\zeta_0 R_{hop}^3}{\lambda^4}$$

where t_1—numeric coefficient of the order of 1/100. Thus for our short hops (R_{hop} ~ 1.5 nm) the characteristic value of wave-shrinkage magneto-resistance is of the order of 10^{-7} and is negligible in comparison with observed strength of magneto-resistance. The negative magneto-resistance in parallel field also can not be described by interference mechanism. This mechanism assumes that at saturation fields the magnetic flux through the area $\zeta_0^{1/2} R_{hop}^{3/2}$ is of the order of flux quantum Φ_0. I our case even in fields of the order of 10 T the relation of discussed magnetic flux to the flux quantum is $\Phi/\Phi_0 \sim 10^{-2}$ and thus no interference magneto-resistance should be observed.

Also one can note that in 2D structures interference magneto-resistance appears only when magnetic field is perpendicular to structures plane while in our fields the negative magneto-resistance is observed in parallel field.

Thus no conventional hopping mechanisms can describe observed picture of magneto-resistance and this magneto-resistance should be ascribed to magnetic phenomena. So we state that to understand magneto-resistance in FTO films one should study hopping conductivity simultaneously with magnetically properties.

By Inoe *et al.*, has been developed theory to explain magneto-restistance when the nearest neighbour hopping occurs in the super paramagnetic granular films [46]. Authors relate negative magneto-resistance to the ordering of magnetic moments of the granules in external magnetic field. Proposed mechanism can not be generalized for non-granular material and especially it can not be applied to the materials with internal ferromagnetic order such as FTO.

4. Conclusions

The detailed study of electronic conductivity of magnetically disordered R(-3)c $Fe_{1.5}Ti_{0.5}O_{3-\delta}$ thin layers shows that conduction electrons are strongly localized causing the Efross-Shklovskii type variable range hopping. The conductivity is attributed to the mixed valences of Fe^{3+}/Fe^{2+}, confirmed by the results from aberration-corrected scanning transmission electron microscopy (STEM) coupled to high-resolution energy electron-loss spectroscopy (EELS) [14]. The hopping nature of conductivity and the magnetic nature of hopping centres result in significant changes of the magneto-resistance. The charge distribution mechanism influences strongly the saturation magnetization, while exchange interactions, as probed with T_c, are not affected.

We believe that we deal with completely disordered samples where Ti ions are randomly distributed between two planes antiferromagnetically ordered with respect to each other. The random character of the distribution of Ti-formed “holes” within the two Fe planes leads to spatial fluctuations of local magnetization. (The situation is to some extent similar to “ferromagnetic glass” considered in [47], although the microscopic mechanism is different). By our hypotheses the anisotropy of magnetic properties and magneto-resistance can be explained by the

magnetic domain structure of magnetically disordered $Fe_{1.5}Ti_{0.5}O_{3-\delta}$. The deep understanding of transport properties of $Fe_{1.5}Ti_{0.5}O_{3-\delta}$ became even more important and interesting, after it has been shown that by particular deposition and post treatment conditions conductivity type inversion (from *n* to *p*) can occur for $FeTiO_3$ [48]. Our preliminary experiment confirms that hole conductivity can be achieved similarly for (Fe_2O_3) and ilmenite ($FeTiO_3$) solid solution. High quality crystallinity, the large room temperature magneto-resistance, room temperature ferromagnetism, possibility to have *n* and *p* type conductivity, are characteristics, to be consider $Fe_{1.5}Ti_{0.5}O_{3-\delta}$ oxide as a potential material for spin and magneto-electronics. The present results will certainly stimulate further *ab initio* calculations as well as guide the elaboration of new homogeneous artificial $Fe_{2-x}Ti_xO_{3-\delta}$ thin films or even $(Fe_2O_3/FeTiO_3)_n$ superlattices.

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