Mechanisms of magnetoelectricity in manganese-doped incipient ferroelectrics

R. O. Kuzian1(a), V. V. Laguta1,2, A.-M. Daré3, I. V. Kondakova1, M. Marysko2, L. Raymond3, E. P. Garmash1, V. N. Pavlikov1, A. Tkach4, P. M. Vilarinho5 and R. Hayn3

1 Institute for Problems of Materials Science NASU - Krzhizhanovskogo 3, 03180 Kiev, Ukraine
2 Institute of Physics, AS CR - Cukrovarnicka 10, 16253 Prague, Czech Republic, EU
3 Aix-Marseille Université, IM2NP CNRS - FST St-Jérôme - Avenue Escadrille Normandie Niemen, F-13397, Marseille Cedex, France, EU
4 IFIMUP and IN-Institute of Nanoscience and Nanotechnology, Department of Physics and Astronomy, Faculty of Science of University of Porto - Rua do Campo Alegre, 687, 4169-007 Porto, Portugal, EU
5 Department of Ceramics and Glass Engineering, CICECO, University of Aveiro - 3810-193 Aveiro, Portugal, EU

received 3 July 2010; accepted in final form 22 September 2010
published online 2 November 2010

PACS 75.85.+t – Magnetoelectric effects, multiferroics
PACS 75.30.Hx – Magnetic impurity interactions
PACS 76.30.Fc – Iron group (3d) ions and impurities (Ti-Cu)

Abstract – We report magnetization measurements and magnetic resonance data for SrTiO3 doped by manganese. We show that the recently reported coexistent spin and dipole glass (multiglass) behaviours are strongly affected by the distribution of Mn ions between the Sr and Ti sites. Motivated by this finding we calculate the magnetic interactions between Mn impurities of different kinds. Both LSDA + U and many-body perturbation theory evidence that magnetic and magnetoelectric interactions are mediated by Mn4+ ions substituting for Ti. We propose two microscopic magnetoelectric coupling mechanisms, which can be involved in all magnetoelectric systems based on incipient ferroelectrics. In the first one, the electric field modifies the spin susceptibility via spin-strain coupling of Mn4+. The second mechanism concerns Mn pairs coupled by the position-dependent exchange interaction.

Copyright © EPLA, 2010

Introduction. – SrTiO3 (STO) and KTaO3 (KTO) doped by manganese have attracted considerable attention exhibiting simultaneous spin and dipole glass behaviours with large non-linear magnetoelectric coupling [1–3]. Such “multiglass” systems extend non-trivially the frame of conventional multiferroicity and give new perspective for studies of the phenomenon and potential application in microelectronic devices.

Both STO and KTO are special representatives of the perovskite family of AB(O3) materials. They are incipient ferroelectrics (IF), i.e. they remain paraelectric down to zero temperature, but exhibit very large dielectric permittivity (~20000 and 5000, respectively) at low temperature due to the softening of a transverse optical mode that corresponds to B sub-lattice oscillations with respect to the almost static rest of the lattice.

The Mn impurities in STO may substitute both for Sr and Ti; they will be denoted as MnA and MnB, respectively. Isolated impurities are paramagnetic, MnA being an isotropic centre with formal valency Mn4+, and a spin $S = 3/2$ [4], while MnA which has valency 2+ and $S = 5/2$, is isotropic at $T > 100 \text{K}$, and axial at low temperature [5]. According to the interpretation of ESR measurements [4,5], which were recently confirmed by density functional theory (DFT) calculations [6,7] and EXAFS experiments [8], the MnB impurity resides in the octahedrally coordinated cubic position B of the perovskite lattice, and MnA is displaced from A position thus forming electric dipoles in addition to magnetic ones.

Ceramic samples of STO doped by 2% of manganese exhibit spin- and polar-glass properties at a temperature below $T_g \approx 38 \text{K}$. Moreover, a substantial non-linear magnetoelectric coupling was measured [1–3]. A similar behaviour for the KTO:Mn system was also found [3]. The interaction of electric dipoles formed by off-central MnA impurities has the same nature as the interaction of other dipole impurities in IF, its mechanism is rather well understood [9]. In this paper we concentrate on magnetic and magnetoelectric interactions in STO : Mn. We show that the presence of off-central Mn2+ ions substituting for MnA...
Sr is necessary but not sufficient to induce the multiglass behaviour, and that the magnetic interactions are mediated by Mn\(^{4+}\) ions substituting for Ti.

Some aspects of the considered problem are interesting from the fundamental point of view. The interaction between ions with different d-shell filling and different spins connected by several bridging ligands requires a generalization of superexchange theory. The dependence of spin-Hamiltonian parameters on the external electric field is a non-trivial application of the ligand field theory for ions in a highly polarizable medium.

**Experiment.** – For our experimental studies we have used two groups of STO:Mn ceramic samples prepared in different labs. We will call them I and II. Type-I ceramics with the formal chemical composition Sr\(_{0.98}\)Mn\(_{0.02}\)TiO\(_3\) were prepared by mixed oxide technology described elsewhere [10]. In particular, reagent grade SrCO\(_3\), TiO\(_2\) and MnO\(_2\) were mixed in appropriate amounts, ball milled, dried and calcined at 1100 °C for 2 h. The calcined powders were again milled, pressed isostatically and sintered at 1500 °C for 5 h. For the type-II ceramics (formal chemical composition Sr\(_{0.96}\)Mn\(_{0.04}\)TiO\(_3\)), instead of MnO\(_2\), powder of MnCO\(_3\) was used. The calcination was performed at 1150 °C for 4 h and the sintering at 1360 °C for 2 h. Both types of samples possess Mn\(^{2+}\)A off-centric impurities and have similar dielectric properties, but as shown below their magnetic responses are strikingly different.

The magnetic measurements were performed using a SQUID magnetometer (MPMS-6S Quantum Design) in the temperature range 4.5–100 K. The zero-field-cooled (ZFC) and field-cooled (FC) susceptibilities were measured in an applied field of 100 Oe. The main experimental result of this paper is illustrated in fig. 1. While magnetic properties of type-I ceramics are similar to that reported in refs. [1,2], namely, they exhibit spin-glass behaviour at \(T < 45\) K (fig. 1a), the type-II ceramics remain paramagnetic down to liquid-helium temperature (fig. 1b). In addition, for the ceramics I the magnetization exhibits a hysteric behaviour with a finite remanence and coercivity (fig. 1c). On the contrary, the magnetic loops measured on ceramics II (fig. 1d) show no hysteresis and remanence. In this case, the magnetization is almost entirely determined by the paramagnetic contribution.

In order to study the distribution of Mn ions in the lattice and their individual magnetic properties—they are the only source of magnetism in our system—we have performed ESR measurements at 9.2 GHz in the standard 3 cm wavelength range at temperatures from 4.2 up to 300 K. An Oxford instrument ESR 900 cryosystem was used. In both types of ceramics we have found the spectra of Mn\(^{2+}\)A and Mn\(^{4+}\)B ions, which were described in detail in our previous paper and other early publications (see, e.g., refs. [4,5]). The main difference between the two types of ceramics revealed by ESR is the ratio of Mn\(^{2+}\)/Mn\(^{4+}\) ion concentration, which is 70/30 and 90/10 for types I and II respectively, as shown in fig. 1e–h. The absolute concentration of Mn\(^{2+}\)A in both ceramics is about 1–1.3% as the ceramics contain also some amount of MnTiO\(_3\) inclusions reflected in ESR spectra by a broad line (see, figs. 1g, h) and observed previously in electron diffraction spectra (ref. [10]). Although in the type-II ceramics about 70% of Mn ions contribute to this MnTiO\(_3\) fraction, it does not markedly influence the magnetic properties of the studied samples (figs. 1b, d) due to relatively small magnetic anomaly of MnTiO\(_3\) at the antiferromagnetic phase transition at 63 K (ref. [11]).

**DFT calculations.** – We have theoretically studied the interactions between Mn ions using LSDA + U and many-body perturbation theory. We have considered the Mn impurities when they occupy nearest neighbour positions, and looked at the various pairs Mn\(_A\)-Mn\(_A\), Mn\(_A\)-Mn\(_B\), and Mn\(_B\)-Mn\(_B\). The Mn\(_A\) ions were shifted in various directions from the symmetric A position.
spin part of the interaction is of Heisenberg type. 

Various Mn pairs in KTaO were considered: one found for the isolated ion \([6]\); for the AA pair, the distance between them, \(d_{AA} = 3.9 \text{ Å}\) \([6]\). The third column shows that the configuration with \(d_{AA} = 3.82\) Å is separated by 695.5 meV from the others by such a large energy, that these will not be observed within the physically relevant temperature range. A similar situation was described in ref. \([15]\) for Li-Li pairs in KTaO. The last column of table 1 represents one of the main theoretical findings of this work, namely, it shows that the magnetic interaction of nearest neighbour Mn\(^{2+}\) ions, for the most probable parallel configuration, satisfies \(|J_{AA}/k_B| < 3\text{ K}\). In fact this value is on the verge of precision of DFT calculations. Despite the large spin value of Mn\(^{2+}\) ions, this interaction cannot be responsible for magnetic susceptibility anomalies at \(T \sim 40\text{ K}\) that we observe for type-I ceramics (fig. 1), and that were reported in previous studies of STO: Mn \([1,2]\).

Table 2 shows the results for a Mn\(^{2+}\)-Mn\(^{4+}\) pair. Here the Mn\(^{2+}\) ion shift was taken to be the same as the one found for the isolated ion \([6]\); for \(d_{AA} > (\sim) 0\) the ions get farther (closer). Finally, for the pair Mn\(^{4+}\)-Mn\(^{4+}\) we have found \(J_{BB} = 9.3\text{ meV}\), i.e. \(J_{BB}/k_B = 107.9\text{ K}\). So, we may conclude that the presence of Mn\(^{4+}\) ions may be responsible for the observed anomalies in magnetic susceptibilities.

**Theory of superexchange.** – To reach a better understanding of the exchange mechanism we have performed analytic calculations of the superexchange interaction between Mn ions within fourth-order many-body perturbation theory. Using resolvent method \([16]\) we obtained a general formula for the magnetic coupling between two spins \(S_1\) and \(S_2\) in terms of hopping integrals \(t_{m \beta n}\) between cations \((im)\) (\(i\) specifies the cation, \(m\) the orbital index) and neighbouring ligands \((\beta n)\) (\(\beta\) specifies the ligand, \(n\) the orbital). Taking the hole point of view (no fermion on the ligand \(p\) orbitals in the ground state) we have established

\[
\text{see eq. (2) above}
\]

where the sum over the cation orbitals \(m\) and \(m'\) is restricted to ground-state occupied ones (abbreviation “occ”). \(\Delta_{ij\beta n}\) is the energy of the excited state (measured with respect to the ground state), where one fermion has moved from \((im)\) to \((\beta n)\), while \(\Delta_{ij}\) is the difference of energy between an excited state with \(N_i - 1\) and \(N_j + 1\) fermions on cation \(i\) and \(j\) respectively, and the ground state (GS) with \(N_i\) and \(N_j\) fermions per cation respectively. If the cations are of the same type, one has \(\Delta_{ij} = \Delta_{ji}\) and \(\Delta_{ij\beta n}\) does not depend on \(i\). The three added terms inside the bracket in eq. (2) correspond to different paths: the first two involve intermediate excited states with \((N_i - 1, N_j + 1)\) fermions on the cations, while the third term corresponds to an excited state with two fermions on the ligands with repulsion \(U_p\) when the holes meet on the same ligand.

The parameters \(t_{m \beta n}\), \(\Delta_{ij\beta n}\) and \(\Delta_{ij}\) were extracted from the analysis of photoemission experiments reported in refs. \([17,18]\). We denote for the BB pair: \(\Delta_{12} = U_{eff}^{B}\), \(\Delta_{ij\beta n} = U_{eff}^{B}\), for the AA pair \(\Delta_{12} = U_{eff}^{A}\), \(\Delta_{ij\beta n} = U_{eff}^{A}\); while for the BA pair \(\Delta_{12} = U_{eff}^{B} - U_{eff}^{A}\) we get farther (closer).
\[
\Delta_{21} = \Delta_{eff}^A - \Delta_{eff}^B + U_{eff}^A, \quad \Delta_{32n} = \Delta_{eff}^C, \quad \text{and} \quad \Delta_{28n} = \Delta_{eff}^D,
\]
where \(\Delta_{eff}^1 = \Delta_1 + J_H/[7/9(N_i - 1) - p_i]\) and \(U_{eff}^i = U_i + J_H[N_i + 11/9 - 2p_i]\), with \(J_H = 5/2B_i + C_i\), \(N_i\) is the number of holes in the ground state of Mn ion and \(p_i\) is the number of doubly occupied orbitals. We use the following experimental values (in eV) for Mn\(_B\): \(B_i = 0.132\), \(C_i = 0.610\), \(\Delta_1 = 2 \pm 0.5\) and \(U_i = 7.5 \pm 0.5\) (table I of ref. [17]), while for Mn\(_A\), \(B_i = 0.119\), \(C_i = 0.412\), \(\Delta_i = 7\) and \(U_i = 5.5\) (tables I, II of ref. [18]). This gives \(\Delta_{eff}^A = 9.2\) eV, \(\Delta_{eff}^B = 4.5 \pm 0.5\) eV, \(U_{eff}^A = 9.9\) eV and \(U_{eff}^B = 11.6 \pm 0.5\) eV. The hopping parameters are expressed in terms of Slater-Koster parameters [19] \(V_{pd\sigma}^{A(B)}\) for Mn\(_A\) (B), they essentially on the cation-ligand distance, we take \(V_{pd\sigma}^{A(B)} = -2.16\) [19]. Following ref. [18], we have assumed that the hopping which links states with \(N + 1\) and \(N\) holes on some cation, is reduced by a factor \(R\) compared to hopping linking states with \(N - 1\) and \(N\) holes. The results (and their comparison with LSDA + U) are presented in table 3 for the parameters \(R = 1.2\) and \(U = 4\) eV, and the shifts are the same as those found in LSDA calculations.

As can be seen, the agreement is qualitative between perturbative calculations and DFT results. In addition, the superexchange theory enables to discuss various tendencies and contributions. The different exchange coupling \(J_{AB}, J_{AB}^d\) and \(J_{AA}\) are proportional to \((V_{pd\sigma}^{A(B)})^4\), \((V_{pd\sigma}^{A(B)}V_{pd\sigma}^{A(B)})^2\) and \((V_{pd\sigma}^{A(B)})^4\), respectively. A crude estimate based on the different distances, leads to \(J_{AB}/J_{BB} \approx 0.1\) and \(J_{AA}/J_{BB} \approx 0.01\). One can also expect a predominant value for \(J_{BB}\) due to geometry: it corresponds to a 180° Mn\(_O\)-O-Mn\(_B\) link, while the other two are 90° ones. The difference between exchange couplings are also due to different number of exchange paths and to difference in charge transfer values \(\Delta_{eff}^A > \Delta_{eff}^B\). The number of paths for \(J_{AA}\) is larger than for the other two, since four ligands and many orbitals come in, against three ligands for \(J_{AB}\) and only one for \(J_{BB}\). Two or more ligands raise the opportunity to have ferromagnetic contributions, which explains reduction of \(J_{AA}\) compared to the other two, further than what was expected just by distance effect.

Mechanisms of magnetoelectric coupling. – We propose two possible mechanisms involving Mn\(_{2+}\) ions, which may be relevant for IF doped by manganese. In the following we consider the solid solution Sr\(_1-x\)Mn\(_x\)Ti\(_1-x\)Mn\(_x\)O\(_3\). The magnetoelectricity implies the dependence of the magnetic susceptibility on an electric field. Up to second order, the magnetic susceptibility may be written

\[
\chi_{ij} = -\frac{\partial^2 F}{\partial H_i \partial H_j} \bigg|_{H=0} = \chi_{0,ij} + \chi_{1,ijk}E_k + \chi_{2,ijkl}E_kE_l.
\]

where the free energy density \(F\), the magnetic and electric field components, \(H_i \) and \(E_j\) are measured in CGS units. To translate this equation in terms of ref. [2] notations with SI units, one should use the relations

\[
\beta_{ij} = (4\pi)^2 \mu_0 \sqrt{\chi_{0,ij}} \approx 1.67 \times 10^{-10} \chi_{0,ij} \text{s/A},
\]

\[
\delta_{ijkl} = 8\pi^2 \mu_0 \epsilon_0 \chi_{2,ijkl} \approx 8.78 \times 10^{-16} \chi_{2,ijkl} \text{m/V A}.
\]

The first mechanism is a one-spin effect: the polarization \(P\) of the lattice, is accompanied by a lattice strain, which is proportional to the square of polarization [20]. The Mn\(_{2+}\) ion has a 3d\(^5\) configuration and a \(4\)F GS, which is split by the ligand field in contrast to the 3d\(^5\) configuration and \(4\)S GS for Mn\(_{3+}\). In a cubic field the Mn\(_{2+}\) ion has a fourfold degenerate \(4\)A2 GS. When the local symmetry becomes axial, an additional splitting arises. Its magnitude depends on the polarization via the strain. This affects the magnetic susceptibility. In a paraelectric phase, the changes are proportional to the square of the external electric field, but in the presence of a net polarization \(P_r\) in a polar phase, a linear dependence appears. Let us note that this mechanism will be effective in any ferroelectric perovskite doped by paramagnetic ions located at B sites and having the 3d\(^5\) configuration.

The contribution of this mechanism to the magnetoelectric susceptibility is given below by eqs. (9) and (11). Substitution of numerical values relevant to the experimental conditions of ref. [2] gives

\[
\chi_{1,zzz} \approx -2.2 \times 10^{-9}, \quad \beta \approx -3.6 \times 10^{-19} \text{s/A},
\]

\[
\chi_{2,zzz} \approx -1.2 \times 10^{-10}, \quad \delta \approx -0.1 \times 10^{-24} \text{m/V A}.
\]

In these estimates, we have used \(x + y = 0.02\), and \(x/y \approx 70/30\), as found in our ESR experiment. The reported experimental values are [2] \(\beta \approx -3 \times 10^{-19} \text{s/A}\) and \(\delta \approx -9 \times 10^{-24} \text{m/V A}\). We see that the paramagnetoelectric susceptibility \(\beta\) is in fairly good agreement, but the biquadratic coefficient is underestimated by this mechanism which cannot be the only argument put forward.

The second mechanism concerns Mn\(_A\)-Mn\(_B\) pairs. As can be seen from tables 2 and 3, the Mn\(_{2+}\) has non-equivalent equilibrium positions in the cell where Mn\(_{2+}\) is present. The superexchange interaction between Mn\(_{2+}\) and Mn\(_{3+}\) strongly depends on the displacement \(d_A\) of the closer Mn. Compared to the closer situation, the case with ions far from each other corresponds to a higher energy \(\Delta E\). As shown in detail in the following section, the lattice polarization increases the number \(N_{P}(P, E)\) of Mn\(_{2+}\) ions lying farther from Mn\(_{2+}\) ions. This leads to a positive \(\chi_{1,zzz}\). In the next section we show that this mechanism seems to be unimportant for the system studied in ref. [2], but it may be very effective for a system where the interaction energy between electric Mn\(_{2+}\)-dipole and \(P_r\) is comparable with \(\Delta E\).
Calculation of non-linear magnetoelectric susceptibility. – Here we quantitatively consider the ideas outlined in the previous section. This section is a little technical and can be safely skipped by someone not interested in the details of computation.

The first mechanism. – In order to estimate its contribution, we follow the ideas of ref. [21]. The Mn$^{4+}$ ion is much more sensitive to the local strain than Mn$^{2+}$. In an octahedral coordination it has a $A_2$ orbital singlet ground state, and the effective spin-3/2 Hamiltonian has the form

$$\hat{H}_B = \mu_B g z z H z S_z + \mu_B g \perp (H_x \hat{S}_x + H_y \hat{S}_y) + D \left( \frac{8}{3} S(S + 1) - \mu_B^2 \sum_{\mu \nu} \Lambda_{\mu \nu} H_{\mu} H_{\nu}, \right)$$

where $\Lambda_{\mu \nu} = g_s - 2 \lambda k \Lambda_{\mu \nu}$, $D = -\lambda^2 (A_{zz} - A_{xx})$, $\Lambda_{\mu \nu} = \sum_{n \neq 0} \langle \phi_n | \hat{L}^\mu | n \rangle \langle n | \hat{L}^\nu | \phi_n \rangle$, $g_s = 2.0023$ is the spin gyromagnetic ratio, $\Lambda$ is the ground (excited) state, $E_0$ and $E_n$ are the corresponding energies, $\hat{L}_{\mu}$ is the $\mu$-th component of the orbital moment operator, $k$ is the orbital reduction factor. Using the ligand field theory [22,23], which perturbatively takes into account $p-d$ hybridization between paramagnetic ion and surrounding ligands, we may obtain [24]

$$A_{zz} = -\Delta g_{cub} (1 - \kappa e_{33}) / 2 \lambda,$$

$$A_{xx} = -\Delta g_{cub} (1 - 5 \kappa e_{33} / 2) / 2 \lambda,$$

where $\Delta g_{cub} = g_{cub} - g_s$ refers to the $g$-value for undistorted cubic lattice, $\kappa \sim -3.5$, $-4$ is the exponent of $p-d$ hopping dependence on distance [19]. The dependence on electric field of the previous equations is only in the strain $e_{33}$. For multiglass samples we may assume that both, the net polarization $P_e$ and the electric field are directed along the axis $Z$, while $\mathbf{P} = P_e + (\epsilon - 1) \mathbf{E} / 4 \pi$. With an external magnetic field also applied along the $Z$-axis, we compute the partition function $Z_B$ and the free energy density $F_B = -g/|v_c| \theta \ln Z_B$, with $g/|v_c|$ the density of Mn$^{4+}$ ions, $v_c$ the host lattice unit cell volume and $\theta \equiv k_B T$. From this free energy, finally derive the linear contribution to the magnetic susceptibility (eq. (3)):

$$\chi_{1,zzz} = -\frac{y}{v_c} \mu_B^2 A_{zz} \left\{ \frac{g_z z \lambda}{\theta} \left[ 5k + \frac{3g_z z \lambda}{2 \theta} \right] - 2 \right\}, \quad (9)$$

where we have taken into account that $D/\theta \ll 1$ for $T = 10 K$. The (double-) prime indicates the (second-) order contribution, with respect to $E$. Similarly, for the second-order contribution, we have

$$\chi_{2,zzz} \approx \frac{y \mu_B^2}{v_c} \left\{ k (\Lambda \Lambda^{'})^2 [10k + 12 g_z z \lambda / \theta] / \theta - \Lambda'' \left\{ \frac{g_z z \lambda}{\theta} \left[ 5k + 3g_z z \lambda / 2 \theta \right] - 2 \right\} \right\}, \quad (10)$$

When we substitute $\kappa = -3.5$, $g_{cub} = 1.992$ [5], $\lambda \approx 135 \text{cm}^{-1}$, [25], $k = 1$, SrTiO$_3$ lattice parameter $a = 3.9 \AA$, $(v_c = a^3)$, and $c/a \approx 1.002$ [6], $\epsilon = (T = 10K) \approx 1500$, and a net polarization $P_e \approx 0.7$, $\mu C / m^2 = 2100 \text{esu/cm}^2$ [10], we obtain the values presented in eqs. (6) and (7).

The second mechanism. – It involves a pair of Mn$_A$-Mn$_B$ ions. There are six available positions for Mn$_A$, three of them are closer to Mn$_B^{2+}$ and lower in energy: the number of Mn$_A^{2+}$ in deep (shallow) wells is $N_1(2)$. Writing $N_1 = n_1 + n_2 + n_3$, and $N_2 = n_4 + n_5 + n_6$, one has in absence of polarization $N_2 / N_1 = \exp(-\Delta E/\theta)$. However with polarization, there is some lift of degeneracy, as can be seen in fig. 2, this leads to a redistribution of level occupancies, and $N_1(2)$ acquires a dependence on the net polarization $P_e$ and on the external electric field $E$.

$$\chi = \chi_0 + \chi_1 xyz + (\chi_2 - \chi_1) N_2(P_e, E), \quad (11)$$

where $\chi_0$ comes from contribution of everything but Mn$_A$-Mn$_B$ pairs, while $\chi_1(J = 1, 2)$ is the susceptibility of a pair $S = 5/2 - S = 3/2$ coupled by the exchange interaction $J_{AB}(d_{AB})$, which depends on the Mn$_A$ position. The dependence of $\chi$ on the electric field comes from

$^1$We have

$$\chi_J = \sum_{S = |S_A + S_B|} \frac{(2S + 1) \exp(-E_S/\theta)}{\sum_{S = |S_A + S_B|} (2S' + 1) \exp(-E_{S'}/\theta)} \chi_S \quad (12)$$

where $E_S = 1/2 J_{AB} |S(S + 1) - S_A(S_A + 1) - S_B(S_B + 1)|$, the magnetic energy of the pair corresponding to the total spin $S$, $\chi_S = \langle \mu_B S \rangle^2 |S(S + 1)/(3\pi v_c)\theta|$ is the corresponding magnetic susceptibility, and the gyromagnetic ratio is $g_s = 1/2 [g_A + g_B + (g_A - g_B) S_A(S_A + 1) - S_B(S_B + 1) / S(S + 1)]$. 17007-p5

---

**Fig. 2**: Changes of Mn$_A$-Mn$_B$ pair energies in polarized medium. Here $E_{loc} = E + \frac{2 \mu^2}{\gamma} P$ is positive, however it can be negative, depending on the relative direction of polarization with respect to the pair Mn$_A$-Mn$_B$. The Lorentz factor $\gamma$ accounts for the deviation of the local field from the simple cubic case, $p \approx Z_A d_A$ is the dipole moment of Mn$_A^{2+}$, $Z_A \approx 2$ is its dynamic charge.
with \( t = pE_{\text{loc}}/\theta \), \( pE_{\text{loc}} \approx cE + \Delta_s \), \( c \approx pe\gamma/3 \) and \( \Delta_s = 4\pi pE_{\text{Pr}}/3 \), \( (\varepsilon \gg 1 \text{ was used}) \). See the caption of fig. 2 for definitions. Finally, making a limited development up to second order in electric field \( E \), we obtain

\[
\chi_{1,zzz} = (\chi_2 - \chi_1) N^2_2(P_r, 0),
\]

\[
\chi_{2,zzz} = (\chi_2 - \chi_1) N^2_2(P_r, 0).
\]

Substituting the values from table 2: \( \Delta E \approx -123 + 144.6 = 21.6 \text{ meV} \), \( J_1 \approx 1.7 \text{ meV} \), \( J_2 \approx 0.5 \text{ meV} \), and \( \gamma \approx -0.2 \) [9], gives \( \Delta_s \approx 16 \text{ meV} \), and a very tiny contribution of this second mechanism to the susceptibilities \( \chi_1 \approx 7.1 \cdot 10^{-15}, \chi_2 \approx 1.6 \cdot 10^{-15} \). However, since \( N^2_2 \) is strongly dependent on \( \Delta E \), the second mechanism could be of the same order than the first one or even exceed it for \( \Delta E \approx \Delta_s \) (then \( \chi_2 \approx 4.6 \cdot 10^{-7}, \chi_2 \approx 1.7 \cdot 10^{-7} \)): this equality can be realized for other concentrations of manganese in SrTiO\(_3\) host, or for other systems (e.g., K\(_{1-x}\)Mn\(_x\)Ta\(_{1-y}\)Mn\(_y\)O\(_3\) [3]).

**Summary.** – We have compared the magnetic properties of two types of ceramic samples of manganese-doped SrTiO\(_3\). Based on the data of ESR measurements we conclude that the spin-glass behaviour is observed only in samples containing an appreciable percentage of Mn\(^{4+}\) ions substituting for Ti, in addition to Mn\(^{2+}\) substituting for Sr. Using LSDA + U supercell calculation we have shown that the exchange interaction between Mn\(^{2+}\) impurities is an order of magnitude smaller than those for Mn\(^{4+}\) - Mn\(^{4+}\) and Mn\(^{4+}\) - Mn\(^{4+}\) pairs. The analytic many-body calculations have shown that the reason for this difference is the interference of various exchange paths for the Mn\(^{2+}\) - Mn\(^{2+}\) pairs combined with different geometry, Mn-O distances, and stability of the Mn\(^{2+}\) ground-state configuration in comparison to other pairs. We conclude that the presence of Mn\(^{2+}\) ions is essential for the formation of a collective magnetic state at low temperature. We propose two microscopic mechanisms of magnetoelectricity in SrTiO\(_3\) : Mn which involve Mn\(^{4+}\) ions.

***

The authors thank M. D. GLINCHUK for fruitful discussions, they acknowledge the PICOS project (Contracts CNRS No. 4767, NASU No. 267) and grant MSMT CR (Project No. 1M06002) for financial support and the IFW Dresden (Germany) which allowed them to use their computer facilities. The institutional research plan AVOZ10100521 is also acknowledged.

**Note added in proofs:** We became recently aware of a related work [26], which to our opinion corroborates the scenario of site-dependent magnetoelectric properties of Mn-doped SrTiO\(_3\).

**REFERENCES**

[1] KLEEMANN W., SHVARTSMAN V. V., BONSAI S., BORISOV P., TKACH A. and VILARINHO P. M., J. Phys.: Condens. Matter, 20 (2008) 434216.

[2] SHVARTSMAN V. V., BONSAI S., BORISOV P., KLEEMANN W., TKACH A. and VILARINHO P. M., Phys. Rev. Lett., 101 (2008) 165704.

[3] KLEEMANN W., BONSAI S., BORISOV P., SHVARTSMAN V. V., MIGA S., DEC J., TKACH A. and VILARINHO P. M., Eur. Phys. J. B, 71 (2009) 407.

[4] MULLER K. A., Phys. Rev. Lett., 2 (1959) 341; MULLER K. A. and BURKARD H., Phys. Rev. B, 19 (1979) 3593.

[5] LAGUTA V. V., KONDAKOVA I. V., BYKOV I. P., GLINCHUK M. D., TKACH A., VILARINHO P. M. and JAETRABKI, L., Phys. Rev. B, 76 (2007) 054104.

[6] KONDAKOVA I. V., KURZAN R. O., RAYMOND L., HAYN R. and LAGUTA V. V., Phys. Rev. B, 79 (2009) 134411.

[7] KVVATKOVSKI O. E., Phys. Solid State, 51 (2009) 982.

[8] LEVIN I., KRAYZMAN V., WOICIK J. C., TKACH A. and VILARINHO P. M., Appl. Phys. Lett., 96 (2010) 052904.

[9] VUGMEISTER B. E. and GLINCHUK M. D., Rev. Mod. Phys., 62 (1990) 993.

[10] TKACH A., VILARINHO P. M. and KHOLKIN A. L., Appl. Phys. Lett., 86 (2005) 172902; Acta Mater., 53 (2005) 5061.

[11] STICKLER J. J., KERN S., WOLD A. and HELLE G. S., Phys. Rev., 164 (1967) 765.

[12] FPLO-7.00-28 (improved version of the original FPLO code by KOEPERNIK K. and ESCHIRG H., Phys. Rev. B, 59 (1999) 1743; http://www.fplo.de). The exchange and correlation potential of Perdew and Wang [13] was employed as well as the FPLO implementation of LSDA + U method in the atomic limit scheme [14].

[13] PERDEW J. P. and WANG Y., Phys. Rev. B, 45 (1992) 12344.

[14] ESCHIRG H., KOEPERNIK K. and CHAPLYGIN I., J. Solid State Chem., 176 (2003) 482.

[15] PROSANDEEV S. A., COCKAYNE E. and BURTON B. P., Phys. Rev. B, 68 (2003) 014120.

[16] AUERBACH A., Interacting Electrons and Quantum Magnetism (Springer-Verlag) 1994.

[17] BOQUET A. E., MIZOKAWA T., SATOHI T., NAMATAME H. and FUJIMORI A., Phys. Rev. B, 46 (1992) 3771.

[18] MIZOKAWA T. and FUJIMORI A., Phys. Rev. B, 48 (1993) 14150.

[19] HARRISON W. A., Electronic Structure and the Properties of Solids (Freeman, San Francisco) 1980.

[20] RIMAI L. and DE MARS G. A., Phys. Rev., 127 (1962) 702.

[21] HOU S. L. and BLOEMERGEN N., Phys. Rev., 138 (1965) A1218.

[22] KUZMIN M. D., POPOV A. I. and ZVEZDIN A. K., Phys. Status Solidi. (b), 168 (1991) 201.

[23] KUZMIN R. O., DARE A. M., SATI P. and HAYN R., Phys. Rev. B, 74 (2006) 155201.

[24] GLINCHUK M. D. and KUZMIN R. O., Physica B, 389 (2007) 234.

[25] ABRAGAM A. and BLEANEY B., Electron Paramagnetic Resonance of Transition Ions (Clarendon, Oxford) 1970, p. 437.

[26] CHODHURY D. et al., arXiv:1009.4792v1 [cond-mat.mtrl-sci].