Pseudo Jahn-Teller Origin of Perovskite Multiferroics, Magnetic-Ferroelectric Crossover, and Magnetoelectric Effects: The d^0-d^{10} Problem

Isaac B. Bersuker

Institute for Theoretical Chemistry, The University of Texas at Austin, Austin, Texas 78712, USA

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The conditions of multiferroicity in d^n perovskites are derived from the pseudo Jahn-Teller effect, due to which ferroelectric displacements are triggered by vibronic coupling between ground and excited electronic states of opposite parity but same spin multiplicity; it takes place for some specific d^n configurations and spin states only. In combination with the high-spin–low-spin crossover effect this leads to a novel phenomenon, the magnetic-ferroelectric (multiferroics) crossover which predicts magnetoelectric effects with exciting functionalities including electric magnetization and demagnetization.

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The interest in materials with coexisting and correlated ferroelectric and magnetic properties (multiferroics) has increased lately due to their potential applications (see [1,2] and references therein). The preparation of such materials encounters difficulties. Solid state ferroelectrics are dielectrics, whereas for nonzero magnetic moments there should be unpaired electrons. In the well-known ferroelectric $BaTiO_3$ with a perovskite ABO_3 structure the d^0 configuration of the Ti^{4+} ion has no unpaired electrons, and attempts to obtain ferroelectricity in perovskites with d^n, $n > 0$, transition metal B ions were unsuccessful for a long time. This prompted some authors to term the situation as a "d^0 mystery" for ferroelectrics. However, more recently quite a number of ferroelectrics-multiferroics, mostly perovskites with configurations d^3-d^7, were obtained and studied [1,2]. The origin of these special properties of perovskite ferroelectrics with d^n configurations does not follow directly from displacive theories; for improper ferroelectrics it is assumed that the inversion center is removed by the magnetic anisotropy that induces polarization via spin-orbital interaction. Note, however, that the latter is rather weak as compared with the vibronic coupling mechanism of proper ferroelectrics discussed below.

Obviously, the origin of multiferroics in proper ferroelectrics lies in a better understanding of the nature of ferroelectricity. Quite a number of publications contribute essentially to the solution of this problem (see, e.g., [3,4] and references therein). In the majority of more recent theoretical papers the authors relay heavily on numerical [mostly density-functional theory (DFT)] calculations of the electronic structure of the crystal as a whole. Such calculations show the summary results of the computer experiment providing important information of the system, in some cases showing indirectly the origins and micromechanisms of the phenomenon. A relatively fuller theoretical treatment [4] takes into account the long-range and short-range interactions within the assumption of fourth-order lattice anharmonicity and with DFT calculation of the parameters. In essence these papers follow the basic ideas initially introduced by Cochran-Anderson-Ginsburg-Landau [5] that explain the spontaneous polarization of the crystal as resulting from the compensation of the local repulsion between the ions by the attractive long-range dipole-dipole interactions in the boundary-optical-phonon displacements of the sublattices ("displacive" phase transitions). Note that in such approaches the specific details of the local electronic structure of the ions, including the d^n configuration of the B ion, are rather obscured.

Meanwhile we suggested in 1966 a totally different approach to the problem [6,7] (see an enhanced and extended formulation in [8]). The theory developed based on this idea was termed "vibronic theory," sometimes called "two-band theory." In this approach, in contrast to the ideas above [5], under certain conditions there is no local repulsion in the off-center displacements of some ions in the unit cell. On the contrary, the local vibronic coupling between the ground and excited states of opposite parity, the pseudo Jahn-Teller effect [7] (PJTE) may lead to spontaneous displacements forming local dipole moments, their cooperative interaction resulting in ferroelectric phase transitions of order-disorder type. This suggestion was in severe dissonance with the dominant ideas at the time [5] (causing a two-year delay and a truncation of our first publication), there was not any experimental or other indirect indication of its feasibility, so our suggestion was not accepted and/or properly cited by other authors in this field.

However, already two-years later, in 1968, the idea of local distortions and order-disorder phase transitions in $BaTiO_3$ was experimentally confirmed in diffuse scattering of x rays [9] (the authors did not cite the 1966 and 1967 papers, but they have sent a letter of recognition afterwards [10]). Evidence of the presence of local distortions in the paraelectric phase and order-disorder phase transitions in crystals of the type $BaTiO_3$ and $KNbO_3$ was then obtained by a variety of experimental methods, including Raman spectra [11], optical refractive index [12], infrared reflectivity [13], x-ray absorption [14], ESR with probing ions [15], XAFS [16], femtosecond resolution light scattering [17], NMR [18], elastic and dielectric measurements [19], etc.

In this Letter we show that the vibronic (PJTE) theory of ferroelectricity [6–8], which is in full qualitative agreement with all experimental observations [11–19], explains also directly the origin of perovskite multiferroics with proper ferroelectricity and formulates the necessary conditions that ABO_3 perovskites with a magnetic d^n configuration of the B ion may be ferroelectric. Moreover, we show also that the multiferroics conditions that emerge from the PJTE for d^n ions with $n = 3$, 4, 5, 6, and 7, are directly influenced by the well-known transition metal high-spin–low-spin crossover, resulting in the coexistence of three phenomena: ferroelectricity (FE), magnetism (M), and spin crossover (SCO). This, in turn, leads to a quite novel phenomenon: magnetic-ferroelectric (multiferroics) crossover (MFCO), creating a rich variety of possible magnetoelectric and related effects. Because of the local nature of the PJTE these effects are not limited to crystalline states, they may occur in molecular, cluster, quantum dots, and thin film formations.

Our proof of multiferroicity is fully based on the vibronic theory of ferroelectricity. Therefore we formulate first the PJTE and the condition of ferroelectric instability in simple terms (for a more elaborate treatment, see [6–8]). Denote by $E(q)$ the adiabatic potential energy surface of an ionic cubic crystal near the high-symmetry (cubic) configuration as a function of low-symmetry displacement q that shift the sublattice of positive (metal) ions with respect to the negative ones (e.g., oxygen), a boundary-optical-phonon displacement (the coherent off-center displacements of the B ions in ABO_3). In case of crystals of $BaTiO_3$ type the displacement of the closed-shell A atom is ignored (this may be inappropriate for crystals like $PbTiO_3$). The lattice becomes unstable with respect to polarization if the curvature $K(q)$ at the point of cubic symmetry is negative,

$$K = (\partial^2 E/\partial q^2)_0 < 0. \tag{1}$$

Putting $E = \langle \psi_0 | H | \psi_0 \rangle$, where H is the Hamiltonian and ψ_0 is the ground state wave function, we get

$$K = \langle \psi_0 | (\partial^2 H/\partial q^2)_0 | \psi_0 \rangle + 2\langle \psi_0 | (\partial H/\partial q)_0 | \psi_0{}' \rangle \tag{2}$$

where $\psi_0{}' = (\partial \psi_0/\partial q)_0$. Denoting the first term in (2) as K_0,

$$K_0 = \langle \psi_0 | (\partial^2 H/\partial q^2)_0 | \psi_0 \rangle \tag{3}$$

and the second one as $K_v = 2\langle \psi_0 | (\partial H/\partial q)_0 | \psi_0{}' \rangle$, $K = K_0 + K_v$, we notice that $K_v < 0$. Indeed, presenting $\psi_0{}'$ in terms of the second order perturbation theory, we get directly

$$K_v = -2\sum_n \frac{|\langle \psi_0 | (\partial H/\partial q)_0 | \psi_n \rangle|^2}{E_n - E_0}. \tag{4}$$

This K_v term thus contributes to the instability of the system. Therefore, if $K_0 > 0$, the K_v contribution is the only source of instability. In a series of papers (see in [7,8,20]) it was proved that for any polyatomic system in the high-symmetry configuration where $\partial E(q)/\partial q = 0$ (force-equilibrated configuration in the q direction)

$$K_0 > 0 \tag{5}$$

and hence the vibronic contribution is the only source of structural instability of any polyatomic system in nondegenerate states. This is the theorem of instability.

The importance of this result is in the different nature of the two contributions, K_0 and K_v. K_0 in Eq. (3) is a diagonal matrix element of second derivatives with regard to the displacement q that includes coherently the local odd displacements of all the atoms, which is a long-range (whole crystal) feature (see more in [8]). On the contrary, K_v contains only off-diagonal matrix elements of first derivatives of the Hamiltonian which, translated to local distortions, does not contain significant intercell interaction terms. Its matrix elements are nonzero when the overlap between the wave functions of the ground state of atoms of one sublattice (oxygen) with the excited state of the atoms of the other sublattice B [Ψ_0 and Ψ_n in Eq. (4)] increases due to the nuclear displacements q, thus enhancing the B-O covalence bonding [7].

The local character of the negative K_v contribution to the curvature means that the instability is essentially of local origin; the long-range interactions presented by K_0 are still important in the realization of the condition of instability $|K_v| > K_0$. The trigger mechanism of spontaneous polarization of the crystal is thus of local origin,

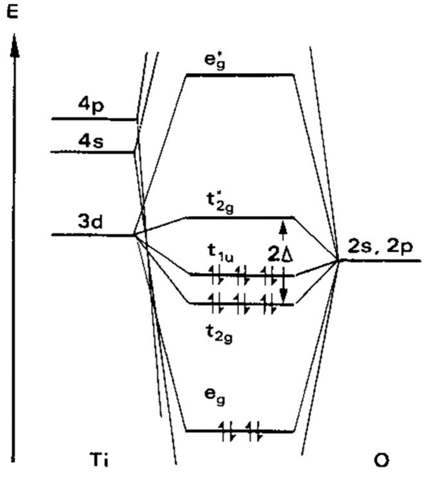

FIG. 1. MO LCAO scheme for a $TiO_6{}^{8-}$ cluster.

directly related to its atomic (electronic) structure, but the polarization depends also on the long-range interactions. In other words, the long-range interaction contributions K_0 by themselves, without the negative local contribution K_v (without the additional covalency [7]), cannot produce the spontaneous polarization of the crystal (see more in [6–8]). This means that we can start with the PJTE in the B center of the cell and, taking into account the denominators in Eq. (4), approximately reduce the problem to a two-level one.

The typical molecular-orbital (MO) energy scheme for an octahedral cluster $BO_6{}^{8-}$ in the approximation of linear combinations of atomic orbitals (LCAO) is shown in Fig. 1 with the MO electron population of the d^0 configuration, e.g., when $B = \mathrm{Ti}$ [6,7,21]. We see that the highest occupied MO (HOMO) in this case is t_{1u} which is a threefold degenerate odd-parity (ungerade) linear combination of mostly oxygen p_π orbitals, while the lowest unoccupied MO (LUMO) is t_{2g}, mostly atomic three d_π orbitals of the transition metal ion B, and the next excited MO is the double degenerate one e_g (the nonbonding oxygen b_{1g} MO is not shown as irrelevant). For the d^0 case the HOMO configuration is thus $(t_{1u})^6 = (t_{1u} \downharpoonleft)^3 (t_{1u} \upharpoonleft)^3$, where the arrows up and down indicate the two spin states; the energy term of this configuration is ${}^1A_{1g}$. The excited state with opposite parity is formed by the one-electron excitation, $(t_{1u} \upharpoonleft) \rightarrow (t_{2g} \upharpoonleft)$ or $(t_{1u} \upharpoonleft) \rightarrow (e_g \upharpoonleft)$, resulting in the lowest excited ungerade term ${}^1T_{1u}$ at the energy gap 2Δ. The PJTE vibronic coupling constant under the polar displacements of the B atom along [111] is thus [see Eq. (4)]

$$F = \langle p_\pi | (\partial H/\partial q)_0 | d_\pi \rangle \tag{6}$$

and the condition of dipolar instability $|K_v| > K_0$ becomes

$$4F^2/K_0 > \Delta. \tag{7}$$

For the d^1 configuration of the B ion instead of the d^0 the HOMO becomes $(t_{1u} \downharpoonleft)^3 (t_{1u} \upharpoonleft)^3 (t_{2g} \upharpoonleft)^1$ with the term ${}^2T_{2g}$, and LUMO (taken into account Hund's rule) is $(t_{1u} \downharpoonleft)^2 (t_{1u} \upharpoonleft)^3 (t_{2g} \upharpoonleft)^2$ with the lowest excited ungerade term ${}^4T_{1u}$. Hence the two closest terms of different parity (that otherwise could mix under nuclear displacements to produce the PJT dipolar distortion), possess different spin multiplicity, and hence they do not mix by the vibronic coupling; the latter does not contain spin operators [7]. In principle, there may be higher in energy electronic configurations of opposite parity with the same spin as the ground state one, but they are at much larger energy gaps Δ, and therefore hardly satisfying the condition of instability (7) [numerical estimate show that the condition (7) is very limiting [7]]. A similar picture emerges for d^2 configurations for which the two lowest terms of opposite parity are ${}^2T_{2g}$ and ${}^5T_{1u}$ (see Table I).

The situation changes for d^3. Indeed in this case the HOMO is $(t_{1u} \downharpoonleft)^3 (t_{1u} \upharpoonleft)^3 (t_{2g} \upharpoonleft)^3$ with the ground state term ${}^4A_{1g}$, and in the low-spin conditions of the strong ligand fields (large t_{2g}-e_g separation in Fig. 1, see, e.g., [21]) the LUMO is $(t_{1u} \downharpoonleft)^2 (t_{1u} \upharpoonleft)^3 (t_{2g} \upharpoonleft)^3 (t_{2g} \downharpoonleft)^1$ with the lowest ungerade term ${}^4T_{1u}$. Therefore for d^3 configurations (e.g., Mn^{4+}) in sufficiently strong ligand fields the situation becomes again favorable for the PJTE and polar distortions, but in this case, distinguished from the d^0 case, the

TABLE I. Necessary conditions that ABO_3 perovskites with the electronic d^n configuration of the B ion possess both ferroelectric and magnetic properties simultaneously; EC = electronic configuration, GS = ground state, LUES = lowest ungerade excited state, FE = ferroelectric, MM = magnetic, MF = multiferroic.

d^n	Example	HOMO EC and GS term	LUMO EC and LUES term	FE	MM	MF
d^0	Ti^{4+}	$(t_{1u})^6$, ${}^1A_{1g}$	$(t_{1u})^5(t_{2g} \upharpoonleft)^1$, ${}^1T_{1u}$	Yes	No	No
d^1	Ti^{3+}, V^{4+}	$(t_{1u})^6(t_{2g} \upharpoonleft)^1$, ${}^2T_{2g}$	$(t_{1u})^5(t_{2g} \upharpoonleft)^2$, ${}^4T_{1u}$	No	Yes	No
d^2	V^{3+}, Cr^{4+}	$(t_{1u})^6(t_{2g} \upharpoonleft)^2$, ${}^3T_{2g}$	$(t_{1u})^5(t_{2g} \upharpoonleft)^3$, ${}^5T_{1u}$	No	Yes	No
d^3, LS	Cr^{3+}, Mn^{4+}	$(t_{1u})^6(t_{2g} \upharpoonleft)^3$, ${}^4A_{2g}$	$(t_{1u})^5(t_{2g} \upharpoonleft)^3(t_{2g} \downharpoonleft)^1$, ${}^4T_{1u}$	Yes	Yes	Yes
d^3, HS		$(t_{1u})^6(t_{2g} \upharpoonleft)^3$, ${}^4A_{2g}$	$(t_{1u})^5(t_{2g} \upharpoonleft)^3(e_g \upharpoonleft)^1$, ${}^6T_{1u}$	No	Yes	No
d^4, LS	Mn^{3+}, Fe^{4+}	$(t_{1u})^6(t_{2g} \upharpoonleft)^3(t_{2g} \downharpoonleft)^1$, ${}^3T_{2g}$	$(t_{1u})^5(t_{2g} \upharpoonleft)^3(t_{2g} \downharpoonleft)^2$, ${}^3T_{1u}$	Yes	Yes	Yes
d^4, HS		$(t_{1u})^6(t_{2g} \upharpoonleft)^3(e_g \upharpoonleft)^1$, ${}^5T_{2g}$	$(t_{1u})^5(t_{2g} \upharpoonleft)^3(e_g \upharpoonleft)^2$, ${}^7T_{1u}$	No	Yes	No
d^5, LS	Mn^{2+}, Fe^{3+}	$(t_{1u})^6(t_{2g} \upharpoonleft)^3(t_{2g} \downharpoonleft)^2$, ${}^2T_{2g}$	$(t_{1u})^5(t_{2g})^6$, ${}^2T_{1u}$	Yes	Yes	Yes
d^5, HS		$(t_{1u})^6(t_{2g} \upharpoonleft)^3(e_g \upharpoonleft)^2$, ${}^6A_{1g}$	$(t_{1u})^5(t_{2g})^4(e_g \upharpoonleft)^2$, ${}^6T_{1u}$	Yes	Yes	Yes
d^6, LS	Fe^{2+}, Co^{3+}	$(t_{1u})^6(t_{2g})^6$, ${}^1A_{1g}$	$(t_{1u})^5(t_{2g})^6(e_g \upharpoonleft)^1$, ${}^3T_{1u}$	No	No	No
d^6, IS_1		$(t_{1u})^6(t_{2g})^5(e_g \upharpoonleft)^1$, ${}^3T_{1g}$	$(t_{1u})^5(t_{2g})^6(e_g \upharpoonleft)^1$, ${}^3T_{1u}$	Yes	Yes	Yes
d^6, IS_2		$(t_{1u})^6(t_{2g})^5(e_g \upharpoonleft)^1$, ${}^3T_{1g}$	$(t_{1u})^5(t_{2g})^5(e_g \upharpoonleft)^2$, ${}^5T_{1u}$	No	Yes	No
d^6, HS		$(t_{1u})^6(t_{2g})^4(e_g \upharpoonleft)^2$, ${}^5T_{2g}$	$(t_{1u})^5(t_{2g})^5(e_g \upharpoonleft)^2$, ${}^5T_{1u}$	Yes	Yes	Yes
d^7, LS	Co^{2+}, Ni^{3+}	$(t_{1u})^6(t_{2g})^6(e_g \upharpoonleft)^1$, ${}^2E_g$	$(t_{1u})^5(t_{2g})^6(e_g \upharpoonleft)^2$, ${}^4T_{1u}$	No	Yes	No
d^7, HS		$(t_{1u})^6(t_{2g})^5(e_g \upharpoonleft)^2$, ${}^4T_{2g}$	$(t_{1u})^5(t_{2g})^6(e_g \upharpoonleft)^2$, ${}^4T_{1u}$	Yes	Yes	Yes
d^8	Ni^{2+}, Cu^{3+}	$(t_{1u})^6(t_{2g})^6(e_g \upharpoonleft)^2$, ${}^3A_{1g}$	$(t_{1u})^5(t_{2g})^6(e_g)^3$, ${}^3T_{1u}$	Yes	Yes	Yes
d^9	Cu^{2+}	$(t_{1u})^6(t_{2g})^6(e_g)^3$, ${}^2E_g$	$(t_{1u})^5(t_{2g})^6(e_g)^4$, ${}^2T_{1u}$	Yes	Yes	Yes
d^{10}	Zn^{2+}	$(t_{1u})^6(t_{2g})^6(e_g)^4$, ${}^1A_g$	$(t_{1u})^5(t_{2g})^6(e_g)^4(ns \upharpoonleft)^1$, ${}^3T_{1u}$	No	No	No

system possess also a magnetic moment created by three unpaired electrons. However, if the ligand field is weak and the separation t_{2g}-e_g is small, the high-spin arrangement of the excited electronic configuration takes place, and the excitation electron occupies the $e_g \uparrow$ orbital instead of $t_{2g} \downarrow$; the LUMO configuration under Hund's rule becomes $(t_{1u}\downarrow)^2(t_{1u}\uparrow)^3(t_{2g}\uparrow)^3(e_g\uparrow)^1$ with the lowest ungerade state $^6T_{1u}$. Here again there is no PJTE on dipolar distortions and no ferroelectric instability. In this way we considered all the d^n configurations with $n = 0, 1, 2, \ldots, 10$, shown in Table I.

It follows from this table that according to the PJTE only B ions with configurations d^3-low-spin, d^4-low-spin, d^5-low-spin and high-spin, d^6-high-spin and intermediate-spin, d^7-high-spin, d^8, and d^9 can, in principle, produce multiferroics, provided the criterion of instability (8) is fulfilled. Transition metal ions B with configurations d^1, d^2, d^3-high-spin, d^4-high-spin, d^6-low-spin, d^7-low-spin, and d^{10} are not expected to produce multiferroics with proper ferroelectricity under this mechanism. Experimentally obtained perovskite multiferroics with such B ions, for example, $Mn^{4+}(d^3)$, $Cr^{3+}(d^3)$, $Mn^{3+}(d^4)$, $Fe^{3+}(d^5)$, $Fe^{2+}(d^6)$, $Co^{2+}(d^7)$, etc. [2], fit well with the conclusions of Table I; there are no multiferroics with d^0, d^1, d^2, and d^{10} configurations in accordance with the predictions of this theory, and for the other d^n configurations there are limitations outlined above.

Note that Table I formulates the necessary conditions of ferroelectricity and multiferroicity; they become sufficient when the quantitative PJTE condition of instability (7) is realized. It requires relatively low energy gaps to the corresponding excited state 2Δ, low rigidity K_0 with respect to ferroelectric displacements, and larger coupling constant F (which increase the covalent B-O wave functions overlap by the ferroelectric displacements). For example, in the series of perovskites ABO_3 with $A =$ Ba, Sr, and Ca, only $BaTiO_3$ is ferroelectric (under ambient conditions), $SrTiO_3$ is a virtual ferroelectric, and $CaTiO_3$ is not ferroelectric, and this fact got a convincing explanation in the vibronic theory [6–8]. Indeed in the series above the size of the ion A decreases from left to right, and accordingly decreases the size of the elementary cell and the Ti-O distance, and this increases the rigidity K_0 and decreases the vibronic coupling constant F. Similarly, the perovskite $CaMnO_3$ with the d^3 configuration of the Mn^{4+} ion is not multiferroic in ambient conditions, but becomes multiferroic under negative pressure or by substitution of Ca with Ba [22,23]; in both cases the Ti-O distance increases improving the condition of instability (7). It explains also why the magnetic crystal $Sr_{1-x}Ba_xMnO_3$ becomes ferroelectric (multiferroic) only at $x \geq 0.45$ [24]. The multiferroicity of these crystals (as many other multiferroics listed in Ref. [2]) confirm the predictions of Table I and add up to the confirmations [11–19] of the vibronic origin of ferroelectricity.

Of special importance is also the fact that, dependent on the ligands of the octahedral environment, some d^n ions with $n = 3$, 4, 5, 6, and 7, may produce two types of magnetic centers, high-spin (HS) and low-spin (LS), and in the d^6 case there may be also intermediate-spin (IS) states (d^3 has two spin configurations in the one-electron excitation). According to our analysis, only d^5 ions follow the necessary condition of potential multiferroics with ligands producing both spin states, but the PJTE condition of instability (7) and the magnetic moments are different in these two cases. For d^3, d^4, d^6, and d^7 ions only one of the two spin states may serve as a candidate of potential multiferroics. On the other hand, in many cases the two spin states are close in energy producing a well-known phenomenon of transition metal spin crossover (SCO), in which case the system can be relatively easily transferred from one spin state to another by external perturbations like heat, light, and magnetic fields (for reviews, see [25]). Since, as shown above, the change of the spin state changes also the ferroelectric state, the SCO is simultaneously a magnetic-ferroelectric (multiferroic) crossover (MFCO).

This coexistence of strongly correlated magnetic, ferroelectric, and spin-crossover phenomena is expected to have very strong magnetoelectric coupling that opens a variety of new possibilities to manipulate the properties of the system with exciting novel functionalities for electronics and spintronics. Here are several examples. (1) For d^3 and d^4 (Cr^{3+}, Mn^{4+}, Mn^{3+}, Fe^{4+}, etc.) ferroelectrics in the LS state in conditions of MFCO, magnetic fields facilitate the LS → HS transition that destroys the ferroelectricity (and multiferroicity), while an electric field in the HS nonferroelectric state may transfer the system to the ferroelectric (multiferroic) LS state, thus realizing electric demagnetization. (2) For d^5 ferroelectrics in conditions of MFCO, if the ferroelectricity is (most probable) different in the two spin states, an electric field may change the spin state (electric magnetization or demagnetization). (3) For d^6 and d^7 (Fe^{2+}, Co^{3+}, Co^{2+}, Ni^{3+}, etc.) in the nonferroelectric LS state under conditions of MFCO, magnetic fields facilitates the LS → HS transition that induces ferroelectricity and hence multiferroicity in a strong magnetoelectric effect (the d^6 LS state is nonmagnetic); in the d^7 nonferroelectric LS state in MFCO conditions, an electric field may transfer the system to the multiferroic state (electric magnetization). (4) The SCO phenomenon is well known to be influenced also by stress, heat, light, and cooperative effects in crystals [25], hence these perturbations can be used to manipulate the MFCO and all the consequent properties including those mentioned above. The dependence of the MFCO on pressure adds a ferroelastic order to the magnetic and ferroelectric ones. (5) There is already a long history of attempts to use transition metal SCO systems as units of magnetic bistability; the difficulty is in the fast relaxation (short lifetime) of the higher in energy spin state [26]. By choosing a system in the MFCO condition, one can increase the lifetime of the excited dipolar (multiferroic) state by applying an external electric field. (6) An important feature of the revealed MFCO is that it is of local origin and hence it does not necessarily require strong cooperative interactions, meaning that, in principle, it may take place as a magnetic-dipolar effect in separate molecular systems, clusters, thin films, etc., provided the condition of instability (7) takes place.

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