EPJ Web of Conferences **29**, 00046 (2012)
DOI: 10.1051/epjconf/20122900046

Multiferroic and magnetoelectric materials -Developments and perspectives

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Abstract. Multiferroic (*MF*) materials with simultaneous magnetic and electric long range order and occasionally, mutual magnetoelectric (*ME*) coupling, have recently attracted considerable interest. The small linear *ME* effect has been shown to control spintronic devices very efficiently, *e.g.* via the classic *ME* antiferromagnet Cr_2O_3 using exchange bias. Similar nano-engineering concepts exist also for *type-I MF* single phase materials, whose magnetic and polar orders have distinct origins like $BiFeO_3$. Strong *ME* coupling occurs in *type-II multiferroics*, where ferroelectricity is due to spiral spin order as in TbMnO3. Record high ME response coming close to applicability arises in stress-strain coupled *multiphase magnetoelectrics* such as PZT/FeBSiC composites. Higher order *ME* response in disordered systems ("*type-III multiferroics*") extends the conventional *MF* scenario toward *ME quantum paraelectric* and *multiglass* materials with polarization-induced control of magnetic exchange, as *e.g.* in $EuTiO_3$, $Sr_{0.98}Mn_{0.02}TiO_3$, and $PbFe_{0.5}Nb_{0.5}O_3$.
Keywords: Magnetoelectrics, Multiferroics, Composites, Multiglass, Relaxors, Spintronics, Sensorics.
PACS: 07.07.Df, 64.70.ph, 75.50.Lk, 75.85+t, 77.80.Jk, 77.84.Lf, 85.75.-d

1 Introduction

A decade ago, Nicola A. Hill posed the provocative question 'Why are there so few magnetic ferroelectrics?' [1]. No doubt, she knew the answer, at least for the oxidic perovskites with the chemical formula ABO_3, where magnetism becomes established via transition metal ions such as Ni^{2+}, Fe^{3+}, Mn^{4+}. They have partially filled *d* shells. while practically all ferroelectric (*FE*) perovskites contain transition metal ions with empty *d* shells, such as Ti^{4+}, Ta^{5+}, W^{6+}. They favor off-centrality due to their ability to form covalent bonds with neigboring oxygen ions. This process is strongly suppressed by real *d* electrons, which strongly discourage multiferroicity, *i.e.* the coexistence of magnetic and electric long-range order [2]. Nevertheless, many research groups became involved studying the rare situation of coexisting order parameters and their coupling.

In particular, the magnetoelectric (*ME*) effect, *viz.* the cross coupling of the order parameters, magnetization $\boldsymbol{M}$ and polarization $\boldsymbol{P}$, to their conjugate fields, $\boldsymbol{E}$ and $\boldsymbol{H}$, enjoyed a breathtaking

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revival [3]. Clearly, upcoming visions were challenging and promising, *e. g.*, switching magnetism with bare electric fields and thus getting rid of overheating in microelectronic devices [4]. Today we encounter a rich variety of multiferroics and magnetoelectrics. More than 400 papers have been published in 2010 in both of these fields, many of them being mutually linked. An updated world of electrically and magnetically polarizable materials is depicted in *Fig.* 1. Its still growing complexity will be subject to this brief overview.

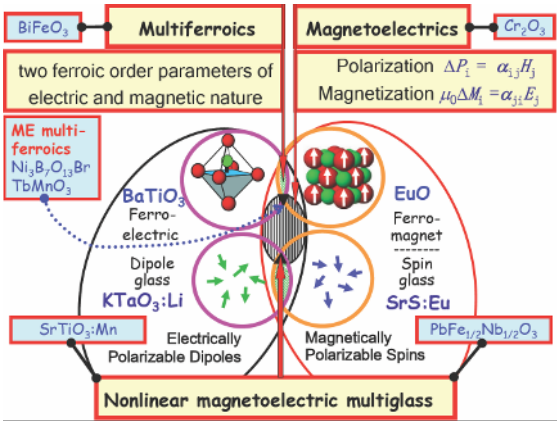

Fig 1. The world of electrically and magnetically polarizable materials including bare ferroics, multi-ferroics, linear magnetoelectrics [5], and dipole-, spin-, and nonlinear *ME* multi-glasses [6,33]

2 Magnetoelectric effect

The linear *ME* effect was first verified on the rhombohedral antiferromagnet Cr_2O_3 [7] and theoretically explored by Landau and Lifshitz [8]. They found that quite stringent symmetry properties must be fulfilled. Time and spatial inversion symmetry, ***T*** and ***I***, respectively, have to be broken, while the combined symmetry operation, ***TI***, must be valid. In this case the free energy density ***F*** of the system contains a contribution $W = -\boldsymbol{\alpha}\mathbf{H}\cdot\mathbf{E}$, which is bilinearly coupled to ***H*** and ***E*** via the linear *ME* susceptibility tensor $\boldsymbol{\alpha}$. In the axial system Cr_2O_3 this term enables the formation of single antiferromagnetic (*AF*) domains by so-called '*ME* cooling' to below the *AF* ordering temperature, T_N = 308 K, in simultaneously applied parallel and antiparallel magnetic and electric fields, respectively [9]

If a system with polar and magnetic properties does not fulfill the above symmetry conditions, it may still be a candidate for higher order *ME* effects. They emerge systematically from a series expansion of the free energy under Einstein summation [10],

$$F(\mathbf{E},\mathbf{H}) = F_0 - \frac{1}{2}\varepsilon_0\chi^e_{ij}E_iE_j - \frac{1}{2}\mu_0\chi^m_{ij}H_iH_j - \alpha_{ij}H_iE_j - \frac{\beta_{ijk}}{2}E_iH_jH_k - \frac{\gamma_{ijk}}{2}H_iE_jE_k - \frac{\delta_{ijkl}}{2}E_iE_jH_kH_l \quad (1)$$

Apart from the field-induced terms coupled to bilinear functions E^2, H^2 and EH via linear susceptibility tensors χ^e_{ij}, χ^m_{ij} and α_{ij}, respectively, increased interest has recently arisen in second-order EH^2 and E^2H, and third-order E^2H^2 effects, synonymously referred to as β, γ, and δ effects, respectively. They are very precisely measured, *e. g.*, by *ME* SQUID susceptometry [11] via the electric field-induced components of the magnetization

$$\mu_0 M_i = -\partial F / \partial H_i = \mu_0\chi^m_{ij}H_j + \alpha_{ij}E_j + \beta_{jki}E_jH_k + \frac{\gamma_{ijk}}{2}E_jE_k + \delta_{jkli}H_jE_kE_l \cdot \quad (2)$$

It involves external *ac* and *dc* electric and magnetic fields, $E = E_{ac}\cos\omega t + E_{dc}$ and H_{dc}, and records the complex first harmonic *ac* magnetic moment, $m(t) = (m' - im'')\cos\omega t$. Under well-defined protocols involving appropriate field amplitudes and directions along the crystal coordinates, the full variety of susceptibility tensor components can be determined. In case of a polycrystalline sample

with volume V the response, m', allows determining orientation averaged coupling parameters α, β and δ,

$$m' = (\alpha E_{ac} + \beta E_{ac} H_{dc} + \gamma E_{ac} E_{dc} + 2\delta E_{ac} E_{dc} H_{dc})(V/\mu_o) \quad (3)$$

The linear *ME* effect is usually very small. *E. g.*, the peak value of the primordial *ME* material Cr_2O_3, $\alpha_{zz}(T \approx 260\ \text{K}) \approx 4$ ps/m [7], denotes an average spin-flip rate of merely $\approx 5 \times 10^{-7}$ spins/(kV/cm) [9]. Much larger effects are expected in the vicinity of the ferroic phase transitions, where suitable components of the χ^e and χ^m tensors diverge and $(\alpha_{ij})^2$ ($\leq \chi^e_{ii}\chi^m_{jj}c^{-2}$ [12]) maximizes. Unfortunately no really existing material even roughly fulfills the condition of two simultaneous ferroic transition.

Recently we have proposed a 'second-best' choice for achieving 'giant' *ME* response, namely the fluctuation regime (large χ^e_{ii}) of a quantum paraelectric material coming close to a *FM* instability (large χ^m_{jj}). This applies to $EuTiO_3$, which is a *G*-type *AF* below $T_N = 5.4$ K, where $\chi^e_{ii} \approx 400$ and $\chi^m_{jj} \approx 100$ due to strong *FM* next-nearest neighbor interaction [13]. *Fig.* 2 shows the *ME* moment m' of a polycrystalline sample of $EuTiO_3$ excited at $T = 4.5$ K with $E_{ac} = 8$ kV/m under '*ME* annealing' [9] in constant $E_{dc} = 80$ kV/m and descending $\mu_0 H_{dc} \leq 1.5$ T. As $\mu_0 H_{dc} \rightarrow 0$, linear behavior with negative slope, $\delta_{eff} = -2.1\times10^{-21}$ sm/VA, indicates a large third-order δ-effect, which is $\approx 200\times$ larger than that of the first explored example of 3rd order *ME* coupling, $Sr_{0.98}Mn_{0.02}TiO_3$ [6] (see below). Closer inspection shows [14] that δ_{eff} contains a contributions due to a second-order β-effect, which becomes allowed due to the formation of net electric polarization upon *ME* annealing.

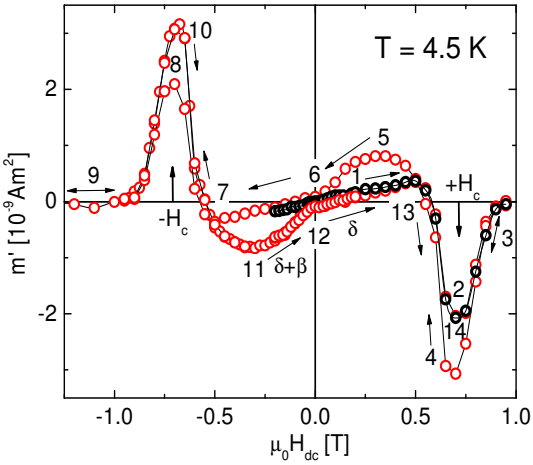

Fig. 2: *ME* response of polycrystalline $EuTiO_3$ at $T = 4.5$ K under external fields E_{ac}, E_{dc}, and $\mu_0 H_{dc}$ (on decreasing from 1.5 T) as indicated. The initial and final slopes, δ and $\delta+\beta$, respectively, and the critical field $\pm\mu_0 H_c$ of the AF-to-PM phase transitions are marked [14]

Most surprisingly, however, the initial *ME* response suddenly changes sign at 0.6 T and develops a sharp peak with 'giant' $m' \approx 3\times10^{-9}$ Am^2 at $\mu_0 H_c = 0.68$ T. At this critical field the system undergoes a phase transition from an *AF* spin-flop to a (saturated) paramagnetic phase. The *ME* response is taking advantage of the critical fluctuations of the (*AF* ordered) transverse magnetization components, $\pm S_x$, and thus fulfills the prediction [12] in an impressive way. Very probably the peak is due to electric field-induced Dzyaloshinskii-Moriya exchange interaction, which gives rise to near-divergent non-diagonal 3rd order *ME* response as $\pm S_x \rightarrow 0$ [14].

3 Multiferroics

Multiferroics (*MF*s) are classified either *single or multiphase*, if the order parameters involved occur in one single compound or in different components of a composite material [15]. Since recently [16] one further distinguishes *type-I* and *type-II single phase MF*s. *Type-I MF*s like $Fe_3B_7O_{13}Cl$, $BiMnO_3$, $BiFeO_3$, $Fe_{2-x}Ga_xO_3$, $LuFe_2O_4$, Fe_3O_4 *etc.* have independent origins of the spontaneous order parameters, $\boldsymbol{P}_s$ and $\boldsymbol{M}_s$ (or AF $\boldsymbol{L}_s$). Contrastingly, in *type-II MF*s like $LiCu_2O_2$, $CuFeO_2$, $Ni_3V_2O_8$, $TbMnO_3$, $HoMnO_3$, $MnWO_4$, $CoCr_2O_4$, Ca_3CoMnO_6, $Y_2Cu_2O_5$ *etc.* the ferroelectricity is primordially due to the magnetism.

Quite often *type-I MF*s reveal high ordering temperatures, but their theory – including the *ME* coupling – can be very complex. Probably the most popular *type-I* single phase *MF* is $BiFeO_3$ with record high ordering temperatures, *AF* T_N = 643K and *FE* T_c = 1103 K. Despite its large variety of different *FE*-ferroelastic and *AF* domains it has ever since been considered a hot favorite for applications in sensorics or spintronics [17, 18].

On the other hand, the theory of *type-II MFs* is symmetry based and straightforward, albeit often quite sophisticated. In most cases the ordering temperatures are very low and the order parameter amplitudes ridiculously small (from an application point of view). *E. g.*, in the orthorhombic perovskite system $TbMnO_3$ it was found that spiral spin ordering due to Dzyaloshinskii-Moriya exchange interaction breaks both $\boldsymbol{T}$ and $\boldsymbol{I}$, and net polarization $\boldsymbol{P} = \boldsymbol{\gamma}(\boldsymbol{r}_j - \boldsymbol{r}_{j+1}) \times (\boldsymbol{S}_j \times \boldsymbol{S}_{j+1})$ becomes induced as depicted in *Fig.* 3 [19]. Also the sinusoidal modulation of the uniaxial *E*-type spin structure in orthorhombic $HoMnO_3$ [20] was shown to produce a sizable improper ferroelectric polarization. Characteristically for *type-II MFs*, it is due to an electronic mechanism apart from the lattice one [21]. Further, in the Ising chain magnetCa_3CoMnO_6 [22] alternating Co^{2+}/Mn^{4+} ionic order creates competing *nearest neighbor FM* and *next-nearest neighbor AF* exchange interactions**.** As a consequence, up-up-down-down ('ANNNI-type') spin ordering arises below $T_N \approx 16$ K. It is accompanied by asymmetric exchange striction, which breaks $\boldsymbol{I}$ and, hence, induces electric polarization below T_N [23].

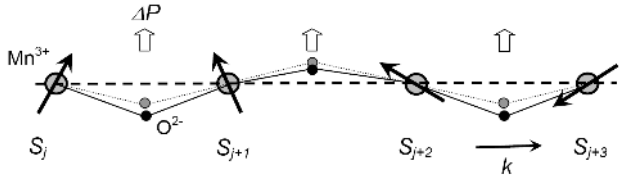

Fig. 3. Counterclockwise spin spiral of $TbMnO_3$ promoting an upward directed electric polarization by forced oxygen displacements [19].

Composite MFs are usuallly based on stress-strain coupling between the order parameters of *FE*-piezoelectric and *FM*-magnetostrictive components like $BaTiO_3$ and $CoFe_2O_4$, respectively [24]. This pioneering self-assembled ceramic material became famous for its large *ME* response, $\alpha_{ME}(BaTiO_3/CoFe_2O_4) = dE/dH = 130$ mV/cm·Oe, which exceeds that of Cr_2O_3 [7] and even that of the record holding single phase *type-I MF* material $TbPO_4$ [25] by factors of about 180 and 20, respectively.

Meanwhile even higher conversion rates are available, and *ME* composites are now considered for applications in transducer, filter and sensor devices [26]. Record high *ME* response can be achieved by taking advantage of resonance effects. One possible design is shown in *Fig.* 4, where amorphous *FM* METGLAS (= FeBSiC) layers are excited by a longitudinal magnetic *ac* field and laterally coupled to a periodically poled *FE* PZT [= $Pb(Zr,Ti)O_3$] piezofiber layer. The conversion factor $\alpha_{ME} = 0.8$ kV/cm·Oe at the resonance frequency $f \approx 2$ kHz [27] exceeds that of archetypical Cr_2O_3 by six orders of magnitude.

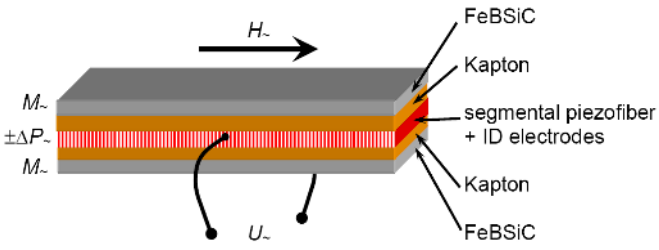

Fig. 4. Schematic *ME* composite consisting of two magnetostrictive FeBSiC layers and a piezoelectric periodically poled PZT piezofiber layer intercalated by Kapton films [27].

4 Multiglasses

The nature of glassy states in disordered materials has long been controversially discussed. In the magnetic community generic *spin glasses* [28] are meanwhile accepted to undergo phase transitions at a static freezing temperature T_g (= glass temperature), where they exhibit criticality and originate well-defined order parameters. Widely accepted, albeit still under debate [29], also polar systems may undergo transitions into generic 'dipolar *or* orientational glass' states [30], which fulfill similar criteria as spin glasses. Hence, it appears quite natural to introduce the term 'multiglass' for a new kind of *MF* material revealing both polar and spin glass properties as discovered in ceramic solid solutions of $Sr_{0.98}Mn_{0.02}TiO_3$ [6]. On one hand, the Mn^{2+} ions being randomly distributed and off-centered from their Sr^{2+}-sites [31] form nanopolar clusters with frustrated dipolar interaction and give rise to a dipolar glass state below $T_g^e \approx 38$ K. On the other hand, frustrated and random Mn^{2+}-O^{2-}-Mn^{2+} superexchange is at the origin of spin glass formation below $T_g^m \approx 34$ K. It should be noticed that both glassy states have unanimously been confirmed by clear-cut aging and rejuvenation effects in their respective *dc* susceptibilities [6]. Observation of biquadratic (δ-type) *ME* interaction - see. *Eq.* (1) - is fully compatible with the low symmetry of the compound and supposed to crucially reinforce the spin glass 'ordering' as schematically depicted in *Fig.* 5 [32].

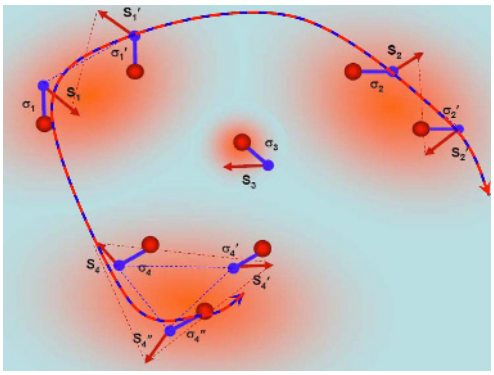

Fig. 5. Multiglass formation in $SrTiO_3$ doped with Mn^{2+} impurities based on *FE* polar clusters (pseudospins $\sigma_j, \sigma_j', \sigma_j''$) and superantiferromagnetic spin clusters (S_j, S_j', S_j'') [32]

In the MF perovskite $PbFe_{0.5}Nb_{0.5}O_3$ (PFN), with Fe^{3+} and Nb^{5+} ions randomly distributed at B sites, two different orderings are about to establish - a soft-mode driven FE one as in $PbTiO_3$, and a super-exchange driven AF one in the percolating Fe^{3+} subspace [33]. Owing to the inherent disorder, however, unconventional phases emerge. The polar phase refers to a so-called relaxor ferroelectric below $T_c^e \approx 385$ K. It results from quenched random electric fields due to the cationic charge disorder

and decays into a polar domain state as known from the related prototype compound $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) [34].

Even more unusual is the coexistence of two magnetic phases both of which fulfill the requirements of the thermodynamic limit. 'Infinitely' large numbers of finite-sized Fe^{3+} clusters without mutual overlap make up a spin cluster glass (CG) coexisting with an AF phase of exchange coupled Fe^{3+} ions. The phase coexistence is compatible with percolation theory. While the AF phase transition at $T_N \approx 153$ K is permitted on the bond-percolated infinite cluster of super-exchange coupled Fe^{3+} spins, the CG transition at $T_g \approx 10$ K (Fig. 6, inset) is restricted to the complementary space accommodating isolated and small clusters of Fe^{3+} ions, where dipolar and super-exchange interaction via oxygen and lead ions warrant glassy bond coherence. On cooling toward the glass transition a finite number of large, but non-percolating spin clusters is undergoing superantiferromagnetic (SAF) blocking as experienced by extra susceptibility response in both magnetization and second-order ME response (E_{ac}= 12.5 kV/m and $\mu_0 H_{dc}$ = 0.2 T; β-effect according to Eq. 3) shown in Fig. 6.

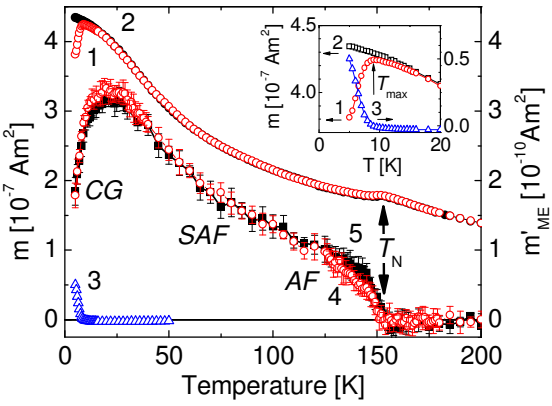

Fig. 6. Magnetic moment m vs. T of PFN (001) obtained on ZFC/FH (curve 1), on FC (2) with $\mu_0 H$ = 0.1T, and on ZFH as TRM (3) (inset: low-T data magnified) (lefthand ordinate). ME moment m'_{ME} vs. T obtained with E_{ac}= 12.5 kV/m on ZFC/FH in $\mu_0 H_{dc}$ = 0.2 T and E_{dc}= 0 (4, open circles) or 50 kV/m (5, solid squares) (righthand ordinate). T_N and dominance of 'phases' AF, SAF and CG (see text) are indicated [33].

5 Applications

Applications have entered the MF agenda from the beginning [5]. To begin with, ME composites are meanwhile established as magnetic field and current sensors, transformers, gyrators, tunable microwave devices, resonators, filters, phase shifters, delay lines etc. [26].

Single phase magnetoelectrics promise to realize low-power electric control of magnetic order [4], while the magnetic control of electric order is much less attractive because of its high energy consumption. As an example, the ME Random Access Memory (MERAM) [35] is based on the electric control of the exchange bias exerted by a ME antiferromagnet like Cr_2O_3 onto an attached FM (multi)layer like $(Pt/Co)_n$, $n \geq 1$ as sketched schematically in Fig. 7.

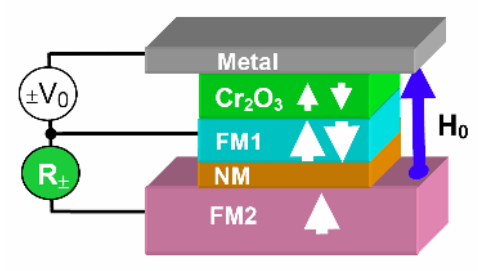

Fig. 7. Schematic view of a MERAM cell based on ME Cr_2O_3(0001) controlling the magnetization of the Pt/Co/Pt trilayer FM1 via voltages $\pm V_0$ and constant magnetic stray field H_0 of a NdFeB thick film FM2. $R_\pm$ is the corresponding giant (or tunneling) magnetoresistance along the trilayer FM1/NM[non-magnetic Cu or MgO]/FM2 [34].

Single phase multiferroics open possibilities of double action involving two order parameters. E. g., in the 4-bit memory of Gajek et al. [36] a thin film of the MF ferro-electromagnet $La_{0.1}Bi_{0.9}MnO_3$ is proposed to serve as a tunnelling layer in a magnetoresistance element showing four different tunnel magneto- and electro resistances (TMR and TER, respectively) when setting the various magnetic and electric states, $\pm\mathbf{M}$ and $\pm\mathbf{P}$. Interestingly, in this case vanishing linear ME coupling between the two order parameters is explicitly welcome. The need of low-temperatures has hitherto impeded any application of this smart idea.

6 Conclusion

Presently still the only room temperature type–I MF material $BiFeO_3$ appears trailblazing for future spintronics applications, while the type-II multiferroics are more challenging from a fundamental point of view because of their fascinating interplay between the different orders. New challenges for theory are brought by ME multiglasses and nonlinear ME effects, which are not as small as hitherto presumed. Among the existing device ideas probably the most promising belong to the field of spintronics such as low current MERAM [35] and MF 2x2 logic cells [36], where the pioneering material chromia, Cr_2O_3, is a promising candidate toward novel applications [35,37].

Acknowledgments

Thanks are due to S. Bedanta (U Bhubaneswar), P. Borisov (U Liverpool), V. V. Shvartsman (U Duisburg-Essen) for their most valuable collaboration within the past few years. Financial support by DFG (SFB 491, KL306/38) and EU (STREP MULTICERAL) is gratefully acknowledged.

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