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Multiferroic materials and heterostructures / Matériaux et hétérostructures multiferroïques

Preamble

Préambule

What does the word "multiferroic" mean? When coining the term in 1994, this was done without ulterior motives, simply by enjoying the beauty of symmetries, permitting the cohabitation of two or all three primary ferroic properties, *ferroelectric, ferromagnetic, and ferroelastic in the same phase*, all forming domains and hysteresis loops, heralding intricate coupling properties. In this definition, the very cradle of "multiferroics" lies in Kêitsiro Aizu's colossal work of 1970, in which he gave all the 773 high-temperature (prototypic) phase/low-temperature (ferroic) phase point group pairs ("species") occurring due to phase transitions, with indication of the number of domain states, comprising *all possible single-phase multiferroic combinations, including implicitly also antiferromagnetic and co-elastic ferroic phases*. The original meaning of the word "multiferroic" has undergone a tacit, more realistic mutation. In its current usage, it designates all kinds of magnetic ferroelectrics, including hetero-phase systems, but with a mainstream trend in electric-field control of ferromagnetism and in all sorts of magnetoelectric interactions.

When working at the Battelle Geneva Research Center, the fascination of the author and of his colleagues Ascher and Janner in magnetic ferroelectrics was kindled in 1958 by G. Smolenskii's talk at a conference in Grenoble, when he announced his work with Ioffe on the synthesis of the first antiferromagnetic ferroelectric perovskite ceramics. Herewith the dream of finding also ferromagnetic ferroelectrics became ubiquitous. On the theoretical side, Dzyaloshinskii's prediction (1959) of the linear magnetoelectric effect in Cr_2O_3 and its measurement by Astrov (converse effect, 1960) and Rado et al. (direct effect, 1961) were most exciting. The renowned Russian crystallography school provided essential symmetry knowledge: e.g., already in 1962 Shuvalov and Belov indicated the 13 magnetic point groups permitting both ferroelectricity and ferromagnetism in a same phase. A strong wave of new science was launched worldwide and a host of applications was proposed for the elegant linear magnetoelectric effect. However, due to its smallness, none of them has been realized up to the present time, nor has a single room-temperature ferroelectric ferromagnet been found.

Hence why such a joyful renaissance of search for magnetic ferroelectrics and associated magnetoelectricity in this century? To my mind, one of the nuclei was Nicola Hill/Spaldin's pertinent question-article in 2000: "Why are there so few magnetic ferroelectrics?" and enthusiastic theory-based follow-up articles with co-workers that served as seeds. But seeds need to fall on fertile soil for yielding seedlings. This fertile soil, the actual scientific background and a powerful modern instrumental arsenal, was in fact ready for action at the beginning of this century, with a host of fully new as well as much improved classical research tools, which we could only dream of in the pioneer period of the 1950s to the 1970s, when often self-built and improvised equipment had to serve. For example, piezoelectric force microscopy and many other scanning probe microscopies, the various improved methods for depositing epitaxial thin and ultrathin films, circular polarized X-rays for detecting non-collinear magnetic order, SQUIDs, high-field superconducting magnets, etc., are great. Or when flicking through the multiferroic literature we may fall into the opinion that really everything is now calculable by first-principles methods. Is that so? Where are the limits? In any case, this tool has already brought enormous stimulation for attacking old problems and imagining new systems. In addition, new fields like spintronics, giant magnetoresistance, ferroelectric tunnel junctions, etc., have sprung up, calling insistently for marriage with energy sparing electric-field-manipulated ferromagnetic order. Having seen the modest beginning, the author is completely flabbergasted by the explosion of new fascinating basic science on the one hand, like the numerous type-II multiferroics with spin spiral generated ferroelectricity, e.g., the direct coupling between polarization and magnetization in $CoCr_2O_4$ (Coi et al. 2009), interphase physics like unidirectional stress effects, domain wall conductivity, etc., and, since Nature does not offer us the ideal all-purpose crystal, most creative attempts at constructing artificial systems of electric-field-controlled ferromagnetism, on the other hand.

Pierre Curie, who announced his famous conjecture in 1894 that materials might exist, which can be electrically polarized by a magnetic field and magnetized by an electric field, would be astonished today to hear that shortly after his conjecture nickel iodine boracite was synthesized in Paris for the first time (Allaire, 1898), the material on which we had the chance of switching for the first time ferromagnetic domains by means of an electric field and ferroelectric domains

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by means of a magnetic field below 60 K (Ascher et al. 1966). But the great joy was dimmed since the electric field did not control the magnetization's sign. Only by applying the stratagem of a magnetic field bias, the desired coupling was achieved. This problem is common to all classical magnetic ferroelectrics (now called type-I multiferroics), lacking direct coupling between polarization and magnetization, providing often mechanical-type *ferroelastic coupling*, but which is not time-reversal-sensitive. This holds also for $BiFeO_3$, in which spontaneous polarization and antiferromagnetic order are coupled via ferroelasticity. Here stratagems are particularly demanding, since a magnetization has to be "grafted" in some way on the antiferromagnetic spin structure, e.g., via exchange bias.

Having much worked with ferroelastic (low-temperature ferromagnetic) ferroelectrics, the author is reminded by the present enthusiasm for multiferroics of another one which was triggered by the "all-optical computer" idea of Rajchman in 1970. Here one of the desirable components was an electrically addressable/optically readout memory. Thus *ferroelastic ferroelectrics* came into play since ferroelastic reorientation equals reorientation of the optical indicatrix, exploitable for contrast formation in polarized light. Initially many workers worldwide ignored entirely strong ferroelastic and electrostrictive deformations, leading to fatigue. Much time and money were wasted. Holographic storage in ferroelectrics, using the photorefractive effect, was also studied in parallel. But suddenly the death-blow for the "all-optical computer" dream was hit by the theoreticians' judgment: "holograms—even three-dimensional ones—do not allow stocking sufficient information per volume!" Astonishingly, both examples show that for emotional and bona fide reasons, crucial questions are often asked too late. Certain issues of the "multiferroic explosion" are probably also not immune against such profoundly human character and will demand utmost scrutiny. This brings the writer to, e.g., the multiferroic favorite $BiFeO_3$. Given its large ferroelastic tilt angle, can we achieve indefinite fatigue-free switching of thin films, free of back-switching and mechanical cross-talk? Probably yes, but how? Many papers seem to avoid intentionally or unintentionally scrutinizing this issue.

Incapable of embracing the entire realm of multiferroics, let us remain with $BiFeO_3$, for which further basic topics are waiting for study. Whereas several microscopies allow looking at the "trees of the forest", we should not forget looking also at the "forest as a whole" of single crystals by classical transmission polarized light microscopy. Here $BiFeO_3$ is unique because of its extremely strong birefringence (Rivera & Schmid 1997), permitting the study of ferroelectric/ferroelastic domains in transmission on thin wafers (down to 8 μm and below). Considering the known high magnetic contribution to birefringence on $(100)_{pc}$ cuts, the optical observability of antiferromagnetic/ferroelastic domains on $(111)_{pc}$-cuts($\perp P_s$), of symmetry lower than rhombohedral, remains a possible issue. The tensorial study of the magnetoelectric *EBB*-effect *vs.* temperature on antiferromagnetic single domains represents another challenge. More generally, the writer has a partiality for all "clean", i.e., mechanics-free magnetoelectric effects, the linear and the quadratic ones. For example, studies of the *EEB*-effect, allowed for the 66 piezomagnetic point groups, are entirely neglected. In this context also, an attempt at representing the rather ill-defined "magnetocapacitance" as a higher-order magnetoelectric tensor may be rewarding.

The near-future will necessitate scrutinizing multiferroic development projects for multiferroic devices. The writer sees this future optimistically, comforted by the story of liquid crystals, for which in the 1970s people considered their future in display very despicably. And look, all serious initial problems of liquid crystal display have rapidly been overcome by fascinating human creativity. In the same optimistic spirit, the author is wishing continuing fascination in multiferroic science, paired with creativity for applications.

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