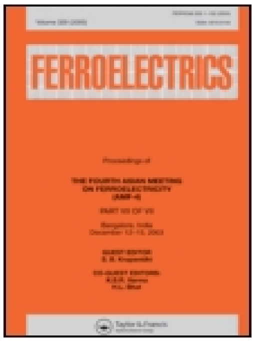

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CRYSTAL PHYSICS OF FERROICS AT ITS BEST: A TRIBUTE TO PROFESSOR HANS SCHMID

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The proceedings of MEIPIC-3 is surely the appropriate forum to pay tribute to Professor Hans Schmid of the University of Geneva, on the occasion of his 65th birthday; in a sense a tribute of a child to the father since it was he who established this series of conferences and since its topic is surely not showing any marks of aging.

Hans Schmid entered the literature in the late fifties, with papers in the field of structural chemistry and crystallography. Later, at the Battelle Institute in Geneva, he became involved in a research project with the aim to investigate structures with anisotropic oxyfluoride octahedra. Proposed by Aloysio Janner and Edgar Ascher, it was to some extent stimulated by the presentation of Georgii Anatolevich Smolenskii from Leningrad at the conference on magnetism held in Grenoble, 1958. In 1966, after mastering the synthesis of boracite single crystals, Hans Schmid excelled with probably his first paper in the field of ferroelectricity[1,2] in which the evidence of ferroelectricity in boracites is given. And the real bombshell exploded soon afterwards. After numerous attempts to verify the possibility of the coexistence of ferroelectric and ferromagnetic ordering, which had been made unsuccessfully in other laboratories, in 1964 comes the discovery of simultaneous and mutually conditioned ferroelectric and ferromagnetic ordering in the Ni-I boracite; it was first reported at the MMM conference in San Francisco, in November 1965, and published in the following year.[3] Here is what Hans had to say himself [4] about the occasion: "...The best candidate appeared to be the Ni-I boracite which exhibited promising anomalies of magnetic susceptibility at about 60 K. When ferromagnetism was established below 60 K, and after several detours, one February night came in 1964 when, at half past two in the morning, in a thin plate of single crystalline Ni-I boracite domains moved both in an electric as well as in a magnetic field; spontaneous Faraday effect was used to monitor the changes. My technician Harry Rieder was present as well and he had patience and enthusiasm to stay till the last drop of helium evaporated. We went home in a strong snow storm but in a state of euphoric excitement...". This discovery can be classified as one of the most significant ones in the field of structural phase transitions. Its importance has been fully appreciated in basic science and, hopefully, may be soon fully appreciated in technology, in connection with the development of basically new devices.

With his already immense knowledge and unmatched activity, Hans Schmid was fully prepared not only to make this sensational finding but also to continue to establish new exciting features of numerous crystals of the boracite-type. In addition to magnetically reorientable spontaneous polarization and electrically reorientable spontaneous magnetization, boracites possess a number of other exciting symmetry and crystallographic properties such as the nonexistence of antiparallel domains and many others; these helped Hans Schmid to get immersed deeply into the crystallographic and symmetry-conditioned properties of ordered single crystals. He proposed several extremely useful classifications and surveys of materials and phenomena; those of magnetoelectric materials[5] and of multiferroic magnetoelectrics[6] can serve as examples. He soon became probably the best ever specialist in the field of polarized light microscopy of twinned crystals. His flawless and complete classification of possibilities to observe ferroelectric and ferroelastic domains in both transmitted and reflected light is a classical paper[7] which leaves hardly anything to add. Studying domains and their motion in applied mechanical, electrical and magnetic fields became a standard but top-level technique in Schmid's laboratory. Together with his coworker J.-P. Rivera they constructed an optical setup which can be used with enviable precision and under extreme conditions. Still, for Hans it is the human eye that plays here the most important role. "...Simplex sigillum veri... all the interesting things we have found, were discovered in a most primitive way, although by means of the most sophisticated pattern recognition machine imaginable, not available on the market, I mean with our eyes, aided by the ordinary light or polarized light microscope. These ... instruments have astonishingly been forgotten by many chemists and physicists since the advent of X-rays, lasers and computers. My predilection for microscopes started ... at the Technical University in Graz by studying bacteria in a biochemistry course and at Batelle, in collaboration with my beloved, too early departed mountain companion Roland Funk, with whom we conceived a patent for electronic watch displays, based on the ferroelectric/ferroelastic 90-degree switching of domains in $BaTiO_3$... Astonishingly, this worked at 1 – 5 volts, just right for wristwatch batteries. For the US version of the patent we had to go to the US Embassy in Bern and swear on the US flag to prove that we were genuine inventors. What a fun! This was a long time ... before liquid crystals became fashionable ...".[8]

Indeed, domain phenomena have accompanied Schmids activities during all his scientific career till today and revealed an immense number of important facts about fundamental material properties, symmetries, phase transitions. The quoted remark on watch displays shows his interest in the practical applications of observed phenomena; but again, typically for Hans Schmid with his passion for order, an extremely useful classification of possible optical contrasts based on domain switching resulted from these considerations.[9]

Looking at Schmid's impressive list of publications, we realize how many essentially different materials he attacked in his investigations. Boracites seem to represent a golden thread of his interests and their continued and systematic studies made them one of the best investigated families of ferroics. But he also synthesizes and investigates a large number of other crystals, always looking for phase transformations and often for magneto-electric properties. Combining reliable data on optical properties, dielectric and magnetic susceptibilities, magnetoelectric interactions, pyroelectric and piezoelectric properties and domain behaviour, together with X-ray analysis and not forgetting the chemical aspects in which Schmid is so well trained, made it possible for his group to elucidate the nature of phase transformations in a number of compounds. Perhaps as an example we may mention the final dot after the long discussion whether $BiFeO_3$ is ferroelectric [10]. Was that easy? Perhaps, but only for those who know how... "After almost twenty years' dispute whether $BiFeO_3$ was ferro-eloectric or antiferroelectric, we have settled that problem in favour of ferroelectricity after a few minutes of etching attack and the observation under the microscope".[8] And similar accummulation of experimental skills led to the discovery, together with Marcos Luján, of "high coercive field ferroelectricity" in the weakly ferromagnetic $KNiPO_4$ or to the final proof, together with Nava Setter, of ferroelectricity in Sr-Cr-sodalite. He recognized the uniqueness of the properties of relaxor ferroelectrics and after mastering their chemical and growth aspects he finally, together with his talented coworker Ye, became involved in the investigations of their domain structures and field-induced transitions which condition their special behaviour.[11] He did react very fast to the discovery of high-Tc superconductors. The immense experience of his group was utilized and, after establishing that YBCO is probably the first superconductor known to be transparent,[12] come several pioneering studies of ferroelastic domain structures in YBCO single crystals,[12] including the discovery of pseudo-symmetry domains made of high densities of ferroelastic domain walls.[13] Beautiful color photographs of twins in these crystals are a crystallographer's delight.

The very active research group founded by Schmid in the Department of Inorganic, Analytical and Applied Chemistry of the University of Geneva, attracted the attention of many distinguished scientists from abroad who considered it their privilege to have the chance to work there for some time. The laboratory is purposefully equipped and seems now to offer the world's most advanced optical microscopy, allowing most precise crystallographic studies under the influence of electric, magnetic and mechanical stress fields, in a wide range of temperatures.

Those who have had the chance to cooperate with Hans Schmid admire his talent to formulate precise questions and design ways to solving them and his internally built sense for systematic classification. He is one of those scholars who leave behind exactly formulated statements, in many cases in the form of tables to which little can be added.

His devotion to work did not prevent him from maintaining an exceptionally warm attention to his coworkers and friends, from having a deep understanding for their human needs and being ready to offer a helping hand in times of crisis. When you talk to him, you will appreciate his warm recollections of his teachers ("...I was lucky enough having had the chance to encounter as a student G. F. Hüttig in Graz, former professor of chemistry in Prague, who taught me the feeling of chemistry and in whose laboratory I fell for the first time in love with the mysteries of magnetism" [8]), as well as his feeling of gratitude to his coworkers ("...I owe so much to Jean-Pierre Rivera, who dedicated 18 years of his life to building up a fine measuring laboratory of magnetoelectricity and crystal optics" [8]). But you will also have fun in listening to Han's recollections of some of the critical moments as the time brought them. "...George Taylor, at that time with RCA at Princeton, played a major role ... After attending a conference on applications of ferroelectrics at IBM - Yorktown Heights, he showed me in his lab prototypes of light gates, skillfully prepared with $Bi_4Ti_3O_{12}$ crystals, hardly believable, considering the 'lousy' monoclinic symmetry and unfavourable plate-like crystal form ... I was so impressed that immediately I wrote a research proposal for Fe-I boracite during my flight back to Geneva, forgetting about our 'lousy' crystals, but advocating the marvelous contrast-efficient 90-degree switching of the optical indicatrix, much superior to $Bi_4Ti_3O_{12}$. I never obtained a contract so rapidly. This time Thomson-CSF at Orsay was enthusiastic and signed, because they also were 'infected' by the worldwide 'all-optical-computer' ideas of Rajchman at RCA, hunting among other things for 'optical page composers'. This project and the follow-up project with the Délégation á l'Informatique on the 'Point mémoire' helped our small group and our families to survive for some years".[8]

MEIPIC-3 at which we can so appropriately express our tribute to Professor Schmid may have been organized at a time when he had to make serious changes in the organization of his scientific life but we who know him well are convinced that he will take many more scientific avenues and be successful in reaching their solutions. All best wishes!

It is a remarkable coincidence that the author of these lines gives, as the location of his main involvement, the place in Central Europe which Hans Schmid as a teenager had to leave in the year 1945, the year which marked the end of that distorted historical period. May this coincidence signal for us all understanding and peace, also in our minds.

Again, all the best for the coming years, Hans.

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