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Robert Collongues

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To cite this version:

Bernadette Bensaude-Vincent, Pierre Teissier. Robert Collongues. 2008. halshs-01070278

HAL Id: halshs-01070278
https://shs.hal.science/halshs-01070278v1

Submitted on 1 Oct 2014

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Collongues, Robert (*b.* Toulouse, France, 1 January 1924; *d.* Villejuif, France, 10 May 1998), *solid-state chemistry, materials science, high temperature devices, metal oxides crystal-growth.*

B. Bensaude-Vincent, P. Teissier, "Robert Collongues" in Noretta Koertge, ed., *New Dictionary of Scientific Biography* (Detroit: Charles Scribner's Sons/Thomson Gale, 2008), Vol. 2, p. 159-64.

Collongues, the heir to a long research tradition dating back to Henry Le Chatelier in the early twentieth century, contributed to the emergence of solid-state chemistry in France. Around 1950, Collongues's early works on crystal-structure defects in iron oxides led him to reappraise the concept of non-stoichiometry and to focus on order-disorder phenomena. Then he promoted the crystal-growth of metal oxides by developing high temperature devices during the 1960s. He became a world leader in refractory materials and single crystal-growth in the 1960s, moved into solid-state ionics during the 1970s, and shifted to optical materials after 1980. His most notable contribution was the founding of a major French research school that promoted solid-state chemistry at the national and international levels.

Childhood and Education.

Robert is the only son of Marie-Louise Trouvé (1898-1979) and Gaston Collongues (1895-1986). During First World War, Gaston was enrolled as a soldier and wounded in 1916. He received a medal (*Légion d'honneur*) in 1961. Marie-Louise worked as an employee of the administration (*préfecture*) of the department of *Haute-Garonne* in Toulouse. Robert was a brilliant student interested both in sciences and literature. At the secondary school Pierre de Fermat in Toulouse he received two *baccalauréats* (GCE A-levels) in 1941: letters and mathematics. After a three-year preparation for the competitive exams of engineering schools, he joined the *École supérieure des industries chimiques de Nancy* (Chemical engineering school in Nancy, France). There he enjoyed laboratory practices in experimental and discovered metallurgy thanks to an engineer internship in a steelworks. In June 1947 he got his chemical engineer degree, on 5 September he married Nelly Sarazin (1921-2001), a student in Nancy, who became a mathematics teacher. They would have three children: Alain (1949), Catherine (1952) and François (1957). Soon after in 1947, Collongues became a PhD student in the laboratory of Professor Georges Chaudron in Paris.

Chaudron and the LCTC.

After World War II, Chaudron was a major figure in the French chemical community, both as a university professor and an industrial adviser. Chaudron had been trained in metallurgy and inorganic chemistry in Le Chatelier's laboratory from 1913 to 1921. In 1939 he became head of the *Laboratoire central des traitements chimiques* (LCTC, Central laboratory for chemical treatments), which had been founded two years before by Georges Urbain in Vitry-sur-Seine, a southern suburb of Paris. Between 1950 and 1962 Chaudron was the director of the most famous French chemical engineering school, the *École nationale supérieure de chimie de Paris* (ENSCP; National superior school of chemistry at Paris), which allowed him to recruit students. From 1951 on, he also worked as a techno-scientific adviser for the *Commissariat à l'énergie atomique* (CEA, Atomic Energy Commission) at Saclay. In 1954 he was elected to the French *Académie des sciences* in the chemistry section and became president of the *Académie* for the year 1971–1972.

In 1947, when Collongues joined Chaudron's laboratory, the LCTC was dedicated to the synthesis and study of metals, metallic alloys, and inorganic solid compounds, especially metal oxides. One major feature of this research center was the hybridization of solid-state physics and physical chemistry methods used to study crystal structures—particularly X-ray diffraction—with metallurgical methods used to characterize inorganic compounds, particularly thermal analysis and magnetism measurements. Chaudron helped to popularize among chemists the notion of "solid solution" commonly used by metallurgists. He thus promoted an interdisciplinary style of research without claiming that he was founding a new discipline.

A second feature of Chaudron's laboratory was its connections with industrial companies. In a period when French scientific research was mostly supported by a state agency created in the 1930s, the *Centre national de la recherche scientifique* (CNRS, National Center for Scientific Research), which encouraged fundamental research, Chaudron was eager to solve technical issues encountered in steel industries, aeronautics, mechanics, and refractory materials companies. In return he received money from these companies, although the LCTC was also the recipient of generous state funding from the CNRS.

Finally, as one of the leaders of the French metallurgy community, Chaudron had international relations with European metallurgists and solid-state physicists. He met many times with Nevill Mott from the University of Bristol in England. He was in touch with the solid-state reactions community, especially the Swedish school of thought headed by Johan

Hedvall. Through inorganic chemistry, he was also connected with European chemists and organized a famous international CNRS conference in Paris during 1948 on chemical "reactions in solid state". Thus, Chaudron's laboratory was one of the rare places in France that intimately combined academic and applied researches and was open to foreign influences.

Early Career.

Collongues was assigned a rather fundamental subject for his PhD, dealing with defects in iron monoxide. This research lasted for seven years, the usual lapse of time for a PhD project in France at that time. In 1954 he defended his thesis, titled "*Contribution à l'étude des propriétés et des modes de décomposition de la phase protoxyde de fer*" (Contribution to the Study of Properties and the Decomposing Ways of the Iron Monoxide Phase). Iron monoxide was known to be a non-stoichiometric compound: instead of following the FeO stoichiometry, its general formula was $Fe_{1-x}O$, with $0<x<0.1$. Below 570°C, the protoxide is decomposed and gives metallic iron and magnetite:

$$\mathbf{4\ FeO \rightarrow Fe + Fe_3O_4} \qquad \textbf{(I)}$$

Collongues's aims were threefold: (1) understanding the mechanisms of (I) by analysis of the kinetics of the reaction; (2) drawing a parallel between the iron monoxide and the steel phase diagrams in order to extend the definition of "solid solution" from intermetallic to ionic compounds; and (3) understanding the physical properties of the solid solution in terms of structure defects. Up to the 1960s, the metal oxides were usually prepared as solid polycrystalline powders, that is, ceramics made up of many grains randomly packed together. Each grain was a single crystal with a typical size of one micrometer or less. Using metallography (metallurgical optical reflection microscopy), Collongues observed the micrometric domains and growing surfaces, and with X-ray diffraction (the Debye-Scherrer powder method) he determined the atomic structure of polycrystals. Collongues was not the first one to study iron monoxide in LCTC. In 1939 Jacques Bénard had defended his PhD thesis, "*Etude de la décomposition du protoxyde de fer et de ses solutions solides*" (Study of the Decomposition of Iron Monoxide and its Solid Solutions). Bénard had used the same techniques to show that (I) occurred without structural changes and without matter transport (i.e., without diffusion). Collongues, however, went further: he tried to link the physical properties (density and electrical conductivity) to the chemical composition and experimental conditions (temperature, quantity of impurities). For this purpose, he used the notion of

“defects”—investigated by the American physicist Frederick Seitz, building on earlier work by the Russian investigator Yakov Frenkel and the Germans Wilhelm Jost, Carl Wagner, and Walter Schottky—and ventured a comparison between the defect crystal structure and a solid solution, which led him to describe the crystal as a dynamic (diffusion and reactions), non-ideal (non-stoichiometric), and disordered (order-disorder phenomena) structure.

Collongues’s PhD research was not really innovative in terms of methods and concepts. The techniques he used to draw phase diagrams and study crystal structures were taken from early twentieth century metallurgy and crystallography. In addition, his approach—based on notions such as defects and structure-dependent properties—followed the path opened by solid-state physics during the 1930s. And yet Collongues opened an avenue of research because he extended the techniques and methods traditionally used to study alloys or model crystals to the investigation of ionic compounds such as non-stoichiometric metal oxides. Thus, he and others—such as Ferdinand A. Kröger at Royal Philips Electronics, at Eindhoven in the Netherlands or John Goodenough at Lincoln Laboratory (MIT)—paved the way towards the science of new materials.

High-temperature Research.

Early in 1953, Chaudron’s laboratory was renamed *Centre d’étude de chimie métallurgique* (CECM; Center for the study of metallurgical chemistry), a name emphasizing the close connection between chemistry and metallurgy without, however, mentioning solid-state physics. In fact, two research programs were developed at the same time. On the metallurgy side, the aim was to obtain metals in their purest state; for instance, aluminium was purified by using the “zone melting” method developed by William Pfann at the Bell Laboratories in New Jersey for germanium in 1952. On the chemistry side, the investigative effort concerned solid-state metal oxides. The laboratory was divided into four different groups.

When Collongues completes his PhD in 1954 at the age of thirty and gets a permanent position at the CNRS, Chaudron created a fifth research group: the High Temperature Section. Devoted to the study of metal oxides, it was placed under Collongues’s supervision. His first two PhD students were women, and later on his group included several female researchers, which was quite unusual in those times. Jeanine Thery continued previous research on iron oxides and ferrites at still higher temperatures than before while Monique Perez y Jorba tackled a new material, zirconia (ZrO_2). With a melting point around 2,680°C, this zirconium oxide was extremely resistant to high temperature, but it went through a dramatic structural

transition around 1,050°C that made it useless for technological purposes. Nevertheless, the CEA, considering zirconia materials as potentially heat resistant, contracted Collongues to study them. Zirconium oxide was finally stabilized by the addition of rare or alkaline earth elements. Up to the 1990s, zirconium and its alloys were massively used to produce tubes in nuclear power plants. Thus, until 1973, Collongues's research group responded to the demand on high performance materials from atomic and military programs.

In the 1960s, Collongues himself considered designing refractory materials for spacecrafts. But in order to meet industrial demands for heat-resistant materials, he had to produce higher temperatures in controlled conditions. With the help of new PhD students, he designed a number of sophisticated furnaces: an "image furnace" in 1960; a high-frequency plasma furnace in 1961 (following the pioneer work of the American, Thomas B. Reed, in 1960); and a direct induction furnace during 1962–1964. These new devices were built and operated thanks to the recruitment of skillful collaborators by the CECM and to the financial support of industrial firms interested in the development of such furnaces. During the 1960s, the group thus built up an expertise in temperatures ranging from 2,000 to 20,000°C. Its reputation was reinforced by the creation of an international journal, the *Revue Internationale des Hautes Températures et des Réfractaires* (International review of high temperatures and refractory materials) edited by Collongues from 1963 to 1976 and dedicated to high temperatures production and refractory crystal compounds. However, the audience of the journal, written in French, was limited to the French-speaking European solid-state chemistry communities.

Crystal-growth.

From 1962 to 1973, Collongues developed a new expertise in single crystal-growth. Here again the innovative strategy was based on the transposition of traditional chemical metallurgy techniques to metal oxides. The group performed the synthesis of single crystals of metal oxides measuring a few centimeters, the first one being calcium oxide, synthesized in 1964 by using the flame fusion method (also called Verneuil's method) related to a plasma furnace. Whereas the physical measurements usually performed on powder crystals could only give average numbers in space, which hid the possible anisotropic properties, with centimeter-size single crystals the crystal was large enough to allow measurements on one single-oriented domain. Moreover, single crystals provided further information on atomic structures. Collongues's group was thus able to make more precise structure determinations

and to measure new anisotropic properties. Moreover, Collongues performed this kind of determinations in a systematic way on a wide variety of metal oxides (zirconium, aluminium, germanium, titanium, and lanthanides).

In 1966 Collongues's research group included 20 people (out of 111 people for the whole CECM). Although all members and Collongues himself still had to pay allegiance to the supreme reigning master, Chaudron, Collongues gained personal recognition. He became a professor at the *Université de Paris* (without a chair in 1964, and with a chair in 1967), was awarded several national science prizes in the 1960s, and in 1966 was elected a member of the National Comity of CNRS (e.g., the ruling body of CNRS) in the inorganic chemistry section. The same year he organized an international conference entitled "*Les mécanismes de la fusion et de solidification*" (Mechanisms of fusion and solidification).

Solid State Ionics.

In 1972 Collongues left the niche where he had "grown up" professionally to create his own laboratory, the *Laboratoire de chimie appliquée de l'état solide* (Laboratory of chemistry applied to the solid state), established within the ENSCP in Paris, where Bénard had succeeded Chaudron as a director. This institution, located in the *Quartier Latin* not far from the *Sorbonne* and other research centers, provided better opportunities for creating links and recruiting students. This strategic move was synchronized with a shift of research interests from refractory to electrical materials, prompted by one single and very promising material: beta-alumina. This ordinary ternary oxide was an inexpensive material largely available in the form $(Al_2O_3)_{11}(Na_2O)_x$, the structure of which had been determined by X-ray diffraction in the 1930s.

During the 1960s it was of interest only to a few crystallographers and ceramists because its good refractory properties qualified it for high temperature furnaces. In 1962, two members of Collongues's group, Jeanine Théry and Daniel Briançon, identified and described a new form of β-alumina, named β"-alumina. The discovery was hardly noticed until suddenly, in 1967, three scientists from the Ford Motor Company at Dearborn, Michigan, reinvented β-alumina. Their two first articles revealed that β-alumina's structural peculiarities led to a high ionic conductivity and that, consequently, β-alumina could be used to make sodium-sulfur batteries for electrical vehicles. This new technology was quite the opposite of the traditional liquid batteries since the electrodes (sodium and sulfur) had to be liquid whereas the electrolyte were solid. Furthermore, in order to liquefy sodium and sulfur and

reach high enough conductivity, the cell had to work at high temperatures (350-400°C). β-alumina and other compounds of its family first appeared to be ideal for solid-state electrolytes because they were high ionic conductivity refractory materials. Despite technological problems (reactivity of liquid sodium at 400°C, electrodes' leakage), solid-state batteries have some distinct advantages over traditional electrolyte: a longer life-time; an easier way of miniaturizing, for example in a thin-film form; a usefulness both in low-pover and high-energy forms; a combination of two functions: separating the electrodes and conducting the ions.

When the energy storage issue became crucial in the early 1970s during the oil crisis, β-alumina became a star material, intensely investigated by hundreds of chemists and physicists from both industry and academic laboratories from mainly the US and Europe. It even prompted the emergence of a new subdiscipline named solid-state ionics dealing with many new "superionic" conducting materials, as it provided a model-material for developing methods of investigation and understanding the physical laws of high ionic conductivity. In the US, Whittingham and Huggins (Stanford University), William Roth, Bruce Dunn (General Electrics) gave particularly striking contributions to the field. Since Collongues's group already had an expertise in β-alumina, big French companies like *Compagnie générale d'electricité* (later renamed Alcatel), *Renault* and *Electricité de France* contracted the group to study its ionic conductivity. New spectroscopic and crystallographic techniques had to be used to detect atomic movements. Therefore, Collongues started a fruitful partnership with solid-state physics and spectroscopy laboratories, the members of his group providing their know-how in the synthesis and the structural characterizations of β-alumina single crystals and the physicists performing more technical characterizations and dealing with physical theories. In the series of eight international conferences on fast ion transportation that took place from 1972 to 1992, Collongues and his group always had significant results to present.

However in the mid-1980s, without having reached an commercial application, the intense exploratory activity on β-alumina came to an end for several reasons: the concern of the companies and states for energy storage declined after the two oil crises, some technical problems still appeared insuperable for application, new high ionic conductors became more promising than β-alumina…. For a few years, Collongues's group went hunting other families of ionic solid conductors, such as the NASICON (Na superionic conductor) family, but it was a swan's song.

Optical Materials.

The group had to move on to a new research topic. An opportunity had opened up in 1979 when a team in the laboratory observed that a laser effect could be obtained with a family of compounds produced by inserting rare earths inside a β-alumina single crystal matrix. It was labeled LNA (Nd-doped lanthanum-hexaluminate) which chemical composition was: $LnMgAl_{11}O_{19}$ (Ln = La_{1-x}, Nd_x [La = Lanthanum; Nd = Neodymium]). The discovery of its potential laser effect resulted from the use of Electron Paramagnetic Resonance (EPR), a technique introduced in the laboratory in 1972 by a newcomer, Jacques Livage, on his return from a postdoctoral stay at Oxford University in England. For optical materials Collongues let the scientific leadership to others, especially Daniel Vivien, because he did not feel comfortable enough with the instrumentation (EPR) and related theories. Nevertheless he supervised the transition from ionic conductors to optical materials as a laboratory manager in charge of research strategies. He did not hesitate to raise funds from the French *Ministère de la défense* (Ministry of defense) as well as from medical companies, he bought new equipments and favored the shift toward quantum chemistry. In the last few years of his directorship, from 1988 to 1993, Collongues worked out a smooth transition in which he allowed more and more autonomy to Vivien, who scientifically was at the heart of the laser project and who became his successor at the head of the laboratory.

The French Research Style.

Collongues's career exemplifies the French way of doing materials research. In the 1960s there was a strong governmental incentive in the United States to create interdisciplinary laboratories investigating all kinds of materials from metals to ceramics to semiconductors and intimately combining science and engineering, but in France the shift from metallurgy to new materials was carried out by a few individuals working in CNRS laboratories under disciplinary labels such as chemistry. A new discipline named solid-state chemistry that embraced all inorganic solid compounds emerged out of the mainstream of inorganic chemistry at the intersection of metallurgy, ceramics, glass materials, and high temperature production. Interdisciplinarity and collaboration between physics and chemistry were the key words. However, most of Collongues's investigations did not require quantum mechanics (except for optical materials). In keeping with a long tradition of applied chemistry initiated by Le Chatelier, Collongues developed physical techniques to study materials structures, and he often used industrial opportunities to start new research programs. Over his long career, he

investigated a wide range of materials: single crystal-growth in the 1960s, solid-state ionics during the 1970s, and optical materials after 1980. Each research cycle reused a part of the expertise acquired during the previous one, while new techniques were introduced in the group by the newcomers.

Thus, Collongues exemplifies the strengths and weaknesses of the French research system. While the CNRS secured job positions and research funds, his group could also rely on industrial contracts but was not encouraged to patent. Researchers were not prone to mobility and tended to stay in the laboratory where they started their career. Thus through teaching and supervising from one generation to the other, they gradually formed a local research school. According to his former students, Collongues was an outstanding teacher, always including new research results in his courses and engaging in discussions with his students. In the laboratory, he was extremely demanding and very strict about clean and well-controlled syntheses, but open-minded enough to accept proposals from his collaborators even if he did not fully understand them. Among his seventy former PhD students, half went into industrial careers. A few of them stayed in the group, whereas others were encouraged to create new independent laboratories of solid-state chemistry: Jean-Claude Gilles became professor at the *École supérieure de physique et de chimie industrielle de Paris* (the Paris Superior School of industrial physics and chemistry) in 1972, Alexandre Revcolevschi at the University of Orsay near Paris in 1977, and Jean-Pierre Boilot at the *École Polytechnique* (Polytechnical school, Palaiseau) in the early 1980s. Jacques Livage created a laboratory at the University of Paris 6 and became one of the world leaders of a new branch of materials chemistry that he himself labeled "*chimie douce*" (soft chemistry) in 1978. By using ambient temperature and low energy bio-inspired chemical reactions, soft chemistry allows the synthesis of a wide range of new materials.

Despite his huge influence on a generation, Collongues never enjoyed international recognition. He did not travel much and was not eager to speak English. His name can hardly be associated with a discovery or a new theory, but he was one of the major cogwheels of the solid-state chemistry machinery in France. Collongues's research school competed—both scientifically and institutionally—with other French groups in the field of materials chemistry, such as the research school headed by Paul Hagenmuller in Bordeaux, the group founded by Félix Trombe at Meudon-Bellevue, and the group around Jean Flahaut at the University of pharmacy in Paris. However, the rivalry did not prevent cooperation among the groups, and so a French community of solid-state chemistry emerged with a common language and specific methods. These were characterized by close connections between chemistry and physics;

between fundamental and applied research; the synthesis and characterization of new solid compounds; and focus on the linear model linking atomic structure to physical properties and properties to applications.

For Collongues's retirement in 1993, the members of the LCAES – most of them being his former students – organized a week-end in the countryside and played several cheerful spectacles to express their admiration and affection to the old master. Soon after, in 1994, Collongues discovered that he had a lung cancer. During four years, he fought with strong energy against the disease, analyzing the medical results like he used to do with chemical ones, giving the impression while speaking with the doctors that he was not the patient but their colleague. Nevertheless he died at the hospital of Villejuif near Paris on 10 May 1998.

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