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FROM SPIN TRANSITION TO DISPLAY AND MEMORY DEVICES

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Abstract : After a presentation of a user-friendly and reliable optical technique to characterize the spin transition phenomenon in iron II derivatives, this paper describes the first realization of a thermally addressed display. This new technology, still at the beginning of its development, is promising for further recording or display applications.

I INTRODUCTION

An interesting feature of some molecular compounds is their ability to have two or more stable electronic states, as a function of their external environment. Their change of electronic ground state can be driven by a change of parameters such as pressure, temperature, or applied strain. If the transition between both states is related to a cooperative effect, the response of the material will be abrupt and the transition phenomenon will be accompanied by a hysteresis, in the loop of which both states will be simultaneously detectable [1]. This memory effect is the basis of applications.

The coordination complexes having a d^n (n = 4,5,6,7) configuration, have already been extensively reported [2] for presenting this type of behaviour, (evidenced by a spin transition-ST), thermally induced. Among them, iron II compounds (d^6) have caught our interest since the magnetic response is a dia-paramagnetic transition, accompanied by a drastic colour change. While, at the beginning of this study, the thermal performances were unsuitable for a practical application of these compounds (T_c around 100 K for the tetrazole derivative $Fe(PTz)_6(BF_4)_2$) [3], outstanding improvements in their chemistry have shifted the working temperature near room temperature[4] and even above (T_c ~ 85 °C for the triazole based molecular material, $Fe(Trz^-)(HTrz)_2(BF_4)$).

This paper will relate the various steps that have led to the realization of a display

based on the iron II derivatives mentioned above, from the optical characterization of the transition to the prototype fabrication.

II SPIN TRANSITION EVIDENCE : THE OPTICAL APPROACH

The spin transition of iron II surrounded by triazole or related molecules is, as said, evidenced by a drastic change of the absorption spectrum in the visible range : the colour of the material changes from white for the High Spin state (HS) to deep purple in the Low Spin (LS) one. The idea is to take profit of this easily detectable change, by optical reading of the transition. For that purpose a test bench has been set up, using :

- a common white light source
- a multimodal optical fiber
- a detection module being either an Optical Multichannel Analyser(OMA), to record the whole spectrum, or a photomultiplier, working on a given wavelength range (here chosen to correspond to the maximum change of response between both states).

Both measurements, reflection and absorption have been performed. The experiments have been made with the high transition temperature triazole derivative $Fe(Trz^{-})_x (HTrz)_{3-x} (BF_4)_{2-x}$.

The first step consisted in defining the best working wavelength for which the signal amplitude is the greatest ; figure 1 presents a detailed absorption spectrum of the HS and LS states. The greatest change is observed for $\lambda = 520$ nm. That corresponds to the electronic transition $^1A_{1g}$----$^1T_{1g}$ This wavelength has been used to record the change of optical index versus temperature over one cycle of warming up and cooling down as shown by figure 2. One notes that the optical data fit exactly those magnetically measured[4] : same transition temperatures and same sharpness.

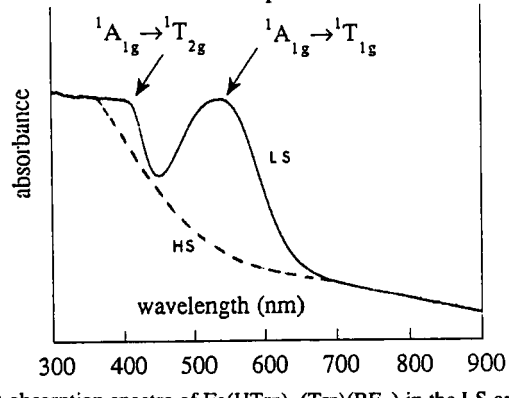

FIGURE 1 : absorption spectra of $Fe(HTrz)_2(Trz)(BF_4)$ in the LS and HS states

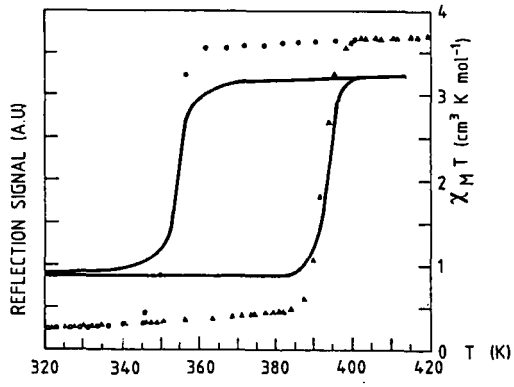

FIGURE 2 : Optical response versus temperature of $Fe(Trz^-)(HTrz)_2(BF_4)$
dotted line : magnetic response versus temperature

This technique has not only been the starting point for the optical assessment with further application in view, but it has also proved to be an efficient characterization tool, being as sensitive and reliable as the magnetic measurement. It enables to cover the whole range of temperature (from 100 K to 100 °C) without requiring a sophisticated equipment.

Its sensitivity is accurate enough to reveal a shift of response over the first write - erase cycles, as presented by figure 3 : the change of the optical behaviour is due to a change of the water content in the layer, H_2O having a great influence on the ligand strength. Moreover the existence of two phases for the generic high temperature triazole derivative has been evidenced. Figure 4 shows the optical response consisting of two hysteresis loops that can be attributed to two different compounds, that have been identified by microanalysis as being $Fe(HTrz)_2(Trz^-)(BF_4)$, and $Fe(HTrz)_3(BF_4)_2$.

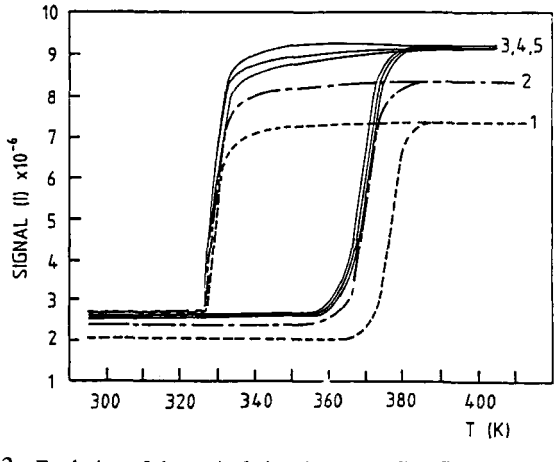

FIGURE 3 : Evolution of the optical signal over the first five write-erase cycles

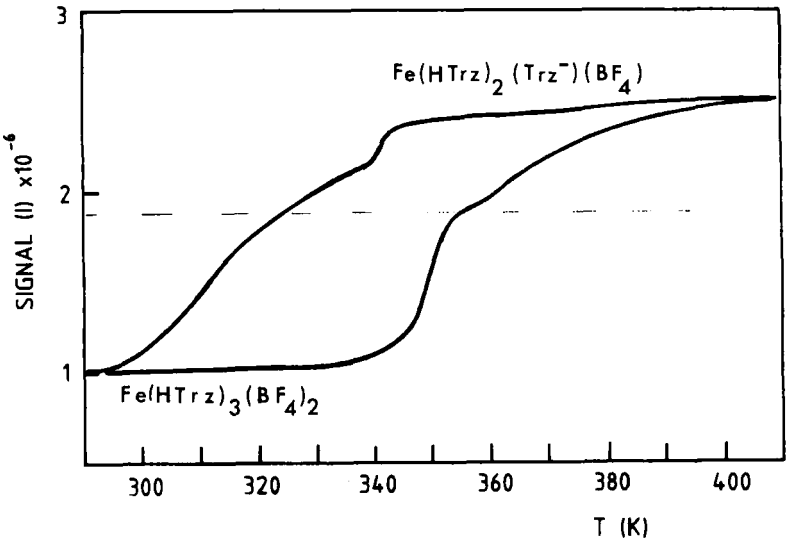

FIGURE 4 : Evidence of a double phase compound

III FROM ST COMPOUNDS TO CONCRETE APPLICATIONS

IIIa Information storage and display : a brief state of the art

The applications of ST compounds, mainly in recording systems and displays, use the hysteresis and the resulting region of bistability. There are already many techniques available in both types of devices.

Concerning the recording systems, it is most interesting to focus on rewritable recording media. Principally, two technical solutions are currently under development : the magneto-optical [5] and the phase change [6] based recording techniques.

The latter consists in detecting the change of reflective index between two phases of a same material (crystalline or amorphous). The writing occurs when warming up locally with a laser beam and quenching the concerned point. By warming up again at a temperature higher than the recrystallization temperature, the data is erased. The basic material is here a GeTe type alloy. While the contrast is easily detectable and consequently the reading easy to perform, such a system requires long erasing time, a high laser power to write and cannot work over too many cycles due to the mechanical fatigue.

The magneto-optical recording technique is the detection of a change of Kerr angle (change of polarization by reflection on a magnetized surface). The active layer is

made of a multilayer system based on rare earth and transition metals alloys or multilayer structures [7], that can be locally magnetized or demagnetized. The writing and erasing steps require to locally heat the active layer under a magnetic field. While a high density of information can be achieved by this technique (0.12 µm per data point), it is highly noise sensitive and the Kerr angle rotations are difficult to detect.

Considering the drawbacks of these other recording techniques, organic spin transition compounds are good candidates as recording media. They do not request high addressing power, their change of state is easy to read, and their stability over many cycles is an intrinsic feature, since the transition is quite purely electronic.

Until recently, the only illustration of such a use of spin transition compounds has been reported by Gütlich et al[8] and refers to the Light Induced Excited Spin State Trapping phenomenon. That consists in freezing the HS state, obtained by local heating through a laser irradiation, at a working temperature (< 50 K) for which the thermal activation is not large enough to make the system return to the stable LS state. This effect does absolutely not use the existence of a hysteresis loop. In fact, the ST molecules reported until this year in the litterature presented critical temperatures below 100 K (110 K for $Fe(Ptz)_6(BF_4)_2$ was the highest reported.transition temperature) that made them unusable in room temperature working devices.

As far as displays are concerned many techniques are available such as plasma screens, fluorescent screens with microtips and so on. The liquid crystal technology is the most developed nowadays, and promising for the future[9]. Nevertheless it is known to have some intrinsic drawbacks such as a relatively long response time, and the limitation of the viewing angle. Some of these problems have found a solution with the introduction of the active matrix technology, addressing each pixel by its own transistor. But the charge retention time remains limited (there are many loss sources in the matrix : resistance losses, coupling of capacitors...), leading to the desactivation of the pixel, and making it necessary to restore it regularly.

Moreover, the speed performance is inversely dependent on the transistor size, so that the electronic part requires very clean production processes. That means that the yield of fabrication decreases rapidly with the size of the screen and that is the main limitation of that technique right now.

In comparison to that ST compounds can find their own field of application, with static image monochromatic, large scale, displays, in a first stage : they do not require to implement an active matrix for addressing and maintaining the information, so that the resulting display should be far cheaper. The next section describes the fabrication of such a device.

IIIb Display fabrication

The use of ST compounds as active part of a display requires deposition of them in a layer of uniform composition. This is done by screen printing technology, using an ink consisting of the ST compound in suspension in a resin which acts as material support and as protection against the environment (water...). The substrate consists of an alumina plate, on which resistive dots and connecting electrodes are previously screen printed. The dots are addressed through columns and lines (figure 5a,b). The addressing step can be monitored through a computer.

The dots, when electrically addressed, act as heat dissipators. When the temperature is over the critical "up temperature" it makes the ST material transit from purple to white.The information is kept as long as the system remains at a temperature within the hysteresis loop (figure 5c).To erase the signal, the system has to be cooled down, under the critical "down temperature". This can be achieved by using a Peltier element.

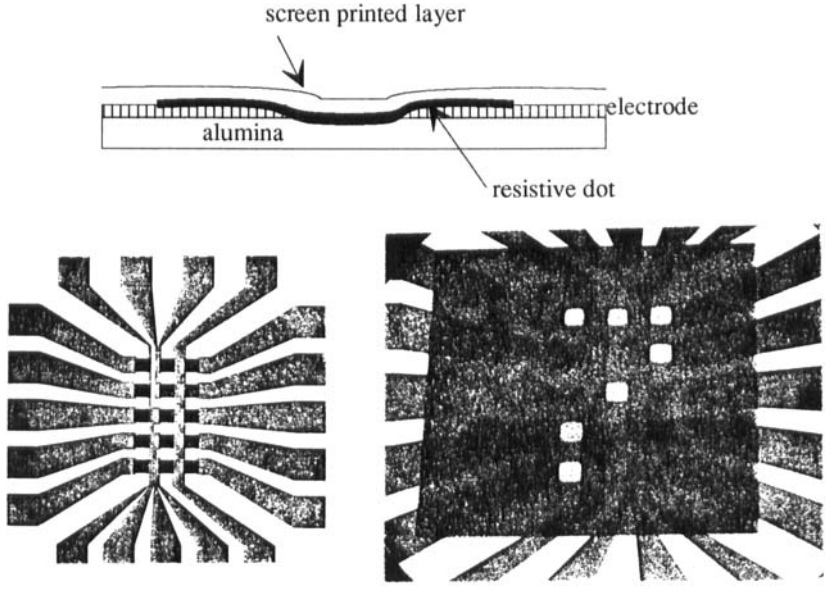

FIGURE 5 : laboratory scale display ; a) cross section of a pixel, b) top view of the substrate, c) addressed ST layer

Various related systems can be derived from the previously described display, depending on the mode of detection : transmission or reflexion. First, the alumina substrate can be replaced by a glass or any other transparent plate. The screen printed

electrodes can be replaced by evaporated "Indium Tin Oxide" (ITO) lines. And instead of working with only one electrode support, one can easily generalize the design to a sandwich consisting of two glass plates, stacked such a way that the ITO electrodes are placed crosswise, with the active ST layer in between, playing the role of the dissipative material (using a more or less dissipative ink support) at the crossing point of the electrodes.

This way it has been possible to fabricate the first ST compound based display, the implementation of which is especially cheap in comparison to the other techniques, and which keeps the information over weeks without having to restore it. An improved prototype consisting of a three digit display has been made in the run of the study. Its applications concern now a restricted area (static signal and global erasing) but using new ways of implementation and making advances in the chemistry of such compounds new perspectives are expectable.[10,11]

A SEM investigation has proved that the smallest crystal size turns around 0,1 μm. Experimentally, such a small size does not impede the phenomenon. Consequently, it makes sense to use the best possible focalization, hence the use of a laser for addressing the system, is relevant. The first attempts in that sense show that the required power is smaller than 5.10^{-2} mW/μm^2, which is far below the usual value of addressing power in magneto-optical displays. The reading can be made by parallel detection through photodiodes or a CCD array, since it occurs in the visible range. In that case, the information density would be comparable to the highest reported in optical recording technology.

IIIc performance of the displays

Even if those prototypes are the very first, some features are already noticeable in terms of relevance and sensibility of use for the ST compounds to be further developed. The energy required for addressing a spot corresponds to a power of the order of a mW over short periods of time (< 1 s). The pixel resolution for screen printed material enables to perfectly distinguish 200 μm large lines separated by 200 μm from each other.The last point is the stability in time, towards chemical changes in presence of water and towards mechanical stresses. First attempts in that sense are quite encouraging, since the intrinsic chemical stability of the material is already reliable while the resistance towards scratches can be decorrelated from the active layer itself and can be ensured by a protective overlayer.

Those characteristics combined with the ease of processability of these compounds make them promising candidates for more sophisticated devices.

IV CONCLUSIONS AND PERSPECTIVES

This paper was devoted to the description of a new type of display, based on ST Molecules, introducing a new display technology. Taking advantage of the fast moving chemistry research in that field, it has been possible to develop those compounds and to realize a prototype. A unique feature of these displays is their very long memory time : at least several weeks at a working temperature of 60 °C for the triazole derivative. A different choice of compounds enables to use room temperature as working temperature.

The next fundamental improvements should concern the width of the hysteresis, which is still of the order of 40 °C.

Another area which deserves further investigation is the molecular behaviour of those compounds, which has not yet been fully understood. If the existence of the hysteresis could be correlated with a molecular behaviour instead of a cooperative one[12], one could enter the field of real molecular electronics, where one molecule would correspond to one data point.

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