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Design and construction of an optical reflectometer for research on spin crossover materials

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Abstract

An optical reflectometer instrument has been design and constructed for research on Spin Crossover Materials, a new kind of compounds which promises to be very significant in molecular memory systems. By using the reflectivity as a physical parameter to investigate the magnetic state of a material, this instrument shows its capability of performing studies of magnetic hysteresis. It mainly consists of a Y-shaped optical fiber, a light source, a sample holder and two optical setups for sampling the reference and reflected signals. Several technical aspects are discussed, like the AC noise electronic filtering, the baseline adjustment, the temperature control, and the remote control of the instruments by GPIB control interface over a virtual instrument platform (LabVIEW®). Measurements of the reflectivity can be performed as a function of temperature from 300 K down to 30 K in a closed cycle cryostat.

Key words: instrumentation, optical reflectance, spin crossover.

Diseño y construcción de un sistema de reflectividad óptica para estudiar materiales de transición de espín

Resumen

Se ha diseñado y construido un instrumento de reflectividad óptica para estudiar Materiales de Transición de Espín, un nuevo tipo de compuestos que prometen ser muy importantes en sistemas de memorias moleculares. Utilizando la reflectividad como parámetro físico para investigar el estado magnético de un material, este instrumento muestra su potencial para estudios de histéresis magnética. Éste consiste, principalmente, de una fibra óptica en forma de Y, una fuente luminosa, un portamuestra y dos sistemas ópticos para registrar la señales de referencia y reflejada. En este trabajo se discuten varios aspectos técnicos tales como el filtro electrónico de ruido AC, el ajuste de la línea base, el control de temperatura, y el control remoto de los instrumentos vía GPIB utilizando una plataforma instrumental virtual (LabVIEW®). Las medidas de reflectividad en función de la temperatura se realizaron en un criostato de ciclo cerrado desde 30 K hasta 300 K.

Palabras clave: instrumentación, reflectividad óptica, transición de espín.

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Introduction

Spin Crossover Materials, SMC, have raise interest in the scientific comunity as possible candidates for optical memories, using their ability to swith between two well defined magnetic states (1, 2). Reported since 1931 (3) this change in their magnetic states was first detected as change between a paramagnetic to diamagnetic state using the Faraday balance for measurements of magnetic susceptibility. Chemically they are a class of inorganic coordination compounds with a central metal ion of d^4 to d^7 electron configuration. This corresponds to the elements Mn^{III}, Fe^{III}, Fe^{II}, Co^{III}, Co^{II} and Ni^{II}. Crystal field theory (4) shows how surrounding ligands of these ions in an octahedral environment can lie in one of two possible electronic states with different spin multiplicity. That makes possible the coexistence of two magnetic state (High Spin (HS) and Low Spin (LS)) among the molecules of a given ensemble and the transition between them, being the latter strongly dependent on the temperature. Moreover, some of these compounds exhibit a hysteresis behaviour in the transition, a feature that makes their temporal state history-dependant. The very origin of this hysteresis is still under research: Modified-classical models of hysteresis, once proposed to explain ferromagnetic phenomena has been applied to these systems with some success (5, 6), although the correspondence between classical hysteresis concepts like domains and the SCM is still to be explained. Nowadays it is widely accepted that the hysteresis in these compounds has its origin in the behavior of an assembly of molecules rather than in the behavior of just one. A complete model could bring to light a way of designing molecular arrangements able to save digital information (2).

The main parameter which determines the transition is the molar fraction of the high spin state, denoted as n_{HS}. In case of hysteresis compounds, the temperatures at which n_{HS} is 0.5 are denoted by $T_{1/2}\uparrow$ or $T_{1/2}\downarrow$, depending on whether the transition is observed with increasing or decreasing temperature. Even though experimentally this transition can be recognized by several analytical methods, like Extended X-Ray Absorption Fine Structure (EXAFS), X-Ray Diffraction (XRD), the Faraday Balance and Differential Scanning Calorimetry (DSC); Mössbauer Spectroscopy is regarded as the most reliable technique to determine n_{HS}.

However, the Mössbauer spectroscopy is a very time-consuming technique for the exploration of the transition so it was clear the need to develop a faster way to recognize and explore it. A new research tool was then proposed in 1996 (7, 8), taking advantage of the change in the Optical Absorption Band with temperature shown by these compounds (9), called Optical Reflectometry. In the following years it proved itself as very useful way to research into the intrinsic mechanism of the transition between HS and LS states (6, 10). An instrument, similar but not equal to that described in reference (8), was developed at the Laboratorio de Magnetismo, Facultad de Ciencias, Universidad Central de Venezuela, to performed optical studies on SCM, which will be explained in the following section (11).

Experimental setup

The Optical Reflectivity R is defined as the ratio of reflected light intensity IntR to incident light intensity IntI at the surface of a material:

$$R = \frac{|Int_R|}{|Int_I|} \qquad [1]$$

In an optical reflectometer instrument this quantity is measured electronically as a function of the temperature of the material, and by recording the value of R the transition between the two magnetic states can then be observed. The assumption that magnetic transition can be followed by an optical quantity lies on the fact that n_{HS} and

R are linear to eachother. This important hypothesis was proven in 1998 by Varret et al. (12).

As an instrument aimed to take light into and from the sample, one important component to be build was a Y-shaped bundle of optical fiber. The fiber has esentially two roles: to carry the light into the sample holder and to collect any reflected light from the sample through the vacuum proofed seals and closed-cycle cyostat (figure 1). Tailored to our purpose, the fiber was manufactured by the EUROFOT Co. (France): Its first branch contains one third of the fibers and conducts the incident light. Its second branch holds the remaining two thirds of fibers, taking the reflected light out of the sample holder. In the central stainless steel tube of 33 cm long are the fibers randomingly packed, and it goes directly into the sample holder. This ratio (1/3-2/3) between the branches was aimed to catch the maximum possible quantity of diffused reflected light.

The sample holder, made of copper and supported by a 33 cm long rod glued to a vacuum-proof cap, see figure 1, fulfill the following requirements: a) gives holding to a temperature sensor and a heating wire (Constantan), b) lets the optical fiber get into the sample space and c) has the necessary thermal inertia for a good temperature control. This assembly is introduced in a close cycle cryostat which has a cold head that lies just underneath of the sample holder (without touching it). The thermal contact between them is achieved with helium gas exchange. Over the rod, lies a home-made electrical feedthrough and the entrance hole of the Y-shaped optical fiber.

A vertical module, see figure 1, gives housing to several instruments associated with the light and temperature measurements: A Mille Luce M-10000 Light Source; a Neocera LTC-11 Temperature Controller; the light detection and filtering circuitry; and a computer with a GPIB interface and

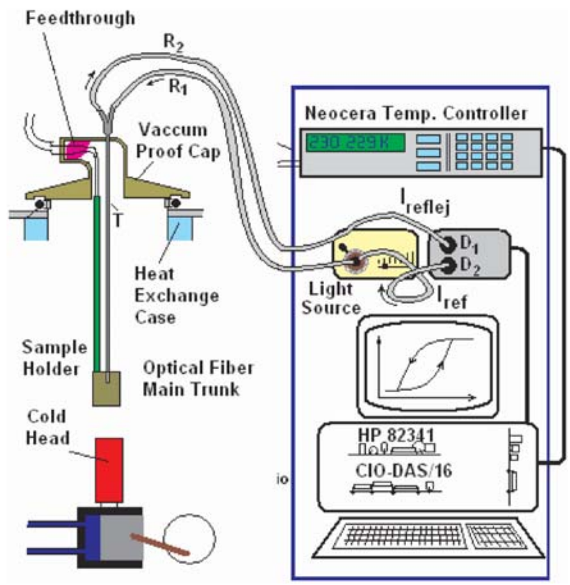

Figure 1. Schematic diagram of the optical reflectometer.

an Analog/Digital Converter (HP 82341 and Computer Board CIO-DAS/JT/16) incorporated to it. The computer program is written over a virtual instrumentation environment, which allows the user to see an instrument-like panel where the control heating power can be controlled, and temperature and reflectivity data of the sample can be monitored. The whole assembly is depicted in figure 1.

The Neocera Temperature Controller acquires the temperature given by a four-wire diode sensor placed on the sample holder, and supplies the heating power to the constantan wire. Since a sharp temperature rate upturning is needed for hysteresis studies, a careful thermal control is needed, hence close loop, used at the beginning of this work, showed an undesirable overshoot; therefore open loop control was finally adopted. The close cycle cryostat allows us to perform studies from room temperature down to 30 K.

In order to obtain the reflectivity we need to measure simultaneously the reflected and incident light intensities. For that, an unbiased photodiode (Edmund Scientific Cat. No. F53-375) connected to a well known Current-Voltage transformation circuit (figure 2) is used. Since the measurement of both intensities can not be strictly done at the same time, a small part of the incident light is diverted into a second detector. The circuit yields a voltage signal (V_0) linear to the incident light intensity (Int_0), as it is expressed by the equation

$$V_o = k * Int_0 + V_{BASE} \qquad [2]$$

where "k" and V_{BASE} represent the circuit constant and the baseline voltage (output voltage with no incident light) respectively.

Raw acquired, the optical signal from the light source exhibited an electrical noise that could be disminished by installing a low pass filter after the Current-Voltage circuit, giving a less noisy signal to ADC Card (11). In figure 3 it is shown the effect of the filter over the signal (1949-2200 s). A Fourier analysis of the noise showed a strong 60 Hz peak together with experimental Bode diagram of this filter are despicted in figure 4, showing the capability of the circuit to attenuate by -55 dB the 60 Hz component. Since the information we are looking for is transfered through a DC voltage level, any AC filtering has no effect on ultimate value of R.

A key detail that must not be overseen ist that the signal has a not-zero baseline V_{BASE} at the Analog/Digital Converter input port even when no light enters the photodiode. Prior to any SCM study, measurement of this baseline voltage was a mandatory procedure: Adjustment of both incident and reflected signal voltages can then be performed by subtracting their respective baseline voltage. The Reflectivity can then be calculated with the quotient of the corrected voltages, as long as both circuits have the same "k" constant:

$$R = \frac{|V_o - Vbase_o|}{|V_I - Vbase_I|} = \frac{|Int_o|}{|Int_1|} \qquad [3]$$

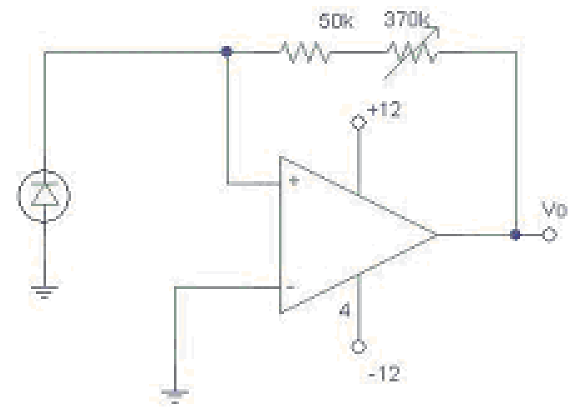

Figure 2. Current-Voltage Circuit.

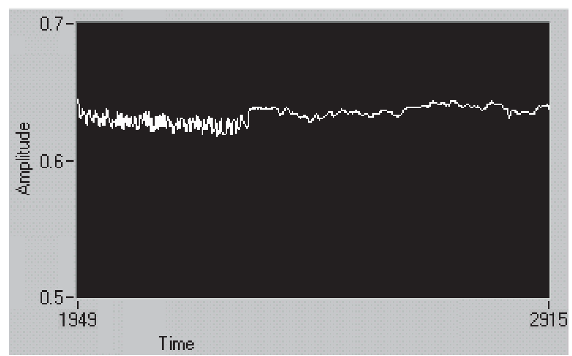

Figure 3. Effect of the Low Pass Filter. From t=1949 s: No Filtered Signal. From t=2200 s: Filtered Signal.

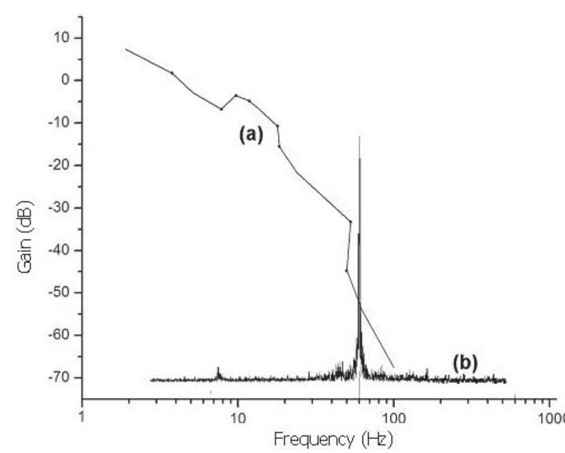

Figure 4. (a) Experimental Bode Diagram. Low Pass Filter (b) Noise Fourier analysis. Note 60 Hz peak. Vertical Scale referred to (a) curve only.

Well done adjustments are obtained when the Reflectivity happens to be immune to small changes in the power of the light source. Any registered change in its value can then thus be regarded to the sample and not to the measuring system.

The software control was done over a virtual instrumentation platform (LabVIEW®), interfacing with two data sources: The temperature controller (by GPIB interface) and the A/D Card. The advantage of virtual instrumentation was clear in this project. Its visual graphical programming environment and very practical-oriented design made it easy to learn and to apply. Many useful libraries are by now offered in the internet and well developed books are available (13, 14). As a matter of fact, the fourier analysis of the acquired signal was straightforward to implement under this environment, avoiding the use of expensive equipment (Spectrum Analyzers). It showed itself to be robust enough on duty, enabling the patient researcher to perform studies in the hysteresis inner zone.

Experimental results and discussion

We have chosen the compound $Fe(btr)_2(NCS)_2(H_2O)$, which has a wide hysteresis cycle among the SCM family, as the initial sample to evaluate the newly built instrument. Thermal aging of the sample is important before any study, otherwise the hysteresis cycle has the undesirable feature of following a not repeatable path. Reported transition temperatures are $T_{1/2}\uparrow$ =123 K and $T_{1/2}\downarrow$=147 K (6). After a ten thermal cycles between 77 and 300 K, it shows an optical response showed in figure 5.

The two cycle swept demonstrates the repeatability of the recorded data, as the second cycle points almost to the first one. The asimetry of the hysteris cycle deserves however some remarks: In the LS state (low temperatures) the reflectivity, which is linear to the magnetic susceptibility, rises with

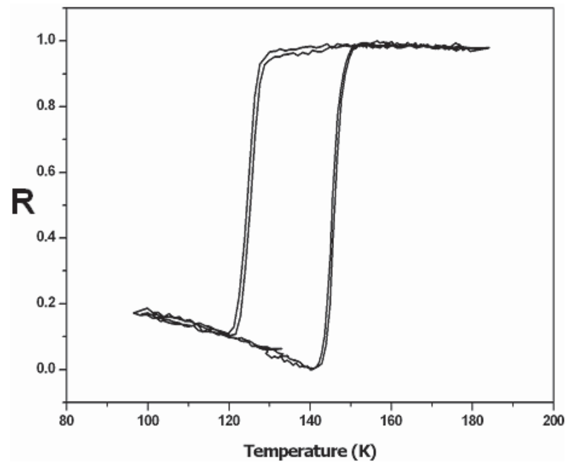

Figure 5. Two cycle reflectivity study of the $Fe(btr)_2(NCS)_2(H_2O)$ compound.

the decreasing temperature as the sample behaves like as paramagnetic substance, obeying thus the Curie law. In the HS state, this statement holds no more, as the molecules contain then an intrinsic magnetic dipole and they interact then in a completely different way.

Up to now, the results not only show the possibility of making optical studies of this magnetic phenomena, but even open the way to apply these data to well developed models of hysteresis behavior.

The following step was focused to explore the inner range of the hysteresis, in an area where not all molecules are switched to LS state. In figure 6 it is shown the obtained response for four cycles, which took about 8 hour to be recorded. Theoretical models of the hysteresis cycle usually require regularly spaced return points between the two saturated states. To achieve this experimentally (points A, B and C of the same figure), careful thermal control is necessary so that the evolution of temperature could effectively turn back where it is wished.

Relative uncertainty of Reflectivity was estimated at 1%, and absolute uncertainty of Temperature at 0,1 K. Although the precision might be redarded to be good, that accuracy in data can only be achieved when

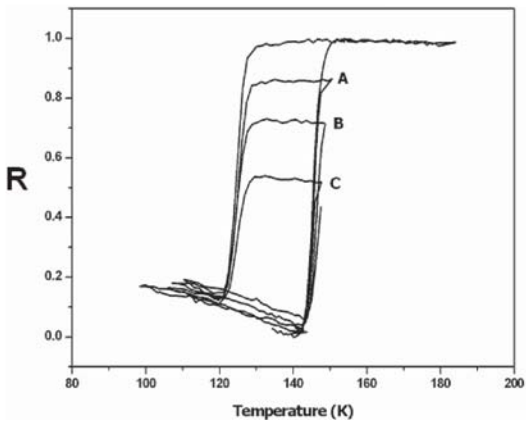

Figure 6. Hysteresis inner zone of the $Fe(btr)_2(NCS)_2(H_2O)$ compound in four cycles.

the baseline voltage adjustment is properly done.

Outlook

This optical tool has emerged fully operative. Nevertheless, several improvements are planned to enhance its research potential, like to provide it with a 550 nm filter (to improve LS-HS reflectivity contrast) and to program the complete automatization of the thermal cycling.

In the other hand, the physics contained in these transitions was certainly enriched by the discovery of the Light Induced Excited Spin State Trapping (LIESST) (9). This effect demonstrated the possibility of switching feature of some SCM between their two magnetic states with light of certain wavelength. In principle, this instrument comes to be suitable to undertake such kind of studies.

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