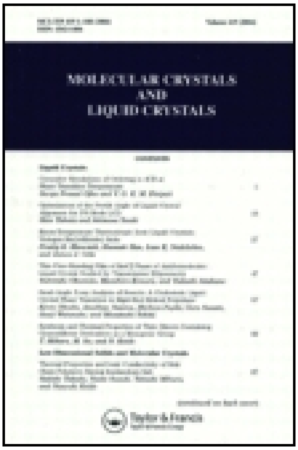


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Simultaneous Reflectivity and Magnetic Measurements on Photomagnetic Solids: Spin-Crossover Solids and a Prussian Blue Analogue

Epiphane Codjovi [a] , Willy Morscheidt [a] , Jelena Jeftic [a] , Jorge Linares [a] , Marc Nogues [a] , Antoine Goujon [a] , Olivier Roubeau [a] , Hector Constant-machado [b] , Arnaud Desaix [a] , Azzedine Bousseksou [d] , Michel Verdaguer [c] & François Varret [a]

[a] Laboratoire de Magnétisme et d'Optique, CNRS-Université de Versailles, 45 Av. des Etats-Unis, 78035, Versailles, Cedex, France

[b] Departemento de Fisica Aplicada, Faculdad de Ingenieria, Universidad Central de Venezuela, Caracas, Venezuela

[c] Laboratoire de Chimie des Métaux de Transition, CNRS-Université P M, Curie 4 place Jussieu, 75252, Paris, Cedex, 05, France

[d] Laboratoire de Chimie de Coordination du CNRS (UP 8241), 205 route de Narbonne, 31077, Toulouse, Cedex, France

Mol. Cryst. and Liq. Cryst., 1999, Vol. 335, pp. 583-592
Reprints available directly from the publisher
Photocopying permitted by license only

Simultaneous Reflectivity and Magnetic Measurements on Photomagnetic Solids: Spin-Crossover Solids and a Prussian Blue Analogue

EPIPHANE CODJOVI[a], WILLY MORSCHEIDT[a], JELENA JEFTIC[a], JORGE LINARES[a], MARC NOGUES[a], ANTOINE GOUJON[a], OLIVIER ROUBEAU[a], HECTOR CONSTANT-MACHADO[b], ARNAUD DESAIX[a], AZZEDINE BOUSSEKSOU[d], MICHEL VERDAGUER[c] and FRANÇOIS VARRET[a]

[a]*Laboratoire de Magnétisme et d'Optique, CNRS – Université de Versailles 45 Av. des Etats-Unis, 78035 Versailles Cedex, France,* [b]*Departemento de Fisica Aplicada, Faculdad de Ingenieria, Universidad Central de Venezuela, Caracas, Venezuela,* [c]*Laboratoire de Chimie des Métaux de Transition, CNRS-Université P M Curie 4 place Jussieu, 75252 Paris Cedex 05 France and* [d]*Laboratoire de Chimie de Coordination du CNRS (UP 8241) 205 route de Narbonne, 31077 Toulouse Cedex, France*

Thermo or photo-chromic properties can be measured using the light reflected by a surface. An apparatus has been designed for coupling to a SQUID Magnetometer. Instrumental improvements and new results on photo-magnetic systems are reported : (i) Spin crossover system $[Fe_xCo_{1-x}(btr)_2(NCS)_2]{\bullet}H_2O$: direct and reverse LIESST, Light Induced Thermal and Optical Hysteresis (LITH/LIOH) (ii) Prussian blue analogue $Rb_{0.52}Co[Fe(CN)_6]_{0.84}, 2.31\ H_2O$: first optical detection of photo-excitation and thermal relaxation of the metastable state.

Keywords: photo-excitation; magnetization; reflectivity; photo-magnetism

INTRODUCTION

Thermo- or photo-chromic properties can be investigated by measuring the light reflected by the surface as a function of temperature or wavelength. Photo-magnetic effects such as LIESST (Light Induced Excited Spin State Trapping) of spin crossover solids[1,2] or photo-excitation of bimetallic cyanides[3,4,5] have been previously investigated using a SQUID magnetometer equipped with an optical fiber for light irradiation[6]. In order to correlate the variations of optical and magnetic properties, we have adapted a reflectivity device for using in conjunction with a SQUID magnetometer. Previous results of increasing quality have been published in references [5-8].

We present the simultaneous measurements, performed on the spin transition solids $[Fe_xCo_{1-x}(btr)_2(NCS)_2]\cdot H_2O$[5,6,7,8], noted [x], and the photo-magnetic Prussian Blue analogue $Rb_{0.52}$ Co $[Fe(CN)_6]_{0.84}$, 2.31 H_2O[4,5,9] to illustrate the main specific character of the system: *reflectivity enables the investigation of the « surface » of the sample, while the magnetic measurements enable the investigation of the bulk.*

A second aspect deals with highly cooperative and absorbing systems. The recently discovered LITH and LIOH phenomena (Light Induced Thermal and Optical Hysteresis)[7,8,10] and the theory[8,11] explain why the LIESST effect becomes hard to perform in the case of strong cooperativity. Also, a large optical absorption in the solid also limits the efficiency of the optical switching processes. It is shown here that the reflectivity technique may enable by-passing both difficulties. This is encouraging for applications to information storage and digital display technology [12].

The SQUID and reflectivity system

The first optical system for the rapid detection of the colour change of spin transition compounds was designed around a Y-shaped optical fiber by O. Kahn and the Laboratoire d'Electronique Philips[13]. The apparatus was completely automated. A novel apparatus for monitoring both incident and reflected light has been developed using a 3-channel temperature controller[14,15], and is used with a SQUID magnetometer. The two flexible branches have been fitted to the light source and detector while a stainless steel tube protects the common branch, see Fig. 1. Two light conducting rods are placed on either side of the

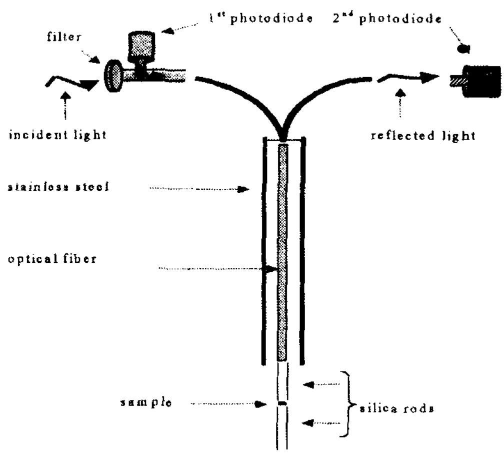


FIGURE 1 The SQUID/reflectivity sample holder

sample to suppress the magnetic signal from the stainless steel tube. The best choice is a silica light-guide, the transmittance of which is not disturbed by the condensation of gases at low temperature, as have been reported in ref.[5]. Calibration of light intensity is performed using a home made bolometer, prior to the experiments. The SQUID magnetometer (Quantum Design MPMS 5) controls time, drives temperature and measures magnetization. The reflectivity device is driven by an other computer (PC) which takes measurements as a function of time (independent of the SQUID), this records the signals provided by a 3-channel temperature controller (Oxford Instruments ITC4 or ITC 502) connected to the photodiodes.

To synchronize the SQUID and reflectivity recordings, we have used the optical reset signal emitted by the SQUID before each measurement. This was realized using a photodiode connected to the third channel of the temperature controller. Alternatively, post-synchronization of the SQUID and reflectivity data files can be made by hand, and the temperatures associated with the optical data can be calculated with the aid of simple software.

The underlying physics

Spectroscopic aspects of photo-magnetism and reflectivity will not be discussed here. We shall briefly outline basic principles for each class of material :

(i) the case of Fe(II) spin crossover compounds is well documented[1]: most crystals are transparent at high-temperatures, in the high-spin (HS) state, and dark purple at low-temperatures, in the low-spin (LS) state, with absorption bands in the red (~ 800nm) and in the green (~500nm) respectively. A high contrast is thus obtained for reflectivity by using either of these bands [13,14,15]. On the other hand, photo-excitation is performed at low temperature, using green/blue light for LS→HS excitation, and red light for the reverse (HS→LS) switching, according to the so-called direct and reverse LIESST effect[2]. An important point is that the metastable state has a long lifetime at low temperature (up to several weeks), and decays through a radiationless process which becomes rapid compared to the experimental time (~ minutes) in the temperature range 60 - 70 K. Thus the use of the memory effect is restricted to the low temperatures, and this is a severe drawback for applications;

(ii) on the contrary, very little is known about the photo-chromic properties of the Co-Fe based Prussian Blue derivative, the photo-magnetic properties of which have been discovered quite recently[3,4,5,9]. This system exhibits photo-excitation and relaxation properties which are reminiscent of spin crossover solids : reversible switching [3], cooperative relaxation [9].

The optical response

We have performed test-experiments on the thermal transitions of cooperative origin exhibited by the spin-crossover solids $[Fe_xCo_{1-x}(btr)_2(NCS)_2]\cdot H_2O$.

In Fig. 2 we show the data for [x=0.5], 1 mg powder sample. The temperature of the sample is varied at a rate of 0.25 K/min around the critical temperature (~110 K). At this temperature the spontaneous relaxation between the two states is extremely fast, and the irradiation results in a negligible photo-excitation. The optical and magnetic signals can be almost perfectly superimposed, using an adequate choice of the vertical scales, and it can be concluded that the optical response is comparable to the magnetic one, i.e. proportional to the HS fraction. It is worth noting that the reflected intensity comes from the surface layers of the sample, down to the penetration depth of the light (typically ~1-10μm), and is thus capable of detecting « surface » effects, such as those previously reported for a [x=0.64] sample [5,6]. Here the surface is observed to behave as the bulk at the thermal spin transition. One can also notice, in Fig. 2, the step-like behaviour of the reflectivity curve, which accurately follows the temperature variations driven by the SQUID computer.

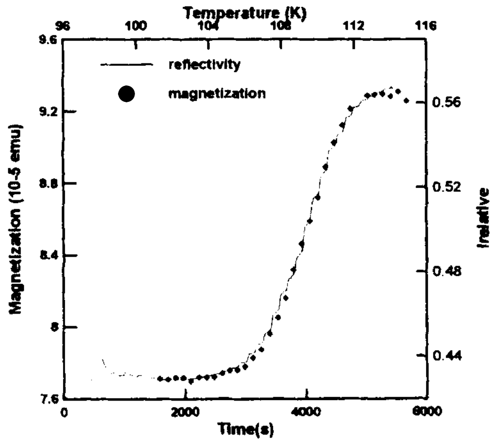


FIGURE 2 Magnetization and reflectivity at thermal spin transition, [x=0.5].

Direct and reverse LIESST of [x=0.64]

The reflectivity and magnetic moment data simultaneously recorded (adapted from[6]) are shown in Fig. 3. In both cases, the reflectivity signal increases during the induced spin conversion, due to the progressive removal of the absorbing centers, in other words due to the bleaching of the sample.

The second important result is the rapid saturation of the optical signal, compared to the magnetic one (in agreement with previous reports[5, 6]). This can be explained by the attenuation of light in the sample, due to bulk absorption. The photo-excitation proceeds in the sample by bleaching successive layers, in a frontal mode.

A third interesting feature deals with the jumps observed on the magnetization signal when the light was switched on and off. The reversibility of the jumps was controlled by chopped light experiments previously reported in ref. [5], and is attributed to the heating of the sample upon irradiation. The use of the Curie law for the paramagnetic case of spin crossover solids enables the evaluation of the temperature increase upon irradiation, ~1K in the present case.

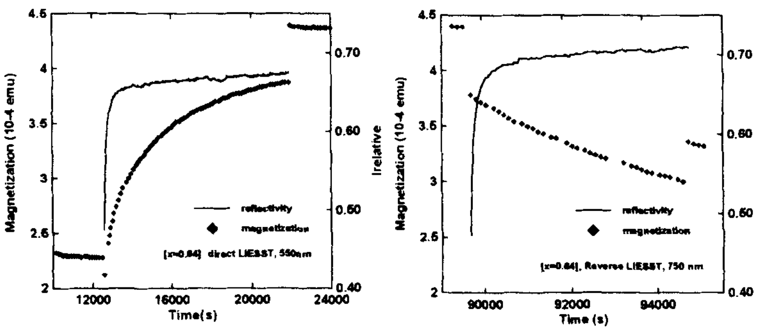


FIGURE 3 Direct (left) and reverse (right) LIESST for 5 mg [x=0.64] at 8K, 25 mW/cm^2. Bulk light attenuation is large, compared to refs.[8,16]

Light-induced bistability of [x=0.5]

Fig. 4 shows the magnetic and optical responses for a 3 mg sample of [x=0.5], under constant irradiation at λ=550nm, 40 mW/cm^2. The observed hysteresis of the steady state (i.e. dynamic equilibrium) is explained by the competition between the constant photo-excitation and a self-accelerated relaxation of cooperative origin[8,11]. We focus here on the difference between the magnetic and optical signals, namely on the low-temperature tail which is enhanced in the magnetic data, and consequently attributed to the bulk part of the sample, submitted to a weaker light intensity.

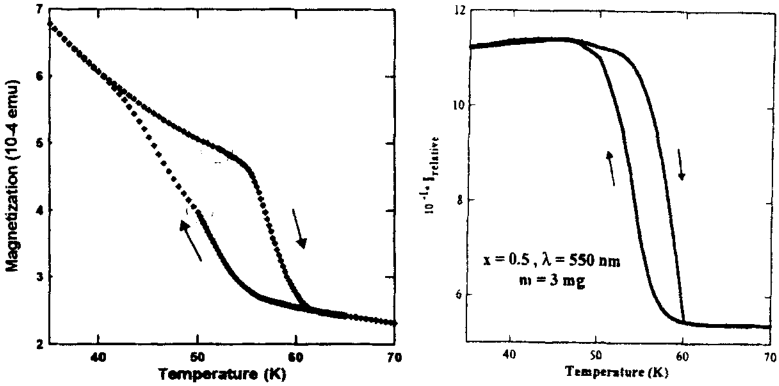


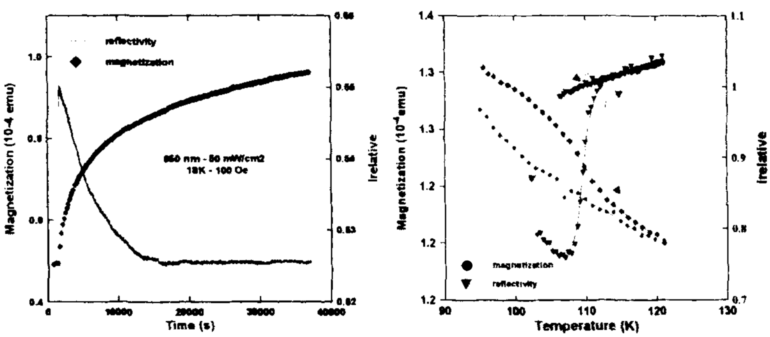
FIGURE 4 Magnetic and optical data for LITH of [x=0.5]. Descending branch 0.2K/2mn → 0.5K/2mn, ascending 0.2K/5mn → 0.5K/5mn). The cycle is completed within 14 h.

It is worth noting that this tail is of kinetic origin, i.e. it is due to the finite time of the experiment. Due to a cumberstone (=temptative) programming of the SQUID sequence, the rate of the temperature sweep changed during the ascending and descending branches of the loop; this resulted in a change in the slope of the magnetic and optical signals (see circled points) which was the clue for the slight kinetic character of the data. At higher temperatures however, the kinetic character is much weaker because the relaxation rate is faster. The high-temperature branch of the optical LITH loop shows better agreement with the expected shape, i.e. drops abruptly. Further data can be found in ref. [16], these illustrate the advantage of the optical detection.

The macroscopic theory which fits these experiments also explains why the LIESST effect may be unsuccessful in the case of highly cooperative solids[8]. The theory introduces a threshold value for the intensity, which drastically increases with the strength of cooperativity. Furthermore, cooperative solids are mostly concentrated compounds which exhibit a large bulk attenuation of light. Then, the LIESST is best achieved at the surface of the sample, and the reflectivity technique is necessary for the case of absorbing solids. This is best illustrated by the following example.

Application to $Rb_{0.52}Co[Fe(CN)_6]_{0.84},2.3\ H_2O$

The photo-magnetic properties of this Prussian Blue analogue are due to an optical electron transfer from Fe^{II} to Co^{III}, followed by the spin conversion of the photo-induced Co^{II}. This creates both the magnetic moments and interactions, and the sample turns from a diamagnet to a ferrimagnet with Tc=21 K [3,4,5,6]. We show in Fig. 5a the photo-excitation curves, indicative of a strong absorption effect (the compound is dark blue).



(a) (b)

FIGURE 5 (a) Photo-excitation of the Co-Fe Prussian Blue Analogue
(b) Thermal decay of the metastable photo-excited state.

In Fig. 5b we show the thermal decay of the metastable state after a brief excitation. We observe little difference between the values derived from the two signals for the decay temperature, thus showing the heating effect is small at this temperature.

It is important to remark that the reflectivity signal evolves in a sense opposite to that observed in the spin crossover systems. The reason has not been clarified yet. We think it should lie in the structureless character of the optical absorption spectrum, associated with a sensitivity of this spectrum to a long-range structural relaxation which might accompany the spin conversion of the photo-induced Co^{II} ions. The reflectivity signal evolves, as expected, in the opposite sense during photo-excitation and decay, and can be used conveniently for a detailed investigation of photo-excitation and relaxation. Due to the cooperative character of relaxation, light-induced bistability[8] is expected to occur as well as in the spin crossover systems.

General aspects of the reflectivity technique

The inherent characteristics of the reflectivity technique can be summarized as follows (we already stressed on the surface selective aspect and on the ability for the case of strongly absorbing materials) . However there remains two inherent aspects which must be faced to :

(i) the heating effect, which is easily controlled by magnetic measurements under a chopped irradiation;

(ii) the trapping effect, i.e. photo-excitation, such as direct or reverse LIESST, which becomes large at low temperature, when the lifetime of the excited state becomes long. This effect can be reduced by switching off the light between the measurements. This requires an external port to the computer which drives the SQUID. In addition, the probe wavelength should be chosen in order to minimize the trapping rate of the system.

Conclusion

Reflectivity is a promising technique for the investigation of photo-switchable materials and for future applications. The technique by-passes some of the difficulties usually encountered. Combining reflectivity and magnetic measurements permits us to distinguish between the surface and the bulk properties, as well as monitoring the heating effect of irradiation.

Acknowledgements

The work was supported by Centre National de la Recherche Scientifique (LMOV is Unité associée URA-1531), the Swiss National Science Foundation (for a post-doctoral grant) and European Communities for a TMR program (Contract TOSS, ERB-FMRX-CT98-0199), and for COST action n° 518.

References

[1] O. Kahn, *Molecular Magnetism* (VCH, New-York 1993).
[2] S. Decurtins, P. Gütlich, C. P. Köhler, H. Spiering, A. Hauser, *Chem. Phys. Letters,* **1,** 139 (1984).
[3] O. Sato, T. Iyoda, A. Fujishima,and K. Hashimoto, *Science* **272,** 704 (1996);.
[4] A. Goujon, *rapport de DEA,* Université d'Orsay (1997).
[5] F.Varret et al ICAME'97 (Intern. Conf. Applic. Mössbauer Effect, Rio de Janeiro Brésil, Sept.1997), *Hyperf. Inter.* **113,** 37 (1998).
[6] H. Constant-Machado, *Ph. D. Thesis,*Université Paris VI, 1997.
[7] A. Desaix, *rapport de DEA,* Université de Rouen (1998).
[8] A. Desaix et al, *Europ. Phys. Journal B.,* vol.**6** n°2, in press.
[9] A. Goujon, O.Roubeau, F. Varret, A. Dolbecq, M.Verdaguer, *in preparation.*
[10] J.F. Letard, O. Kahn et al, *Inorg. Chem.* **37,** 442 (1998).
[11] F. Varret et al, *present conference,*C33.
[12] O. Kahn, J. Kröber, C. Jay, *Adv. Mat.,* **4,** 718 (1992).
[13] O. Kahn, E. Codjovi, *Phil. Trans. R. Soc. London A* **1996,** 354, 359.
[14] W. Morscheidt et al, *Meas. Science and Technology* **9,** 1311 (1998).
[15] W. Morscheidt, *rapport de DEA,* Université Paris 6 (1997).
[16] O. Roubeau et *al, present conference*C39.