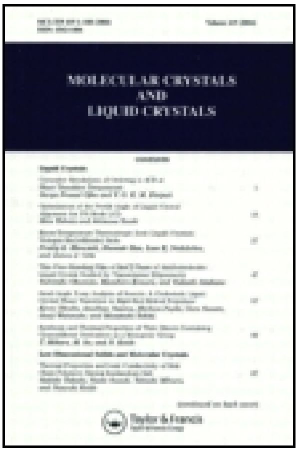

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Thermally Induced Dilution of the Photo-Induced Magnetic State of Prussian Blue Analogues

F. Varret [a] , A. Goujon [a] , K. Boukheddaden [a] , M. NoguÈS [a] , A. Bleuzen [b] & M. Verdaguer [b]

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

[b] Lab. Chimie Inorganique et Matériaux Moléculaires, CNRS, Univ. Pierre et Marie Curie, 4 pl. Jussieu, Paris Cedex 05, 75252, France

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Thermally Induced Dilution of the Photo-Induced Magnetic State of Prussian Blue Analogues

F. VARRET[a], A. GOUJON[a], K. BOUKHEDDADEN[a],
M. NOGUÈS[a], A. BLEUZEN[b] and M. VERDAGUER[b]

[a]*Lab. Magnétisme et Optique CNRS-Université de Versailles, 45 Av. Etats-Unis, 78035 Versailles Cedex, France; fvarret@physique.uvsq.fr and* [b]*Lab. Chimie Inorganique et Matériaux Moléculaires, CNRS-Univ. Pierre et Marie Curie, 4 pl. Jussieu, 75252 Paris Cedex 05, France*

We report on recent progress in the control of dilution of photo-induced magnetic structures, by using thermal activation of the steric relaxation of the photo-excited electronic state. Experimental data relative to Rb- and Cs- based Prussian Blue Analogues are reported in terms of dynamic phase diagrams : Curie temperature vs concentration in photo-excited species. The building-up of correlations, due to steric interactions during the thermal relaxation process, is discussed.

Keywords: photomagnetism; relaxation; diluted magnetic systems

Photo-magnetic Prussian Blue Analogues C_x Co $[Fe(CN)_6]_{y.}$, z H_2O, where C is an alkaline cation, here abbreviated C-PBA, undergo the photo-induced process[1]:

$$Co^{III}(LS,S=0) + Fe^{II}(LS,S=0) \rightarrow Co^{II}(HS,S=3/2) + Fe^{III}(LS, S=1/2).$$

Among the generic appealing features of photo-induced magnetic structures lies the ability of controlling at will the concentration of magnetic moments in a given sample. In[2] we presented the first dilution phase diagram obtained this way (Tc vs relative concentration in photo-induced magnetic moments), obtained with the Rb-based Prussian Blue Analogue $Rb_{0.52}$ Co $[Fe(CN)_6]_{0.84}$, 2.31 H_2O, here abbreviated Rb-PBA. Complementary literature on photo-excitation in PBAs can be found in references[3-5].

For the needs of the coming discussion, we refer to a recent theoretical work[6] devoted to the dynamics of spin-crossover networks, which are the archaetyp of "molecular bistable networks" (MBN). PBAs can be described as MBNs, as long as photo-excitation or relaxation can be considered as a "single-molecule" processes occurring in Co-Fe pairs. MBNs were modelled through the Ising-like hamiltonian, including short- and long-range interactions (of steric origin).

Here we present further experimental dilution data, and a homogeneous stochastic simulation of the dilution effect[3]. The experimental phase diagrams are discussed with respect to the possible onset of correlations.

The simplest way for obtaining at will diluted systems would consist in controlling the irradiation parameters (intensity, time). In Figure 1 we show the field-cooled (FC) magnetisation curves of Rb-PBA, recorded after different photo-excitation times.

The magnetic ordering temperature is observed to keep a constant value, Tc ~22 K, after a very short irradiation time (~10'). This feature reveals an inhomogeneous character of photo-excited Rb-PBA[4], due to bulk absorption of light in this deep blue material : the partially excited sample contains a "top" layer completely photo-excited, a "frontier" layer inhomogeneously excited, and a "bottom" layer, unexcited. Due to the properties of cooperative, self-accelerated relaxation[7], this frontier layer rapidly decays, and after a while the photo-excited state can be considered as a bi-layer, made of a saturated leyaer and an unexcited layer. The thickness of the excited top layer basically depends on the photo-excitation intensity and time.

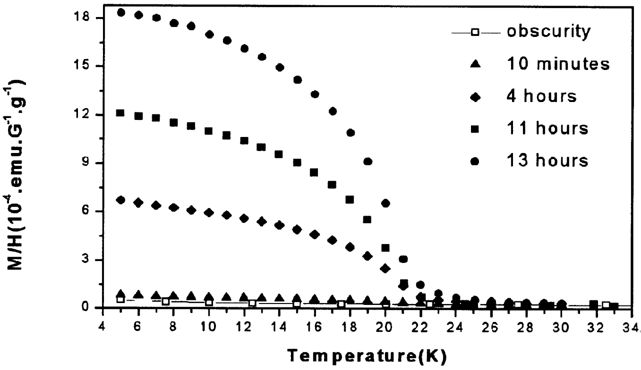

FIGURE 1 FC magnetisation of Rb-PBA before and after different irradiation times at $\lambda > 665$nm, T=10K, H=50Oe, P = 50 mW/cm^2.

To overcome this drawback inherent to the photonic nature of the process, we defined[2] a two-step procedure: (i) a long-time illumination "saturates" the sample, till a given penetration depth; (ii) then, a controlled thermal annealing induces first the decay of the frontier and afterwards progressively induces the homogeneous decay of the saturated part of the sample. Such a bulk process provided the desired correlation between the concentration in magnetic moments (vertical scale) and the magnetic ordering temperature, i.e. the dynamic dilution phase diagram of the photo-induced magnetic structure , reported in Figure 2.

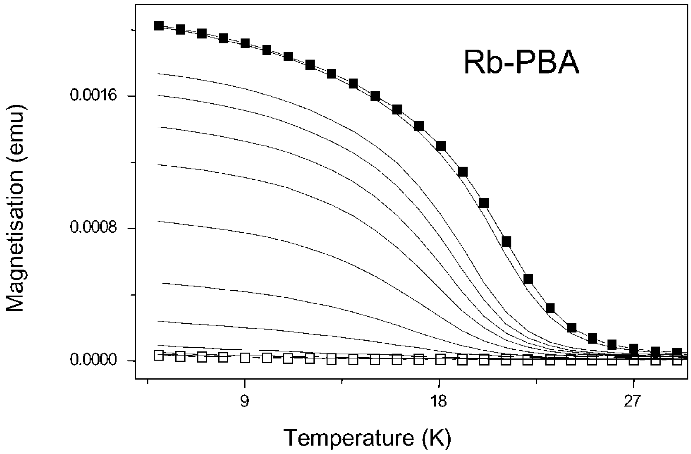

FIGURE 2 FC curves (H= 40 Oe), Rb-PBA after photo-excitation (750 nm, 30 mW/cm^2, 8 K, 12hours), and successive thermal annealing stages [5→T_{max}→5 K] with T_{max}=60, 70, 80, 85, 90, 95, 96, 98K; temperature sweep rate was 0.5K/min (after [2]).

Here we present further dilution data on the same Rb-PBA and on an other analogue formulated $Cs_{0.175}Co[Fe(CN)_6]_{0.72}$, 4 H_2O (Cs-PBA). We performed appropriate initial photo-excitation and successive *isothermal* annealing stages, 3à0 min. each, at temperatures progressively increased in the range [90-95K], for Rb-PBA, and [130-150K] for Cs-PBA. After each annealing stage, the sample was cooled down rapidly, and the FC curves measured. The corresponding phase diagrams have been derived, see Figures 3, 4, by assuming that the low-temperature (4 K) FC magnetisation linearly depends on the concentration in photo-induced magnetic species Fe^{III}_{LS}, Co^{II}_{HS}. The Tc value was taken as the inflection point of the photo-induced contribution to the magnetisation curve. Such correction for the unexcited part of the sample revealed to be crucial for the Cs-PBA data.

A striking point in Figure 3 is the discrepancy of the two sets of data, however obtained with the same sample after identical photo-excitation. For the second set, performed at sizeably lower temperatures and longer times, the Tc value remained high even for very diluted states. In other words the percolation threshold value was

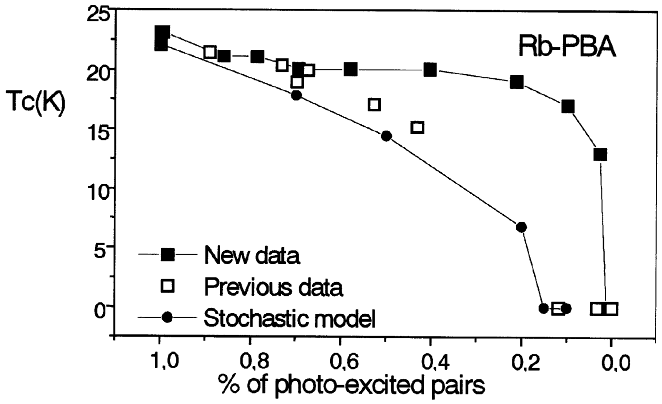

FIGURE 3 The dilution phase diagram of photo-excited Rb-PBA, derived from the previous [2] and new [3] data.

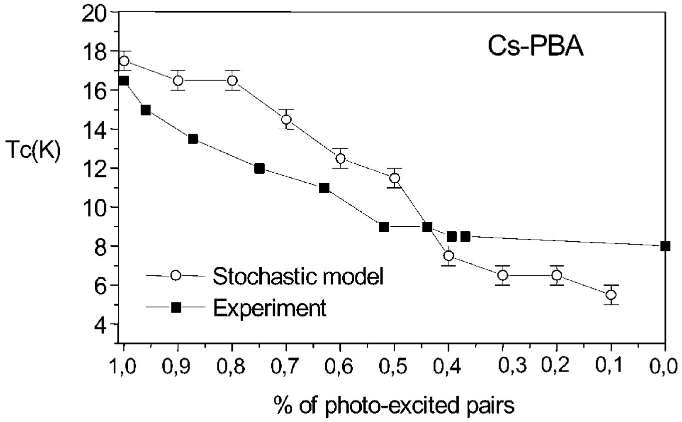

FIGURE 4 The dilution phase diagram of Cs-PBA (data from [3]).

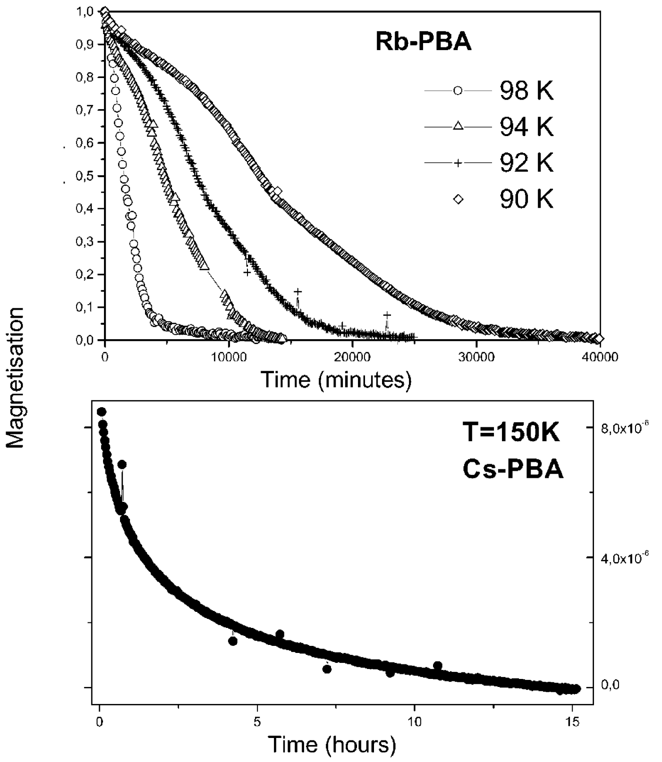

FIGURE 5 "Steric" relaxation curves for the photo-excited state of Rb-PBA (left) and Cs-PBA (right), after[3]. The measured magnetisation was considered as a linear function of concentration in magnetic pairs.

sizeably higher. We interpret this feature as an inhomogeneous effect due to the onset of correlations associated with steric interactions, during the relaxation. The picture is that of concentrated "clusters", which have the longer lifetimes and mainly contribute to the critical phenomena which define Tc.

Such steric interactions are responsible for the abrupt character of the spontaneous transition (i.e. thermo-induced) in molecular bistable networks, such as spin transition solids[7,8], valence tautomeric compounds[9] and Na- and K- PBAs[1]. Cs-PBA under study here also exhibits near ~250K a spontaneous thermal change [3,*Polyhedron*] following the $Co^{III}(LS) + Fe^{II}(LS) \leftrightarrow Co^{II}(HS) + Fe^{III}$ (LS) conversion, but the smooth variation implies the steric interactions to be weak. On the contrary, strong steric interactions in Rb-PBA[4,5] have been inferred from the self-accelerated character of relaxation. Typical relaxation curves are reported in Figure 5 (previous page).

The effect of the annealing time, observed in the "cooperative" system, Rb-PBA, illustrated in Figure 2, can be explained by consideration of correlations associated with the steric interactions. Indeed our recent investigation of the Ising-like model[6] with both short- and long-range interactions, has shown that the onset of correlations was favoured by longer annealing times (associated with lower temperatures). The correlations can also explain the presence of long "tails" in the isothermal relaxation curves of Rb-PBA.

Stochastic model (after [3]) and discussion :

Relevant comparison of the Rb- and Cs-PBA data, due to their difference in genuine Co^{II}(HS) content, requires the help of a model for the building-up of the photo-excited state, pure and diluted. The simplest approach, assuming independent "single-molecule processes" consisted in successively selecting suitable Co-Fe pairs for the photo-induced process. Homogeneous diluted states are built-up during the step-by-step procedure, and can as well represent the structural states provided by a correlationless relaxation of the photo-excited state.

Computations were performed in a cubic sample, with 10×10×10 $C_xCo[Fe(CN)_6]_y$ units. Several independent runs (typically 10) were used to average the results. The scatter of the data, see Figure 6, essentially originates from structural differences between different runs. Each computation run was made of the following stages:

(i) location of all $Fe(CN)_6$ vacancies and C^I cations : at random.

(ii) assignment of all initial Co^{II} (according to the detailed stoichiometry) : as close as possible to the $Fe(CN)_6$ vacancies (for steric reason, Co^{II}(HS) > Co^{III}(LS)) ; if needed, random choice.

(iii) assignment of all initial Fe^{III} (if present, according to Mössbauer data) : as close as possible to the Co^{II}(HS) sites (due to electrostatic energy) ; if needed, random choice.

(iv) selection of photo-excitable Co^{III}(LS) : close to the largest number of $Fe(CN)_6$ vacancies (at least one) ; if needed, random choice.

(v) selection of a neighbouring Fe^{II}(LS), close to the photo-excitable Co^{III}(LS), and photo-transformation of the pair.

Stages iv-v were renewed till all photo-excitable Co^{III}(LS) were found (non-excitable CoIII are those which have no neighbouring vacancy) .

The magnetic properties of the system at any stage of the building-up procedure were simulated by Metropolis technique. We used Ising model with first-neighbour magnetic interaction only, the strength of which was fitted to the Tc value of the photo-excited state. Actually Tc values were derived from the computed specific heat curves at zero field. We show in Figure 6 the corresponding FC curves.

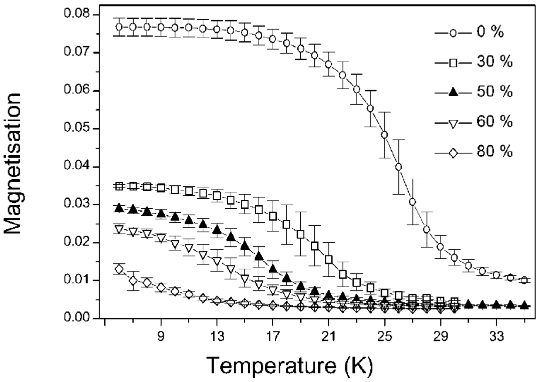

FIGURE 6 The computed static magnetisation curves, for different stages of the building-up of the photo-excited state (after [3]).

The experimental dilution data of Cs-PBA, see Figure 4, qualitatively agree with the phase diagram computed in the homogeneous correlationless simulation. This is consistent with the weakness of steric interactions, already reported, and therefore supports the pertinence of the simulation approach. On the contrary, the discrepancies concerning Rb-PBA (Figure 3) illustrate the interaction effects in this system. These discrepancies could be qualitatively explained at the microscopic scale by the Ising-like dynamic approach (*vide supra*). Alternatively, the observed inhomogeneous effects could also be attributed, at the macroscopic scale, to the transient instability[10] which is inherent of any cooperative system. To our best knowledge, the resulting spatio-temporal properties are not yet described theoretically. Therefore, definitive conclusion on the short- or long-range range character of these correlations cannot be given.

CONCLUSION

Magnetic measurements provided a novel application: the Curie temperature was used as a sensitive probe of the thermally activated dilution of a magnetic system. The phase diagrams revealed the occurrence of inhomogeneities associated with the onset of correlations. A further study is needed, with complementary techniques (diffraction, diffusion..) providing direct access to the spatial properties.

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