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A first order reversal curve investigation of pressure hysteresis in multiferroics spin transition compound

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Spin crossover multiferroic $[\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2]$ is investigated for the first time with the first order reversal curve (FORC) diagram method for its hysteretic pressure behavior. The experimental setup allows the measurements of the high spin fraction as the function of temperature, light intensity, and pressure. The experimental FORC diagrams obtained in compression and releasing modes show significant differences which are in disagreement with the classical Preisach model. Also, stronger kinetic effects are evidenced in the compression mode and possible explanations of this effect considering the viscoelastic behavior are provided. © 2008 American Institute of Physics. [DOI: [10.1063/1.2831335](https://doi.org/10.1063/1.2831335)]

I. INTRODUCTION

In the last few years, the interest in the field of multiferroic materials experienced an obvious increase. Basically, multiferroics represent those materials where there is a coupling between several order parameters, the most known case being the ferromagnetic-ferroelectric coupling. Essentially, one can change the electric polarization with a magnetic field and, vice versa, the electric field can tune the sample magnetization.¹ Even if ferroelectricity and ferromagnetism/antiferromagnetism seemed to exclude each other, in 1960,² a material with both properties was discovered. Single phase¹ or composite³ magnetoelectric multiferroic materials were synthesized and investigated not just for exploring the fundamental science of phase control and magnetoelectric interactions but mostly for the potential impact in recording industry. Among data storage, applications based on exchange bias phenomena⁴ or tunnel junctions^{5,6} were envisaged as well.

The coupling between a number of order parameters could be encountered not only for the above mentioned systems; it can be encountered also in spin transition compounds where a modification in temperature, pressure, magnetic or electric field, or under light pumping may switch the system between a low spin (LS) and a high spin (HS) state or vice versa.⁷ Due to these modifications, the magnetic properties switch from a diamagnetic (LS) to paramagnetic (HS) behavior [in the most usual case of Fe(II) compounds]; the color and also the vibrational properties and distance between metal ion and ligand change (the HS state has a bigger volume than the LS state). When the elastic interactions inside the spin transition compound overcome a threshold

value, the LS ↔ HS crossover exhibits a first order phase transition with hysteresis. Usually, the multiferroic response is converted into the fraction of the HS molecules, n_{HS} . Like in the case of *magnetoelectrical multiferroics*, the main applications foreseen for *spin transition multiferroics* are in data storage solution industries,^{8,9} and also as displays¹⁰ or sensors in cancer treatment¹¹ or food storage.¹²

The thermal hysteresis and light-induced thermal hysteresis of spin transition materials were recently investigated with the first order reversal curve (FORC) technique.^{13–15} We showed with the thermal FORC in diluted compounds (where Fe is substituted by the “spin crossover nonactive” ion such as Co, Zn, or Ni) that one has to assume a distribution of concentration coefficients in order to explain the apparent correlation of the gap energy Δ between HS and LS states with the interaction parameter J .¹⁵ Also, the FORC method proved to be an excellent fingerprint of the kinetic effects in light-induced thermal hysteresis of spin crossover.¹⁴

Our previous FORC studies of the thermal hysteresis in spin transition materials proved that the switching properties are essentially linked to distributions of intrinsic parameters controlling local hysteretic properties. The results suggest that the switching properties through the channel of elastic interactions are connected to the particle size and consequently to the particle size distribution. The concept of like-spin domains was introduced¹⁶ by analogy to ferromagnetism. Additional FORC measurements based on further control parameters (pressure in the present case) could add valuable information to the fundamental understanding of the spin transition materials. As a direct consequence of the spin transition multiferroic molecular structure, the pressure and temperature have opposite effects (see Fig. 1).

In this paper, we report on pressure hysteresis investigated for the first time with the FORC method after our

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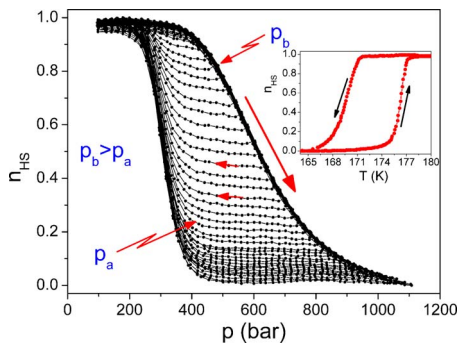


FIG. 1. (Color online) FORCs for pressure hysteresis at constant temperature $T=178$ K with returning points on the descending branch of the major hysteresis loop—the releasing mode. Inset: thermal major hysteresis loop on the same compound measured at $p=600$ bars.

recent study of the correlation between thermal and pressure hysteresis loops.¹⁷ We also discuss the pressure hysteresis properties in the framework of the classical Preisach model¹⁸ for the spin transition multiferroic $[\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2]$.¹⁹

II. EXPERIMENTAL SECTION

The spin crossover compound $[\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2]$ (cooperative phase) has been recently studied for its thermal, pressure,¹⁷ and light-induced switching properties under continuous irradiation²⁰ or short pulse laser irradiation.¹⁰ The sample powder was prepared, as described in Ref. 20.

The pressure FORC was measured with our integrated temperature-pressure reflectivity platform recently fully automatized, as described in Ref. 17. The improvement of the setup was absolutely necessary due to the huge number of experimental data required by the FORC experiment that could not be done manually. The principle of pressure-FORC measurements is similar to those where the temperature¹⁵ or magnetic field²¹ are the driving forces, see Figs. 1 and 2. Doing this systematically, one obtains a set of FORCs, and the double mixed derivative of the high spin fraction with respect to the reversal pressure (p_b) and the actual pressure (p_a) is proportional to the FORC distribution (see the inset of Fig. 2). FORC distribution can be measured both on the descending or ascending branches. Our previous FORC investigations (controlled by temperature at ambient pressure)¹⁵ did not show any sizable difference between the diagrams recorded in the warming and cooling modes at the

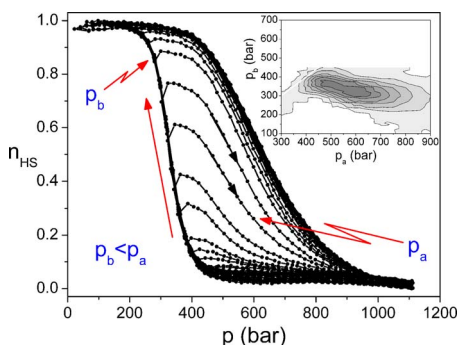


FIG. 2. (Color online) FORCs for pressure hysteresis at constant temperature $T=178$ K with returning points on the increasing branch of the major hysteresis loop—the compression mode. Inset: FORC diagram represented in the (p_a, p_b) plane.

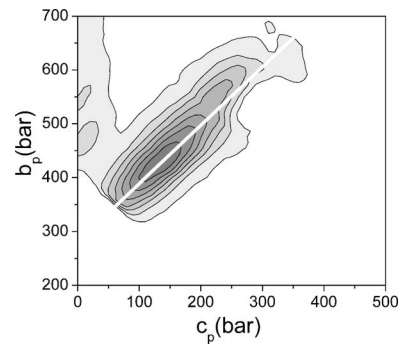


FIG. 3. FORC diagram represented in the coercivity and bias plan for the releasing mode (Fig. 1).

thermal spin transition. However, sizable differences were observed at the light-induced thermal hysteresis¹² due to the kinetic aspects inherent to the photoexcitation process.

It is worth remarking that a preliminary knowledge of the temperature-pressure phase diagram of the spin transition is needed for determining the best temperature value for a pressure-FORC investigation (in any case above the thermal hysteresis loop at ambient pressure). Also, it should be checked that the saturated state can be effectively reached. Compounds presenting a wide thermal hysteresis will not reach saturation and pressure switching in the opposite ways would require different temperatures, see Ref. 22, for example. In the present case, the hysteresis width ~ 6 K required a maximum pressure of ~ 1100 bars close to the limit of our device. Thanks to further improvements, the system now reaches 3.2 kbars, thus providing pressure-FORC access to a wider range of spin transition multiferroics.

III. RESULTS AND DISCUSSION

The experimental FORCs in releasing and compression modes have been shown in Figs. 1 and 2, respectively. For the compression mode, the derived FORC diagram is inserted in Fig. 2. For convenience we present the FORC diagrams (Figs. 3 and 4, respectively, derived from Figs. 1 and 2) in the coercivity-bias representation (p_c, p_b) previously introduced for the thermal hysteresis:¹⁵ $b_p = (p_a + p_b)/2$ and $c_p = (p_a - p_b)/2$, respectively.

A simple inspection of Figs. 1 and 2 shows a striking difference between the FORC curves in the compression and releasing modes: while those of Fig. 1 remain flat over a wide pressure interval, those of Fig. 2 exhibit an initial jump

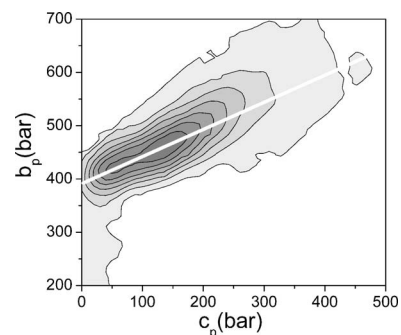


FIG. 4. FORC diagram represented in the coercivity and bias plan for the compression mode.

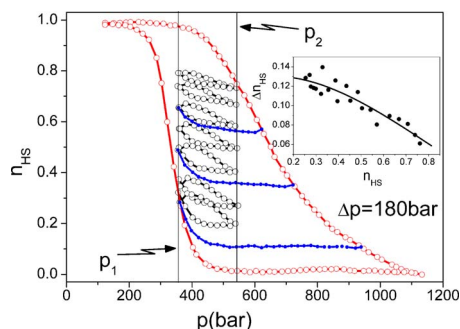


FIG. 5. (Color online) The congruence loops between pressure p_1 and p_2 , where $p_2 - p_1 = 180$ bars. For selected loops, we indicated the complete path followed by the sample. Inset: variation of the height of the minor loops as a function of the average high spin fraction.

and then rapidly decrease, far before reaching the major loop branch. The initial jump revealed to have a kinetic character, and the general shape of the set curves is rather similar to the one observed during our investigation of the light-induced hysteresis.¹² The FORC diagrams shown in Figs. 3 and 4 can also be understood in the light of a kinetic effect larger in the compression mode (Fig. 4), leading to a broader distribution in coercivity and to the presence of a reversible component.¹²

The reason why kinetic effects are enhanced in the compression mode is not clearly understood at the present time. A trivial explanation might be the *ex situ* location character of the pressure probe which may sizably delay the actual pressure variations. Specific experiments with an *in situ* probe should be designed and future experiments with further multiferroic systems will probably help clearing up this instrumental problem. An alternative explanation in terms of interdomain interactions, leading to “moving Preisach models,”²³ does not seem appropriate for creating such a huge difference between the compression and releasing modes. The kinetic effect—if its intrinsic character happens to be confirmed—might rather be considered in terms of the viscoelastic response of the material to applied stresses, for which structural investigations under pressure might help. We suspect a possible impact of the pressure-induced structural transition observed above ~ 6 kbars.²⁴ In order to illustrate the departure from a classical Preisach system, we also performed the so-called congruency test¹⁸—in pressure—see Fig. 5.

If one analyzes the problem from a more practical point of view, congruency property describes, in fact, the susceptibility of the system at a given pressure variation. A congruent system will show the same susceptibility regardless of the number of the HS state molecules in the system. Systematic experimental studies of congruency in our system have shown a noncongruent behavior with a significant decrease of susceptibility at higher HS fraction.

The standard representation in magnetism of the congruency experiment is the dependence of the difference between the maximum ($n_{\text{HS}}^{\text{max}}$) and the minimum ($n_{\text{HS}}^{\text{min}}$) high spin fraction values obtained during the pressure cycling $p_1 \rightarrow p_2 \rightarrow p_1$ as a function of the average high spin fraction during the same cycling: $\Delta n_{\text{HS}} = f(n_{\text{HS}})$, where $\Delta n_{\text{HS}} = n_{\text{HS}}^{\text{max}} - n_{\text{HS}}^{\text{min}}$ and

$n_{\text{HS}} = (n_{\text{HS}}^{\text{max}} + n_{\text{HS}}^{\text{min}})/2$. The results are inserted in Fig. 5. Even if the data are a little bit noisy, the general trend can be observed easily, decreasing Δn_{HS} with increasing high spin fraction. This departure from the congruency property also seems tightly associated with the trapezoidal shape of the major hysteresis loop.

IV. CONCLUSIONS

We presented, for the first time, a FORC investigation of the pressure hysteresis of the spin transition multiferroics [Fe(PM-BiA)₂(NCS)₂] proving that the pressure FORCs strongly differ in the compression and releasing modes. We also showed that the system is not congruent with respect to pressure variations and exhibits kinetic effects in the compression mode. Further investigations are needed.

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