



## SUPERPARAMAGNETISM IN HEXANITROFERRATES, $K_2M[Fe(NO_2)_6]$ WHERE M is Pb, Sr, Zn, Ca

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### Abstract:

Detailed variable temperature Mossbauer, Infrared, measurements and variable temperature magnetic susceptibility were carried out on  $K_2Pb [Fe(NO_2)_6]$  to investigate the electronic structure and correlate it to the observed unusual magnetic hyperfine interaction in this system. All these results are then further extended to the other systems where lead has been substituted with strontium, zinc and calcium, because of their structural similarity. This was further confirmed by detailed variable temperature Mossbauer spectral measurements on the above-mentioned systems. The transition temperature in all these systems was found to be 45 K. These results exactly match with those of  $K_2Ba[Fe(NO_2)_6]$  reported earlier. All these results indicate the existence of superparamagnetic relaxation in these types of complexes, generated as a result of nano size dimension, which is evident from the synthetic procedure adopted

**IndexTerms:** Hexanitroferrates, superparamagnetism,

### I. INTRODUCTION

In a previous report (1) it was established that the compound with a formula  $K_2BaFe(NO_2)_6$  (dipotassium barium hexanitroferrate) was found to exhibit unusual magnetic and electronic relaxational properties. This was attributed to  $^5E$  ground state of the iron ion in the high spin state which originated from the  $^5T_2$  ground state splitting into the  $^5E$  and  $^5B_2$  due to Jahn - Teller distortion. The doubly degenerate ground state of the molecule is the one responsible for the magnetic behaviour, temperature dependent Mossbauer spectral properties. In most cases the manifestation on the quadrupole coupling constant which will be temperature dependent (2). Theoretical simulations of the Mossbauer spectrum coupled with Jahn-Teller distortion (3) have never been realized experimentally especially for the six line pattern with peculiar intensity ratio of 1:2:3:2:1.

However there are few examples of  $Fe^{2+}$  systems with a quintet spin ground state showing magnetic hyperfine split Mossbauer spectra in the low temperature regime. This could be due to the various types relaxation mechanisms, such as spin lattice relaxation (4), spin -spin relaxation (5,6), superparamagnetic relaxation (7,8), and the magnetic phase transition due to a change from cubic to tetragonal phase (9,10). There is also evidence for the low value of magnetic hyperfine field compared to the free ion resulting from the significant covalency as pointed out by several authors (11,12).

Even though the high spin  $Fe^{2+}$  systems do have a high quadrupole coupling constant there are few systems in which low value is reported. The low value of the quadrupole coupling constant is attributed to the reduction in the spin orbit coupling for the  $Fe^{2+}$  ions and the Jahn-Teller distortion (11,13-15). We report here a series of Iron complexes having the general formula  $K_2M[Fe(NO_2)_6]$  where M= Pb, Sr, Zn, Ca where in we observe a low quadrupole coupling constant especially at high temperature and a magnetic hyperfine splitting at low temperature from 45 K and down. These compounds were earlier reported to have a singlet spin ground state, conclusions were purely extracted from the room temperature magnetic susceptibility (16), optical (16,17) and Mossbauer spectral studies (18). It must be mentioned here that these compounds are not crystalline, because of the

quick precipitation from the aqueous solutions, making it impossible to carry out the single crystal X-ray structure determination. The reason may be due the formation of small independent magnetic domines. This forced us to carry out a low temperature investigation using magnetic susceptibility, infrared, Mossbauer spectroscopic techniques on  $K_2Pb [Fe(NO_2)_6]$  and extend it to other systems. The EXAFS data on  $K_2Pb [Fe(NO_2)_6]$  and its interpretation were reported earlier (19).

## 2. Materials and Methods:

The compounds were prepared according to the previously reported procedure (16). The purity of the compounds was checked. Infrared spectrum at room temperature was recorded on Brucker model IF 66V Fourier transform IR spectrometer. Variable temperature IR was recorded with a Bomem single beam FT IR spectrometer. A Leybold Helium close cycle cryostat attached to a Leybold-Heracus, Veriotemp,HRI, variable temperature controller was used for the measurements. Mossbauer spectra were recorded in Canberra S-100 Mossbauer spectrometer fitted with a Wissel constant acceleration drive. The source  $Co^{57}$ -Pd (Amersham 50mCi) and the absorber was kept stationary in the Helium dewar fitted with Mylar windows. The source, absorber and the detector were carefully centered and aligned under operating conditions to ensure reliable and reproducible geometry. All the velocity calibrations were done using the natural Iron foil of 25  $\mu$  thickness. The velocity range selected was from -10 to +10 mm/sec. Measurements at variable temperature were done by using a variable temperature MD-306 bath cryostat which is of gas exchange type. The sample temperature was monitored by using a calibrated Rh-Fe sensor which is connected to the ITC-4 temperature controller. Spectra were recorded in the temperature range from 300-15K. in the absence of an external magnetic field. All the spectral patterns were fitted with a computer programme using the Lorentzian line shape unless otherwise specified. The isomer shift parameter is reported with respect to natural iron foil. Magnetic susceptibility measurements were carried out on a powder sample at a field of 1.4 T. using a SQUID in the temperature range of 4.2 K. to 300 K. The error in the temperature was  $\pm 0.2$  K. and susceptibility was within 1%. The magnetic susceptibility was corrected for the underlying diamagnetism using Pascal constants.

## 3. Results and Discussion:

**Magnetic susceptibility:** The magnetic susceptibility ( $\chi$ ) and the inverse magnetic susceptibility ( $\chi^{-1}$ ) versus temperature for the Pb compound are shown in Fig 1 A. The magnetic data for the Ba compound is already reported (1). A similar data for the other compounds with Ca, Sr, and Zn clearly confirms that there is no contribution from these ions towards magnetic susceptibility. The Mossbauer spectra and the magnetic susceptibility data of  $K_2Ba [Fe(NO_2)_6]$  down to 4.2 K have been already reported (1). It is seen that the lead salt just like its barium analogue (1) is a paramagnet down to 30 K. It undergoes a long-range ordering around 20-25 K. as predicted by EXAFS, as also supported by Mossbauer spectroscopy (vide infra). The experimental data was fitted with Bleaney-Bowers expression to extract out the information of exchange interactions. The fitting gave  $g = 3.6285$ ,  $2J = -20.1$   $cm^{-1}$  and  $\theta = -17K$ , for an S value of 2. The fit of the experimental data with a net spin  $S = 2$  is a clear indication of the fact that the ground state of the iron atom is high spin quintet in contact to the earlier suggestion of a singlet as ground state (18). A negative value of the exchange coupling constant and the  $\theta$  value reveal the presence of anti-ferromagnetic interaction. These results on the lead containing lattice are fairly close to the barium lattice having a value of  $2J = -14$   $cm^{-1}$ , and  $\theta = -1.3$  K. The long range ordering at low temperature is indicative of the superparamagnetic relaxation.

### 3.1 Variable temperature Infrared spectroscopy:

The room temperature IR spectrum of the compound  $K_2Pb[Fe(NO_2)_6]$  correlates very well with the already reported values (16). The variable temperature IR spectra are shown in Fig 1 B. The temperature dependent IR spectra show some interesting features which give additional proof for the contribution of the spin-lattice relaxation and the appearance of the hyperfine lines in the Mossbauer spectra only at low temperatures. The IR spectral lines corresponding to  $\nu_{asym}$ ,  $\nu_{sym}$  and  $\delta$  of  $NO_2$  groups become considerably sharpened especially below 50 K. as is evident from the figures, though the sharpening process on cooling is gradual throughout the temperature region. This is indicative of the long vibrational relaxation time. Since the spin lattice relaxation involves the transfer of the Zeeman energy of the spin system to phonon modes, the sharpening of the FT IR lines and the consequent formation of the hyperfine lines-again a second order process-may be interpreted as due to the decoupling of the lattice phonon modes from the electronic wave function at low temperatures, and hence the loss in efficiency of the transfer of the Zeeman energy of spin system to the phonon modes of the lattice. This increases the  $T_1$  leading to the appearance of the hyperfine lines in Mossbauer spectrum.

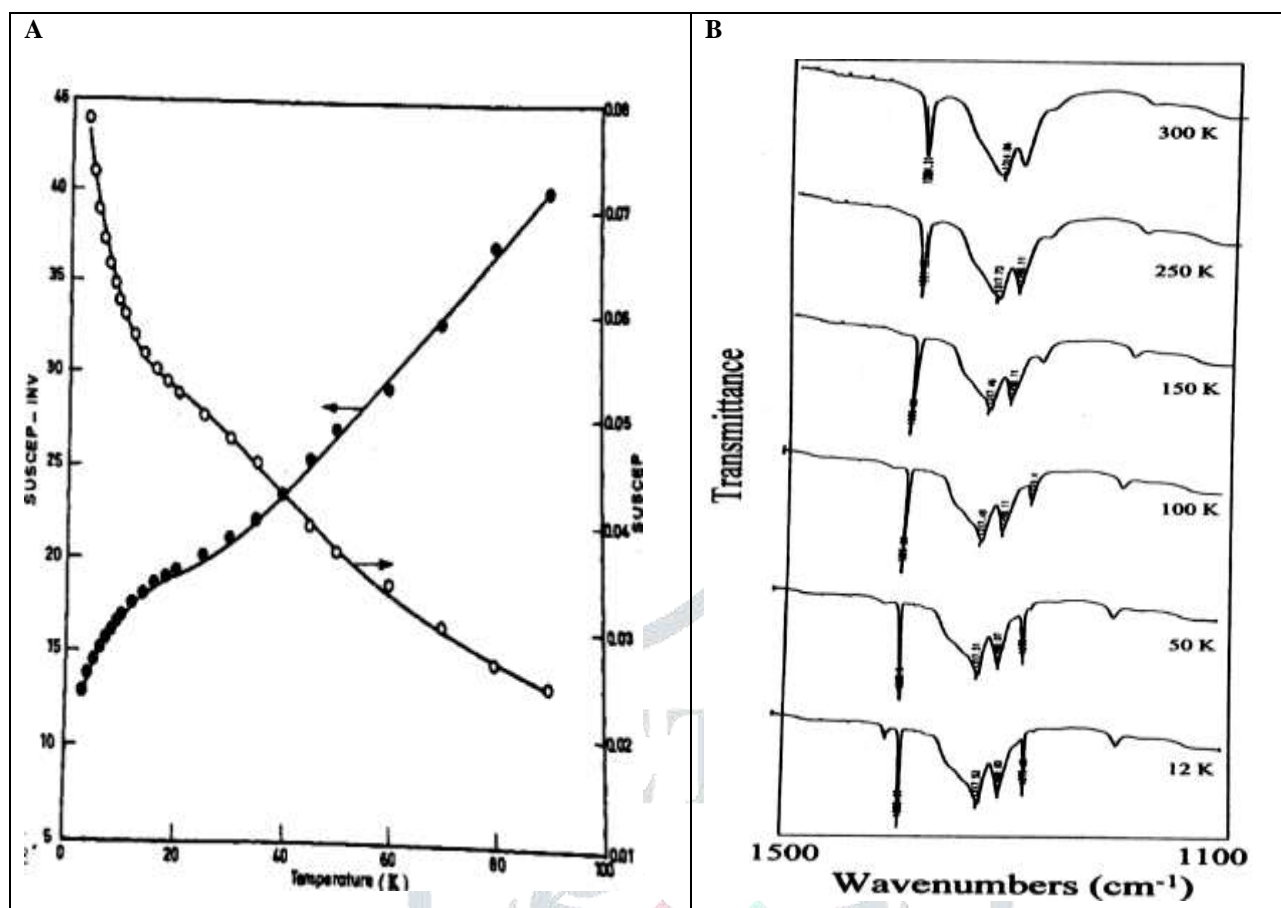


Fig 1: (A) Plot of magnetic susceptibility ( $\chi$ ) and inverse magnetic susceptibility ( $\chi^{-1}$ ) versus temperature for  $K_2Pb [Fe(NO_2)_6]$ . Experimental (●●●●●), and fitted (—) (B) Variable temperature infrared spectrum of  $K_2Pb [Fe(NO_2)_6]$ , in the range of  $1500cm^{-1}$  to  $1100cm^{-1}$ .

### 3.2 Mossbauer spectroscopy:

The Mossbauer spectrum of all the compounds with  $M=Pb, Sr, Ca$  and  $Zn$  are shown in Fig. 2 and the extracted spectral parameters of all these compounds are listed in Table 1. Since the Mossbauer spectral properties of all these compounds are similar it is only necessary to discuss the spectral properties of the  $Pb$  compound alone in detail and compare the results with other compounds.

Mossbauer spectra of the dipotassium lead hexanitroferrate recorded down to 15K are shown in Fig. 2 C. The spectral parameters derived from the simple splitting are given in Table 1. At 298 K, the spectrum is purely a quadrupole split doublet with quadrupole coupling constant of 0.62 mm/sec and the isomer shift is 0.36 mm/sec. The isomer shift value of this compound over a wide range of temperatures is rather low when compared to other normal high spin  $Fe^{2+}$  compounds. The low value could be due to the reduced spin-orbit coupling and the temperature dependence of this could be explained in terms of Jahn-Teller effect. The quadrupole coupling constants are also found to be temperature dependent, with the values constantly decreasing with decrease in temperature. The value of  $\Delta E_Q$  is almost zero at 15 K. It is very much clear from Fig. 2 C that the magnetic hyperfine interactions begin to show up at 45 K. The resolution is much better at 15 K. These spectral characteristics suggest the presence of long-range magnetic ordering. The departure of the integrated intensities from the normal ratio 3:2:1:1:2:3 for the six lines and the substantial difference in the line positions indicate the competitive nature of the quadrupole term and the hyperfine term as function of temperature in the Mossbauer Hamiltonian. This is obvious from the temperature dependent magnetic field and

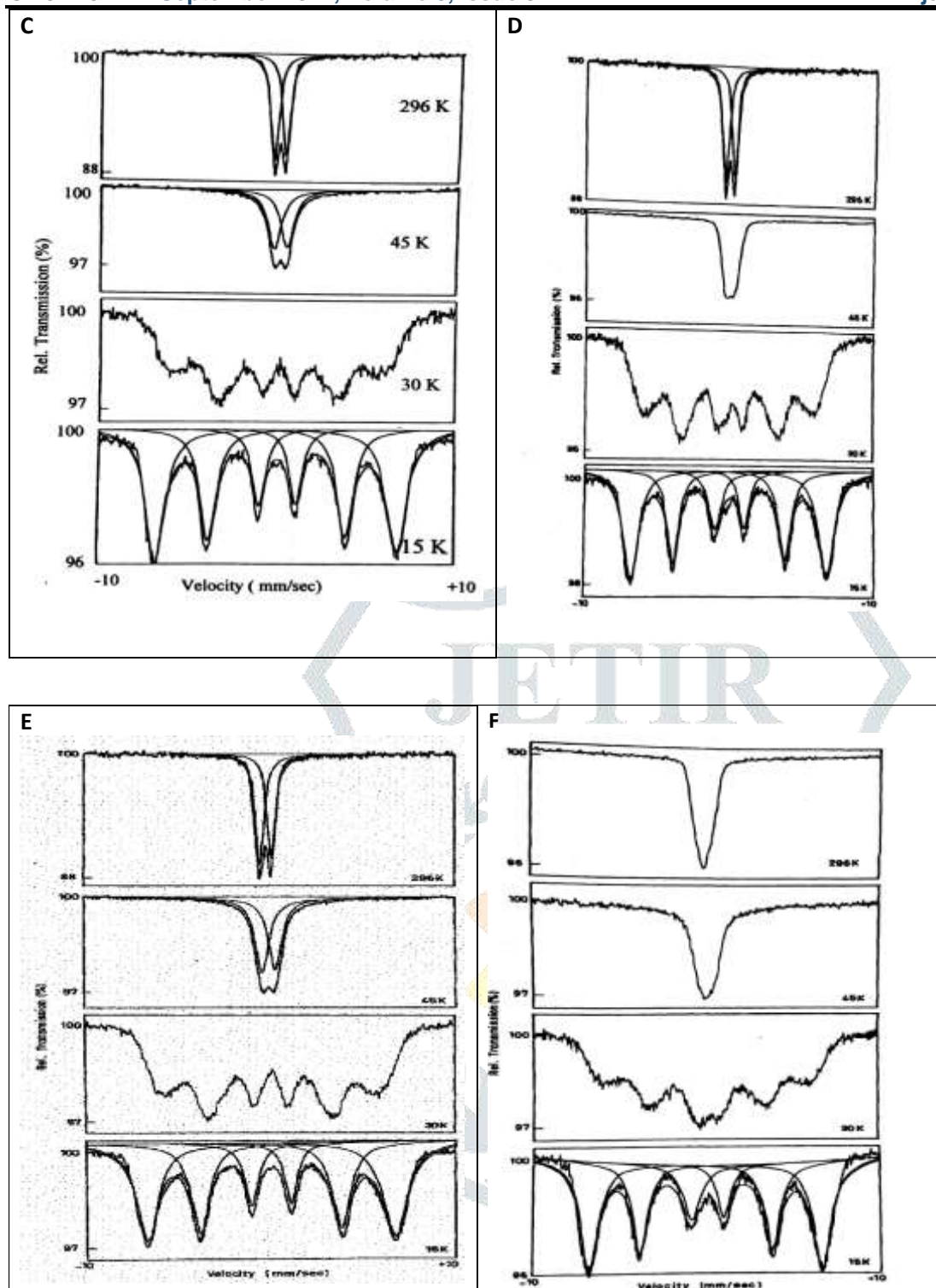


Fig 2: Variable temperature <sup>57</sup>Fe Mossbauer Spectra of polycrystalline (C) K<sub>2</sub>Pb [Fe(NO<sub>2</sub>)<sub>6</sub>] (D) K<sub>2</sub>Sr [Fe(NO<sub>2</sub>)<sub>6</sub>] (E) K<sub>2</sub>Zn [Fe(NO<sub>2</sub>)<sub>6</sub>] (F) K<sub>2</sub>Ca[Fe(NO<sub>2</sub>)<sub>6</sub>] in the absence of external magnetic field.

quadrupole coupling constant. From the line position of the spectral patterns at 15K, the magnitude of magnetic field at the site of the nucleus is calculated to be 41.6 T. It shows that there are four unpaired electrons which should definitely come from the high spin state of the iron atom with a <sup>5</sup>T<sub>2</sub> ground state. Moreover, it is clear from the spectral patterns at low temperature that the internal magnetic field is temperature dependent. This temperature dependence is a manifestation of the spin lattice relaxation due to the spin-orbit coupling of the quintet ground state, the explanation for which is exactly the same as barium analogue (1). It is

**Table 1: Variable temperature Mossbauer spectral parameters for the K<sub>2</sub>M[Fe(NO<sub>2</sub>)<sub>6</sub>] where M= Pb, Sr, Zn, Ca. All the spectra were recorded in the absence of an external magnetic field. δ (isomer shift, w.r.t. natural iron foil, mm/sec), ΔE<sub>Q</sub> (Quadrupole coupling constant, mm/sec), H<sub>int</sub> (Internal magnetic field, Tesla, T).**

T/K	Pb			Sr			Zn			Ca		
	$\delta$	$\Delta E_Q$	$H_{int}$	$\delta$	$\Delta E_Q$	$H_{int}$	$\delta$	$\Delta E_Q$	$H_{int}$	$\delta$	$\Delta E_Q$	$H_{int}$
300	0.36	0.62	0.0	0.40	0.68	0.0	0.42	0.60	0.0	0.40	0.70	0.0
	$\pm 0.02$	$\pm 0.02$		$\pm 0.02$	$\pm 0.02$		$\pm 0.02$	$\pm 0.02$		$\pm 0.02$	$\pm 0.02$	
45	0.53	0.71	0.0	0.56	0.71	0.0	0.52	0.80	0.0	0.58	0.68	0.0
	$\pm 0.02$	$\pm 0.02$		$\pm 0.02$	$\pm 0.02$		$\pm 0.02$	$\pm 0.02$		$\pm 0.02$	$\pm 0.02$	
30	0.49	0.09	35.6	0.53	0.10	35.5	0.49	0.20	35.4	0.51	0.10	35.0
	$\pm 0.02$	$\pm 0.02$		$\pm 0.02$	$\pm 0.02$		$\pm 0.02$	$\pm 0.02$		$\pm 0.02$	$\pm 0.02$	
15	0.47	0.03	41.6	0.51	0.02	42.2	0.46	0.0	41.5	0.46	0.04	41.1
	$\pm 0.02$	$\pm 0.02$		$\pm 0.02$	$\pm 0.02$		$\pm 0.02$			$\pm 0.02$	$\pm 0.02$	

interesting to note that the Mossbauer spectral results for the other compounds with Sr, Ca and Zn as divalent ion follow that of lead. We did not measure the temperature dependent susceptibility for these systems because of the similarity in the Mossbauer spectral data. The variable temperature Mossbauer spectral patterns for  $Sr^{2+}$ ,  $Zn^{2+}$ ,  $Ca^{2+}$  are shown in Fig 2 (D, E, F) respectively. These spectral patterns show similar behavior with almost similar ordering temperatures. The isomer shift and quadrupole coupling constants are found to be temperature dependent similar to that of the lead compound. The one-to-one correspondence of these compounds is especially noticeable in the Mossbauer spectral patterns at 30K and 15 K. The magnitude of the internal magnetic field calculated from the line positions, is also found to be temperature dependent. The spectral parameters extracted from the simple fitting procedure are reported in Table 1, respectively. All these experimental details show that the hexanitroferrates have similar electronic structural and relaxational properties irrespective of the counter ions. The divalent ion do not seem to play any major role except to provide the charge compensation for the  $[Fe(NO_2)_6]^{4-}$  anion which dominate the properties. A relatively larger value of the line width for all these compounds even at 15K does indicate that the relaxational processes are still not complete. Also, the orientational ordering at low temperature results in the large magnetic field.

#### 4. Conclusion:

The structure of  $K_2Pb [Fe(NO_2)_6]$  probed through the EXAFS technique indicate a distorted octahedron with respect to the Fe atom, the distortion originating from the  $NO_2$  group co-ordinated to the Fe atom (19). The positions of other atoms are in complete agreement with the earlier derived crystal structure on the basis of powder method. Though the average bond distance of 1.95 Å for Fe-N is indicative of the low spin state for the  $Fe^{2+}$ , experimental facts from susceptibility and Mossbauer spectroscopy give us a clear evidence for the  $^5T_2$  ground state of the Fe atom in  $[Fe(NO_2)_6]^{4-}$  subjected to Jahn-Teller distortion as against the prediction of the  $^1A_1$  ground state by earlier work. The orbital states must have split into a doublet and a singlet by the Jahn-Teller effect. The final states are however, made up of vibronic and spin orbit states and hence the rationale behind the observation of magnetic hyperfine interaction through relaxation mechanism explainable by Blume-Tjon theory (20). The ligand field at the iron site may be reduced by disposing all the  $NO_2$  groups in such a fashion as to reduce the  $\pi$  overlap between the ligand and the metal orbital in a distorted fashion, may be with a lower symmetry. This reduced  $\pi$ -orbital contribution to the ligand field might have facilitated the formation of high spin state for the iron atom. Also, the quick precipitation of the samples resulted in the formation of nano structures, the individual magnetic field of which are aligned in all possible direction. At low temperatures the orientational ordering of the nano structured domains and the associate superparamagnetic relaxation.

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