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Dielectric and charge transport properties of the spin crossover complex $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$

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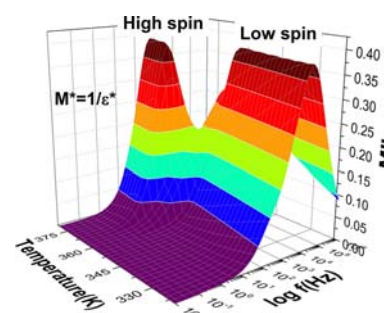
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Spin crossover compounds are considered to be a viable alternative for creating display, memory and switching devices due to the bistability of their magnetic, optical, mechanical and electrical properties. This Letter presents the study of the dielectric and transport properties of the $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ ($\text{Htrz} = 1\text{H-}1,2,4\text{-triazole}$) complex in a wide temperature and frequency range. Our results reveal a singular behavior of the dielectric modulus upon the spin transition in conjunction with the switching of the conductivity between the high spin and low spin states.



1 Introduction Spin crossover (SCO) compounds are molecular complexes or extended coordination networks of $3d^4\text{--}3d^7$ transition-metal ions in a pseudo-octahedral coordination sphere. They display a bistability of the high spin (HS) and low spin (LS) electronic configurations, which manifests in optical, electrical, magnetic and mechanical properties. The transition between the two states can be triggered by various external stimuli, such as temperature, magnetic field, pressure and light irradiation [1, 2].

Electrical transport properties of these compounds have been recently studied at microscopic [3, 4], nanoscopic [5, 6] and single molecule levels [7–12]. All these interesting findings in conjunction with the possibility to synthesize SCO compounds as thin films, nanoparticles and other nano-objects [1, 13–15] motivated us to seek for a better understanding of the charge transport phenomena

in these materials. This Letter aims to provide an in depth analysis of the electrical properties of the SCO compound $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ (**1**). This compound is very promising for electronic devices as it presents a very robust spin transition above room temperature with a hysteresis loop of about 25 K. In a previous work [3] we have revealed the dependence of the DC electrical conductivity on the spin state of **1** and we have shown that the HS form is less conductive than the LS state, contrary to the results reported by Prins et al. [6] on smaller particles. In order to bring more information about the electrical behavior of this SCO material, we have carried out a broadband AC analysis. The nanocrystalline sample (200 nm mean size, nearly spherical particles used here is the same as described in Ref. [3] as **C1**. (For more sample information see also the Supporting Information.) The powder was pressed inside a

Teflon sample holder between two stainless steel electrodes and its complex impedance was determined using a Novocontrol BDS 4000 broadband dielectric spectrometer between 320 K and 380 K in a frequency range of 10^{-2} – 10^6 Hz.

2 Results and discussion

2.1 AC conductivity The real part of the AC conductivity (σ'), recorded in the heating and cooling modes, is reported in Fig. 1. Starting from a cut-off frequency, which depends both on the temperature and the spin-state of the compound, the AC conductivity obeys a power law at high frequencies. This behaviour is characteristic to low mobility, disordered systems where σ' obeys the “universal dielectric response (UDR)”:

$$\sigma'(\omega) = \sigma_{\text{dc}} + Af^n = \sigma_{\text{dc}} \left[1 + \left(\frac{f}{f_c} \right)^n \right], \quad (1)$$

where n ($0 < n \leq 1$) was interpreted by means of many-body interactions among charge carriers [16]. The cut-off frequency f_c can be assimilated with the charge hopping frequency [17]. As shown in Fig. 1c, the values of exponent n are very close (0.47 and 0.44, respectively) in the HS and LS states, which indicates that the conduction mechanism at high frequencies is probably the same in the two-spin states.

Below f_c , the AC conductivity increases slowly with increasing frequency depending on the spin state. In the LS state, $\sigma'(f)$ exhibits more clearly a step-like increase in the range 1 – 10^3 Hz, which can be a signature of a Maxwell–Wagner-type contribution of depletion layers at grain boundaries of the powder. This behaviour is clearly ob-

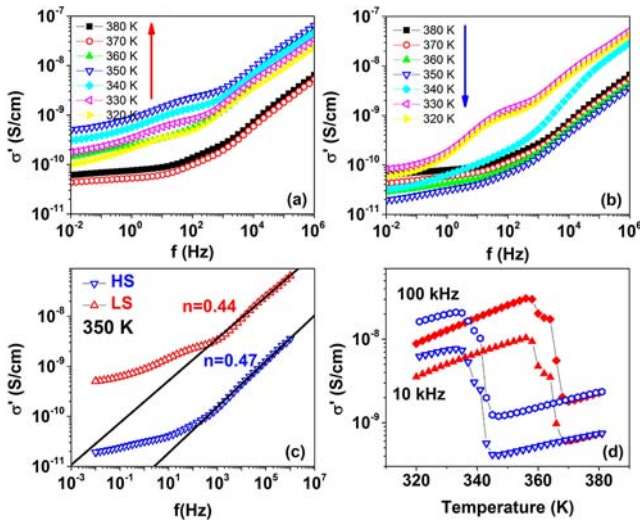


Figure 1 Real part of the AC conductivity of **1** as a function of frequency, measured at selected temperatures in the (a) heating and (b) cooling modes. (c) Conductivity spectra at 350 K in the HS and LS states. The fits of the high-frequency part of the spectra are also shown. (d) Thermal hysteresis of σ' recorded at 10 kHz and 100 kHz.

served in Fig. 1b at 320 K and 330 K in the LS state. In this case the interfacial polarization effectively reduces the conductivity by one decade at low frequencies. The values of the AC conductivity measured at 10^{-2} Hz are in good agreement with those obtained from our previous DC electrical measurements ($\sim 10^{-9}$ S cm $^{-1}$ at 355 K, heating mode) [3]. The important finding here is that the electrical conductivity displays a spin state dependence in the whole studied frequency range, showing a thermal hysteresis loop (Fig. 1d) characterized by the same switching temperatures (LS to HS at 367 K upon heating, HS to LS at 342 K upon cooling) as detected in magnetic and optical measurements [3]. The conductivity of the LS state exceeds by more than one order of magnitude that of the HS state both in the DC and AC regimes, which is of primary importance for applications requesting fast data rate.

2.2 Dielectric permittivity and electrical modulus

Figure 2 displays the frequency dependence of the real part of the complex dielectric permittivity, which is a measure of stored energy. The region at low frequencies is dominated by an important dispersion caused by electrode polarization. The measured value of ϵ' increases with decreasing frequency at each temperature. The temperature dependence of the dielectric permittivity (real part) exhibits a wide hysteresis loop of 25 K (see the inset of Fig. 2) and the value of the permittivity (recorded at 1 kHz) decreases by 5 times when the compound is switched from the LS to the HS state. The strong decrease of the permittivity in the HS state is rather unusual in SCO compounds [18] and should be linked to the charge transport properties of this complex. This important variation of the permittivity makes **1** an attractive material for electronic capacitive storage devices.

For a better understanding of the relaxation process with respect to the material properties we have considered the electric modulus formalism ($M^*(f) = 1/\epsilon^*(f)$). This approach enables us to circumvent the effects of electrode and space charge polarization, which might mask the dielectric relaxation. The frequency dependence of M'' re-

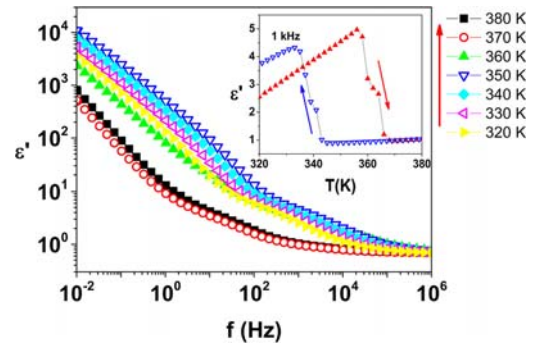


Figure 2 Real part of the dielectric permittivity of **1** as a function of the frequency, measured at selected temperatures in the heating mode. The inset shows the thermal hysteresis loop of ϵ' recorded at 1 kHz.

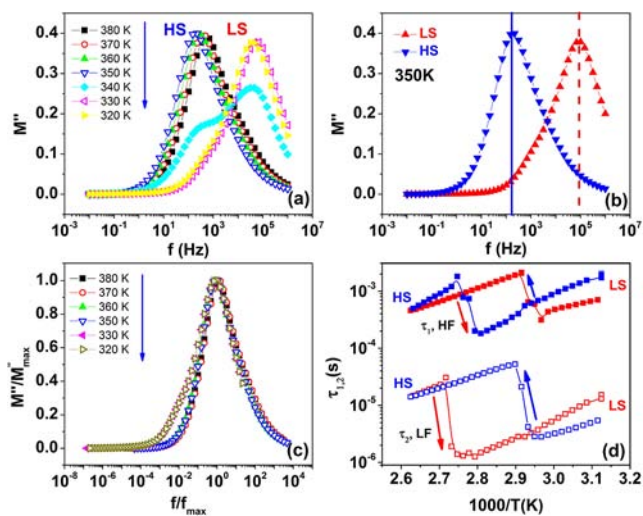


Figure 3 (a) Dielectric loss modulus M'' of **1** at selected temperatures in the cooling mode. (b) Spin state dependence of M'' at 350 K. (c) Plot of the normalized loss modulus (M''/M''_{\max}) as a function of the reduced frequency (f/f_{\max}). (d) Thermal hysteresis loops of the HN relaxation times ($\tau_{1,2}$).

corded at different temperatures reveals two loss peaks, which characterize the two spin states (Fig. 3a). Remarkably, when switching the material from the LS to the HS state the loss peak frequency exhibits a spectacular drop by about three orders of magnitude (Fig. 3b). When the transition is in progress (for example at 340 K) the two loss peaks co-exist. This is the sign of a phase separation as expected for a first-order phase transition. Figure 3(c) displays the scaled electric modulus vs. the scaled frequency. We observe a perfect overlap of the scaled relaxation peaks in a given spin state, but a significant difference exists between the HS and LS curves. This means that the dynamical processes are the same at each temperature in a given phase, but change with the spin state of the compound.

A Havriliak–Negami (HN) empirical equation was used to describe the frequency dependence of the loss peak as follows [19]:

$$M^* = M' + iM'' = M_{\infty} - \frac{M_{\infty} - M_0}{[1 + (i\omega\tau_M^*)^{\alpha}]^{\beta}}, \quad (2)$$

where M_{∞} , M_0 , are the modulus at the high and low frequency limits, respectively, τ_M is the HN characteristic relaxation time, while the parameters α and β describe the distribution of relaxation time. We have fitted the experimental loss modulus data by two HN functions. The plot of the two HN (mean) relaxation times, τ^1 and τ^2 , as a function of the reciprocal temperature (Fig. 3d) reveals the same thermal hysteresis as observed also for σ' and ε' . The same temperature behaviour was obtained for the other HN parameters ($\Delta M = M_{\infty} - M_0$, α and β) as well. While a quantitative link is difficult to establish between the relaxa-

tion and charge transport phenomena it is tempting to correlate the drop of the relaxation frequency with that of the conductivity, i.e. in the HS state the electrical conduction mechanism is governed by a long range hopping process (lower frequency), while the charge transport in the LS state occurs by a short range hopping (higher frequency) mechanism. Similar to what was reported for other phase change materials [20] the higher hopping frequency and thus the higher conductivity of the LS form might be related to the significant stiffening of the crystal lattice in this phase.

3 Conclusions In conclusion, we observed an unprecedented behavior of the complex permittivity upon the spin transition in the compound $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$. We have shown that the dielectric relaxation frequency is strongly dependent on the spin state of the complex, denoting different relaxation mechanisms, which could be related to the structural changes (lattice deformation) between the two spin states. The AC and DC conductivities as well as the dielectric constant and the dielectric relaxation frequency exhibit a hysteretic behavior, with an important drop when going from the LS to the HS state. All these observables represent a different facet of the charge carrier dynamics in the system, conferring unique properties to this material and making it interesting for threshold switching and memory devices as well as thermally variable capacitors. The observed interplay between the molecular spin states and electrical properties call also for magneto-transport studies, which are in progress.

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