Piezoresistive Effect in the $[Fe(Htrz)_2(trz)](BF_4)$ Spin Crossover Complex

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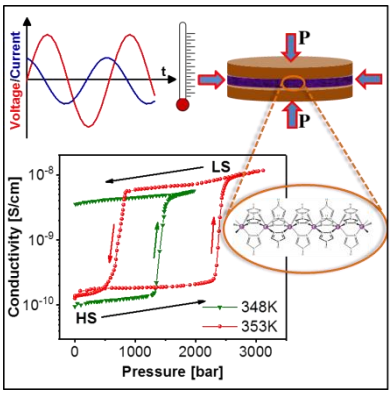
ABSTRACT: We report on the effect of hydrostatic pressure on the electrical conductivity and dielectric permittivity of the $[Fe(Htrz)_2(trz)](BF_4)$ (Htrz = 1H-1,2,4, triazole) spin crossover complex. Variable temperature and pressure broadband impedance spectrometry revealed a piezo-resistive effect of more than one order of magnitude for pressures as low as 500 bar, associated with a large pressure-induced hysteresis of 1700 bar. The origin of the piezo-resistive effect has been attributed to the pressure induced spin-state switching in the complex and the associated P,T phase diagram was determined.



Bistable molecular complexes that can exist in two interchangeable states can act as switches under external stimuli. In this context, molecular spin crossover (SCO) compounds present a special interest due to their response to various external stimuli that might lead to a wide range of potential applications.[1,2] In these systems, the electronic configuration of the metal can be conveniently switched from the so-called low spin (LS) to a high spin (HS) electronic configurations in response to an external stimulus such as temperature, pressure, light irradiation, etc.[3] This spin-state switching leads to a pronounced change of various material properties, including optical, magnetic, mechanical, and electrical characteristics. Since bulk SCO materials are in general highly insulating[4] their electrical properties have been largely ignored and received growing interest only in the past few years – in parallel with the emergence of nanoscale SCO materials[5]. To date, most of the studies have been focused on the thermal bistability of the electrical properties.[4-12] A few studies have evidenced also remarkable switching of electrical transport properties under electrical stimuli[12-15] and light irradiation.[16-17]

Pressure is also a very useful parameter to control the spin-state of these materials. Indeed, it is well known that due to the substantial volume difference between the LS and HS states (typically between 1 – 10 % unit cell volume change), an applied pressure stabilizes the LS state.[3] In general, a ca. 10 – 20 K upshift of the spin transition is observed under an applied hydrostatic pressure of 1 kbar.[18-23] This effect could be very useful in order to 'push' the spin transition to higher temperatures where the thermal activation of charge carrier mobility should allow for higher conductivity. Besides the upshift of the spin transition temperature, pressure is also expected to increase the conductivity by itself due to the increasing density of the material, which is expected to enhance the charge carrier hopping rates.[24] In addition, at constant temperature an applied pressure can also trigger the spin transition leading, in some cases, to a pressure induced bistability.[25-26]

To explore these potentially very useful phenomena we carried out conductivity measurements as a function of temperature and pressure on the benchmark $[Fe(Htrz)_2(trz)](BF_4)$ (**1**) spin crossover complex. At atmospheric pressure this compound exhibits a pronounced conductivity switching when cycled around the spin transition temperature[6], a phenomenon which was exploited in a series of micro- and nanoelectronic test devices.[7-9,12]

Magnetic measurements were used to confirm the thermal SCO in the polycrystalline sample around 365 K as well as the well-known thermal hysteresis of about 40 K width[27] (see Fig. S2 – S3 in the Supporting Information, SI for the magnetic data and other sample characterization details). The conductivity, the electric modulus and the dielectric permittivity of the sample recorded at atmospheric pressure at different temperatures are also reported in the SI (Fig. S4-S6) and are comparable with the data recorded on the same complex previously[28]. It should also be noted that, prior to the measurements under pressure, the good reproducibility of the spin transition was controlled over 8 consecutive thermal cycles (Fig. S7). For high pressure measurements the powder was slightly pressed to a thickness of 1.96 mm between two parallel electrodes of 15 mm diameter within a Teflon ring and sealed by epoxy glue so that no losses or changes in the thickness of the sample may occur. The electrodes were connected by flexible leads to high-pressure feed-through connectors in a commercial high pressure cell (Novocontrol Technologies). Silicone oil was used as a pressure transmitting medium and the electrode assembly, including the inner powder layer, was fully immersed in oil to provide hydrostatic conditions. It was confirmed that the silicone oil has negligible effect on the measured electrical signal. Pressure can be changed in small steps of ca. 10 bar up to 3 kbar both on compression and decompression. A schematic of the high pressure setup is presented in the SI (Fig. S1). Of particular inter-

est of the setup is the possibility to carry out pressure as well as temperature scans at fixed temperature and pressure values, respectively, providing a rather unique tool to explore the P,T phase diagram along different paths in a finely resolved manner. The complex impedance at fixed P, T values was measured using a Novocontrol BDS40 broadband dielectric spectrometer by sweeping the frequency of the applied ac voltage (V_{rms} = 1 V) between 0.1 Hz and 1 MHz.

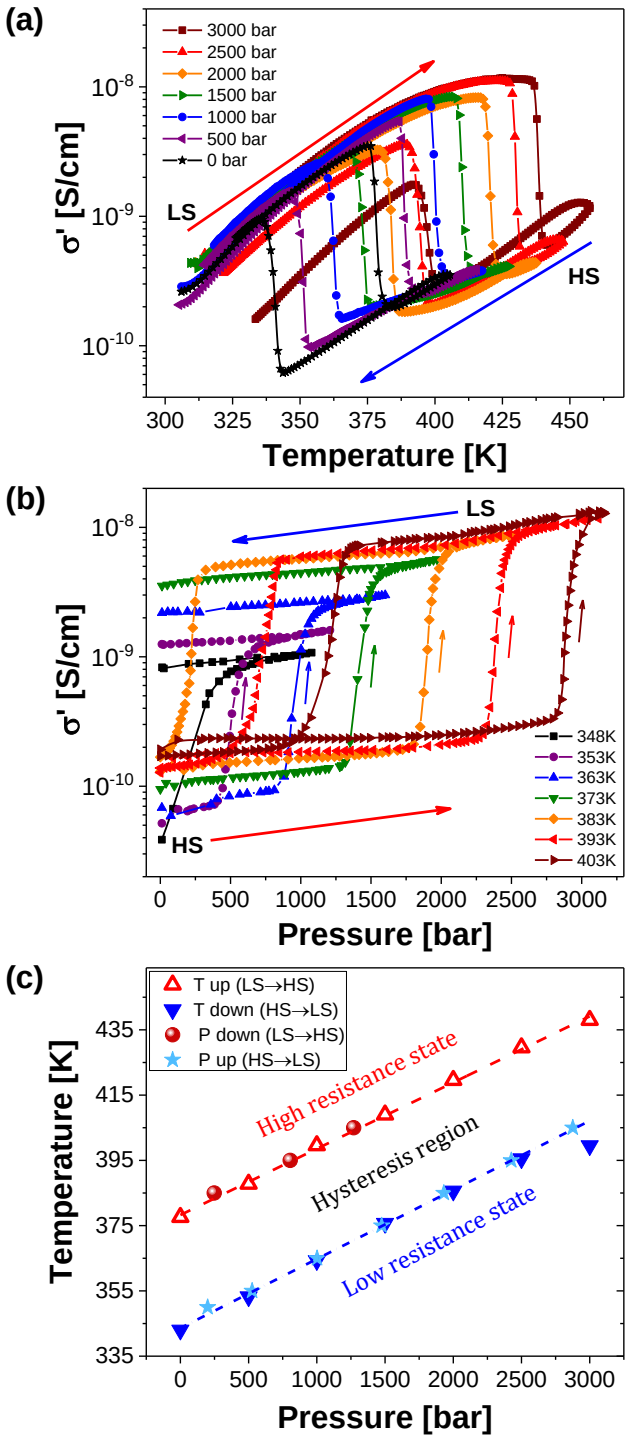


Figure 1. (a) Temperature dependence of the real part of the AC conductivity recorded at 10 kHz at various applied pressures, (b) pressure dependence of the electrical conductivity at 10 kHz recorded at various temperatures and (c) the phase diagram in P,T coordinates.

Figure 1a shows the temperature dependence of the real part of the AC conductivity (10 kHz) recorded between 300 and 450 K at fixed pressure values. The electrical conductivity displays a spin state dependence with a thermal hysteresis loop and a more conducting LS state. By applying an external pressure a progressive shift of the thermal hysteresis loop toward higher temperatures is observed. When going from 1 atm and 3 kbar the barycenter of the hysteresis is displaced from 355 K to 415 K, while the hysteresis width (~39 K) remains nearly constant throughout the whole pressure range.

Figure 1b displays complementary experiments wherein the conductivity was measured at constant temperature values while sweeping the pressure between 1 atm and 3 kbar. For each curve, the temperature was first raised above 410 K, so that the sample switches to the HS state in order to make possible to switch it back to the LS state by increasing the pressure. When the pressure is applied at a temperature above the LS→HS transition temperature this leads to piezo-hysteresis loops, whose width is virtually constant (~1680 bar). On the other hand, when the pressure is applied within the thermal hysteresis region a piezoresistive switching effect is obtained, characterized by a sharp remnant drop of the resistance of more than one order of magnitude within a pressure range of ca. 500 bar. Obviously the origin of this remarkable piezo-resistive effect is related to the pressure-induced spin-state switching properties of the SCO complex **1.** This can be better appreciated in the P-T phase diagram shown in Figure 1c, which was constructed using both temperature and pressure scan data. The perfect overlap between these data points highlights the outstanding stability of the spin transition during repeated cycling at high temperatures (up to 435 K) and high pressures (up to 3 kbar) simultaneously. Piezoresistive switching is possible within the hysteresis region, which is delimited by the coexistence lines. The slope of the cooling/compression coexistence line is ca. 21.2 ± 0.5 K/kbar, while that of the heating/decompression line is 20.9 ± 0.4 K/kbar. The observed pressure induced shift of the spin transition is somewhat lower than that reported previously for the same SCO complex studied by magnetic methods (29 ± 7 K/kbar)[29], but falls in the typical range expected for ferrous SCO complexes.[19] On the other hand, the virtually constant hysteresis width up to 3 kbar is a less common effect. In fact, for most of the studied SCO compounds, the hysteresis width decreases with increasing pressure. In the case of **1**, the Clapeyron slope can be estimated as $dP/dT = \Delta S/\Delta V = 28 \pm 3$ K/kbar on the basis of reported entropy[27] and volume[30] changes associated with the SCO. The conventional mean-field Ising-like model of SCO[31] predicts also a linear increase of the transition temperature at a rate of 25 K/kbar, which is in reasonable agreement with the experiment. On the other hand, this theory predicts a monotonous decrease of the hysteresis width to 20 K at 3 kbar (see the SI for more details on the model), which is not observed in our data. As discussed in ref. 32, this discrepancy between experiment and theory is likely to occur due to the anharmonicity of the lattice and, in particular, the volume dependence of the bulk modulus.

Remarkably, the conductivity in the LS state exceeds with more than one order of magnitude that in the HS state throughout the whole range of applied pressures. The switching amplitude $(\sigma'_{LS}-\sigma'_{HS})/\sigma'_{HS}$ slightly increases with pressure from ~15 (1 atm) to ~30 (3 kbar). This might be explained by an increase of the thermal activation energy of the conductivity in the HS state under pressure, while it remains nearly unchanged in the LS state (see Figs. S8-S9 in the SI). Another important finding is the significant increase of the conductivity of the sample near the spin transition for an applied external pressure of 3 kbar. As it can be inferred

from Figure 1a the main contribution to this pressure-induced enhancement of the conductivity comes from the upshift of the spin transition temperature which, in turn, leads to an increased thermal activation of the charge transfer. Nevertheless a clear intrinsic pressure effect on the conductivity can be also denoted in the isothermal curves in Figure 1b. Similar to that observed in organic materials[24], this latter effect most likely finds its origin in the enhanced overlap of the molecular orbitals under pressure leading to higher charge carrier mobility (hopping rate).

The pressure effect on the dielectric properties has been also investigated. Figure 2a displays the pressure dependence of the real part of the dielectric permittivity recorded at selected temperatures (see also Fig. S12 for the temperature scans at fixed pressures). Similar to the conductivity data, ε' displays a pressure-induced hysteresis for temperatures above the hysteresis region, while a pressure-induced switching of ε' can be obtained inside the hysteresis. Contrary to the behavior of σ', the switching amplitude of the dielectric constant $(\varepsilon'_{LS}-\varepsilon'_{HS})/\varepsilon'_{HS}$ increases considerably when increasing the pressure. To better understand the origin of this phenomenon the data were also analyzed in the electric modulus formalism ($M^* = 1/\varepsilon^*$).[28] The data shown in Figure 2b and Fig. S12 suggest that the observed variation of ε' is not an intrinsic property of our sample, but most likely related to a higher contribution from the electrode and interface polarization effects at high pressure and temperature values. The modulus data also gives access to the characteristics of the charge carrier relaxation processes in the two spin states. Figures 2c and 2d show the frequency dependence of the imaginary part of the electrical modulus M" during the compression and decompression process, respectively. One can observe loss peaks around 30 Hz and 30 kHz characteristic of the HS and LS states, respectively. As it was discussed in ref. 33, the higher relaxation (i.e. hopping) frequency in the LS state is perfectly in line with the higher conductivity of this phase. One can depict also a slight shift of the relaxation peaks (in a given spin state) towards higher frequencies, which can be also correlated with the pressure induced increase of the conductivity observed in Fig. 1b. Hence the pressure effect on the conductivity can be interpreted as an increase in charge carrier mobility.

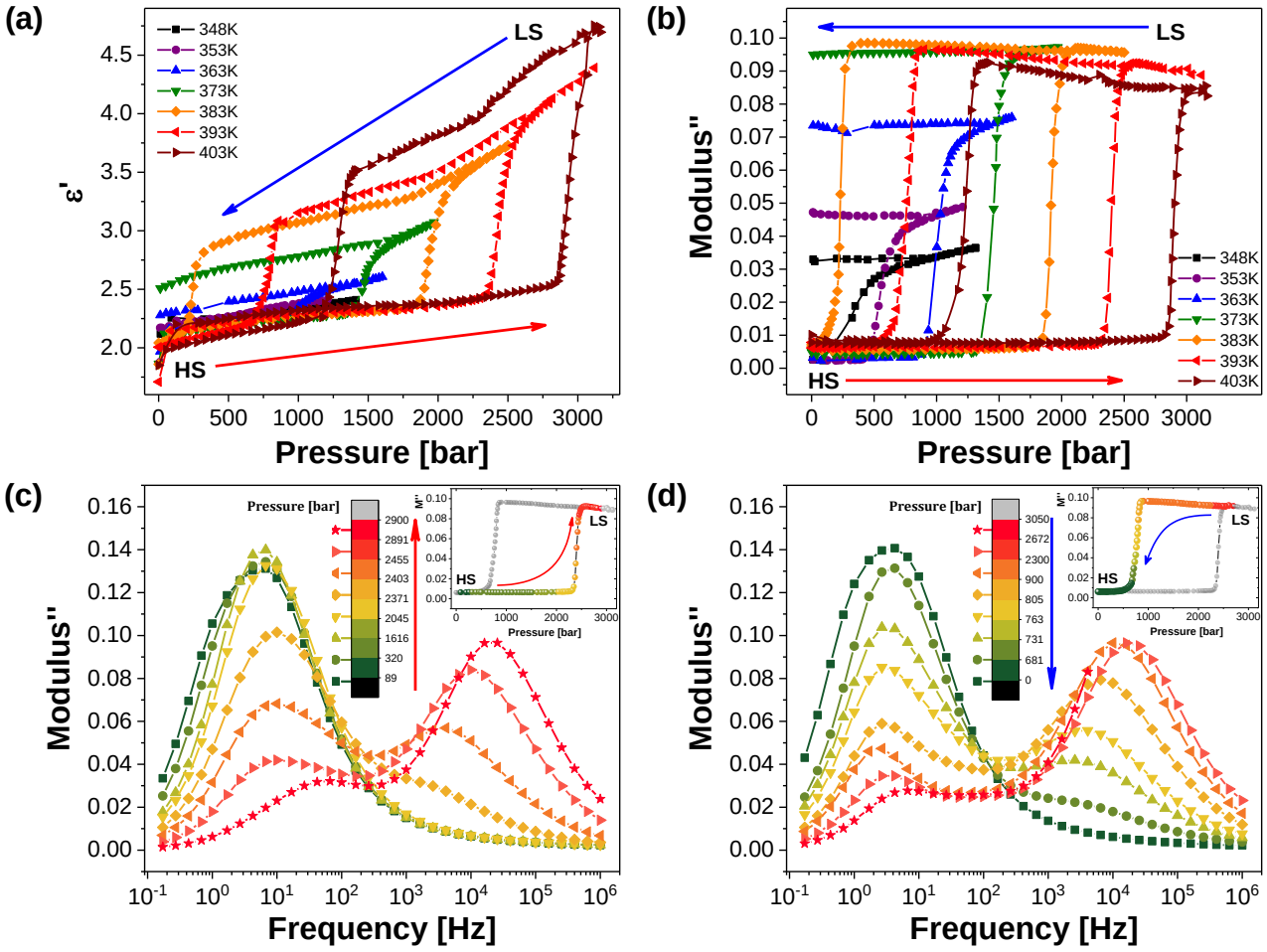


Figure 2. Pressure dependence of (a) the dielectric permittivity (real part) and (b) the electric modulus (imaginary part) recorded at 10 kHz for various temperatures. (c-d) Frequency dependence of the imaginary part of the electrical modulus recorded at 393 K for various pressure values in the loading and unloading modes. Inset: corresponding pressure hysteresis at 10 kHz

In summary, we observed a significant pressure-induced increase of the conductivity in the spin crossover complex $[Fe(Htrz)_2(trz)](BF_4)$ as well as a pronounced piezoresistive effect at the spin transition, accompanied by a large piezo-hysteresis loop. These results open up new perspectives for technological applications such as pressure sensors and actuators with electrical output.

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Supporting Information Available:
The SI section contains details about the high pressure experimental setup as well as details regarding synthesis and characterization, magnetic properties and dielectric measurements under varying frequency, pressure, temperature and time of the sample. A theoretical study based on the Ising-like model is also presented.

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