Analysis of phase transitions in spin-crossover compounds by using atom – phonon coupling model

A Gîndulescu¹,², A Rotaru², J Linares¹, M Dimian², and J Nasser³
¹GEMaC, CNRS-UMR 8635, Université de Versailles St. Quentin en Yvelines, 78035 Versailles, France
²Stefan cel Mare University, Electrical Engineering and Computer Science, Suceava, Romania
³Lab. LISV, Université de Versailles St. Quentin en Yvelines, 78035 Versailles, France
E-mail : jlinares@physique.uvsq.fr, aurelian.rotaru@gmail.com

Abstract. The spin – crossover compounds (SCO) have become of great interest recently due to their potential applications in memories, sensors, switches, and display devices [1-3]. These materials are particularly interesting because upon application of heat, light, pressure or other physical stimulus, they feature a phase transition between a low-spin (LS) diamagnetic ground state and a high-spin (HS) paramagnetic state, accompanied by color change. The phase transition can be discontinuous (with hysteresis), in two steps or gradual. Our analysis is performed by using the atom – phonon coupling (APC) model which considers that neighboring molecules are connected through a spring characterized by an elastic constant depending on molecules electronic state. By associating a fictitious spin to each molecule that has -1 and +1 eigenvalues corresponding to LS and HS levels respectively, an Ising type model can be developed for the analysis of metastable states and phase transitions in spin-crossover compounds. This contribution is aimed at providing a review of our recent results in this area, as well as novel aspects related to SCO compounds behavior at low temperature. In the framework of the APC model, we will discuss about the existence of metastable and unstable states, phase transitions and hysteresis phenomena, as well as their dependence on sample size.

1. Introduction

The spin – crossover compounds (SCO) have become of great interest recently due to their potential applications in memories, sensors, switches, and display devices [1-3]. These materials are particularly interesting because upon application of heat, light, pressure or other physical stimulus, they feature a phase transition between a low-spin (LS) diamagnetic ground state and a high-spin (HS) paramagnetic state, accompanied by color change. The phase transition can take a variety of shapes depending on the material characteristics.

Spin crossover phenomena occurs in some octahedrally coordinated transition metal compounds with 4 to 7 electrons in the 3d orbital. As a consequence of the splitting of the energy of d orbitals into the $t_{2g}$ and $e_g$ sets in a ligand field, octahedral complexes may exist in high or low spin states. The transition takes place due to the competition between $\delta$ and $\Pi$, where $\delta$ is the splitting energy between the $t_{2g}$ and $e_g$ orbitals and $\Pi$ is the spin pairing energy (see figure 1).
The spin crossover or spin transition between the two states of a SCO leads to different physical properties of the systems such as magnetic, optic, structural and vibrational which can be determined using a very wide range of characterization techniques: structural characterization, magnetic susceptibility measurements, X-Ray diffraction, Raman spectroscopy, infrared and UV-visible spectroscopy, calorimetric, reflectance and ellipsometry measurements and optic microscopy [4-6]. While in the LS state we can talk about a diamagnetic material, in the HS state the compound is paramagnetic. The transition might be followed by a color change of the material. Most of the SCO found in LS state have a pink or violet color, while in the HS state they are colorless, pale yellow or white.

According to the type and the intensity of the interactions between the molecules, the SCO compounds present different types of spin transition, with or without hysteresis. The transitions with hysteresis present a considerable industrial interest, due to their applicability, for example, in information storage. The presence of hysteresis may be associated with the presence of very strong long-range interactions within the solid or with a change of crystallographic phase (in which case the system is called strongly cooperative).

The article is aimed at providing a review of our recent results in this area as well as novel aspects related to SCO compounds behavior at low temperature. The first part will introduce the Ising model and its applicability to describe SCO, followed by a short presentation of the atom-phonon coupling (APC) model. The third section presents the role of the parameters in the APC model. Next sections are dedicated to relaxation dynamics in SCO, the size effect on their behaviour and a low temperature analysis of obtained metastable and unstable states.

2. The Ising model

2.1. Configuration diagram

The configuration diagram representing the variation of the potential energy $E$ in function of the Fe-ligand distance for the case when the compound is in the HS state, respectively in the LS state is shown in figure 2. The energy difference between the two states is given mainly by the ligand field force around Fe(II). The variation of the Fe-ligand field leads to a transition between the LS state and HS state.
2.2. Thermodynamic aspects

As we mentioned earlier the interactions between the molecules (intermolecular interactions) play an important role in the phase transitions and influence the shape of the graphical representation of the high spin fraction with the variation of the temperature. In the case in which the hysteresis is present (figure 3) the system’s response is going to follow two different paths when the sample is heated and cooled. In the figure $T_{1/2}^\uparrow$ is the transition temperature in heating, $T_{1/2}^\downarrow$ while is the one in cooling. The hysteresis width is given by:

$$\Delta T = T_{1/2}^\uparrow - T_{1/2}^\downarrow$$

so for a given temperature that is comprised between the two temperatures defined earlier, the system can be either in the HS state, either in the LS state, depending on its previous state. If $N_{HS}$ and $N_{LS}$ are the number of molecules in HS state, respectively LS state, we can characterize the macroscopic state of our system using a parameter called the high spin fraction, defined as $n_{HS} = N_{HS}/(N_{HS}+N_{LS})$.

In order to study the behavior of SCO, a theoretical approach is used, in which to each spin we associate a fictitious operator $\langle \sigma \rangle$ with two eigenvalues: +1 for the HS state and -1 for the LS state.
If we consider that molecules do not interact with each other, the energy of a molecule is given by:

$$E = \pm \frac{\Delta}{2},$$

where $\Delta$ is the energy difference between the minimal energies of the two states, the minus sign corresponding to the LS state, while the plus is for the HS state. Taking into account the Boltzmann law and the degenerescences for the two states $g_{LS}$ and $g_{HS}$ the “mean” state of a molecule at a certain temperature is given by:

$$<\sigma> = \frac{-g_{LS} \exp(\beta \times \Delta/2) + g_{HS} \exp(-\beta \times \Delta/2)}{g_{LS} \exp(\beta \times \Delta/2) + g_{HS} \exp(-\beta \times \Delta/2)},$$

where $\beta = \frac{1}{k_B T}$

or

$$<\sigma> = \frac{r \exp(-\beta \times \Delta) - 1}{r \exp(-\beta \times \Delta) + 1}$$

if we consider $r = \frac{g_{HS}}{g_{LS}}$.

We consider $N$ is the total number of molecules, $N_{HS}$ the number of molecules in the HS state, we can define the high spin fraction $n_{HS}$:

$$<\sigma> = \frac{N_{HS} \times 1 + (N - N_{HS}) \times (-1)}{N} = n_{HS} - (1 - n_{HS})$$

from which, $n_{HS}$, is given by:

$$n_{HS} = \frac{<\sigma> + 1}{2}$$

If we consider that the molecules are interacting with each other, the term that describes in a phenomenological manner the interaction between the molecules (i) and (j) has the following form:

$$- J \sigma_i \sigma_j.$$ If the variable $J$ is positive then the energy $- J \sigma_i \sigma_j$ is minimal because $\sigma_i$ and $\sigma_j$ have the same value being in the same state. Therefore the total energy of the system for a number of $N$ molecules is given by:

$$\frac{\Delta}{2} \sum_{i=1}^{N} \sigma_i - \sum_{i<k} J \sigma_i \sigma_j$$

where the first sum takes into consideration all the molecules, while the second one refers to the pairs between neighboring molecules.

We apply the mean field approximation technique in order to find the average value of $\sigma$. For this we consider a particular molecule (i) isolating in equation (7) the part where this molecule interferes:

$$\frac{\Delta}{2} \sigma_i - \sigma_i \sum_{j \text{neighboring} \text{molecules}} J \sigma_j$$

or

$$\frac{\Delta}{2} \sigma_i - \frac{1}{2} \sum_{j \text{neighboring} \text{molecules}} J \sigma_j$$

$$\sigma_i$$
From equation (9) we can consider that the molecule is under the influence of an “effective” energy gap:

\[ \Delta_{\text{eff}} = \Delta - 2 \sum_{j, \text{neighboring molecules}} J_{ij} \sigma_j \]  

so the energy of the molecule (i) is given by the following formula:

\[ \frac{\Delta_{\text{eff}}}{2} \hat{\sigma}_i \]  

The mean field approximation neglects the fluctuations in time of this \( \Delta_{\text{eff}} \) replacing it with its average value:

\[ \langle \Delta_{\text{eff}} \rangle = \Delta - 2 J p \langle \sigma \rangle, \]  

where \( p \) is the number of the nearest neighbors of a lattice site. In the mean field approximation each molecule of the crystal is submitted only to the action of the effective field, so we have again \( N \) independent molecules, placed in a uniform field, but this time it depends on the average value \( \langle \sigma \rangle \) of the system. In the mean field approximation the energy of the molecule (i) can be calculated using the formula presented below:

\[ E = \left[ \frac{\Delta - 2 J p \langle \sigma \rangle}{2} \right] \hat{\sigma}_i \]  

Therefore the energy of a molecule found in the LS state is \( E_{\text{LS}} = -\frac{\Delta - 2 J p \langle \sigma \rangle}{2} \), while for the one found in the HS state has the following form:

\[ E_{\text{HS}} = \frac{\Delta - 2 J p \langle \sigma \rangle}{2} \]  

giving an average value of \( \langle \sigma \rangle \):

\[ \langle \sigma \rangle = \frac{r \exp \left( -\beta \frac{\Delta - 2 J p \langle \sigma \rangle}{2} \right) - 1}{r \exp \left( -\beta \frac{\Delta - 2 J p \langle \sigma \rangle}{2} \right) + 1} \]  

3. The atom-phonon coupling model

Although the Ising model offers an accurate description of the main characteristics of spin crossover phenomena, along with the models introduced by Wajnflasz and Pick [7] and Bousseksou et al. [8] do not offer an explanation on the physical origin of the intermolecular interactions and the exchange like constants are just phenomenological parameters. In order to be able to describe the interactions as well as the exchange like constants, the atom – phonon coupling (APC) model [9, 10] was introduced, which considers that neighboring molecules are connected through a spring characterized by an elastic constant depending on molecules electronic state. By associating a fictitious spin to each molecule that has -1 and +1 eigenvalues corresponding to LS and HS levels respectively, an Ising type model can be developed for the analysis of metastable states and phase transitions in spin-crossover compounds.

This model considers that neighboring atoms are connected to each other with a spring characterized by an elastic constant which depends on the atoms electronic states: \( C_{LL} = \lambda \) when both atoms are in the LS state, by \( C_{HH} = \nu \) when both are in the HS state and by \( C_{HL} = \mu \) when the atoms are in different states.

Using the Ising – like model approach in the APC model, we assume that each atom has associated a fictitious – spin operator \( \hat{\sigma} \) which can take one of the two eigenvalues +1, respectively -1, corresponding to the electronic states of the atom (HS, respectively LS). The ratio between the degeneracy of the fundamental LS level \( g_{\text{LS}} \) and that of the excited HS level \( g_{\text{HS}} \) defines the degeneracy factor: \( r = g_{\text{HS}} / g_{\text{LS}} \). The resulting Hamiltonian of the system formed by a number of \( N \) atoms disposed in chain is:
\[ H = \sum_{i=1}^{N} \frac{A}{2} \hat{\sigma}_i + \sum_{i=1}^{N} \frac{p_i^2}{2m_a} + \sum_{i=1}^{N} \frac{k_{i,i+1}}{2} \left( u_{i+1} - u_i \right)^2 \]  

(15)

where: \( \Delta \) is the energy gap between the LS and HS states, the second sum is the kinetic energy of the chain, \( u_i \) is the displacement of \( i \) – atom from its equilibrium position, \( m_a \) is the mass of the atom, \( k_{i,i+1} \) is the elastic constant that can take one of the three values \( \lambda, \nu \) or \( \mu \) mentioned above, depending on the states of atoms \( i \) and \( i+1 \).

Therefore, using the Ising – like model, \( k_{i,i+1} \) can be written as:

\[
k_{i,i+1} = \frac{\lambda + 2\mu + \nu}{4} + \frac{\nu - \lambda}{4} (\hat{\sigma}_i + \hat{\sigma}_{i+1}) + \frac{\lambda - 2\mu + \nu}{4} \hat{\sigma}_i \cdot \hat{\sigma}_{i+1}
\]

(16)

and the Hamiltonian (1) can be rewritten by using the following expression:

\[
H = -\sum_{i=1}^{N} h_i \hat{\sigma}_i - \sum_{i=1}^{N} J_{i,i+1} \hat{\sigma}_i \cdot \hat{\sigma}_{i+1} + \sum_{i=1}^{N} \left[ \frac{p_i^2}{2m_a} + \frac{\lambda + 2\mu + \nu}{8} (u_{i+1} - u_i)^2 \right]
\]

(17)

In the above equation, the first sum could be considered as a Zeeman – like interaction where each spin \( \hat{\sigma}_i \) is under the influence of an effective field \( h_i \), while the second sum resembles to an exchange – like interaction between the two neighboring spins \( \hat{\sigma}_i \) and \( \hat{\sigma}_{i+1} \). In this case the effective field will be given by: \( h_i = -\{4\Delta + (\nu - \lambda)(u_{i+1} - u_i)^2 + (u_{i+1} - u_i)^2\}/8 \), while the interaction between the spins \( i \) and \( i+1 \) can be calculated using the formula \( J_{i,i+1} = (\lambda - 2\mu + \nu)(u_{i+1} - u_i)^2 / 8 \). One can observe now that the total Hamiltonian of our system is formed by a classical Ising Hamiltonian and a phonon Hamiltonian that can be solved using methods from the theory of magnetism.

By using the mean-field approximation in the APC model, we replace the elastic constants \( k_{i,i+1} \) with one effective constant \( K \) which does not depend on the site. Therefore the effective field and the exchange coupling constant presented above are constant and we can note them with \( h \) and \( J \). The total Hamiltonian can be studied now by using the transfer matrix so one arrives at the following two equations: \( m = \langle \hat{\sigma}_i \rangle \), \( s = \langle \hat{\sigma}_i \hat{\sigma}_{i+1} \rangle \), where \( \langle \cdot \rangle \) are the thermal mean values.

Therefore, in the mean field approximation, the thermal mean value of the phonon Hamiltonian \( \langle H_{phon} \rangle \) has the following expression (the formula was determined by using the calculations from [10]):

\[
\langle H_{phon} \rangle = \frac{\hbar \omega_0 (\lambda)}{2} \sum_{i} \sin \left( \frac{i \pi}{N} \right) \coth \left( \frac{\beta \hbar \omega_0 (\lambda)}{2} \sum_{i} \sin \left( \frac{i \pi}{N} \right) \right)
\]

(18)

where \( i = 0, \pm 1, \ldots, \pm \left( \frac{N}{2} - 1 \right) \), \( \beta = \frac{1}{k_B T} \) and \( K \) is calculated using the following formula:

\[
K = \frac{\lambda + 2\mu + \nu}{4} + \frac{\nu - \lambda}{4} m + \frac{\lambda - 2\mu + \nu}{4} s
\]

(19)

The maximum phonon angular frequency \( \omega_0 (\lambda) \) for a periodic chain with an elastic constant \( \lambda \), is given by \( \omega_0 (\lambda) = 2\sqrt{\lambda/m_a} \).

The self consistent equations for the two parameters considered in this problem, \( m \) and \( s \), were derived in [10] and they can be expressed as follows:
where the effective field and effective exchange coupling constants are expressed by:

\[
h = -\frac{\Delta}{2} - \lambda \frac{\langle H_{\text{phon}}(K) \rangle_I}{N} + \frac{\nu}{4K} \text{ and } J = -\frac{\lambda}{2} - 2\mu + \nu \frac{\langle H_{\text{phon}}(K) \rangle_I}{N} \]

(22)

From the equations (20) – (22) for \(m\) and \(s\) one can find at low temperature the metastable states of a SCO compound. Using the equation for \(m\) one can also find easily the value of the high spin fraction by applying the following expression: \(n_{HS} = (m+1)/2\).

Throughout this article we have used the following parameters [10]:

- The energy gap: \(\delta = \frac{\Delta}{\hbar \omega_d(\lambda)}\);
- The reduced temperature: \(t_r = \frac{k_B T}{\hbar \omega_d(\lambda)}\)

4. The role of the atom – phonon coupling model parameter \(C_{IH}/C_{LL}\)

The parameters used in the APC model can be determined experimentally using calorimetric measurements (for the energy gap \(\delta\) and the degenerescence \(r\)), Brillouin spectroscopy for the elastic constant ratios, inelastic diffusion of neutrons, inelastic diffusion of X-rays [11, 12]. The hysteretic properties of a system depend highly on \(C_{IH}/C_{LL}\) ratio, their influence can be observed in the figure 4.

![Figure 4](image_url)

**Figure 4.** \(n_{HS}\) variation in function of reduced temperature for different values of \(C_{IH}/C_{LL}\) using \(C_{HH}/C_{LL} = 0.2\), \(r = 5\), \(\delta = 0.55\), \(N = 50\).

When two neighbouring atoms are in different states, the elastic constant \(C_{IH}\) between them can take values between \(C_{LL}\) and \(C_{HH}\). The figure 4 presents the variation of the high spin fraction in
function of temperature for different values of the ratio: \( C_{LH}/C_{LL} \). The figure shows the importance of the parameter’s value in obtaining results experimentally observed:

a. gradual spin conversion is obtained for \( C_{LH} = (C_{LL} + C_{HH})/2 \), in this case \( C_{LH}/C_{LL} = 0.70 \);

b. the limit value below which hysteresis is obtained is \( C_{LH}/C_{LL} = 0.55 \);

c. a typical hysteresis can be observed for \( C_{LH}/C_{LL} = 0.49 \);

d. a more abrupt and pronounced hysteresis can be achieved for values of \( C_{LH}/C_{LL} = 0.40 \).

From the figure we can also conclude that \( T_{1/2} \) is slightly shifted towards smaller values of temperatures when the ratio \( C_{LH}/C_{LL} \) decreases. When \( C_{LH} \) takes values closer to \( C_{LL} \) the hysteresis becomes more abrupt. From an application point of view the last case presented is very important because the two electronic states HS and LS are very well defined.

5. Relaxation dynamics

A molecule can pass from the HS state to the LS state in two different ways, either by nonradiative relaxation from \( ^5T_2 \) to \( ^1A_1 \), either using the reverse LIESST effect by irradiation with light in the absorption band [13]. While the latter mechanism has a fast kinetics of the order of ps for a molecule, the direct relaxation from \( ^5T_2 \) to \( ^1A_1 \) is much slower (on the order of ms), being the subject of studies that try to determine the relaxation in time of the photo-excited states after application of a laser impulse.

The relaxation process is mainly determined by the tunnel effect at low temperatures (\( T < 30 \)K) and thermally activated for higher temperatures (\( T > 40 \)K). Many studies were undertaken by Hauser and his research group [13, 14] that rely on the properties of the HS state energy barrier in order to understand the properties of the cooperative relaxation. The relaxation rate \( k_{HL} \) on the thermal activation regime is:

\[
K_{HL}(T,n) = k \exp\left(-\frac{E_a}{k_B T}\right)
\]

where \( k \) is the relaxation rate at high temperature and \( E_a \) is the activation energy given by:

\[
E_a = E_0 - E_{HS}
\]

The energy difference between the two potential wells \( E_{HS} \) is given by:

\[
E_{HS} = \frac{A}{2} + \frac{E_{\text{photon}}}{N}
\]

so we can rewrite the equation:

\[
K_{HL}(T,n) = k \exp\left(-\frac{E_a}{k_B T}\right) = k \exp\left(-\frac{A - \delta}{2} \frac{\langle H_{\text{ph}}(K) \rangle_T}{N t_r}\right)
\]

Where:

\[
A = \frac{E_0}{\hbar \nu_{\text{cut}}(\lambda)}
\]

The variation in time for the high spin fraction can be calculated using the following expression:

\[
\frac{dn}{dt} = -nk \exp\left(-\frac{A - \delta}{2} \frac{\langle H_{\text{ph}}(K) \rangle_T}{2 t_r}\right)
\]
Using this equation, the relaxation curves that take into account the factors that can interfere in the real situations such as dilution, size or the temperature of the system [15, 16] are presented in the figure 5.

![Figure 5. Relaxation curve without using light irradiation using: $\delta = 0.6, t = 0.03, N = 2000, r = 5, A = 0.8, k = 100$.](image)

Another representation that allows us to analyze the relaxation mechanism is the Arrhenius representation in which: \( \ln(k_{HL}) = f(n_{HS}) \) (figure 6) [16].

![Figure 6. Arrhenius diagram using $\delta = 0.6, t = 0.03, N = 2000, r = 5, A = 0.8, k = 100, x = 0.5, y = 0$ [16].](image)

In the figure 6 Arrhenius’s diagram form presents two slopes and not a straight line like in the case of Hauser’s model which comes in good agreement with the experimental data. Using the equation
The theoretical results were superposed with the experimental data obtained for \( [\text{Fe}_{0.5}\text{Zn}_{0.5}(\text{btr})_2(\text{NCS})_2]\text{H}_2\text{O} \) (figure 7).

![Figure 7](image-url)

**Figure 7.** Relaxation curves at different temperatures obtained for \( [\text{Fe}_{0.5}\text{Zn}_{0.5}(\text{btr})_2(\text{NCS})_2]\text{H}_2\text{O} \) after photo-excitation with light having the wavelength of 550nm wavelength. The continuous lines were calculated using the equation (28).

The final part of the curve is called ‘relaxation queue’ and it was explained by Hauser as being determined by the progressive installation of correlations created by the short range interactions. The figure clearly shows that the relaxation curves obtained theoretically are very well superposed on the one’s obtained experimentally including the relaxation tail. In Hauser’s model, the last part of the curve could be reproduced only if another term is included, accounting for the short range interactions [17-19]. The theoretical relaxation curves including this term are presented in the figure 8.

![Figure 8](image-url)

**Figure 8.** Relaxation curves at different temperatures obtained after photo-excitation with light having the wavelength of 550 nm wavelength. The continuous lines are the theoretical lines from Hauser’s model.
6. Size effect

The size effect plays an important role from an applications point of view such as information storage. One of the most important analysis are based on finding the smallest size for which the system keeps its properties. In order to find the influence of the system’s size on the width of the hysteresis cycle we have simulated the dependence of the n_HS fraction for different sizes of the chain of molecules.

Two important ratios that are parameters in the APC model influence highly the hysteretic properties of a system: the ratio between \( C_{HH} \) and \( C_{LL} \) and the ratio between \( C_{LH} \) and \( C_{LL} \) [20].

There is a strong dependence of the hysteresis width on the ratios \( C_{HH}/C_{LL} \) and \( C_{LH}/C_{LL} \) which offers an explanation for different results regarding the size effect in SCO. Following this idea we have simulated in a 1D SCO system the dependence of the hysteresis width in function of the number of molecules \( N \) for different values of \( C_{LH}/C_{LL} \) (figure 9).

The figure 9 shows that for both values of the ratio \( C_{LH}/C_{LL} \) the hysteresis loop disappears for a chain of 8 molecules. We can notice a variation of the hysteresis width with the chain’s size is followed by saturation, which corresponds to an infinite system.

![Figure 9](image)

**Figure 9.** The dependence of the hysteresis loop width in 1D systems on the number of molecules for different values of \( C_{LH}/C_{LL} \) using \( C_{HH}/C_{LL} = 0.4 \), \( r = 5 \), \( \delta = 0.55 \).

7. Low temperature metastable states

An interesting phenomena observed in spin crossover compounds is the LIESST effect. Experimentally, it has been shown, first by Moussa et al [21] and recently by Neville et al [22] that in the case of a two-step thermal spin transition, by irradiating the sample at low temperature, the system can be photoexcited only 50% from the high spin fraction. By using the APC model we have been able to reproduce this kind of behavior [23, 24]. The results are displayed in figure 10.
Figure 10. The variation of $n_{HS}$ with reduced temperature for $C_{LL}/C_{LL} = 0.69$, $C_{HH}/C_{LL} = 0.226$, $r = 30$, $\delta = 0.606$, $N = 50$.

8. Conclusion
In this report the atom-phonon coupling model has been applied to a 1D spin crossover systems. Only the elastic force constant of the spring which links two atoms first neighbors is assumed to be depending on the electronic states of both atoms. As shown in the figure 4 the atom-phonon coupling model leads to spin conversion with or without first order phase transition depending on the values of the elastic constant between LS and HS atoms. On the bases of good agreement between simulated results and experimental one we can conclude the APC model can be applied to describe the relaxation process into a system with spin conversion. At low temperature we have obtained metastable states at $n_{HS} = 0.5$. These states can be associated to the “incomplete” photoconversion excited states obtained by irradiating the samples. We have presented a study on the size effect in the spin crossover compounds: our results point to the fact that to reduce the size of a system and keep the properties of its hysteresis loop, it is necessary to choose materials with $C_{HH}/C_{LL}$ ratio as small as possible.

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