Vol 18 No 6, June 2009
1674-1056/2009/18(06)/2557-08

Chinese Physics B

© 2009 Chin. Phys. Soc.
and IOP Publishing Ltd

# Ferroelectricity in a diatomic Ising chain as investigated by the elastic Ising model*

Guo Yun-Jun(郭云均), Wang Ke-Feng(王克锋), and Liu Jun-Ming(刘俊明)†

*Laboratory of Solid State Microstructure, Nanjing University, Nanjing* 210093, *China*

*International Center for Materials Physics, Chinese Academy of Sciences, Shenyang* 110016, *China*

(Received 5 January 2009; revised manuscript received 12 January 2009)

An elastic Ising model for a one-dimensional diatomic spin chain is proposed to explain the ferroelectricity induced by the collinear magnetic order with a low-excited energy state. A statistical theory based on this model is developed to calculate the electrical and magnetic properties of $Ca_3CoMnO_6$, a typical quasi-one-dimensional diatomic spin chain system. The calculated ferroelectric polarization and dielectric susceptibility show a good agreement with recently reported data on $Ca_3Co_{2-x}Mn_xO_6$ ($x \approx 0.96$) (*Phys. Rev. Lett.* **100** 047601 (2008)), although the predicted magnetic susceptibility does not coincide well with experiment. We also address the rationality and deficiency of this model by including a first-order correction which improves the consistency between the model and experiment.

**Keywords:** multiferrocity, elastic Ising model, diatomic Ising spin chain
**PACC:** 7540D, 7580, 7780

## 1. Introduction

The phenomenon of both ferroelectricity and magnetism existing simultaneously in compounds, the so-called multiferrocity, has shown great potential for both practical applications and fundamental studies.[1−8] The magnetoelectric (ME) coupling between the frustrated magnetic orders and ferroelectricity in several systems has been investigated in the past few years, although the microscopic mechanism still remains unclear.[9−12] It is deduced that the spiral magnetic order is the origin of multiferrocity on one occasion, as the spin current picture[9,10] and the Dzyaloshinskii–Moriya interaction (DMI)[13,14] are believed to play the crucial roles[11,12] for the magnetic frustration of spiral magnetic order. Some works based on these mechanisms show the ferroelectricity to be consistent with experiment for quite a number of spiral spin ordered systems.[15,16]

However, recent discoveries show the existence of magnetism-driven ferroelectricity in the system with collinear spin order, in which the mechanisms of spiral magnetic order fail to work well on the ME coupling.[17,18] In Ref.[18], Choi *et al* suggested that the ferroelectricity in the system of $Ca_3Co_{2-x}Mn_xO_6$ ($x \approx 0.96$) is driven by exchange striction. $Ca_3Co_{2-x}Mn_xO_6$ can be viewed as a doped $Ca_3Co_2O_6$ material where the Co ions are partially replaced by Mn ions, and the parallel diatomic Ising spin chains of $CoMnO_6$ form a triangular lattice in the *ab*-plane. Along the *c*-axis, the $CoMnO_6$ chain consists of face-sharing $CoO_3$ trigonal prisms and $MnO_3$ octahedral prisms, and we find the intrachain interactions along the *c*-axis are much stronger than the ones between $CoMnO_6$ chains.

In the $Ca_3Co_{2-x}Mn_xO_6$ system, while $x = 1$, the Mn and Co ions will alternate in each chain occupying the high-spin and low-spin sites, and each Ising chain has an up–up–down–down ($\uparrow\uparrow\downarrow\downarrow$) magnetic order in the ground state.[18,19] Different from the ferroelectricity driven by spiral magnets, in this system with an FM exchange interaction between the nearest-neighbor spins, the exchange striction in each spin chain, which shortens the bonds between the parallel spins and stretches the bonds between antiparallel spins, is responsible for the electric polarization. This exchange striction mechanism is attributed to the elastic energy in the Ising-like model to be constructed below.

To explain quantitatively the ferroelectricity induced by exchange striction for $Ca_3Co_{2-x}Mn_xO_6$, we start from a one-dimensional spin chain, with which

*Project supported by the National Natural Science Foundation of China (Grant Nos 50832002, 10674061 and 10874075), and the National Key Projects for Basic Research of China (Grant Nos 2006CB921802 and 2009CB623303).
†Corresponding author. E-mail: liujm@nju.edu.cn

an elastic Ising model will be proposed. We assume that $Ca_3CoMnO_6$ consists of parallel one-dimensional diatomic spin chains which are independent of each other, as the interchain exchange interaction is much smaller than the one in the spin chain. Then we deal with only a single diatomic spin chain, in which the long range is suggested to be unbroken.

With a low-excited-state assumption and its first-order correction, we address the rationality of the elastic model by applying it to investigate the ferroelectricity generation in $Ca_3Co_{2-x}Mn_xO_6$ and temperature dependences of polarization, magnetic susceptibility and dielectric susceptibility. The major aim of this work is to illustrate the suggestion in Ref.[18] for the mechanism of ferroelectricity in the Ising spin chain system.

## 2. Model and formulation

We start from the diatomic Ising model for a single one-dimensional spin chain. For such a chain with alternating magnetic ions Mn and Co, we consider the nearest-neighbor FM interaction ($J_{\rm F} > 0$) and next-nearest-neighbor AFM interaction ($J_{\rm AF} < 0$). In Fig.1(a) we draw schematically two forms of diatomic spin chains aligned along the $c$-axis. As expected, the ground state has an up–up–down–down magnetic order if $-J_{\rm AF}/J_{\rm F} > n/(1+n^2)$, where $n = S_{\rm A}/S_{\rm B}$.[18,19] The Hamiltonian for such an Ising model is

$$H = -J_{\rm F}\sum_{\langle ij\rangle} S_i \cdot S_j - J_{\rm AF}\sum_{[ij]} S_i \cdot S_j - h\mu_{\rm B} g_{\rm l}\sum_i S_i + \frac{1}{2}\sum_i k_i r_i^2, \qquad (1)$$

where subscript $\langle ij\rangle$ refers to the nearest-neighbor spin pair and $[ij]$ the next nearest-neighbor pair, $S_i$ represents the spin of ion on site $i$, $h$ denotes the external magnetic field, $\mu_B$ is the Bohr magnon, $g_l$ is the Lande factor and $k_i$ is the stiffness factor for the ion on site $i$.

### 2.1. Elastic interaction

Taking account of the exchange striction effect, for an FM interaction, there is an attraction force between two ions with parallel spins, and a repulsion force between ones with antiparallel spins. As shown in Fig.1(a), where the dashed circles represent the original ion positions without exchange striction, the up–up–down–down spin order with alternating Mn and Co ions which breaks the inversion symmetry has two configurations (the left and right chains) inducing opposite polarizations.[18] Take the first configuration for example (the left chain in Fig.1(a)), all the Mn ions have an upward displacement while all the Co ions displace downwards. Taking the upward direction as the positive $c$-axis, we have the total electric polarization at temperature $T = 0$ for the Ising chain:

$$P\,(T=0) = \sum_{i=1}^{2N} P_i = N\,(P_{\rm Mn} + P_{\rm Co})\,, \qquad (2)$$

where $N$ is the number of Mn and Co ions in a unit volume, $P_i$ is the electric polarization of the ion on site $i$ defined with respect to the position with no exchange striction. Here $P_{\rm Mn}$ and $P_{\rm Co}$ are the electric polarizations defined with respect to the shift of Mn and Co ions, respectively. The exchange force competing with the restoring force from the crystal lattice causes the displacement of the ions.

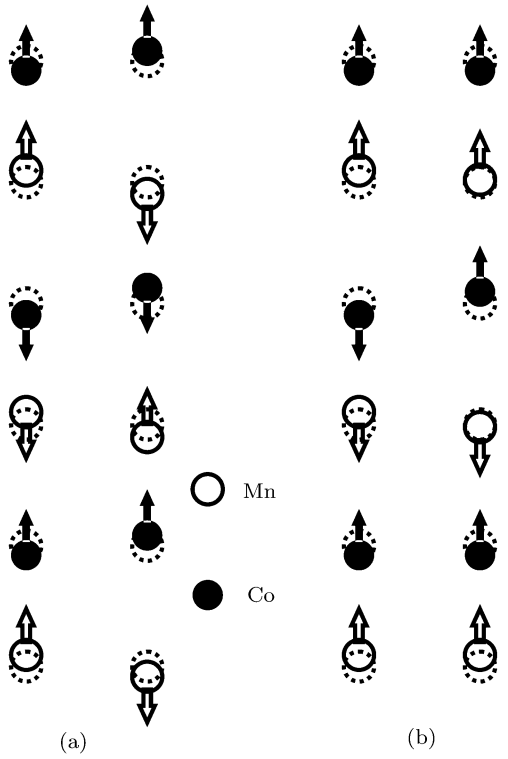



**Fig.1.** (a) Two configurations of the up–up–down–down Ising chain with alternating Mn and Co ions. The dashed circles represent the original positions of the ions and the arrows indicate the spin directions. (b) Change of polarization upon one spin flipping from the configuration in the left chain into the right one.

Along these lines, an elastic Ising model is introduced to describe the exchange striction and the exchange energy terms $J_{\rm F}$ and $J_{\rm AF}$ should contain a

long-range elastic term:[20]

$$J = J_0((r_{ij}/r_0)^{12} - (r_{ij}/r_0)^6), \tag{3}$$

where $r_{ij}$ is the distance between the ions on site $i$ and site $j$, and $r_0$ is the original distance between two ions without elastic exchange. Considering the elastic exchange associated with the next-nearest-neighbor terms ($J_{\mathrm{AF}}$), no symmetry breaking can be found to cause effective exchange striction. This indicates that the elastic interaction should only apply to the nearest-neighbor interaction $J_{\mathrm{F}}$. We denote the displacement of the ion on site $i$ as $r_i$, then the distance $r_{ij}$ can be represented as: $r_{ij} = r_0 + r_i + r_j$. Since $r_i$ is a relatively small quantity with respect to $r_0$, the elastic energy can be cut-off only to the first order.

## 2.2. Ferroelectricity at ground state

From the Hamiltonian in Eq.(1), together with the elastic energy in Eq.(3) for the nearest-neighbor terms ($J_{\mathrm{F}}$), one obtains the ion equilibrium position by minimizing $H_1$ with respect to $r_i$. Therefore with the displacement $r_i$, the electric polarization in the ground state ($T = 0$) in Eq.(2) can be expressed as

$$\begin{aligned} P(T=0) &= \sum_{i=1}^{2N} Q_i \cdot r_i \\ &= N\bigg(Q_{\mathrm{Mn}} \cdot \frac{12 J_{\mathrm{F}} S_{\mathrm{Mn}} \cdot S_{\mathrm{Co}}}{r_0 k_{\mathrm{Mn}}} \\ &\quad - Q_{\mathrm{Co}} \cdot \frac{12 J_{\mathrm{F}} S_{\mathrm{Mn}} \cdot S_{\mathrm{Co}}}{r_0 k_{\mathrm{Co}}}\bigg), \end{aligned} \tag{4}$$

where $Q_i$ is the electric charge of the ion on site $i$ ($Q_{\mathrm{Mn}}$, $Q_{\mathrm{Co}}$).

For the $Ca_3Co_{2-x}Mn_xO_6$ system, the parallel Mn–Co chains along the $c$-axis form a triangular lattice in the $ab$-plane. The interchain distance is $a$ =5.24 Å (1 Å=0.1 nm) and the intrachain distance is $r_0$ =2.65 Å.[21–23] The number of Mn–Co couples in a unit volume $N$ =$1.57\times10^{28}$ m$^{-3}$. Then we have $Q_{\mathrm{Mn}} = 4e$ and $Q_{\mathrm{Co}} = 2e$. The spin for the Mn ion is $S_{\mathrm{Mn}} = 3/2$, and for the Co ion is $S_{\mathrm{Co}} = 1/2$.

Furthermore, for $Ca_3Co_{2-x}Mn_xO_6$, six Mn–O bonds form an octahedral prism, while six Co–O bonds form a trigonal prism. Three of the six Mn–O (or Co–O) bonds have an angle $\theta_{\mathrm{Mn}}$ (or $\theta_{\mathrm{Co}}$) from the Mn–Co chain along the $c$-axis, while the others have the angle $\pi - \theta_{\mathrm{Mn}}$ (or $\pi - \theta_{\mathrm{Co}}$). We treat the covalent bond equivalent to a Coulomb interaction with equivalent charge $Q*_{\mathrm{Mn}} = \alpha Q_{\mathrm{Mn}}$, $Q*_{\mathrm{Co}} = \alpha Q_{\mathrm{Co}}$ and $Q*_O = \alpha Q_O$ where $Q_O = 2e$ is the charge of the oxygen ion. Only considering the interaction along the $c$-axis, the Coulomb interaction from these six bonds can be regarded as a harmonic oscillator when the displacement is small, so that the stiffness factors for these bonds can be evaluated. We have the Coulomb interaction $F$ for the Mn–O bonds and Co–O bonds:

$$\begin{aligned} F &= \frac{3}{4\pi\varepsilon_0} \cdot \bigg(\frac{Q_\mu Q_{\mathrm{O}} \alpha^2 \cos(\theta_\mu)}{(R_\mu - r_\mu/\cos(\theta_\mu))^2} \\ &\quad + \frac{Q_\mu Q_{\mathrm{O}} \alpha^2 \cos(\pi - \theta_\mu)}{(R_\mu - r_\mu/\cos(\pi - \theta_\mu))^2}\bigg) \\ &\approx \frac{3 Q_\mu Q_{\mathrm{O}} \alpha^2}{\pi\varepsilon_0 R_\mu^3} \cdot r_\mu, \\ &\mu = \mathrm{Mn},\ \mathrm{Co}, \end{aligned} \tag{5}$$

where $\varepsilon_0$ is the dielectric constant in vacuum, the length of the Mn–O bond is $R_{\mathrm{Mn}} = 1.905$ Å, the length of the Co–O bond is $R_{\mathrm{Co}} = 2.140$ Å.[21–23] So the stiffness factor can then be expressed as

$$k_\mu = \frac{3 Q_\mu Q_{\mathrm{O}} \alpha^2}{\pi\varepsilon_0 R_\mu^3},\ \mu = \mathrm{Mn},\ \mathrm{Co}. \tag{6}$$

Taking $\alpha = 0.4$, we obtain $k_{\mathrm{Mn}} = 2.89\times10^2$ N/m, the stiffness factor for Mn–O bonds, and $k_{\mathrm{Co}} = 1.01\times10^2$ N/m, the factor for Co–O bonds.

## 2.3. Temperature dependence

Subsequently, we investigate the temperature dependency of electric polarization. At a nonzero $T$, some of the Mn and Co spins may flip due to the thermal activation. As an approximation we only consider the low-excited-state (LES) at a low $T$, which means that the ferroelectricity is generated from the LES associated with the ground state of the up–up–down–down magnetic order. Consequently, the ferroelectricity is sensitive to the magnetic order (or spin configuration of the chain) but the latter can be very stable because of the strong intra-chain exchange interaction. To understand this 'sensitivity' and 'stability', one may consult Ref.[18]. The measured electric polarization for $Ca_3Co_{2-x}Mn_xO_6$ ($x$ = 0.96) cooled down to 3.1 K is much smaller than the one cooled down to 2 K. Furthermore, it is expected that the electric polarization as a function of $x$ reaches its maxima at $x$ =1, and falls down quickly with decreasing $x$. Upon a magnetic field $h$ being applied along the chain direction ($h$ = 4 T, 7 T), the electric polarization is partially suppressed but does not disappear. We therefore argue that $Ca_3Co_{2-x}Mn_xO_6$ can be well

approached by the present diatomic spin chain model under the LES assumption.

Now we discuss the dynamics of spin flip at a given low $T$. The dynamics may prefer a single spin flip sequence rather than a collective one due to the low-excited state. The dynamic can be calculated within the mean-field approximation. While a Co ion has its spin flipped, as shown in Fig.1(b) for an example (from the left chain to the right chain), its own displacement will turn to the opposite direction and its two nearest-neighbor Mn ions will return to their original positions where no electric polarization appears. The change of polarization for one spin flip can be represented as

$$\Delta P = -2(P_{\rm Mn} + P_{\rm Co}). \tag{7}$$

The excited energy for this spin flip is under $h = 0$:

$$\Delta E_\mu = 4J_{\rm AF} \cdot S_\mu^2,\ \mu = {\rm Mn, Co}. \tag{8}$$

According to the Boltzmann statistics, the probability for the Mn/Co spin flip can be defined as

$$\omega_\mu = \exp\left(\frac{4J_{\rm AF} \cdot S_\mu^2}{kT}\right) \Big/ \left(1 + \exp\left(\frac{4J_{\rm AF} \cdot S_\mu^2}{kT}\right)\right),$$
$$\mu = {\rm Mn,\ Co}, \tag{9}$$

where $k$ is the Boltzmann constant. For $Ca_3Co_{2-x}Mn_xO_6$, $S_{\rm Mn}/S_{\rm Co} = 3$. At $h = 0$, equation (8) gives $\Delta E_{\rm Mn} = 9\Delta E_{\rm Co}$. At the low-excited state, $\omega_{\rm Mn}$ is negligible with respect to $\omega_{\rm Co}$ since $\omega_{\rm Mn} \approx \omega_{\rm Co}^9 \sim 0$, noting that $\omega_{\rm Co}$ itself is also a small quantity ($\omega_{\rm Co} < 1$).

## 2.4. Polarization, magnetic and dielectric susceptibilities

Under the LES assumption, it is easy to derive the temperature dependence of the electric polarization ($P_{\rm LES}$) under zero field ($h = 0$) along the chain direction:

$$\begin{aligned} P_{\rm LES}(T) &= N(P_{\rm Mn} + P_{\rm Co}) - N\omega_{\rm Co}\Delta P \\ &= N(P_{\rm Mn} + P_{\rm Co}) \cdot (1 - 2\omega_{\rm Co}). \end{aligned} \tag{10}$$

Given a finite $h$, the excited energy for the spin flip, equation (8), can be rewritten as

$$\Delta E_\mu^\pm = -4J_{\rm AF} \cdot S_\mu^2 \pm \mu_{\rm B} g_{\rm l} h \cdot S_\mu,\ \mu = {\rm Mn, Co}, \tag{11}$$

where the superscript '+' of $\Delta E_\mu$ refers to the case with spins parallel to $h$, and '–' to the case with spins antiparallel to $h$. Same as Eq.(9), we define the probability for the Mn/Co spin flip as

$$\begin{aligned} &\omega_\mu^h = \left(\omega_\mu^+ + \omega_\mu^-\right)/2, \\ &\omega_\mu^\pm = \exp\left(-\frac{\Delta E_\mu^\pm}{kT}\right) \Big/ \left(1 + \exp\left(-\frac{\Delta E_\mu^\pm}{kT}\right)\right), \\ &\mu = {\rm Mn,Co}. \end{aligned} \tag{12}$$

Similar to the discussion for $\omega_{\rm Mn}$, we can also have $\omega_{\rm Mn}^h \sim 0$. In the ground state, the numbers of spins in parallel and antiparallel to $h$ are the same, so the electric polarization becomes:

$$P_{\rm LES}(T) = N(P_{\rm Mn} + P_{\rm Co}) \cdot \left(1 - \left(\omega_{\rm Co}^+ + \omega_{\rm Co}^-\right)\right). \tag{13}$$

Following the discussion above, the AFM order of Mn spins in the low-excited state is rigid with respect to Co spins and the Mn spin flip is very hard since $\omega_{\rm Mn}^h \sim 0$. Therefore, the nearest-neighbor exchange interactions for Co spins are cancelled because the two nearest-neighbor Mn spins of each Co spin are opposite. The Co ions themselves can then be seen as an Ising chain with AFM exchange interaction. Under a weak magnetic field, the magnetic susceptibility under the low-excited-state:

$$\chi_{\rm LES} = M/h = \frac{N\mu_{\rm B} g_{\rm l} S_{\rm Co}}{h} \cdot \left(\omega_{\rm Co}^+ - \omega_{\rm Co}^-\right). \tag{14}$$

The dielectric susceptibility along the $c$-axis can be calculated by

$$\varepsilon_c = \frac{\left\langle P^2 \right\rangle - \langle P \rangle^2}{N k_{\rm B} T}. \tag{15}$$

Noting that $P = (N - 2n)(P_{\rm Mn} - P_{\rm Co})$ where $n$ is the number of flipping Co spins. Here we simply express $\omega_{\rm Co}^h$ as $\omega$ for short. For an $N$-spin chain, the probability for $n$ spin flips with $N - n$ retained is

$$\rho_n = C_N^n \omega^n (1 - \omega)^{N-n}, \tag{16}$$

yielding

$$\begin{aligned} \langle n \rangle &= \sum_{n=0}^{N} n \cdot \rho_n = N\omega, \\ \left\langle n^2 \right\rangle &= \sum_{n=0}^{N} n^2 \cdot \rho_n = N\omega(N\omega + 1). \end{aligned} \tag{17}$$

The dielectric susceptibility under a magnetic field $h$ along the chain direction is

$$\varepsilon_{\rm LES} = \varepsilon' + \frac{2(P_{\rm Mn} + P_{\rm Co})^2}{k_{\rm B} T} \left(\omega_{\rm Co}^+ + \omega_{\rm Co}^-\right), \tag{18}$$

where $\varepsilon'$ is the dielectric susceptibility for other ions in the system.

### 2.5. First-order correction

From Eqs.(13), (14) and (18) we can calculate $P_{\rm LES}$, $\chi_{\rm LES}$, and $\varepsilon_{\rm LES}$ as a function of $T$ and compare them with experimental data. Nevertheless, before we do this, it is necessary to pay attention to the applicability of the LES assumption at high temperatures. We look at the transition point $T_{\rm C}$ of ferroelectricity where the ferroelectricity disappears. Equation (7) tells us that at $T_c$, the number of flipping spins is about $N/2$, i.e. 25% of the total spins in the chain. This number can no longer be treated as a small quantity, and the LES assumption will no longer be valid when the temperature approaches $T_c$ for the ferroelectricity. A correction to the model for application to relatively high temperature becomes necessary, and the correction for the LES assumption is made for the first order below.

When a Co spin flips (noting here that no more flip of Mn spins is concerned since $\omega_{\rm Mn} \sim 0$), we denote this spin as spin $L1$ in Fig.2, and the probability for flipping of its two next-nearest-neighbor spins (also Co spins) which are denoted as $L2$ in Fig.2 is no longer $\omega^h_{\rm Co}$ as defined in Eq.(12) but always 50%, no matter what the magnetic field $h$ is. The electric polarization contributed from these two flipping spins (i.e. the two spins next-nearest-neighboring to spin $L1$) is zero. We then count all these spins over the whole spin chain and they can be removed from a counting for those flipping spins which contribute to the electric polarization. For a small $h$, their contribution to magnetization can also be neglected. Consequently, the effective number of spins in the chain is no longer a constant but a variable depending on $T$ and $h$:

$$N_{\rm eff}\,(T) = N \cdot \left(1 - \frac{\eta_{\rm Co}\,(T,h)}{2} \cdot \left(\omega^+_{\rm Co} + \omega^-_{\rm Co}\right)\right), \quad (19)$$

where $\eta_{\rm Co}$ represents the number fraction of Co spins to be removed per spin flip, noting that $\eta_{\rm Co}$ tends to be 2.0 at $T \to 0$ K and 1.0 as $T \to T_c$ (where almost half of Co spins flip and the other half remain static). Therefore, it is easy to obtain the following expressions for $\eta_{\rm Co}$, according to the Boltzmann statistics

$$\eta_{\rm Co}\,(T,h) = 2 - \left(\omega^+_{\rm Co} + \omega^-_{\rm Co}\right). \quad (20)$$

Replacing $N$ in Eq.(10) with $N_{\rm eff}(T)$, we obtain the electric polarization and magnetic susceptibility with a first-order correction:

$$P_{\rm tot}\,(T) = N\,(P_{\rm Mn} + P_{\rm Co}) \cdot \left(1 - \left(\omega^+_{\rm Co} + \omega^-_{\rm Co}\right)\right) \times \left(1 - \frac{\eta_{\rm Co}\,(T,h)}{2} \cdot \left(\omega^+_{\rm Co} + \omega^-_{\rm Co}\right)\right), \quad (21)$$

$$\chi_{\rm tot} = M/h = \frac{N\mu_{\rm B} g_{\rm l} S_{\rm Co}}{h} \cdot \left(\omega^+_{\rm Co} - \omega^-_{\rm Co}\right) \times \left(1 - \frac{\eta_{\rm Co}\,(T,h)}{2} \cdot \left(\omega^+_{\rm Co} + \omega^-_{\rm Co}\right)\right). \quad (22)$$

For the dielectric susceptibility, a simple substitution cannot produce a proper result. Denoting the effective probability for a Co spin flip by $W_{\rm Co}$, the electric polarization can be written as

$$P_{\rm tot}\,(T) = N\,(P_{\rm Mn} + P_{\rm Co})\,(1 - 2W_{\rm Co}), \quad (23)$$

and $W_{\rm Co}$ can be got from Eqs.(21) and (23):

$$W_{\rm Co} = \left(1 + \frac{\eta_{\rm Co}(T,h)}{2} - \frac{\eta_{\rm Co}(T,h)}{2} \cdot \left(\omega^+_{\rm Co} + \omega^-_{\rm Co}\right)\right) \times \frac{\omega^+_{\rm Co} + \omega^-_{\rm Co}}{2}. \quad (24)$$

Replacing $\omega_{\rm Co}$ in Eq.(18) by $W_{\rm Co}$, one obtains the dielectric susceptibility with the first-order correction

$$\varepsilon_{\rm tot} = \varepsilon' + \frac{2\,(P_{\rm Mn} + P_{\rm Co})^2}{k_{\rm B}T} 2W_{\rm Co}. \quad (25)$$

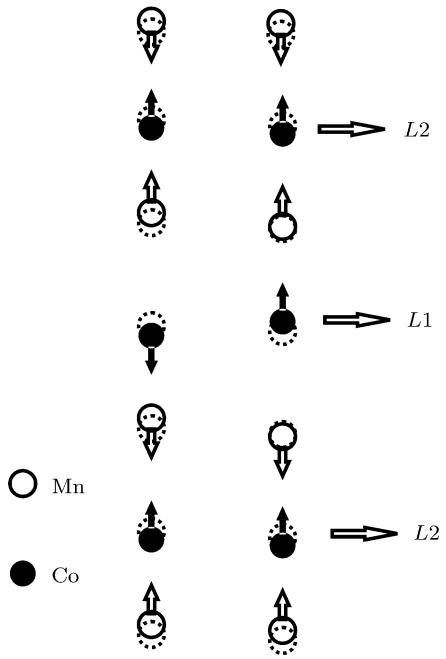



**Fig.2.** Ground state of the diatomic Ising spin chain is shown as the left chain. A flipped Co spin ($L1$) and its two next-nearest-neighbor spins ($L2$) are shown in the right chain.

## 3. Results and discussion

### 3.1. Comparison with experiment

In this section, we present our model calculation of the temperature-dependent electric polariza-

tion, magnetic susceptibility, and dielectric susceptibility, and compare them with measured data taken from Ref.[18]. For such a calculation, we need the values of parameters $J_{\rm AF}$ and $J_{\rm F}$.

Unfortunately, accurate values of these two parameters for $Ca_3Co_{2-x}Mn_xO_6$ ($x \approx 0.96$) are not available to us so far. We may employ the data for $Ca_3Co_2O_6$, the base system for $Ca_3Co_{2-x}Mn_xO_6$. It was reported that $J_{\rm F} \sim 22$ K,[24] and $J_{\rm F} \sim 15$ K.[25] By substituting these two parameters into Eq.(4), one obtains the electric polarization in the ground state $P_{\rm gs} \sim 130\,\mu{\rm C/m^2}$ for $J_{\rm F} \sim 22$ K, and $\sim 89\,\mu{\rm C/m^2}$ for $J_{\rm F} \sim 15$ K. The results both have the same order of magnitude as the measured data $P \sim 90\,\mu{\rm C/m^2}$ at $T = 2$ K.[18] We take $J_{\rm AF} = -10$ K in order to meet the condition for the up–up–down–down magnetic order: $(-J_{\rm AF}/J_{\rm F} > S_{\rm A}/S_{\rm B}/(1 + (S_{\rm A}/S_{\rm B})^2) = 0.3$.

Figures 3(a)–3(c) present the calculated electric polarization in the low-excited state, $P_{\rm LES}$ (open square dots, LES), and that after a first-order correction, $P_{\rm tot}$ (open circle dots, tot), as a function of $T$ under several values of field $h$. The measured data taken from Ref.[18] are plotted too in the figures (solid circles, exp.) for comparison. It is clearly shown that the temperature dependence of $P_{\rm LES}$ and $P_{\rm tot}$ shows similar behavior with measured polarization. Nevertheless, $P_{\rm LES}(T)$ is much larger than the measured ones, indicating that the LES assumption does not work well at high temperatures. This is reasonable since the LES approximation itself applies only to the low temperature.

Given a first-order correction to the low-excited state, the calculated polarization $P_{\rm tot}$ shows much better consistency with measured one over the whole temperature range. This consistency indicates that the present model reasonably describes the ferroelectricity generation in $Ca_3Co_{2-x}Mn_xO_6$ ($x \approx 0.96$). The first-order correction results in a smaller polarization with respect to $P_{\rm LES}$. This is easily understood since the first-order correction considers more spin flipping events which are unfavorable for ferroelectricity generation.

Figures 4(a) and 4(b) present the calculated magnetic and dielectric susceptibilities as a function of $T$ for a comparison with experimental data. It is seen that the calculated magnetic susceptibility ($\chi_{\rm LES}$ and $\chi_{\rm tot}$) under $h = 0.2$ T and dielectric susceptibility ($\varepsilon_{\rm LES}$ and $\varepsilon_{\rm tot}$) under $h = 0$ are on the same order of magnitude with measured data ($\chi$ and $\varepsilon$). For details, while the measured $\chi(T)$ does not change much over the range for measurement, the calculated $\chi_{\rm LES}(T)$ and $\chi_{\rm tot}(T)$ are both zero at $T = 0$ and then increase up to their respective maxima before falling slowly in the high temperature range. The inconsistency between the calculated and measured $\chi$ is remarkable, but the susceptibility under the first-order

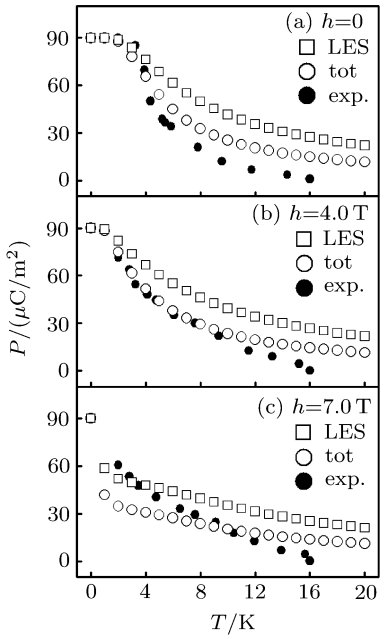



**Fig.3.** Electric polarization as a function of temperature $T$ calculated under the LES assumption (LES) and after the first-order correction (tot), and taken from experiment (exp.) (Ref.[18]). (a) $h = 0$ T. (b) $h = 4$ T. (c) $h = 7$ T.

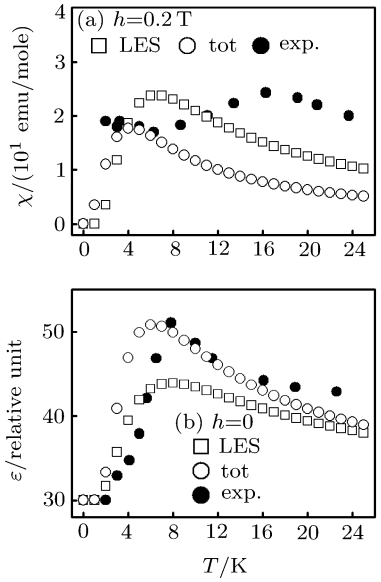



**Fig.4.** (a) Magnetic susceptibility $\chi$ and (b) dielectric susceptibility $\varepsilon$ as a function of temperature $T$ calculated under the LES assumption (LES) and after the first-order correction (tot), and taken from experiment (exp.) ($\varepsilon'$ here is 30) (Ref.[18]).

correction, $\chi_{\rm tot}(T)$, is well consistent with the rigorous solution of the one-dimensional AFM Ising model.[26] The magnetic susceptibility in Ref.[18] was defined as $\chi = M/h$, while in our model no spontaneous magnetization is possible because of the up–up–down–down magnetic order, which has zero magnetic susceptibility $\chi = 0$ at $T \to 0$. It is suggested that the magnetic property of CCMO cannot be simply explained by an Ising model and other contributions such as low-$T$ quantum fluctuations seem to be important.

It should be addressed that the calculated dielectric susceptibility shows quite similar temperature dependence to the measured one, and they both exhibit the single peak pattern against temperature. We also observe that $\varepsilon_{\rm tot}$ has much better consistency with $\varepsilon_{\rm LES}$, indicating the significance of the first-order correction at high temperatures (e.g. $T > 4$ K).

### 3.2. Discussion

Our model focuses on a single diatomic Ising spin chain and the predicted ferroelectricity cannot be in perfect consistency with the measured data for a parallel-aligned spin chain system with interchain interactions. This is reflected by the difference between the calculated data and measured ones in Figs.3 and 4, even after the first-order correction. In this paper, we suggest an unbroken long range order, which cannot be realized in the true system. It is found that the exchange interaction between the diatomic chains is responsible for the stability of the long range order, and then a qualitative discussion for the effect of the interchain interaction on the ferroelectricity is to be presented below.

As mentioned earlier in subsection 2.1, the diatomic Ising chain has two configurations with opposite polarization directions. In the ground state ($T = 0$) the polarization for all the chains has the same direction,[18] but it may not at high temperature. That means, at high temperature, a whole chain (or some part of a chain) may flip together, which is not considered in our model. For this reason, the polarization we calculated is higher than the measured data over almost the whole temperature range. The interchain exchange interaction absent from our Hamiltonian is apparently thought to be responsible for these flip events, and the external magnetic field is expected to suppress them according to experiments. In our model, the external magnetic field gives suppression to the polarization of a single chain. Meanwhile it also reduces the probability for flip of a whole chain (or some part of a chain), since a rigid magnetic order would prevent such an event from occurring. These two competing effects lead to the intersection of measured polarization curves under strong magnetic fields and under zero field, so that the calculated polarization under $h > 0$, shown in Figs.3(b) and 3(c), has better consistency with measured data than the case of $h = 0$ shown in Fig.3(a).

As for the magnetic susceptibility, the magnetization of the $Ca_3Co_{2-x}Mn_xO_6$ ($Ca_3Co_2O_6$) system was fully investigated in previous works.[27−32] These works illustrated the important role of the interchain exchange interaction for the magnetization, and predicted that the present spin chain Ising model is not proper to calculate the magnetic susceptibility of $Ca_3Co_{2-x}Mn_xO_6$. The good consistency of calculated dielectric susceptibility with experiments even without consideration of the interchain interaction confirms the applicability of the present model.

What should be mentioned here is that the inconsistency between our calculation and experimental data grows with temperature. High order correction of LES assumption may be a reason for this inconsistency, and the long range order, which is supposed to be unbroken in the whole paper, is not so stable in the real system that a suppression of polarization for the breaking of long range order may be an effective correction to our model.

## 4. Conclusion

In summary, an elastic Ising model is constructed to explain the exchange striction in the $Ca_3Co_{2-x}Mn_xO_6$ system, and also the ferroelectricity generated from the collinear spin order. A statistic solution to this model under the low-excited state assumption and the first-order correction has been presented. The calculated dielectric and ferroelectric properties at the ground state and low-excited state agree well with the experiment. The elastic exchange energy in the up–up–down–down magnetic order is considered to be responsible for the ion displacements and thus the ferroelectricity.

# References


[1] Khomskii D I 2006 *J. Magn. Magn. Mater.* **306** 1
[2] Tokura Y 2006 *Science* **312** 1481
[3] Cheong S W and Mostovoy M 2007 *Nat. Mater.* **6** 13
[4] Fiebig M 2005 *J. Phys.* D **38** R123
[5] Feng H J and Liu F M 2007 *Chin. Phys.* B **17** 1874
[6] Ge B H, Li F H, Li X M, Wang Y M, Chi Z H and Jin C Q 2008 *Chin. Phys.* B **17** 3163
[7] Zhang Y, Deng C Y, Ma J, Liu Y H and Nan C W 2008 *Chin. Phys.* B **17** 3910
[8] Xu F, Bai Y, Ai F and Qiao L J 2008 *Chin. Phys.* B **17** 4562
[9] Katsura H, Balatsky A V and Nagaosa N 2005 *Phys. Rev. Lett.* **95** 057205
[10] Jia C, Onoda S, Nagaosa N and Han J H 2007 *Phys. Rev.* B **76** 144424
[11] Sergienko J A, and Dagotto E 2006 *Phys. Rev.* B **73** 094434
[12] Sergienko J A, Şen C and Dagotto E 2006 *Phys. Rev. Lett.* **97** 227204
[13] Dzyaloshinskii I 1964 *Sov. Phys. JETP* **19** 960
[14] Moriya T 1960 *Phys. Rev.* **120** 91
[15] Li Q C, Dong S and Liu J M 2008 *Phys. Rev.* B **77** 054442
[16] Kim J H, Lee S H, Park S I, Kenzelmann M, Harris A B, Schefer J, Chung J H, Majkrzak C F, Takeda M, Wakimoto S, Park S Y, Cheong S W, Matsuda M, Kimura H, NodaY and Kakurai K 2008 *Phys. Rev.* B **78** 245115
[17] Chapon L C, Radaelli P G, Blake G R, Park S and Cheong S W 2006 *Phys. Rev. Lett.* **96** 097601
[18] Choi Y J, Yi H T, Lee S, Huang Q, Kiryukhin V and Cheong S W 2008 *Phys. Rev. Lett.* **100** 047601
[19] Fisher M E and Selke W 1980 *Phys. Rev. Lett.* **44** 1502
[20] Zhu X and Landau D P 2006 *Phys. Rev.* B **73** 064115
[21] Rayaprol S, Sengupta K and Sampathkumaran E V 2003 *Solid State Commun.* **128** 79
[22] Zubkov V G, Bazuev G V, Tyutyunnik A P and Berger I F 2001 *J. Solid State Chem.* **160** 293
[23] Wu H, Haverkort M W, Hu Z, Khomskii D I and Tjeng L H 2005 *Phys. Rev. Lett.* **95** 186401
[24] Hardy V, Lambert S, Lees M R and Paul D Mck 2003 *Phys. Rev.* B **68** 014424
[25] Kageyama H, Yoshimura K, Kosuge K, Azuma M, Takano M, Mitamura H and Goto T 1997 *J. Phys. Soc. Jpn.* **66** 3996
[26] Baxter R J 1982 *Exactly Solved Models in Statistical Mechanics* (London: Academic Press) p34
[27] Kudasov Y B 2006 *Phys. Rev. Lett.* **96** 027212
[28] Yao X Y, Dong S and Liu J M 2006 *Phys. Rev.* B **73** 212415
[29] Yao X Y, Dong S and Liu J M 2006 *Phys. Rev.* B **74** 134421
[30] Yao X Y, Dong S, Xia K, Li P L and Liu J M 2007 *Phys. Rev.* B **76** 024435
[31] Li P L, Yao X Y, Gao F, Zhao C, Yin K B, Weng Y Y, Liu J M and Ren Z F 2007 *Appl. Phys. Lett.* **91** 042502
[32] Li P L, Yao X Y, Wang K F, Lu C L, Gao F and Liu J M 2008 *J. Appl. Phys.* **104** 054111