Soft mode characteristics of up-up-down-down spin chains: The role of exchange interactions on lattice dynamics

Y. J. Guo,1,2 Y. J. Gao,1 C. N Ge,1 Y. Y. Guo,3 Z. B. Yan,2 and J.-M. Liu2,a)
1 School of Physics and Electronic Engineering, Jiangsu Second Normal University, Nanjing 210013, China
2 Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, China
3 College of Electronic Science and Engineering, Nanjing University of Posts and Telecommunications, Nanjing 210003, China

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In this work, the dynamics of a diatomic chain is investigated with \( \uparrow \downarrow \downarrow \) spin order in which the dispersion relation characterizes the effect of magnetic interactions on the lattice dynamics. The optical or acoustic mode softening in the center or boundary of the Brillouin zone can be observed, indicating the transitions of ferroelectric state, antiferromagnetic state, or ferroelastic state. The coexistence of the multiferroic orders related to the \( \uparrow \downarrow \downarrow \) spin order represents a type of intrinsic multiferroic with strong ferroelectric order and different microscopic mechanisms. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4918767]

In 1960s, Cochran and Anderson proposed a lattice dynamic theory in which the ferroelectric (FE) transition is related with a certain mode of lattice vibration in crystals.1–4 Since then, ferroelectricity can be treated as a problem of lattice dynamics. Such a microscopic mechanism of FE transition is named as the soft mode theory. Here, the terminology “softening” implies a gradual freezing of the lattice vibration frequencies. As the square of vibration frequency \((\omega^2)\) approaches to zero and becomes negative, the vibration mode with non-real frequency appears, indicating the lattice instability.5

In recent years, great attention has been paid to a new type of ferroelectrics, the multiferroics, which accommodate simultaneously the FE and specific spin orders.6–8 In the framework of Landau theory, coexisting ferroelectricity and magnetism may produce the cross-magnetoelastic coupling. This coupling is, however, weak in proper ferroelectrics, since the ferroelectricity and magnetism in these materials are antithetic in terms of electronic structure. Therefore, much attention is paid to the so-called “improper ferroelectricity,” which originates from specific spin orders with broken spatial inversion symmetry. These spin orders include spiral spin order,6–11 E-type antiferromagnetic (AFM) order,12,13 or collinear \( \uparrow \downarrow \downarrow \uparrow \) spin order.14–16 These materials have been named as intrinsic multiferroics and consequently, the magnetoelastic coupling must be very strong, since the specific spin orders are one of the ingredients for ferroelectricity generation. Along this line, the mechanism for FE transition is totally different from the structure transition in conventional displacive FE systems. An interesting issue here is how the vibration modes couple with the spin orders and whether the vibration mode would “soften” in these intrinsic multiferroics?

The strong coupling between these two ferroic orders in intrinsic multiferroics makes the control of electrical polarization by external magnetic field or the control of magnetism by electric field possible, and also is expected to appear in static properties and dynamical responses.17–20 As investigated by Pimenov et al., the far-infrared spectroscopy in TbMnO3 and GdMnO3 presents a single-peak structure only under electric field \( E^\parallel//a\)–axis, which indicates an excitation from electric field responses.18 The frequency of the absorption peak at wave-number \(~20\) cm\(^{-1}\) is much lower than phonon frequencies at \(~100\) cm\(^{-1}\) and just fall on the region of spin wave. Therefore, the electrically driven spin excitations, termed as electromagnons, can be seen as the response of spin order to lattice vibration. Such peculiar phenomena stimulate great enthusiasm both experimentally and theoretically, and subsequently electromagnons were observed in a series of materials such as Gd1–xTbxMnO3, DyMnO3, Eu1–xYxMnO3, and RMn2O5.21–24 With respect to electromagnons, the impact of spin order on lattice vibration mode is relatively insignificant. Although frequency red–shifting in the low-lying optical phonon in TbMnO3, GdMnO3, and Eu0.75Y0.25MnO3 was claimed,25–27 no sufficient experimental measurements indicated the frequency softening substantially into zero or negative zone in accompanying the construction of FE order.

Regarding the microscopic mechanism for the improper ferroelectricity in these intrinsic multiferroics, one has sufficient reason to believe that the magnetic interactions would surely affect the dynamics of lattice.28 Experimentally, the low FE transition temperature and small polarization in intrinsic multiferroics may be the obstacles to the observation of soft mode behavior. Considering the totally different mechanisms for ferroelectricity in displacive ferroelectrics and intrinsic multiferroics, it is attractive to examine theoretically whether the vibration mode softening would happen and what is the difference in the soft mode behavior between the two types of ferroelectrics. It is known that in multiferroic \( R\)MnO3 (\( R = \)Gd, Tb, and Dy) with spiral spin order, the Dzyaloshinskii-Moriya interaction (DMI) is responsible for...
the FE order. For collinear multiferroics (Ca$_3$CoMnO$_6$ or orthorhombic RMnO$_3$ with $R$ = Ho, Y), the FE order originates from the exchange striction, which is considered to be much stronger than DMI. In this sense, the soft mode phonon, if any, would be more probably appear in the latter cases. In this work, we choose a diatomic chain with ↑↓↑↓ IIsing magnet, as a simplified model to multiferroics Ca$_3$CoMnO$_6$ and intend to explore the correlation between the magnetic interactions and lattice vibrations.

Fig. 1 presents a diatomic chain with alternating A and B ions, while the up-up-down-down magnetic would cause coherent ion displacement. While in multiferroic lattices, magnetic interactions must be taken into consideration in addition to the conventional dynamics, such as the exchange interaction. According to previous work, in the system with ↑↓↑↓ spin order or E-type AFM order, a contraction or stretching force would be generated from each parallel or anti-parallel spin pair. Such effect, named as exchange striction, is known to be responsible for the ionic displacement in multiferroics with linear spin order, and an elastic Ising model is supposed to be essential in lattice dynamics.

It is noted that the dimensionality issue of spin order is not concerned here, i.e., we treat a one-dimensional spin chain, which is a unit in a three-dimensional spin system. Therefore, one is allowed to deal with the one-dimensional system as the simplest model to illustrate the lattice dynamics. Thus, to describe the lattice vibration of this diatomic chain, the Hamiltonian should include the following terms:

$$H = H_E + H_C + H_M$$

$$= \frac{1}{2} k \sum_i (r_{i+1} - r_i)^2 + \frac{1}{4\pi\varepsilon_0} \sum_{ij} \frac{Q_i Q_j}{R_{ij}}$$

$$- \sum_{ij} J_{ij} S_i \cdot S_j - \sum_{ij} J_{ij} S_i \cdot S_j,$$

(1)

where $H_E$ denotes the harmonic elastic potential with stiffness factor $k$; $H_C$ presents the long-range Coulomb potential; and $H_M$ is the magnetic term of Ising model. Subscripts $i$ and $j$ represent the ions (or spins) on $i$-th and $j$-th sites ($i < j$); $r_i$ is the displacement of ion on $i$-th site with respect to the equilibrium position, while $r_{ij} = r_i - r_j$; and $R_{ij} = |r_{ij} + (i - j)d|$ is the distance between ions on sites $i$ and $j$; the lattice constant is $2a$; $\varepsilon_0$ is the vacuum dielectric permeability. $J_{ij}$ is the exchange interaction; $\left(\ldots\right)$ concerns the nearest-neighbor (NN) spin-pairs, while $\left[\ldots\right]$ denotes the next nearest-neighbor (NNN) ones. For $i = 2n$, $S_i \sim S^A$, $Q_i \sim Q_A$, while $S_i \sim S^B$, $Q_i \sim Q_B$ at $i = 2n + 1$. $S^A$ and $S^B$ represent the spins of ions A and B and they only take the values of ±1, while $Q_A = -Q_B = Q$.

The exchange interactions $J_{ij}$ originated from the quantum effect of identity principle, are very intricate, and an explicit form for this interaction is still absent. But it can also be addressed $J_{ij}$ should be the function of relative displacement $r_{ij}$. To take account of this dependence, one can expand the $J_{ij}(r_{ij})$ function in a Taylor series

$$J_{ij} = J_{ij0} + \frac{1}{2} \mu J_{ij0}^2 + O(r_{ij}^3), \quad \mu = 1, 2, 3.$$

(2)

Here, subscripts $\mu = 1, 2, 3$ represent the magnetic interaction between the NN A-B ions, NNN A-A ions, or NNN B-B ions, respectively.

Following the traditional approach, the equation of dynamics can be written as

$$m_A \ddot{r}_{2n} = k(r_{2n+1} - r_{2n-1} - 2r_{2n}) - 2\gamma \sum_{p=1}^{\infty} \left[ \frac{2r_{2n} - r_{2n+2p} - r_{2n-2p} - 2r_{2n} - r_{2n+2p-1} - r_{2n-2p+1}}{(2p)^3} \right]$$

$$m_B \ddot{r}_{2n+1} = k(r_{2n+2} + r_{2n-2} - 2r_{2n+1}) + 2\gamma \sum_{p=1}^{\infty} \left[ \frac{2r_{2n+1} - r_{2n+2p+1} + r_{2n-2p+1} - 2r_{2n+1} - r_{2n+2p} + r_{2n-2p+2}}{(2p)^3} \right]$$

(3)

where $\gamma = Q^2/4\pi\varepsilon_0 a^3$ defining the strength of long range Coulomb interactions and $m_A$ and $m_B$ are the atomic mass of A and B. It can be easily deduced that the solution of Eq. (3) takes the form of $r_{2n} = A_0 + A \exp[i(\omega t - (2n)a)]$ and $r_{2n+1} = B_0 + B \exp[i(\omega t - (2n+1)a)]$. Such lattice wave functions indicate an oscillation of A/B ions in their new equilibrium position with the coherent displacement

$$\delta = B_0 - A_0 = \frac{\alpha_1}{k - \frac{q}{\varepsilon_0} \frac{1}{3}\gamma}.$$

(4)
Here, $\zeta(3) = 1/1^3 + 1/2^3 + 1/3^3 + \cdots \approx 1.202$.
To get a concise expression, we define certain variable
\[
\begin{align*}
\xi' &= k - \beta_2(\cos 2qa - 1) + \gamma \sum_{p=1}^{\infty} \frac{1 - \cos(2p)qa}{(2p)^3} - \frac{1}{(2p-1)^3} \\
\xi'' &= k - \beta_3(\cos 2qa - 1) + \gamma \sum_{p=1}^{\infty} \frac{1 - \cos(2p)qa}{(2p)^3} - \frac{1}{(2p-1)^3} \\
\eta &= \left[ k \cos qa - \gamma \sum_{p=1}^{\infty} \cos(2p-1)qa \right]^2 - (\beta_1 \sin qa)^2 \\
\Delta &= (m_A \xi'' - m_A \xi')^2 + 4m_A m_B \eta.
\end{align*}
\]
Thus, the dispersion relation yields
\[
\omega^2_\alpha(q) = \frac{1}{m_A m_B} \left[ m_A \xi' + m_B \xi'' \pm \sqrt{\Delta} \right].
\] (6)

Equation (6) presents a similar form as the dispersion relation of diatomic chain model in reference book, while $\xi'$ and $\xi''$ can be regarded as the correction of the stiffness factor ($k$) under long range Coulomb interaction ($\gamma$) and magnetic elastic term ($\beta$).

In the following, the dispersion relations of the optical branch $\omega^2_\alpha(q)$, as shown in Fig. 2, and the acoustic branch $\omega^2_\alpha(q)$, as shown in Fig. 3, as a function of reciprocal lattice vectors $q$, respectively, are plotted with different parameters $k, \gamma, \beta_1, \beta_2,$ and $\beta_3$; parameter $\gamma$ is defined as the unit strength of interactions ($\gamma = 1$). It is shown that at $\Delta < 0$, $\omega^2_\alpha(q)$ would take complex values, which are just plotted as a constant $\epsilon$ in Figs. 2 and 3, where $\epsilon$ is an infinitesimal negative number, representing the softening of vibration mode.

We perform a series of calculation of the phonon modes, given different parameters ($k, \beta_1, \beta_2$, and $\beta_3$). For simplicity, we impose $\beta_2 = \beta_3, \gamma = 1, m_A = 1,$ and $m_B = 0.5$, and then change the values of $\beta_1, \beta_2,$ and $k$. A choice of other set of parameters ($\gamma, m_A, and m_B$) does not change the phonon spectra in a qualitative sense.

**FIG. 2.** Dispersion relation $\omega^2_\alpha(q)$ of optical branch (a) for a set of $\beta_3(\beta_1)$ values from $-0.5$ to $0.1$, inserted at $k = 1.2$ and $\beta_1 = 0.1$; (b) for a set of $\beta_1$ values from $0.1$ to $0.4$, inserted at $k = 1.2$ and $\beta_2 = \beta_3 = 0.1$; (c) for a set of $\beta_2(\beta_3)$ values from $-0.15$ to $0.15$, inserted at $k = 0.8$ and $\beta_1 = 0.1$; and (d) for a set of $\beta_1$ values from $0$ to $0.6$, inserted at $k = 0.8$ and $\beta_2 = \beta_3 = 0.1$. $\epsilon$ is an infinitesimal negative number.

**FIG. 3.** Dispersion relation $\omega^2_\alpha(q)$ of acoustic branch (a) for a set of $\beta_2(\beta_1)$ values from $-0.35$ to $-0.05$, inserted at $k = 1.2$ and $\beta_1 = 0.1$; (b) for a set of $\beta_1$ values from $0.05$ to $0.35$, inserted at $k = 1.2$ and $\beta_2 = -0.3$; (c) for a set of $\beta_2(\beta_1)$ values from $-0.3$ to $0.3$, inserted at $k = 0.8$ and $\beta_1 = 0.1$; and (d) for a set of $\beta_1$ values from $0$ to $0.3$, inserted at $k = 0.8$ and $\beta_2 = \beta_1 = 0.1$. $\epsilon$ is an infinitesimal negative number.

The calculated dispersion relations $\omega^2_\alpha(q)$ are summarized in Fig. 2 for a set of $\beta_1, \beta_2(\beta_3)$ values at $k = 1.2$ and $k = 0.8$. Results suggested that small $k, \beta_1$ and big $\beta_2(\beta_3), \gamma$ favor the softening of the optical phonons both in the center and on the boundary of Brillouin zone. We consider the acoustic branch and the mode softening in the center of Brillouin zone, which indicates the ferroelastic transitions. The calculated dispersion relations $\omega^2_\alpha(q)$ are presented in Fig. 3 at $k = 1.2$ and $0.8$ with a set of $\beta_1$ and $\beta_2(\beta_3)$. In comparison with the optical phonon, the acoustic mode softening in the center of Brillouin zone requires small $k, \beta_1$ and $\beta_2(\beta_3)$, as well as big $\gamma$.

As discussed before, softening of vibration mode can be contributed into two aspects: one concerns correction of the stiffness factor $k$ under long range Coulomb interaction $\gamma$ and magnetic elastic term $\beta_2(\beta_3)$, with the parameter $\xi'$ (or $\xi''$) < 0; the other denotes the instability of lattice vibration originated from $\Delta < 0$. Figs. 2 and 3 show the soft mode in the center of Brillouin zone originates from the former effect, both for optical mode and acoustic mode; while the latter would be mainly responsible for the softening in the boundary of Brillouin zone. A bit of more detailed analysis on the dispersion relations is given.

The mode softening indicates the non-real frequency of vibration mode, which appears at $\Delta < 0$ and/or $\omega^2_\alpha < 0$. In the center of Brillouin zone ($q = 0$), given $\beta_2 = \beta_3$, one has $\xi' = \xi''$, and, thus, one always has $\Delta \geq 0$. Therefore, the mode softening appears only at $\omega^2_\alpha < 0$. For satisfying $\omega^2_\alpha < 0$, we have
\[
k - \frac{7}{8} \gamma \zeta(3) < 0 \quad \text{and} \quad 2 \left[ k - \frac{7}{8} \gamma \zeta(3) \right] \left( k + 2 \beta_2 - \gamma \frac{\ln 2}{2} - \beta_1^2 > 0. \right.
\] (7a)
For meeting $\omega^2_\alpha < 0$, one has
\[
k - \frac{7}{8} \gamma \zeta(3) < 0 \quad \text{or} \quad 2 \left[ k - \frac{7}{8} \gamma \zeta(3) \right] \left( k + 2 \beta_2 - \gamma \frac{\ln 2}{2} - \beta_1^2 < 0. \right.
\] (7b)
IV. No phase transition relevant with the phonon mode
We consider the exchange striction mechanism related to the soft phonons, since these two equations show no correlation. To this stage, it seems for us to reach a new type of multiferroics with high Curie temperature and large electrical polarization.

Now, we apply the present theory to Ca$_3$CoMnO$_6$ as an example. Referring to our previous work, we take $k \sim 195$ N/m and $\gamma \sim 111$ N/m. The exchange interaction $J$ is hard to obtain and we assume $J = J_{\mu} = (m_{\mu}p_{\mu})^2$ with parameter $\lambda$ adjustable and $\beta_\mu = \lambda(\mu - 1) / 2$. By choosing $\lambda = 12$, we obtain $\beta_1 = 1.63$ N/m, $\beta_2 = 0.37$ N/m, and $\beta_3 = 0.19$ N/m. For $\lambda = 18$, one has $\beta_1 = 3.77$ N/m, $\beta_2 = 0.86$ N/m, and $\beta_3 = 0.44$ N/m. With all these parameters, it can be concluded the softening of vibrations would not be observed in Ca$_3$CoMnO$_6$, even with the ferroelectric order. In most systems, since the magnetic term $\beta_\mu$ is much smaller than parameters $k$ and $\gamma$, a critical system of ferroelectric transition may be more probable to realize the phonon softening in this type.

In summary, we have investigated the role of magnetic interactions on the lattice dynamics in a diatomic spin chain model and calculated the dispersion relationship for the softening of vibration modes. It is predicted that the soft mode is mainly dependent on the short-range lattice elastic energy, long-range Coulomb interactions, and exchange interactions. Along this line, the soft phonons representing the FE, AFE, and ferroelastic orders are coupled with the $\uparrow \downarrow \downarrow$ spin order. Given the different mechanisms, a new type of multiferroics with such coexisting ferroic orders may be proposed, while more comprehensive investigation of possible materials fitting this category is still required.

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\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig4}
\caption{Phase diagram of (a) parameters $k$ and $\beta_2$, as $\beta_1 = 0.01$; (b) parameters $k$ and $\beta_1$, as $\beta_2 = 0.1$. (c) Parameters $\beta_1$ and $\beta_2$, as $k = 1.2$; (d) parameters $\beta_1$ and $\beta_2$, as $k = 1.0$.}
\end{figure}

Equations (7) and (8) define various regions in the parameter space for the phonon mode softening in the center of Brillouin zone or on the boundary of Brillouin zone, marking the FE, AFE, or ferroelastic transitions possible. The corresponding phase diagrams are presented in Fig. 4: ferroelastic phase in region I, FE and AFE phases in region II, ferroelastic and FE phases in region III, and ferroelastic, FE, and AFE phases in region IV. No phase transition relevant with the phonon mode occurs in other regions.

Furthermore, the lattice dynamics origins for these phase transitions can be understood from Eqs. (7) and (8), respectively. First, if no spin interactions are considered, i.e., no exchange striction mechanism related to the $\uparrow \downarrow \downarrow \downarrow$ spin order is involved, one has $J_{\mu} = m_{\mu} = 0$. In this case, the softening of the optical phonon modes in the center of Brillouin zone occurs as $\text{ln}2 - \gamma < 0$. If the $\uparrow \downarrow \downarrow \downarrow$ spin ordering is considered, the softening ensues at $k - \text{ln}2 - \gamma < 0$. Therefore, one can argue that in the region $\text{ln}2 < k / \gamma < 7/8 - \gamma$, the FE transition is most likely driven by the $\uparrow \downarrow \downarrow \downarrow$ spin order.

In Eq. (4), the coherent ion displacement $\delta$ indicates that the ferroelectricity originates from the exchange striction, similar to Ca$_3$CoMnO$_6$ system. However, as seen from Eq. (7a), the softening of optical phonons in the center of Brillouin zone suggests a displaceable ferroelectricity, much stronger than the former one. We can also deduce displacement $\delta$ to be irrelevant to the soft phonons, since these two equations show no correlation. To this stage, it seems for us...