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Anharmonic phonon properties in $Eu_{0.5}Ba_{0.5}TiO_3$

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Phonon properties have been studied using reduced sound velocity of $Eu_{0.5}Ba_{0.5}TiO_3$ (EBTO). To achieve this aim, the anharmonic phonon-phonon interaction and the spin-phonon interaction were used. It was shown that the reduced sound velocity of multiferroic EBTO exhibits a kink at $T_N = 1.9$ K. This anomalously reduced sound velocity can be interpreted as an effect of vanishing magnetic ordering above T_N. What's more, the ferroelectric subsystem cannot be influenced by the magnetic subsystem above T_N for $T_N \ll T_C$ in the EBTO. It was found that the reduced sound velocity decreases as T increases near ferroelectric transition T_C. That is to say, the sound velocity softens near ferroelectric transition T_C. It is also noteworthy that the reduced sound velocity softens when the R^E (the coupling between the ferroelectric pseudo-spins and phonons), $V^{(3)}$ and $|V^{(4)}|$ (the third- and fourth-order atomic force constants of the anharmonic phonons, respectively) increase. These conclusions are all in good accordance with the experimental data and theoretical results.

Keywords: *anharmonic phonon-phonon interaction; reduced sound velocity; multiferroics*

1. Introduction

$Eu_{0.5}Ba_{0.5}TiO_3$ (EBTO) has a ferroelectric phase transition temperature ($T_C = 213$ K) and an antiferromagnetic phase transition temperature ($T_N = 1.9$ K) [1–4]. EBTO represents the coexistence of ferroelectric and antiferromagnetic orders, and for this reason, it has attracted much attention [1–6]. $EuTiO_3$ has a low Neel temperature ($T_N \sim 5.3$ K) typical of G-type antiferromagnetism. $BaTiO_3$ has a Curie temperature of ferroelectricity $T_C \sim 400$ K. In addition, Rushchanskii et al. [6] took a 50/50 (Eu, Ba)TiO_3 ordered alloy as a starting point and calculated the properties of EBTO using the first principles approach. Rowan-Weetaluktuk et al. [7] studied the effects of phonon mode softening at T_C in EBTO by Mössbauer spectroscopy. At last but not least, the reduced sound velocity is a powerful technique to study the properties of lattice. Further, many researchers have used microscopic theoretical approaches to study the multiferroic properties of EBTO [5, 7–9]. Especially, Wesselinowa [8] investigated the origin of the multiferroicity of EBTO. Nevertheless, they have not studied the reduced sound velocity of EBTO. To the best of our knowledge, little microscopic theoretical work has been done on reduced sound velocity in multiferroic EBTO. In this paper, we have studied the phonon properties using the reduced sound velocity.

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2. The model

The Hamiltonian of the EBTO can be described as [8]:

$$H_{mu} = H^M + H^E + H^{ME} + H^{PH} \tag{1}$$

H^M is the Hamiltonian of the magnetic subsystem (MS) $EuTiO_3$:

$$H^M = -\frac{1}{2}\sum_{[ij]} J_1(i,j) P_i \cdot P_j - \frac{1}{2}\sum_{\langle ij\rangle} J_2(i,j) P_i \cdot P_j \tag{2}$$

P_i is the magnetic spin at the site i, [ij] and $\langle ij\rangle$ denote the sum of the nearest neighbor (nn) magnetic spins and the next-nearest neighbor (nnn) magnetic spins, respectively. $J_1 > 0$ and $J_2 < 0$ are the exchange coupling constants of the nn magnetic spins and the nnn magnetic spins, respectively.

H^E is the Hamiltonian of the electrical subsystem (ES) $BaTiO_3$:

$$H^E = -\Omega\sum_k S_k^x - \frac{1}{2}\sum_{kl} I_{kl} S_k^z S_l^z \tag{3}$$

S_k^x and S_k^z are the pseudo-spins at the site k. The exchange coupling constant between the nn pseudo-spins is $I_{kl} > 0$ the ES, and the tunneling frequency is Ω.

H^{ME} is the Hamiltonian of the coupling between MS and ES:

$$H^{ME} = -K\sum_{ij}\sum_{kl} S_k^z S_l^z P_i \cdot P_j \tag{4}$$

where K is the magnetoelectric (ME) coupling constant.

H^{PH} is the Hamiltonian of the phonon and phonon-spin/ phonon-pseudospin interactions:

$$\begin{aligned} H^{PH} &= -\sum_q F^M(q) A_q P_{-q}^z \\ &- \frac{1}{2}\sum_{qq_1} R^M(q,q_1) A_q A_{-q_1} P_{q_1-q}^z \\ &- \sum_q F^E(q) A_q S_{-q}^z - \frac{1}{2}\sum_{qq_1} R^E(q,q_1) A_q A_{-q_1} S_{q_1-q}^z \\ &+ \frac{1}{2}\sum_q (B_q B_{-q} + \omega_0^2 A_q A_{-q}) \\ &+ \frac{1}{3}\sum_{qq_1} V^{(3)} A_q A_{-q_1} A_{q_1-q} \\ &+ \frac{1}{4}\sum_{qq_1q_2} V^{(4)} A_{q_1} A_{q_2} A_{-q-q_2} A_{-q_1+q} \end{aligned} \tag{5}$$

The first two terms describe the coupling between the magnetic order parameters and the phonons, while the following two terms refer to the coupling between the ferroelectric pseudo-spins and phonons. The last term is the harmonic phonon Hamiltonian, where ω_0 is the harmonic phonon frequency of the lattice mode. $A_q = \sqrt{1/2\omega_0}(a_q + a_q^+)$, $B_q = i\sqrt{\omega_0/2}(a_q^+ - a_q)$. $V^{(3)}$ and $V^{(4)}$ are the third- and fourth-order atomic force constants of the anharmonic phonons, respectively [10].

3. Reduced sound velocity

The reduced sound velocity [11–13]:

$$\tilde{v} = \sqrt{1 - H^2} \tag{6}$$

where:

$$H = \sqrt{\frac{R^M\langle P^z\rangle + R^E\langle S^z\rangle - V^{(4)}\langle A^2\rangle - 2V^{(3)}\langle A\rangle}{2\omega_0^2}}.$$

According to the method described in the literature [11], the $\langle A\rangle$ can be written as:

$$\begin{aligned} \langle A\rangle &= [2F^M(k)\langle P^z\rangle + 2F^E(k)\langle S^z\rangle \\ &- \frac{1}{N}\sum_q V^{(3)}\langle 2\bar{N}_q + 1\rangle]/[\omega_0 - \sum_{q_1} R^M(k)\langle P^z\rangle \\ &- \sum_{q_1} R^E(k)\langle S_{q_1-q}^z\rangle + \frac{1}{N}\sum_q V^{(4)}\langle 2\bar{N}_q + 1\rangle] \end{aligned} \tag{7}$$

where $\bar{N}_q = 1/[\exp(\bar{\omega}_q/T) - 1]$.

The expression of the magnetization can be solved on the basis of Callen method [14]:

$$\langle P^z\rangle = \frac{(\Phi + 1 + P)\Phi^{2P+1} - (\Phi - P)(\Phi + 1)^{2P+1}}{(\Phi + 1)^{2P+1} - \Phi^{2P+1}} \tag{8}$$

Here, $\Phi = \frac{1}{N}\sum_k \frac{1}{e^{\beta E_M(k)} - 1}$, $E_M = \langle P_k^z\rangle(J_{10}' - J_{1k}' + J_{20} - J_{2k}) + F^M(O)\langle A\rangle + \frac{1}{2}R^M(O)\langle A^2\rangle$, $J_{10}' = n_1 J_1'$, $J_{1k}' = J_1'\sum_{[ij]} e^{ik(i-j)}$, $J_{20} = n_2 J_2$, $J_{2k} = J_2\sum_{\langle ij\rangle} e^{ik(i-j)}$ and $J_1' = J_1 + 2K\sum_{[kl]}\langle S_k^z S_l^z\rangle$ (n_1 and n_2 are the numbers of nn and nnn spins, respectively).

The z-component of the pseudo-spin $\langle S^z\rangle$, following the method of Teng et al. [15], can be written as:

$$\langle S^z\rangle = (\delta/2\omega_E)\tanh(E_E/2k_BT) \tag{9}$$

where $E_E^2 = I_E^2 + \Omega^2$, $I_E = I_1\sum_l\langle S_l^z\rangle$ and $I_1 = I/2 + 2K\sum_{[ij]}(\langle P_i^+ + P_j^-\rangle + \langle P_i^z P_j^z\rangle)$.

4. Results and discussion

The parameters of the model have been used for the ES (electrical) and the MS (magnetic) systems: $J_1 = 0.8$ K, $J_2 = -0.5$ K, $\Omega = 5$ K , and the bare phonon frequency (i.e. harmonic phonon frequency) $\omega_0 = 253$ cm^{-1} [8, 16], $F^E = 3$ cm^{-1}, $F^M = 0.8$ cm^{-1}, $R^E = -3.0$ cm^{-1}, $R^M = -1.0$ cm^{-1}, $V^{(3)} = 0.5$ cm^{-1},

$V^{(4)} = -2.5$ cm^{-1}, the spin P = 3.5 and the pseudo-spin S = 0.5. These parameters can produce $T_C = 213$ K and $T_N = 1.9$ K.

Fig. 1 to Fig. 4 show how the reduced sound velocity ($\tilde{v}$) vary with temperature (T). It has been found that the reduced sound velocity of EBTO exhibits a kink at $T_N = 1.9$ K. This anomalous reduced sound velocity can be interpreted as an effect of vanishing magnetic ordering above T_N. In addition, the ES can not be influenced by the MS above T_N for $T_N \ll T_C$ in the EBTO. This theoretical conclusion obtained from the study is in good accordance with the phonon energy [8] and other experimental results [6, 7]. It has also been found that the reduced sound velocities will soften at T_C. That is to say, the sound velocity is softened near ferroelectric transition temperature T_C. These results are the same as the theoretical data of Wesselinowa [8] and the experimental results of Rowan-Weetaluktuk et al. [7].

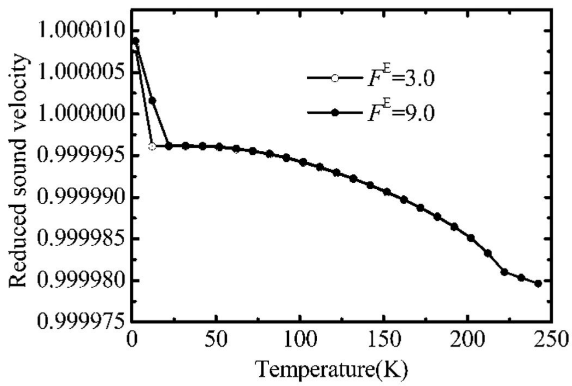

Fig. 1. Plot of reduced sound velocity $\tilde{v}$ vs. T for different values of $F^E = 3.0$ K, 9.0 K.

Fig. 1 and Fig. 2 show how the reduced sound velocity $\tilde{v}$ change with the temperature for different values of F^E and R^E, respectively. It is found that the T_N moves to higher temperature with the increase of these two parameters. This behavior can be explained as the enhancement of coupling between the ferroelectric pseudo-spins and phonons. It is noteworthy that the reduced sound velocity softens with the increase of R^E. The conclusion is in good accordance with the experimental data [2, 3, 5–7].

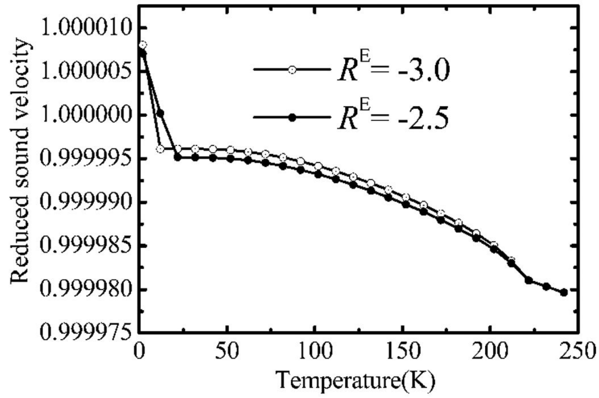

Fig. 2. Plot of reduced sound velocity $\tilde{v}$ vs. T for different values of $R^E = -2.5$ K, -3.0 K.

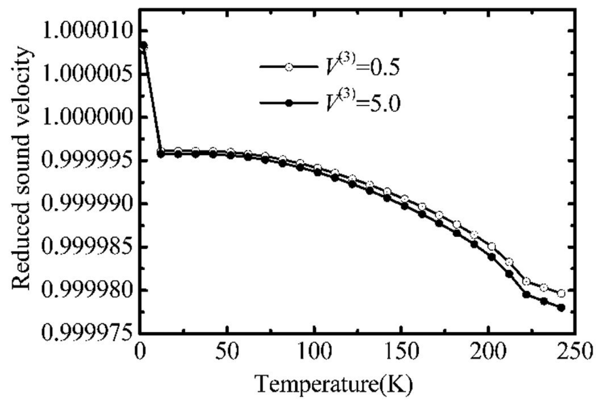

Fig. 3. Plot of reduced sound velocity $\tilde{v}$ vs. T for different values of $V^{(3)} = 0.5$ K, 5.0 K.

Fig. 3 and Fig. 4 show how the reduced sound velocity $\tilde{v}$ change with temperature for different values of $V^{(3)}$ and $V^{(4)}$, respectively. It has been found that the reduced sound velocity softens with the increase of $V^{(3)}$ and $|V^{(4)}|$. As mentioned earlier, $V^{(3)}$ and $V^{(4)}$ are the third- and fourth-order atomic force constants of the anharmonic phonons, respectively. Then, the increase of the values of $V^{(3)}$ and $|V^{(4)}|$ means that the lattice distortions increases too. This result is also in good agreement with the experimental data [2, 3, 5]. A similar result has also been obtained in the sound velocity of $BiFeO_3$ [11].

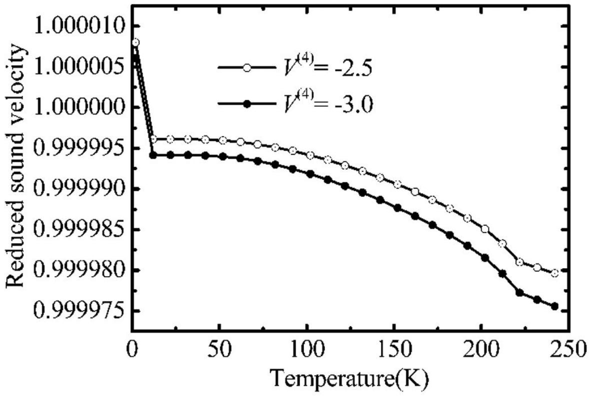

Fig. 4. Plot of reduced sound velocity $\tilde{v}$ vs. T for different values of $V^{(4)} = -2.5$ K, -3.0 K.

5. Conclusion

Phonon properties have been studied using the reduced sound velocity in EBTO. To achieve this aim, the anharmonic phonon-phonon interaction and the spin-phonon interaction have been introduced. It has been shown that the reduced sound velocity of multiferroic EBTO exhibits a kink at $T_N = 1.9$ K. This anomalous reduced sound velocity can be interpreted as an effect of vanishing magnetic ordering above T_N. What's more, the ES is insensitive to MS above T_N for $T_N \ll T_C$ in the EBTO. It has been found that reduced sound velocity decreases as T increases near ferroelectric transition T_C. That is to say, the sound velocities are softened near ferroelectric transition T_C. It is also noteworthy that the reduced sound velocity soften with the increase of R^E, $V^{(3)}$ and $|V^{(4)}|$. These conclusions are in good accordance with the experimental and theoretical data.

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