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PHONON PROPERTIES OF A MULTIFERROIC $BiFeO_3$ IN CUBIC PHASE

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Abstract: Multiferroic (MF) materials exhibit a highly coupled, spontaneous ferroelectric polarization and magnetization. Coupling between electrical and magnetic properties in multiferroic materials makes them a promising material for the design of multifunctional device applications, but also because of the interesting physics found in this class of materials. The role or absence of phonon softening in order to explain ferroelectric transition and the phonon modes symmetry in $BiFeO_3$ are some important questions still needs to be answered. Very little is known about the behaviour of phonons in magnetoelectric multiferroics. The investigations of phonons have in the past played a crucial role in the understanding of classic ferroelectrics. Motivated to determine and understand the role of phonons in multiferroics, we have undertaken the theoretical investigation on the phonon properties of $BiFeO_3$ in its cubic phase by applying lattice dynamical simulation method based on de Launey angular force (DAF) constant model. The calculated zone centre phonon frequencies agree well with available results. The phonon spectrum of $BiFeO_3$ is calculated along the three symmetry directions. Some modes of $BiFeO_3$ are coming out to be negative, representing the soft modes.
Keywords: Multiferroic materials, lattice dynamics, zone centre phonons, phonon dispersion.

Introduction

Multiferroics (MF) are the materials that enfold physics for various future technological applications and have received worldwide attention from the scientific community working in the field of materials sciences ([1], [2]). Coupling between electrical and magnetic properties is particularly interesting in multiferroic materials, which present simultaneously two or more ferroic or antiferroic order parameters. The ferroelectric [3] and antiferromagnetic properties of $BiFeO_3$ based systems, showing T_{Curie}=1090 K and $T_{Néel}$= 640 K [4], have been known for a long time, but the possibility of making devices operating at room temperature [5] gave a new burst to bismuth ferrite. The coexistence of ferroelectricity and antiferromagnetism at room temperature makes $BiFeO_3$ one of the most interesting multiferroic materials. These materials are promising for various technological applications such as information storage, spintronics, and sensors. In recent years, these compounds have

been the focus of attention in view of their possible application as multifunctional materials essential for modern microelectronics. In its ferroelectric phase, $BiFeO_3$ belongs to the R3c [6] space group, which derives from the ideal (paraelectric) Pm3m cubic perovskite group by a small distortion along the [111] cubic directions [7].

In order to understand some of the exotic ferroelectric and ferromagnetic properties of bulk $BiFeO_3$, it is important to determine the zone center phonons and interatomic interactions in this material. We have therefore, performed a systematic study of phonon properties of the perovskite-like multiferroics $BiFeO_3$ in cubic phase using theoretical short range force constant model [8]. The calculated results are compared with other calculated results [9].

Crystal Structure and Methodology

In the cubic phase of $BiFeO_3$, we have a Bi atom at (a/2,a/2,a/2), a Fe atom at (0,0,0), an oxygen at (a/2,0,0)(O_1), a second at (0,a/2,0)(O_2) and a third at (0,0,a/2)(O_3). Zone centre phonon vibration modes (Γ (O_h)) in cubic ABO_3 perovskites are split by symmetry into three T_{1u} modes and one T_{2u} mode (all of which are triply degenerate). The T_{1u} modes are active only in the infrared while the T_{2u} mode is inactive both in the infrared and Raman spectra (silent mode). The symmetry of these phonons at the Γ point (in terms of the O_h representation) is

$$\Gamma\ (O_h) = 4T_{1u} + T_{2u}$$

There are possibilities of occurrence of some imaginary frequencies at the zone boundary. The imaginary frequency corresponds to unstable mode. The unstable mode determines the nature of the phase transitions and the dielectric responses of the compounds.

In the present investigation a de Launey angular force (DAF) constant model [8] has been used to study the phonons in the $BiFeO_3$ to check whether softening of phonons are there or not in some crystal symmetry directions as it is supposed to be connected to phase changes in these compounds. In DAF model, the relative displacement of the reference atom and one of the neighbours is considered. The restoring force on the reference atom is taken to be proportional to the component of the relative displacement perpendicular to the line joining the two atoms at their equilibrium positions. The forces due to all neighbours are calculated separately and summed up together. Different force constants are used for the various categories of neighbours and the net force on the reference atom is obtained by summing over the contribution from all the neighbours.

The present calculation involves four central force constants α_1, α_2, α_3, α_4 and four angular force constants α_1', α_2', α_3' and α_4' between Fe-O, Bi-O, Bi-Fe and O-O atoms respectively

up to third nearest neighbour. The calculated dynamical matrix of (15x15) is reduced to three matrices of the order (5x5) at zone centre (ZC) [10]. Zinenko et al. [9] have performed lattice dynamics calculation of cubic phase of $BiFeO_3$ by using a nonempirical model of an ionic crystal with inclusion of dipole.

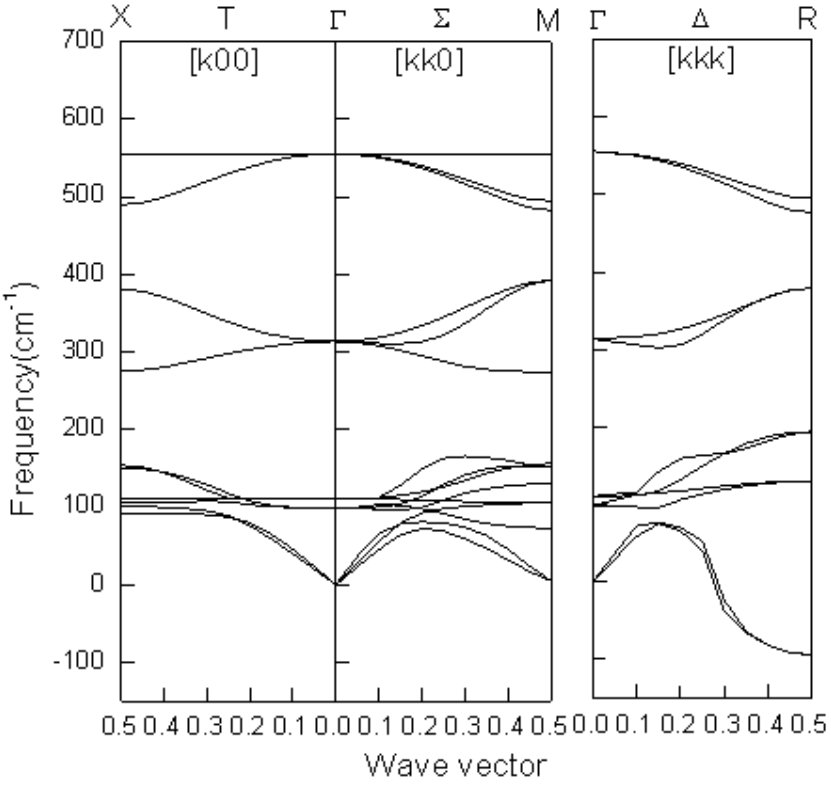

FIG.1: Phonon dispersion curves of $BiFeO_3$

In the present calculation the interatomic force constants are obtained by fitting the calculated results of Zinenko et al.[9] obtained by disregarding the long-range dipole interaction at the ZC for TO mode of infrared active phonon frequencies. The force constants thus calculated are listed in table 1. Taking these force constants as input parameters, the dynamical matrix is solved at the ZC as well as along three symmetric directions (k00), (kk0) and (kkk). The ZC phonons thus obtained are listed in table 2 along with other results [9]. The phonon dispersion curves thus obtained in three symmetric directions for $BiFeO_3$ are shown in fig. 1.

TABLE 1: Values of force constants (10^3 dyne cm^{-1})

Compound	Force constants							
	α_1 (Fe–O)	α_1' (Fe-O)	α_2 (Bi-O)	α_2' (Bi-O)	α_3 (Bi-Fe)	α_3' (Bi-Fe)	α_4 (O-O)	α_4' (O-O)
$BiFeO_3$	94.0	9.0	- 14.0	12.0	86.0	4.5	-2.50	0.265

TABLE 2: Calculated zone centre phonon frequencies in cm^{-1}

ZC phonons of $BiFeO_3$				
Modes	T_{1u}	T_{1u}	T_{1u}	T_{2u}
Present work	555	314	99	111
Other work [9]	555	314	99	109

Results and Discussion

The table 1 presents the calculated inter-atomic force constants $BiFeO_3$. It is observed that force constant α_2 between Bi-O atoms has a considerable negative value, indicating a sizable coupling between Bi and O atoms along Bi-O chain, which

does not, allows the displacement of Bi atom against O atoms. It is obvious from table 1 that the force constant α_1 between Fe-O is strongest among all other interatomic interactions in $BiFeO_3$. This suggests that the covalent bonding between (Fe-O) is strongest than that between (Bi-O), (O-O) and (Bi-Fe). The interatomic force constants presented in table 1 are taken as input parameter and the matrix is solved at zone centre. The zone centre phonons thus obtained are listed in table 2. It is obvious from table 2 that the present calculation of zone centre phonons of cubic $BiFeO_3$ gives no unstable TO mode. The zone centre phonons are in good agreement with other theoretically calculated results [9]. Unfortunately there are no experimental results available to compare the present calculation.

The dynamical matrix is solved in the three symmetric directions and complete phonon dispersion spectrum is obtained and are shown in figure 1. It is obvious from calculated phonon dispersion curves of $BiFeO_3$ in figure 1 that phonon branches are distributed almost uniformly throughout in all symmetric directions. The calculated eigen frequencies and eigen vectors suggest that the top most part of phonon dispersion curves consist of three phonon

branches and are due to Fe atom vibrations, the middle three branches at about 315 cm^{-1} are due to Bi atom vibrations, and the lower nine branches are due to Bi and O atom vibrations.
The main issue of the present calculation is to verify the occurrence of softening of modes at the boundary of Brillouin Zone (BZ) along major symmetry directions.
The softening of phonons and instability of modes are the features which are supposed to be connected to phase transitions in these compounds. It is found from present calculation that the cubic phase of $BiFeO_3$ has some unstable modes at the zone boundary, having an imaginary frequency. This is in agreement with other calculation also [9]. The most unstable modes in $BiFeO_3$ were found at R points as shown in figure 1 whereas there is softening of modes at M point. The unstable modes have eigenvectors that involve motion of the oxygen ions and may be viewed as coupled librational modes of the FeO_6 octahedra. The inactive T_{2u} mode involves alternating in-phase and out-of-phase rotation of adjacent (corner-sharing) octahedral in successive planes in the crystal [11]. The unstable phonons of the cubic phase of $BiFeO_3$ are there at Brillouin Zone boundary suggest possible distortion in cubic phase of $BiFeO_3$. The unstable mode is an indication of change in cubic phase of $BiFeO_3$ and is in agreement with other calculations [12].

Conclusion

- The zone centre phonons and phonon dispersion curves of $BiFeO_3$ have been calculated by applying a short range force constant model.
- We found a soft mode of along [kk0] and imaginary frequencies along [kkk] direction. The soft and unstable mode suggests possible distortion in cubic phase.
- We observed that the longitudinal inter-atomic force constant between nearest neighbour Bi and O atoms has a considerable negative value, indicating a sizable coupling between Bi and O atoms along Bi–O chain.
- It is worth to mention here that the proposed force constant model, with small number of parameters, gives a satisfactory description of phonon spectra of $BiFeO_3$.

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