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DYNAMICAL STUDY OF PHONONS IN FERROELECTRIC LEAD TITANATE

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Abstract.- Lattice dynamical formalism using rigid ion model with long range coulomb forces and short range axially symmetric forces has been applied to the crystal of lead titanate in tetragonal phase. All zone center phonons and a few zone boundary phonons were used in determining the force constant parameters both at room temperature and close to T_c by nonlinear least squares analysis. The results indicate that the Ti-O short range forces are at least one order of magnitude larger than the Pb-O forces. Moreover oxygens retain an effective charge of 73% of their free ion value, whereas titaniums possess only 67% of their free ion charge. The eigenvector calculations of the lowest optic mode of E-symmetry correspond to the prediction by Last, whereas in BaTiO₃ the computed eigenvectors confirm the description of the soft mode due to Slater. The parameters obtained, have been utilized to compute elastic and piezoelectric properties of PbTiO₃. The calculations of the zone centre phonons near T_c reveal that the small anharmonic forces could lead to the observed frequency changes.

The importance of lattice dynamics in studying the structural phase transitions in cubic perovskite structures was first realized by Cochran.¹ No work has, however, appeared in literature dealing with the interatomic forces in tetragonal phase and their variations with temperature. Lead titanate is one example of this class and undergoes a ferroelectric-paraelectric phase transition at 493°C, below which the crystal symmetry is tetragonal (C_{4v}^1) with one formula unit in the unit cell. According to Shirane et al.² the unit cell structure may be described by placing Pb (K=1) at the cell corners, Ti (K=2) at $(\frac{1}{2}, \frac{1}{2}, u)$ and oxygens (K=3,4,5) at $(\frac{1}{2}, \frac{1}{2}, v)$, $(\frac{1}{2}, 0, w)$, $(0, \frac{1}{2}, w)$; where $u = 0.541$, $v = 0.112$ and $w = 0.612$ with $a_0 = 3.904 \text{ \AA}$ and $c_0 = 4.15 \text{ \AA}$. Group theoretical analysis for zone centre phonons shows that the 12 optical modes should be classified as follows:

$$3A_1(Pb, Ti, O)_z + 4E(Pb, Ti, O)_{x,y} + B_1(O)_z$$

The subscripts x,y,z denote the displacement directions of the ions included in bracket. In the rigid ion formalism the potential energy of an ionic crystal can be written as the sum of short range repulsive and long range coulomb forces. For lead titanate considering ion pair potentials for all interactions for distances less than 3.5 Å, the short range part of potential energy may be elaborated as follows:

$$\phi_{S.R.} = 4\phi_{13}(r_{13}) + 4\phi_{14}(r_{14}) + 4\phi'_{14}(r'_{14}) + \phi_{23}(r_{23}) + \phi'_{23}(r'_{23}) + 4\phi_{24}(r_{24}) + 8\phi_{34}(r_{34}) + 4\phi_{45}(r_{45}) \quad (1)$$

where r' are second neighbor distances. Each short range potential is assumed to be of axially symmetric type. The potential minimum equations were worked out in the manner suggested by Katiyar.³ These conditions were in turn used to compute five tangential force constant parameters, namely, B_{13} , B_{14} , B_{23} , B_{23} and B_{24} . In order to reduce the number of force constant parameters further we assumed that the radial force constants may be interrelated by Born-Meyer type of potential function,⁴ i.e.

$$A_{34} = A_{45} e^{-\alpha_{0-0}(r_{34}-r_{45})} \quad (2)$$

with similar relations for other $A_{KK'}$. The constant α_{0-0} can be related to n_{0-0} in Pauling's potential function⁴ as follows:

$$\alpha_{0-0} = (n_{0-0} + 1)/R_{0-0}^0 \quad (3)$$

where R_{0-0}^0 corresponds to the distance between the two oxygens in contact. These transformations allowed us to reduce the number of undetermined parameters to eleven, namely, n_{Rb-0} , n_{Ti-0} , n_{0-0} , A_{14} , A_{23} , A_{45} , B_{14} , B_{34} , B_{45} , Z_{Pb} and Z_0 . The value of n_{0-0} was fixed to 7 as given by Pauling and the remaining 10 parameters were obtained by least squares fit to the zone centre phonons⁵ and a few zone boundary phonons⁶ using the method suggested by Katiyar and Mathal.⁷ Reasonably good agreement between the calculated and the observed frequencies was obtained except for $A_1(TO_3)$ phonon in which case the calculated frequency is 578 cm^{-1} whereas the observed frequency was 646 cm^{-1} . This and other small disagreements may be due to the neglect of the polarisabilities of the ions into the rigid ion model.

The values of the best fitted parameters were used to compute the axially symmetric force constant parameters and they are as follows: $A_{13} = 19.25$, $A_{14} = 38.01$, $A_{14} = 6.94$, $A_{23} = 192.80$, $A_{23} = 48.89$, $A_{24} = 122.80$, $A_{34} = 4.85$, $A_{45} = 6.27$, $B_{13} = -2.62$, $B_{14} = -7.27$, $B_{14} = -2.02$, $B_{23} = -25.10$, $B_{23} = -0.49$, $B_{24} = -14.31$, $B_{34} = -1.38$ and $B_{45} = -2.01$; all in the units of $e^2/2v$.

The parameters shown above appear to be physically acceptable. The large values of A_{23} , A_{23} and A_{24} indicates that there are strong forces between Ti and O ions, whereas the oxygen-oxygen interactions (A_{34}, A_{45}) are considerably weaker. The ionic charge obtained for Pb ion is $1.695e$ and for the oxygen ion is $-1.456e$. These values suggest highly ionic character of the crystal.

From the eigen vector calculations the normal mode picture for the soft mode corresponding to $E(TO_1)$ is drawn in Fig. 1. In this mode both Ti and O ions move against Pb ions along x- or y-axis. Similar movements occur in the soft mode $A_1(TO_1)$ along z-direction. This description of the soft mode is in agreement with the proposal by Last⁸ for $BaTiO_3$. We have carried out the above calculations for $BaTiO_3$ as well and the eigen vector calculations for the lowest dipolar mode suggest that both Ba and O ions move against the Ti ions along the principal axes which is in agreement with the picture proposed by Slater⁹ for $BaTiO_3$.

We have also adjusted our force constant parameters to obtain reasonably good agreement between the observed¹⁰ and the calculated frequencies close to the phase

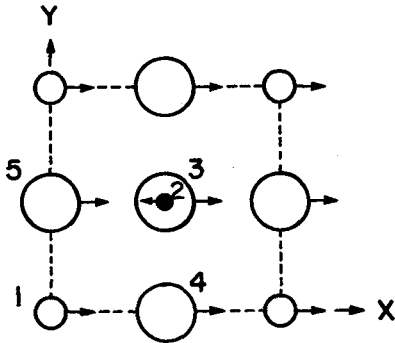


Fig. 1: Normal mode picture for $E(T0_1)$ mode ions have been projected on the xy -plane.

transition temperature ($\sim 493^\circ\text{C}$) in PbTiO_3 . The lowest optic mode $E(T0_1)$ varies from 88 cm^{-1} to 54 cm^{-1} , whereas the lowest $A_1(T0_1)$ decreases to 62 cm^{-1} from 147 cm^{-1} . A close look at the force constant variations reveals very small changes in their values except for the parameters A_{24} , A_{34} and A_{45} , whose values decrease by about 20-30% near T_c . Perhaps relatively small anharmonic forces could explain such changes.

The acoustic wave propagation in piezoelectric crystals has been discussed in detail by Hutson and White.¹¹ Following their approach we have computed piezoelectric and elastic coefficients for lead titanate using the force constant parameters obtained from phonon frequencies fit. The calculated values of elastic constants are as follows (in units of 10^{11} N/M^2): $C_{11} = 1.327$, $C_{12} = 0.846$, $C_{13} = 0.891$, $C_{33} = 0.934$, $C_{44} = 0.801$ and $C_{66} = 0.927$; and those of piezoelectric coefficients are given below (in units of 10^{-12} C/N): $d_{15} = 45.52$, $d_{31} = -15.07$, $d_{33} = 51.00$.

In above calculations we have used the values of $\epsilon_{11}/\epsilon_0 = 125.6$ from the work of Frey and Silberman and $\epsilon_{33}/\epsilon_0 = 30.0$ (dielectric constant along c -axis) as reported by Bhide et al. Unfortunately no single crystal measurements exist in the literature to compare with our calculations. We have also computed these coefficients for BaTiO_3 and except for C_{44} they compare well with the calculations of Devonshire.¹²

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