

Nonlinear lattice dynamical theory for valence transition in rare earth compounds

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Abstract. A nonlinear lattice dynamical theory is proposed to explain the mode softening in intermediate valence compound $\text{Sm}_{0.75}\text{Y}_{0.25}\text{S}$. In this theory we consider the breathing motion of the electron shells of Sm-ion to be nonlinear, and depend on temperature, resulting in strong electron-ion coupling. We calculate the salient features of the nonlinear breathing potential, which resembles the ϕ^4 potential for second order ferro-electric transitions. We also calculate the temperature dependence of LO(L) frequency for this compound, showing that at transition temperature (about 200 K) this mode freezes.

Keywords. Nonlinear lattice dynamics; rare earth compounds.

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1. Introduction

In recent years valence fluctuation and its instabilities in rare earth intermediate valence compounds (IVC) have been the subject of intense theoretical as well as experimental research (Mook *et al* 1978, 1979; Kress *et al* 1981; Dernier *et al* 1976; Bilz *et al* 1979; Penny *et al* 1975). Under the influence of valence fluctuation, strong anomalies in the phonon dispersion curves of several systems of IVC are observed. These anomalies manifest themselves in the softening of the longitudinal optic and acoustic modes at the zone boundary and at the middle of the zone ($\frac{1}{4}\frac{1}{4}\frac{1}{4}$) respectively. Large phonon linewidths are observed (Holland Moritz *et al* 1988; Wakabayashi 1980) for longitudinal modes. Transverse modes, however, remain unaffected during the valence transition. Particular interest about these phonon anomalies is that they behave unusually with temperature (Maple and Wohlleben 1971; Guntherodt *et al* 1977). For $\text{Sm}_{0.75}\text{Y}_{0.25}\text{S}$ mixed valence alloy, the softening becomes largest at about 200 K.

A look into the electronic structure of rare earth samarium atom reveals that the phonon anomalies are expected to occur due to the presence of localized, partly-filled 4f shells. In normal state, divalency is favoured for samarium ion. The two energy levels $4f^n(5d6s)^m$ and $4f^{n-1}(5d6s)^{m+1}$ are nearly degenerate and may become the same by two methods. One of these methods is application of pressure. For example, due to the application of pressure SmS transforms to metal at 6 Kbar from usual zero pressure semiconductor phase (Jayaraman *et al* 1970) corresponding to valence transition from Sm^{2+} to Sm^{3+} state. The same phenomenon occurs if the composition of Sm is changed by alloying with other rare earth atom. When SmS is

alloyed with YS, a similar transition occurs for $\text{Sm}_{1-x}\text{Y}_x\text{S}$ ($x > 0.15$). In this case, a localized $4f$ electron is promoted to the delocalized ($5d6s$) band, reducing the Coulomb screening of the core. This also results into large volume collapse. This phenomenon gives rise to resonant coupling of the phonon modes with lattice when the valence fluctuation rate is on the same time scale as the lattice vibration. If it proceeds on a time scale somewhat faster than that of phonons, phonon anomalies are expected for the LO branch at L point and the LA branch at $(\frac{1}{4}\frac{1}{4}\frac{1}{4})$.

A survey of literature reveals that the phenomenon of mode softening of LA $(\frac{1}{4}\frac{1}{4}\frac{1}{4})$ branch in SmYS alloy was first reported by Mook *et al* (1978, 1979) from neutron scattering measurements. More recently this phenomenon is explained (Bilz *et al* 1979; Kress *et al* 1981) by considering breathing deformation of the samarium ion, although they did not report any exact result on temperature dependence of any mode. Wakabayashi (1980) reported calculation of phonon line-width of longitudinal and acoustical modes as a function of wave vector using a charge fluctuation model. There is, however, no direct evidence of the softening of LO branch from the neutron scattering measurements at a particular temperature, as the measurement of these phonons was rather difficult because of the uncertainties associated with large error bars. It is revealed from the optical measurements and the results of X-ray diffraction that the LO phonon mode gets soft at the valence transition. Dernier *et al* (1976) who have determined the temperature dependence of the mean square displacements of sulphur ions $\langle u_s^2 \rangle$, suggest strong softening of optic phonons at valence transition. Valence transition in such a case is associated with a large negative thermal expansion. Apart from the anomalous increase of $\langle u_s^2 \rangle$ with temperature, Holland Moritz *et al* (1988) reported the temperature dependence of optical phonon linewidth from neutron scattering measurements. Softening of the LO(L) mode has been observed around 200 K.

Until now no effort has been made to interpret the temperature dependence of the LO phonons at the zone boundary for $\text{Sm}_{0.75}\text{Y}_{0.25}\text{S}$. Theoretical attempts have been made to explain the phonon dispersion curves of this compound at 300 K using model approaches (Mook *et al* 1978, 1979; Entel and Seitz 1981; Wakabayashi 1980; Gupta 1987). These approaches fairly reproduce the large LO–TO splitting at L point. However, no attempt has been made to predict the variation of optical phonon frequency with temperature. In the present paper we explain the origin of the temperature dependence of LO mode in the mixed valence compound $\text{Sm}_{0.75}\text{Y}_{0.25}\text{S}$. We propose a nonlinear lattice dynamical theory for mixed valence compounds in which nonlinear breathing motion of electron shell is considered to couple strongly with the lattice. For this purpose, we consider one-dimensional lattice for SmYS system where we associate, in addition to the displacement of cations and anions, the nonlinear breathing potential of fourth order at the samarium ion site. In order to understand the salient features of the proposed 1-D nonlinear lattice dynamical theory, we discuss briefly the different solutions of the equation of motion for different physical situations. We solve the equation of motion in the nonlinear breathing coordinate of the samarium ion for LO phonon at L point. We calculate the energy and temperature dependence of this optic mode. From our analysis we find that similar to LA modes at $(\frac{1}{4}\frac{1}{4}\frac{1}{4})$, the LO(L) phonons also softens at the valence transition temperature. Finally we give satisfactory explanation of the anomalous temperature dependence of LO(L) mode which are caused by the valence fluctuation of Sm ion by interpreting it in terms of fourth order nonlinear breathing motion of the electrons.

2. Nonlinear lattice dynamical theory

For explaining the specific dynamical properties such as phonon dispersion curves and soft modes, we consider one-dimensional chain of samarium and sulphur atoms. The essential feature of the present approach is that the cation (samarium ion) is considered to be nonlinearly deformable due to the breathing motion of electron shells and the anharmonicity in the breathing potential can be expressed in terms of electron shell breathing displacement of samarium ion as

$$\phi(b) = \sum_{n=1}^{\infty} (g_{2n}^b b^{2n}) \quad (1)$$

where g_{2n}^b are core-shell coupling constants due to breathing of Sm. For our present analysis we keep the terms only up to $n = 2$.

In $\text{Sm}_{0.75}\text{Y}_{0.25}\text{S}$ alloy, since yttrium ion is lighter than samarium, it does not affect the phonon anomalies. Its local mode is well separated between the optical and acoustic branches of the host compound. In fact, Y is only considered as a doping agent for SmS system to crossover into an intermediate valence state. At the zone boundary the LO mode consists of motion of next neighbour sulphur atoms in opposite direction, causing a maximum volume deformation of the samarium atomic volume resulting in large phonon anomalies at the zone boundary (see figure 1). Because of the symmetry of LO branch at L point we can consider one sublattice (Sm) to be at rest position because of large mass and other sublattice (S) moves in the opposite direction. We treat the anomalous phonon behaviour in the Λ direction of the Brillouin zone where the quasi one-dimensional treatment for the NaCl structure can be applied.

The Hamiltonian for a sublattice consisting of samarium and sulphur ions (as in figure 2), can be written as

$$H = \frac{1}{2} [M_1 \dot{U}_1^2 + M_2 \dot{U}_2^2 + M_e \dot{W}_2^2 + M_e b^2 + f[(U_1 + b) - (U_3 + W_3)]^2 + f[(U_2 + W_2) - (U_1 - b)]^2 + g_2^b b^2 + \frac{1}{2} g_4^b b^4 + g_2^d W_2^2] \quad (2)$$

where U_1 , U_2 and $W_{2,3}$ are the displacements of the cation core (Sm), the anion core (S) and the anion electronic shell relative to the core respectively. The coordinate b measures the change of the cation shell radii because of breathing. The f state is characterized by the positive b whereas the d state is characterized by negative b . g_2^b and g_4^b are coupling constants for breathing deformation potential at Sm ion site. f is short range force constant between the cation and anion. g_2^d is the coupling constant for polarizable deformation of sulphur ion. M_1 , M_2 and M_e are the masses of Sm, S and electron respectively.

From the Hamiltonian we can write the equation of motion in the nonlinear breathing coordinate b corresponding to longitudinal optic LO(L) mode for the unit

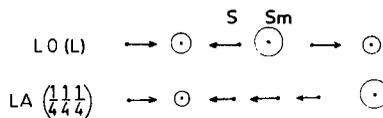


Figure 1. Vibrational mode of longitudinal optic and acoustic phonons at the zone boundary for $\text{Sm}_{0.75}\text{Y}_{0.25}\text{S}$.

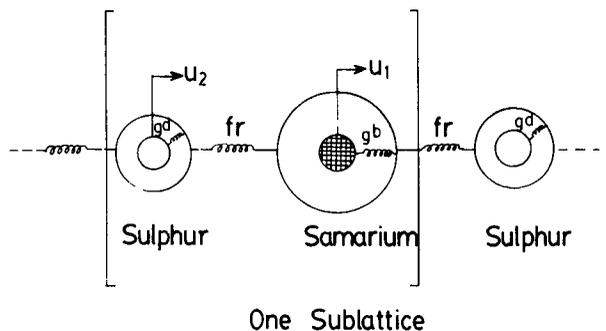


Figure 2. A sublattice of $\text{Sm}_{0.75}\text{Y}_{0.25}\text{S}$ consisting of samarium and sulphur atoms in one dimension.

cell (see figure 2) in the adiabatic approximation ($M_e = 0$) as

$$(2f + g_2^b)\ddot{b} + 3g_4^b b^2 \ddot{b} + 6g_4^b b \dot{b}^2 + 2f/M_2(g_2^b b + g_4^b b^3) = 0. \quad (3)$$

Equation (3) remains invariant under the parity operation. We use a new variable $x = b^2$, which on substitution in (3) results to

$$(\alpha x + \beta)\ddot{x} - \frac{\beta}{2}\left(\frac{\dot{x}^2}{x}\right) + \left(\frac{\alpha}{2}\right)\dot{x}^2 + \frac{4f}{M_2}(g_2^b x + g_4^b x^2) = 0 \quad (4)$$

with $\alpha = 3g_4^b$ and $\beta = 2f + g_2^b$.

For solving (4) we multiply it by $2\dot{x}$ and integrate once to get

$$(\alpha x + \beta)\dot{x}^2 - \beta \int_0^t \left(\frac{\dot{x}^3}{x}\right) dt + \frac{4f}{M_2} \left(g_2^b x^2 + \frac{2}{3}g_4^b x^3\right) - 2C' = 0 \quad (5)$$

where $2C'$ is a constant of integration.

For solving (5), we assume that at $t = 0, x = x_0$ with x_0 as turning point. In that case (5) will be a single valued analytic function of x_0 within a quarter period of oscillation or within a half period in case of oscillation which do not traverse through the origin. Therefore we can define

$$I(x) = \int_0^t \left(\frac{\dot{x}^3}{x}\right) dt = \int_{x_0}^x \left(\frac{\dot{x}^2}{x}\right) dx. \quad (6)$$

Using (6), eq. (5) can be written as a linear first order differential equation as

$$x(\alpha x + \beta) \frac{dI(x)}{dx} - \beta I(x) + \gamma Q(x) = 0 \quad (7)$$

where

$$\gamma = \frac{8fg_4^b}{3M_2}$$

$$Q(x) = x_0^3 + \frac{3}{2}\left(\frac{g_2^b}{g_4^b}\right)x_0^2 - \lambda \quad (8)$$

and

$$\lambda = \frac{3M_2C'}{8fg_4^b}.$$

Equation (7) can be solved easily by using a suitable integrating factor, resulting in

$$I(x) = \frac{-\gamma}{\alpha x + \beta} \left[\frac{x^3}{2} + \frac{3}{2} \left(\frac{g_2^b}{g_4^b} \right) x^2 + \lambda - C_0 x \right] \quad (9)$$

with

$$C_0 = \frac{x_0^2}{2} + \frac{3g_2^b}{2g_4^b} x_0 + \frac{\lambda}{x_0}. \quad (10)$$

Substitution of $I(x)$ in (5) gives the solution for oscillations in the breathing motion as

$$\dot{x}^2 = -\frac{8f}{9M_2} \frac{x F(x)}{(x + \beta/\alpha)^2} \quad (11)$$

where

$$F(x) = x^3 + \left(\frac{3}{2} \right) \left[\frac{\beta}{\alpha} + \frac{g_2^b}{g_4^b} \right] x^2 + 3 \left(\frac{g_2^b}{g_4^b} \right) \left(\frac{\beta}{\alpha} \right) x - \left(\frac{\beta}{\alpha} C_0 \right) - \lambda. \quad (12)$$

Equation (11) can be solved for the frequency of the oscillation, $\omega (= 2\pi/T)$, by writing it in the form

$$T = \int_0^\infty dt = \int_{-x}^x \left[\frac{2}{3} \left\{ - \left(\frac{2f}{M_2} \right) \frac{x F(x)}{4(x + \beta/\alpha)^2} \right\}^{1/2} \right]^{-1} dx. \quad (13)$$

The energy of a given mode is the potential energy of the mode at the turning point, and is given by

$$E = \frac{g_4^{b^2}}{4f} \left(x_0^3 + \frac{3}{2} \left(\frac{g_2^b}{g_4^b} + \frac{\beta}{\alpha} \right) x_0^2 + 3 \left(\frac{g_2^b}{g_4^b} \right) \left(\frac{\beta}{\alpha} \right) x_0 \right). \quad (14)$$

The effective potential of the oscillator in terms of relative breathing displacement is given by

$$V_{\text{eff}}(x) = \frac{1}{2} \frac{g_4^b}{f} F \left(\frac{-\beta}{\alpha} \right) - \frac{1}{18} \frac{\beta^2}{f} \frac{\left(x + F \left(\frac{-\beta}{\alpha} \right) \right)}{\left(x + \frac{\beta}{\alpha} \right)^2}. \quad (15)$$

Here, the first term represents the contribution from the potential energy whereas the second term is from the kinetic energy of the oscillator.

3. Analysis of allowed oscillations

The nature of the oscillation in the squared core shell breathing coordinate can be analyzed. For this purpose we first examine the solutions given by polynomial $Q(x)$ and $F(x)$. The nature of the polynomial $Q(x)$ depends on one intrinsic parameter

g_2^b/g_4^b and one variable parameter λ . To find out the nature of the polynomial, we follow the Descartes Rule of signs for positive and negative roots. We analyze the solution of $Q(x)$ for six cases:

- (a) $g_2^b > 0, \lambda > \frac{1}{2}(g_2^b/g_4^b)^3$ for which $Q(x)$ has one positive and two negative roots
- (b) $g_2^b > 0, 0 < \lambda < \frac{1}{2}(g_2^b/g_4^b)^3$, in this case $Q(x)$ has one positive and two negative roots
- (c) $g_2^b < 0, \lambda < 0$, as both the parameters are negative, two roots of $Q(x)$ become imaginary. Only one negative root is possible
- (d) $g_2^b < 0, \lambda > 0$; Reverse situation to case (c) occurs as $Q(x)$ has one positive root. Rest two roots are imaginary
- (e) $g_2^b < 0, \frac{1}{2}(g_2^b/g_4^b)^3 < \lambda < 0$, in this specified interval $Q(x)$ has two positive roots and one negative root
- (f) $g_2^b < 0, \lambda < \frac{1}{2}(g_2^b/g_4^b)^3$, this interval allows $Q(x)$ to have two positive and one negative roots.

The behaviour of $Q(x)$ can be qualitatively sketched as $Q(x) \rightarrow \infty$ for $x \rightarrow \infty$ and $Q(x) \rightarrow -\infty$ for $x \rightarrow -\infty$. Thus the polynomial $Q(x)$ determines the maximum or minimum squared amplitude of the oscillations. The minima or maxima of $Q(x)$ are at 0 and $-(g_2^b/g_4^b)$. Since x_0 is one of the roots of the polynomial $F(x)$, we can write $F(x)$ in the form

$$F(x) = (x - x_0) T(x) \quad (16)$$

with

$$T(x) = x^2 + cx + d$$

where

$$c = x_0 + \left(\frac{3}{2}\right) \left(\frac{\beta}{\alpha} + \frac{g_2^b}{g_4^b}\right)$$

$$d = x_0^2 + \left(\frac{3}{2}\right) \left[\left(\frac{\beta}{\alpha}\right) + \left(\frac{g_2^b}{g_4^b}\right) \right] x_0 + 3 \left(\frac{g_2^b}{g_4^b}\right) \left(\frac{\beta}{\alpha}\right).$$

$T(x)$ is a quadratic equation having two real roots x_1 and x_2 where one is greater than the other. We can solve (16) analytically by knowing x_1, x_2 so that the allowed oscillations can be analyzed using the polynomial $F(x)$. The complete set of oscillations is obtained in between the largest positive root of $Q(x)$, x_{02} if $\beta > 0$ and with the smallest positive root, x_{01} , if $\beta < 0$. We analyze $F(x)$ for four cases.

Case I $g_2^b > 0, \beta > 0$.

Only symmetrical oscillations traversing the origin are possible. As λ decreases from infinity to zero, the amplitude of the allowed oscillation also decreases from infinity to zero. At a particular value of λ the oscillation is harmonic. $\lambda_{\text{harmonic}}$ is given by

$$\lambda_{\text{harmonic}} = \left[-\left(\frac{3}{2}\right) \left(\frac{g_2^b}{g_4^b}\right) + \left(\frac{\beta}{2\alpha}\right) \right]^2 \left(\frac{\beta}{2\alpha}\right)$$

provided that

$$\frac{\beta}{\alpha} > 3 \left(\frac{g_2^b}{g_4^b}\right).$$

Case II $g_2^b < 0, \beta > 0$.

$F(x)$ has two equal negative roots with value $(-\beta/\alpha)$. Symmetrical oscillations are obtained for the positive root of $F(x)$. These oscillations are traversing the origin. For $\lambda < \lambda_{\text{harmonic}}$, $F(x)$ has one real root x_{02} . For $\lambda = \lambda_{\text{harmonic}}$ the oscillation tends to harmonic nature. For $\lambda_{\text{critical}} < \lambda < \lambda_{\text{harmonic}}$, $F(x)$ has one positive and two negative roots. Critical value of λ occurs for the value $x_{\text{critical}}^2 (x_{\text{critical}} + (\frac{3}{2})g_2^b/g_4^b)$ where x_{critical} is the positive root of $F(x)$. When the value of λ equals the $\lambda_{\text{critical}}$ then no oscillation is obtained meaning that for the critical value of λ the frequency of oscillation reduces to zero. For $\frac{1}{2}(g_2^b/g_4^b)^3 < \lambda < \lambda_{\text{critical}}$, $F(x)$ has again two positive roots $x_2 < x_{02}$ and one negative root. In this limit the oscillations are localized in either of the two equivalent potential wells. The minimum and maximum squared displacements are x_2 and x_{02} respectively.

Case III $g_2^b < 0, \beta = 0$.

In this case, $F(x) = x^2(x + (\frac{3}{2})g_2^b/g_4^b)$ for $\lambda = 0$. Hence $F(x)$ has double root of the equation for $x = 0$ and one negative root. Only the harmonic oscillation at $\lambda = 0$ traversing the origin is possible. Localized oscillations are obtained for $\frac{1}{2}(g_2^b/g_4^b)^3 < \lambda < 0$.

Case IV $g_2^b < 0, \beta < 0$.

In this case, $F(x)$ possesses three positive roots x_{01}, x_1, x_2 . For the value $\lambda_1 < \lambda < 0$, oscillations through the origin are possible where λ_1 is given for $x = -\beta/\alpha$ as

$$\lambda_1 = \left(\frac{-\beta}{\alpha} + \frac{3g_2^b}{2g_4^b} \right) \frac{\beta^2}{\alpha^2}.$$

Here the relation between the roots is $0 < x_{01} < -\beta/\alpha < -g_2^b/g_4^b < x_2$. When $\lambda = \lambda_1$, x_{01} and x_1 tends to $-\beta/\alpha$ giving the oscillations to be harmonic. For $\frac{1}{2}(g_2^b/g_4^b)^3 < \lambda < \lambda_1$ roots of $F(x)$ are $x_1 < -\beta/\alpha < x_{01} < -g_2^b/g_4^b < x_2$ and localized solutions are obtained from x_{01} and x_2 , as λ tends to $\frac{1}{2}(g_2^b/g_4^b)^3$, x_2 tends to $-g_2^b/g_4^b$.

Further on analyzing the shape of the effective potential with respect to the variation of the amplitude of oscillation of the anharmonic oscillator, we gain more information about the nature of the potential. For $g_2^b > 0, \beta > 0$, V_{eff} has a single well structure of varied shape. When $g_2^b < 0, \beta > 0$ the effective potential becomes anharmonic for large amplitude waves. V_{eff} is a single well structure but it decreases below a certain value in the interval developing into a double well structure with a hump at the origin. Here the acceleration of the oscillator reverses sign three times between two turning points. For a particular value of λ less than $\lambda_{\text{critical}}$, the oscillations are localized in either of the two wells. This type of behaviour of the potential (i.e. double well with a hump at origin) are commonly observed for ferroelectric phase transition (Bilz *et al* 1980; Bilz *et al* 1987a, b) and is also relevant to the materials showing valence transition.

4. Numerical analysis and discussion

The analytical treatment of the allowed oscillations for the LO mode at L point for $\text{Sm}_{0.75}\text{Y}_{0.25}\text{S}$ compound reveals that eq. (13) together with eq. (14) represents the trajectory of the oscillator in relative breathing displacement coordinate of the cation

(Sm) in b space. Equation (13) can be numerically solved for four different cases. Depending on two parameters, $-\beta/\alpha$ and g_2^b/g_4^b it gives rise to four different physical situations. Though we have analyzed all the cases and also know the nature of the potential, but looking to the problem of mode softening in SmYS alloy, case II is more relevant. Qualitatively this case corresponds to ferroelectric phase transition when a particular mode softens at transition temperature. This phenomenon is analogous to the valence fluctuation case although they have different origins.

By the numerical analysis of (13) and (14) we acknowledge many information like the nature of breathing motion, variation of the velocity with time for different displacements, its time and energy (or temperature) dependence and variation of frequency with energy and temperature. Values of parameters chosen for case II are $g_2^b = -160.90$ N/m, $g_4^b = 804.52$ N/m and $f = 321.81$ N/m which are determined from phonon properties of SmYS alloy.

The velocity of the oscillator as a function of time for three initial displacements are shown in figure 3. For small initial displacements, the particle oscillates at the bottom of the well and the oscillations are harmonic in nature. For larger initial displacements, the particle reaches the central hump of the potential. The velocity of the oscillator with respect to the time changes significantly. Around the middle of the path the velocity of the oscillator is very fast showing anharmonic nature. For

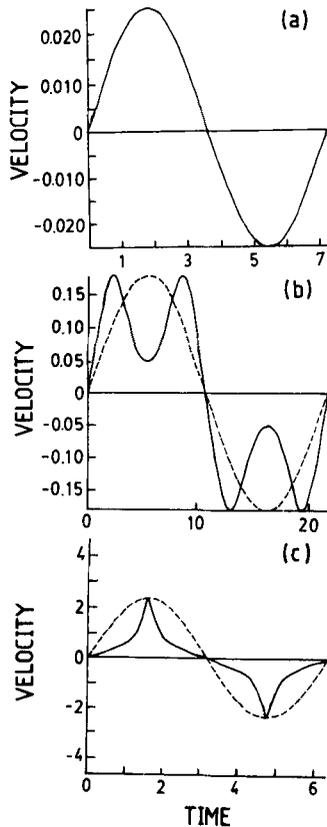


Figure 3. Velocity of the oscillator as a function of time for three initial displacements. (a) $w_0 = 0.475$, (b) $w_0 = 0.59$, (c) $w_0 = 1.0$.

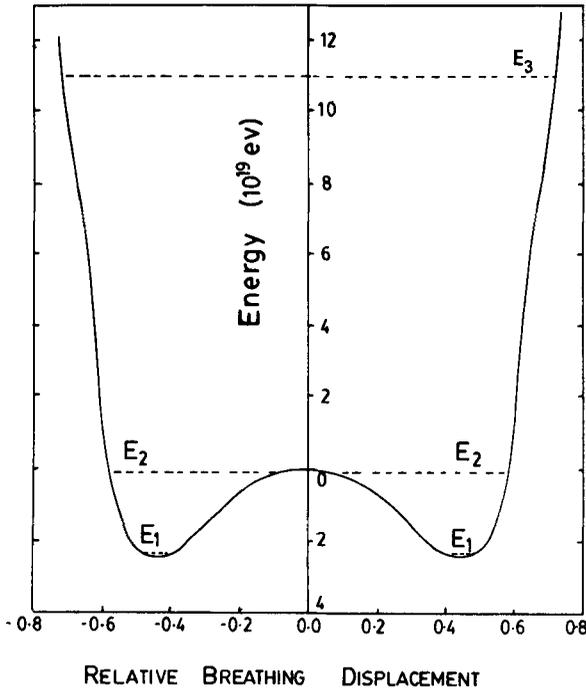


Figure 4. Energy of the oscillator as a function of initial displacements.

further higher values of displacement, the oscillations become solitary deviating largely from harmonic nature. To understand more about the nature of oscillation, the breathing energy of oscillation as a function of these three initial displacements and time are shown in figures 4 and 5.

For low energy values, the oscillator has a very small amplitude showing harmonic behaviour and is confined in either of the potential well, which is $4f^6$ valence state of Sm ion. On increasing the energy (or temperature) of oscillations corresponding to a critical breathing displacements, the oscillations are near to the central hump of the potential corresponding to intermediate valence state where the two states $4f^6$ and $4f^55d^1$ are nearly degenerate. Here the oscillations become anharmonic, taking long time to travel through the central hump. Consequently, the oscillations get frozen at the origin resulting in an infinite time period. Further increase in energy leads to highly anharmonic oscillations. The particle is away from the central hump and such a state can be characterized as delocalized ($4f^55d6s$) band for Sm-ion. Around the central hump of the well, strong hybridization occurs due to the presence of degenerate levels, which reduces the frequency of oscillation at that energy (or temperature). This fact gives rise to softening of LO phonon mode around the transition temperature (T_c).

In order to understand the nature of the oscillations in double well potential we study the variation of frequency with temperature. In figure 6 we plot the LO(L) phonon frequency of SmYS as a function of temperature. The region in left of transition temperature belongs to the highly localized $4f^6$ state and the interaction of electrons with the ion is harmonic. For low temperature longitudinal LO(L) mode, the harmonic frequency is about 10 THz. As temperature increases, the harmonic frequency falls

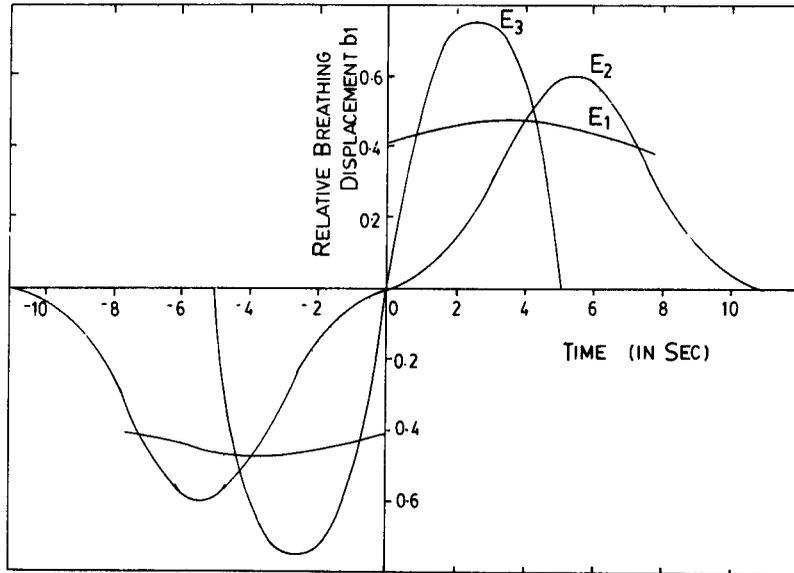


Figure 5. Time dependence of the energy of the oscillator for three initial energy levels.

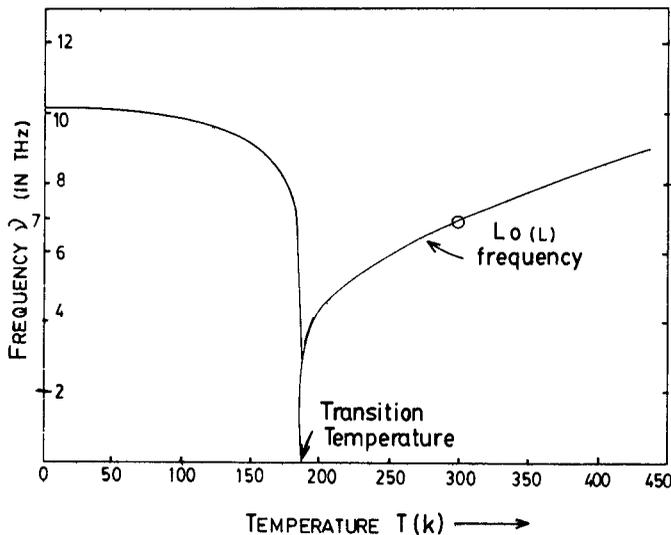


Figure 6. The LO(L) frequency of $\text{Sm}_{0.75}\text{Y}_{0.75}\text{S}$ is plotted as a function of temperature.

down to zero when the oscillations cross over the central hump of the potential resulting into softening of this mode. On further increase in temperature corresponding to increase in energy the frequency of breathing motion increases which signifies the delocalized band.

The measurement of LO(L) frequency as a function of temperature has not been reported so far. This fact restricts our comment on the exactness of our results. But qualitatively, the present theory satisfactorily explain the softening of LO(L) phonon in SmYS alloy due to valence transition. A direct comparison of our results with the

LO(L) phonon linewidth measurements (Holland Moritz *et al* 1988) support our findings.

In the present paper, we have qualitatively analyzed the softening of the LO phonon mode at the zone boundary by considering nonlinear breathing deformation of electron shell of the Sm ion in $\text{Sm}_{0.75}\text{Y}_{0.25}\text{S}$. The electron breathing deformation arises from the on-site $f \rightarrow d$ hybridization of nearly degenerate $4f$ and $5d$ levels, giving rise to the valence transition from Sm^{2+} (insulator with $4f^6$) to Sm^{3+} (metal with $4f^5 5d^1$) state. We emphasize that the strong coupling between the breathing motion of electron with the lattice phonon increases significantly around the T_c resulting in mode softening.

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