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Effects of pressure and temperature on the vibronic as well as the thermodynamic properties of LiYF_4 and LiYbF_4

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Abstract

Since the tetragonal lithium rare earth fluoroscheelites are excellent laser media with a wide bandgap, studies of their vibronic and thermodynamic properties would help render valuable insights in contriving better technology towards achieving higher lasing efficiency. Hence, in this paper, we try to enunciate a brief account on lattice dynamical calculations of the pressure as well as the temperature dependence of various underlying physical phenomena of two such para-elastic scheelites, namely, LiYF_4 and LiYbF_4 . Our computations based on a rigid ion model yield a good deal of parity with the measured Raman data of LiYF_4 . These are then comfortably extended for LiYbF_4 , to give way to a useful comparative analysis for further studies.

1. Introduction

Studies of pressure and temperature dependence of relevant physical properties of any worthy system often open up windows offering many interesting features which can then be used for further technological upliftment in eventually making it more and more market friendly. Here we give a brief outline of lattice dynamical calculations on pressure and temperature studies of one such system, rich in practical applicability. The tetragonal fluoroscheelites LiYF_4 and LiYbF_4 , doped with trivalent rare earth ions (e.g. Nd^{3+} , Pr^{3+} , Ho^{3+} . . .) cater to several optical domains of application primal to which is the wide-range (UV–IR) thermally tunable solid state lasers with astoundingly high efficiency. These lithium compounds display remarkably low lasing thresholds due mainly to their superior thermal and optical properties and hence, are of increasing demand in industry. Several studies [1–7] have already been pursued in exploring such a type of complex crystal with a wide range of detail. As an extension to these bountiful works carried out over the years, here we present a comprehensive understanding of how the crystal structure and also the phonon spectra respond at the microscopic level to high pressure and high temperature, on the basis of a rigid ion model.

Pressure reduces the volume of a substance causing thereby significant changes in its electronic and vibronic states, chemical bonding and also, atomic packing. Therefore,

investigations of pressure-dependent optic and thermodynamic properties frequently offer a unique possibility of imbibing a wealth of information on the crucial properties of materials at high pressure. The other thermodynamic variable, which also plays an equally important role in understanding condensed matter, is temperature. It is instrumental in altering the equilibrium interatomic spacing leading to the thermal expansion as well as in changing the phonon occupation numbers. This two-fold action of temperature on the phonon frequencies is chiefly responsible for the anharmonicities that arguably fosters anomalous behaviour in the dynamical response of the crystal. Cowley [8], in his microscopic theory of ferroelectricity attributed the phenomena to anharmonic interactions between the normal modes of vibration. Hence it would be quite utile to understand the response of the crystal structure and the phonon modes of both the fluoroscheelites at the microscopic level to different pressures and temperatures on the basis of lattice dynamical calculations. In the following sections we continue with a handful of discussions on the high-pressure behaviour of their thermodynamic properties and also their related anharmonicities.

2. Vibrational eigenstates

Lithium rare earth fluorides generally crystallize in the tetragonal scheelite structure at ambience with the space group of $I4_1/a$, having two formula units per primitive cell. A detailed group theoretical analysis [5,6] of this system reveals that all 36 zone centre phonon modes are distributed among the various irreducible representations of the C_{4h} factor group, according to

$$\Gamma : 3A_g + 5A_u + 5B_g + 3B_u + 5E_g + 5E_u.$$

Here, the modes of E_g and E_u symmetry are doubly degenerate. While B_u modes are optically inactive, the A_u and E_u modes are infra-red (IR) active, and the A_g , B_g and E_g modes are Raman active.

In our previous paper [9], we reported an optimized rigid ion model in the quasi-harmonic approximation to satisfyingly derive the crystal potential, which includes as few as only five unknown parameters. Because of the strong ionic character of the system, the potential consists mainly of long-range Coulombic attractive as well as short-range Born–Mayer-type repulsive terms. Yet we have to include a weak van der Waals-type attractive potential as a third term in the potential function simply to account for the polarizability of the highly electronegative fluorine ions. The empirical parameters used in the potential function are chosen in such a way as to satisfy the criteria of both static and dynamic equilibrium, and the minimum enthalpy structure, so obtained, is subsequently used for all our lattice dynamical calculations. All our complex computations have been carried out using the current version of the software DISPR [10], developed at Trombay.

From their high-pressure Raman experiments on LiYF_4 Wang *et al* [11] observed the first singularity at 6 GPa. Our computations (figure 1) suggest that the discontinuity in the Raman spectra of LiYF_4 may be initiated at a pressure of 5.8 GPa due to a dynamical instability of a transverse acoustic phonon mode at a small wavevector along the $[1\ 3\ 0]$ direction. For LiYbF_4 , our predicted value of the corresponding instability pressure is 5.5 GPa. Table 1 gives an overview of how the structural parameters in fluoroscheelites change with pressure. As can be seen, variation under the influence of pressure, in the mean square displacements (in the form of isotropic temperature factors, B_{iso}) of rare earth atoms is significant. Both pressure and temperature have interesting effects on the vibrational eigenstates of the fluoroscheelites under study, as we show in the following sections.

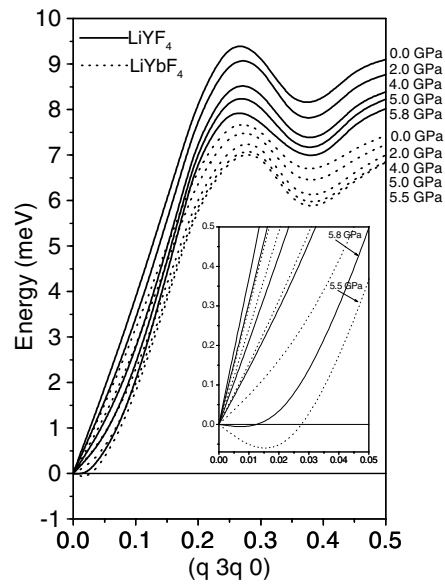


Figure 1. The calculated pressure variation of a transverse acoustic phonon branch along $[q\ 3q\ 0]$, the direction of dynamical instability. The solid curves refer to LiYF₄, while the dotted ones refer to LiYbF₄.

Table 1. Calculated structural parameters (at 0 K) and isotropic temperature factors B_{iso} (at 300 K) of LiRF₄ (R:Y, Yb) at an ambient pressure as well as a pressure near the dynamical instability. The quantities within brackets represent the measured values (see, for example, [1]) of some of the parameters. The temperature of the experimental quantities is 293 K. Atomic positions are: Li(0, 0, 0); R(0, 0, 1/2); F(u, v, w) and equivalent sites in the space group of $I4_1/a$.

	LiYF ₄		LiYbF ₄	
	$P = 0.0$ GPa	$P = 5.0$ GPa	$P = 0.0$ GPa	$P = 5.0$ GPa
a (Å)	5.145(5.164)	5.020	5.114(5.132)	4.997
c (Å)	10.820(10.741)	10.698	10.679(10.590)	10.554
u	0.7913(0.7817)	0.7901	0.7926(0.7817)	0.7914
v	0.1667(0.1645)	0.1651	0.1684(0.1645)	0.1671
w	0.6717(0.6687)	0.6668	0.6725(0.6687)	0.6669
B_{iso} (Å ²)				
Li	1.240	1.192	1.220	1.177
R	0.565	0.642	0.553	0.615
F	0.967	1.049	0.948	1.010

2.1. The pressure dependence of the Raman active phonon modes

LiYF₄ is a positive uniaxial birefringent crystal and its tetragonal unit cell consists of Y³⁺ ions and LiF₄³⁻ tetrahedra. For such a type of scheelite system, group theory predicts 13 Raman active phonon modes. Of these, six are external modes, namely, two rotations of A_g and B_g symmetry and four translations of 2B_g and 2E_g symmetry [12]. The remaining seven are, however, internal modes of the LiF₄ tetrahedra. Since there is no energy gap between the internal and external vibrations, the phonon modes, in general, have a mixed character. Raman scattering, as we know, results from a transition polarizability. Following [13], the various

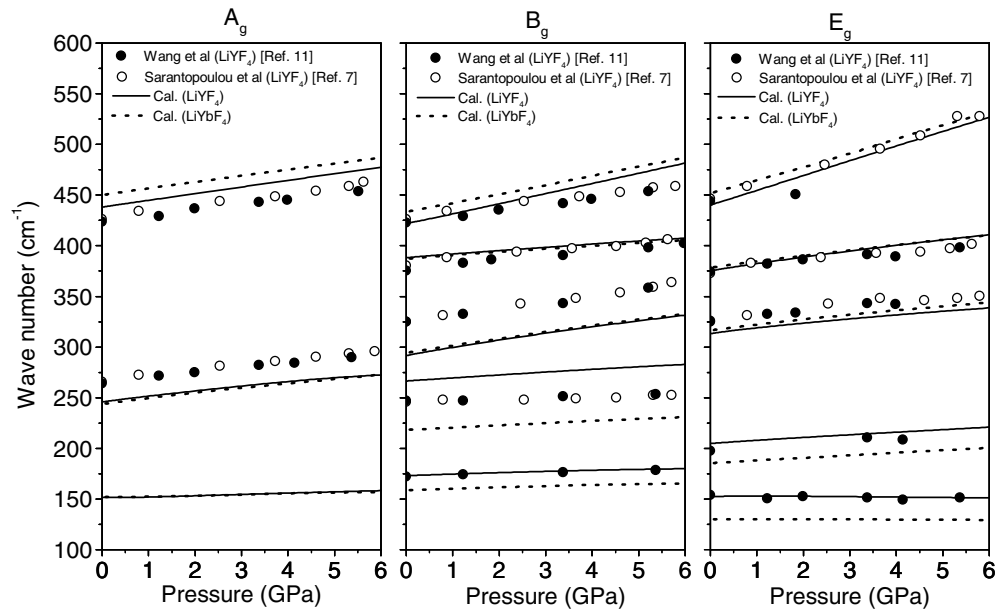


Figure 2. The pressure dependence of Raman active phonon frequencies of LiYF_4 and LiYbF_4 . The solid curves refer to our calculated values for LiYF_4 , and the dotted curves to LiYbF_4 . The circles (open and closed), however, represent the measured data (see e.g. [7, 11]). To compare the computed data with the experimental data, all the calculations were performed at 300 K, suitably taking account of the thermal pressure.

Raman polarizability tensors associated with the present system are represented as follows:

$$\begin{aligned}
 A_g &: \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix} & B_g &: \begin{pmatrix} c & d & 0 \\ d & -c & 0 \\ 0 & 0 & 0 \end{pmatrix} \\
 E_g &: \begin{pmatrix} 0 & 0 & e \\ 0 & 0 & f \\ e & f & 0 \end{pmatrix} & E_g &: \begin{pmatrix} 0 & 0 & -f \\ 0 & 0 & e \\ -f & e & 0 \end{pmatrix}.
 \end{aligned}$$

The pressure dependence of the Raman active phonon frequencies is plotted in figure 2. Our lattice dynamical calculations show a good match for the measured Raman data. While the calculated E_g modes are seen to agree fairly well with the experimental ones in the entire frequency range, for the other Raman modes, the agreement seems to be rather qualitative, due mainly to the initial discrepancy observed at ambience, as attested by table 2. Figure 2 further illustrates that the low-lying Raman frequencies of LiYF_4 and LiYbF_4 exhibit apparent shifts in the B_g and E_g modes. This strongly supports the findings of Sarantopoulou *et al* [7], in establishing that the low-frequency modes of $2B_g$ and $2E_g$ symmetry (external modes) are highly sensitive to rare earth substitution. The decrease of the frequency of one E_g mode (153 cm^{-1} in LiYF_4 and 130 cm^{-1} in LiYbF_4) with increasing pressure may be viewed in solidarity with Ganguly and Nicol [14] as an outcome of the rotational displacement of the LiF_4^{3-} tetrahedra.

Table 2. Comparison between the experimental (at 300 K) (see e.g. [5, 7, 11]) and the calculated (at 0 and 300 K) Raman active phonon frequencies of LiYF₄, along with their respective Grüneisen parameters (Γ).

Experimental 300 K	Phonon frequency (cm ⁻¹)		Γ	
	Calculated		Experimental	Calculated
	0 K	300 K		
151(A _g) ^a	151(A _g)	151(A _g)	—	0.630
153(E _g) ^b	153(E _g)	152(E _g)	0.167	0.185
172(B _g) ^b	174(B _g)	173(B _g)	0.479	0.416
197(E _g) ^b	207(E _g)	205(E _g)	1.048	0.857
246(B _g) ^c	268(B _g)	266(B _g)	0.368	0.487
265(A _g) ^c	250(A _g)	246(A _g)	1.501	1.799
326(E _g + B _g) ^c	318(E _g)	313(E _g)	0.963	1.033
	297(B _g)	292(B _g)	1.66	1.754
375(E _g + B _g) ^c	380(E _g)	375(E _g)	0.973	0.623
	391(B _g)	388(B _g)		1.219
426(A _g + B _g) ^c	442(A _g)	438(A _g)	0.956	1.068
	428(B _g)	422(B _g)		1.699
446(E _g) ^c	449(E _g)	440(E _g)	2.519	2.428

^a [5].^b [11].^c [7].

2.2. Pressure dependence of infrared active phonon modes

High-pressure IR spectra, in tune with similar other prevalent techniques, elucidate changes in bonding properties of compressed crystals and allow identification of phase transition [15]. Since the present system is highly polar, it has a natural tendency to display strong IR spectra. Figure 3 depicts the calculated pressure variation of IR active phonon modes in LiYF₄ and LiYbF₄, obtained from our model. Interestingly, there are appreciable shifts in one transverse optic A_u mode (26% for 316 cm⁻¹ in LiYF₄ and 23% for 321 cm⁻¹ in LiYbF₄) and one transverse optic E_u mode (24% for 410 cm⁻¹ in LiYF₄ and 21% for 418 cm⁻¹ in LiYbF₄) under the influence of pressure. There are no experimental data available for comparison with the calculations.

2.3. Temperature dependence of Raman active phonon modes

To get an idea of how phonon frequencies depend on equilibrium interatomic spacing as well as on phonon occupation numbers in case of the zone centre ($q = 0$) optical modes, we have to resort to studying the Raman as well as the IR spectra, as functions of temperature. Temperature is more subtle in its effect than pressure. With increase in temperature, atomic motions acquire anharmonic character, leading to shifts in phonon frequencies and excitation widths. Optical phonons generally happen to depend on temperature in two distinct ways. Firstly, phonon frequencies become altered due to the thermal expansion of the crystal lattice, resulting in what is termed as an ‘implicit effect’. Secondly, there are also shifts in phonon frequencies arising out of the higher order terms (e.g. cubic, quadratic, etc) in the crystal potential, causing ‘explicit effect’. While the former effect is obtained from the volume dependence of phonon frequencies, the latter one is, however, associated with the anharmonic interaction of phonons. Though small enough, anharmonic terms contribute quantitative as

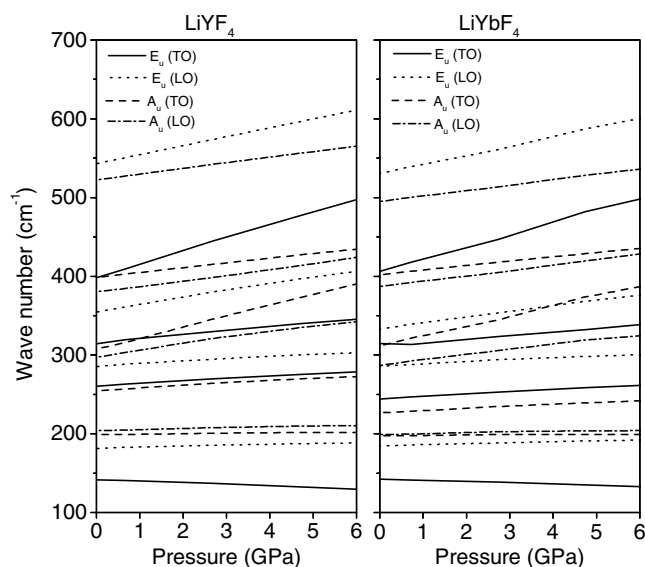


Figure 3. The theoretical plots showing the pressure dependence of the IR active phonon frequencies of LiYF₄ and LiYbF₄. Calculations were performed at 300 K, suitably taking account of the thermal pressure.

well as qualitative corrections to the physical properties of a crystal. The implicit contribution reflects the effect of the change in equilibrium interatomic spacing which accompanies a change in temperature. For the mode $i (= qj, j$ being the mode index), it may be expressed as [16]

$$\left(\frac{\partial \omega_i}{\partial T}\right)_{\text{implicit}} = \left(\frac{\partial \omega_i}{\partial V}\right) \left(\frac{\partial V}{\partial T}\right) = -\Gamma_i \omega_i \alpha_v(T) \quad (1)$$

where $\Gamma_i (= -\frac{\partial \ln \omega_i}{\partial \ln V})$ and $\alpha_v(T) (= \frac{1}{V} \frac{\partial V}{\partial T})$ are respectively the Grüneisen parameter for the i th mode and the volume thermal expansion coefficient. Generally, phonon frequencies increase on decreasing volume since the force constants become larger. Hence, the differential of frequency with volume is calculated first, which naturally turns out to be negative and then we search for the fractional change in volume with temperature to finally determine the volume effect, using equation (1). The explicit effect, on the other hand, may be evaluated for the long-wavelength phonon modes through a perturbative approach.

In the study of anharmonicities, especially the fractional implicit contribution is known to follow systematic trends depending on the type of bonding between the atoms particularly in a given vibrational mode [17]. Bonds, weak or strong, generally stiffen as they shorten by virtue of their intrinsic anharmonicity, though strong bonds are shortened very slightly [18] and their softening is also relatively slight. Unlike in covalent crystals, where phonon occupation driven explicit effect dominates, ionic crystals are seen to generally favour the thermal expansion driven implicit effect. Our computed volume-driven implicit contribution thus corroborates, to a reasonable extent, the measured temperature–Raman results, as is obvious from figure 4. As it appears from our results (table 3), the effect of explicit anharmonicity in the fluoroscheelite structure is not very significant and hence, we may hold that lattice dynamics is aptly able to explain the thermodynamic properties of the fluoroscheelite family. We further observe that modes of higher wavenumbers are prone to get more reduced with the increase in temperature in both the fluoroscheelites.

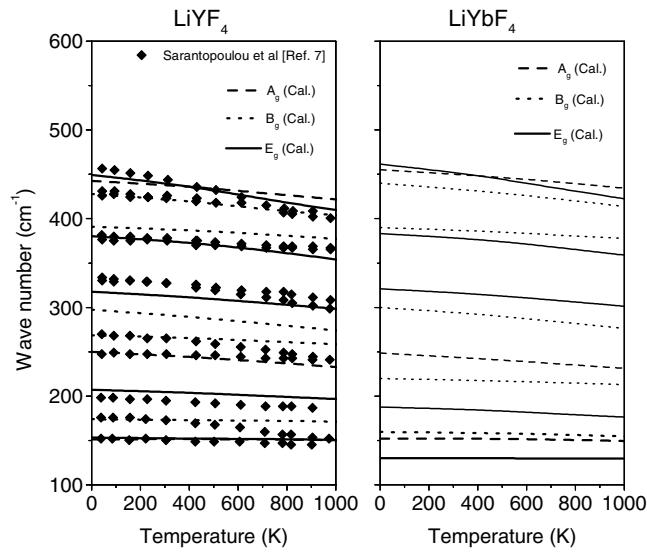


Figure 4. Temperature dependence of Raman active phonon frequencies of LiYF₄ and LiYbF₄. The solid diamonds represent the measured data (see e.g. [7]), while the curves, the calculated (implicit effect) results.

Table 3. Comparison between the experimental Raman mode frequencies of LiYF₄ at 0 K, obtained by extrapolation of the fitting to $\omega(T)$ (see e.g. [7]) and our calculated results at the same temperature. The temperature derivatives ($d\omega/dT$) of these frequencies at 300 K are also being tabulated below.

Modes	Phonon frequency, ω_0 (cm ⁻¹)		$d\omega/dT$ (cm ⁻¹ K ⁻¹)	
	Experimental	Calculated	Experimental	Calculated
A _g	—	151	—	-0.004
	269.2	250	-0.021	-0.021
	432.8	442	-0.023	-0.022
B _g	177.4	174	-0.020	-0.004
	246.7	268	-0.006	-0.006
	331.4	297	-0.026	-0.024
	381.9	391	-0.015	-0.023
	428.9	428	-0.018	-0.034
E _g	154.9	153	-0.005	-0.001
	201.8	207	-0.013	-0.008
	330.7	318	-0.020	-0.015
	376.0	380	-0.012	-0.011
	460.0	449	-0.057	-0.051

2.4. Temperature dependence of infrared active phonon modes

The calculated implicit temperature dependence of IR active phonon modes for both the fluoroscheelites are plotted in figure 5. The longitudinal A_u modes decrease maximum with temperature at 303 cm⁻¹ in LiYF₄ and at 293 cm⁻¹ in LiYbF₄. On the other hand, for the transverse A_u modes, appreciable shifts are found to occur for mode at 316 cm⁻¹ in LiYF₄,

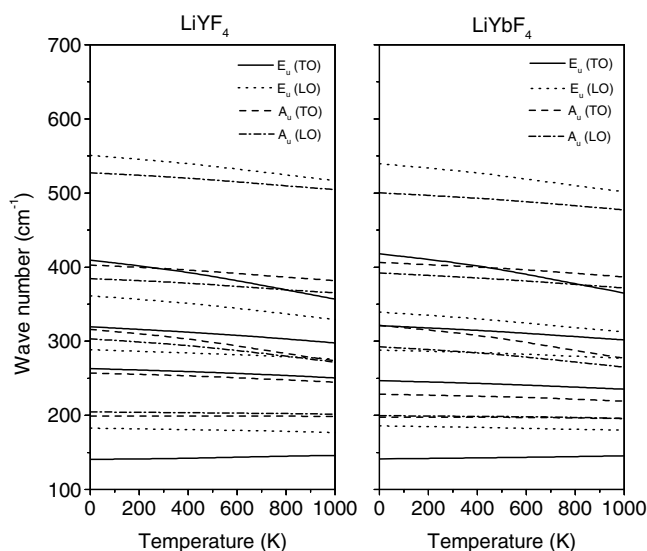


Figure 5. Calculated temperature dependence (implicit effect) of IR active phonon frequencies of LiYF₄ and LiYbF₄.

whereas it is 321 cm⁻¹ for LiYbF₄. A variation of about 13% happens to the transverse E_u modes at 410 cm⁻¹ in LiYF₄ and at 418 cm⁻¹ in LiYbF₄ in the 0–1000 K temperature range. Furthermore, longitudinal E_u modes (361 cm⁻¹ in LiYF₄ and 339 cm⁻¹ in LiYbF₄) are also observed to suffer similar decrements.

3. Phonon density of states

The phonon spectrum for the present system has been calculated [9] by integrating over 1088 wavevectors within the irreducible Brillouin zone, with an energy resolution of 1 meV. For comparison with the neutron scattering data, the calculated phonon spectrum is subsequently weighted with the neutron scattering cross sections of the constituent atoms of both the fluoroscheelites. Figure 6 shows a comparison of the neutron weighted total one-phonon density of states of LiYF₄ and LiYbF₄ at ambience and at 5 GPa (near the instability region). At ambient pressure, the phonon density of states extends upto 70 meV for both the fluoroscheelites, while it is 75 meV when the pressure shoots to 5 GPa. The compression of Y–F and Li–F bonds may be regarded as a possible cause of the extension of phonon density of states unto 75 meV. As pressure increases, shifts in the peak positions become evident only above 25 meV. In LiYF₄, the acoustic mode peak shifts by about 11%, while it is nearly 6% for LiYbF₄. However, the dispersive optic branches for both the crystals translate in the energy scale under the influence of pressure more or less in a similar way (3–11%). The partial dynamical contributions arising from various atomic units are also calculated, as shown in figure 7. For rare earth ions, the effect of pressure is apparently negligible. Furthermore, lighter mass and a stronger neutron scattering cross section of the fluorine atoms ensure that they make a significant dynamical contribution in the neutron weighted density of states. With the increase in pressure, a notable change in the phonon spectrum is observed for Li atoms towards the higher energy side. While there is a dip at around 63 meV in the partial density of states of Li at ambience, a sharp peak seems to sprout at 5 GPa.

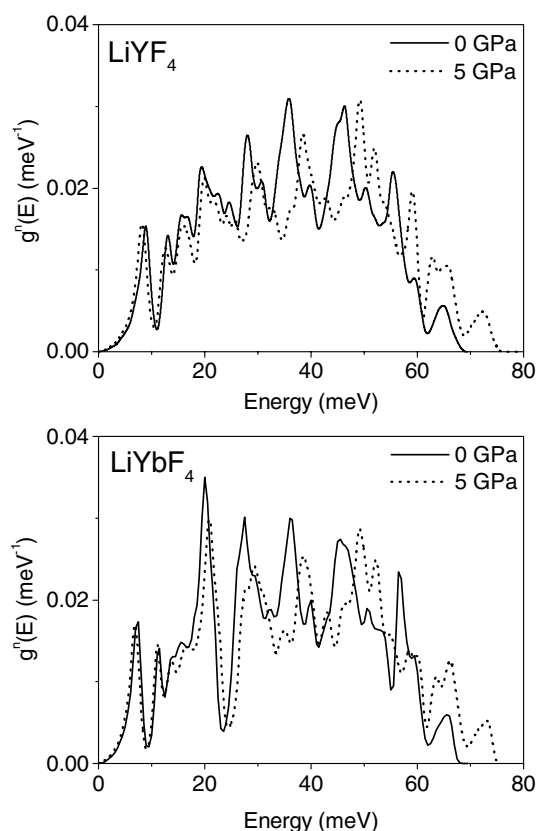


Figure 6. Comparison of the neutron weighted total one-phonon density of states of LiYF₄ and LiYbF₄ at ambient and at a pressure of 5 GPa.

4. Compressibility and the equation of state

The equation of state broadly transpires the pressure–volume–temperature relationship of materials, the utility of which lies in the meaningful interpretation of various physical phenomena at arbitrary temperature and matter density. We have computed the bulk modulus for LiYF₄ as 69 GPa, which is somewhat lower than the reported measured value of 80 GPa [19]. For LiYbF₄, our calculated value is 75 GPa. As is obvious from figure 8, the compressibility is anisotropic in both the fluoroscheelites, with a and c being the least compressible. The linear compressibilities for lattice parameters a and c are predicted by our model as 6.0×10^{-3} and 2.3×10^{-3} GPa⁻¹, against 5.4×10^{-3} and 2.6×10^{-3} GPa⁻¹ of LiYbF₄. Hence we observe that unlike the lattice parameter a and volume V , the other lattice parameter c decreases more in LiYbF₄ under the influence of pressure (figure 8).

The temperature variation of the measured elastic constants yield the volume compressibility, as worked out by Sarantopoulou *et al* [7] for LiYF₄. We have computed compressibilities upto 1000 K, using our model. Here too, we come across a modest agreement, as indicated by figure 9. However, it is interesting to note that LiYbF₄ is more compressible (about 7%) at 1000 K, in comparison to LiYF₄.

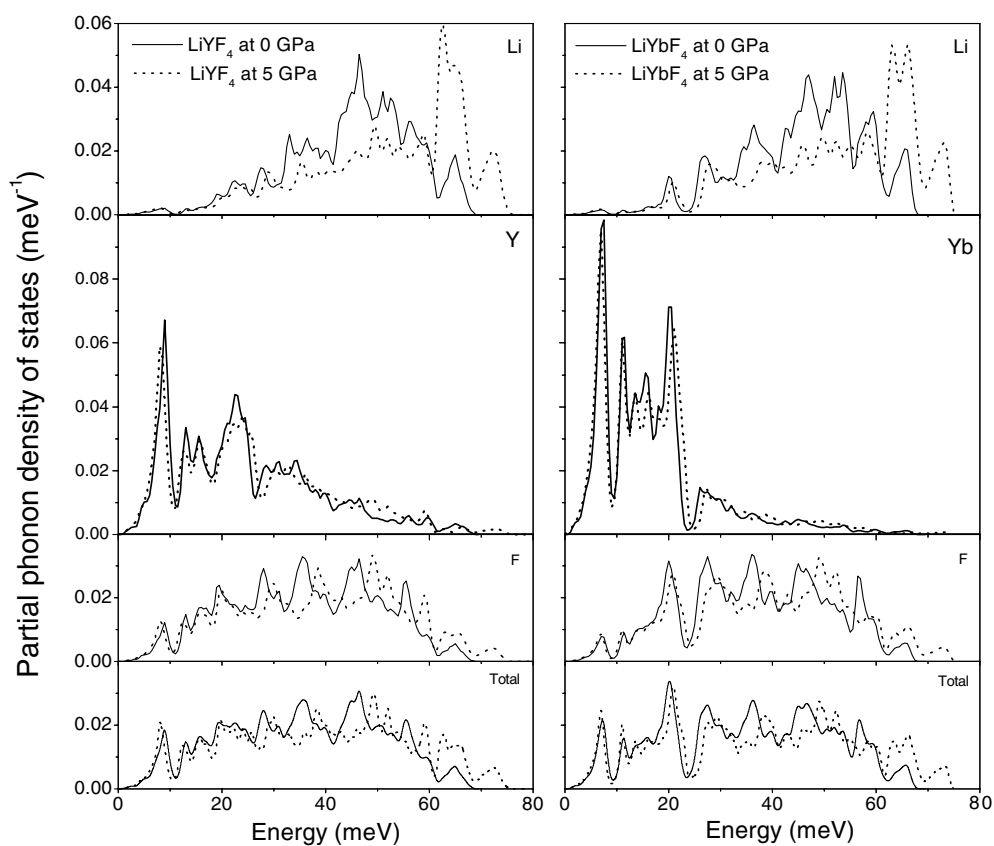


Figure 7. The calculated partial phonon densities of states for the constituent atoms Li, Y(Yb) and F, together with the total one-phonon density of states of LiYF₄ and LiYbF₄ at ambience and at a pressure of 5 GPa.

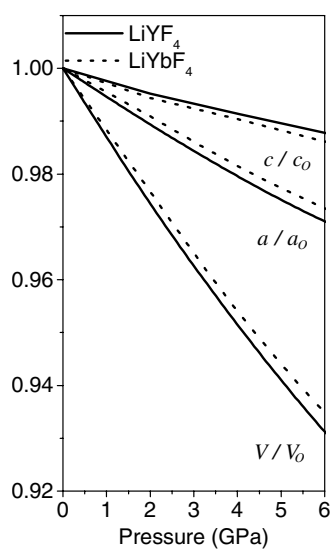


Figure 8. Computed equations of state for LiYF₄ (solid curve) and LiYbF₄ (dotted curve).

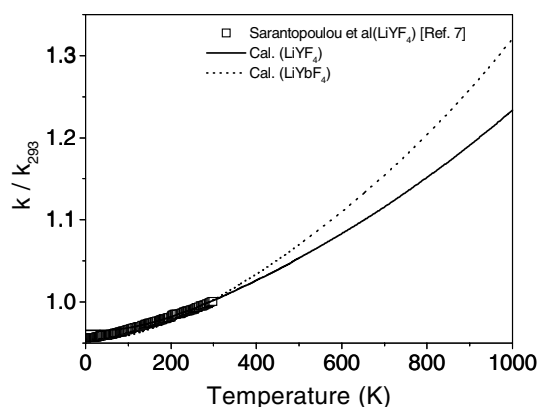


Figure 9. Comparison of the calculated and the experimental volume compressibilities in LiYF₄, at $P = 0$ GPa. The solid curve represents our calculations while the open squares, the measured ones (see e.g. [7]). Our calculated results (dotted curve) for LiYbF₄ are also shown.

5. Conclusions

We have endeavoured in this paper to ascertain various vibronic and thermodynamic properties of the lithium rare-earth fluoroscheelites under the influence of pressure and temperature. The calculated pressure and temperature-dependent Raman data of LiYF₄ are in good agreement with the available measured ones. Furthermore, our computations yielding the volume compressibility data of LiYF₄, also strongly favour the respective reported values. In addition, we have been able to predict various IR active phonon modes of LiYF₄ at different pressures and temperatures, and extend our results to shed light on how the phonon density of states transforms itself for every individual atom at a certain pressure, near the dynamical instability. Finally, our calculations have also enabled useful predictions of various macroscopic thermodynamic properties of LiYbF₄, for which, however, no sufficient measured data are reported to be available at hand.

Acknowledgments

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