Lattice vibrations in high-pressure phases of LiYF$_4$

A. Sen$^1$, S. L. Chaplot and R. Mittal

Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai 400085, India

Abstract

Possible variations in the dynamical behaviour of LiYF$_4$ due to its several structural changes under pressure are examined by making use of the complementary techniques of quasi-harmonic lattice dynamics and molecular dynamics simulations. The phonon spectra in the entire Brillouin zone together with the respective Gibbs free energies are calculated for the three high-pressure polymorphs of LiYF$_4$ (that are stable at $T = 0$) with a view to better understand their relative stabilities as functions of pressure and temperature. The present work predicts anomalous thermal expansion at low temperatures in phases I and II$_a$ while irreversibility of phase II $\rightarrow$ phase III transition on subsequent pressure release. Molecular dynamics simulations provide qualitative impressions about a temperature-driven second-order transition and also of kinetic effects in the subsequent pressure-driven first-order phase transformation.

1 Introduction

Ternary rare-earth halide LiYF$_4$, which has drawn considerable interest[1,2,3,4,5,6,7,8,9,10] as a laser host material, displays several structural phase transitions[4,6,8] upon compression. While isostructural CaWO$_4$ has a scheelite ($I4_1/a$) to wolframite ($P2_1/c$) kind of high-pressure phase transformation, LiYF$_4$ displays an intermediate fergusonite phase (viz. $I2/a$, above room temperature and $P2_1/c$, in the low temperature region) associated with a soft phonon mode[5]. Further, the axial ratio in both the compounds evolves in a different way under the effect of pressure[10]. Recently, the post-fergusonite phase of LiYF$_4$ has been predicted as wolframiteline monoclinic one[8,9].

$^1$ Present address: Department of Physics, Indian Institute of Technology, Kanpur 208016, India; Electronic address: asen@iitk.ac.in
With the advent of high-energy synchrotron X-rays and sophisticated pressure cells, high-pressure lattice dynamics has gained considerable momentum in recent years as it enables a direct comparison of experimental findings obtained either by the inelastic scattering processes or through some other techniques like ultrafast X-ray diffraction[11]. In this work, we have carried out extensive lattice dynamical calculations in the quasiharmonic approximation (QHA) for various individual high-pressure phases (e.g. I, IIa and III in Fig. 1) of LiYF$_4$ that may help analyze experimental observations. The same interatomic potential as developed earlier[3] for lattice dynamical calculations under ambient conditions is made use of here again for high-pressure studies. Gibbs free energies are calculated for various high-pressure phases of LiYF$_4$ in order to have a better understanding of their relative stabilities in terms of volume compression and vibrational entropy. We further examine their respective phonon dispersions and phonon density of states. The second-order phase transitions and the kinetic effects in the first-order phase transformations are specifically investigated by molecular dynamics simulations. Finally, a pressure-temperature (P-T) phase diagram associated with LiYF$_4$ is plotted to qualitatively gauge the underlying physics of phase transitions at the microscopic level.

2 Vibrational Properties

2.1 Raman and infrared active modes

From the previous works[2,3,5], we know that the ambient scheelite phase ($I4_1/a$, Z=4) of LiYF$_4$ has a total of 36 vibrational degrees of freedom per primitive cell. However, the two high-pressure phases (IIa and III in Fig. 1) possess 72 phonon modes at each wavevector due to doubling of the primitive cell. Since both these high-pressure phases of LiYF$_4$ belong to the same space group($P2_1/c$, Z=4), the common irreducible representation of the phonons at the zone center is given by

$$\Gamma: 18A_g + 18A_u + 18B_g + 18B_u,$$

of which $A_g$ and $B_g$ modes are Raman active while modes of ungerade symmetry (viz. $A_u$ and $B_u$) remain infrared active. Although our calculated high-pressure phases have 36 Raman active modes in all, the ambient fergusonite structure has only 18 such frequencies. It may be further noted that the degeneracy of the $E_g$ and $E_u$ modes which were present in phase I (scheelite) of LiYF$_4$ is lifted in the high-pressure phases. Table 1 yields a comparison of our calculated zone centre normal modes between phases IIa and III at respectively 13 and 18 GPa. Phase IIa has a soft $A_g$ mode at 18 cm$^{-1}$ which hardens
considerably to 92 cm\(^{-1}\) in phase III. Most other modes harden slightly in going from phase IIa to phase III. The vibrational frequencies for each of the phases are computed by diagonalization of the respective dynamical matrices using the software DISPR[13], developed at Trombay.

2.2 Phonon dispersion relations

To compare the phonon dispersion in various phases, we resort to the common high symmetry direction of \(\Gamma\), which is labeled as the \(c\) axis for phase I (\(I4_1/a\)) while it is the \(b\) axis for the other high-pressure(monoclinic) phases of similar space group symmetry (i.e. \(P2_1/c\)). From our group theoretical calculations, we obtain for the irreducible representations of all the normal modes in the three phases as follows:

- Phase I \(\rightarrow\) \(\Lambda\): \(8\Lambda_1 + 8\Lambda_2 + 10\Lambda_3\) (\(\Lambda_3\) being doubly degenerate)
- Phase IIa and Phase III \(\rightarrow\) \(\Lambda\): \(36\Lambda_1 + 36\Lambda_2\)

Phonon dispersions of various polymorphs in LiYF\(_4\) are displayed in Figure 2 along with the available inelastic neutron scattering data.[2] The experimental data[2] for the phase I at zero pressure fit well with the lattice dynamical calculations[3]. Due to doubling of the unit cell in going from phase I to phase IIa, the Brillouin zone in phase IIa is halved and so there is an apparent folding back of the dispersion branches from zone boundary (of phase I) to zone center (of phase IIa). This leads to several optic phonons at the zone center in phase IIa at low energies. We find a very low energy zone-center optic mode in phase IIa, indicating the onset of a possible high-pressure phase transition at a pressure close to 13 GPa. This espouses our previous MD observations[8]. The soft-alike phonon branch of phase IIa may be identified as the longitudinal \(A_g\) mode [Table 1] as noted earlier. A crossover between an acoustic phonon mode and a low frequency optic mode is observed in phase IIa and also in phase III. We further notice that two acoustic phonon branches of \(\Lambda_2\) symmetry in the phase III are too closely dispersed to remain distinguishable.

2.3 Phonon density of states

To have an overview of the range and extent of various phonon modes in all the three phases, we integrate over all the phonons with an energy resolution of 0.5 meV at each wave vector on a \(16 \times 16 \times 16\) mesh within the irreducible Brillouin zone. As Figure 3 suggests, the energy distribution extends by nearly 10 % in switching from phase I to phase IIa while the change in the extent is negligible for the phase III transition. In order to check whether it is due to the pressure effect, we compare the respective frequency distribution for phase IIa
and phase III at the same pressure of 13 GPa. One may notice that though the distribution patterns slightly differ, the extent remain quite the same. If one is further interested in looking for individual contributions of the constituent atoms to the entire frequency distribution, partial density of states (PDOS) are to be estimated by atomic projections of the one-phonon eigenvectors.

The labeling of the crystallographic axes viz. $a$, $b$, and $c$ varies in high-pressure phases as per convention adopted for specific space groups. In view of these differences, we choose right-handed orthogonal $x$, $y$ and $z$ axes as follows: $z$ along $c$ and $x$ along $a$ in phase I ($I4_1/a$); $z$ along $b$ and $x$ along $c$ in phases IIa and III ($P2_1/c$). Our calculated PDOS for various atoms in various phases are portrayed in Figure 4. $Y$ atoms are found to contribute largely up to 60 meV while $Li$ atoms make it (especially with polarization along $x$ and $y$) in the higher energy side of the density of states (DOS). However, $F$ atom contributions are spread over the entire energy range as if to replicate the total DOS to a considerable degree. Such variations in atomic contributions are partly due to the mass effect.

3 Thermodynamic Properties

3.1 Heat capacity and Debye Temperature

From the DOS calculations derived out of our simulated data for all the three phases of LiYF$_4$, we compare the respective heat capacities at constant pressure ($C_P$) as a function of temperature. Figure 5(a) demonstrates how $C_P$ changes for different high-pressure phases. We observe that although initially constant pressure heat capacity for phase III runs lower, it goes up above the room temperature and in the process, even surpasses phase IIa. The reason is that as we go on increasing temperature ($T$), the difference $C_P(T) - C_V(T) \equiv \alpha V^2(T)BV T$ (where $C_V(T)$ is the constant volume heat capacity and $B$ is the isothermal bulk modulus) becomes significantly large, as inset of Figure 5(a) suggests, due to the existence of much higher thermal expansion $\alpha V(T)$ in phase III than that in phase IIa. A detailed discussion on $\alpha V(T)$ follows in the next subsection.

We compare the Debye temperature $\theta_D(T)$ for the various phases [Figure 5(b)] as derived from the calculated $C_V(T)$. It is observed that in the very low temperature region (say, $< 20$ K), $\theta_D$ differs a lot from phase to phase (about 14 % increase for I$\rightarrow$IIa and about 26 % increase for IIa$\rightarrow$III) while at higher temperatures (say, 300 K), it comes closer for phases IIa and III as difference gets minimal (about 2 % only).
3.2 Gr"uneisen parameter and thermal expansion

Lattice anharmonicity, which leads to a volume dependence of phonon frequencies($\omega_i$), is described by the mode Gr"uneisen parameter\cite{14} given as

$$\gamma_i = -\frac{\partial \ln \omega_i}{\partial \ln V}$$

(1)

It is the only kind of anharmonicity that can be taken care of within the framework of quasiharmonic approximation. Moreover, Gr"uneisen parameter is an important quantity as it describes the thermoelastic behaviour of materials at high pressures and temperatures. It has both the microscopic and macroscopic definition, the former relating to the vibrational frequencies of atoms in a material (Eq. 1) while the latter, to familiar thermodynamic properties such as heat capacity and thermal expansion. Unfortunately, the experimental determination of $\gamma_i$, defined in either way, is often not so easy, since the microscopic definition requires a detailed knowledge of the phonon dispersion spectrum of a material, whereas the macroscopic definition calls for experimental measurements of thermodynamic properties at high pressures and temperatures. In this perspective, theoretical model calculation may be of great relief. Figure 6 displays our calculated average $\gamma_i$ for various phonon energies and in various phases. It can be seen that below 10 meV, there is a significant number of modes with negative Gr"uneisen parameter in phase I as well as phase IIa, while phase III modes have all positive $\gamma_i$.

The effect of pressure on the volume coefficient of thermal expansion($\alpha_V$) can be studied through mode Gr"uneisen parameters($\gamma_i$) in the entire Brillouin zone. In the quasiharmonic approximation, each phonon mode of energy $E_i$ contributes to the thermal expansion by way of $(\frac{1}{BV})\gamma_i C_{Vi}$, where $C_{Vi}$ denotes the specific heat (at constant volume) contribution of the $i^{th}$ mode and $V$ the lattice volume. This procedure suits well to the ambient fluoroscheelite system because explicit anharmonicity (which arises mainly out of thermal amplitudes) is not very significant\cite{5} compared to the implicit effect that involves phonon frequency change with volume (as obtained from $\gamma_i$).

Figure 7(a) demonstrates the variation of $\alpha_V$ as a function of temperature. It is also apparent that the scheelite as well as the initial high-pressure phase of LiYF$_4$ have negative thermal expansion in the low temperature limit (below 100 K). It may be because $\gamma_i$ has large negative values for phonons below 10 meV in these two phases. However, the third phase has no such anomaly, since it has all positive gammas for phonons of all energies (Fig. 6). The contributions to $\alpha_V$ from phonons of different energies (corresponding to various phases of LiYF$_4$) are displayed in Figs. 7(b), (c) and (d) respectively.
We observe that at low temperatures (e.g. 20 K), contribution of modes up to 10 meV are quite significant to $\alpha_V$, but as temperature is increased (e.g., 300 K) higher energy modes get more populated and hence, contribute in a large way to the volume thermal expansion.

### 3.3 Mean squared displacements and thermal anisotropy

In order to gain some insight over how the phonons of various energies are polarized in various phases of LiYF$_4$, we plot (see Figure 8) the partial contributions of these phonons to the mean squared thermal amplitude of the constituent atoms. The mean squared displacement of atom $k$ along $\alpha$ direction is given by

$$U_{\alpha\alpha}(k, T) = \langle u_{k\alpha}^2 \rangle_T = A \frac{\hbar}{m_k} \int_0^\infty \frac{(n + 1/2)}{\omega} g_{k\alpha}(\omega) d\omega,$$

where $n = \left[ \exp \left( \frac{\hbar \omega}{kT} \right) - 1 \right]^{-1}$; $g_{k\alpha}(\omega)$ is the partial density of states associated with an atom $k$ whose mass is $m_k$; $A$ is the normalization constant such that $\int g_{k\alpha}(\omega) d\omega = 1$. As Figure 8 suggests, the modes at very low energies involve equal displacements of all the atoms that correspond to the acoustic modes. Interestingly, between 2 and 9 meV, Y and F atoms have larger amplitudes than what relatively light-weight Li atoms possess. It may be noted that the basic structure (scheelite) of LiYF$_4$ comprises a pair of strongly bonded LiF$_4$ tetrahedra and loosely bonded YF$_8$ polyhedra[10]. Larger amplitudes of F atoms in the first two phases mark the presence of librations of the LiF$_4$ tetrahedra.

Our calculated values of equivalent isotropic thermal parameters for Li, Y and F atoms in the ambient (i.e., P=0) scheelite phase of LiYF$_4$ are found to be 17, 9 and $14 \times 10^{-2}$ Å$^2$ as against the respective experimental[15] values of 20, 10 and $17 \times 10^{-2}$ Å$^2$. A detailed comparison of the anisotropic thermal parameters ($U_{\alpha\alpha}$) at different temperatures among the different phases of LiYF$_4$ is further given in Table 2. It may be interesting to note that while Y and F atoms have comparable atomic displacements along the three directions in all the high-pressure phases of LiYF$_4$, Li atoms, in contrast, show larger anisotropy along the $z$ direction in phase I, along the $y$ direction in phase II and again along the $z$ direction in phase III.
3.4 Free energy and phase stability

A pressure-temperature phase diagram generally portrays various equilibrium phases at constant temperature (T) and pressure (P) with the lowest Gibbs free energy (G). From phonon calculations, the temperature dependent vibrational free energy at various hydrostatic pressures for various phases of LiYF₄ can be estimated in the quasiharmonic approximation. Thermodynamically, we may write\[16\]

\[ G_n(P, T) = U_n - TS_n + PV_n \]  

(3)

where \( U_n, S_n \) and \( V_n \) refer respectively to the internal energy, the vibrational entropy and the lattice volume of the \( n^{th} \) phase. The lattice excitations are treated in this work within the quasiharmonic approximation where the full Hamiltonian at a given volume is approximated by a harmonic expansion about the equilibrium atomic positions and anharmonic effects are included through the implicit volume dependence of the vibrational frequencies. Hence, the vibrational Gibbs free energy (\( G_{\text{vib}}^n \)) is found to be satisfyingly accurate.

To include vibrational effects in the present phase diagram, we have calculated dynamical matrices separately for each of the three phases (viz. I, IIa and III) at pressure intervals of 2 GPa on a 4 \( \times \) 4 \( \times \) 4 mesh throughout the irreducible Brillouin zone comprising 64 wavevectors. In order to rationalize the behaviour of this dynamical simulation, we calculate\[17\] the enthalpy vs. pressure curves for all the three known structures of LiYF₄ and notice that the enthalpy changes (due to internal energy and volume) are predominant in pressure-driven transitions over free energy changes (due to vibrational energy and entropy). Perhaps this is why most of the first-principles phase diagram calculations of pressure-driven phase transitions\[18\] do not include vibrational entropies, though configurational contributions are always taken into account. The other reason for this may be that vibrational entropy differences between phases are assumed to be quite small as we come across in this particular case too.

The stability of a crystalline phase is largely determined by the minimization of the Gibbs free energy\[19\]. We have compared the phase-wise free energy and the outcome is shown in Figure 9. We note from Fig. 9(a) that at 300 K the free energy plot of the phase I joins smoothly at 6 GPa to that of phase IIa, which is consistent with the nature of second order phase transition. Beyond 8 GPa, phase III has a lower free energy indicating the greater stability of this phase and also the onset of a first order phase transition from phase IIa to phase III. However, the transition pressure as obtained through the MD simulations\[8\] is higher than 8 GPa due to hysteresis. We observe the
greater stability of phase III at high pressures arises primarily due to its lower volume, while the vibrational energy remains lower and the entropy becomes higher in phase III providing an additional stability. From the plot of differences in vibrational Gibbs free energy ($\Delta G$) at 300 K as a function of pressure (Fig. 9(b)), we find that $G$ for phase III is lower (above 8 GPa) than that for phase IIa. It is also observed (Fig. 9(c)) that $\Delta G$ between phase IIa and phase III structures decreases with temperature. Another point to note from the plots of relative free energy vs. temperature (at 8 GPa) is that in the very low temperature region (say, below 100 K), free energy difference shows an anomalous behaviour. It may be attributed to the fact that there is a greater density of low frequency modes in phase IIa than in phase III (due to the soft phonon modes in the former phase). Table 1 supports this view, where several vibrational modes have been compared between phase IIa and phase III. At low temperatures, these low frequencies are populated, thereby lowering the free energy.

The above comparison of the Gibbs free energies in various phases provides the phase diagram for the first order phase transitions. However, the second order transitions and also kinetic effects such as hysteresis in the first order transitions are better illustrated through molecular dynamics simulations. A qualitative impression of the phase transitions in LiYF$_4$ is given in Fig. 10 with increasing pressure and temperature (see caption of Fig. 10). It stands our earlier observation[8] that phase II possesses two different space groups (viz. phase IIa: $P2_1/c$; phase IIb: $I2/a$) existing in two different ranges of temperature. The low temperature phase IIa involves small displacements of some of the $F$ atoms from their ideal positions of body-centered symmetry in phase IIb. The transition IIa $\rightarrow$ III occurs at a much higher pressure of 14 GPa than the equilibrium phase boundary at 8 GPa due to hysteresis at the time scale of the simulation and is found irreversible on release of pressure.

4 Conclusions

We have demonstrated in this work that a lattice dynamics-molecular dynamics study can eventually lead one to calculate the vibrational free energy and other essential thermodynamic functions of a rare-earth ternary halide in various high-pressure phases. Effort has been made to shed light on the understanding of some important physical phenomena associated with the phase equilibria. Further, our results have the potential ingredients to help analyze the experimental inelastic scattering data, if high-pressure (along with low temperature) phonon measurements are to be carried out in future.
Acknowledgements

A. S. would like to express his deep sense of gratitude to the Council of Scientific and Industrial Research (CSIR, New Delhi), India, for rendering necessary financial assistance throughout the work and acknowledge as well the continuous encouragement and care taken by Dr. M. Ramanadham and Dr. V. C. Sahni.

References

[1] E. Sarantopoulou, Y. S. Raptis, E. Zouboulis and C. Raptis, Phys. Rev. B 59, 4154 (1999).
[2] S Salaïn, A. Bulou, M. Rousseau, B. Hennion and J. Y. Gesland, J. Phys.: Condens. Matter 9 6957 (1997).
[3] A. Sen, S. L. Chaplot, and R. Mittal, Phys. Rev. B 64 024304 (2001).
[4] F. J. Manjon, S. Jandl, K. Syassen and J. Y. Gesland Phys. Rev. B 64, 235108 (2001).
[5] A. Sen, S. L. Chaplot, and R. Mittal, J. Phys.: Condens. Matter 14 975 (2002).
[6] A. Grzechnik, K. Syassen, I. Loa, M. Hanfland, and J. Y. Gesland Phys. Rev. B 65, 104102 (2002).
[7] L. van Pieterson, M. F. Reid, and A. Meijerink, Phy. Rev. Lett. 88 067405 (2002); D. Åberg and S. Edvardsson, Phys. Rev. B 65 045111 (2002); D. Åberg, S. Edvardsson, and M. Engholm, Phys. Rev. B 68 195105 (2003); A Collombet, Y. Guyot, M. F. Joubert, M. Laroche, J. Margerie, R. Moncorge and E. Descroix, Phys. Rev. B 68 035115 (2003).
[8] A. Sen, S. L. Chaplot, and R. Mittal Phys. Rev. B 68 134105 (2003).
[9] Sa Li, Rajeev Ahuja and Börje Johansson, J. Phys.: Condens. Matter 16 S983 (2004).
[10] D. Errandonea, F. J. Manjón, M. Somayazulu, and D. Häusermann, J. Solid State Chem. 177 1087 (2004); D. Errandonea, M. Somayazulu, and D. Häusermann, physica status solidi (b) 235 162 (2003); D. Errandonea, M. Somayazulu, and D. Häusermann, physica status solidi (b) 231 R1 - R3 (2002).
[11] R. W. Schoenlein et al, Science 274 236 (1996); R. Rischel et al, Nature (London) 390 490 (1997); C. Rose-Petruck et al, Nature (London) 398 310 (1999); A. Cavalleri et al, Phys. Rev. Lett. 85 586 (2000).
[12] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices*, (Clarendon: Oxford University Press, 1954); G. Venkataraman, L. A. Feldkamp, and V. C. Sahni, *Dynamics of perfect crystals*, (Cambridge: MIT Press, 1975).

[13] S. L. Chaplot, 1992 (unpublished).

[14] E. Grüneisen, *Theorie des festen zustandes einatomiger element*, Annals Physik 12 257 (1912).

[15] E. Garcia and R. R. Ryan, Acta Crystallogr., Sect. C: Cryst. Struct. Commun. 49, 2053 (1993)

[16] T. L. Hill, *An Introduction to Statistical Thermodynamics*, (Reading, Massachusetts: Addition-Wesley Pub. Co., 1960).

[17] A. Sen, PhD Thesis, University of Mumbai (Mumbai), 2003.

[18] F. Ducastelle, *Order and Phase Stability in Alloys*, (Amsterdam: Elsevier Science Pub. Co., 1991); D. de Fontaine, *Cluster Approach to Order-Disorder Transformation in Alloys*, Solid State Physics 47 33 (1994); A. Zunger, *First Principles Statistical Mechanics of Semiconductor Alloys and Intermetallic Compounds* in NATO ASI on Statics and Dynamics of Alloy Phase Transitions, (New York: Plenum Press) 361 (1994).

[19] S. L. Chaplot, Phys. Rev. B 36 8471 (1987).
Table 1
Comparison of calculated zone-center phonon frequencies between phase IIa (P = 13 GPa) and phase III (P = 18 GPa) of LiYF$_4$ at T = 0 K.

|       | $A_g$ |       |       |       | $A_u$ |       |       | $B_u$ |
|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Phase IIa | 18    | 92    | 115   | 127   | 0     | 0     | 0     | 0     |
| Phase III | 95    | 107   | 162   | 151   | 80    | 82    | 0     | 0     |
| Phase IIa | 155   | 151   | 193   | 165   | 87    | 128   | 115   | 142   |
| Phase III | 166   | 175   | 217   | 200   | 185   | 156   | 152   | 183   |
| Phase IIa | 178   | 214   | 227   | 250   | 196   | 206   | 199   | 195   |
| Phase III | 215   | 225   | 260   | 277   | 266   | 268   | 220   | 205   |
| Phase IIa | 286   | 271   | 293   | 314   | 293   | 298   | 277   | 230   |
| Phase III | 303   | 313   | 316   | 316   | 310   | 299   | 304   | 259   |
| Phase IIa | 324   | 317   | 336   | 398   | 343   | 352   | 310   | 278   |
| Phase III | 334   | 363   | 369   | 404   | 358   | 356   | 315   | 337   |
| Phase IIa | 371   | 377   | 384   | 417   | 408   | 382   | 345   | 368   |
| Phase III | 413   | 410   | 438   | 431   | 434   | 436   | 370   | 383   |
| Phase IIa | 429   | 436   | 461   | 447   | 455   | 463   | 388   | 410   |
| Phase III | 435   | 443   | 496   | 476   | 463   | 473   | 437   | 435   |
| Phase IIa | 473   | 463   | 507   | 478   | 495   | 497   | 477   | 495   |
| Phase III | 506   | 481   | 531   | 509   | 514   | 539   | 494   | 526   |
| Phase IIa | 546   | 562   | 577   | 614   | 578   | 623   | 553   | 552   |
Table 2
Calculated anisotropic thermal parameters (in units of $10^{-4}\text{Å}^2$) for the constituent atoms at various temperatures of 20 and 300 K associated with the three high-pressure phases of LiYF₄. It may be noted that in the scheelite phase ($I4_1/a, Z=4$), all the $F$ atoms are symmetrically equivalent. See text for the labeling of $x$, $y$, $z$ directions.

| Sp. Temp. (K) | Uₓₓ (P=4 GPa) | Uᵧᵧ (P=4 GPa) | Uzz (P=4 GPa) | Uₓₓ (P=13 GPa) | Uᵧᵧ (P=13 GPa) | Uzz (P=13 GPa) | Uₓₓ (P=18 GPa) | Uᵧᵧ (P=18 GPa) | Uzz (P=18 GPa) |
|---------------|----------------|----------------|---------------|----------------|----------------|---------------|----------------|----------------|---------------|
| Li            | 20             | 63             | 63            | 88             | 54             | 72            | 60             | 58             | 64            |
| 300           | 137            | 137            | 224           | 98             | 144            | 109           | 95             | 114            | 189           |
| Y             | 20             | 17             | 17            | 14             | 13             | 12            | 17             | 11             | 12            |
| 300           | 107            | 107            | 71            | 63             | 52             | 94            | 39             | 42             | 51            |
| F(1)          | 20             | 41             | 41            | 40             | 36             | 36            | 36             | 29             | 28            |
| 300           | 154            | 154            | 124           | 108            | 103            | 112           | 70             | 130            | 106           |
| F(2)          | 20             |                |               | 36             | 38             | 42            | 33             | 30             | 34            |
| 300           |                | 112            | 113           | 162            | 88             | 88            | 106            |
| F(3)          | 20             |                |               | 36             | 36             | 38            | 31             | 36             | 31            |
| 300           |                | 110            | 108           | 121            | 78             | 78            | 106            |
| F(4)          | 20             |                |               | 35             | 36             | 35            | 34             | 45             | 36            |
| 300           |                | 103            | 100           | 113            | 93             | 127           | 106            |
Fig. 1. Crystal structures of LiYF$_4$ belonging to (a) phase I, (b) phase IIa, (c) phase IIb and (d) phase III.

Fig. 2. Comparison of phonon dispersion relations along the same high symmetry direction of $\Lambda$ in the three phases of LiYF$_4$ at respectively 0, 13 and 18 GPa. Lines refer to our calculations while symbols represent the experimental data [2].

Fig. 3. (a) Calculated phonon density of states, g(E), in the three phases of LiYF$_4$ at respectively 4, 13 and 18 GPa; (b) comparison of g(E) in the two high-pressure phases at the same pressure of 13 GPa.

Fig. 4. Calculated partial density of states for the constituent atoms with contributions from polarizations along three orthogonal directions in the three phases of LiYF$_4$ at respectively 4, 13 and 18 GPa. Since phase I is of tetragonal symmetry, the contributions along $x$ and $y$ directions are identical for this phase. The relationship between the orthogonal directions and the crystallographic axes is given in section IIIC.

Fig. 5. Calculated (a) heat capacity ($C_P$) and (b) Debye temperature($\theta_D$) as a function of temperature for the three phases of LiYF$_4$ at respectively 4, 13 and 18 GPa. The inset depicts the difference of $C_P(T)$ and $C_V(T)$ over the same temperature region.

Fig. 6. Calculated average mode Grüneisen parameter($\gamma_i$) as a function of phonon energy for the three phases of LiYF$_4$ at respectively 4, 13 and 18 GPa.

Fig. 7. Calculated volume thermal expansion coefficient ($\alpha_V$) as a function of temperature for the three phases of LiYF$_4$ at respectively 4, 13 and 18 GPa. (b), (c) and (d) demonstrate how phonons of different energies (in phase I, phase IIa and phase III respectively) contribute to $\alpha_V$ at 20 and 300 K.

Fig. 8. Calculated thermal mean squared displacements (on a semi-logarithmic scale) of the constituent atoms for (a) phase I, (b) phase IIa and (c) phase III due to phonons of various energies at 300 K. Insets in (a), (b) and (c) refer to the same but on an expanded scale up to 10 meV for the respective phases of LiYF$_4$ at 4, 13 and 18 GPa. It may be noted that in phases IIa and III, there are four symmetrically different F atoms, however, only the average contributions of all the F atoms are shown here.

Fig. 9. (a) Comparison of the Gibbs free energy per atom as a function of pressure in all the three phases of LiYF$_4$, as obtained from the lattice dynamical calculations at $T = 300$ K. The variation in Gibbs energy difference ($\Delta G$) is plotted in (b) with pressure(P) and in (c) with temperature(T) giving a qualitative impression of the first order phase transition that takes place in switching from phase IIa to a dynamically more favourable phase III. Inset in (c) shows $\Delta G$ vs. $T$ up to 200 K on an expanded scale.

Fig. 10. Results of phase transitions as observed in MD simulations runs with increasing pressures at several constant temperatures (phase I $\rightarrow$ phase II(a/b) $\rightarrow$ phase III) and also with increasing temperatures at several constant pressures (phase IIa $\rightarrow$ phase IIb). The transitions among the phase I, IIa and IIb are found to be reversible while phase III retains on decompression to P=0. The dashed line indicates the phase boundary between phase II and phase III as determined by quasiharmonic free energy calculations.