Phonon density of states, free energy, and anharmonicity of LiKSO₄

Narayani Choudhury, S. L. Chaplot, and K. R. Rao

Nuclear Physics Division, Bhabha Atomic Research Centre, Trombay, Bombay 400085, Maharashtra, India

(Received 26 February 1986)

LiKSO₄ has been investigated extensively by a variety of techniques recently. The phonon density of states of this material is now calculated for its two phases $P6_3$ (C_6^6) and P31c (C_{3v}^4) using the rigid molecular-ion model within the external mode formulation. The partial density of states associated with translations of each species of atoms and translations and rotations of the "molecules" SO_4^{-2} are individually derived in the two phases. The free-energy difference and vibrational energy for the two phases are also evaluated. We have also analyzed the anharmonic behavior in the system at $q \approx 0$, using perturbation theory in order to understand its role in the rotational dynamics of SO_4^{-2} ions.

I. INTRODUCTION

Extensive studies of phase transitions in LiKSO₄ have been carried out during this decade using a variety of experimental techniques dealing with macroscopic and microscopic physical properties of the system. Thermal expansion,¹ piezoelectric and elastic,² pyroelectric,³ polariza-tion and ferroelectric,⁴ and dielectric⁵ behavior have been studied. X-ray diffraction,⁶ neutron diffraction,^{7,8} and thermal analysis⁸ have been used to identify various phases and the underlying crystal structure. Infrared ab-sorption,⁹ Raman scattering,^{9,10} electron-paramagnetic resonance,¹¹ Brillouin scattering,¹² inelastic neutron scattering,¹³ and high-pressure¹⁴ techniques have given detailed information on the lattice spectra and some information on the dynamical aspects underlying the phase transitions. The interest in this system is because of its pyroelectric and ferroelectric behavior, the large number of phase transitions, and observation of incommensurate lattice in certain temperature regions. It is stated that the series of phase transitions observed in LiKSO₄ is very peculiar and has never been observed in any material of this simple inorganic type. Many phases possess hexagonal symmetry and are associated with the $P6_3$ (C_6^6) space group; this phase seems to appear rather reentrantly. The detailed theoretical study of lattice dynamics of this phase and of another phase P31c carried out by us¹⁵ recently derived impetus because of this feature as well as a goal of understanding the Raman spectra¹⁰ of the two phases.

The phase transition occurring at around 210 K while cooling involves a space-group change from $P6_3$ (C_6^6) to P31c (C_{3v}^4) as established on the basis of Raman intensity redistribution^{10(a),10(b)} of the lithium translational mode and sulfate internal modes across the transition temperature. It is also said^{10(c)} that the phase transition is associated with cooperative reorientation of one of the SO₄⁻² tetrahedra in the unit cell either by rotation of about 60° around the c axis or by rotation of 108° about an appropriate axis passing through sulfur and normal to the c axis. In a recent study^{10(c)} of Raman-active lowfrequency external modes, it is argued that the reorientation of SO_4^{-2} "molecules" is likely to take place about an axis normal to the *c* axis. Computer simulation¹⁶ studies, however, show that large rotations do not occur only about any single unique axis; they occur about more than one axis, as in the case of other ionic systems like NH₄Cl (Ref. 17).

Our objective in the present work has been (a) to evaluate one-phonon and two-phonon density of states to study how the effect of the reorientations of sulfates manifests itself in the density of states, (b) to study how the thermodynamical parameter, namely, the free energy changes because of these reorientations, and (c) to examine the role of anharmonicity in understanding temperature-dependent Raman data. In Sec. II we briefly outline the latticedynamical model used in these studies. Section III gives the details for evaluation of one-phonon and two-phonon densities of states and free energy. The one-phonon density of states is determined by solving the secular equations, based on external mode formalism, for a large number of wave vectors in the Brillouin zone. It has been resolved into a partial density of states corresponding to translations of Li⁺ and K⁺ ions and translational and rotational modes of SO_4^{-2} molecular ions, using the information on eigenvectors. The two-phonon density of states may help in the analysis of Raman data. The Raman experiments^{10(c)} have revealed that the low-frequency rotational $E_1(TO)$ mode at 40 cm⁻¹ in the P6₃ phase is quite broad (width is nearly 40 cm⁻¹). Below the transition temperature a new E mode appears at 64 cm⁻¹ (width of about 10 cm^{-1}) in the P31c phase. So also an E_2 mode at 52 cm^{-1} changes to a mode at 61 cm^{-1} . The quasiharmonic calculations¹⁵ do not agree with these findings; across the phase transition instead of the E_1 mode at 44 cm⁻¹ an E mode appears at 27 cm⁻¹, although the E_2 mode at 39 cm⁻¹ has a corresponding E mode at 45 cm⁻¹. We have summarized how one can reconcile the apparent contradiction between experimental results and quasiharmonic lattice-dynamics results in Sec. V on the basis of an approximate anharmonic theoretical approach outlined in Sec. IV.

II. LATTICE-DYNAMICAL MODEL

Recently we reported results of lattice-dynamical studies pertaining to the $P6_3$ and P31c phases of LiKSO₄.¹⁵ We were able to analyze and understand several aspects of the Raman spectra¹⁰ of these two phases on the basis of the lattice-dynamical calculations. Comparison of experimental and theoretical mode frequencies has been mostly satisfactory. Therefore, we believe that the theoretical model provides a basis for further studies of the dynamical behavior of the system making use of the interatomic potential function used therein. We have carried out the study of the details of density of states and related aspects which is the subject matter of this paper. Computer experiments have also been carried out by us; a preliminary report of this work is given in Ref. 16.

The dynamical analysis¹⁵ was based on eigenvalues and eigenvectors of the dynamical matrix associated with the crystal assuming that the interactions among the constituents of the lattice can be described either by the rigid-ion model or by the rigid-molecular-ion model¹⁸ within the usual quasiharmonic approximation. The rigid-ion model yields the external modes of the lattice as well as the internal modes of the SO₄⁻² ions in the crystal; the rigidmolecular-ion model gives the external modes only as governed by the external mode formalism.¹⁹ It may be noted that, in the rigid-molecular-ion model, only the nonbonded interactions between pairs of atoms are taken into account, and the intramolecular interactions do not enter into consideration. We have restricted the present study to external modes only as they are the modes that are affected most by changes in crystal structure.

The atom-atom potential function is comprised of a long-range Coulomb interaction and a short-range Born-Mayer-type repulsive interaction. The potential energy between two nonbonded atoms (Kk) and (K'k') separated by a distance r is given by

$$V(r) = \frac{e^2}{4\pi\epsilon_0} \frac{Z(Kk)Z(K'k')}{r} + a \exp\left[-\frac{br}{R(Kk) + R(K'k')}\right],$$
 (1)

with $1/(4\pi\epsilon_0)=9\times 10^9 \text{N m}^2/\text{C}^2$, a=1822 eV, and b=12.364. R(Kk) and Z(Kk) are the effective radius and charge of the atom (Kk) belonging to the unit K. Evaluation of these parameters using physicochemical considerations, equilibrium structure, equilibrium conditions, cohesive energy, etc., is described in Ref. 15. The parameters Z(Kk) and R(Kk) used in the rigid-molecular-ion model are 0.95, 0.55, 1.1, and -0.65 for the charges, and 1.375, 1.95, 1.0, and 1.35 Å for the radii of Li, K, S, and O atoms, respectively.

There are two formula units of LiKSO₄ per unit cell associated with $P6_3$ or P31c phases. In the external mode formalism¹⁹ there are, therefore, 24 degrees of freedom associated with each unit cell and the size of the dynamical matrix is 24×24 . Computer program DISPR (Ref. 20) has been used to calculate the dynamical matrices and solve the secular equation, and this took about 45 sec on the NORSK 560 computer for each wave vector.

III. FREQUENCY DISTRIBUTION OF EXTERNAL MODES AND FREE ENERGY

The space-group symmetry allows us to confine numerical evaluations to wave vectors within the irreducible Brillouin zone (IBZ). The sizes of the IBZ for the $P6_3$, and P31c are $\frac{1}{12}$ and $\frac{1}{6}$ of their respective Brillouin zones. The partitioning of the IBZ adopted for calculations is shown in Fig. 1. We sampled within the IBZ 112 wave vectors in the case of the $P6_3$ phase and 224 wave vectors in the case of the P31c.

A. One-phonon density of states

The frequency distribution of phonons or one-phonon density of states $g(\omega)$ is defined as

$$g(\omega) = A \int_{BZ} \sum_{j} \delta(\omega - \omega_{j}(\mathbf{q})) d\mathbf{q} = A \sum_{j,p} \delta(\omega - \omega_{j}(\mathbf{q}_{p})) d\mathbf{q}_{p} ,$$
(2)

where A is a normalization constant such that $\int g(\omega)d\omega = 1$; $w_j(\mathbf{q}_p)$ is the phonon frequency of the *j*th normal mode of a phonon of wave vector \mathbf{q}_p , p being the mesh index in the partitioned IBZ, and $d\mathbf{q}_p$ provides the weight factor corresponding to the volume of the *p*th mesh in q space. The root sampling method is used in obtaining $g(\omega)$.

Figures 2(a) and 2(b) show the total one-phonon density of states of external modes of LiKSO₄ in the P6₃ and P31c phases respectively; the $g(\omega)$ for the P31c phase is shifted by about 10 cm⁻¹ towards higher frequencies in the region of 0-50 cm⁻¹, compared to that of the P6₃ phase. It may be noted that there are certain band gaps in the $g(\omega)$ of both the phases. A band gap of about 10 cm⁻¹ is noticed around 145 cm⁻¹ and another of nearly 280 cm⁻¹ around 350 cm⁻¹. The latter large band gap clearly separates the lithium translatory mode at around 500 cm⁻¹ from the lower external modes. However, these

FIG. 1. Partitioning of the irreducible Brillouin zone in the a^*b^* plane used in calculation of density of states. The wave vectors sampled correspond to the central point of each mesh; each wave vector sampled was given a weight proportional to the volume of the mesh surrounding it.





FIG. 2. One-phonon density of states of $LiKSO_4$ in the $P6_3$ and P31c phases.

lithium modes are also coupled with some low-frequency internal modes (see Ref. 15), and therefore they shift to lower frequencies. These features have a remarkable similarity with the observations made recently in the case of Li_2SO_4 (Ref. 21).

B. Partial density of states

Corresponding to the 24 degrees of freedom of external modes per unit cell in LiKSO₄ there are 24 modes for any wave vector **q**, and correspondingly there are 24 branches (*j* is the branch index) of dispersion relation. There are 24-component eigenvectors associated with each one of the 24 modes. The eigenvector $\xi(\mathbf{q})$ contains detailed information of displacement components for each of the atoms and the molecules; the translatory and rotatory displacements of molecules are identifiable separately. The eigenvector $\xi(\mathbf{q})$ is, therefore, a direct sum of the mass (moment-of-inertia)—weighted translatory (rotary) partial eigenvectors $\xi_{j,v/\mu}^{t/r}(\mathbf{q})$ of the atoms and molecules. For the sake of clarity, we may note that

$$\boldsymbol{\xi}_{j}(\mathbf{q}) = \sum_{\boldsymbol{\nu},\boldsymbol{\mu}} \left[\boldsymbol{\xi}_{j\boldsymbol{\nu}}^{t}(\mathbf{q}) \oplus \boldsymbol{\xi}_{j\boldsymbol{\mu}}^{t}(\mathbf{q}) \oplus \boldsymbol{\xi}_{j\boldsymbol{\mu}}^{r}(\mathbf{q}) \right] \,. \tag{3}$$

Here v and μ are the atomic and molecular indices, and tand r represent translational and rotatory components. Each partial eigenvector is a three-dimensional vector consisting of translatory displacement components along the Cartesian axes or rotatory displacement components about the Cartesian axes.

The partial density of states $g^{t/r}(\omega)$ associated with each of the partial eigenvectors is defined by the relation

$$g_{i}^{t \mid r}(\omega) = A \sum_{\substack{\text{cell} \\ \nu \mid \mu \in i}} \sum_{j,p} \delta(\omega - \omega_{j}(\mathbf{q}_{p})) \mid \boldsymbol{\xi}_{j,\nu \mid \mu}^{t \mid r}(\mathbf{q}_{p}) \mid^{2} d\mathbf{q}_{p} \qquad (4)$$

 $\sum_{\text{cell}, \nu \mid \mu \in i}$ indicates that the summation is carried out over all the atoms or molecules of the same *i*th species in the unit cell.

The partial one-phonon density of states associated with the translatory modes of Li⁺, K⁺, and the SO₄⁻² ions as well as the rotatory modes of SO₄⁻² ions are shown separately in Fig. 3 for both the phases. From comparison of the partial density of states with the total one-phonon density of states, we observe that several prominent peaks in the one-phonon density of states can be associated unambiguously with specific dynamical behavior of the individual constituents of the unit cell. We note that the peak at ≈ 50 cm⁻¹ in the one-phonon density of states is predominantly due to sulfate librations, that at nearly 100 cm⁻¹ due to translatory modes of potassium, and that at nearly 500 cm⁻¹ due to translations of lithium.

The partial density of states also indicates that the phase transition from $P6_3$ to P31c affects the translations of potassium ions and translations and rotations of SO_4^{-2} ions, the lithium translations being largely unaffected. Since the immediate environment of the SO_4^{-2} (which rotates) is a set of lithium atoms and not that of potassium, it is somewhat surprising that the potassium atoms are affected and not the lithium atoms. However, since the lithium vibrations occur at rather high frequencies, they may be expected to show smaller change.



FIG. 3. Partial density of states of LiKSO₄ in $P6_3$ and P31c phases. Partial densities associated with translations of K and Li atoms and of SO₄⁻² molecules and that of rotations of SO₄⁻² are shown separately.

C. Free energy and vibrational energy

The frequency distribution $g(\omega)$ can be used in the evaluation of free energy, vibrational energy, and specific heat of the solid.

1. Free energy

In the quasiharmonic approximation free energy per unit cell of volume V at temperature T with contribution from the static potential energy, vibrational energy, and vibrational entropy is given by

$$F(V,T) = U(V) + \sum_{i} \left\{ \frac{1}{2} \hbar \omega_{i} + k_{B} T \ln \left[1 - \exp \left[-\frac{\hbar \omega_{i}}{k_{B} T} \right] \right] \right\}$$
(5)

where U(V) is the static lattice energy per unit cell, \hbar the Planck's constant, and k_B the Boltzmann constant. The summation extends over all normal modes in the Brillouin zone. A normalization is used to obtain the free energy per unit cell containing two formula units or the free energy per mole of LiKSO₄.

The free energy is calculated using Eq. (5) as a function of temperature only, keeping volume V constant, as the lattice constant variation over the temperature range 200-400 K is small and assuming that the crystal can be in either of the phases over this temperature range. Since our interest is only to compare the difference in the free energies $\Delta F(V,T)$ of the two phases, as brought about by large-scale reorientations of the SO_4^{-2} ions, we assume that (a) the internal modes are identical in the two phases and (b) the variations in the phonon frequencies due to variations in temperature are negligible compared to changes in $g(\omega)$ due to reoriented sulfates. We have used the $g(\omega)$ computed for the two phases to calculate the free energy of external modes. The static lattice energies



FIG. 4. Free energy F(V,T) as a function of temperature for the $P6_3$ and P31c phases.

have been calculated as -24.3933 eV per unit cell for $P6_3$ and -24.3911 eV per unit cell for P31c phases.

Figure 4 shows the results of calculation of F(V,T) for the two phases. We observe that the F(V,T) for the two phases are quite close and indistinguishable on the scale of the figure; the free energy of $P6_3$ at all temperatures is, however, slightly lower than that of P31c. As the freeenergy curves do not cross each other, we are unable to arrive at any phase transition temperature based on our calculations. This lacuna may be due to the fact that we have not taken into account anharmonic interactions and other changes in the structure accompanying reorientation of sulfates. $\Delta F(V,T)$, the difference in free energies of the two phases, is rather small, only of the order of 0.01 eV. The recent single-crystal neutron-diffraction experiments⁷ are noteworthy in this context as they have revealed that the so-called phase II which contains the P31cphase is, in reality, a mixed phase of $P6_3$ and P31cphases and that it is not possible to transform the entire crystal to the P31c phase.

2. Vibrational energy

In the quasiharmonic approximation, the vibrational energy E_{vib} is given by

$$E_{\rm vib} = \sum_{i} (n_i + \frac{1}{2}) \hbar \omega_i = \int (n_i + \frac{1}{2}) g(\omega_i) \hbar \omega_i \, d\omega_i \,, \qquad (6a)$$

$$n_i = \left[\exp\left[\frac{\hbar\omega_i}{k_B T}\right] - 1 \right]^{-1}.$$
 (6b)

Using an appropriate normalization, the vibrational energy per degree of freedom is expressed in temperature units. Note that in the classical limit at high temperatures the vibrational energy per degree of freedom in a solid is simply k_BT .

Vibrational energy E_{vib} , taking into account the external modes only, is shown as a function of temperature in Fig. 5. The asymptotic classical value corresponding to



FIG. 5. Vibrational energy as a function of temperature for LiKSO₄.

(7)

 k_BT per degree of freedom is reached at high temperatures. From the low-temperature intercept on the energy axis we derive that the zero-point energy per unit cell is 0.29 eV which corresponds to a temperature of 140 K per degree of freedom. When internal vibrations are taken into account the zero-point energy comes out to be about 360 K.

D. Two-phonon density of states

As the two-phonon density of states, involving wave vectors \mathbf{q} and $-\mathbf{q}$, are of significance in relation to optic experiments, we have evaluated this information also. The two-phonon density of states is computed using the expression

$$g_{2}(\omega) = \sum_{q=1}^{p} \sum_{j=1}^{24} \sum_{j'=1}^{24} \left\{ [n_{j}(\mathbf{q})+1][n_{j'}(-\mathbf{q})+1]\delta(\omega-\omega_{j}(\mathbf{q})-\omega_{j'}(-\mathbf{q})) + n_{j}(\mathbf{q})[n_{j'}(-\mathbf{q})+1]\delta(\omega+\omega_{j}(\mathbf{q})-\omega_{j'}(-\mathbf{q})) + [n_{j}(\mathbf{q})][n_{j'}(-\mathbf{q})+1]\delta(\omega+\omega_{j}(\mathbf{q})+\omega_{j'}(-\mathbf{q})) \right\},$$

and is shown in Fig. 6. A discussion of its possible implications with reference to the Raman data is given in Sec. V.

IV. ANHARMONICITY IN LiKSO4

In the Introduction, we have already referred to the changes observed in the Raman experiments^{10(c)} in the frequencies and widths of the doubly degenerate rotational modes at the phase transition. (The rotational modes of the A representation are unaffected.) The observed shifts in mode frequencies could be due to anharmonic effects. In a complex crystal, like LiKSO₄, it is quite difficult to



FIG. 6. Two-phonon density of states in $P6_3$ and P31c phases of LiKSO₄.

estimate the anharmonic effects rigorously unless one uses elaborate computations. However, one can make certain simplifying assumptions and arrive at qualitative trends in the shifts of selected phonons as a function of temperature. We have based the following study on the approach recently taken by Kuchta and Luty²² for studying the frequencies of anharmonic librational modes at zero wave vector for the α phase of solid nitrogen. The librations are considered as uncoupled oscillators with the frequencies determined by the one-dimensional crystal potential along a direction specified by the harmonic eigenvector of these modes. We have, as discussed in Sec. II, considered the atom-atom potentials consisting of a Coulombic part and a short-range Born-Mayer repulsive part and studied anharmonic aspects of all normal modes at $q \approx 0$ along c^* in the P6₃ and P31c phases. The potential $V(\theta_i)$ is computed corresponding to any normal coordinate θ_i of *i*th excitation at q=0, by displacing Li and K atoms and SO_4^{-2} molecules and also by rotating SO_4^{-2} molecules in a manner specified by the eigenvector of the mode under consideration. For $|\theta_j| \leq \langle \theta_j^2 \rangle^{1/2}$; the potential $V(\theta_j)$ can be expressed by a polynomial in θ_i given by

$$V(\theta_j) = a_{0,j} + a_{2,j}\theta_j^2 + a_{3,j}\theta_j^3 + a_{4,j}\theta_j^4 .$$
(8)

The coefficients $a_{2,j}$, $a_{3,j}$, and $a_{4,j}$ of the harmonic and anharmonic terms in this expression are useful in determining the harmonic frequencies and anharmonic shifts; the coefficients are determined by least-squares fitting $V(\theta_j)$ to Eq. (8). The appropriate moment of inertia I of the oscillator is given by,

$$I_{j} = \sum_{k} m_{k} | \mathbf{u}_{k,j}^{t} |^{2} + \sum_{k} \underline{I}_{k} | \mathbf{u}_{k,j}^{r} |^{2}.$$
(9)

Here k runs over all atoms and molecules in the primitive cell and \mathbf{u}_k^t and \mathbf{u}_k^r represent the translational and rotational displacement vectors, for unit θ_j , of the kth atom/molecule with a moment of inertia \underline{I}_k . Expression (10) gets slightly modified when \underline{I}_k is nondiagonal. The harmonic frequency is given by the expression

$$\omega_j = \left[\frac{2a_{2,j}}{I_j}\right]^{1/2},\tag{10}$$

and from perturbation theory at $q \approx 0$ the anharmonic shifts due to third- and fourth-order terms are given by²²

8612

 \parallel \frown \mid

	חחתעו	I. INCOULD OF AIRING	IIIOIIIC calculations (III		j, uic marmonic mequery, ag	111 1111 M CONT	e more medacined or		
Representation	ωj	$\Delta_j^{(3)}$	$\Delta_j^{(4)}$	$\Omega_j(0)$	Representation	ωj	$\Delta_j^{(3)}$	$\Delta_j^{(4)}$	0) ⁽ υ
		P 63 phase					P31c phase		
E_1	44 ^a	0	6.68 (2)	51 ^a	E	27ª	-0.66	15.70	42
	100	0	0.4	100		46	0.02	0.76 (2)	47
	491	0	6.15 (30)	497		84	0	0.19	84
						91	0	2.87 (14)	94
E_2	39	-0.06	1.21 (2)	40		100	0	0.51 (1)	101
	82	-0.04	0.59 (1)	83		491	0	5.71 (15)	497
	89	-0.02	1.76 (1)	91		493	0	5.58 (12)	499
	493	- 5.09	5.64 (23)	494					
B	109	0	0.20 (1)	109	B	109	0	0.23 (1)	109
	145	0	1.01 (8)	146		145	0	1.05 (9)	146
	214	0	3.16 (34)	217		214	0	3.29 (42)	217
	534	0	6.64 (77)	541		534	0	6.63 (77)	541
V	120	-2.41 (34)	2.65 (132)	120	Ł	120	-2.39 (34)	2.63 (131)	120
	200	-0.02	-1.08 (8)	199		200	-0.03	-1.05 (5)	199
	561 ^a	-0.12	-64.1 (275)	497 ^a		561 ^a	-16.6 (279)	-22.3 (300)	522'
^a Results for the mo	des at $q \approx 0$ a	long c.							



FIG. 7. Potentials for the E_1 and A modes and E and Amodes in P63 and P31c phases in LiKSO4. Dashed curves indicate the harmonic part of the potential. The potential for A modes are purely harmonic, and hence corresponding dashed lines cannot be shown.

$$\Delta_j^{(3)} = -\frac{7.5\hbar}{I_j^3} \left[\frac{a_{3,j}}{\omega_j^2}\right]^2 \tag{11}$$

and

$$\Delta_j^{(4)} = 3.0\% \left[\frac{a_{4,j}}{(I_j \omega_j)^2} \right], \qquad (12)$$

respectively. The renormalized frequency $\Omega_i(T)$ at any temperature T is given by

$$\Omega_j(T) = \omega_j + (\Delta_j^{(3)} + \Delta_j^{(4)})[2n_j(T) + 1] .$$
(13)

Figure 7 shows the nature of potentials $V(\theta_i)$ for some of the E- and A-type modes in the $P6_3$ and P31c phases as typical examples. Using the coefficients of the leastsquares fitted potential,²³ the third- and fourth-order shifts are computed (Table I). Figure 8 shows the plot of renormalized frequency as a function of temperature for all long-wavelength modes. We observe from Table I that the rotational E_1 mode at 44 cm⁻¹ and the lithium trans-latory A mode at 561 cm⁻¹ are highly anharmonic in the $P6_3$ phase. In the P31c phase the lowest-frequency rota-tional E mode at 27 cm⁻¹ and lithium translatory A mode at 561 cm^{-1} are anharmonic. All other modes do not exhibit perceptible anharmonicity. Further, this 27 cm^{-1} libratory E mode is so anharmonic that it is not quite appropriate to use perturbation theory for this mode. However, in Fig. 9 we have shown a plot of shifted

п



FIG. 8. Renormalized mode frequencies in the $P6_3$ and P31c phases of LiKSO₄ as a function of temperature.

frequency of this mode as a function of temperature as given by the perturbation approach by the dotted lines. One may note that the steep increase in frequency of this mode is unrealistic and reflects the limitations of such a perturbation calculation.

We believe that a more realistic estimate of the shift in frequency for such highly anharmonic modes may be attempted via a modified perturbation approach, in which the harmonic frequency on the right-hand side of Eqs. (11) and (12) is replaced by the renormalized frequency. Figure 9 shows the results of such a modified perturbation calculation also for the $27 \text{-cm}^{-1} E$ mode in the P31cphase and also for the $44 \text{-cm}^{-1} E_1$ libratory mode in the $P6_3$ phase, compared with results of the perturbation theory discussed in the earlier paragraph. The modified perturbation scheme results in reduced shifts.

In order to examine the validity of the modified perturbation procedure, we have carried out a classical calculation which is valid for high temperatures. We consider a classical oscillator of moment of inertia I in a potential $V(\theta)$. The period of oscillation τ of the oscillator is given by

$$\tau = 2 \int_{\theta_{\min}}^{\theta_{\max}} \frac{d\theta}{\dot{\theta}} = 2 \int_{\theta_{\min}}^{\theta_{\max}} \frac{d\theta}{\{(2/I)[E - V(\theta)]\}^{1/2}} .$$
(14)

Here θ_{\min} and θ_{\max} are the turning points of the oscillator and

$$E = V(\theta_{\min}) = V(\theta_{\max}) = 2k_B T$$
(15)



FIG. 9. Comparison of the results of perturbation (dashed lines), modified perturbation (solid lines), and classical theory (open and solid circles) with reference to low-frequency E and E_1 rotational modes in LiKSO₄.

for the classical oscillator. Using the potential $V(\theta_j)$, we numerically compute the period and hence the frequency $(\omega = 2\pi/\tau)$ of the oscillator at any temperature. From Fig. 9 we observe that the classical frequency derived thus corresponding to 300 and 350 K are quite close to the results of the modified perturbation approach, suggesting that the latter scheme does provide a fair estimate of the anharmonic frequencies at these temperatures.

V. SUMMARY

The phonon density of states for LiKSO₄ in the phases $P6_3$ and P31c is obtained by making use of the rigidmolecular-ion model within the framework of external mode formalism. It is observed that the frequency region below 50 cm⁻¹ is populated to a greater extent in the $P6_3$ phase compared to that in the P31c phase. Detailed analysis based on study of the partial density of states shows that this change in frequency distribution is principally due to the lower-frequency libratory modes of SO_4^{-2} in the $P6_3$ phase. The difference in free energy corresponding to the two phases is of the order of 0.01 eV in the temperature range 200-400 K, suggesting that the two phases can coexist over this temperature range.

Qualitatively, agreement between the Raman data^{10(c)} and results of lattice-dynamical results¹⁵ may be said to be fair, although detailed comparison may reveal certain discrepancies. This feature is especially prominent as far as the low-frequency long-wavelength E_1 and E_2 modes are concerned. From Fig. 2 of Ref. 15 it may appear as if the frequencies, derived theoretically, tend to become soft as one goes from the $P6_3$ phase to the P31c phase, contrary to what is observed experimentally in Raman experiments.^{10(c)} There are several aspects of the present study that can be related to the experimentally observed^{10(c)} frequency shifts of sulfate libratory modes and lithium translatory mode and the large widths of the low-frequency rotational mode.

We observe from Fig. 6 that the two-phonon density of states (with phonons of wave vectors q and -q) in $P6_3$ is composed of three peaks below 400 cm⁻¹ at nearly 65, 110, and 200 cm⁻¹ while that of the P31c phase is made up of four peaks at around 15, 65, 120, and 200 cm⁻¹, apart from the δ function at $\omega = 0$. The peak at 65 cm⁻¹ in the $P6_3$ phase is rather broad and asymmetric. To the extent that the two-phonon density of states is sampled in the Raman experiments, one may expect differences in the line shapes due to this dissimilar feature in the two-phonon density of states.

Secondly, from the results of study of anharmonic effects given in Table I and Fig. 8, we note that only two out of the 21—optic modes, are highly anharmonic. The remaining modes are mostly not affected by anharmonicity. The low-frequency rotational mode (44 cm⁻¹ in the $P6_3$ phase and 27 cm⁻¹ in the P31c phase) and the lithium translatory modes at 561 cm⁻¹ (in both $P6_3$ and P31cphases) are the modes that are affected by anharmonicity.

- D. P. Sharma, Pramana 13, 232 (1979); T. Ranga Prasad, Y. C. Veneedhar, L. Iyengar, and K. V. Krishna Rao, Pramana 11, 81 (1978); R. Ando, J. Phys. Soc. Jpn. 17, 937 (1962).
- ²D. P. Sharma, Pramana 13, 223 (1979); B. Mroz, T. Krajewski, T. Breczewski, W. Chomka, and D. Sematowicz, Ferroelectrics 42, 459 (1982).
- ³T. Breczewski, T. Krajewski, and B. Mroz, Ferroelectrics 33, 9 (1981); D. R. Madhu and P. S. Narayanan, Nucl. Phys. Solid State Phys. (India) 24C, 335 (1981).
- ⁴S. Fujimoto, N. Yasuda, H. Hibino, and P. S. Narayanan, J. Phys. D 17, L35 (1984).
- ⁵R. Cach, P. E. Tomaszewski, P. Bastie, and J. Barnarel, Ferroelectrics 53, 337 (1984); M. Delfino, G. M. Loiacono, W. A. Smith, A. Shenlov, Y. M. Tsuo, and M. I. Bells, J. Solid State Chem. 31, 131 (1980).
- ⁶A. J. Bradley, Philos. Mag. 49, 1225 (1925); S. Chung and Th. Hahn, Z. Kristallogr. Kristallgeom. Kristallphys. Kristallchem. 137, 447 (1973); M. Karippinen, J. O. Lundgren, and R. Liminga, Acta Crystallogr., Sec. C 39, 34 (1983); P. A. Sandomirskii, S. S. Meshalkin, and I. V. Rozhdestvenskaya, Kristallografiya 28, 67 (1983) [Sov. Phys.—Crystallogr. 28, 33 (1983)]; P. E. Tomaszewskii and K. Lukaszewicz, Phase Trans. 4, 37 (1983); P. E. Tomaszewskii and K. Lukaszewicz, Phys. Status Solidi A 71, K53 (1982); A. Meng and Q. J. Cao, Acta Phys. Sinica 32, 1196 (1983); Y. X. Gu, *ibid.* 32, 525 (1983); Q. W. Yan, *ibid.* 33, 435 (1984); A. Meng and Q. J. Cao, *ibid.* 31, 1405 (1984); S. S. Xie et al., *ibid.* 33, 235 (1984).
- ⁷S. Bhakay-Tamhane, A. Sequeira, and R. Chidambaram, Acta Crystallogr., Sec. A 37 (Suppl.), C108 (1981); S. Bhakay-Tamhane, A. Sequeira, and R. Chidambaram, *ibid.* 40, 1648 (1984); S. Bhakay-Tamhane, A. Sequeira, and R. Chidambaram (unpublished); S. Bhakay-Tamhane, A. Sequeira, and R. Chidambaram, Solid State Commun. 53, 197 (1985); A. M. Balagurov, B. N. Savenko, M. Dlouha, S. Vratislav, and Z. Jirak, Phys. Status Solidi A 83, K117 (1984); A. M. Balagurov, I. D. Dutt, Z. Gheorghiu, B. N. Savenko, and L. A. Shuvalov, Phys. Status Solidi A 51, 367 (1979); A. M. Balagurov, V. I. Gordeliy, M. Z. Ishmukhametov, V. E. No-

In Fig. 9 we have compared the results of anharmonic calculation via perturbation, modified perturbation, and classical approaches for anharmonic rotational modes. Results of the modified perturbation approach are perhaps indicative of the realistic anharmonic shifts possible in the system. We believe that the results of quasiharmonic calculations¹⁵ have to be viewed with caution as anharmonicity plays a very important role in renormalizing some of the mode frequencies. As discussed above, certain lowfrequency rotational modes have hardened, while one of the lithium translatory modes has softened due to anharmonicity. Qualitatively, the anharmonic studies may be said to be in agreement with Raman experimental results associated with SO_4^{-2} reorientations and lithium translatory modes in so far as the anharmonic nature of the modes is concerned.

ACKNOWLEDGMENTS

We are grateful to Dr. A. P. Roy for his comments on the manuscript.

- vozhila, B. N. Savenko, and V. D. Shibaev, Nucl. Instrum. Methods 193, 617 (1982).
- ⁸Li Yin-yuan, Solid State Commun. 51, 355 (1984).
- ⁹J. Hiraishi, N. Taniguchi, and H. Takahashi, J. Chem. Phys. **65**, 3821 (1976).
- ¹⁰(a) M. L. Bansal, S. K. Deb, A. P. Roy, and V. C. Sahni, Solid State Commun. **36**, 1047 (1980); (b) M. L. Bansal, S. K. Deb, A. P. Roy, and V. C. Sahni, Pramana **20**, 183 (1983); (c) M. L. Bansal and A. P. Roy, Phys. Rev. B **30**, 7307 (1984).
- ¹¹F. Holuj and M. Drozdowski, Ferroelectrics 36, 379 (1981); C. H. A. Fonseca, G. M. Ribeiro, R. Gazzenelli, and A. S. Chaves, Solid State Commun. 46, 221 (1983); N. C. Mishra, K. Murthy, and U. Ramesh, Nucl. Phys. Solid State Phys. (India) 26C, 323 (1983).
- ¹²M. Drozdowski, F. Holuj, and M. Czajkowski, Solid State Commun. 45, 1005 (1983).
- ¹³G. Eckold, Th. Hahn, and B. O. Hildmann, Acta Crystallogr. Sec. A Suppl. 40, C-374 (1984).
- ¹⁴S. Fujimoto, N. Yasuda, and H. Hibino, Phys. Lett. A 104, 42 (1984).
- ¹⁵S. L. Chaplot, K. R. Rao, and A. P. Roy, Phys. Rev. B 29, 4747 (1984).
- ¹⁶S. L. Chaplot and K. R. Rao, Bull. Mater. Sci. 7, 31 (1985).
- ¹⁷S. L. Chaplot and K. R. Rao, Phys. Rev. B 33, 4327 (1986).
- ¹⁸K. R. Rao, S. L. Chaplot, P. K. Iyengar, A. H. Venkatesh, and P. R. Vijayaraghavan, Pramana 11, 251 (1978).
- ¹⁹G. Venkataraman and V. C. Sahni, Rev. Mod. Phys. **42**, 409 (1970).
- ²⁰S. L. Chaplot, Report No. BARC-972, 1978, Bhabha Atomic Research Center (Trombay, Bombay, Maharashtra, India) (unpublished).
- ²¹R. Fruh and E. Cazzenelli, Solid State Commun. 9&10, 95 (1983).
- ²²B. Kuchta and T. Luty, Chem. Phys. Lett. **92**, 462 (1982); B. Kuchta and T. Luty, J. Chem. Phys. **78**, 1447 (1983).
- ²³We have used the quasiharmonic calculations reported in Ref. 15 to obtain the frequencies ω_j . However, the nature of anharmonic shifts listed in Table I is unlikely to change if ω_j are obtained from a harmonic calculation at zero temperature.