Intrinsic anharmonicities in the $BX_4{}^{2-}$ orthorhombic sublattice

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We have measured the room-temperature polarized Raman spectra of the internal modes of K_2SO_4 and K_2SeO_4 under hydrostatic pressure up to 10 GPa in a backscattering configuration. It was found that phonons involving the motion of selenium atoms have distinctive pseudoanharmonicities that can be traced to isotopic natural abundances. Accordingly, a reinterpretation is given to the origin of the fourth-order anharmonicity (g_4 coupling constant) within the quartic potential formalism as representing dynamical isotopic effects in the cluster picture. We found that this analysis may be extended to other molecular systems with either phonon instabilities or order-disorder commensurate-incommensurate phase transitions.

I. INTRODUCTION

Isostructural A_2BX_4 compounds showing the paraelectric orthorhombic *Pnam* (D_{2h}^{16}) space group with four molecules per unit cell have attracted interest because the wide variety of structural changes that they present, of which, the modulated phase is distinctive. Of these the most studied is K_2SeO_4. Its second-order phase transition, from the paraelectric into the incommensurate stage, is characterized by the softening of the Σ_2,Σ_3 extended branch with $\omega_j(\bar{q})$ tending to zero at $\bar{q}\simeq(1/3,0,0)$.[1] Below T_I ($\simeq$129 K), the wave vector $\bar{q}_\delta=[1-\delta(T)]\bar{a}^*/3$ is characteristic of an unidimensional modulation with δ going discontinuously to zero at the lock-in transition ($T_c=93$ K). The Brillouin zone then folds along $\bar{a}$ three times and the system becomes weakly ferroelectric. This sequence of structural changes is shared with compounds like Rb_2ZnCl_4, Rb_2ZnBr_4, and K_2ZnCl_4, among others.

In contrast, K_2SO_4 whose β paraelectric phase is a prototype for the whole A_2BX_4 family, has the orthorhombic (paraelectric)—orthorhombic (ferroelectric) sequence in common with K_2SeO_4 but without the intermediate incommensurate phase.[2]

There have been numerous attempts to understand the paraelectric lattice instability in K_2SeO_4 and in particular, the origin of the incommensurate phase. The proposed mechanisms range from the coupling of translation motion of the potassium ions with the rotation motion of $SeO_4{}^{2-}$,[1] in a rigid ion approximation; to a local fourth-order potential addition to the shell model.[3] This last, Fig. 1, represents a one-dimensional diatomic chain with polarizable anionic clusters and rigid cations. The origin of nonlinearity is attributed to the quartic polarizability of the chalcogenide anions and related cluster. It leads analytically to a lock-in transition at $2\pi/3$. More recently, Massa *et al.*[4] presented experimental evidence for mode softening precursors in the electron-phonon interactions.

All these approaches involve in a fundamental way the role of the $BX_4{}^{2-}$ sublattice, and, since in many cases there are inconsistencies in the current literature, we decided to compare with Raman scattering, the behavior of $SeO_4{}^{2-}$ and that of $SO_4{}^{2-}$ at room temperature under high hydrostatic pressure.

Our aim is to elucidate from the experimental point of view what may differentiate the inner dynamics of these two sublattices, and then compare our results with an appropriate theoretical model to aid the understanding of the appearance of a modulate phase in these relatively simpler systems.

The study of K_2SeO_4 and K_2SO_4 only implies an isoelectronic chalcogenide replacement in the formula unit. Hence, they present an ideal situation for this kind of comparative work. The reported x-rays studies at room temperature do not reveal any distinctive anomaly in these two compounds.[5,6] Accordingly, we describe below the polarized Raman spectra of the internal modes of K_2SeO_4 and K_2SO_4 under high hydrostatic pressure up to 10 GPa at room temperature in a backscattering configuration.
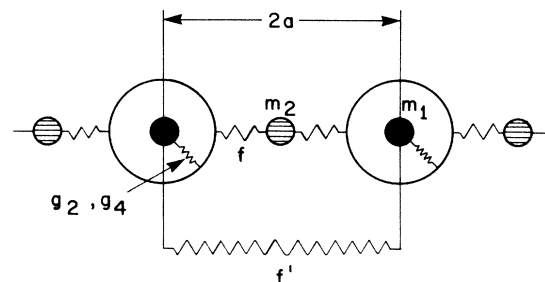

FIG. 1. Shell-cluster model; M_1,M_2 effective ionic masses of $BX_4{}^{2-}$ anion and A_2 cation. f,f' first- and second-nearest-neighbor coupling constants. g_2,g_4 harmonic and quartic shell-core coupling constants (from Ref. 3).

II. EXPERIMENT

Single crystals of K_2SO_4 and K_2SeO_4 were grown by slow evaporation of aqueous solutions at room temperature. The pressure is applied by an opposed anvils type cell.[7] One anvil is the cylindrical 10 mm diameter and 10 mm thick, optically flat sapphire window. An oriented small single crystal and a ruby chip, for pressure calibration purposes, were put in the 300 μm hole of a Cu-Be gasket. The pressure transmitting fluid was a mixture of methanol-ethanol in a 4:1 ratio. Frequency positions were established against the calibrated (5145 Å) plasma lines. Pressure points were verified before and after each run since we observed some window deterioration around 5—6 GPa. Our estimated error is about 0.1 GPa.

Pressure phase diagrams have been studied by Pistorius and Rapoport[8] and Press et al.[9] No structural phase transition was expected or found at room temperature with increasing pressure up to 10 GPa.

III. RESULTS

Our results are displayed in Figs. 2(a),2(b) and 3(a),3(b). The points represent experimental data while solid lines are least-square fits to the data with polynomial expressions of the type

$$\omega = \omega_0 + \sum_n A_n p^n \ . \tag{1}$$

Atmospheric pressure peak positions are summarized as zero-order fitting parameters (ω_0) in Table I. They are in agreement with previously reported spectra.[10,11]

The $XO_4^{2-}(v_2,v_4,v_1,v_3)$ vibrational modes are in well-defined spectral regions as for the free molecule. Figures 2(a) and 2(b) show the behavior of the symmetric (v_2) and antisymmetric (v_4) bending modes for K_2SO_4 and K_2SeO_4 under pressure. It should be noted that the weakest $v_4(B_{1g})$ mode was not plotted since it tended to merge with the background from the backscattering configura-
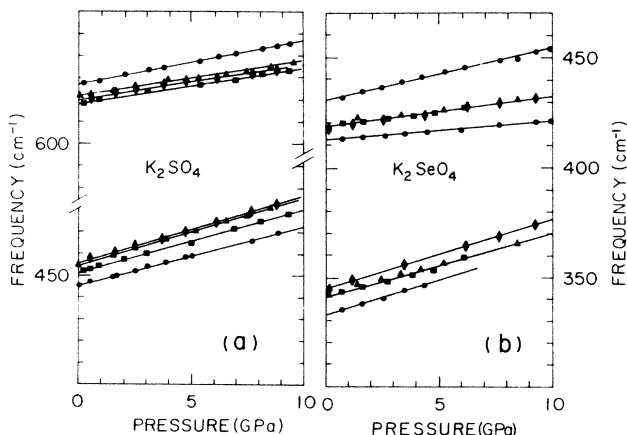
tion. Nevertheless, we were able to verify that it has the same behavior as the other v_4. The one-to-one correlation between the two compounds for every phonon is evident and the frequency-pressure relation is generally linear.

The results for the stretching region (v_1,v_3) are shown in Figs. 3(a) and 3(b). $B_{1g}(v_1,v_3)$ modes that are almost degenerate with their A_g counterparts were not considered because leakages of the latter modes made their position uncertain. Even though the overall frequency versus pressure dependence has the same slope for both compounds there is a definite departure from a linear behavior in the v_3 phonons of K_2SeO_4. These [Fig. 3(b)] do not show a break in the slope. Their behavior with pressure is continuous, implying the possible absence of a random librational motion and pointing toward intrinsic anharmonicities within the SeO_4^{2-} sublattice.

The fitted linear coefficients of Eq. (1), (A_1), were used to calculate mode Grüneisen parameters, γ_j, for all observed modes (j) using the equation

$$\gamma_j = -\frac{d \ln\omega_j}{d \ln V} = \frac{A_1(j)B}{\omega_0(j)} \ , \tag{2}$$

where B is the bulk modulus. We have used an empirical rule[12] to calculate the bulk modulus of K_2SO_4 since to the best of our knowledge the elastic constants have not been determined. It relates the bulk moduli and the molecular densities of the two materials by

$$\frac{B(2)}{B(1)} = \left|\frac{\rho(2)}{\rho(1)}\right|^4 \ , \tag{3}$$

with $B(1)=26.7$ GPa as previously calculated for K_2SeO_4 (Ref. 13) and densities (ρ) obtained from lattice constants.[5,6] Thus, $B(2)\simeq15.4$ GPa for K_2SO_4. Every inter-

FIG. 2. Pressure dependence of the bending modes of (a) K_2SO_4 and (b) K_2SeO_4: ●, A_g; ■, B_{1g}; ▲, B_{2g}; ◆, B_{3g}. The polynomial fit is shown as solid lines.
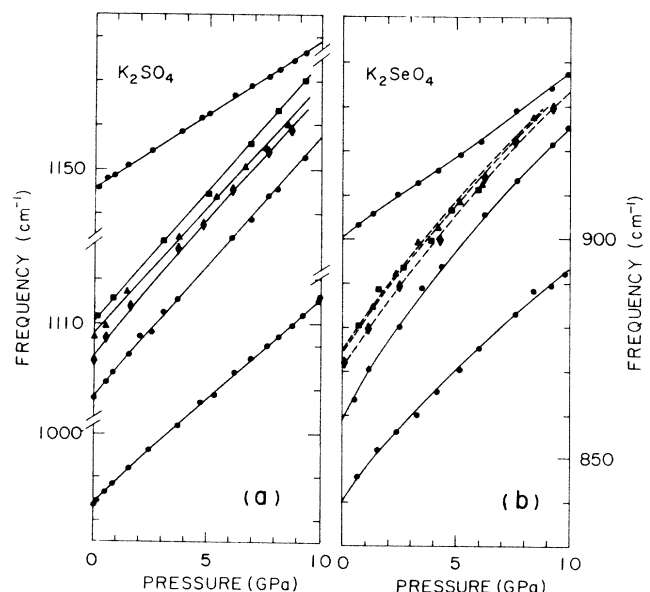
FIG. 3. Pressure dependence of the stretching modes of K_2SO_4 and K_2SeO_4: ●, A_g; ■, B_{1g}; ▲, B_{2g}; ◆, B_{3g}. The polynomial fit is shown as full and dashed lines.

TABLE I. Peak position of the internal vibrational modes of K_2SeO_4 and K_2SO_4 at atmospheric pressure and coefficients of a polynomial fit to the expression $\omega = \omega_0 + \sum_n A_n p^n$. A weak unresolved peak has been observed in some of our A_g spectra at the frequency indicated by the question mark. It does have a direct correlation with the internal mode assignments.

Mode	K_2SeO_4 ω^a (cm^{-1})	ω_0 (cm^{-1})	A_1 (cm^{-1}GPa^{-1})	A_2 (cm^{-1}GPa^{-2})	K_2SO_4 ω^b (cm^{-1})	ω_0 (cm^{-1})	A_1 (cm^{-1}GPa^{-1})
A_g	334	332.8	3.1		447	445.5	2.7
	414	412.3	0.89		618	616.9	1.2
(aa)	430	430.5	2.4		628	626.7	2.0
(bb)	841	841.1	6.5	-0.14	983	984.7	4.6
(cc)	865	862.2	7.8	-0.15	1192	1093.8	5.7
	901	900.2	3.7		1144	1145.7	3.3
B_{1g}	342	340.5	3.0		453	451.6	2.8
(ba)	420	418.3	1.4		620	618.7	1.6
	437				633		
	841				983		
	874	876.7	6.2		1111	1110.7	5.8
	900				1144		
					1165(?)		
B_{2g}	344	342.6	2.8		456	455.0	3.0
(ac)	421	420.4	1.3		622	621.6	1.5
	875	874.5	7.0	-0.10	1109	1106.3	6.2
B_{3g}	346	344.8	3.2		457	455.3	3.1
(bc)	417	417.6	1.5		623	620.3	1.3
	871	871.6	7.5	-0.14	1104	1104.5	5.7

[a]Reference 11.
[b]Reference 10.

nal mode of each vibrational group has a Grüneisen parameter of the same order of magnitude. Table II shows the mean values for each vibrational group of K_2SeO_4 and K_4SO_4. The only exception to this trend is observed, as in the case of K_2SeO_4,[13] for the ν_3 mode (A_g, 1146 cm^{-1}, atmospheric pressure) whose Grüneisen parameter $\gamma'(\nu_3) = 0.0145$, is distinctive within its group. These mode Grüneisen parameters, as expected for ionic solids, are not correlated with frequency for either compound. Anharmonic contributions in SeO_4^{2-} are reflected here in that a polynomial fit needs significant second-order terms, as shown in Table I, i.e., linear mode Grüneisen parameters would only be an approximation.

IV. DISCUSSION

A clue to the origin of the difference between SO_4^{2-} and SeO_4^{2-} internal vibrational modes is that the antisymmetric ν_3 stretching eigenmodes imply the motion

TABLE II. Mean values of the Grüneisen parameters of each internal vibrational group of K_2SO_4 and K_2SeO_4.

	$\overline{\gamma}(\nu_2)$	$\overline{\gamma}(\nu_4)$	$\gamma(\nu_1)$	$\overline{\gamma}(\nu_3)$
K_2SO_4	0.099	0.038	0.072	0.082
K_2SeO_4[a]	0.24	0.096	0.21	0.22

[a]Reference 13.

of the tetrahedral center atom.[14] While the former anion contains an isotopic composition with only small mass differences (^{32}S, 95%; ^{33}S, 0.76%; ^{34}S, 4.22%; ^{36}S, 0.014%),[15] the latter one has to add the presence of a wide variety of Se isotopes (^{74}Se, 0.37%; ^{76}Se, 9.02%; ^{77}Se, 7.58%; ^{78}Se, 23.52%; ^{80}Se, 49.82%; ^{82}Se, 9.19%).[15] [The idea of growing crystals of K_2SeO_4 (^{80}Se) was abandoned due to the excessive cost that it implies. However, samples of K_2ZnCl_4 (^{35}Cl) are in active consideration.] The oxygen contribution is present for both anions. We note that K_2SeO_4 near degenerate phonons of the B_{1g}, B_{2g}, B_{3g} species at about 875 cm^{-1} are precisely those that are likely to be affected by these atoms. Having four molecules per unit cell, the likelihood of four tetrahedral replicas is small so we also understand the frequency versus pressure quadratic dependence of the ν_1 (841 cm^{-1}, atmospheric pressure) symmetric mode as a result of a many-body dynamical interaction. This is to some extent manifested on the oxygen isotopic side band of this phonon, shown in Fig. 4, where we found structureless line shapes at any temperature in contrast with those reported for K_2SO_4 by Montero et al.[10]. Hence, we have pointed out the origin of intrinsic anharmonic, or perhaps, now more properly, pseudoanharmonic, effects in SeO_4^{2-} sublattice and consequently, we are driven to consider a model in which extra anharmonicities play a distinctive role.

As it was pointed out above, a one-dimensional model, Fig. 1, has been put forward that includes a local fourth-order anisotropy potential,[3] i.e., a second-order oscillator,
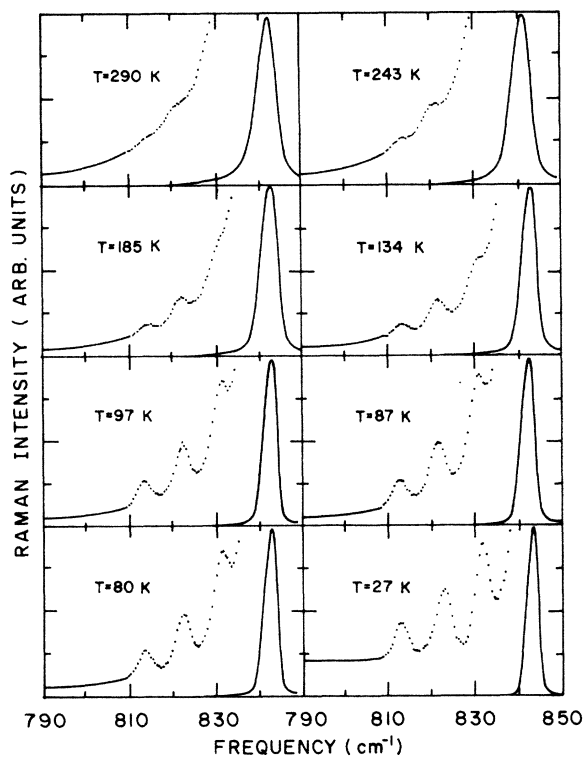
FIG. 4. Temperature dependence of the oxygen isotopic side band of the v_1, A_g mode of K_2SeO_4.

in considering the electron interaction of a shell-core cluster picture for the SeO_4^{2-} sublattice. The harmonic version is well known for its success in describing the lattice dynamics of innumerable compounds.[16] The additional introduction of a g_4 quartic coupling constant is determinant for ferroelectric phase transitions as well as for nonlinear excitations in several systems considered displacive. However, this treatment does not discriminate between K_2SeO_4 and K_2SO_4. If one chooses to consider that the atom polarizability in the shell picture is totally taken into account by harmonic terms, as it is quite likely since S and Se are isoelectronics, one obtains the same commensurate-phase—transition sequence for both compounds. Lattice instability in this approximation is attributed to a negative (electron) shell-(ion) core coupling constant g_2.

In the nonlinear version,[17] the additional higher-order term, i.e., the nonlinear interaction between electrons and ions resulting in the g_4 coupling constant, is thought to give origin to the double-well picture (see Ref. 17, Sec. II B, α, β) in a displacive environment only.

We interpret the g_4 coupling constant as a pseudoanharmonic macroscopic counterpart of a many-body problem that results when the natural isotopic composition is explicitly considered in the lattice dynamics. They may be thought of as intrinsic impurities of the BX_4^{2-} sublattice. With this additional term, the perfect translation symmetry in the classical sense is regained. g_2,

within this interpretation, would still play the role assigned in the harmonic approximation for hybridization in the cluster.

This interpretation for the nonlinear force gives a more intrinsic character to each member of the A_2BX_4 orthorhombic family. We know that some of its components such as Rb_2ZnCl_4 or K_4ZnCl_4 share the same orthorhombic (paraelectric)—incommensurate—orthorhombic (ferroelectric) phases with K_2SeO_4. However, they have a different dynamical behavior at T_I. No soft phonon has been found in the paraelectric phase of either Rb_2ZnCl_4 (Ref. 18) or K_2ZnCl_4 (Ref. 19). We interpret this as a consequence of the dynamical disorder introduced in the normal phase by rubidium ([85]Rb, 72.15%; [87]Rb, 27.85%) (Ref. 15) and chlorine ([35]Cl, 75.53%; [37]Cl, 24.47%) (Ref. 15) atoms. Hwang[20] has already pointed this out in the lattice dynamics of molecular compounds and earlier, Wu and Sutherland[21] estimated the relative percentage of various isotopic compositions for CCl_4 to be 31.6% for [35]Cl$_4$; 42.2% for [35]Cl$_3$ [37]Cl; 21.1% for [35]Cl$_2$ [37]Cl$_2$; 4.7% for [35]Cl [37]Cl$_3$; and 0.4% for [37]Cl$_4$. This means that in the paraelectric phase of $A_2ZnCl_4(A:K,Rb)$ systems the chlorines, due to their positions in the tetrahedras, not only introduce extra pseudoanharmonicities, as Se in K_2SeO_4, but also lower the effective symmetry. A statistically weighted percentage of D_{2h}^{16} (Pnam) forbidden modes are naturally allowed at some sites of the ideal paraelectric phase. Then the order-disorder picture at T_I, rather than the displacive one, is a natural consequence. This is also evidenced in hydrostatic pressure phase diagrams for the commensurate-incommensurate transition. Rb_2ZnCl_4, K_2ZnCl_4, and Rb_2ZnBr_4 have positive-pressure coefficients,[22] while a negative one is found for K_2SeO_4,[9] in agreement with Samara criterion.[23]

On the other hand it also suggests that the cluster model would be successful to describe the phonon instability in other compounds such as $SrTiO_3$,[24] where titanium has a well differentiated isotopic family ([46]Ti, 6.88%; [47]Ti, 7.32%; [48]Ti, 73.99%; [49]Ti, 5.46%; [50]Ti, 5.25%),[15] and that in blue bronzes, $X_{0.33}MoO_3$ ($X=K,Rb$), ([92]Mo, 15.86%; [94]Mo, 9.12%; [96]Mo, 16.50%; [97]Mo, 9.45%; [98]Mo, 23.75%; [100]Mo, 9.62%),[15] where the commensurate-incommensurate phase transition involves a distortion of the MoO_6 octahedra.[25] We observe that replacement of molybdenum by isoelectronic tungsten[26] produces drastic changes pointing toward a more important role of mass differences than the one regularly assigned.

V. CONCLUSION

We have measured the internal modes spectra of K_2SeO_4 and K_2SO_4 up to 10 GPa. The reported behavior shows explicitly that v_3 phonons involving the motion of the selenium atoms have distinctive pseudoanharmonicities that can be traced to isotopic natural abundances. We found that the analysis may be extended to other systems with either phonon instabilities or phase transformations. On the other hand, we reinterpret the g_4 coupling con-

stant within the quartic potential formalism[3] as given containing dynamical isotopic effects thus reinforcing the idea of a deformable sublattice as the proper description of the lattice dynamics in molecular compounds.

We wish to emphasize that in spite that nonlinear potentials lead to consider, within the context of the above discussion, the isotopic presence as a sufficient condition for a commensurate-incommensurate phase transition, we still like to think as only a necessary ingredient in the delicate balance of forces present in systems that develop that kind of structural transformations. This is also consistent with the quoted experimental results.[1,18,19]

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