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Original scientific paper

INFRARED SPECTRA OF THE SULFATE ION TRAPPED IN POTASSIUM SELENATE – A COMPARISON WITH SULFATE DOPED POTASSIUM CHROMATE*

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The FT-IR spectra of SO_4 doped K_2SeO_4 were recorded at room (RT) and liquid-nitrogen temperature (LNT). The sulfate ions occupy sites of C_s symmetry. This leads to a complete removal of the degeneracy of the *E and* F_2 modes. Exactly nine bands originating from the internal $^{32}SO_4$ vibrations were found at both RT and LNT. Bands due to $^{34}SO_4$ species could also be detected for the ν_3 and ν_4 mode components. Nine (out of the ten possible) second order transitions of the S–O stretchings were precisely measured at LNT. The harmonic frequencies of the S–O stretchings were calculated. The comparison with the SO_4 doped K_2CrO_4 shows that (i) the sulfate ions are more distorted in a selenate than in a chromate host lattice; (ii) the anharmonicity constants of the x_{13i} type are larger that those of the x_{3i3j} type (iii) the ratio x_{13i}/x_{3i3j} of the anharmonicity constants appears to be smaller in the case of selenate than in the case of chromate host compound and (iv) most probably, mechanical anharmonicity dominates over the electric one. The possible reasons for these findings are discussed.

Key words: IR spectra; doped crystals; isolated ions; sulfate ion distortion; harmonic frequencies; anharmonicity constants.

INTRODUCTION

A number of crystals having the structure of β-K_2SO_4 are known: K_2SO_4, K_2SeO_4, $(NH_4)_2SO_4$, K_2CrO_4, K_2MnO_4, $(NH_4)_2BeF_4$, Rb_2SeO_4 *etc.* Most of these have been very extensively studied by both diffraction and spectroscopic methods. The structure refinements [1–6] reveal the great similarity between the compounds; they all crystallize in the orthorhombic space group *Pnam*, with four formula units in the crystal cell. All ions are situated on mirror planes. The tetrahedral anions are fairly regular. The oxygen (*i.e.* fluorine – in BeF_4 compounds) atoms either participate in the hydrogen bonding as proton acceptors (in the case of NH_4 compounds) or are 'coordinated' to the univalent metal cations (K, Rb, Tl *etc.*). It might be interesting to mention that although $(NH_4)_2SeO_4$ and $(NH_4)_2CrO_4$ crystallize in the monoclinic crystal system (space group *C2/m*), still their structure shows a number of similarities with the compounds of the β-K_2SO_4 type (*e.g.* all ions in the structure are at symmetry planes *etc.* [7,8]).

The spectroscopic studies are also numerous [9–15]. Both IR (transmission and reflection) and Raman techniques were employed in the assignment of the sulfate internal modes in K_2SO_4 [9]. The LO and TO mode frequencies were measured and reported too. Much attention was also paid to the study of pressure/temperature induced phase transitions in $(NH_4)_2SO_4$ [10–15].

Directly related to the present work are the studies of doped and mixed crystals, particularly those in which various polyatomic ions were 'isolated' in the host matrix [16–34]. Of special interest are those concerned with sulfate doped alkali halides [25–29] and SO_4 ions 'isolated' in a related isostructural compound (selenate, chromate, manganate or ferrate) [30–34]. In the latter studies conventional grating instruments have been used, so the results were (with a few exceptions) limited to reporting the frequencies of the $\nu_3(SO_4)$ and $\nu_4(SO_4)$ mode components.

Some time ago we studied the FT–IR spectra of sulfate doped K_2CrO_4 [35] at LNT. The high signal-to-noise ratio allowed us to measure accurately the fundamental as well as second-order transition frequencies and to calculate the anharmonicity constants and the harmonic frequencies for the antisymmetric stretching

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SO_4 vibrations. In this work a more thorough investigation of sulfate doped K_2SeO_4 was done. The results are presented and compared with those for SO_4 doped K_2CrO_4 [35, 36].

EXPERIMENTAL

Sulfate doped potassium selenate was prepared from K_2CO_3 and H_2SeO_4. The selenic acid already contained a small amount of SO_4 impurities (although both chemicals were declared as being of reagent grade purity). Sulfate enriched samples (mole ratio of about 5%) were used for the measurement of the weak $\nu_1(SO_4)$ and $\nu_2(SO_4)$ bands which were otherwise completely masked by the high frequency wings of the intense $\nu_3(SeO_4)$ and $\nu_4(SeO_4)$ mode. Sulfate doped K_2CrO_4 was prepared from mixtures of K_2CrO_4 and K_2SO_4. The spectra were recorded from KBr pellets on a Perkin Elmer 1720 FT–IR spectrometer. The spectral resolution was about 1 cm^{-1}. In order to have high quality spectra (high signal-to-noise ratio) one thousand spectra were accumulated. For sharp bands the measured frequencies are accurate to within 0.2–0.3 cm^{-1}. The integrated band intensities (I) were estimated as a product of the full width at half-maximum intensity (FWHMI = $\Delta\nu_{1/2}$) and the absorbance (A) of the band. In order to sharpen the absorptions (reducing the number of 'hot' transitions, mainly two-phonon bands in which low frequency lattice phonons take place), low temperature studies were performed using a flow cryostat cooled with liquid nitrogen.

RESULTS: GENERAL CONSIDERATIONS AND APPEARANCE OF THE SPECTRA

Initially, we shall briefly consider the spectra of β–K_2SO_4, in order to demonstrate the advantages of studying isolated ions, particularly ions which are subject to isomorphous isolation.

The LNT IR spectra of a KBr disk containing pure K_2SO_4 are shown in Fig. 1. The application of group-theoretical methods (under the $\mathbf{k} = 0$ approximation) reveals that two bands originating from ν_1, three from ν_2 and five bands from both ν_3 and ν_4 are expected to appear in the powder IR spectra, as a consequence of both site-group and correlation-field splitting effects. Furthermore, in IR transmission studies (especially in ionic crystals, and in the vicinity of strong IR bands) the spectrum appears to be a result of superimposed transmission and reflection [37]. This is a consequence of the LO–TO splitting of the IR active modes (not predicted by the unit-cell group-theory approximation), leading to a high reflectivity of the sample in the frequency regions between ν(TO) and ν(LO) [38]. To summarize, a powder IR transmission spectrum is of relatively little value if one wishes to correlate the spectral and structural properties of the investigated material.

Things become even worse if one studies the second order transitions (two-phonon bands and true

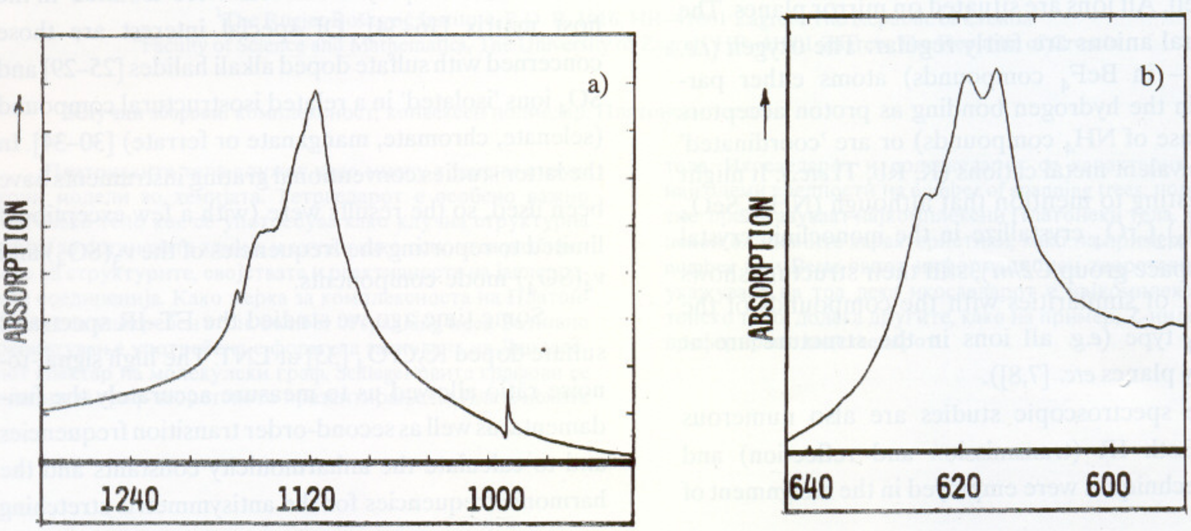

Fig. 1 . LNT IR spectra of a KBr disk containing pure K_2SO_4 in the region of the SO_4 stretching (a) and antisymmetric bending modes (b).

overtones) of pure K_2SO_4, in order to gain some knowledge of the anharmonicity of the SO_4 stretching vibrations. The spectrum (cf. Fig. 2) is very rich, as a result of relaxation of the selection rules for multi-phonon transitions. No band in this part of the spectrum could be simply assigned to a particular transition, as we discussed in our previous paper [35].

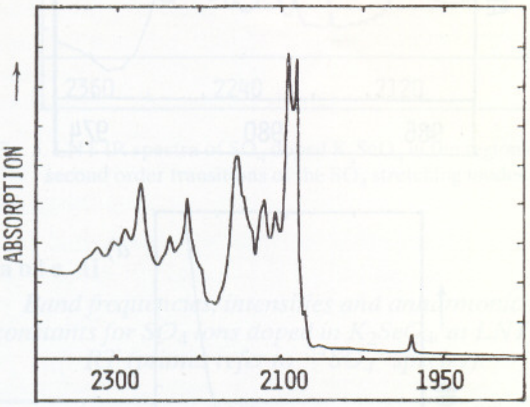

Fig. 2. LNT IR spectra of pure K_2SO_4 in the region of second order transitions of the SO_4 stretching modes

When sulfate ions are doped (at low concentration) in K_2SeO_4 (K_2CrO_4), they are more or less 'isolated'. This means that (i) interactions of identical oscillators (which cause Davydov splittings and the dispersion of phonon courves) and (ii) interactions (long-range electrostatic forces) leading to LO–TO splitting of the sulfate modes, can both be neglected. In such cases the number of bands (due to internal SO_4 vibrations)* in the vibrational spectra and their activity may be predicted using site-group [39], rather than by ordinary unit cell-group analysis [40]. The results of these group theoretical considerations are given in Fig. 3.

As a consequence of the C_s site symmetry, all degeneracies are removed and the forbidden ν_1 and ν_2 modes become allowed. The spectral picture of SO_4 doped K_2SeO_4 at LNT (and also at RT) is in excellent agreement with these predictions, all nine bands being clearly detectable (Fig. 4). The frequencies of the components of ν_3 and ν_4 modes are in a good agreement with those reported by other authors [30–34], but ν_1 deviates by about 5 cm^{-1} with respect to the value (985 cm^{-1}) found by Hájek *et al.* [33]. As far as we know the components of the symmetric SO_4 bending have not been detected so far in this class of (isomorphous) solid solutions.

Some much weaker bands were found in the region of the ν_3 mode and one in the region of ν_4. Three of them were assigned to vibrations of the $^{34}SO_4$ species. In order to confirm this assignment, we made an approximate normal coordinate analysis for a 'free' SO_4 ion and its $^{34}SO_4$ and $S^{18}O_4$ isotopomers. The GVFF method was employed [41]. The geometry of the sulfate ion (regular tetrahedron, $R(S\text{–}O) = 147.2$ pm) was taken from the work of Murray-Rust *et al.* [42]. The set of force constants used and the output results (vibrational frequencies) are presented in Table I.

The accumulation within the interferometer, of a great number of spectra allows even very weak bands to be detected, such as the overtones and combination bands of the components of the ν_1 and ν_3 modes.** The corresponding region of the IR spectra is presented in Fig. 5.

Knowing the frequencies of both fundamental and second-order transitions allows one to calculate the anharmonicity constants [44]. The anharmonicity constant for the $2\nu_1$ vibration was estimated from the IR spectrum of pure K_2SO_4 (Fig. 2), taking the mean value of the unit-cell group components as the frequency of the ν_1 fundamental [36]. Previous studies [35]

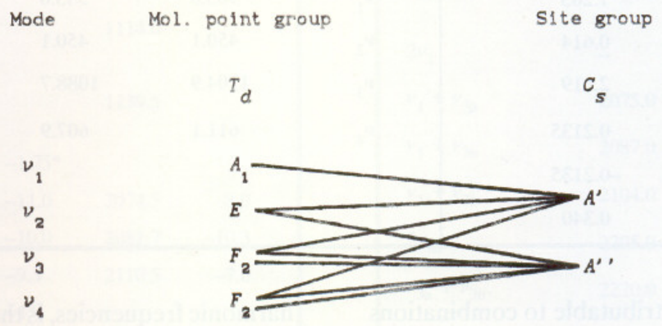

Fig. 3. Correlation between the molecular point group and the site group of sulfate ions isolated in K_2SeO_4

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* The external modes of the sulfate ions absorb in the FIR region (below 200 cm^{-1}) and will not be discussed in the present work.

** Since the sulfate ions are *isolated* in the selenate matrix, and the frequencies of the SO_4 stretching vibrations are well above all other (*i.e.* SeO_4 stretching and/or bending) frequencies, terms *localized phonons* [43] or *localized vibrations* are often used. These are exponentially attenuated (rather than plane) waves. For simplicity the terms *fundamental mode* (vibration), *overtone* and *combination band* are used throughout the text, rather than *phonon*, *true overtone* and *two-phonon band* – which are more conveniently used in pure crystals.

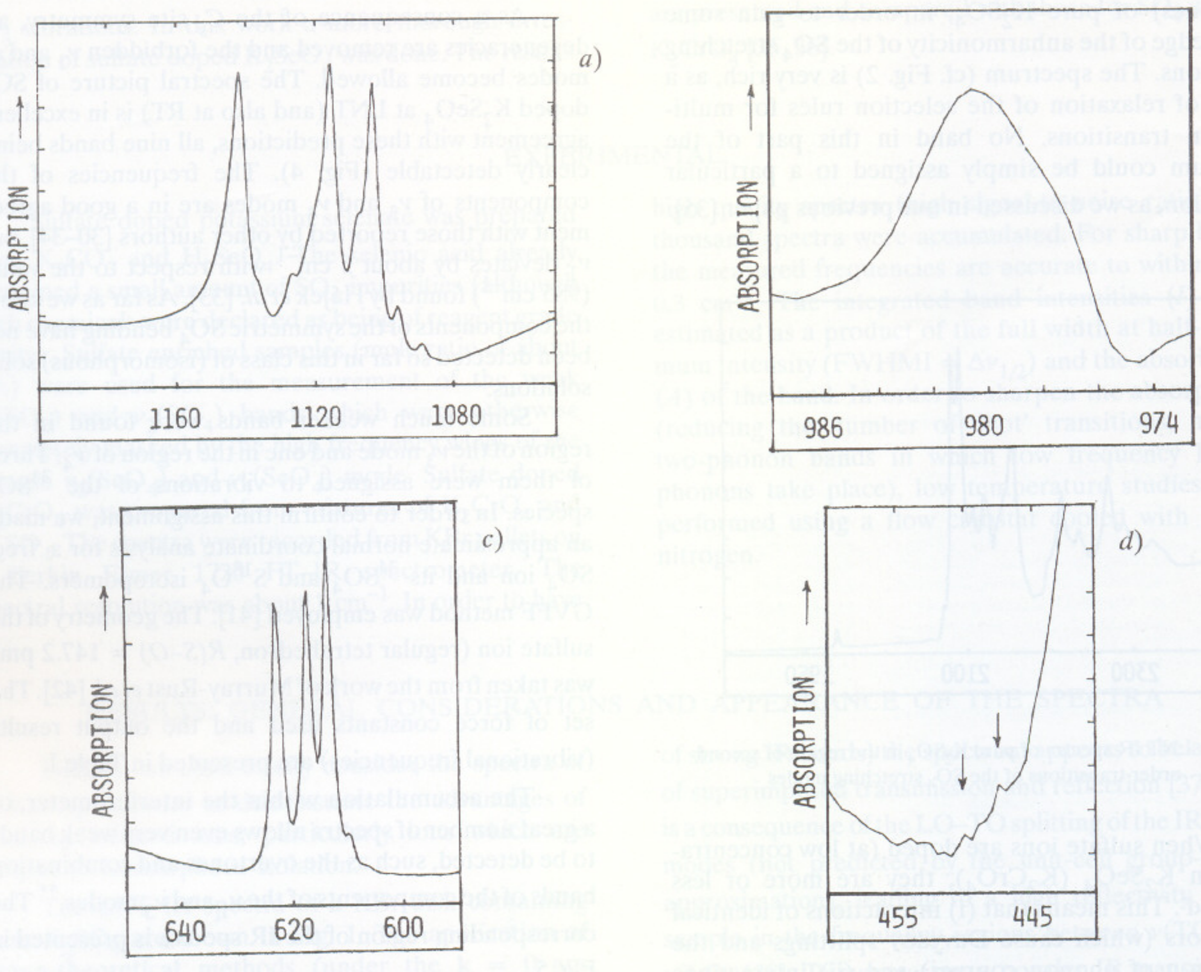

Fig. 4. LNT IR spectra of SO_4 doped K_2SeO_4. (a) $\nu_3(SO_4)$; (b) $\nu_1(SO_4)$; (c) $\nu_4(SO_4)$ and (d) $\nu_2(SO_4)$ region

Table I

Force constants and calculated frequencies for various SO_4 isotopomers ($f_{\alpha\alpha} = -f_{\alpha\alpha}'$ was assumed [45])

Force constant	Value/($N \cdot cm^{-1}$)	Mode	$^{32}SO_4$ ν/cm^{-1}	$^{34}SO_4$ ν/cm^{-1}	$^{32}S^{18}O_4$ ν/cm^{-1}
f_r	7.263	ν_1	983.0	983.0	926.8
f_{rr}	0.614	ν_2	450.1	450.1	424.3
$d^2 f_\alpha$	2.019	ν_3	1104.9	1088.7	1073.9
$d^2 f_{\alpha\alpha}$	0.2135	ν_4	611.1	607.9	581.7
$d^2 f_{\alpha\alpha'}$	–0.2135				
$0d^2(f_{r\alpha} - f_{r\alpha'})$	0.340				

have shown that no bands attributable to combinations of stretching and bending modes could be found in the IR spectra, thus suggesting that the corresponding anharmonicity constants are negligibly small. Since the site symmetry of the sulfate ions is low, all degeneracies are removed, and equations for the non-degenerate case might be applied [44]. The calculation of the harmonic frequencies, is therefore, straightforward. All data are summarized in Table II. Data for SO_4 doped K_2CrO_4 are given for comparison in Table III. The calculated harmonic frequencies are given in Table IV.

Fig. 6 shows that there is a good correlation between the intensity of the second-order transitions and the corresponding values of the anharmonicity constants.

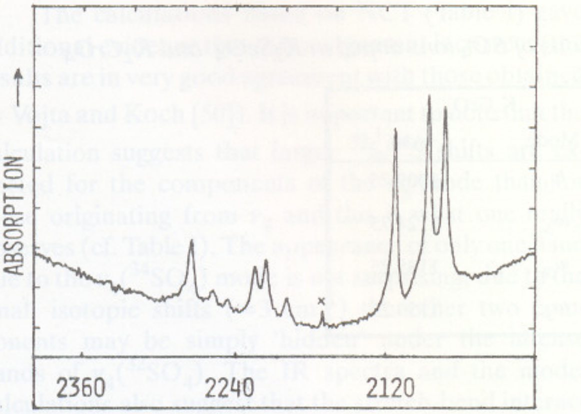

Fig. 5. LNT IR spectra of SO_4 doped K_2SeO_4 in the region of the second order transitions of the SO_4 stretching modes

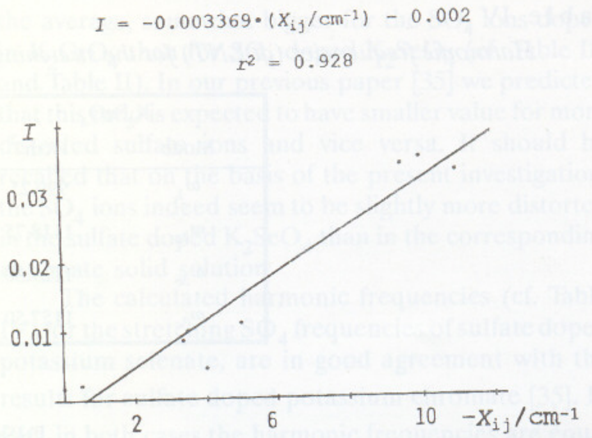

Fig. 6. Intensity of the bands due to second order transitions vs anharmonicity – a least-squares best-fit line

Table II

Band frequencies, intensities and anharmonicity constants for SO_4 ions doped in K_2SeO_4, at LNT and RT (primes refer to $^{34}SO_4$ species).

Mode	LNT			RT	
	ν/cm^{-1}	I/(arb. units	x_{ij}/cm^{-1}	ν/cm^{-1}	x_{ij}/cm^{-1}
ν_{2a}	447.5	0.0011		447.5	
ν_{2b}	450.0	0.0019		451.5	
ν_{4a}'	610.0	–			
ν_{4a}	613.5	0.85		614.0	
ν_{4b}	617.0	0.70		617.5	
ν_{4c}	623.0	0.62		622.5	
ν_1	980.5	0.043		978.0	
ν_{3a}'	1089.5	0.031			
ν_{3b}'	1096.5	0.073			
ν_{3a}	1103.5	3.2		1104.5	
???	1108.3	–			
ν_{3b}	1115.5	4.3		1114.0	
ν_{3c}'	1127.1	–			
ν_{3c}	1142.0	4.5		1139.5	
$2\nu_1$	–	–	–1.75*		
$\nu_1 + \nu_{3a}$	2073.0	0.033	–11.0	2074.5	–8.0
$\nu_1 + \nu_{3b}$	2086.0	0.035	–10.0	2081.7	–10.3
$\nu_1 + \nu_{3c}$	2113.0	0.034	–9.5	2110.5	–7.0
$2\nu_{3a}$	2199.0	0.0045	–4.0		
$\nu_{3a} + \nu_{3b}$	2115.5	0.010	–3.5	2216.3	–2.2
$2\nu_{3b}$	2224.3	0.0085	–3.35		
$\nu_{3a} + \nu_{3c}$	2245.5	0.0018	0.0		
$\nu_{3b} + \nu_{3c}$	2257.0	0.0022	–0.5		
$2\nu_{3c}$	2274.0	0.011	–5.0	2269.5	–4.75

*Estimated value (see text for details)

Table III

LNT frequencies and anharmonicity constants for SO_4 ions doped in K_2CrO_4 [35, 36] (primes refer to $^{34}SO_4$ species)

Mode	ν/cm^{-1}	x_{ij}/cm^{-1}
ν_{4a}	612.0	
ν_{4b}	616.5	
ν_{4c}	622.5	
ν_1	984.0	
ν_{3a}'	1092.5	
ν_{3b}'	1099.5	
ν_{3a}	1106.5	
ν_{3c}'	1110.5	
ν_{3b}	1117.5	
???	1127.5	
ν_{3c}	1133.5	
$2\nu_1$	–	–1.75*
$\nu_1 + \nu_{3a}$	2075.0	–15.5
$\nu_1 + \nu_{3b}$	2087.0	–14.5
$\nu_1 + \nu_{3c}$	2104.0	–13.5
$2\nu_{3a}$	2205.0	–4.0
$\nu_{3a} + \nu_{3b}$	2220.0	–4.0
$2\nu_{3b}$	2227.0	–4.0
$\nu_{3a} + \nu_{3c}$	2239.0	–1.0
$\nu_{3b} + \nu_{3c}$	2250.0	–1.0
$2\nu_{3c}$	2258.0	–4.5

*Estimated value (see text for details)

Table IV

Harmonic frequencies (at LNT) for the stretching vibrations of SO_4 *ions doped in* K_2SeO_4 *and* K_2CrO_4

K_2SeO_4		K_2CrO_4	
Mode	ν/cm^{-1}	Mode	ν/cm^{-1}
ω_1	999.25	ω_1	1009.25
ω_{3a}	1118.75	ω_{3a}	1124.75
ω_{3b}	1129.30	ω_{3b}	1135.25
ω_{3c}	1157.50	ω_{3c}	1150.25

DISCUSSION

According to Ross [45], the frequencies of the normal vibrations for a "free" SO_4 ion are 983 (ν_1), 450 (ν_2), 1105 (ν_3) and 611 cm^{-1} (ν_4). When these values are compared with the frequencies (cf. Table II) of the nine fundamentals observed for the isolated ions, one may conclude that the symmetry of these ions deviates only slightly from the ideal T_d symmetry; the largest splitting of the ν_3 mode components at LNT is 38.5 cm^{-1} which compared with the centro-frequency (ν_c = 1120.3 cm^{-1}) of the ν_3 mode gives $\approx$ 3.5 % as a value for the relative splitting of the antisymmetric stretching vibration. The relative splittings of the ν_4 (antisymmetric bending) and ν_2 (symmetric bending) modes are much less pronounced (~1.5 %, and 0.55 %, respectively), indicating that the effects of angular distortion are somewhat smaller than those caused by the bond length distortion. Both findings suggest that the sulfate ions are only 'slightly' distorted, this conclusion being further confirmed by the low intensity of the symmetric stretching and bending mode components (these modes are IR forbidden for ions with T_d symmetry).

Another estimate for the degree of distortion of the studied SO_4 ions may be made on the basis of their geometry. The method of Baur [46] is widely used for that matter, although more involved methods are also known [47–49]. Assuming that the geometry of the isolated SO_4 ions is basically the same as in pure β-K_2SO_4, one may calculate the distortion indices [46] *DI(SO), DI(OO)* and *DI(OSO),* which are measures for the departure of the S–O distances, O···O separations and O–S–O angles, respectively, from their mean values. The values calculated on the basis of the structural data [1] give *DI(SO)* = 0.0034 and *DI(OSO)* = 0.0024. One should, then, conclude that both diffraction and spectroscopic results suggest that the sulfate ions are more distorted with respect to the S–O distances than with respect to the O–S–O angles.

However, it is questionable to what extent the results obtained by X-ray diffraction *on pure substances* are transferable to the *dopant ions* in mixed crystals. Usually, it is *a priori* assumed that the geometry of the structural units (in this case sulfate ions) does not change significantly during isomorphous isolation [49]. This is, of course, only an approximation. It is known from the literature that some of the K···O distances in K_2SeO_4 are slightly shorter and other slightly longer than the corresponding distances in K_2CrO_4 [1,4]. Assuming that the same holds for the K···O separations built with the O atoms of the dopant SO_4 ions, one would expect that the shorter K···O contacts will induce additional lengthening of the somewhat longer S–O bonds and vice versa. So, it is not surprising that the SO_4 ions doped in K_2SeO_4 are *slightly more distorted* than those doped in K_2CrO_4, at least when S–O distances are taken into consideration.*

The spectra of SO_4 doped K_2SeO_4 and K_2CrO_4 *are* in agreement with this assumption (cf. Table II and III), the relative splitting $\Delta\nu/\nu_c$ for the ν_3 mode components of SO_4 doped K_2CrO_4 being $\approx$2.5 % (significantly smaller than the splitting of SO_4 doped K_2SeO_4). With appropriate modifications (to make it more quantitative), this simple method may be used to quantify the distortion of a dopant polyatomic ion in a series of isomorphous host crystals, for which the approach of Baur [46] or any of the other approaches based on crystallographic data are not applicable.

Weak bands are usually found in the vicinity of the intense absorptions due to the components of ν_3 and ν_4 modes (cf. Fig. 4 and Table II). Some of them are, probably, combinations of the ν_1 mode with low-frequency lattice modes, as shown by Lewis and Sherman [28]. Another reason for the appearance of bands in this region is the existence of $^{34}SO_4$ ions (the abundance of ^{34}S in the natural sulfur is about 4.3 %). An empirical assignment of these bands was made on the basis of their position; they are all 'shifted' to low wavenumbers, with respect to the corresponding $^{32}SO_4$ bands.

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* In line with this, the comparison of the RT and LNT data (cf. Table I) also suggests that the SO_4 ions are somewhat more distorted at LNT. This finding may be explained in terms of the unit cell contraction at low temperatures, the entities (ions) being packed more tightly. This may be expected to increase the order of the K··O 'bonds', resulting in a more distorted sulfate ion.

The calculations based on NCT (Table I) gave additional evidence that this assignment is correct (the results are in very good agreement with those obtained by Vojta and Koch [50]). It is important to note that the calculation suggests that larger $^{32}S/^{34}S$ shifts are expected for the components of the ν_3 mode than for those originating from ν_4 and this is what one really observes (cf. Table I). The appearance of only one band due to the $\nu_4(^{34}SO_4)$ mode is not surprising; due to the small isotopic shifts (≈ 3 cm^{-1}) the other two components may be simply 'hidden' under the intense bands of $\nu_4(^{32}SO_4)$. The IR spectra and the model calculations also suggest that the stretch-bend interaction force constants are not the same for all four S–O bonds; hence the slightly different isotopic ratios for the ν_3 mode-components.

Nine bands due to second-order transitions were clearly identified in the LNT IR spectra of the SO_4 ions trapped in both K_2SeO_4 and K_2CrO_4 (Table II, Table III and Fig. 5). Only five such bands were resolved at RT (the bands at RT are significantly broader, partly due to the presence of 'hot bands', but also due to phonon collisions which reduce the mean-life of the excited states [51]). Due to insufficient data at RT, only the LNT spectra will be further discussed in more detail.

The anharmonicity constants of the type x_{3i3j} are several times smaller than those of the x_{13i} type. The reason for this seems to be clear : for sulfate ions which are only slightly distorted, the forms of the normal modes are expected to be close to those in 'free' SO_4 The symmetry coordinates of the following type (the r_i's are the four S–O distances in the sulfate ion)

$$S_1 = 1/2\,(\Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_4)$$

$$S_{3a} = 1/2\,(\Delta r_1 + \Delta r_2 - \Delta r_3 - \Delta r_4)$$

$$S_{3b} = 1/2\,(\Delta r_1 - \Delta r_2 + \Delta r_3 - \Delta r_4)$$

$$S_{3c} = 1/2\,(\Delta r_1 - \Delta r_2 - \Delta r_3 + \Delta r_4)$$

may be used, to a first approximation, if one wishes to describe the four stretching vibrations. Now, for an ion with T_d symmetry the atomic displacements along S_{3i} and $-S_{3i}$ are equivalent by symmetry (they are transformed into each other by the application of a suitable $\hat{S}_4$ operation). As a consequence, all odd terms in the potential energy expansion of the ν_3 mode components vanish. For a slightly distorted sulfate ion, these terms are expected to be of much smaller value than the even ones. On the other hand, no symmetry operation transforms the displacement along S_1 into $-S_1$, allowing cubic (as well as higher-order) terms to exist. Hence, the doubly excited ν_3 components are 'less anharmonic' compared to the combinations of ν_1 and ν_3.

The ratio of the anharmonicity constants, x_{13i}/x_{3i3j}, might further be of interest. This ratio is, on the average, somewhat bigger for the SO_4 ions doped in K_2CrO_4 than for SO_4 doped K_2SeO_4 (cf. Table III and Table II). In our previous paper [35] we predicted that this ratio is expected to have smaller value for more distorted sulfate ions and vice versa. It should be recalled that on the basis of the present investigation, the SO_4 ions indeed seem to be slightly more distorted in the sulfate doped K_2SeO_4 than in the corresponding chromate solid solution.

The calculated harmonic frequencies (cf. Table IV) for the stretching SO_4 frequencies of sulfate doped potassium selenate, are in good agreement with the results for sulfate doped potassium chromate [35]. In fact, in both cases the harmonic frequencies are equal within 10 cm^{-1}.

Finally, the correlation found between the intensity of the second order transitions and the corresponding anharmonicity constants (Fig. 6) strongly suggests that the anharmonicity is predominantly mechanical in nature. In the dipole approximation, the intensity (*i.e.* transition moment) of an overtone transition is proportional to the square of the integral:

$$<\psi_i(\mathbf{q})\,|\hat{q}\,|\,\psi_{i+2}(\mathbf{q})>$$

where $\varphi_i(\mathbf{q})$ are the true ('anharmonic') wave functions of an arbitrary mode. In principal, similar expressions may be written for the transition probability of a combination vibration. In accordance with the condition of completeness the wave functions may be expanded as a series of harmonic-oscillator eigenfunctions $\phi_i(\mathbf{q})$:

$$\psi_i(\mathbf{q}) = \sum_{j=0}^{\infty} c_{ij}\,\phi_j(\mathbf{q})$$

The c_{ij} coefficients for which $i = j$, are the basic terms in the expansion; all other terms appear due to the anharmonicity present. It is (at least intuitively) clear that the larger the anharmonicity, the larger will be the coefficients c_{ij} ($i \neq j$), and consequently, the larger is the intensity of the second order transition. This, naturally, produces a correlation (although not necessarily a linear one). If, on the other hand, large electrical anharmonicity was present (arising from non-linear terms in the dipole moment expansion) than the correlation in Fig. 6 would be a mere coincidence. One finds this assumption rather improbable, and consequently less satisfying.

Further work on sulfate doped $SrCrO_4$, $BaCrO_4$ and $BaSeO_4$ is in progress.

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Резиме

ИНФРАЦРВЕНИ СПЕКТРИ НА СУЛФАТНИ ЈОНИ КАКО ПРИМЕСИ ВО КАЛИУМСЕЛЕНАТ – СПОРЕДБА СО СУЛФАТНИ ЈОНИ ВО КАЛИУМ ХРОМАТ –

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Клучни зборови: инфрацрвени спектри; кристали со примеси; изолирани јони; деформација на SO_4 јони; хармониски фреквенции; константи на анхармоничност.

Фуриетрансформни инфрацрвени спектри на калиум селенат онечистен со сулфатни јони се снимани на собна и на ниска температура. Сулфатните јони лежат на рамнини на симетрија. Како резултат на тоа доаѓа до потполно отстранување на дегенерацијата на нивоата од E и F_2 симетриски тип. Во областа на внатрешните вибрации од $^{32}SO_4$ групациите се најдени точно девет ленти. За ν_3 и ν_4 модовите, регистрирани се и ленти од $^{34}SO_4$ изотопомерите. Прецизно се измерени спектралните параметри на девет (од вкупно 10) премини од втор ред, што се во врска со валентните S–O вибрации. Пресметани се и хармониските фреквенции на валентните модови. Споредбата со SO_4 „онечистен" K_2CrO_4 покажува дека: (i) сулфатните јони се подеформирани во селенатна, отколку во хроматна матрица; (ii) константите на анхармоничност од x_{13i} тип се поголеми од оние од x_{3i3j} тип; (iii) односот x_{13i}/x_{3i3j} е помал за сулфатни јони вградени во селенатна матрица; (iv) најверојатно, е доминантна механичка анхармоничност на вибрациите. Дискутирани се можните причини за овие наоди.