Lattice Vibration Spectra. LXXV. IR Single Crystal Reflection Spectra of $Sr(ClO_3)_2$

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Polarized infrared reflection spectra of $Sr(ClO_3)_2$ single-crystal plates are recorded and analysed for the frequencies of the transversal and longitudinal optical zone-centre phonon modes and other oscillator parameters by Kramers-Kronig analyses and both the classical 3 parameter (dielectric sum-function) and the 4 parameter (factorized form) oscillator-fit methods. The frequencies computed are compared with the results of previous single-crystal Raman studies. Because of the great distortion of the ClO_3^- ions (site symmetry C_1), no intraionic coupling of the ClO vibrations to symmetric (ν_1) and asymmetric (ν_3) stretching modes occurs. The TO/LO splittings of respective ClO unit-cell group modes rank like the vector elements of the corresponding ClO bonds with respect to the crystal axes.

Key words: Strontium chlorate; IR reflection spectra; Oscillator-fit calculations; LO phonon modes.

1. Introduction

The energies (frequencies) of transversal optical (TO) and longitudinal optical (LO) phonons of solids are available from inelastic neutron scattering techniques as well as from IR reflection spectra using Kramers-Kronig analyses and oscillator-fit procedures, respectively (see for example [1]). In the case of compounds which crystallize in acentric space groups, the TO and LO phonon modes can also be established by single-crystal Raman experiments [2–4]. We have performed such Raman studies on $Sr(ClO_3)_2$ single crystals [3]. However, assignment of the spectra obtained was not unequivocally possible. In order to confirm and complete these results we recorded polarized single-crystal IR reflection spectra of $Sr(ClO_3)_2$ and calculated the TO and LO phonon energies using the fitting procedures mentioned above [1]. More recent investigations on LO phonons of acentric compounds using both IR and Raman experiments are scarce (see, for example, Razzetti et al. [5]).

$Sr(ClO_3)_2$ crystallizes in the space group Fdd2-C_{2v}^{19} with $Z=8$. X-ray single-crystal structure data are reported in [6]. The result of group theoretical treatment (unit-cell group C_{2v}) is given in Table 1 [6].

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2. Experimental

Single crystals as large as 27 cm^3 in size were grown from aqueous solutions by controlled evaporation at 40 °C [7].

For the IR studies, the crystals were cut to give plates of about $(12 \times 12 \times 3)$ mm^3 in size. The surface were (100) and (001) planes, respectively. The orientation of the crystal axes was determined by both X-ray and optical methods [8].

The measurements were performed at near normal incidence on a Bruker IFS-114 Fourier transform interferometer in the range 40–1800 cm^{-1}. An aluminium mirror was taken as a reference. Polarized IR radiation was obtained using gold wire grid-type polarizers with polyethylen and KRS5 substrate for the low and high frequency region, respectively.

The polarized IR reflection spectra were converted into the dielectric dispersion relations by means of

Table 1. Unit-cell group analysis of zone centre phonon modes of $Sr(ClO_3)_2$.

C_{2v}	n	n_T	$n_{T'}$	n_R	n_i	
A_1	13	z	3	3	6	IR, RA
A_2	13	–	4	3	6	RA
B_1	14	x	4	3	6	IR, RA
B_2	14	y	4	3	6	IR, RA

n, total amount of irreducible representations; n_T, translations; $n_{T'}$, translational modes; n_i, internal (stretching and bending) modes of the ClO_3^- ions.

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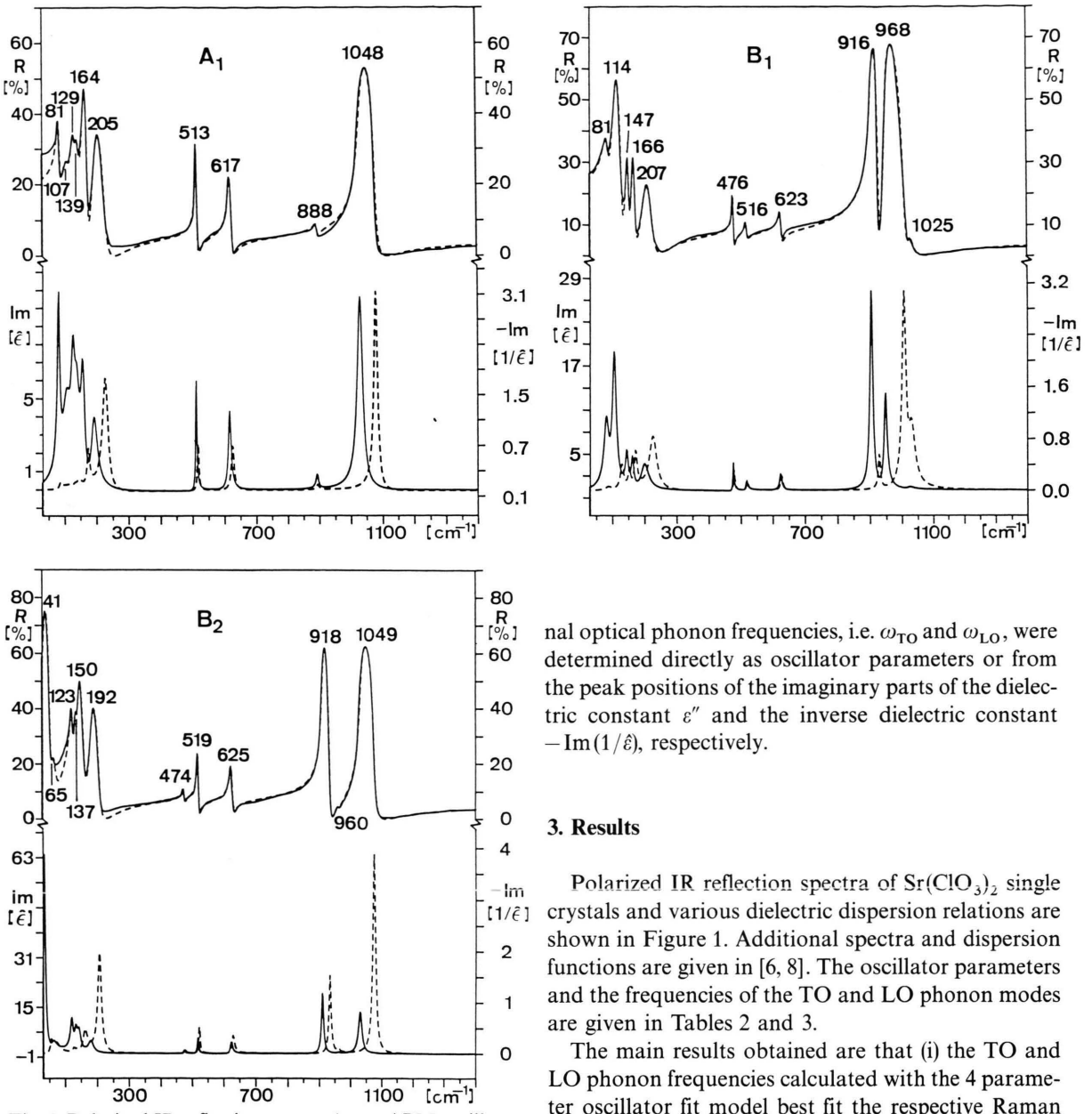

Fig. 1. Polarized IR reflection spectra (– – –, 4 PM oscillator fit) and dispersion functions (——, ε''; – – –, $-\mathrm{Im}(1/\hat{\varepsilon})$ of $Sr(ClO_3)_2$ single crystals; A_1: (100), $\boldsymbol{E} \parallel c$; B_1: (001), $\boldsymbol{E} \parallel a$; B_2: (001), $\boldsymbol{E} \parallel b$.

both Kramers-Kronig analyses and oscillator-model calculations using the classic dielectric sum function (3 parameter model) as well as the factorized form of the dielectric function (4 parameter model). Details are given elsewhere [1, 8]. The transversal and longitudinal optical phonon frequencies, i.e. ω_{TO} and ω_{LO}, were determined directly as oscillator parameters or from the peak positions of the imaginary parts of the dielectric constant ε'' and the inverse dielectric constant $-\mathrm{Im}(1/\hat{\varepsilon})$, respectively.

3. Results

Polarized IR reflection spectra of $Sr(ClO_3)_2$ single crystals and various dielectric dispersion relations are shown in Figure 1. Additional spectra and dispersion functions are given in [6, 8]. The oscillator parameters and the frequencies of the TO and LO phonon modes are given in Tables 2 and 3.

The main results obtained are that (i) the TO and LO phonon frequencies calculated with the 4 parameter oscillator fit model best fit the respective Raman data (see Tables 3 and 4 and Fig. 2), (ii) the damping constants γ_{LO} are not always larger than γ_{TO} as it is reported in [10] for the one oscillator case (see Table 2), (iii) the Raman band at 1074 cm^{-1} is unequivocally a LO mode of the ClO stretching vibrations, and not a two phonon band as discussed in [3]*,

* The lack of LO modes for the $ClO_{(1)}$ and $ClO_{(2)}$ vibrations in the A_1 (LO) Raman spectrum of $Sr(ClO_3)_2$ discussed in [3] is due to the small TO/LO splittings of these vibrations in species A_1.

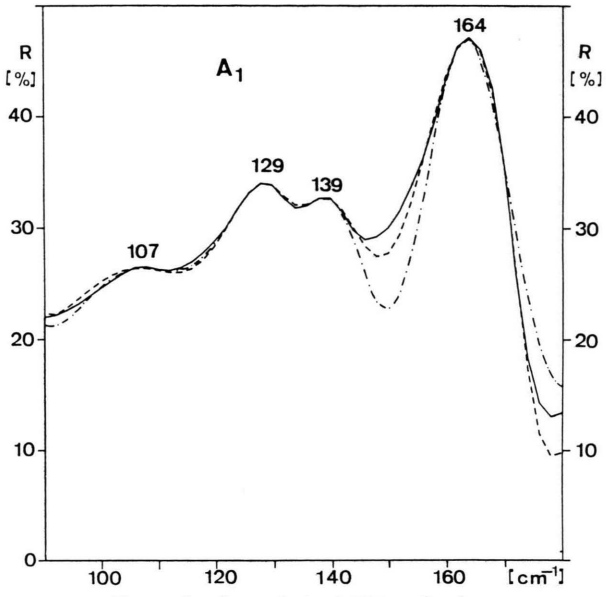

Fig. 2. Oscillator fit of a polarized FIR reflection spectrum ($\boldsymbol{E} \parallel c$) of a (100) face of $Sr(ClO_3)_2$; – – –, 4 PM model; – · – · –, 3 PM model.

and (iv) the TO/LO splittings of the ClO stretching vibrations mainly reflect the vector elements of the ClO bonds with respect to the crystal axes (see Table 5), i.e. the band intensities, which are expected on the assumption that the vibrations of the three ClO arms of the ClO_3^- ions are intraionically uncoupled [3].

4. Discussion

The results obtained confirm the recent findings [1] that, owing to the strong distortion of the ClO_3^- ions in $Sr(ClO_3)_2$, intraionic coupling of the ClO stretching vibrations to a symmetric and two asymmetric ones does not occur. The vector element of a hypothetical symmetric ClO stretching mode (ν_1) would be largest with respect to the c axis of the structure, i.e. 42.67 compared to 17.64 and 34.75 with respect to the a and b axes, respectively, and, hence, the lowest energy ClO stretching mode, which would be the symmetric one in the case of undistorted ClO_3^- ions, should possess the greatest intensity and TO/LO splitting in species A_1. This is not the case, as shown in Fig. 1 and Table 2.

However, there are two findings which cannot be interpreted so far. (i) The TO/LO splitting (and the intensity) of the $ClO_{(2)}$ band of species B_2 are too small compared to the corresponding vector element (see Table 5). This too small TO/LO splitting may be caused by unit-cell group interaction effects (interionic coupling) or by partial intraionic coupling of the respective ClO vibrations in the case of the mode under discussion. (ii) The oscillator strength of the $ClO_{(1)}$

Table 2. Oscillator parameters (cm^{-1}) of the zone-centre phonon modes of $Sr(ClO_3)_2$ obtained from IR single-crystal reflection spectra by the 4 parameter oscillator fit method.

$4\pi\varrho$ [a]	ω_{TO}	γ_{TO}	ω_{LO}	γ_{LO}	Assignment [b]
A_1 $\varepsilon_\infty = 2.37$					
1.03	82	8.9	86	9.9	T′
0.99	109	29.8	114	23.8	R
0.85	128	16.5	133	12.6	R
0.50	137	16.1	147	18.3	R
0.56	158	14.7	174	9.6	T′
0.47	191	23.2	228	19.6	T′
0.06	511	4.4	517	5.3	$\delta_{(ClO_3)}$
0.07	616	10.2	625	10.5	$\delta_{(ClO_3)}$
0.01	893	10.0	894	9.8	$\nu_{(Cl-O_{(1)})}$
0.22	1029	21.4	1078	13.7	$\nu_{(Cl-O_{(3)})}$
B_1 $\varepsilon_\infty = 2.54$					
1.89	82	18.4	88	17.1	T′
2.54	107	15.0	130	12.5	T′ ?
0.34	145	10.4	153	9.4	R
0.25	163	9.8	172	10.6	T′ ?
0.47	200	26.7	227	27.9	T′
0.04	476	4.3	478	5.5	$\delta_{(ClO_3)}$
0.02	517	6.8	519	7.9	$\delta_{(ClO_3)}$
0.03	624	8.9	627	9.0	$\delta_{(ClO_3)}$
0.34	905	11.2	929	7.8	$\nu_{(Cl-O_{(1)})}$
0.15	947	10.8	1007	14.6	$\nu_{(Cl-O_{(2)})}$
0.01	1022	18.5	1028	24.3	$\nu_{(Cl-O_{(3)})}$
B_1 $\varepsilon_\infty = 2.57$					
13.2	36	7.4	56	9.1	T′
0.77	63	19.2	73	25.0	R
0.80	122	10.5	127	8.6	R
0.57	135	10.9	139	9.9	R
0.57	144	12.5	162	15.3	T′
0.42	181	20.2	209	13.7	T′
0.01	475	5.4	476	5.8	$\delta_{(ClO_3)}$
0.05	518	5.2	523	5.5	$\delta_{(ClO_3)}$
0.05	624	8.2	629	9.9	$\delta_{(ClO_3)}$
0.18	911	8.3	934	8.1	$\nu_{(Cl-O_{(1)})}$
0.00	960	8.1	960	8.5	$\nu_{(Cl-O_{(2)})}$
0.18	1031	13.6	1076	10.7	$\nu_{(Cl-O_{(3)})}$

[a] $4\pi\varrho_j = \varepsilon_\infty(\omega_{LO_j}^2 - \omega_{TO_j}^2)/\omega_{TO_j}^2 \prod_{\substack{k=1 \\ k\neq j}}^{N} (\omega_{LO_k}^2 - \omega_{LO_j}^2)/(\omega_{TO_k}^2 - \omega_{TO_j}^2)$ [1, 9]. (For comparison with experimental 3 PM data see [8].)

[b] R, T′, δ, ν, librational, translational, bending and stretching modes, respectively; assignment of the librations and translational modes (lattice vibrations) is only tentative.

Table 3. TO and LO phonon energies of the ClO_3^- internal vibrations (species A_1) of $Sr(ClO_3)_2$ obtained from both single-crystal Raman spectra and IR reflection measurements (peaks of the dispersion relations of the imaginary part of the dielectric constant ε'' and the dielectric loss function $-\mathrm{Im}(1/\hat{\varepsilon})$, evaluation procedures see [1]); data of species B_1 and B_2 see [8].

KKA [a]		3 PM [b]		4 PM [c]				Raman data [3]	
ε''	$-\mathrm{Im}(1/\hat{\varepsilon})$	ε''	$-\mathrm{Im}(1/\hat{\varepsilon})$	ε''	$-\mathrm{Im}(1/\hat{\varepsilon})$	OP [d]			
ω_{TO}	ω_{LO}	ω_{TO}	ω_{LO}	ω_{TO}	ω_{LO}	ω_{TO}	ω_{LO}	ω_{TO}	ω_{LO}
512	517	511	517	511	517	511	517	510	516
615	625	615	625	615	625	616	625	615	622
893	895	893	893	893	893	893	894	–	–
1031	1077	1029	1079	1029	1077	1029	1078	1021	1074

[a] Kramers-Kronig analysis. – [b] 3 Parameter oscillator-fit method. – [c] 4 Parameter oscillator-fit method. – [d] Oscillator parameters (see Table 2).

Table 4. TO and LO phonon energies (cm^{-1}) of the internal ClO_3^- vibrations (species A_2, B_1, and B_2) obtained from single-crystal Raman spectra [3] and IR reflection measurements (oscillator parameters of the 4 PM oscillator-fit calculations, see Table 2).

A_2	B_1			B_2		
Raman	Raman	IR		Raman [a]	IR	
	ω_{TO}	ω_{TO}	ω_{LO}	ω_{TO}/ω_{LO}	ω_{TO}	ω_{LO}
481	475	476	478	475	475	476
511	516	517	519	520	518	523
620	623	624	627	627	624	629
898	899	905	929	892	911	934
959	944	947	1007	962	960	960
1023	1021	1022	1028	1024, 1074	1031	1076

[a] oblique phonons [3].

band of species B_1 is too large compared to the TO/LO splitting of this band (see Table 5).

The unit-cell group splitting of the ClO stretching modes (see Table 6) are different for the vibrations of the three ClO arms. The frequencies of the various modes range $B_2 > B_1 > A_2 > A_1$ for the $ClO_{(1)}$ modes, $B_1 > B_2 \approx A_2 > A_1$ for the $ClO_{(2)}$ ones, and $B_2 \approx A_1 > B_1 \approx A_2$ for the $ClO_{(3)}$ vibrations. The maximum unit-cell group splittings range $\Delta\nu_{ClO_{(1)}} > \Delta\nu_{ClO_{(2)}} \approx \Delta\nu_{ClO_{(3)}}$. These different unit-cell group splittings can be realized by the dipole-dipole interaction model. As basis of this discussion, the hypothetical phonon frequencies ω_0, which are affected neither by the local field E_{loc} nor by long-range electric forces [11], are chosen (see Table 6).

Table 5. Vector elements (pm) [3] of the ClO arms of the ClO_3^- ions with respect to the crystal axes of $Sr(ClO_3)_2$ (VE) and both TO/LO splittings (cm^{-1}) and oscillator strengths (OS) (see Table 2) of the respective ClO stretching vibrations (ClO bond lengths (pm) [6] in parentheses).

	$ClO_{(1)}$ (150.7)			$ClO_{(2)}$ (147.4)			$ClO_{(3)}$ (145.8)		
	VE	TO/LO	OS	VE	TO/LO	OS	VE	TO/LO	OS
x (B_1)	98.2	24	0.340	123.6	60	0.149	27.5	6	0.005
y (B_2)	106.9	23	0.183	73.2	0	0.003	76.0	45	0.180
z (A_1)	40.6	9	0.072	33.1	1	0.009	120.5	49	0.221

Table 6. Unit-cell group splittings of the ClO stretching modes (cm^{-1}) of $Sr(ClO_3)_2$ (the hypothetical phonon frequencies ω_0 are calculated with the equation $\omega_0^2 = (2\omega_{TO}^2 + \omega_{LO}^2)/3$ [11]).

Species	$ClO_{(1)}$	$ClO_{(2)}$	$ClO_{(3)}$
A_1	893	945	1046
A_2	898	959	1023
B_1	913	967	1024
B_2	919	960	1046
Mean values of ω_0	906	958	1035

The ClO_3 bending modes are strongly intraionically coupled. A detailed interpretation of these modes, for which ω_0 phonon frequencies may be calculated in the same manner as for the stretching modes, in terms of intensities, TO/LO splittings, and unit-cell group splittings is therefore not straightforward. The same is true for the lattice modes (translational vibrations)

and librations of the ClO_3^- ions in the low-frequency region of the spectra. For the assignment of these modes see Table 2.

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