In this investigation no fine structure of the Auger lines due to vibrational levels of N_2^{K+} and N_2^{2+} has been found. The main reason for this is the instrumental width of about 0.6 eV at energies of the Auger group A. In order to detect any vibrational structure the resolution of the spectrometer should be increased at least by a factor of two.

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On the Phonon and Polariton Spectrum of $LiJO_3$ *

R. CLAUS, H. W. SCHRÖTTER, and H. H. HACKER

Sektion Physik der Universität München, Lehrstuhl Prof. BRANDMÜLLER

and S. HAUSSÜHL

Institut für Kristallographie der Universität Köln

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Raman spectra of the polar A, E_1 and the non polar E_2 species of $LiJO_3$ are presented. The number of phonons expected by group theory has been calculated. LO-TO splitting of two E_1-phonons could be observed and the polariton associated with the A(z) phonon at 795 cm^{-1} has been recorded.

Since NATH and HAUSSÜHL detected the strong second harmonic generation of a ruby laser in Lithtium Iodate [1] and an extremely great piezoelectric longitudinal effect parallel to [001] was detected [2], the $LiJO_3$ crystal has become of great common interest. The present paper will deal with the vibrational species of the optical phonons observed by Raman scattering experiments.

Theory

$LiJO_3$, which belongs to the crystal symmetry class C_6, as could be shown three years ago [3, 4], has the Raman scattering tensors [5]

$$A(z)\begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix}; \quad E_1(x)\begin{pmatrix} 0 & 0 & c \\ 0 & 0 & d \\ c & d & 0 \end{pmatrix};$$

$$E_1(y)\begin{pmatrix} 0 & 0 & -d \\ 0 & 0 & c \\ -d & c & 0 \end{pmatrix}; \quad E_2\begin{pmatrix} e & f & 0 \\ f & -e & 0 \\ 0 & 0 & 0 \end{pmatrix};$$

$$E_2\begin{pmatrix} f & -e & 0 \\ -e & -f & 0 \\ 0 & 0 & 0 \end{pmatrix}.$$

The E_2 species are doubly degenerate unpolar modes while the A and E_1 species are both infrared and Raman active. The E_2 species can easily be observed separately using $x(yx)y$ scattering geometry, while the A and E_1 species in general will mix. In order to find adequate scattering geometries for separation, one will have to examine the scattering efficiencies using the well-known formula for the scattering intensity of an uniaxial piezoelectric crystal, given by LOUDON [5]. Thus, using a phonon wave vector propagating in the xy-plane along the bisecting line of the x and y axes, the most general

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Reprint requests to Dr. H. W. SCHRÖTTER, *D-8000 München 13*, Amalienstraße 54.

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effective scattering tensors for the LO and TO modes will be

$$\mathrm{TO}_1\begin{pmatrix} a\,\alpha & 0 & 0 \\ 0 & a\,\alpha & 0 \\ 0 & 0 & b\,\alpha \end{pmatrix}; \qquad \mathrm{TO}_2\begin{pmatrix} 0 & 0 & \frac{(c-d)\,\alpha}{\sqrt{2}} \\ 0 & 0 & \frac{(c+d)\,\alpha}{\sqrt{2}} \\ \frac{(c-d)\,\alpha}{\sqrt{2}} & \frac{(c+d)\,\alpha}{\sqrt{2}} & 0 \end{pmatrix},$$

$$\mathrm{LO}\begin{pmatrix} a\,\alpha\,\mu_3 & 0 & c\left(\alpha\,\mu_1+\frac{\beta}{\sqrt{2}}\right)-d\left(\alpha\,\mu_2-\frac{\beta}{\sqrt{2}}\right) \\ 0 & a\,\alpha\,\mu_3 & d\left(\alpha\,\mu_1+\frac{\beta}{\sqrt{2}}\right)+c\left(\alpha\,\mu_2-\frac{\beta}{\sqrt{2}}\right) \\ c\left(\alpha\,\mu_1+\frac{\beta}{\sqrt{2}}\right)-d\left(\alpha\,\mu_2-\frac{\beta}{\sqrt{2}}\right) & d\left(\alpha\,\mu_1+\frac{\beta}{\sqrt{2}}\right)+c\left(\alpha\,\mu_2-\frac{\beta}{\sqrt{2}}\right) & b\,\alpha\,\mu_3 \end{pmatrix}.$$

The TO_1 modes are polarized parallel to the z-axis and the TO_2 modes perpendicular to it. The most general case of the LO-tensor as given above, where the electrical and mechanical polarizations are not collinear, may be simplified however, using $\mu_1 = 1/\sqrt{2}$; $\mu_2 = 1/\sqrt{2}$; $\mu_3 = 0$, as the phonon wave vector is propagating in the symmetry plane. Therefore $x(zz)y$ scattering geometry will isolate the $A(z)$ phonons, and $x(zx)y$ geometry the E_1 phonons. Any 'mixing' may occur for instance only due to diffuse reflections.

An identification of the LO-modes of type E_1 will be possible using a scattering geometry, where the phonon wave vector is propagating along the z-axis of the crystal. LO-modes can in this case only be of type A, so all Raman active E_1 phonons will be TO modes. This method has been used and described during the last few years [6].

Furthermore, measurements using near forward scattering may confirm the assignment of the $E_1(TO)$ phonons. Due to momentum conservation $\boldsymbol{k}_p = \boldsymbol{k}_i - \boldsymbol{k}_s$ (i = incident, s = scattered, and p = phonon) of the phonon and photons it is obvious that all Raman active phonons will have their smallest wave vector at straight forward scattering. Polar TO-modes will then be strongly coupled to the electromagnetic field, and the energy of the vibrational quanta will be of mixed type: partly mechanical and partly electromagnetic. These energy quanta known as polaritons show a frequency dependence due to the wave vector and may therefore move towards smaller wave numbers for decreasing scattering angles [7–9].

Experimental

Two experimental arrangements were used.

1. PH 1 Spectrometer by Coderg with a Spectra Physics He-Ne-Laser Mod. 125.

2. A Jarrell-Ash double monochromator with a Spectra Physics Ar^+-Induction Laser Mod. 140. A low temperature cell used together with both arrangements was made by Coderg.

All spectra presented in this paper were recorded with 2 cm^{-1} slit width and 1 cm^{-1}/sec.

Discussion

An analysis by group theory gives the number of external and internal vibrations that can be observed by Raman scattering experiments [10, 11]. The results are presented in Table 1. As $LiJO_3$ is a typical ion crystal, an 'internal' spectrum can only appear due to the JO_3^- groups. The corresponding Raman lines can be separated from the crystal spectrum by measuring an aqueous solution of $LiJO_3$, where the JO_3^- ions are isolated. Corresponding spectra recorded by us showed a very strong polarized line

Species	Internal	External		Observable number of Raman lines
		Transl.	Libr.	
A	2	2	1	5
B	2	1	1	only infrared active
E_1	4	4	2	5 without LO-TO-splitting
E_2	4	2	2	4

Table 1. Predicted number of phonons by group theory.

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at about 800 cm^{-1} and a more weak one at 160 cm^{-1}. Furthermore, two depolarized lines at 325 and 345 cm^{-1} could be observed. All these Raman lines were very broad, so the wave numbers may be within an error of about 8 cm^{-1}. Fig. 1 shows the vibrational species of a single crystal of $LiJO_3$. Comparing these spectra with Table 1 and the solution spectra, the following assignments are suggested. The A(z) species at 147 and 795 cm^{-1} and E_2 species at 342 and 766 cm^{-1} belong to the internal spectrum. As the E_2 phonon at 824 cm^{-1} is very weak using $y(xy)x$ scattering, this part of the spectrum was rerecorded with about doubled sensitivity as can be seen on the E_2 phonon at 766 cm^{-1}. At the same time the sample was removed and replaced in order to show that the Raman line at 795 cm^{-1} is the A-phonon which appears due to false scattering light. The intensity is changed and cannot be reproduced.

Since the E_1 species are polar modes, splitting into LO and TO modes may occur as mentioned above. The calculated effective scattering tensors for LO modes with their phonon wave vector parallel and perpendicular to the z-axis, respectively, showed, that E_1 modes will appear for right angle scattering only using extraordinary incident photons and ordinary scattered photons or vice versa. Due to the strong double refraction of the crystal it was necessary to correct the course of the incident ray for instance by a prism, so that the scattering angle inside the crystal was $\pi/2$. The experimental arrangements for $\boldsymbol{k}_p \parallel \boldsymbol{z}$ and $\boldsymbol{k}_p \perp \boldsymbol{z}$ are shown in Fig. 2 a and b, respectively. Only a small scattering volume was used in order to avoid trouble with optical activity. A screen as sketched in Fig. 2 a and b was used for this purpose. Backward reflection of the incident photons on the second surface inside the crystal was diminished by attaching the crystal on a prism with paraffin oil. The prism was arranged with its edge parallel to the scattering direc-

Wave number	Assignment	Wave number	Assignment
95	E_2	460	E_1 LO
147	A	766	E_2
172	E_1	769	E_1
243	A	795	A
328	$E_1 + A$	824	E_2
342	E_2	845	E_1 LO
354	A		

Table 2. Assignments and wave numbers (± 2 cm^{-1}) of the observed Raman lines.

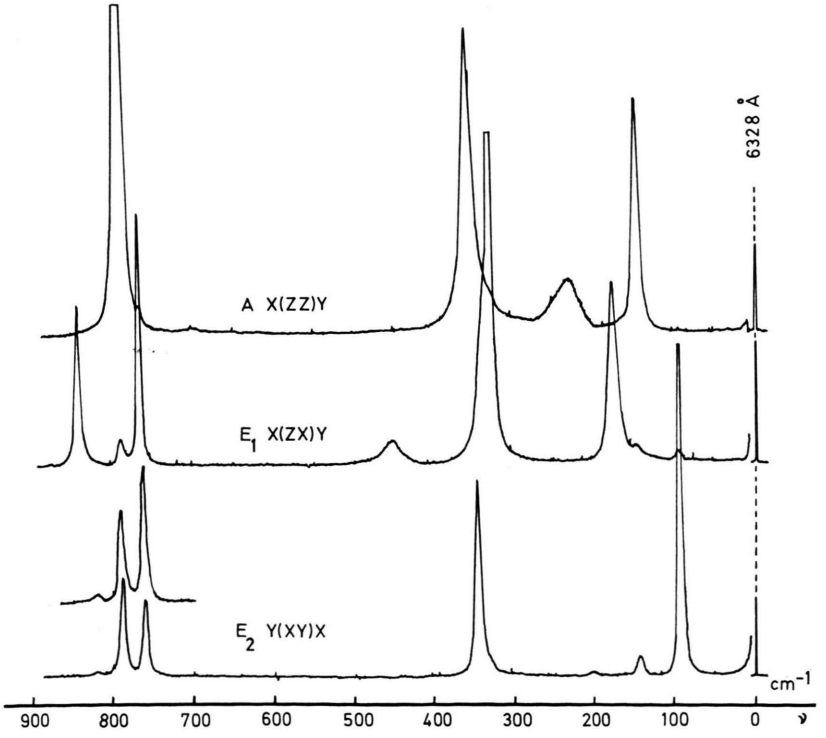

Fig. 1. Vibrational species of $LiJO_3$. See Table 2.

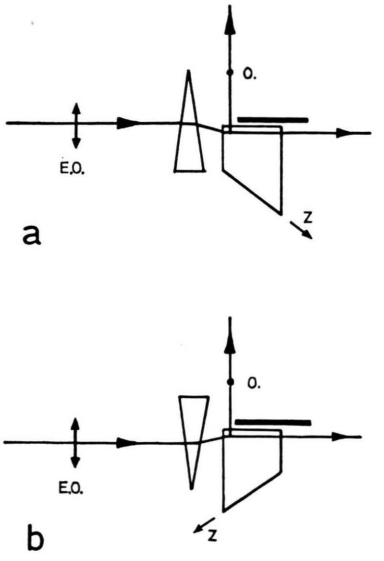

Fig. 2. Experimental arrangements used for identification of E_1(LO)-modes.
a) $\boldsymbol{k}_p \parallel \boldsymbol{z}$ b) $\boldsymbol{k}_p \perp \boldsymbol{z}$

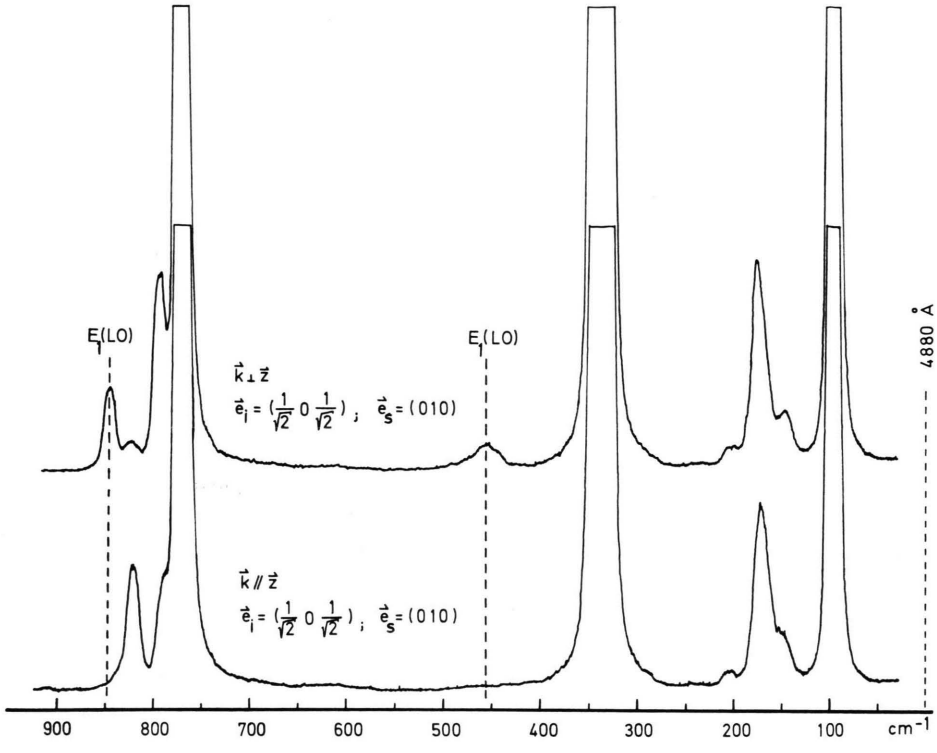

Fig. 3. Spectra, used for identification of $E_1(LO)$-modes. e_i and e_s are unit vectors parallel to the polarization of the incident and scattered photons, respectively.

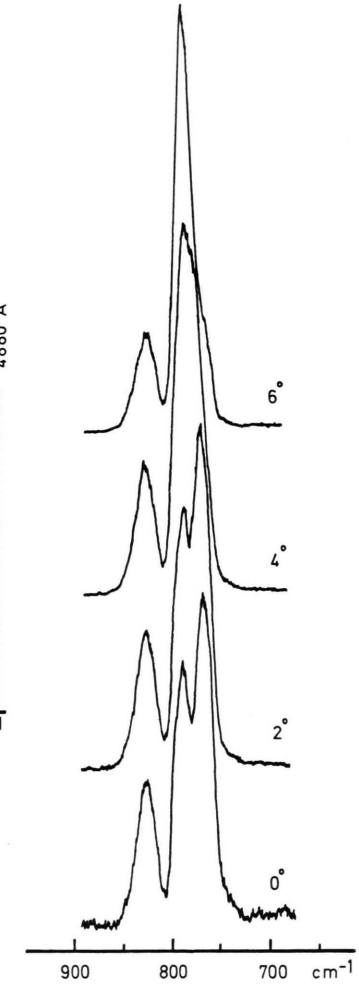

Fig. 4. Polariton associated with the A(z)-phonon at 795 cm^{-1}. Near forward scattering from 6° to 0°$=x(yy)x$ scattering geometry was used. The spectra were recorded at −150 °C.

tion so that no photons reflected on its second surface could reach the volume of the crystal projected into the doublemonochromator. Figure 3 shows that the Raman lines at 460 and 845 cm^{-1} can be assigned as $E_1(LO)$-modes, and the phonons at 328 and 769 cm^{-1} will be the corresponding TO-modes at lower frequencies. All these Raman lines therefore belong to the internal spectrum. As group theory shows that there should be 5 doubly degenerate phonons, much experimental work was done in the search for the two missing E_1 phonons. The phonon at 328 cm^{-1} shows a shoulder which might suggest that two E_1 phonons are superimposed, however, even at −150 °C no good resolution could be obtained in order to determine the precise wave numbers.

Near forward scattering from 7° to 0° showed that no polariton associated with any of the $E_1(TO)$ modes could unambiguously be observed. Experiments were made at room temperature and −150 °C. As, however, the A(z)-phonons of the $LiJO_3$ crystal are polar modes, too, they might show polariton behaviour as TO-modes. Experiments using $x(yy)x$ scattering geometry were successful. Figure 4 shows the polariton associated with the A-phonon at 795 cm^{-1} moving from 795 to about 770 cm^{-1} with decreasing scattering angle from 6° to 0°. The phonon at 795 cm^{-1} can be observed at the same time due to backward reflection on the second surface inside the crystal. The E_2 phonon at 824 cm^{-1} appears because of the tensor component R_{yy}. However, it will not show any polariton behavior, as the E_2 modes are not infrared active, so it can be used as a standard line, as well as the A phonon at 795 cm^{-1} in the spectra of Fig. 4.