Effect of an electric field on the polariton Raman spectra of lithium niobate crystals

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The effect of an electric field on the polariton Raman spectra of lithium niobate crystals was investigated as a function of the field direction and scattering geometry. The electrooptic coefficient for the near-infrared was determined from experimental data on these spectra. It was shown that the application of the field to the crystal resulted in violation of the selection rules, and forbidden lines appeared in the Raman spectrum.

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INTRODUCTION

Raman scattering (RS) in crystals placed in an external electric field was investigated in Refs. 1 and 2. The influence of the electric field was found to reduce to the appearance of forbidden lines in the case of centrosymmetric crystals ($SrTiO_3$ and $KTaO_3$) and to an increase in the intensity of Raman scattering by low-frequency vibrations in the $Ba_2NaNb_5O_{15}$ crystal. There are also two papers[3,4] in which studies are reported of the dependence of the frequency of the parametric generation line in nonlinear crystals on the applied electric field. However, there are no published studies of the effect of an external electric field on the overall shape of polariton Raman spectra. Such studies can be a source of information on the dependence of the refractive index on the electric field in nonlinear crystals, and on the connection between polariton Raman spectra and the electrooptic effect.

In the present paper we report an investigation of the dependence of polariton Raman spectra corresponding to the A_1 and E vibrations in lithium niobate crystals on the external electric field in the range 0–5×10^4 V/cm. The nature of the variation in the refractive index in these cases is determined.

1. EXPERIMENTAL METHOD

The polariton spectra were recorded photographically in the STE-1 spectrograph, using a well-kown method.[5] The telescopic system described in Ref. 6 was used to obtain the frequency-angle dependence of the spectra. The light source was an argon laser producing the 514.5 and 488.0 nm lines. A cadmium sulfide crystal was used as the filter suppressing the laser radiation. The spectra scattered by A_1-polaritons were recorded in the $X(ZZ)X+\Delta Y$ geometry, using excitation at the 514.5 nm line. Spectra scattered by high-frequency E-polaritons were recorded in the $X(ZY)X+\Delta Y$ geometry (excitation at the 488.0 nm line). Moreover, the $Z(XY)Z+\Delta Y$ geometry (excitation at the 514.5 nm line) was used to record scattered spectra in the direction of the optic axis of the crystal.

The electric field was applied to the crystal with the aid of brass-foil electrodes glued to their surface. To avoid electrical breakdowns in air, the crystals were inserted into an optical chamber filled with VM-1 oil. The electric field was applied to crystals, ~1 mm thick, in the direction of the Z or Y optic axis. Electrical breakdown in the lithium niobate crystals was observed for field strengths in the range 6×10^4 to 8×10^4 V/cm.

A vacuum liquid-nitrogen optical cryostat was used to record spectra scattered by crystals cooled down to 100 K.

2. SCATTERING OF LIGHT IN THE DIRECTION PERPENDICULAR TO THE OPTIC AXIS OF THE CRYSTAL

Let us now consider the experimental data when the exciting radiation propagates along the crystallographic X axis, whereas the electric field is applied along the Y or Z axis. For the $X(ZZ)X+\Delta Y$ scattering geometry that corresponds to the excitation of A_1-polaritons, the shape of the spectrum did not change for fields up to 5×10^4 V/cm and was identical with the corresponding spectrum given in Ref. 7, which was recorded in the absence of the electric field.

In the case of scattering of light by high-frequency E-polaritons ($X(ZY)X+\Delta Y$ scattering geometry), with the electric field applied in the direction of the optic axis of the crystal, the shape of the spectrum was again found to remain unaltered but, when the direction of the electric field was parallel to the crystallographic Y axis, the polariton spectra were found to have undergone a change (see Figs. 1a–c). The spectrum shown in Fig. 1a was recorded in an electric field of 5×10^4 V/cm, applied along the Y axis, and Fig. 1c shows the spectrum obtained with the same field applied in the reverse direction. Figure 1b shows the spectrum recorded in zero field. It is clear from Figs. 1a–c that the application of the external field in the direction of the Y axis results in a shift of the limiting wavelength of light scattered by high-frequency E-polaritons by the amount $\Delta\lambda=0.5$ nm. The direction of the shift depends on the direction of the applied electric field.

The application of the external electric field to the lithium niobate crystals is accompanied by a change in the refractive index, which is due to the electrooptic effect. Since the quasimomenta of the quasiparticles participating in the scattering process depend on the refractive index, a change in the refractive index should lead to a change in shape of the polariton Raman spectra. Conservation of wave vectors at zero light-scattering angle under $X(ZY)X+\Delta Y$ scattering geometry has the form

$$K=2\pi(\nu_0 n_e{}^0-\nu' n_0{}')=2\pi(\nu_0-\nu')n_0{}^*, \tag{1}$$

where K is the wave vector of the polariton, ν_0 and ν' are the

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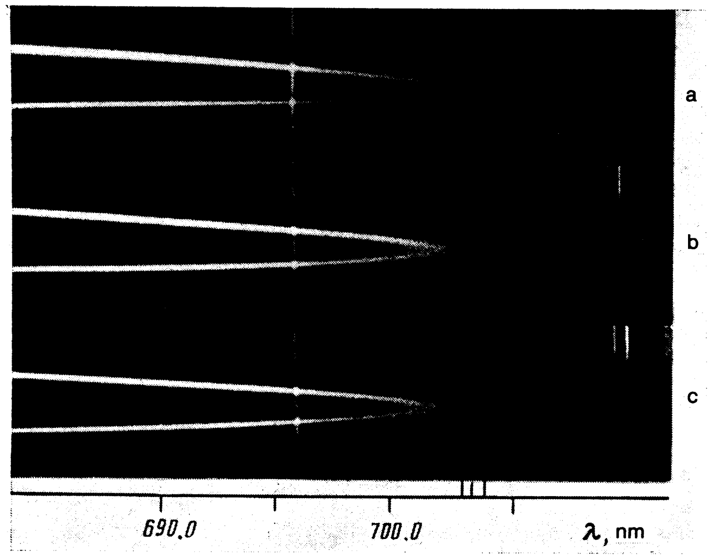

FIG. 1. Effect of an electric field on the spectra of high-frequency E-polaritons in lithium niobate: a—5×10^4 V/cm applied along the Y axis, b—no field, c—5×10^4 V/cm applied along the Y axis in the opposite direction.

frequencies (in cm^{-1}), $n_e{}^0$ and n_0' are the refractive indices for exciting and scattered light, respectively, and n_0^* is the refractive index of the crystal for the ordinary wave at infrared frequencies. The external electric field shifts the limiting frequency ν' by the amount $\Delta\nu'$ which, in accordance with (1), can be found from the expression

$$\Delta\nu'=\nu_0\left(\Delta n_e{}^0-\frac{\nu'}{\nu_0}\Delta n_0{}'-\frac{\nu}{\nu_0}\Delta n_0{}^*\right)(n_0{}'-n_0{}^*)^{-1},\quad \nu=\nu_0-\nu'. \tag{2}$$

The quantities $\Delta n_e{}^0$, $\Delta n_0'$, Δn_0^* in this expression are the increments on the corresponding refractive indices. These increments are found from the shape of the refractive index indicatrix. In particular, when the field is applied in the direction of the crystallographic Y axis, the increments are given by:[8]

$$\Delta n_0=-{}^1/{}_2 r_{22}n_0{}^3E_y,\quad \Delta n_e=0.$$

Substituting these expressions in (3), we obtain

$$\Delta\nu'={}^1/{}_2[\nu'(n_0{}')^3r_{22}E_y+(\nu_0-\nu')(n_0{}^*)^3r_{22}{}^*E_y](n_0{}'-n_0{}^*)^{-1}. \tag{3}$$

where r_{22} and r_{22}^* are the electrooptic coefficients corresponding to the frequencies of the scattered radiation ($\lambda=0.7\,\mu$m) and of the polariton wave ($\lambda\ +1.6\,\mu$m), and E_Y is the applied field.

It is shown in Ref. 9 that the coefficient r_{22} remains constant in the range 0.7–2.5 μm. Hence, assuming that $r_{22}=r_{22}^*$, we can use (3) to calculate the electrooptic coefficient r_{22} for the near infrared. Its value turns out to be 1.2×10^{-10} cm/V, which is in agreement with direct measurements reported in Ref. 10.

When the electric field is parallel to the optic axis of the crystal, the expression for the shift of the limiting frequency assumes the form

$$\Delta\nu'=-{}^1/{}_2[\nu_0(n_e{}^0)^3r_{33}E_z-\nu'(n_0{}')^3r_{13}E_z-(\nu_0-\nu')(n_0{}^*)^3r_{13}{}^*E_z]$$
$$\times(n_0{}'-n_0{}^*)^{-1}. \tag{4}$$

Since there are no published data on the values of r_{33}, r_{13}, and r_{13}^* for lithium niobate, it is not possible to estimate the frequency shift on the basis of (4). It may be assumed that the absence of appreciable shifts of the limiting frequency in polariton spectra is connected with the mutual cancellation of positive and negative terms in (4).

3. SCATTERING IN THE DIRECTION OF THE OPTIC AXIS OF THE CRYSTAL

Let us now consider results obtained by investigating polariton spectra when light is scattered in the direction of the optic axis of the crystal. Figure 2 shows photographs of polariton spectra in the $Z(XY)Z+\Delta Y$ geometry, obtained (a) in the absence of the electric field and (b) when a field of 5×10^4 V/cm was applied along the Y axis. It is clear from this figure that, when the field is applied, there is a break-

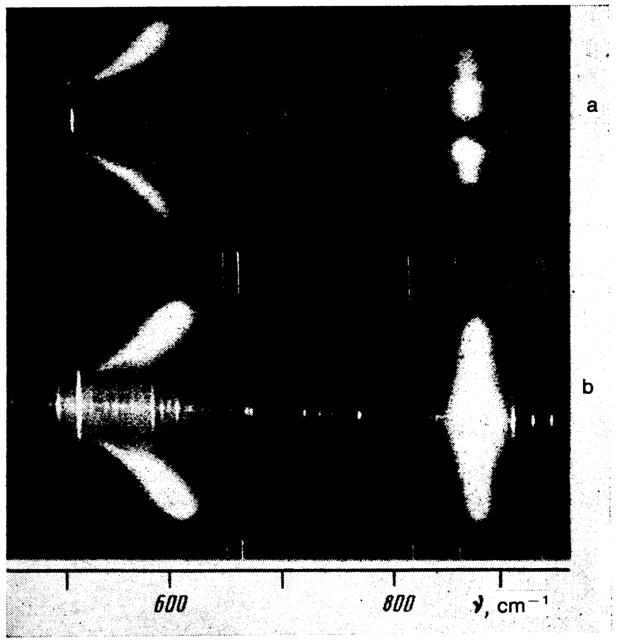

FIG. 2. Effect of an electric field on polariton spectra of lithium niobate. $Z(XY)Z+\Delta Y$ geometry: a—without field, b—5×10^4 V/cm applied along the Y axis.

down in selection rules, which was considered in Ref. 11 for the $Z(XY)Z + \Delta Y$ geometry used here. In particular, it was found that the longitudinal A_1-vibration at 880 cm^{-1} was detected even though it was forbidden for this particular geometry.

The application of the electric field along the Y axis leads to a reduction in the symmetry of the crystal from the original group C_{3v} to a group containing only the identity symmetry transformation. The A_1 and E vibrations are then transformed into fully symmetric vibrations. Thus, under these conditions, the A_1-type longitudinal vibrations should be present in the Raman spectrum in the $Z(XY)Z + \Delta Y$ scattering geometry, and this was, in fact, confirmed experimentally.

We note that analogous changes in the recorded spectra are observed even in the absence of the external field after prolonged (about one hour) irradiation (for the same scattering geometry) by laser light when the crystal is cooled down to liquid-nitrogen temperatures. This can be explained by the appearance of internal local electric fields $E \sim 5 \times 10^4$ V/cm perpendicular to the optic axis of the crystal.

CONCLUSIONS

We have thus established, for the first time, that the application of an external electric field of 5×10^4 V/cm to lithium niobate crystals leads to a change in the parameters of polariton Raman spectra. This is accompanied by a shift in the limiting frequency of polariton scattering ($\Delta\lambda = 0.5$ nm) and a change in the intensity distribution in the spectrum. These effects are observed only when the field is perpendicular to the optic axis of the crystal. Analysis of the polariton spectra enables us to estimate changes in the refractive index, the values of the electrooptic coefficients, and the strength of the internal electric field that appears in the crystals when they are exposed to laser light at low temperatures.

The dependence of the limiting frequency of polariton scattering on the applied electric field, which we have found, is determined by the value of the electrooptic coefficient r_{22}. In view of this, it is possible to estimate the magnitude of analogous changes in polariton scattering spectra due to other electrooptic crystals. In particular, it follows from the data reported in Ref. 10 that the shift of the limiting frequency of polariton scattering by lithium tantalate should be of the same order as for lithium niobate. The magnitudes of the electrooptic coefficients of barium-strontium niobate are greater by an order of magnitude than the corresponding values for lithium niobate crystals. We may therefore expect substantially greater shifts of the limiting frequency when an external electric field is applied to the latter crystal. We also note that the shift of the limiting frequency of polariton scattered light, which we have observed when an external field was applied to the crystal, can be exploited in local measurements of inhomogeneous electric fields.

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