PHYSICAL REVIEW B VOLUME 26, NUMBER 6 15 SEPTEMBER 1982

Brillouin spectra of $K_{1-x}Li_xTaO_3$ under poled and zero-field-cooled conditions

L. L. Chase, E. Lee, and R. L. Prater*
Physics Department, Indiana University, Bloomington, Indiana 47405

L. A. Boatner
Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

(Received 26 March 1982)

The Brillouin spectra of $KTaO_3$ single crystals containing 5.6 mol % lithium have been investigated as a function of temperature in the temperature range below 77 K. The results obtained for both poled and zero-field-cooled (ZFC) samples are in agreement with the presence of a tetragonal ferroelectric phase below a transition temperature T_c of approximately 60 K. A 50% step discontinuity was observed in the elastic constant c_{33} below T_c. The value of the saturated polarization calculated from this change in c_{33} with the use of electrostrictive data is 0.27 C/m^2. The sharp Brillouin components and the anisotropy of the elastic constants in both the ZFC and poled samples imply that the absolute magnitude and axis of the polarization are constant over dimensions on the order of the laser focal spot (i.e., 50 to 100 micrometers in diameter). The existence of antiphase domain boundaries between much smaller regions of reversed polarization, however, is suggested by the results of Raman scattering experiments.

I. INTRODUCTION

Potassium tantalate ($KTaO_3$) is an incipient ferroelectric material that can be converted to a ferroelectric by the addition of rather low-threshold quantities of niobium which replaces tantalum in the $KTaO_3$ lattice[1] or sodium which replaces some of the potassium ions.[2] The addition of either Nb or Na to $KTaO_3$ results in a ferroelectric phase that appears below a transition temperature T_c whose value increases rapidly with increasing concentration of the substituted ion.

Recently, the properties of this induced ferroelectricity have been extensively investigated using a number of experimental techniques including acoustic resonance, dielectric constant measurements, and Raman scattering.[3–5] The characteristics of these "mixed-crystal" ferroelectrics were found be be qualitatively similar to those of the perovskite-structure ferroelectrics such as $KNbO_3$ and $BaTiO_3$, although a greater range of properties (i.e., multicritical points and crossovers from first- to second-order transitions) occur over the full range of mixed-crystal compositions.

In contrast to the case of ferroelectrics formed by the addition of either Nb or Na to $KTaO_3$, the situation regarding the characteristics of the related material formed by replacing potassium with lithium to produce $K_{1-x}Li_xTaO_3$ (KLT) is somewhat uncertain. Results of dielectric and elastic measurements on the KLT system have recently been reported,[6,7] which differ markedly from those obtained for $KTa_{1-x}Nb_xO_3$ (KTN) or $K_{1-x}Na_xTaO_3$ (KTNa). In particular, the conclusion was drawn from those results that there is no macroscopic spontaneous polarization induced at any temperature in KLT for $x < 0.16$. This conclusion was based primarily on the absence of an elastic step anomaly analogous to that observed in both KTN and KTNa when a spontaneous polarization occurs below T_c. A polarization could be produced and "frozen into" the KLT samples, however, by decreasing the temperature in the presence of an applied electric field. It was suggested that, since these properties were analogous to those of spin-glasses, KLT should be regarded as a dipole glass.[7,8] In a subsequent study of optical birefringence in similar KLT samples, Courtens[9] observed behavior that was characteristic of a tetragonal, "ordered, polar phase" with domain sizes on the order of 100 μm. This effect was found even in samples which were cooled through T_c with no applied electric field.

Raman scattering and optical depolarization measurements reported by Prater *et al.*[10] resulted in a third description of the low-temperature phase of KLT, which differs from the conclusions of Courtens only in the size of the domains. Although the $k=0$ transverse-optic (TO) branch developed a splitting at low temperatures into the usual A_1 (TO) and E (TO) components typical of a tetragonal ferroelectric phase, the expected extraordinary phonon with a frequency that varies with the direction of propagation was not observed in unpoled KLT samples. Instead, scattering was observed from TO phonons of all wave-vector orientations, as indicated by the "powder-pattern" type of intensity distribution. There were, however, fairly sharp edges in the spectra which occurred at the energies of the pure A_1 (TO) and E (TO) phonons observed in the same samples when a poling electric field produced a single domain. These Raman results imply that the domain size is not more than a few optical wavelengths ($< 1 \mu$m), so that TO phonons propagating in all directions participate in the scattering regardless of the scattering geometry. On the other hand, the sharp peaks observed in unpoled material at the same energies as the A_1 (TO) and E (TO) phonons of the monodomain state imply that the polarization must be quite uniform within these small domains and that each domain has a polarization of essentially the same magnitude. Finally, a polarized beam of light was depolarized after transmission through the unpoled samples—in contrast to the nearly single-domain type of birefringence observed by Courtens.[9] These depolarization results were used to estimate a maximum domain size of about 0.2 μm in the samples used in the Raman experiments.[10]

While the difference between the birefringence[9] and Raman results[10] might be attributable to differences in the single-crystal samples, the previously reported failure to observe any changes in the elastic constants at T_c using acoustic flexure resonance[7] remains a puzzling result. In the present work the results of a Brillouin scattering investigation of both unpoled and poled samples of KLT are presented and we find that, in contrast to the earlier reports,[4] the expected step discontinuities in the elastic constants do, in fact, occur at T_c. The magnitude of the elastic constant change Δc_{33} is used, together with electrostrictive constants and Raman data, to estimate the low-temperautre limit of the polarization P_s. Birefringence data of the type reported by Courtens[9] were also obtained using some of our more recent samples. These differences in sample behavior apparently result from a selection of the axis of polarization by random or macroscopic strain distributions.

II. EXPERIMENT

Two different single-crystal samples, each grown with 5.6 mol % lithium in the melt,[11] were employed in the Brillouin scattering experiments. One crystal was prepared with six (100) faces and the other with two (001) and four (110) faces. Electrodes were placed on a (001) face of each sample using silver conducting paint so that the samples could be poled into a single domain below T_c. The samples were held with the opposite face in electrical contact with a copper holder using a layer of silver conducting paint. This holder was closed except for small optical access holes, and a heater and exchange gas system allowed selection and control of the sample temperature to an accuracy of about 0.1 K.

Brillouin scattering data were obtained using the 5145-Å line of a single-mode argon laser and an electronically swept and stabilized triple-pass Fabry-Perot interferometer followed by a grating monochromator that rejected light outside of the free spectral range of interest. Two scattering configurations were used with the two different samples. For one sample the incident and scattered beams were along $\langle 110 \rangle$ and $\langle 1\bar{1}0 \rangle$ directions so that acoustic phonons propagating along a cube axis perpendicular to the poling field were selected. For the second sample the laser beam was along a $\langle 100 \rangle$ direction, and the scattered light was observed along the $\langle 001 \rangle$ poling axis through a small hole in the electrode so that the $\langle 101 \rangle$ phonons were selected. The birefringence of the samples was monitored by polarizating the incident laser light at 45° to the poling axis, and the transmitted laser light was detected through a polarizer set at 90° to the incident polarization direction.

Brillouin spectra were obtained for both samples with and without a poling field in order to search carefully for any possible differences between the zero-field-cooled (ZFC) state and the poled state which might indicate the presence of the type of dipole glass phase suggested previously for the ZFC state.[7,8] In particular, the absence of a macroscopic polarization in the proposed ZFC dipole glass state would be expected to lead either to significantly reduced changes in the elastic constants below T_c or to a broadening of the Brillouin components in comparison to the poled state.

The $VV+VH$ Brillouin data observed using a poled sample with a phonon wave vector $\vec{q}\,||\,[101]$ are shown in Fig. 1. The polarization of the incident and scattering light is identified as V for polarization normal to the plane of scattering or H for components parallel to that plane. The first such letter refers to the incident laser polarization and the second to the polarization of the scattered light. In the $VV+VH$ data of Fig. 1, a phonon

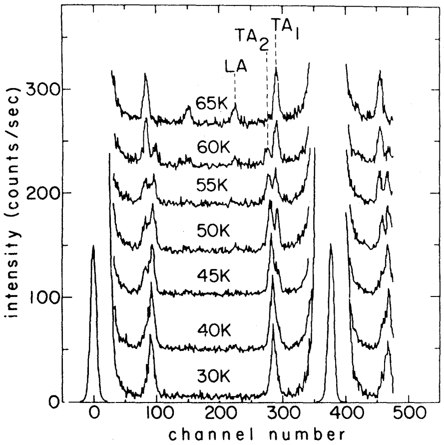

FIG. 1. Brillouin spectra of KLT with $x=0.056$ for $VV+VH$ polarizations. The free spectral range is 113.5 GHz and the labeled TA_1, TA_2, and LA peaks correspond to the same order as the unshifted peak at channel number 375.

peak labeled TA_2 appears below T_c ($T_c \approx 60$ K for this sample) and grows rapidly in intensity until it becomes the strongest feature in the spectrum below about 45 K. The frequency, polarization, and appearance of this phonon below T_c all imply that it is the mixed, quasishear mode TA_2, polarized in the plane containing the polar axis of the ferroelectric phase. This peak disappears, for example, in the *HH* or *HV* geometry, as expected for the TA_2 mode.[12] The quasilongitudinal mode labeled LA in Fig. 1 decreases in intensity as T decreases below T_c. The intensities of the LA and TA_2 modes in this geometry are proportional to $(p_{12}+p_{13})^2/v_{\mathrm{LA}}^2$ and $(p_{12}-p_{13})^2/v_{\mathrm{TA}}^2$, respectively, where the p_{ij} are photoelastic tensor components and v_{LA} and v_{TA} are the phonon velocities.[12] The significantly diminished LA intensity found for $T<60$ K implies that $p_{13}\approx -p_{12}$. On the other hand, the vanishing of the TA mode above T_c requires that $p_{13}\approx p_{12}$ above T_c. Together these results imply that either p_{13} or p_{12} changes sign below T_c. Another major intensity change near T_c is observed as a fourfold increase in the *VV* intensity of the LA phonon propagating perpendicular to the polar axis along a ⟨100⟩ direction. The intensity of this mode is proportional to p_{31}^2 in the ferroelectric phase and to p_{21}^2 in the cubic phase. This result, therefore, implies that the low-temperature value of p_{31} is about twice as large as the value of p_{21} in the cubic phase.

The frequencies of the five phonons observed in the $\vec{q}\parallel\langle 100\rangle$ and $\vec{q}\parallel\langle 101\rangle$ scattering geometries are indicated in Fig. 2 at various temperatures above and below T_c. The only phonons with clearly measurable frequency shifts below or near T_c are the $\vec{q}\parallel\langle 100\rangle$ LA phonon and the $\vec{q}\parallel\langle 101\rangle$ TA_2 quasishear mode. At each temperature the five measured frequencies are sufficient to determine five of the six elastic constants of the tetragonal phase. Above T_c the three cubic elastic constants are obtained from the frequencies of the four observable phonons. The results, which are summarized in Fig. 3, were obtained from the Brillouin frequencies by the use of standard expressions which have been summarized elsewhere.[12] The properties of $KTaO_3$ used in obtaining the c_{ij} were the density $\rho=6.97$ g/cm^3 and the refractive index $n=2.3$. The anisotropy of the refractive index in the tetragonal phase below T_c is of the order of 0.01 (Ref. 19) and was therefore neglected.

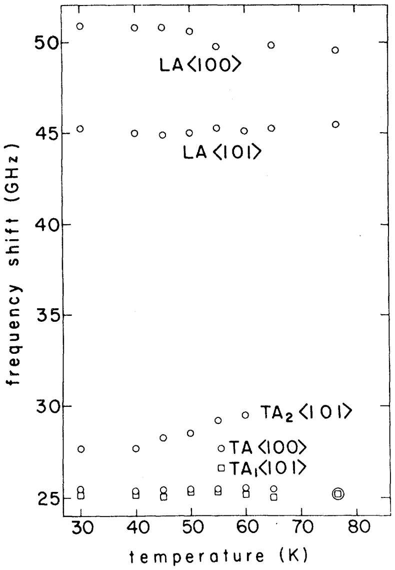

FIG. 2. Temperature dependence of the frequencies of observed acoustic modes for the two selected propagation directions, ⟨100⟩ and ⟨101⟩. The accuracy of the measurements is about 1%.

The results obtained for the unpoled samples depended upon the position of the laser beam in the sample. This is illustrated in Fig. 4 which shows the spectrum observed at 40 K at two points separated by a distance on the order of a millimeter. The scattering wave vector is along a pseudocubic axis. The lower trace clearly shows the presence of scattering from at least two regions with different directions for the tetragonal polar axis. The peak labeled LA ⟨001⟩ represents scattering from an LA phonon propagating along a polar axis with a velocity given by $(c_{33}/\rho)^{1/2}$. The mode labeled LA ⟨100⟩ is due to an LA phonon propagat-

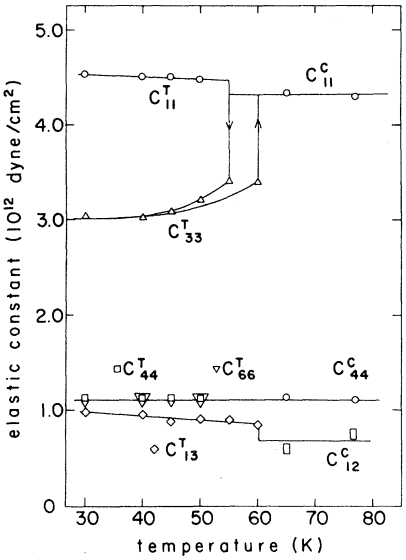

FIG. 3. Elastic constants of KLT with $x=0.056$ as a function of temperature. These results are calculated from the data of Fig. 2, which is obtained from two different samples with $T_c \simeq 60$ K. The superscripts C and T refer to the cubic and tetragonal phases, respectively. The relative precision of these constants is about 1% but the absolute values have an uncertainty ranging from 1.4% in c_{11}^T to about 10% in c_{33}^T and 20% in c_{13}^T. This large uncertainty in the two latter constants is due to the propagation of uncertainties in the expressions used in the calculation.

ing in a direction perpendicular to a polar axis with a velocity $(c_{11}/\rho)^{1/2}$. The values of c_{11} and c_{33} obtained from the frequencies of these phonons are in close agreement with the values given in Fig. 3 for poled samples. Only one transverse mode is observed in the lower trace of Fig. 4 because the shear velocities for the two polar-axis orientations are given by either $(c_{44}/\rho)^{1/2}$ or $(c_{66}/\rho)^{1/2}$ and $c_{44}=c_{66}$ to within the accuracy of our measurements, as is evident in Fig. 3. These results imply that the elastic anisotropy in the unpoled ZFC samples is equal to that found for the poled samples. The spectrum in the upper trace of Fig. 4 is indicative of a sample region in which the phonons propagate only in a region or regions in which the polar axis is perpendicular to the phonon wave vector. This, in fact, is a much more typical spectrum of the ZFC samples. Such spectra apparently imply regions, comparable in size to the ~ 50 μm^3 volume of the sample probed by the Brillouin scattering, in which the polar axis is unchanged. This is consistent with the "single-domain" type birefringence which was often observed in the unpoled samples used in the present work as well as those used by Courtens.[9] On the other hand, in none of these samples were we able to observe the anisotropic Raman frequency of the extraordinary TO phonon below T_c^{10}—as would be expected for single domains with dimensions $\gtrsim 10$ μm. The only apparent way to reconcile the Raman results with the Brillouin and birefringence experiments is to assume that strains in the lattice select a preferred axis of polarization over regions on the order of 100 μm in size, but that there are, in fact, antiphase domain walls separating regions of *reversed* polarization of dimensions $\lesssim 1$ μm. It is also possible that the polarization reversal would not have a substantial effect on either the optical anisotropy or on the acoustic phonon frequencies and linewidths, since those properties are sensitive only to the absolute magnitude and axis of the polarization and not to the direction of the polarization along the axis. The observation of depolarization, rather than birefringence, in the samples used for the earlier Raman work[10] implies then that microscopic strains in those samples caused the axis of polarization to change over shorter distances than in the present samples.

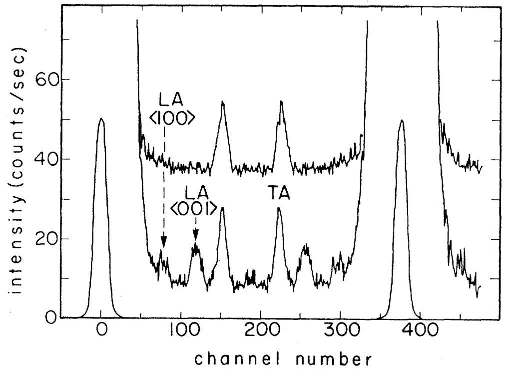

FIG. 4. Brillouin spectra observed for an unpoled sample of KLT at $T=35$ K. The upper and lower traces were obtained for two different regions of the sample separated by about 1 mm. The polarizations selected are $HH+HV$. The free spectral range is 62.2 GHz, and the peaks labeled LA ⟨100⟩, LA ⟨001⟩, and TA are in the same order as the elastic peak in channel number 375.

III. DISCUSSION

The observation of sharp phonon peaks and an elastic anisotropy for phonons of wavelength on the order of 1 μm implies that the low-temperature phase has a polarization which is quite uniform in magnitude over regions with dimensions much larger than a micrometer, and that the magnitude of the polarization is nearly the same in all regions. The magnitude of this polarization can be estimated from the measured elastic constants through the use of the relations derived by Pytte[13] who considered the coupling of the acoustic and soft optic modes in perovskite ferroelectrics.

The third- and fourth-order anharmonic terms of this type can be written[13]

$$H_a = \sum_{i,\lambda,\lambda',l} G_{i\lambda\lambda'}\epsilon_i(l)Q_\lambda(l)Q_{\lambda'}(l) + \tfrac{1}{2}\sum_{i,j,\lambda,l} H_{ij\lambda}\epsilon_i(l)\epsilon_j(l)Q_\lambda^2(l) \,, \tag{1}$$

where $\epsilon_i(l)$ is the strain tensor component in unit cell l, Q_λ is the TO mode (mass-normalized) eigenvector, and $G_{i\lambda\lambda'}$ and $H_{ij\lambda}$ are the third- and fourth-order anharmonic coefficients, respectively. We neglect the fourth-order term and consider the electrostrictive terms in $G_{i\lambda\lambda'}$. The changes in the elastic constants are then given, in contracted notation for $G_{i\lambda\lambda'}$, by[13]

$$\begin{aligned} \Delta c_{11} &= \Delta c_{12} = -G_{12}^2 D_3^T \,, \\ \Delta c_{33} &= -G_{11}^2 D_3^L \,, \\ \Delta c_{44} &= -G_{44}^2 D_1^{L,T} \,, \\ \Delta c_{66} &= 0 \,, \end{aligned} \tag{2}$$

with $D_\lambda^{L,T}$ defined by

$$D_\lambda^\mu = \left[\frac{4\rho\langle Q_\lambda\rangle^2}{M\Omega_{\lambda\mu}^2(0)} \right] (1+\omega^2\tau_{\lambda\mu}^2)^{-1} \,, \tag{3}$$

where $\langle Q_\lambda \rangle$ is the amplitude of the static distortion below T_c, $\lambda = 1,3$ corresponds to the E and A components, respectively, of the $\mu = L$ (longitudinal) and $\mu = T$ (transverse) optic modes, ω is the acoustic-phonon frequency, $\Omega_{\lambda\mu}(0)$ is the frequency of the branch λ at the zone center, $\tau_{\lambda\mu} = \Gamma_{\lambda\mu}/\Omega_{\lambda\mu}^2(0)$, where $\Gamma_{\lambda\mu}$ is the damping constant of the branch λ at $q=0$, and M is the mass of the unit cell.

The electrostrictive constants of $KTaO_3$ have recently been measured over a large temperature range by Uwe and Sakudo[14] who fit their results to free-energy density terms of the form

$$H = \tfrac{1}{2}\sum_{i,j} c_{ij}\epsilon_i\epsilon_j + \sum_{i,\lambda,\lambda'} g_{i\lambda\lambda'}\epsilon_i P_\lambda P_{\lambda'} \,, \tag{4}$$

where $g_{i\lambda\lambda'}$ is an electrostrictive coefficient and P_λ is the polarization. They obtained (in cgs units) values of

$$\begin{aligned} g_{11} &= 3.5 \pm 0.4 \,, \\ g_{12} &= -0.2 \pm 0.3 \,, \\ g_{44} &= 0.4 \pm 0.3 \,. \end{aligned} \tag{5}$$

The $G_{i\lambda\lambda'}$ may be obtained from the $g_{i\lambda\lambda'}$ by relating P_λ to $\langle Q_\lambda \rangle$. We obtain the following relationships,

$$P_\lambda = \frac{e^*}{vm_e}\langle Q_\lambda \rangle \,, \tag{6}$$

$$G_{i\lambda\lambda'} = \frac{e^{*2}}{vm_e} g_{i\lambda\lambda'} \,, \tag{7}$$

where e^* is the effective charge of the TO vibration, v is the unit-cell volume, and m_e is an effective mass which can be expressed in terms of the tantalum and oxygen masses as $m_e = 3m_T m_0/(m_T+3m_0)$. By combining Eqs. (2), (3), (6), and (7) we arrive at the following result for Δc_{ij},

$$\Delta c_{ij} = \left[\frac{4\rho}{Mm_e} \right] \left[\frac{e^{*2}P_0^2 g_{kl}^2}{\Omega_{\lambda\mu}^2(0)} \right] (1+\omega^2\tau_{\lambda\mu}^2)^{-1} \,, \tag{8}$$

with k, l, and μ related to i and j as in Eq. (2).

The parameters $\Omega_{\lambda\mu}(0)$ and $\Gamma_{\lambda\mu}$ can be obtained from the Raman data[10] for KLT with 5.4 at. % Li. The effective charge e^* has been determined by Uwe and Sakudo[14] to be $e^* = 4.8 \times 10^{-19}$ cgs, in agreement with several dielectric results on $KTaO_3$. The low-temperature limiting value of $\Delta c_{33} = c_{11}$ (cubic) $- c_{33}$ (tetragonal) can then be used with the second part of Eq. (2) to obtain P_0 (the saturation value of the polarization at $T \ll T_c$) from the largest electrostrictive coefficient g_{11}. The parameters used are $\rho = 6.97$ g cm^{-3}, $\Omega_{3T}(0) = 80$ cm^{-1}, $\omega \approx 40$ GHz, $\Gamma_{3T} \approx 10$ cm^{-1}. The resulting polarization is $P_0 = 0.27$ C m^{-2}, which is a factor of 3 larger than the "electret polarization" obtained by Höchli *et al.*[7] from acoustic resonance measurements on samples cooled with an electric field applied along a [001] direction.

In principle, this value of P_0 could be verified by using the first and third parts of Eq. (2). Unfortunately, the values of g_{12} and g_{44} in Eq. (5) are too small and uncertain to give meaningful values of Δc_{11}, Δc_{12}, or Δc_{44}. Furthermore, there is no measurable change in c_{44} in Fig. 3, and although the small changes in c_{11} and c_{12} are equal in magnitude, they are opposite in sign to the predictions of Eq. (2). These small changes can, therefore, be attributed primarily to the fourth-order anharmonic term in Eq. (1).

Fleury and Lazay carried out Brillouin and Raman scattering experiments on tetragonal $BaTiO_3$,[15] and their results are in notable contrast to the case of KLT. In $BaTiO_3$, the pure shear mode TA_1 along [101] was enhanced and shifted by coupling to the soft, overdamped E (TO) phonon. Thus the constant c_{44} and elasto-optic coefficient p_{44} were most strongly affected by the coupling, whereas no shift or enhancement of this phonon was observable in KLT because the E (TO) phonon remains underdamped at an energy of about 45 cm^{-1}.

IV. CONCLUSIONS

The Brillouin spectra of KLT clearly show the presence of an elastic step below the transition to the tetragonal phase. The sharp Brillouin components and the observed elastic anisotropy show, first, that a large polarization develops which is fairly uniform in *magnitude* over regions with dimensions the order of 50 – 100 μm, and second, that this magnitude is uniform from one region to the next. It is possible, however, that there are much smaller domains of *reversed* polarization within these regions, which could explain the lack of an anisotropic extraordinary mode frequency in the Raman spectra. Except for this possibly strain-dependent domain structure, we see no significant differences between poled and zero-field-cooled samples, and it is therefore unlikely that KLT is a true "dipole glass" in the ZFC state.

ACKNOWLEDGMENTS

The research at Indiana University was supported in part by National Science Foundation Grant No. DMR81-05005. Oak Ridge National Laboratory is operated by the Union Carbide Corporation for the U.S. Department of Energy under Contract No. W-7405-eng-26.

---

*Permanent address: Bell Telephone Laboratories, Holmdel, New Jersey.

[1] S. Triebwasser, Phys. Rev. 114, 63 (1959).
[2] T. G. Davis, Phys. Rev. B 5, 2530 (1972).
[3] U. T. Höchli and L. A. Boatner, Phys. Rev. B 20, 266 (1979).
[4] Y. Yacoby and A. Linz, Phys. Rev. B 9, 1712 (1974).
[5] R. L. Prater, L. L. Chase, and L. A. Boatner, Phys. Rev. B 23, 221 (1981).
[6] U. T. Höchli, H. E. Weibel, and L. A. Boatner, Phys. Rev. Lett. 41, 1410 (1978).
[7] U. T. Höchli, H. E. Weibel, and L. A. Boatner, J. Phys. C 12, L563 (1979).
[8] F. Borsa, U. T. Höchli, J. J. van der Klink, and D. Rytz, Phys. Rev. Lett. 45, 1884 (1980).
[9] Eric Courtens, J. Phys. C 14, L37 (1981).
[10] R. L. Prater, L. L. Chase, and L. A. Boatner, Phys. Rev. B 23, 5904 (1981).
[11] L. A. Boatner, A. H. Kayal, and U. T. Höchli, Helv. Phys. Acta 50, 167 (1977).
[12] R. Vacher and L. Boyer, Phys. Rev. B 6, 639 (1972).
[13] E. Pytte, Phys. Rev. B 5, 3758 (1972).
[14] H. Uwe and T. Sakudo, J. Phys. Soc. Jpn. 38, 183 (1975).
[15] P. A. Fleury and P. D. Lazay, Phys. Rev. Lett. 26, 1331 (1971).