Far-infrared soft mode behavior in PbSc\textsubscript{1/2}Ta\textsubscript{1/2}O\textsubscript{3} thin films

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Temperature dependences of the optic phonons in PbSc\textsubscript{1/2}Ta\textsubscript{1/2}O\textsubscript{3} sol-gel films deposited on sapphire substrates were studied by means of Fourier transform far-infrared transmission spectroscopy in the temperature range 20-900 K. Four films displaying different B-site order with both ferroelectric and relaxor behavior were studied. In all cases the TO mode near 80 cm\textsuperscript{-1} at 10 K softens on heating to \approx 45 cm\textsuperscript{-1} following the Cochran law with extrapolated critical temperature near 700 K (400 K above the temperature of dielectric maximum, \(T_m\)), but above 600 K its frequency remains stabilized. It can be assigned to the A\textsubscript{1} component of the ferroelectric soft mode inside polar clusters which form below the Burns temperature near 700 K. In the ordered PST film another mode activates below \(T_m\) in infrared spectra near 60 cm\textsuperscript{-1} exhibiting also anomalous temperature dependence due to its coupling with the former mode. It is assigned to the A\textsubscript{1} component of the F\textsubscript{2g} Raman active mode. Central mode, which appears below the Burns temperature in the THz range, is assigned to the dynamics of polar clusters. It slows down on cooling and vanishes from our spectral range below \(T_m\). Another overdamped excitation assigned to the E component of the soft mode appears near 30 cm\textsuperscript{-1} at low temperatures.

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I. INTRODUCTION

Ferroelectric relaxors, in particular complex perovskites with the general formula PbB\textsubscript{1/2}B\textsuperscript{′′}\textsubscript{1/2}O\textsubscript{3} and PbB\textsubscript{1/2}B\textsuperscript{′′}\textsubscript{1/2}O\textsubscript{3}, are of high interest due to their excellent dielectric, electrostrictive, and pyroelectric properties. A discovery of giant piezoelectric response in relaxor based crystals by Park and Shrouf\textsuperscript{10} turned attention of scientific community to better understanding the relaxor ferroelectricity.

Lead magnesium niobate PbMg\textsubscript{1/3}Nb\textsubscript{2/3}O\textsubscript{3} (PMN) and lead scandium tantalate PbSc\textsubscript{1/2}Ta\textsubscript{1/2}O\textsubscript{3} (PST) are model representatives of the relaxor ferroelectrics which exhibit high and broad maxima in the real \(\varepsilon'(T)\) and imaginary \(\varepsilon''(T)\) part of the dielectric permittivity which shift with the increasing frequency to higher temperatures. No ferroelectric (FE) phase transition occurs in PMN without bias electric field, while PST exhibits a spontaneous FE transition. Its temperature depends on the ordering of B-site ions (Sc and Ta). Disordered PST undergoes FE transition at \(T_c \sim 270\) K, while \(T_c\) of the ordered sample appears near 300 K without typical relaxor behavior above \(T_c\).

It is well known that the peculiar dielectric properties of relaxors are connected with a broad dielectric relaxation (we call it central mode (CM) in analogy with inelastic scattering experiments) below the polar phonon frequencies. It stems from the dynamics of nanoscopic inhomogeneities - polar clusters. Many low-frequency experimental dielectric data exist on the behavior of CM in FE relaxors, but much less data were published about dielectric response in the MHz and GHz range and THz data are practically missing in the literature. Neutron diffuse scattering in PMN revealed\textsuperscript{2} the CM below the Burns temperature, \(T_d \approx 620\) K, where the polar nanoclusters appear. However, its frequency was not determined.

Very recently, infrared (IR) transmission and microwave dielectric data of PMN have shown that the CM has characteristic frequency near 20 cm\textsuperscript{-1} (0.6 THz) at \(T_d\) and its frequency dramatically slows down to sub-Hertz region on cooling to freezing temperature \(T_f\) near 200 K. Simultaneously the relaxation broadens on cooling, giving rise to frequency independent losses between 100 Hz and 100 GHz at temperatures below \(T_d\). Dielectric studies of PST up to 33 GHz revealed a two-component CM\textsuperscript{14}; however its behavior at high temperatures near \(T_d\) was not studied. One of the aims of this study is to investigate the CM at high temperatures to confirm its vanishing (merging with the soft mode response) above \(T_d\).

Lattice dynamics of PMN was studied by means of Raman, IR and inelastic neutron scattering spectroscopy\textsuperscript{(8,9,12,13,14)}. It was shown\textsuperscript{8,13} that the lowest frequency transverse optic phonon (TO\textsubscript{1}) \(\omega_{SM}\) follows the Cochran law

\[
\omega_{SM} = A \sqrt{T_d - T}
\]

with the extrapolated critical temperature near the Burns temperature \(T_d \approx 620\) K. It indicates that the TO\textsubscript{1} frequency \(\omega_{SM}\) can be assigned to the FE soft mode (SM) in polar clusters. The questions arise: Is it the general behavior typical for all FE relaxors? What is the behavior of relaxors with the spontaneous FE phase...
Raman lines are seen not only in B-sites ordered samples, should be expected in the spectra. However, first-order et al. which are determined by the interatomic force constants. as the mode activity is given by the phonon eigenvectors. Raman scattering is sensitive to short-range (nm) order, to modes activated by the zone folding as it was assumed center of the parent Pm3m cubic structure rather than activated modes belong prevailingly to the Brillouin-zone. It would mean that the Raman-phonons and one silent F $^{1}u$ T $^{a}$ modes were observed in the Raman spectra of paraelectric phase. Siny et al. explained the activity of the phonons in Raman spectra by doubling of the unit cell in the paraelectric phase due to the 1:1 B-site ordering. In this case the space group is Pm3m and the factor group analysis yields the following optic vibration modes:

$$\Gamma = A_{1g}(R) + E_{g}(R) + F_{1g}(-) + 4F_{1u}(IR) + 2F_{2g}(R) + F_{2u}(-). \quad (2)$$

It means that 4 Raman and distinct 4 IR active modes should be expected in the spectra. However, first-order Raman lines are seen not only in B-sites ordered samples, but also in the disordered PST and in other relaxors like PMN. Siny et al. explained this Raman activity by local short-range B-site ordering in chemical clusters. Namely, Raman scattering is sensitive to short-range (nm) order, as the mode activity is given by the phonon eigenvectors which are determined by the interatomic force constants.

Another assignment was suggested recently by Hlinka et al. They argued that Raman scattering in relaxors is primarily due to anisotropic polar clusters rather than to 1:1 B-site ordering. It would mean that the Raman-activated modes belong prevalingly to the Brillouin-zone center of the parent Pm3m cubic structure rather than to modes activated by the zone folding as it was assumed by Siny et al.

Also results of the pulsed neutron atomic pair-density function analysis by Egami et al. speak in favor of such a picture. They have shown that the Burns temperature $T_d$ is the local Curie temperature below which the polar clusters are formed, but the local polarization of Pb persists up to $\sim 1000$ K several hundreds of Kelvins above $T_d$. Probably both mechanisms of mode activation in Raman spectra have to be considered and to distinguish between them requires more detailed studies, particularly at very high temperatures near the B-site ordering temperature. Comparison of the Raman spectra with properly evaluated IR spectra is also necessary.

Factor-group analysis in the R3m rhombohedral ferroelectric phase with the doubled unit cell due to B-site ordering yields the following optic modes:

$$\Gamma = 7A_{1}(R, IR) + 2A_{2}(-) + 9E(R, IR), \quad (3)$$

and $1A_{1} + 1E$ acoustic modes. It means that up to 16 TO modes simultaneously Raman and IR active plus corresponding 16 LO Raman active modes can be expected in the spectra of the ferroelectric phase. IR active modes in bulk PST ceramics were studied by means of IR reflectivity. The spectra revealed correlation between the degree of 1:1 B-site ordering and appearance of an extra mode at 315 cm$^{-1}$. The high-frequency wing of the CM was observed above room temperature in the reflectivity spectra below 30 cm$^{-1}$. However, the accuracy of IR reflectivity technique is limited at low frequencies and high temperatures. In this case transmission measurements are more accurate and more sensitive to absorption mechanisms, but for this purpose, due to high absorption, thin films are needed. The aim of this study is to investigate temperature dependence of the low-frequency polar phonons and CM in PST films with various B-site order in a broad temperature interval 20 - 900 K. It should allow us to shed more light on the lattice and polar-cluster dynamics between $T_c$ and the Burns temperature $T_d$.

II. EXPERIMENT

PST thin films were prepared by chemical solution deposition on sapphire substrates, which are transparent in the far IR. Four films of various degree of order were investigated: disordered (annealed at 700°C for 1 min), slightly ordered (annealed at 850°C for 1 min), 50% ordered (annealed at 850°C for 1 hour) and 78% highly ordered (annealed at 800°C for 48 hours). The degree of ordering was determined by the X-ray diffraction from $\{1\over 2,1\over 2,1\over 2\}$ superlattice peak intensity and the size of the ordered regions was investigated using TEM dark-field imaging. The thickness of the films was about 500 nm, plane-parallel (0001) oriented sapphire substrates were 0.5 mm thick. The unpolarized IR transmission spectra were taken using FTIR spectrometer Bruker IFS 113v at temperatures between 20 and 900 K with resolution of 0.5 cm$^{-1}$. A helium-cooled Si bolometer operating at 1.5 K was used as detector, an Optistat CF cryostat with polyethylene windows was used for cooling, and a high-temperature cell SPECAC P/N 5850 was used for the heating. The investigated spectral range was determined by the transparency window of the sapphire substrate; at 20 K up to 450 cm$^{-1}$ (15 THz), at 900 K the sample was opaque already above 190 cm$^{-1}$.

III. SPECTRA EVALUATION

IR transmission spectra of 78% ordered PST film at selected temperatures are shown in Fig. 1. Dense osci-
FIG. 1: IR transmission spectra of the 500 nm thick 78% ordered PST film deposited on sapphire substrate (490 µm) for various temperatures. Frequencies of the central mode (CM), split TO$_1$ soft mode (SM) and TO$_2$ phonon are marked. Absorption peak near 380 cm$^{-1}$ is a phonon peak from the sapphire. Small peak near 220 cm$^{-1}$ at 300 K is an instrumental effect.

The overall transmission decreases on heating, mainly due to the increase in multi-phonon absorption of the sapphire substrate. The spectra were taken at more than 20 temperatures. At each temperature the spectra of a bare sapphire substrate and the PST film on the substrate were measured. The complex transmittance of the two-layer system was computed by the transfer matrix formalism method including interference effects. Model of the sum of damped quasi-harmonic oscillators in the form

$$
\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) = \varepsilon_\infty + \sum_{j=1}^{n} \frac{\Delta\varepsilon_j \omega_j^2}{\omega_j^2 - \omega^2 + i\omega\gamma_j} \quad (4)
$$

was used for the expression of the complex permittivity $\varepsilon^*$ of the films. $\omega_j$, $\gamma_j$ and $\Delta\varepsilon_j$ denote the frequency, damping and contribution to the static permittivity of the $j$-th polar mode, respectively. The parameter $\varepsilon_\infty$ describes the high-frequency permittivity originating from the electronic polarization and from the polar phonons contribution above the spectral range studied.

IV. RESULTS AND DISCUSSION

Real ($\varepsilon'$) and imaginary ($\varepsilon''$) parts of permittivity $\varepsilon^*$ of the 78% ordered PST thin film calculated from the fit of transmission spectra in Fig. 1 are shown in Fig. 2. The frequencies of maxima of $\varepsilon''$ correspond to the mode frequencies. Parameters of the modes above 200 cm$^{-1}$ were fixed during our fits at temperatures above 300 K because the substrate was opaque and this range is omitted in the figure. We note that the mode parameters correspond very well to parameters obtained from the bulk IR reflectivity spectra published in Ref. 21. It shows that the phonon parameters are not influenced by possible strain or size effect in our thin films. We believe that the IR transmission spectra are more sensitive than the IR reflectivity spectra. It could be the reason why we could see also the splitting of the TO$_2$ mode although it was
not resolved in the IR reflectivity spectra.

The most important mode anomalies were observed in the range below 100 cm\(^{-1}\). Temperature dependences of the polar mode frequencies are plotted in Fig. 3. A new heavily damped (i.e. \(\gamma_j/\omega_j > 1\)) excitation appears on cooling below 700 K at frequencies near 30 cm\(^{-1}\). This mode is not manifested by a minimum in the IR transmission spectra, but rather by enhanced broad absorption at below 40 cm\(^{-1}\). This excitation does not seem to be of usual one-phonon origin, and we assign it to dynamics of polar clusters (i.e. CM).

Disappearance of the CM above 700 K is manifested by an enhancement of the low-frequency transmission, although the high-frequency transmission continues to decrease on heating, as expected due to increase in damping of polar phonons and multi-phonon absorption (see Fig. 1). On cooling to \(T_c \approx 300\) K, CM slows down to microwave range and vanishes below \(T_c\) from our spectral range.

Another heavily damped excitation arises in our IR spectra below \(T_c\) near 30 cm\(^{-1}\) and remains in the spectra down to the lowest temperatures. The origin of this excitation was not fully understood until recently (in analogy to PMN, where it also appears) it could be explained by activation of the acoustic phonon branches due to the local unit cell doubling or translation symmetry breaking). However, now it seems to us more probable that it is just the E component of the split \(F_{1u}\) SM (for this explanation see below).

Let us stress that our static permittivity in Fig. 2 does not correspond to experimental low-frequency permittivity, because strong dielectric dispersion exists below the phonon frequencies. Bovtun et al. combined high-frequency and microwave dielectric spectra of PST ceramics between 1 MHz and 36 GHz with the IR reflectivity spectra, and revealed two dispersion regions below phonons. One, nearly temperature independent, was estimated to near 1 THz and corresponds well to our heavily damped mode near 30 cm\(^{-1}\) below \(T_c\). Second relaxation was seen at temperatures below 350 K in the high-frequency range and it slows down and broadens on cooling. At higher temperatures it merges with the far IR spectra so that it corresponds to the relaxation below \(T_d\) near 30 cm\(^{-1}\) assigned to the dynamics of polar nanoclusters. This relaxation is responsible for the pronounced dielectric anomaly near and above \(T_c\). The relaxation does not completely vanish at low temperatures, because our dielectric data at 1 MHz and 8 GHz obtained on PST thin films of various B-site order show permittivity between 300 and 400 at 20 K whereas the phonon contribution to permittivity is only about 100 (see Fig. 2). This is not surprising because a small dielectric dispersion (constant dielectric losses) was observed in many relaxors at low temperatures.

The lowest-frequency phonon (marked TO\(_1\)) with the symmetry \(F_{1u}\) has the frequency near 45 cm\(^{-1}\) at high temperatures. It starts to harden below 550 K and it seems to split below \(T_c\). For illustration, in Fig. 3 we fitted the temperature dependences of both components by the Cochran law, but rather different extrapolated critical temperatures (700 and 1000 K, respectively) were obtained. The realistic value could be somewhere in between, but anyway, the softening ceased near 600 K and above the Burns temperature of about 700 K the expected hardening is not appreciable.

Both components of the TO\(_1\) SM have their counterparts also in Raman spectra, but the assignment of the modes in Raman spectra is more speculative. One mode near 56 cm\(^{-1}\) dominates the Raman spectrum below 100 cm\(^{-1}\) in the paraelectric phase. If we assume that it is Raman active due to the B-site ordering, it should be of \(F_{2g}\) symmetry, stemming from the Brillouin zone boundary of simple cubic perovskite structure. Its frequency is by about 10 cm\(^{-1}\) higher than that of the \(F_{1u}\) mode in our IR spectra (Fig. 3). At low temperatures a triplet appears in Raman spectra with frequencies about 50, 60 (strong peak) and 80 cm\(^{-1}\) (at 100 K). The mode near 80 cm\(^{-1}\) corresponds to the \(A_1\) component of our \(TO_1\) SM, which may activate in Raman spectra below \(T_c\). The mode near 50 cm\(^{-1}\) could be assigned to the E component of the cubic \(F_{2g}\) mode and is seen only in Raman spectra, although it could be also (weakly) IR active. The mode near 60 cm\(^{-1}\) frequency could correspond to the E component of the TO\(_1\) SM (see Fig. 3) or to \(A_1\) mode from the split \(F_{2g}\) mode. The latter explanation is more realistic because this mode is the strongest one in the Raman spectra, and its strength decreases in IR spectra with increasing disorder at the B-sites (see Fig. 3). This would mean that the mode near 30 cm\(^{-1}\) should be assigned to the E component of the polar SM (\(F_{1u}\)). This mode should remain IR active up to 700 K due to the dielectric anisotropy in polar clusters, but

![Figure 3: Temperature dependences of the polar mode frequencies in 78% ordered film. The lowest frequency mode below 30 cm\(^{-1}\) (marked as CM) is overdamped, therefore the frequency of loss maximum corresponding to \(\omega_\text{CM}/\gamma_\text{CM}\) is plotted. Two kinds of the Cochran fit of the SM (shown by solid and dashed lines) are discussed in the text.](image-url)
it is probably screened by the CM at high temperatures. This assignment sheds a new light on softening of both
types near 80 and 60 cm$^{-1}$. The higher-frequency mode
softens and because both modes are of the same A$_1$ sym-
metry so that they can bilinearly couple which results
also in partial softening of the lower-frequency mode due
to the mode repulsion.

Let us discuss the question how the polar-phonon pa-
rameters in PST are influenced by the different B-site or-
dering. The difference is best remarkable at 20 K, where
the phonon damping is minimized and the phonons up to
400 cm$^{-1}$ can be resolved in our IR spectra. Transmis-
sion spectra of four PST films with various order are com-
pared at 20 K in Fig. 4. One can see that the TO$_2$ spli-
ting (two minima near 230 cm$^{-1}$) is appreciable only in
the highest ordered film. TO$_1$ splitting below 100 cm$^{-1}$
is less and less pronounced with the decrease in ordering,
but mostly due to the increase in the linewidths.

Reaney et al. correlated the intensity of Sc-Ta
stretching mode in PST seen at 315 cm$^{-1}$ with the degree
of B-site order. One can see this mode clearly in 50% and
78% ordered films, in the other two samples only a weak
shoulder appears (Fig. 4). Unfortunately, we cannot es-
ablish any quantitative correlation between the intensity
of this mode and the degree of order. Namely, the spe-
tra of 78% ordered and disordered films were measured
on substrates which were not polished on the bottom sur-
face, while the other two substrates were well polished on
both surfaces. Matted bottom surface causes parasitic
diffuse scattering of the IR beam at higher frequencies
which is responsible for the lower value of the transmis-
sion peak at 400 cm$^{-1}$ in the corresponding film spectra.
Fortunately, the quality of the rear substrate surface has
no influence on our spectra below 200 cm$^{-1}$ because the
IR beam with wavelength larger than 50 µm does not feel
its roughness.

Temperature dependences of the mode frequen-
cies in disordered PST film are plotted in Fig. 5. The mode
near 60 cm$^{-1}$ appears only below 100 K due to the line
broadening compared to ordered film. Its lower strength
than in ordered sample gives evidence that it is the A$_1$
component of the F$_{2g}$ Raman mode. The A$_1$ compo-
nent of the TO$_1$ SM exhibits behavior similar to that in
the 78% ordered film: it softens on heating towards the
Burns temperature which ceases above 700 K. CM ap-
pears below 650 K and slows down below our spectral
range on cooling. The new heavily damped mode (prob-
able the E component of the F$_{1u}$ SM) appears below
T$_c$ at 30 cm$^{-1}$. This mode was observed in all studied PST
films as well as in the PMN film. In Ref. 8 we suggested
that the overdamping of the SM in the inelastic neutron
scattering spectra of PMN (so called ”waterfall” effect) is
only an apparent effect. We suggested that the SM were
underdamped (as in IR spectra) but disappeared from
the neutron spectra due to its overlapping with the CM
which approached the THz range near T$_d$. The SM and
CM behavior in PMN and PST is therefore very similar,
but to our knowledge, PST was not studied by inelas-

![FIG. 4: Low-temperature IR transmission spectra of PST films with various B-site order.](image)

![FIG. 5: Temperature dependences of the polar mode frequen-
cies in disordered PST film.](image)
tic neutron scattering so that no similar comparison is possible.

In conclusion, our IR transmission spectra of variously ordered PST thin films show qualitatively the same behavior: soft TO phonon of F$_{1u}$ symmetry splits on cooling below the Burns temperature. $A_1$ component hardens and follows the Cochran law with extrapolated critical temperature slightly above the Burns temperature. The low-frequency E component is clearly seen at low temperatures, but it is probably active up to $T_d$, where it is screened by the overdamped CM with similar frequency. CM stemming from dynamics of polar clusters appears below the Burns temperature and slows down to $T_c$. Similar behavior was observed also in the PMN relaxor so it seems that such a phonon and CM behavior is general for most perovskite relaxor ferroelectrics.

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1. G. A. Samara, Solid State Physics, Advances in Research and Applications, Vol. 56. San Diego: Academic Press, 240-458 (2001).
2. S.-E. Park, T. S. Shrouf, J. Appl. Phys. 82, 1804 (1997).
3. N. Setter, L. E. Cross, J. Mater. Sci. 51, 2478 (1980).
4. F. Chu, N. Setter, A. K. Tagantsev, J. Appl. Phys. 74, 5129 (1993).
5. S. Kamba and J. Petzelt, Piezoelectric Single Crystals and Their Application, Ed. by S. Troler-McKinstry, L. E. Cross and Y. Yamashita, Penn State University, 257, 2004.
6. E. Buixaderas, S. Kamba, and J. Petzelt, Ferroelectrics 308, 131 (2004).
7. K. Hirota, Z.-G. Ye, S. Wakimoto, P. M. Gehring, and G. Shirane, Phys. Rev. B 65, 104105 (2002).
8. S. Kamba, M. Kempa, V. Bovtun, J. Petzelt, K. Brinkman, and N. Setter, cond-mat/0412017.
9. V. Bovtun, S. Kamba, A. Pashkin, M. Savinov, P. Samoukhina, J. Petzelt, Ferroelectrics 298, 23 (2004).
10. F. Chu, N. Setter, C. Elissaké, and J. Ravez, Mat. Sci. Eng. B 38, 171 (1996).
11. V. Bovtun, V. Porokhonskyj, J. Petzelt, M. Savinov, J. Endal, C. Elissaké, and C. Malibert, Ferroelectrics 238, 17 (2000).
12. I. G. Siny, R. S. Katiyar, and A. S. Bhalia, Ferroelectrics Review, 2, 51 (2000).
13. S. Wakimoto, C. Stock, Z.-G. Ye, W. Chen, P. M. Gehring, and G. Shirane, Phys. Rev. B 66, 224102 (2002).
14. for review of neutron scattering in relaxors see for example G. Shirane and P. M. Gehring, in Morphotropic Phase Boundary Perovskites, High Strain Piezoelectrics, and Dielectric Ceramics, ed. K. M. Nair, W. K. Wong-Ng, A. Bhalia, D. Viehland, D. Suvorov, in Ceramics Transactions, 136, 17 (2003).
15. N. Setter and I. Laulicht, Appl. Spectrosc. 41, 526 (1987).
16. I. G. Siny and T. A. Smirnova, Fiz. Tverd. Tela 30, 823 (1989), Ferroelectrics 90, 191 (1989).
17. U. Bismayer, V. Devarajan, and P. Groves, J. Phys.: Condens. Matter 1, 6977 (1989).
18. B. Mihailova, U. Bismayer, B. Gütter, M. Gospodinov, and I. Konstantinov, J. Phys.: Condens. Matter, 14, 1091 (2002).
19. B. Gütter, B. Mihailova, R. Stosch, U. Bismayer, M. Gospodinov, J. Mol. Structure, 661-662, 469 (2003).
20. I. M. Reaney, J. Petzelt, V. V. Voitsekhovskii, F. Chu and N. Setter, J. Appl. Phys. 76, 2086 (1994).
21. J. Petzelt, E. Buixaderas, and A. V. Pronin, Mater. Sci. Eng. B 55, 86 (1998).
22. J. Hlinka, I. Gregora and J. Pokorný, and M. Iwata, submitted to Phys. Rev. B.
23. T. Egami, E. Mamontov, W. Dmowski, S. B. Vakrushev, Fundamental Physics of Ferroelectrics, AIP Conference Proceedings 677, 48 (2003).
24. K. Brinkman, PhD. Thesis, EPF Laussane 2004.
25. M. Born and E. Wolf, Principles of Optics, Oxford, Pergamon, 1960.
26. O. S. Heavens, Rep. Prog. Phys. 22, 1 (1960).
27. J. Hlinka, T. Ostapchuk, J. Petzelt, D. Nourjini, and S. Kamba, submitted to Phys. Rev. Lett.