Splitting of the ferroelectric phase transition in a laser radiation field and self-focusing of light in the incommensurate phase

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Continuous laser radiation is found to split the second-order ferroelectric phase transition in mixed $Sn_2P_2(Se_xS_{1-x})_6$ crystals whose phase diagrams have a Lifshitz point separating the transitions to the commensurate and incommensurate phases. The splitting is greater when the polarization of the laser light is parallel to the spontaneous polarization vector of the crystal. The findings are explained phenomenologically by considering the interaction with the order parameter and its spatial derivatives, which is quadratic in the field. Strong self-focusing is observed in the incommensurate phase when the latter is induced by a change in composition or an increase in laser power. The polarization dependence of the self-focusing is correlated with the photoinduced broadening of the incommensurate phase. It is concluded that the splitting is due primarily to the photoelastic effect, which becomes anomalously large in the incommensurate phase near the Lifshitz point due to the increased compliance of the lattice to spatially nonuniform elastic deformations.

The mixed crystals $Sn_2P_2(Se_xS_{1-x})_6$ are intrinsic ferroelectrics whose phase diagram contains a Lifshitz point[1,2] that separates the transitions to the commensurate and incommensurate (IC) phases. The $P2_1/c \rightarrow Pc$ phase transition of the second kind in $Sn_2P_2S_6$ occurs at $T_0 = 339$ K. When some of the sulfur is replaced by selenium, the line of continuous phase transitions splits smoothly into lines of transitions of the first and second kinds that bound the IC phase.[3,4]

Strong self-focusing of laser radiation in the IC phase of $Sn_2P_2(Se_xS_{1-x})_6$ ferroelectric solid solutions and significant photoinduced broadening were reported in Ref. 5. It was found that near the Lifshitz point, an increase in x enhances the optical nonlinearity of the IC phase and increases the photoinduced splitting; the addition of selenium also causes broadening (i.e., the IC phase exists in a wider temperature interval). In this paper we analyze the splitting by considering how the laser radiation and IC phase interact when the wavelength, power, and polarization of the laser light are varied and the chemical composition of the $Sn(Pb)_2P_2S(Se)_6$ solid solutions is changed (the composition determines the nature of the phase transitions and the width E_g of the forbidden gap of the crystals). A phenomenological model is used to explain the observed behavior.

We employed cw He-Ne (6328 Å, 0.06 W) and Kr lasers (6471 Å, 1 W; 6764 Å, 0.06 W) to irradiate the crystals. The radiation power was regulated by calibrated neutral light filters and was recorded by an IMO-2. The temperatures and behavior of the phase transition were found by recording the temperature dependence of the transmission of a low-power probing signal of fixed wavelength near the absorption edge.[3] The probing light was generated by a light bulb and a DFS-24 spectrometer selected the wavelength, which depended on the composition of the crystals. The coaxial probe and the excitation (laser) beams were focused on the crystal by a long-focus lens ($f = 140$ mm). The diameter (0.03 mm) of the laser beam at the waist was greater than the corresponding diameter of the probing beam, which enabled us to record the transmission temperature curves directly where the laser beam passed through. The crystal temperature was measured to within 0.1 K and changed at a rate of less than 0.5 K/min. The single crystals were grown by the vapor transport technique[3] and shaped into parallelepipeds 1–3 mm on a side. The X axis of the coordinate system pointed along the [100] crystallographic direction, which was parallel to the spontaneous polarization axis to within the measurement error. The Y axis was normal to the (010) symmetry plane of the monoclinic unit cell.[6]

EXPERIMENTAL RESULTS

Self-focusing of He–Ne laser radiation occurs in $Sn_2P_2(Se_xS_{1-x})_6$ crystals with $x > 0.2$, for which an intermediate IC phase is present, and it increases with the broadening (i.e., with the width of the temperature interval in which the IC phase exists). Broadening and enhanced self-focusing were also observed when the power P of the laser radiation was increased at a given composition (e.g., for $x = 0.4$, Fig. 1). The data indicate that the Lifshitz point may shift in the phase diagram toward lower Se concentrations when the crystal is irradiated by intense laser light, i.e., we have a Lifshitz line in T, P, x space.

Figure 2(a) shows the temperature dependence of the transmission of the probing radiation near the bifurcation point on the T, x diagram for an unirradiated $Sn_2P_2(Se_{0.1}S_{0.8})_6$ crystal. The kink at $T_0 = 303$ K is typical of phase transitions of the second kind,[3] in agreement with the results found in Refs. 4 and 7, where other properties were studied. When the crystal was irradiated by light from the krypton laser ($\lambda = 6471$ Å, polarization roughly along the X axis), the transmission curve had another discontinuity at $T = T_c$ corresponding to the jump in E_g during a phase transition of the first kind (Fig. 2(b). The ferroelectric phase transition is thus split, and the difference $T_i - T_c$ reaches 2 K for $P = 0.5$ W [here T_i and T_c are the temperatures at which the kink (para-IC phase transition of the sec-

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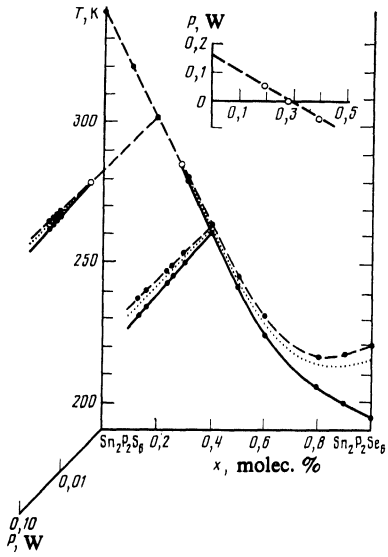

FIG. 1. Phase transition temperatures in mixed $Sn_2P_2(Se_xS_{1-x})_6$ crystals as functions of concentration and laser power. ●, experimentally measured phase transition temperatures; ○, calculated positions of the Lifshitz point. The solid and dashed lines correspond to transitions of the first and second kinds, respectively. The dotted line shows the expected temperatures for direct para→ferroelectric phase transitions calculated using (1). The insert shows the projection of the Lifshitz line on the P, x plane.

ond kind) and jump (IC-ferroelectric transition of the first kind) occur]. We note that this difference is greater than the value $T_i - T_x \approx 1.5$ K found in unirradiated $Sn_2P_2(Se_{0.4}S_{0.6})_6$.

The splitting of the phase transition is accompanied by strong self-focusing of the laser radiation, which is characteristic of the IC phase in $Sn_2P_2(Se_xS_{1-x})_6$ crystals.[5] Local heating and photostimulated shift are responsible for the change in T_i and T_c during illumination (and hence also for the change in the temperature T_0 of the expected direct transition from the para to the ferroelectric phase). As the power increases, the enhanced splitting (first unambiguously detected for $P \geq 0.3$ W, cf. Fig. 3) is accompanied by an increase in the size of the jump in the transmission. This indicates that the transition to the ferroelectric phase becomes a sharper transition of the first kind because the distance from the Lifshitz point increases with P. A similar behavior is also observed as the concentration x moves away from the value corresponding to the Lifshitz point.[3]

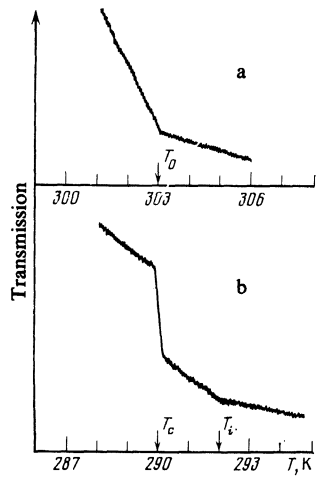

FIG. 2. Temperature curves for the transmission of probing light ($\lambda = 5953$ Å) by an $Sn_2P_2(Se_{0.2}S_{0.8})_6$ crystal with (b) and without (a) irradiation by a laser beam of power 0.5 W.

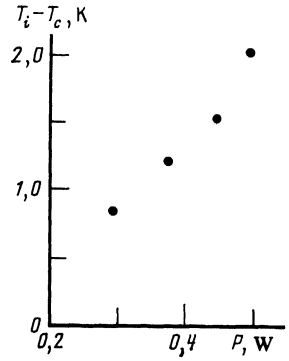

FIG. 3. Temperature width of the IC Phase in $Sn_2P_2(Se_{0.2}S_{0.8})_6$ versus laser power.

According to the theoretical predictions in Ref. 1, the width of the IC phase should increase quadratically with distance from the Lifshitz point, and indeed this is the case for the T, x diagram of $Sn_2P_2(Se_xS_{1-x})_6$, for which we find that $T_i - T_c = 45.8\ (x - x_L)^2$ with $x_L = 0.28$. We will show below that $T_i - T_c$ should also increase quadratically near the Lifshitz point when plotted in the P, T plane for $x = \text{const}$. We then find that $P_L \approx 0.06$ W for $x = 0.2$. On the other hand, for $x = 0.4$ (for which the IC phase is present in unirradiated crystals), the data in Ref. 5 indicate that the Lifshitz point lies at "negative" powers ≈ -0.06 W. The diagram in Fig. 1 plots T_i and T_c versus P to semilogarithmic scale for two values of x under the assumption that T_0 is constant (we did not estimate the local laser-induced heating of the crystal). We used the relation

$$(T_0 - T_c)/(T_i - T_0) \approx 4.4, \tag{1}$$

which is valid in the single-harmonic approximation.[1] The Lifshitz line in the P, T, x plane separates the surface $T_0(P,x)$ for para→ferroelectric phase transitions of the second kind from the surface $T_i(P,x)$ for para→IC transitions of the second kind. On the Lifshitz line the latter surface coalesces smoothly with $T_c(P,x)$, the surface for IC→ferroelectric phase transitions of the first kind. The insert in Fig. 1 shows the projection of the Lifshitz line on the P, x plane. We have assumed that the ferroelectric phase transition in $Sn_2P_2S_6$ splits for laser powers greater than 0.15 W.

We now examine what happens when the polarization of the laser light changes. Our crystals belong to the monoclinic class and thus are optically inactive along directions in or normal to the (010) symmetry plane. At 300 K, the spontaneous polarization axis [100] in $Sn_2P_2S_6$ make a $\approx 45°$ angle with the plane containing the optic axes.[8] Combined with the dielectric measurements in Ref. 9, observations of the conoscopic pattern show that the same situation also occurs for the $Sn_2P_2(Se_{0.4}S_{0.6})_6$ crystals used in the polarization

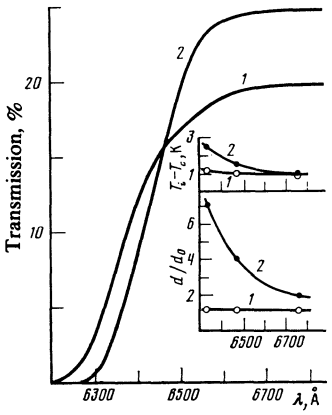

FIG. 4. Spectral curves for transmission of light traveling along the Z axis and polarized along the Y (1) and X (2) axes for an $Sn_2P_2(Se_{0.4}S_{0.6})_6$ crystal. The insert shows the broadening $T_i - T_c$ of the IC phase and the self-focusing d/d_0 as functions of the wavelength for $P = 0.02$ W and Y- and X-polarized light (d/d_0 is the relative change in the diameter of the laser beam cross section after transmission by the crystal at $T = T_c$).

measurements. The measurements can therefore be carried out using a laser beam along the Z axis (in the plane of symmetry normal to [100] which is polarized along the X or Y axes. If the beam travels along the Y axis, the polarization vector will be either in or normal to the plane containing the optic axes. In either case, the projections of the field vector E ($E^2 \propto P$) on the spontaneous polarization axis are similar in magnitude.

We found that for a laser power $P = 0.02$ W, the self-focusing and light-induced broadening of the IC phase were greatest when E was parallel to X and could hardly be observed for $E \| Y$ (insert to Fig. 4) or $E \| Z$. When the beam traveled along the Y axis, the self-focusing and broadening were roughly the same for both polarizations (insert in Fig. 5) and smaller in magnitude than for $E \| X$ with the light beam along the Z axis. These results indicate that self-focusing and broadening occur if E has a nonzero projection on the spontaneous polarization axis of the crystal.

The splitting and self-focusing increase with the Se content.[5] This may be due in part to a decrease in the gapwidth E_g as x increases, so that the laser photon energy $\hbar\omega$ approaches E_g. Figures 4 and 5 show the transmission of a crystal measuring 2 mm on a side as a function of wavelength for the experimental configurations described above; the composition was $x = 0.4$ and the temperature was $T = T_i + 5$ K. The inserts show that the photoinduced broadening of the IC phase and the maximum self-focusing d/d_0 (the relative change in the diameter of the laser beam transmitted through the crystal at T_c) both decrease as λ increases for a fixed $P = 0.02$ W. The crystal was transparent to radiation at the longer wavelength 6764 Å, and in this case the broadening and self-focusing were insignificant. However, it should be noted that for light with $E \| X$, the self-focusing was appreciably greater than for $E \| Y$ (Fig. 4), even though the absorption was less.

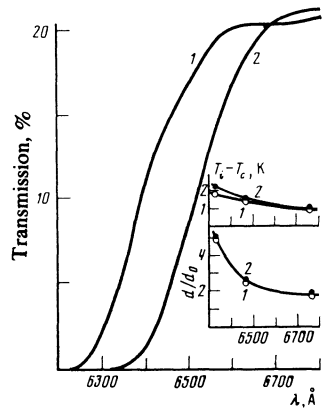

FIG. 5. Spectral curves for transmission by $Sn_2P_2(Se_{0.4}S_{0.6})_6$ of light propagating along the Y axis and polarized in (1) and normal to (2) the plane containing the optic axes. The insert plots $T_i - T_c$ and d/d_0 as functions of the laser wavelength ($P = 0.02$ W) for the in-plane and normal polarizations.

These results suggest that light absorption processes involving changes in the free carrier concentration are not dominant. This is confirmed by the finding that the broadening and self-focusing are the same for light polarized in or normal to the plane of the optic axes, in spite of the fact that the edge absorption is highly anisotropic for these polarizations (the spectral transmission curves are separated by nearly 100 Å, cf. Fig. 5). Differences in light absorption are thus unimportant as long as the projections of E on the spontaneous polarization axis are the same. The critical nonlinear increment near the IC phase transition is therefore significant only for the refractive index n_x and increases as $\hbar\omega$ approached E_g, which occurs if λ is decreased or if the gap E_g is narrowed by changing the composition x.

In the above discussion we have considered self-focusing near the Lifshitz point. However, we also investigated $(Pb_y Sn_{1-y})_2P_2Se_6$ solid solutions with a broad IC phase (i.e., far from the Lifshitz point). The width of the IC phase for these solutions increases from 28K at $y = 0$ to 105K at $y = 0.4$. Moreover, E_g increases with y, so that radiation from He – Ne and Kr lasers can be used. We found that there was less self-focusing in the IC phase as y increased. Thus, d/d_0 was equal to 9, 5, and 1 for solutions with $y = 0$, 0.2, and 0.4, respectively, for $P = 0.06$ W ($\lambda = 6764$ Å). For $y = 0.4$, self-focusing was not observed even for $\lambda = 6471$ Å at $P = 0.06$ W.

DISCUSSION

We will analyze the experimental data discussed above by using the thermodynamic potential

$$\Phi = \Phi_0 + \frac{\alpha}{2}\eta^2 + \frac{\beta}{4}\eta^4 + \delta(\nabla\eta)^2$$

$$+ g(\nabla^2\eta)^2 - r\eta^2E^2 - \varkappa(\nabla\eta)^2E^2 \qquad (2)$$

for an intrinsic ferroelectric with a spatially nonuniform order parameter η. The coefficients β, g, r, and $\varkappa$ are positive and independent of T in the range considered, while $\alpha = \alpha_T(T - T_0)$ depends linearly on T, where T_0 is the Curie temperature. The coefficient δ can be expanded as a series $\delta = \delta_x(x - x_L)$ in terms of the concentration near the Lifshitz point.[1] In principle, the term ηE must also be retained

in (2), because the optical rectification in the crystal generates a *dc* electric field. However, the effect of the interaction ηE should be to make the IC phase narrower.[10] In the present case the ηE term is probably negligible.

We denote the renormalized expansion coefficients in (2) by

$$\alpha/2-rE^2\equiv\alpha^*, \quad \delta-\varkappa E^2\equiv\delta^*. \tag{3}$$

At the Lifshitz point we have[1,2]

$$\alpha^*\equiv 0, \quad \delta^*\equiv 0. \tag{4}$$

Below the Lifshitz point, $\delta^*<0$ and a phase transition occurs from the initial para-phase to the IC phase with wave vector

$$q_0^2=-\delta^*/2g. \tag{5}$$

The concentration and field dependences

$$T_i-T_c\approx(\delta^*)^2/g\alpha_T=[\delta-\varkappa E^2]^2/g\alpha_T \tag{6}$$

hold in the IC region, starting at the Lifshitz point. It is clear from (4) that the laser field splits the phase transition if $E^2>\delta/\varkappa$, while (6) implies that the width of the IC phase depends quadratically on P for fixed x and that the photoinduced broadening increases with x as we move away from the Lifshitz point. This behavior is observed experimentally.

We now estimate the value of the coefficient $\varkappa$ in (1). Assume that an IC phase of width 1 K forms in a crystal with concentration $x=x_L$ for a laser beam of power 0.5 W (these are close to the experimental values). If we take $\delta=0$, $g\approx q_{\max}^{-4}$ (where $q_{\max}$ is the diameter of the Brillouin zone), Curie-Weiss constant $C=\alpha_T^{-1}\approx 10^5$ K^{-1} (Ref. 9), laser field $E\sim 10^4$ V/cm, and interatomic field $E_m\sim 10^6$ V/cm, we find that $\varkappa\sim 30q_{\max}^{-2}E_m^2$ from the relation $(C\varkappa^2/g)(E/E_m)^4=1$, which follows from (6). According to (3) and (5), the wave vector of the structural deformation should increase with P as $q_0\sim(P-P_L)^{1/2}$ in the IC phase of an intrinsic ferroelectric; this dependence is similar to the concentration behavior $q_0\propto(x-x_L)^{1/2}$. We also note that because of the renormalization (3) of the coefficient α, the laser light field alters the temperature T_0 for direct transition from the para to the ferroelectric phase.

Finally, we consider the self-focusing of low-power laser radiation in the IC phase. Heating and the electrooptic and photoelastic effects are the primary factors[11] responsible for nonlinear lens-like action in crystals. The self-focusing is probably not due to heating or electrooptic effects, because otherwise one could not explain why self-focusing occurs only in the IC phase and not in the para and ferroelectric phases. The most plausible explanation is that the photoelastic effect plays a dominant role. In this case the nonlinear focusing occurs because the crystal deformation produced by electrostriction is nonuniform over the beam section.

The lattice compliance to deformations with $q_0\neq 0$ increases abruptly during formation of the IC phase, because the mixed system of linearly coupled acoustic and soft optical branches is unstable.[12] Since the piezooptical coefficients are proportional to the elastic compliance, strong self-focusing may occur if the compliance increases at the characteristic wave vectors $k\sim 10^3$ cm^{-1} for the radial intensity distribution in the waist of the laser beam. However, this self-focusing must be highly anisotropic, whereas little anisotropy is found experimentally.[5] We can account for this discrepancy if the deformation in the low-symmetry monoclinic crystal is due to a combination of several elastic moduli. In addition, the nonlinear coupling between the elastic waves and the soft optical branch is also important. For instance, it was found in Ref. 4 that the velocity of longitudinal ultrasound (which drops abruptly at T_i and T_c) is also lower in the IC phase near the Lifshitz point in $Sn_2P_2(Se_xS_{1-x})_6$. This decrease is correlated with the temperature behavior of the self-focusing.[5]

As we go away from the Lifshitz point, q_0 moves continuously from the center of the Brillouin zone and may reach $\sim 10^7$ cm^{-1} for $Sn_2P_2Se_6$. This apparently explains why self-focusing occurs in crystals with $x>x_L$ but not for $x<x_L$ (in the latter case, $q_0=0$). The IC phase becomes much broader when some of the Sn is replaced by Pb, so that $q_0\gg k$ and the self-focusing disappears.

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