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Photoluminescence determination of the pressure and temperature of the shock wave induced by a picosecond laser pulse in the layered semiconductor GaSe

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The pressure and temperature of the shock waves generated by a picosecond laser pulse in the layered semiconductor gallium selenide were determined by shock-induced changes of the photoluminescence spectra. The peak pressure was measured to be about 13 kbar, while the temperature remained the same during the measured time range. Our results are consistent with the pressure measurements made with a piezoelectric transducer.

INTRODUCTION

Shock-wave dynamics is an active area of research because of its technological importance.[1] The high pressure and high temperature associated with shock waves can initiate chemical and physical processes in materials such as bond dissociations,[2,3] structural phase changes,[4] and redistribution of energy among vibrational[5] and electronic states.[6] Since many of the above phenomena take place on a picosecond time scale, new ultrafast diagnostic methods are required to resolve them. There are various techniques to generate and characterize shock processes. The current techniques of generating shock waves, namely impact production[7] and rapid localized heating via nanosecond laser pulses,[8] do not provide the overall necessary time resolution.

It is well known that the semiconductor energy band structure changes under pressure. For GaSe, the energy band-gap shrinks under pressure[9,10] causing the shift of both the absorption and luminescence spectra.[11–13] In this paper, we present the first time-resolved photoluminescence measurements to monitor the onset of the shock wave in the layered semiconductor GaSe.[14] We used the excite-and-probe technique to determine the shock-wave pressure and temperature microscopically in a semiconductor on a picosecond time scale. We find that the peak pressures as determined by the photoluminescence technique are of the same order of magnitude for equal laser-pulse energy, such as those measured by a piezoelectric transducer.[15] This shows that picosecond laser techniques are not only useful in the generation of shock waves, but also useful in the study of shock effects in condensed matter. Although the ability to simultaneously measure temperature accurately in the shocked state exists with the technique described in this paper, no temperature changes were observed because of the small (~ 13 kbar) shock pressures produced in the present study.

METHODS AND MATERIALS

The shock wave in GaSe was launched from an aluminum-metal foil which was in contact with the GaSe sample. The shock wave was generated in the foil by ablation via the absorption of a focused intense picosecond laser pulse. As the shock propagated through the GaSe, its effect was studied by the spectrum analysis of the photoluminescence generated by a weak picosecond probe laser pulse. A schematic diagram of the experimental setup is shown in Fig. 1. The laser system has been described elsewhere.[15] It consists of an oscillator and three amplifiers. The system produces an 8 ps, 1054 nm pulse which is used for the generation of shock waves in the aluminum foil. Part of the 1054 nm pulse was frequency doubled by passing it through a potassium dihydrogen phosphate (KDP) crystal to produce a 6 ps, 527

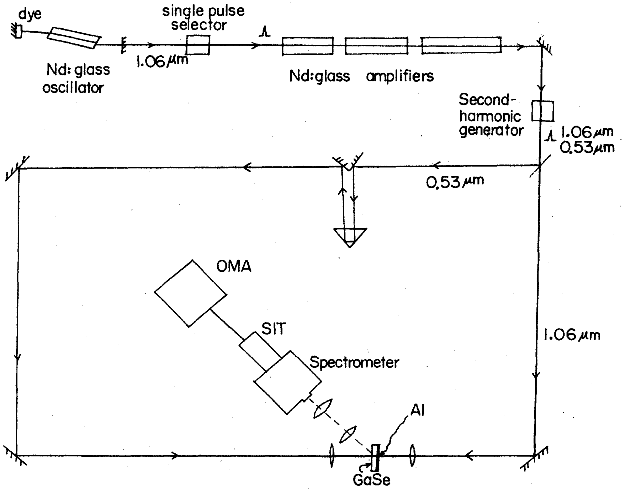

FIG. 1. Schematic of the experimental setup.

nm probe laser pulse for photoluminescence generation in the GaSe sample. The 527 nm pulse was optically delayed so that it arrived at the GaSe after the 1054 nm pulse hit the aluminum foil to allow time for the shock wave to reach the probe region near the surface of the GaSe. By changing the delay time τ between the 1054 and 527 nm pulses, we were able to study the profile of the shock effect in the GaSe and obtain information of the pressure and temperature in the shock waves.

The GaSe sample had a thickness of about 20 μm with the c axis of the crystal parallel to the thickness of the sample. The sample was pressed against a 35 μm thick aluminum foil and they were loaded between two $\frac{1}{2}$ inch thick Pyrex plates. Mineral oil or water was added to all interfaces to ensure efficient mechanical coupling. A $\sim$30 mJ, 1054 nm, 8 ps pulse was focused by a 18 cm focal-length lens to a $\sim$0.75 nm diameter spot on the aluminum foil at the aluminum-Pyrex interface while a $\sim$50 μJ, 527 nm, 6 ps probe pulse was focused to a $\sim$0.5 mm diameter spot by a 10 cm focal-length lens on the GaSe at the GaSe-Pyrex interface right behind the 1054 nm laser spot on the Al foil. Care was taken in aligning the two laser beams so that the shock was launched from the aluminum foil into the laser probe region in the GaSe. The thickness of the probe region is roughly equal to the penetration depth of the 527 nm laser pulse which is about 5 μm. The photoluminescence of the GaSe was collected and passed into a $\frac{1}{4}$-m Spex spectrometer, detected by a Princeton Applied Research (PAR) silicon intensified target (SIT), and analyzed by a PAR optical multichannel analyzer (OMA) II. All experiments were performed at room temperature. The energy of the pulse was monitored by a photodiode and measured on an oscilloscope. The spectral shift in the GaSe photoluminescence changed monotonically over the range of laser energy employed in our study. As a result, the energy of the 1054 nm laser pulse was kept constant to within 10% and so was the energy of the 527 nm pulse to normalize the probing effect. The photoluminescence spectra were measured as a function of delay time between the 1054 and 527 nm pulses. The zero time was determined by an optical Kerr gate.[16]

RESULTS AND DISCUSSION

The photoluminescence spectra of the GaSe excited by the 527 nm laser pulse are shown in Fig. 2. Unlike the other figures, Fig. 2(a) is obtained without the 1054 nm laser pulse hitting the aluminum foil. Figures 2(b), 2(c), and 2(d) are obtained with the 527 nm pulse delayed by 11, 18, and 29.5 ns with respect to the 1054 nm pulse, respectively. The peaks of the luminescence for Fig. 2(c) and 2(d) are shifted to a lower energy. A series of the GaSe luminescence spectra have been measured for delay time up to 45 ns. We find that the red-shift of the GaSe luminescence peak starts at around 13–14 ns delay time, maximizes at $\sim$18 ns, and decreases slowly for a longer delay time.

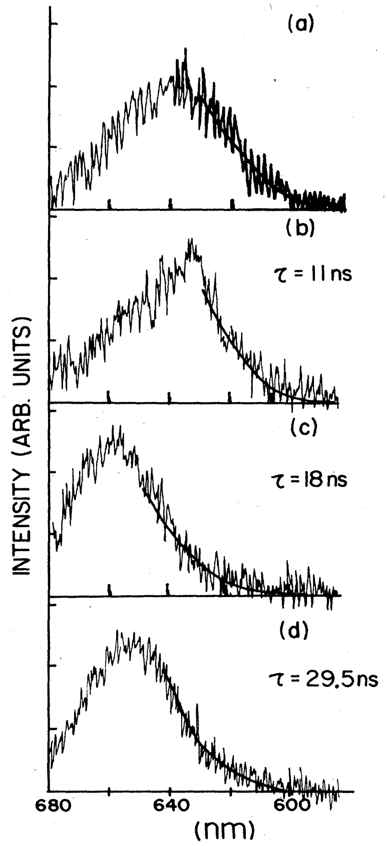

FIG. 2. Photoluminescence spectra of GaSe excited by 527 nm laser pulses, and shocked by a 1054 nm laser pulse on the attached foil. (a) No excitation from 1054 nm laser pulses on Al foil, $E_p=1.954$ eV. (b) Delay time between 1054 and 527 nm pulses is 11 ns, $E_p=1.954$ eV. (c) Delay time is 18.1 ns, $E_p=1.878$ eV. (d) Delay time is 29.5 ns, $E_p=1.906$ eV.

The photoluminescence spectra and kinetics of the ϵ-GaSe excited by 527 nm picosecond laser pulses were previously reported by Yao and Alfano.[17] There are two components in the spectra. The first component is the result of a spontaneous emission which is due to the exciton-carrier scattering when the excitation intensity is low and due to the electron-hole recombination when the excitation intensity is high. The second component is caused by a stimulated emission which is probably due to the recombination across the indirect band gap. In this experiment, the intensity of the 527 nm laser pulse was kept low to avoid stimulated emission.

The exact form of time-integrated photoluminescence intensity of the high-energy tails of the GaSe spectra is[17]

$$I(\hbar\omega)\propto\int_0^\infty dx\{\hbar\omega-[E_g(x)+P(x)C]\}^{1/2}\times\exp\left[-\alpha x-\frac{\hbar\omega-[E_g(x)+P(x)C]}{kT_L(x)}\right], \tag{1}$$

where x is the distance measured from the surface of GaSe along the c axis, α is the absorption coefficient for the probe pulse, $I(\hbar\omega)$ is the intensity of the spectra at different energies $\hbar\omega$, $E_g(x)$ is the energy gap of GaSe at lattice temperature $T_L(x)$, $P(x)$ is the shock-wave pressure, and C is the pressure coefficient of the band gap. Since both the shock-wave pressure and temperature profiles are not known in advance, it is necessary to use an approximation given by Eq. (2), below, in order to extract the temperature and the pressure of the shock wave, i.e.,

$$I(\hbar\omega) \propto (\hbar\omega - \tilde{E}_g)^{1/2} \exp[-(\hbar\omega - \tilde{E}_g)/kT_e] , \qquad (2)$$

where $\tilde{E}_g$ is the measured direct band gap which is related to the peak energy of the photoluminescence by $E_p = \tilde{E}_g + \frac{1}{2}kT_e$, T_e being the electronic temperature. The electronic temperature T_e and the lattice temperature T_L are assumed to be locally equal because of rapid thermal relaxation.[17] In Eq. (2), the electronic temperature T_e is assumed constant within the absorption depth of a 527 nm laser pulse.

The $\tilde{E}_g$ is related to the direct energy gap E_g by $\tilde{E}_g = E_g + PC$, where P is the shock-wave pressure which is also assumed constant within the absorption depth of a 527 nm pulse. The value of E_g is 2.02 eV for ϵ-GaSe at $T_L = 300$ K and shifts to the red by 0.47 meV/K.[18] According to the result of Belen'kil *et al.*,[10] the C value of GaSe under uniaxial pressure is less than zero when $T_L > 80$ K. The pressure coefficient of the GaSe band-gap energy is derived from the optical-absorption study[11,12] ranges from -4.2 to -6.9 meV/kbar at room temperature. We have measured the emission spectra of GaSe in a diamond anvil cell at about 350 K. The C value obtained is about -6 meV/kbar.[13]

Equation (2) was used to fit (solid line) the high-energy tails of Figs. 2(a)–2(d). For Fig. 2(a), the peak value is $E_p = 1.954$ eV and $T_e = 434$ K. The electronic temperature T_e is higher than the room temperature, 300 K, due to the heating of the GaSe sample by the tightly focused 527-nm laser pulses. The temperature rise of the lattice can be estimated using thermal pressure generated by this probe pulse inside the GaSe sample. The pressure $P(x) = d\epsilon_{\text{abs}}(x)/dx = \alpha\epsilon(0)e^{-\alpha x}$, where $\epsilon_{\text{abs}}(x) = \epsilon(0)e^{-\alpha x}$, $\epsilon(0)$ is the reflectance corrected energy per unit area on the GaSe surface ($\sim 1.3 \times 10^5$ ergs/cm^2), and α is the absorption constant at 527 nm ($\sim 2 \times 10^3$ cm^{-1}).[19] Assuming the ideal-gas model can be applied, the change of the temperature ΔT is $\Delta P/nk = 88$ K, where $\Delta P = P_{\text{surface}} = 0.26$ kbar, n is the molecular density of GaSe ($\sim 2.1 \times 10^{22}$ cm^{-3}), and $k = 1.38 \times 10^{-16}$ ergs deg^{-1} is Boltzmann's constant. This increase ΔT on the surface of the probe region is the same order of magnitude as the experimentally observed value of 134±20 K in Table I. The simple ideal-gas approximation is expected to give a ΔT with approximately a factor of 2 smaller than the true ΔT because the assumption corresponds to a Grüneisen parameter of $\frac{2}{3}$ rather than the $\sim\frac{4}{3}$, which is usually representative of room-temperature lattice modes.[20] Using a temperature T_e of 434 K and the red-shifted peak observed (1.954 eV), the equation $\tilde{E}_g = E_p - \frac{1}{2}kT_e$ yields the value $\tilde{E}_g = 1.935$ eV. This is consistent with the calculated value E_g due to the thermal red-shifting using the equation $\tilde{E}_g = 2.02$ eV–0.47 meV $(T_e - 300) = 1.938$ eV.[19]

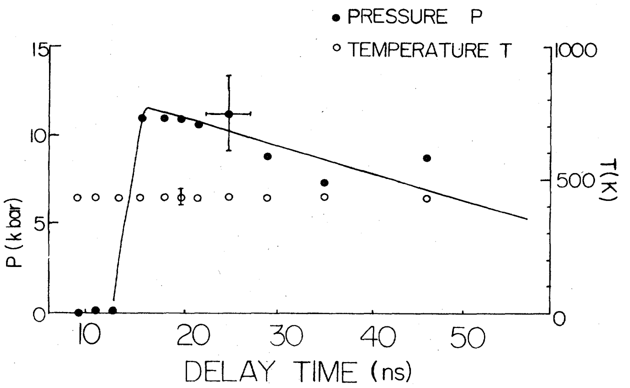

FIG. 3. The fitted temperatures and pressures of shock waves in GaSe at various delay times from 9 to 45 ns. The open circles represent the temperatures T_e, and the solid circles represent the pressures.

Now the form for $I(\hbar\omega)$ in Eq. (1) can be used to refit the high-energy tails of the curves in Fig. 2. Assuming that $P(x)$ is the same as the pressures obtained in Fig. 3, $T_L(x)$ is given by $300 + (\Delta T)\exp(-\alpha x)$, $\Delta T = 134$ K, and $C = -6$ meV/kbar, Eq. (1) fits the curves well. The parameters used to fit the high-energy tail of the spectra are given in Table I. There is an uncertainty in the x value in Eq. (1). The GaSe photoluminescence decay time is ~ 400 ps,[17] and for shock propagation velocity of $\sim 2 \times 10^5$ cm/s the corresponding pressure location uncertainty is ~ 0.8 μm.

The extracted average pressures and temperatures at different delay times are plotted in Fig. 3. The open circles indicate the temperatures and the solid circles indicate the shock-wave pressure. The pressure increases from 0 kbar at 13 ns to ~ 13 kbar at 17 ns, and decreases to ~ 7 kbar at 35 ns. The peak shock pressure has the same order of magnitude at that measured with the transducer for shock waves produced under similar conditions.[15] The temperature remains at about 434 K from 9 to 45 ns. More detailed study of the shock front risetime

TABLE I. Parameters used to fit the high-energy tails of the spectral profiles displayed in Fig. 2.

Figure	Delay time (ns)	E_p (eV)	T_e (K)	$\tilde{E}_g$ (eV)	E_g (eV)	P (kbar)
2(a)		1.954±0.010	434±20	1.935±0.011	1.938	0
2(b)	11	1.954	434	1.935	1.938	0
2(c)	18	1.878	434	1.859	1.938	13
2(d)	29.5	1.906	434	1.886	1.938	8.7

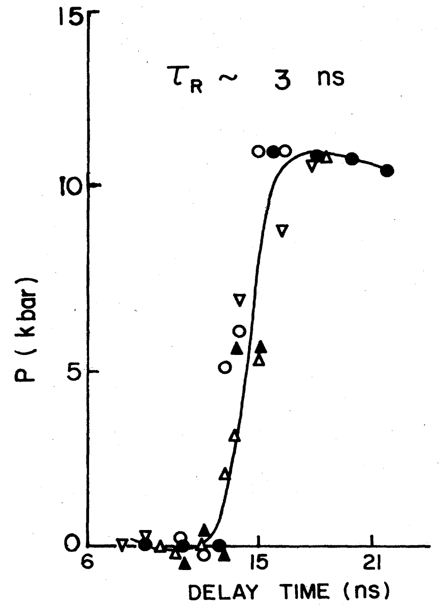

FIG. 4. A more detailed study of the shock front risetime τ_R. Data are obtained from different runs on the same GaSe sample.

is shown in Fig. 4. The risetime of the pressure is ~ 3 ns. The time resolution of the measurements is restricted by the GaSe photoluminescence decay time which is ~ 400 ps (Ref. 17) at low-excitation intensity and the shock transit time through the probing region which is about 2 ns in our experiment.

The shock-wave risetime can be estimated from the bulk velocity as follows. The plastic wave shock velocity (13 kbar is certainly above the yield stress for GaSe) is associated with the bulk velocity.[20] Yet 13 kbar represents a relatively low shock amplitude so that the shock velocity can be estimated from the infinitesimal bulk velocity given[21] by $C_B=(C_1^2-4/3C_s^2)^{1/2}$, where C_1 and C_3 are the longitudinal and shear (transverse) sound velocities. If the GaSe parallel to the c-axis values are $C_1=2.5\times10^5$ cm/s, $C_s=1.2\times10^5$ cm/s,[22] one finds $C_B\cong2.1\times10^5$ cm/s. Similarly, for aluminum, $C_1=6.3\times10^5$ cm/s, $C_s=3.1\times10^5$ cm/s, and $C_B\cong5.2\times10^5$ cm/s. Since the elastic-plastic signal propagates at the bulk velocity, the transit time through the Al foil and GaSe layer is

$$t_B=35\ \mu\text{m}/C_B(\text{Al})+20\ \mu\text{m}/C_B(\text{GaSe})\cong16.9\ \text{ns}\ .$$

The transit time for the small amplitude elastic precursor is

$$t_e=35\ \mu\text{m}/C_1(\text{Al})+20\ \mu\text{m}/C_1(\text{GaSe})\cong13.6\ \text{ns}\ .$$

Therefore, the shock-wave risetime should be $t_B-t_e=3.3$ ns which agrees with the experimental risetime of 3 ns.

The transit time of the longitudinal waves through both the Al foil and the GaSe sample is 13.6 ns which should be equal to the threshold time at which the shock-wave pressure starts to increase. The observed threshold time is about 13 ns which is close to the calculated 13.6 ns. The difference may be due to unevenness in the Al and the GaSe thickness.

Calculating the laser-induced pressures expected in the GaSe sample is a different task usually requiring the running of a complicated computer code.[23] One can, however, estimate the decay time of the laser-induced shock wave relatively simply by considering the volume expansion (and the associated pressure decrease) of the plasma contained between the unvaporized portion of the aluminum foil and the confining Pyrex plate.

For simplicity, we assume that a plasma pressure of 10 kbar is supporting a peak pressure of about 10 kbar in the GaSe and calculate the time necessary for that plasma pressure to decay to 1 kbar. That time must be of the same order of magnitude as the approximately 70 nsec seen in Fig. 3. If the plasma is considered to be an ideal gas undergoing adiabatic expansion from $P_0=10$ kbar to some pressure P, then

$$P=P_0\left[\frac{A_0}{A}\right]^{\gamma}\left[\frac{l_0}{l}\right]^{\gamma}\ , \tag{3}$$

where A and l are the plasma cross section and thickness (in the direction of shock propagation), respectively. Allow, again for simplicity, the plasma to be monatomic ($\gamma=1.4$), and the expansion to be one dimensional ($A=A_0$).

The plasma expansion time can then be estimated from

$$l=l_0+2u_pt\ , \tag{4}$$

where u_p is the particle (flow) velocity at the aluminum-plasma boundary with the expansion assumed symmetrical (even though one boundary is characterized by aluminum and the other by Pyrex). u_p can be estimated from $\rho_aU_su_p=P^*$, where $P^*=5$ kbar is an average pressure, $\rho_a=2.7$ g/cc, and $U_s=5.2\times10^{15}$ cm/s is the bulk velocity in the aluminum (the particle velocity is continuous across the plasma-aluminum interface). From Eqs. (3) and (4),

$$t=\left[\left[\frac{P_0}{P}\right]^{1/\gamma}-1\right]\frac{\rho_al_0U_s}{2P^*}\ , \tag{5}$$

so that the l_0 associated with 10 kbar determines the expansion time to the pressure P.

A value for l_0 can be obtained by assuming an "initial" plasma dimension equal to the vaporization depth l_{00}, in the aluminum, a corresponding pressure P_{00}, and then using Eq. (3) to calculate the adiabatic expansion to 10 kbar. For an optical-absorption constant $\alpha'\cong10^6$ cm^{-1} at 1054 nm, $l_{00}=0.02$ μm, is reasonable.

P_{00} can be crudely approximated from

$$P(x)=\frac{d\epsilon_{\text{abs}}}{dx}=\alpha'\epsilon(0)e^{-\alpha'x}\ , \tag{6}$$

with $\epsilon(0)\cong10^7$ ergs/cm^2 ($\sim7\times10^7$ ergs/cm^2 focused laser pulse and 90% reflectivity). Thus, $P(0)\cong10$ Mbar and $P(0.02\ \mu\text{m})\cong750$ kbar. Because of competing processes (e.g., acoustic losses during laser deposition time and lateral expansion effects) the true $P(0)$ will be lower than the 10 Mbar estimate. Thus, an approximate average value of $P_{00}=1$ Mbar will be used.

The approximate result for l_0 is then, via $l_0 \cong l_{00} \cdot (P_{00}/P_0)^{1/\gamma} = 0.54\ \mu\text{m}$. That value, when substituted into Eq. (5) yields $t = 38$ ns, in very good agreement (considering the crude approximations used) with the 70 ns of Fig. 3.

In conclusion, the techniques of time-resolved photoluminescence measurements of the pressures and temperatures of the picosecond laser-induced shock wave in a semiconductor are described. The peak pressure measured in our experiment is the same order of magnitude as that measured by the quartz transducer using laser pulses of the same energy.[15] The temperature of the unshocked or shocked semiconductor remains almost unchanged.

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[1] G. E. Duvall, Inter. Sci. and Technol. **16**, 45 (1963).

[2] S. J. Arnold, W. G. Brownlee, and G. H. Kimbell, J. Phys. Chem. **74**, 8 (1970).

[3] G. A. Adadurov, I. M. Barkalov, V. L. Tal'roze, V. I. Gol'danskii, A. N. Dremin, T. N. Ignatovich, A. N. Mikhailov, and P. A. Yampol'skii, Polym. Sci. USSR **7**, 196 (1965).

[4] D. B. Hayes, J. Appl. Phys. **45**, 1208 (1974).

[5] D. S. Moore, S. C. Schmidt, and J. W. Shaner, Phys. Rev. Lett. **50**, 1819 (1983).

[6] G. E. Duvall, K. M. Ogilvie, R. Wilson, P. M. Bellamy, and P. S. P. Wei, Nature (London) **296**, 846 (1982).

[7] S. B. Kormer, A. I. Funtikov, V. D. Urbin, and A. N. Kolesnikova (unpublished); A. H. Jones, W. M. Isbell, and C. J. Maiden, J. Appl. Phys. **37**, 3493 (1966).

[8] R. M. White, J. Appl. Phys. **34**, 2123 (1963); N. C. Anderholm, Appl. Phys. Lett. **16**, 113 (1970).

[9] A. J. Niilisk and J. J. Kiss, Phys. Status Solidi **31**, K91 (1969).

[10] G. L. Belen'kil, E. Yu, Salaev, R. A. Suleimanov, and E. I. Mirzoev, Fiz. Tverd. Tela (Leningrad) **22**, 3153 (1980) [Sov. Phys.—Solid State **22**, 1842 (1980)].

[11] J. M. Besson, K. P. Jain, and A. Kuhn, Phys. Rev. Lett. **32**, 936 (1974).

[12] V. V. Panfilov, S. I. Subbotin, L. F. Vereskchagin, I. I. Ivanov, and R. T. Molchanova, Phys. Status Solidi B **72**, 823 (1975).

[13] K. P. Leung, R. R. Alfano, and H. King (unpublished).

[14] K. P. Leung, S. S. Yao, A. G. Doukas, R. R. Alfano, and P. Harris, Bull. Am. Phys. Soc. **24**, 724 (1984).

[15] K. P. Leung, S. Yao, and R. R. Alfano, *Shock Waves in Condensed Matter 1983,* edited by J. R. Asay, R. A. Graham, and G. K. Straub (Elsevier, Amsterdam, 1984), p. 343.

[16] M. A. Duguay and J. W. Hansen, Appl. Phys. Lett. **15**, 192 (1969).

[17] S. S. Yao and R. R. Alfano, Phys. Rev. B **27**, 2439 (1983).

[18] J. P. Voitchovsky and A. Mercier, Nuovo Cimento **22B**, 273 (1974).

[19] G. Antonioli, D. Bianchi, V. Emiliani, P. Podini, and P. Franzosi, Nuovo Cimento **54B**, 211 (1979).

[20] N. W. Asheroft and N. D. Mermin, *Solid State Physics* (Holt, Rinehart and Winston, New York, 1976), pp. 494 and 495.

[21] Ya. B. Zel'dovich and Yu. P. Rarzer, *Physics of Shock Waves and High-Temperature Hydrodynamic Phenomena* (Academic, New York, 1967), Chap. 11.

[22] Kh. M. Khalilov and K. I. Rzaev, Kristallografiya **11**, 929 (1966) [Sov. Phys.—Crystallogr. **11**, 786 (1967)].

[23] D. Salzmann, S. Eliezev, A. D. Krumbein, and L. Bitter, Phys. Rev. A **28**, 1738 (1983).

[24] C. H. Skeen, J. D. O'Keefe, D. L. Crouse, C. N. McDowell, and C. M. York (unpublished); P. Harris, J. Appl. Phys. **49**, 1281 (1981).