Nonlinear optical properties of incommensurate phase of a ferroelectric crystal

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The ferroelectric crystal $(NH_4)_2BeF_4$ was investigated by the optical second harmonic generation (SHG) method. It was observed that sufficiently intense lasing is observed in the incommensurate phase only if the radiation propagates along the structure modulation direction, regardless of the polarizations of the pump and second-harmonic fields. These results are explained on the basis of methods of the theory of four-dimensional groups with account taken of the change in the local characteristics of the crystal when modulation of its structure sets in. It follows from the equation obtained for the SHG that the presence of incommensurate modulation changes the synchronism conditions. The approach employed can be easily extended to include other optical properties of incommensurate structures.

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INTRODUCTION

Nonlinear-optics methods, particularly generation of harmonics, are now widely used to study the structures and properties of solids. These effects are due to nonlinearities of the dielectric susceptibility of the medium, which are described by tensors of third and higher ranks. In the case of perfect crystals, the symmetry of their structure imposes a number of restrictions on these tensors, and the presence of translational invariance makes it easy to obtain the connection between the local and macroscopic nonlinear dielectric susceptibilities and thus measure in experiment the local characteristics of the medium. Thus, the nonlinear dielectric susceptibility that gives rise to SHG is described in the dipole approximation by a third-rank tensor d_{ijl}; from group-theoretical considerations, all its components vanish only if the crystal unit cell is centrosymmetric.[1] This permits effective utilization of the SHG method for the study of phase transitions connected with the onset of acentric structures, and particularly transitions into ferroelectric phases. The available data[2,3] on the connection between the values of d_{ijl} and the spontaneous polarization $\mathbf{P}_S$ cannot only reveal the presence of a polar ferroelectric phase, but in a number of cases also to determine the temperature dependence of $\mathbf{P}_S$. The high sensitivity of the methods makes these studies more accurate than, say, direct measurements of the spontaneous polarization. Since the spontaneous polarization in ferroelectric crystals is either a parameter of the ordering (intrinsic ferroelectrics) or is closely connected with it (extrinsic ferroelectrics), the SHG method can yield data on the order parameter and on its dependence on external factors (temperature, pressure, etc.).

In many recently discovered crystals[4-11] an intermediate phase is observed between the para- and ferroelectric phases, with a spatially inhomogeneous order parameter. The possible existence of such structures was predicted in Refs. 12 and 13, where their onset was attributed to condensation of the soft mode in other than a singular point of the Brillouin zone of the paraphase. In fact, in crystals with K_2SeO_4 structure phonon condensation was observed at the point

$$\mathbf{q}=(1-\delta)\mathbf{a}^*/l, \tag{1}$$

where δ is the incommensurability parameter, l is an integer, and $\mathbf{a}^*$ is the paraphase reciprocal-lattice vector.[5,6,9] This changes not only the point group of the crystal, but also the values of the elementary translations. To describe the produced phase it is necessary either to consider a superstructure with a macroscopic and temperature-dependent period, or else dispense entirely with consideration of translational invariance in its usual sense.[14] In any case, this leads to an inhomogeneous change of the local values of d_{ijl} and should therefore be reflected in the SHG process, and was in fact first observed experimentally in Ref. 15. Since the appearance of macroscopic inhomogeneities of the crystal structure complicates greatly the measurements of its local characteristics, experimentally of this kind become particularly important.

MEASUREMENT PROCEDURE

The experiments were performed on the $(NH_4)BeF_4$ crystal. According to Refs. 4 and 5, this crystal is incommensurate in the temperature interval from $T_c = 175$ K to $T_i = 185$ K. The space groups of its ferroelectric ($T < T_c$) and paraelectric ($T > T_c$) phases are $Pn2_1a$ and $Pnma$ respectively. Consequently, for both the unit cell and for the crystal as a whole $d_{ijl} = 0$; the nonzero components in the ferroelectric phase are d_{211}, d_{222}, d_{233}, d_{112}.

The samples were rectangular parallelepipeds ($4 \times 5 \times 6$ mm) with edges parallel to the crystallographic axes. At this syngony they coincide with the axes of the refraction ellipsoid, so that when the pump radiation propagates parallel to one of the crystallographic axes with polarization along another axis there is no birefringence. This makes it possible to measure each of the components of the tensor d_{ijl} separately, as well as to check on the accuracy of the orientation during the course of the experiment. The axes are oriented accurate to within ±15′. The experiments were performed on six samples and the results averaged.

To measure the SHG intensity $I(2\omega)$, the pumping was with coherent-radiation pulses of wavelength $\lambda = 1.06$

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μm, repetition frequency 25 Hz, and power 2 MW. The SHG intensity was registered with an AI-4096 pulse-height analyzer and fed to an automatic recorder. The registration system is described in greater detail in Ref. 16. The temperature variation was kept constant and did not exceed 0.1 K/min during the entire experiment, so that $I(2\omega)$ could be measured continuously with accuracy ±10%.

EXPERIMENTAL RESULTS

In accord with the selection rules, $I(2\omega)$ in the paraelectric phase should vanish in the dipole approximation. Highly sensitive apparatus, however, records an SHG signal even from centrosymmetric crystals. This may be due to imperfection of the crystal structure, as well as to the quadrupole, octupole, etc. effects. According to Ref. 1, the contribution from the quadrupole effects to $I(2\omega)$ does not exceed 10^{-4} of $I(2\omega)$ in the d_{111} component of quartz even if the synchronism conditions are satisfied. Kurtz[17] concluded on the basis of numerous experimental data that the relative SHG intensity in centrosymmetric crystals does not exceed 10^{-3}. In our case the intensity $I(2\omega)$ in the paraelectric phase of $(NH_4)_2BeF_4$ did not exceed $10^{-4}-10^{-3}$ of the SHG intensity in quartz regardless of the beam direction. This signal is apparently due mainly to crystal-structure defects.

Sufficiently intense SHG is observed in the incommensurate phase only if the radiation propagates along the a axis. In this phase $I(2\omega)$ is maximal near T_c (on the order of 10^{-2} of the SHG in quartz), and increases sharply on going into the heterophase, if the corresponding d_{ijl} is allowed, or drops to the level of the signal in the paraphase if $d_{ijl}=0$ (Fig. 1). The highest intensity is observed in the component d_{333}, a certain stretching of the signal being observed into the ferroelectric phase; this signal does not exceed 0.1 of the intensity at the maximum. It appears that the effect in question is connected with a certain smearing of the phase transition. When the sensitivity of the apparatus was increased (the averaging was carried out over a larger number of pulses), a similar effect was observed also in the remaining d_{ijl} components. In all other respects the results agree within the limits of error with the data of Ref. 15.

When the radiation propagates perpendicular to the a axis, the intensity $I(2\omega)$ remains practically unchanged in the transition from the paraphase to the incommensurate phase, regardless of the polarizations of the pump and second-harmonic fields, and increases strongly on

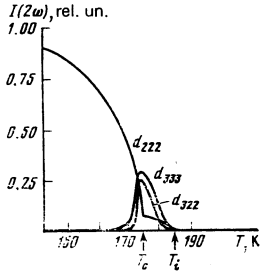

FIG. 1. Temperature dependence of the SHG intensity in the crystal $(NH_4)_2BeF_4$. The radiation propagates along the a axis.

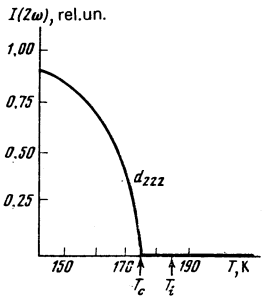

FIG. 2. Temperature dependence of the SHG intensity in the crystal $(NH_4)_2BeF_4$. The radiation propagates along the c axis.

going to the heterophase if the corresponding component $d_{ijl}\neq 0$ (Fig. 2).

DISCUSSION OF RESULTS

1. Effect of structure modulation on the local crystal characteristics

To explain the results, we examine the effect of structure modulation on the local properties of the incommensurate phase of the crystal. In the initial paraelectric phase the coordinates of the atoms were described by the vectors

$$\mathbf{R}_0(\mathbf{n},\mu,\varkappa)=\mathbf{n}+\mathbf{r}_0(\mu,\varkappa), \tag{2}$$

where

$$\mathbf{n}=n_1\mathbf{a}+n_2\mathbf{b}+n_3\mathbf{c},$$

n_i are integers; **a**, **b**, and **c**, are the basis vectors of the structure; $\varkappa$ is the number of the molecular grouping of the atoms in the cell; n is the number of the atom in the given group. Upon condensation of the soft mode with wave vector **q** the atoms shift to the points

$$\mathbf{R}(\mathbf{n},\mu,\varkappa)=\mathbf{R}_0(\mathbf{n},\mu,\varkappa)+\mathbf{u}(\mathbf{n},\mu,\varkappa), \tag{3}$$

where the displacement field **u** takes the form

$$\mathbf{u}(\mathbf{n},\mu,\varkappa)=\sum_{\{\mathbf{q}\}}\mathbf{f}(\mathbf{q},\mu,\varkappa)\exp(i\mathbf{q}\mathbf{n}). \tag{4}$$

Here $\{\mathbf{q}\}$ is the set of wave vectors making up the "star" of the soft mode, and **f** is the amplitude of the structure modulation. It is obvious that the set $\{\mathbf{f}\}$ is determined by the form of the oscillation corresponding to the soft mode.

Consider some local characteristic $w(\mathbf{n})$ of the n-th unit cell of the crystal in the paraphase. In the general case w can be a scalar, vector, or tensor of any rank. Since the structure in the paraphase is translationally invariant, we have

$$w(\mathbf{n})=w_p(\mathbf{n})=\text{const}.$$

The change of w on going to the incommensurate phase is due to the dissplacements of the atoms from their initial positions. As shown earlier, the structure becomes in this case translationally invariant and consequently the relation $w_{inc}=w_{inc}(\mathbf{n})$ assumes a more complicated form. If the displacements of the atoms are small enough (much less than the parameters of the initial unit cell), then the quantity $w_{inc}(\mathbf{n})$ can be expanded in powers of these displacements. Confining ourselves to the first two terms of the expansion and taking (4) into account, we get

$$w_{\text{inc}}(\mathbf{n})=w_p(\mathbf{n})+\frac{1}{2}\sum_{\{q\}} W(\mathbf{q})\exp(i\mathbf{qn}), \tag{5}$$

where

$$W(\mathbf{q})=2\sum_{i\mu\varkappa}\frac{\partial w_p(\mathbf{n})}{\partial u_i(\mathbf{n},\mu,\varkappa)}f_i(\mathbf{q},\mu,\varkappa). \tag{6}$$

The sum in (5) describes the changes produced in the local characteristic $w(\mathbf{n})$ by the modulation of the structure. Summing in (5) and using (1), we get

$$w_{\text{inc}}(\mathbf{n})=w_p(\mathbf{n})+W(\mathbf{q})\cos[2\pi n_1(1-\delta)/l]. \tag{7}$$

If we take the volume element to be the ferroelectric-phase cell and recognize that the value of q for a given crystal depends only on δ, then

$$w_{\text{inc}}(\mathbf{n})=w_p(\mathbf{n})+W(\delta)\cos(2\pi\delta n_1). \tag{8}$$

It must be recognized here that now

$$n=n_1\mathbf{a}_l+n_2\mathbf{b}+n_3\mathbf{c},$$

where $\mathbf{a}_l=l\mathbf{a}$, and in expression (6) for $W(\delta)$ we must sum over all the atoms of the cell of the ferroelectric phase. On going from the incommensurate to the ferroelectric phase, $\delta\to 0$ and

$$w_f(\mathbf{n})=w_p(\mathbf{n})+W(0). \tag{9}$$

As seen from (8) and (9), the changes of the local characteristic in transitions into the incommensurate and into the ferroelectric phases are determined respectively by the quantities $W(\delta)$ and $W(0)$. Since the derivatives in their definition (6) do not depend on δ, the changes of $w(n)$ are proportional to the displacements of the atoms in these transitions, which can be of the same order[7,9].

However, a substantial difference between $w_{\text{inc}}(\mathbf{n})$ and $w_f(\mathbf{n})$ can be the result of unequal symmetries of the structures of the corresponding phases. This is easiest to show by using group-theoretical methods. The corresponding formalism for commensurate phases has been adequately developed. The analogous methods for incommensurate phases are still under development and the question of the effect of the symmetry of a modulated structure on its local characteristic has heretofore not been considered.

2. Group-theoretical analysis of modulated structure

To construct the three-dimensional space group of an incommensurate phase it is necessary to find the common period of the functions (2) and (4). As follows from (1) and (4), this period is macroscopically large (at small δ) and temperature dependent (since $\delta=\delta(T)$]. The determination of the physical properties of phases with such superstructures is a very complicated task. To simplify the problem, it was proposed[14,18] to carry out the analysis in $(3+d)$-dimensional space $V_3\oplus V_d$, where V_3 is a three-dimensional Euclidean space with basis $\{\mathbf{a},\mathbf{b},\mathbf{c}\}$ and V_d is a d-dimensional Euclidean space of vectors that are reciprocal to $\{\mathbf{q}\}$. In our case, according to (1), $d=1$ and this is equivalent to a transition to four-dimensional space, where the additional coordinate is connected with the displacement of the field $\mathbf{u}$ relative to the initial structure. The symmetry of the incommensurate phase is described by four-dimensional space groups, a general analysis of which was presented earlier.[19] Methods of determining the four-dimensional group of a crystal modulated in accord with (3) and (4) were proposed in Ref. 14. The data on the form of the functions $\mathbf{f}$ were taken from Refs. 6 and 20. The obtained four-dimensional symmetry group of the incommensurate phase is made up of a translations subgroup and an identity element. A detailed derivation is given in Ref. 21. The projection of this group on three-dimensional space contains identity elements and translations in the bc plane whose values agree with the translations in the paraelectric phase. There is no translational invariance in the a direction. On going to the ferroelectric phase, the projection of the four-dimensional group obtained in this manner on V_3 agrees with $Pn2_1a$ with a doubling of the elementary translation along the a axis; this agrees with the experimental data[19] and confirms the validity of the analysis. The group-theoretical treatment shows therefore that a crystal in an incommensurate phase can be represented as layer perpendicular to the a axis, within which translational invariance is conserved. The rotation group of each layer is made up of only the identity element, so that all the components of the tensor d_{ijl} can be nonvanishing.

It must be noted that this result depends substantially on the form of the functions $\mathbf{f}$, i.e. on the form of the oscillation corresponding to the soft mode. Thus, if we neglect the orientational degrees of freedom of the molecular groups (the data of Ref. 6 show that their contribution to $\mathbf{f}$ is actually not too large), then the symmetry of the layers is higher, and this restricts the number of nonzero d_{ijl} components.

To draw quantitative conclusions concerning the character of the change of the values of d_{ijl} on going from layer to layer, we must use relations (5) and (6) between the crystal structure modulation parameters and its local characteristics.

3. Generation of optical second harmonic in the incommensurate phase of the crystal

The SHG intensity is determined by the value of the nonlinear polarization of the medium:

$$P_i^{(2)}(\mathbf{n},t)=4d_{ijl}(\mathbf{n})E_j^{(1)}(\mathbf{n})E_l^{(1)}(\mathbf{n})\exp i[(\mathbf{k}(1,j)+\mathbf{k}(1,l))\mathbf{n}-2\omega t], \tag{10}$$

where $E_j^{(1)}(\mathbf{n})$, ω, and $\mathbf{k}(l,j)$ are the amplitude, frequency, and wave vector of the field of the pump with polarization along the axis j. Since the conversion efficiency far from synchronism is low, the variation of $E^{(1)}(n)$ with the coordinate can be neglected and we can put

$$\mathbf{E}^{(1)}(\mathbf{n})=\mathbf{E}^{(1)}(0)\equiv\mathbf{E}^{(1)}. \tag{11}$$

Following the analysis above, we find for d_{ijl} in the incommensurate phase, according to (5),

$$d_{\text{inc}\,ijl}(\mathbf{n},\delta)=D_{ijl}(\delta)\cos(2\pi\delta n_1), \tag{12}$$

where $D_{ijl}(\delta)$ is defined in accord with (6). It is taken into account here that $d_{ijl}=0$ in the paraphase. Since the period of $d_{ijl}(\mathbf{n},\delta)$ and the wavelength of the pump field are much larger than the dimensions of the ele-

mentary volume $a_l bc$ isolated by us, we can consider SHG in a quasi-continuous medium with slowly varying value

$$d_{nijl}(\mathbf{R}, \delta) = D_{ijl}(\delta) \cos(2\pi\delta \mathbf{R} a_l^*). \quad (13)$$

Then, following Ref. 22, we obtain for the second-harmonic field intensity

$$E_i^{(2)} = -\frac{32\pi i\omega^2}{k(2,i)Sc^2} E_j^{(1)} E_l^{(1)} \int_V dV\, d_{nijl}(\mathbf{R}, \delta) \exp(i\Delta\mathbf{k}\mathbf{R}), \quad (14)$$

where

$$\Delta\mathbf{k} = \mathbf{k}(1,j) + \mathbf{k}(1,l) - \mathbf{k}(2,i),$$

S is the pump-beam cross section and V is the volume in which the nonlinear interaction takes place. The integral in (14) is proportional to S if the vectors $\Delta\mathbf{k}$ and $\mathbf{a}$ are parallel, and is proportional to

$$\frac{4a(\pi S)^{1/2}}{\delta \sin\theta} J_1\left\{\delta\left(\frac{S}{4\pi a_l^2}\right)^{1/2} \sin\theta\right\},$$

if they make an angle θ. Here J_1 is a Bessel function of first order. Inasmuch as for $(NH_4)BeF_4$ we have $\delta < 0.1$,[5] $a_l \approx 15$ Å, and S is macroscopic in size (of the order of 1 mm^2), we find that the SHG intensity is maximal at $\theta = 0$. It follows from the experimental results that in this case the SHG intensity is higher by one order of magnitude than in the allowed d_{ijl} component in the ferroelectric phase. At $\theta = \pi/2$ the intensity, according to estimates, decreases by a factor 10^5–10^7, i.e., it becomes much less than the signal in the paraphase. It is therefore impossible to separate the contribution of the structure modulation to the SHG in this case. We consider from now on only the case $\theta = 0$. Then in the incommensurate phase

$$I(2\omega) = \frac{c}{2\pi S}\left|\frac{16\pi\omega^2 L}{k(2,i)c^2} D_{ijl}(\delta) E_j^{(1)} E_l^{(1)}\right|^2 \left\{\varphi_+^2 + \varphi_-^2 + 2\varphi_+\varphi_- \cos\left(\frac{\delta L}{a_l}\right)\right\}, \quad (15)$$

where L is the length of the crystal and

$$\varphi_\pm = 2\sin\left[\left(\Delta k \pm \frac{\delta}{a_l}\right)\frac{L}{2}\right]\left[\left(\Delta k \pm \frac{\delta}{a_l}\right)L\right]^{-1}.$$

As shown earlier, the symmetry of incommensurate phase imposes no restrictions on the form of the tensor $D_{ijl}(\delta)$, i.e., all its components can be nonzero. The contribution to the SHG on account of the modulation of the structure is maximal if $\theta = 0$, i.e. if the radiation propagates along the direction of the structure modulation, as was in fact observed in experiment (see Figs. 1 and 2). On going to the ferroelectric phase ($\delta = 0$) the symmetry of the crystal rises to $Pn2_1a$ and the tensor $D_{ijl}(\delta = 0)$ corresponds to this class of rhombic syngony. Equation (15) then goes over into the usual expression for the SHG intensity in a perfect crystal. It is interesting to note that, as follows from (15), in the incommensurate phase the synchronism conditions for SHG are changed. The generation intensity has sharp maxima at

$$\Delta k = \pm\delta/a_l. \quad (16)$$

Estimates show that this condition can be satisfied when δ is of the order of 10^{-3}, i.e., near the transition into the ferroelectric phase.[5] In fact, the SHG intensity in the incommensurate phase is maximal near T_f, but in view of the strong temperature dependence of δ in this region and in view of the presence of small temperature gradients, it is difficult to satisfy the condition (16) over the entire volume of the sample.

For the estimate of the SHG intensity in the incommensurate phase we note that far from T_f the quantity Δk is much less than δ/a_l, and therefore the ratio of the intensity $I(2\omega)$ in the incommensurate phase to $I(2\omega)$ in the ferroelectric phase is approximately equal to $[D_{ijl}(\delta)\Delta k a_l / D_{ijl}(0)\delta]^2$. Substituting $\Delta k = 10^{-3}\pi/a_l$, $a_l = 15$ Å, and $\delta = 0.02$ and assuming that $D_{ijl}(\delta) \approx D_{ijl}(0)$ we find that this ratio is of the order of 10^{-2}. When T_f is approached, Δk and δ/a_l become comparable in value because of the decrease of δ, leading to an increase of φ_- and to an increase of $I(2\omega)$, which can then become of the same order as $I(2\omega)$ in the ferroelectric phase, as was indeed observed in experiment.

Thus, a group-theoretical analysis in four-dimensional space and allowance for the influence of the modulation of the structure on the local characteristics of the crystal explain fully the experimental results. The SHG method is quite effective in the study of incommensurate phases of ferroelectrics, and the modulation direction is easily determined with its aid. It follows from (15) that by using the standard procedure for the determination of the coherence length one can obtain the dependence of $I(2\omega)$ on the crystal length L, and the form of this dependence is determined by the values of Δk and δ. If the refractive indices at the frequencies ω and 2ω are known with high accuracy, this makes it possible to determine the incommensurability parameter δ. Quantitative measurements of the absolute SHG intensity in the presence of the same data permit a determination of the amplitude of the modulation of the nonlinear susceptibility.

[1] N. Bloembergen, Nonlinear Optics, Benjamin, 1965, Chaps. 1 and 5.
[2] V. S. Gorelik, O. P. Maksimov, G. G. Mitin, and M. M. Sushchinskiĭ, Fiz. Tverd. Tela (Leningrad) **16**, 1688 (1973) [Sov. Phys. Solid State **16**, (1973)].
[3] J. Jerphagnon, Phys. Rev. B **2**, 1091 (1970).
[4] A. P. Levanyuk and D. G. Sannikov, Fiz. Tverd. Tela (Leningrad) **18**, 423 (1976) [Sov. Phys. Solid State **18**, 245 (1976)].
[5] M. Iizumi and K. Gesi, Solid State Commun. **22**, 37 (1977).
[6] M. Iizumi, J. D. Axe, G. Shirane, and K. Shimaoka, Phys. Rev. B **15**, 4392 (1977).
[7] H. Jakobi, Zs. Krist. **132**, 434 (1970).
[8] C. J. De Pater and C. van Dijk, Phys. Rev. B **18**, 1281 (1978).
[9] K. Gesi and M. Iizumi, J. Phys. Soc. Jpn. **45**, 1777 (1978).
[10] D. Kucharzyk, A. Pietransko, and K. Lukashewicz, Crystallogr. A **33**, S4 (1978).
[11] Y. Shiroishi, A. Nakata, and S. Sawada, J. Phys. Soc. Jpn. **40**, 911 (1976).
[12] E. M. Lifshitz, Zh. Eksp. Teor. Fiz. **11**, 255 (1941).
[13] L. D. Landau and E. M. Lifshitz, Statisticheskaya fizika (Statistical Physics), Part 1, Nauka, 1976, p. 506. [Pergamon].
[14] A. Janner and T. Janssen, Phys. Rev. B **15**, 643 (1977).
[15] K. S. Aleksandrov, A. N. Vtyurin, and V. F. Shabanov, Pis'ma Zh. Eksp. Teor. Fiz. **28**, 153 (1978) [JETP Lett. **28**, 143 (1978)].
[16] V. P. Ermakov, I. S. Kabanov, and V. F. Shabanov, Prib. Tekh. Eksp. No. 1, 190 (1979).

[17]S. K. Kurtz, Acta Crystallogr. A 28, 5231 (1972).
[18]P. M. de Wolff, Acta Crystallogr. A 30, 777 (1974).
[19]A. Onodera and Y. Shiozaki, J. Phys. Soc. Jpn. 46, 157 (1979).
[20]T. S. Kuntsevich and N. V. Belov, Kristallografiya 16, 5 (1971) [Sov. Phys. Crystallogr. 16, 1 (1971)].
[21]V. F. Shabanov, A. N. Vtyurin, and S. Ya. Vetrov, Preprint IFSO-103F, Krasnoyarsk, 1979.
[22]F. F. Zernike and J. E. Midwinter, Applied Nonlinear Optics, Wiley, 1973, Chap. 2.

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Crystal growth control by electromagnetic radiation

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Gas epitaxy of narrow-band semiconductors irradiated by wide-spectrum lamps is experimentally investigated. It is shown that the application of definite doses of ultraviolet radiation accelerates the growth, improves the crystal quality, and lowers the epitaxy temperature. The mechanisms of the action of the radiation are investigated. Questions involved in the control of deviation from stoichiometry are considered. The possibility of using ultraviolet lasers for epitaxy is discussed.

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1. The possibilities of nonthermal selective action of electromagnetic radiation on matter are receiving ever increasing attention of late. Much progress has been made in such applications of laser radiation as the stimulation of chemical reactions[1,2] and isotope separation.[3–5] The present paper is devoted to a new trend that has set in recently, namely the stimulating action of radiation on crystal growth.[6–10] This group of questions is of great importance in microelectronics, progress in which is closely connected with introduction of epitaxial technology methods in manufacture.

Following the first reports[6–9] of the use of broad-spectrum electromagnetic radiation for the growth of epitaxial semiconductor layers, many interesting results were obtained, particularly accelerated growth of epitaxial layers of germanium, silicon, and gallium arsenide[6–8] and of the tellurides of cadmium and lead.[9] However, attempts to use lasers were unsuccessful. Progress in this research was impeded to a considerable degree by the insufficient understanding of the mechanism of growth under irradiation conditions.

We report here experimental and theoretical research on the mechanisms of gas epitaxy of narrow-band semiconductors using xenon-lamp illumination, and determine the feasibility of the use of lasers. It is shown that under certain conditions ultraviolet (UV) irradiation increases the growth rates, improves the quality of the crystalline films, lowers the epitaxy temperatures, and affords a possibility of controlling the deviations from stoichiometry. A unique feature here is the strictly measured dose and the relatively low power of the UV irradiation. Thus, the use of lasers with properties that deviate from definite norms (with respect to intensity, spectral composition, and operating regime) is more or less useless.

2. Experiments on the epitaxial growth of layers 5 to 100 μm thick were performed on the compounds PbTe, $Pb_{1-x}Sn_xTe$, and HgTe under conditions of sublimation transport of the matter through the gas phase in a semi-enclosed volume of a quartz reactor in a hydrogen atmosphere. The light flux was used both to heat the reaction system (in conjunction with resistive heating) and for nonthermal action on the growth of the epitaxial layers. A diagram of the experimental setup is shown in Fig. 1. Among its distinguishing features is the presence of a radiation source, of an optical window in the reaction chamber, and of an optical system for the entry of the radiation into the reaction volume.

The radiation source was a DKSR-3000 ultrahigh-pressure xenon lamp emitting at 0.2 to 1.5 μm, with 10% of the power in the ultraviolet, 35% in the visible,

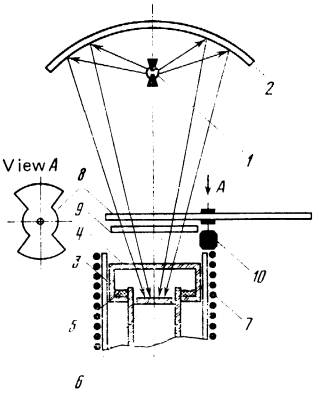

FIG. 1. Experimental setup for the study of the mechanism of the effect of optical irradiation on the growth of epitaxial semiconductor layers: 1—radiation source, 2—elliptic reflector, 3—quartz reactor, 4—optical-quartz window, 5—source of matter carried through the gas phase, 6—substrate, 7—resistance heater, 8—rotating shutter, 9—light filter, 10—motor.

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