[7]V. A. Golenishchev-Kutuzov, V. V. Samartsev, N. K. Solovarov, and B. M. Khabibulin, Magnitnaya kvantovaya akustika (Magnetic Quantum Acoustics), Nauka, 1977.
[8]R. M. Valishev, Candidate's dissertation, Kazan' State Univ., 1966.
[9]V. N. Vasyukov, G. N. Neĭlo, A. D. Prokhorov, and G. A. Tsintsadze, Fiz. Tverd. Tela (Leningrad) 19, 2389 (1977) [Sov. Phys. Solid State 19, 1399 (1977)].
[10]S. N. Lukin, Candidate's Dissertation, Donetsk Physicotech Inst., 1975.
[11]R. S. Rubins and S. K. Jani, J. Chem. Phys. 66, 3297 (1977).
[12]N. G. Kabanova, S. N. Lukin, G. N. Neĭlo, and L. F. Chernysh, Kristallografiya 21, 1235 (1976) [Sov. Phys. Crystallogr. 21, 716 (1976)].
[13]S. N. Lukin, E. D. Nemchenko, and L. G. Oranskii, Prib. Tekh. Eksp. No. 4, 116 (1974).
[14]R. W. G. Wyckoff, Crystal Structures, 3, Interscience, 1951.
[15]B. Bleaney and K. D. Bowers, Proc. Phys. Soc. London **A65**, 667 (1952).
[16]R. B. Hemphill, P. L. Donoho, and E. D. McDonald, Phys. Rev. **146**, 329 (1966).
[17]N. B. Karlov and A. A. Manenkov, Itogi nauki, Radiofizika. Kvantovye usiliteli (Science Summaries, Radiophysics, Quantum Amplifiers) VINITI, 1966, p. 62.
[18]R. Orbach, Proc. Phys. Soc. London **A264**, 458 (1961).
[19]K. W. H. Stevens, Rep. Prog. Phys. **30**, 189 (1967).
[20]K. P. Lee and D. Walsh, Can. J. Phys. **47**. 1753 (1969).
[21]V. N. Vasyukov, S. N. Lukin, and G. A. Tsintsadze, Fiz. Tverd. Tela (Leningrad) **20**, 2260 (1978) [Sov. Phys. Solid State **20**, 1304 (1978)].
[22]W. M. Walsh, Phys. Rev. **114**, 1473 (1959).
[23]L. K. Aminov, Zh. Eksp. Teor. Fiz. **48**, 1398 (1965) [Sov. Phys. JETP **21**, 934 (1965)].
[24]L. K. Aminov, In: Paramagnitnyĭ rezonans (Paramagnetic Resonance), No. 3, Kazan' Univ. Press, 1968, p. 3.
[25]N. Shrivastava, Phys. Rep. **C20**, 137 (1975).

Translated by J. G. Adashko

Crystal optics of phases with incommensurable superstructures

V. A. Golovko and A. P. Levanyuk

Moscow Evening Metallurgical Institute
(Submitted 25 April 1979)
Zh. Eksp. Teor. Fiz. 77, 1556–1574 (October 1979)

The characteristics of linear and nonlinear crystal optics in dielectrics with incommensurable superstructures are investigated theoretically for the case of ammonium fluoroberyllate. The optical properties can be described by a spatially periodic distribution of the dielectric constant and nonlinear susceptibility tensors which depend on the order parameter. The form of the tensors can be established on the basis of the phenomenological theory. The fields are determined by solving the Maxwell equations. Effects similar to the spatial dispersion effects, but more pronounced, are found. Moreover, a periodic dependence of the reflection coefficient on the position of the boundary with respect to the superstructure, and the appearance of ellipticity in the reflected light, are predicted. For the nonlinear properties it is shown that there is noticable second harmonic generation due to low local symmetry. The influence of the surface results in the appearance of additional components of the harmonic field and in their periodic dependence on the position of the boundary with respect to the superstructure. This is most manifest on propagation of the wave along the axis of the superstructure. Qualitative agreement is observed between the theory and the only known experiment on second harmonic generation by the incommensurable phase. Quantitatively, however, the difference is appreciable and may be ascribed to the domain structure of the incommensurable phase. The analysis shows that the existence of a multidomain structure may result in a considerable increase of harmonic generation in the incommensurable phase.

PACS numbers: 78.20.Dj, 78.20.Bh, 42.65.Cq

Phases with incommensurable superstructures whose periods greatly exceed the interatomic distances but are smaller than the optical wavelengths λ have by now been observed in a large number of dielectrics (see, e.g., Refs. 1–3). It is natural to expect the propagation of light in such structures to have certain singularities, particularly those similar to the singularities known from crystal optics with spatial dispersion. The presence of spatial dispersion leads to a number of qualitatively new effects, the magnitude of which is determined by the ratio a/λ or $(a/\lambda)^2$, where a is the radius of the intermolecular interaction.[4] On the other hand, optical effects due to the superstructure should be determined by an analogous parameter in which a is replaced by d, where d is the period of the superstructure, and must therefore be much more strongly pronounced and much easier to observe in experiment.

One can hope that an experimental study of the optical properties of incommensurable phases will yield new data on their structure and singularities. The results of the first experiments[5] turned out to be quite inter-

 0038-5646/79/100780-10$02.40

esting; second-harmonic generation was observed in the incommensurable phase of ammonium fluoroberyllate, and its character differed from the character of the generation observed in the commensurable polar phase (no generation of second harmonic was observed at all in the high-temperature nonpolar phase).

In light of the foregoing, it is important to study theoretically the crystal optics of incommensurable phases, to which the present paper is in fact devoted. The magneto-optical effect in media with helical magnetic structure were investigated in Ref. 6; it was shown that under certain conditions total reflection of light is observed, the reflection coefficient oscillates with changing frequency of the light and with changing crystal thickness, and the rotation of the plane of polarization can reach appreciable values. We are interested in noncommensurable phases produced in structural phase transitions, where effects of another kind should manifest themselves. We emphasize that optical effects in such phases do not reduce merely to a more pronounced manifestation of effects known from the optics of ordinary crystals with spatial dispersion. Definite peculiarities should be possessed here by boundary effects. In fact, whereas in an ordinary crystal the position of the boundary can vary only by an integer number of lattice periods, in a crystal with a superstructure the change can be a fraction of a period of the superstructure, and this should lead, for example, to a periodic change in the reflection coefficient, depending on the position of the boundary relative to the distribution of the order parameter.

In the present paper, the structure of the incommensurable phase is described in the macroscopic approximation—as a spatial periodicity of the order parameter, in analogy with the procedure used in Refs. 7 and 8. From the point of view of the optical properties, the incommensurable phase is represented as a periodic spatial inhomogeneity of the dielectric tensor and of the linear dielectric susceptibility tensor in the region of the optical frequencies. The optical properties of cholesteric liquid crystals are described in similar fashion,[9] but the character of the structure, and therefore also the employed approximation, the analysis method, and a number of investigated phenomena is in our case different than in the case of liquid crystals. The macroscopic approach makes it possible to express the final results in terms of the constants of the thermodynamic potential in the Landau theory of phase transitions and in terms of some other quantities, which can be determined in principle from independent experiments.

By way of example we consider ammonium fluoroberyllate. The choice of this substance is dictated by the fact that the incommensurable phase was investigated in relatively great detail both from the theoretical[8,10,11] and the experimental[2,5] points of view.

1. STRUCTURE OF INCOMMENSURABLE PHASE OF AMMONIUM FLUOROBERYLLATE

A most important role in the study that follows is played by the local symmetry of the incommensurable phase. We must therefore first consider its structure, which determines the character of the periodicity of the optical quantities.

The incommensurable phase of ammonium fluoroberyllate exists in a temperature interval from 96 to −90 °C (Ref. 2).[1)] The symmetry group of the high-temperature phase $T>-90$ °C is $D_{2h}^{16}(Pnam)$, while out of the polar phase ($T<-96$ °C) is the group $C_{2v}^{9}(Pn2_1a)$.[12] In the polar phase the period along the x axis is doubled and the spontaneous polarization is directed along the y axis. The irreducible representation of the D_{2h}^{16} group, which gives as a subgroup the group C_{2v}^{9} with doubling of the period along the x axis, is the second of the representation designated in Ref. 13 by the number $T70$.[2)]

This representation is two-dimensional, therefore the density function $\rho(\mathbf{r})$ (Ref. 15) takes below the phase-transition temperature the form

$$\rho=\rho_{\rm init}(\mathbf{r})+\eta\varphi_1(\mathbf{r})+\xi\varphi_2(\mathbf{r}).$$

It is easy to show that depending on the ratio of the coefficients η and ξ, the function $\rho(\mathbf{r})$ has a symmetry of one of the three space groups: if $\eta/\xi=\pm1$, the group C_{2v}^{9} is realized; if $\eta/\xi=0,\infty$—the group C_{2h}^{5}; in all the remaining cases—the group C_s^2 with a specular slip plane perpendicular to the z axis.

In the incommensurable phase, the ratio η/ξ varies periodically depending on the coordinate x.[8] Since the period $d=2\pi/k_0$ of this change is large compared with the lattice periods, we can speak of local symmetry of the structure. It follows from the foregoing that the local symmetry of the incommensurable phase of ammonium fluoroberyllate is the symmetry of the group $C_s^2(P11a)$ with parameters periodic in x.

Using the results of Refs. 8 and 10, we can represent the dependence of the parameters η and ξ on the coordinate x in the form

$$\begin{gathered}\eta=\rho_0\cos k_0x+\rho_0^3a_1\cos 3k_0x+\rho_0^5\sum_{n\geq2}a_n\cos(2n+1)k_0x,\\ \xi=\rho_0\sin k_0x-\rho_0^3a_1\sin 3k_0x+\rho_0^5\sum_{n\geq2}(-1)^na_n\sin(2n+1)k_0x,\end{gathered}\tag{1}$$

where a_n are quantities of zeroth or higher order in ρ_0. It follows from (1) that under certain transformations $x\to x'$ the parameters η and ξ go over into each other. These transformations—translations and reflections of the x axis relative to the coordinate system fixed by the choice of the phase in (1)—are given in the table; it is indicated in the first and second rows how η and ξ are transformed in this case.

It is now easy to establish the character of the periodicity of the different quantities. We consider, for example, the component of the local dielectric tensor ε_{xy}. As follows from the transformation properties of the order parameter, in first-order approximation we have

$$\varepsilon_{xy}\sim(\eta^2-\xi^2).$$

Therefore under the indicated transformations of x, the quantity ε_{xy} transforms in accordance with the third row of the table, from which it is seen that the period of the function $\varepsilon_{xy}(x)$ is equal to π/k_0 and this function is even. Consequently, the Fourier series of this function contains only $\cos 2mk_0x$. Inasmuch as it reverses sign under the transformation $x \to x + \pi/2k_0$, the number m in the argument of cosines should be odd. Thus, the Fourier series of this function takes the form

$$\varepsilon_{xy} = \sum_{n=0}^{\infty} A_n \cos(2n+1)2k_0x. \tag{2}$$

Using the properties of the representation according to which η and ξ transform, it can be shown that formula (2) remains valid when combinations of η and ξ raised to any power is taken into account in ε_{xy}.

We can establish in similar fashion the form of the Fourier series of the diagonal components of the tensor ε_{ik}, which are invariant under symmetry transformations of the group D_{2h}, and are consequently proportional to $\eta^2 + \xi^2$:

$$\varepsilon_{xx}, \varepsilon_{yy}, \varepsilon_{zz} \sim \sum_{n=0}^{\infty} B_n \cos 4nk_0x. \tag{3}$$

The components ε_{xz} and ε_{yz} are equal to zero, since the local-symmetry group has a mirror plane perpendicular to the z axis.

These considerations can be used for a tensor of any rank. The nonzero components contain an even number of indices z, and their Fourier expansion, depending on whether the number of indices x and y is even or odd, takes the form (2), (3) or the same form as for the components of the polar vector $P_x \sim (\eta\eta' + \xi\xi')$ or $P_y \sim \eta\xi$:

$$P_x = \sum_{n=1}^{\infty} C_n \sin 4nk_0x, \quad P_y = \sum_{n=0}^{\infty} D_n \sin(2n+1)2k_0x. \tag{4}$$

If we average expressions (2)–(4) over the superstructure, then only expression (3), which has a dc component at $n=0$, remains unequal to zero. Therefore the only nonzero components in the incommensurable phase of ammonium fluoroberyllate are likewise the average components of any tensor which have an even number of indices x, y, or z, just as for a crystal of class D_{2h}. Thus, with respect to homogeneous actions the incommensurable phase has the same symmetry as the high-temperature phase; in this sense, their point groups coincide.

Having ascertained the general character of the dependence of the components ε_{ik} on x, which enabled us to draw a number of conclusions that are valid in all orders of approximation in ρ_0, we now refine for the concrete calculations the dependence of the tensor ε_{ik} on the order parameter in the lower-order approximations. The diagonal components ε_{ik} can depend only on invariants made up of η and ξ. All three invariants of second degree (with account taken of the first derivatives) are written out in the thermodynamic potential in Ref. 8. When (1) is substituted, the yield, accurate to terms $\sim\rho_0^6$, expressions of the type

$$a\rho_0^2 + b\rho_0^4 \cos 4k_0x.$$

We have 11 invariants of fourth degree; two of them were written out in Ref. 8, and the remaining ones contain derivatives of η and ξ. Upon substitution of (1) all lead to expressions of the type

$$a\rho_0^4 + b\rho_0^4 \cos 4k_0x.$$

Therefore the diagonal components, accurate to terms $\sim\rho_0^6$, are equal to $(l = 1, 2, 3)$

$$\varepsilon_{ll} = \varepsilon_{0l} + \gamma_{1l}\rho_0^2 + \gamma_{2l}\rho_0^4 + \gamma_{3l}\rho_0^4 \cos 4k_0x. \tag{5}$$

Among the combinations of η and ξ which transform like ε_{xy}, there are three combinations of second degree:

$$\eta^2 - \xi^2, \quad \eta\xi' + \eta'\xi, \quad (\eta')^2 - (\xi')^2$$

and eight combinations of fourth degree. With account taken of (1), and accurate to terms $\sim\rho_0^6$, all are proportional to $\cos 2k_0x$. Inasmuch as $\varepsilon_{xy} = 0$ in the high-temperature phase (at $\rho_0 = 0$), we have

$$\varepsilon_{xy} = \varepsilon_{yx} = \rho_0^2(\zeta_1 + \zeta_2\rho_0^2) \cos 2k_0x. \tag{6}$$

We neglect the local gyrotropy, which results in increments $\sim a/\lambda$, and the absorption of light; therefore all the coefficients in the components in the tensor ε_{ik} are real.

2. ELECTROMAGNETIC WAVES IN THE INCOMMENSURABLE PHASE (LINEAR CASE)

In the approximation linear in the field intensity, the question of the propagation of light in the incommensurable phase is a variant of the problem of wave propagation in periodic structure. A definite specific feature of the considered question is that an important role is played in it by the anisotropy of the tensor ε_{ik}. Before we carry out an analytic investigation, we present some qualitative considerations. As shown above, the amplitude of the periodic term in the diagonal components ε_{ik} is proportional to ρ_0^4, while in the component ε_{xy} it is proportional to ρ_0^2. It is therefore natural to expect the presence of the incommensurable structure to affect to the greatest degree that wave for which the component ε_{xy} is significant. This is a wave traveling along the z axis, inasmuch as ε_{xy} gives rise to a transverse polarization-vector component that should influence noticeably the wave propagation. If the wave proceeds along the x or y axis, the component ε_{xy} yields only longitudinal polarization, which plays a relatively smaller role. Thus, one should expect, within the framework of the linear theory, the presence of the superstructure to affect primarily waves propagating along the z axis. However, as will be shown below, boundary effects peculiar to the incommensurable phase, manifest themselves most clearly for waves propagating along the x axis.

We write down the equation of an electromagnetic wave of frequency ω:

TABLE I.

	x'						
	$x+\pi/2k_0$	$x+\pi/k_0$	$x+3\pi/2k_0$	$-x$	$-x-\pi/2k_0$	$-x-\pi/k_0$	$-x-3\pi/2k_0$
η	$-\xi$	$-\eta$	ξ	η	$-\xi$	$-\eta$	ξ
ξ	η	$-\xi$	$-\eta$	$-\xi$	$-\eta$	ξ	η
ε_{xy}	-1	1	-1	1	-1	1	-1

$$\frac{\partial^2 E_i}{\partial x_k^2}-\frac{\partial^2 E_k}{\partial x_i \partial x_k}+\frac{\omega^2}{c^2}\varepsilon_{ik}(x)E_k=0. \quad (7)$$

We seek the solution of this equation, as usual, in the form

$$E_i(\mathbf{r})=u_i(x)e^{i\mathbf{k}\mathbf{r}}, \quad (8)$$

where $u_i(x)$ are periodic functions with the period of the superstructure. Substituting this expression in (7), we obtain the equation for u_i:

$$u_i''-\delta_{i1}u_x''+2ik_x u_i'-i\delta_{i1}k_k u_k'-ik_i u_x'-k^2u_i+k_ik_ku_k+\omega^2c^{-2}\varepsilon_{ik}u_k=0, \quad (9)$$

where δ_{i1} is the Kronecker symbol, and the prime denotes differentiation with respect to x.

We consider the solution of Eq. (9) in those cases when the wave propagates along one of the coordinate axes. If we are dealing with the x axis, Eq. (9) yields the system $(k_x=k)$

$$\varepsilon_{xx}u_x+\varepsilon_{xy}u_y=0, \quad (10a)$$

$$u_y''+2iku_y'-k^2u_y+\omega^2c^{-2}(\varepsilon_{yx}u_x+\varepsilon_{yy}u_y)=0, \quad (10b)$$

$$u_z''+2iku_z'-k^2u_z+\omega^2c^{-2}\varepsilon_{zz}u_z=0. \quad (10c)$$

This system has two solutions,

$$u_z\neq 0, \quad u_x=u_y=0;$$

$$u_x\neq 0, \quad u_y\neq 0, \quad u_z=0,$$

corresponding to two possible polarizations of the normal waves in the absence of a superstructure. The component u_z is determined from (10c). If we substitute in the equation the expression (3) for ε_{zz} and take into account the initial terms of the expansion (5), we can easily show that the general structure of the solution is of the form

$$u_z=C\left[1+\rho_0^4\sum_{n\geq 1}(A_n^{(1)}\cos 4nk_0x+iB_n^{(1)}\sin 4nk_0x)\right]. \quad (11)$$

Here and below C is an arbitrary constant, $A_n^{(1)}$, $B_n^{(1)}$, and the similar quantities with indices are real combinations of parameters that determine the dependence of ε_{ik} on η and ξ.

The concrete form of the solution can be obtained in the form of an expansion in powers of ρ_0. Substituting in (10c) ε_{zz} from (5), we seek the solution in the form

$$u_z=u_{0z}+\rho_0^2u_{1z}+\rho_0^4u_{2z}+\ldots, \quad k_1=k_{01}+\rho_0^2k_{21}+\rho_0^4k_{21}+\ldots,$$

where k_1 is the wave vector for the given solution. Using the known procedure and recognizing that $k_1/k_0 = d/\lambda \ll 1$, we obtain accurate to terms $\sim\rho_0^6$

$$E_z=u_ze^{ik_1x}=C\left[1+\frac{\omega^2\gamma_{33}\rho_0^4}{16c^2k_0^2}\left(\cos 4k_0x-i\frac{k_1}{2k_0}\sin 4k_0x\right)\right]e^{ik_1x}. \quad (12)$$

The quantity k_1, accurate to terms $\sim\rho_0^8$, is determined by the usual expression in terms of the component ε_{zz} averaged over the superstructure.

Using (2) and (3), we find from (10a) and (10b) that u_x and u_y are represented by series of the type

$$u_x=C\rho_0^2\sum_{n\geq 0}[A_n^{(2)}\cos(2n+1)2k_0x+i\rho_0^4B_n^{(2)}\sin(2n+1)2k_0x],$$

$$u_y=C\left[1+\rho_0^4\sum_{n\geq 1}(C_n^{(2)}\cos 4nk_0x+iD_n^{(2)}\sin 4nk_0x)\right]. \quad (13)$$

Just as in the preceding case, we seek the solution of the equations in the form of expansions in ρ_0. We have

$$E_x=-\frac{\rho_0^2}{\varepsilon_{01}}C\left[\zeta_1+\left(\zeta_2-\zeta_1\frac{\gamma_{11}}{\varepsilon_{01}}\right)\rho_0^2\right]\cos 2k_0xe^{ik_2x},$$

$$E_y=C\left[1+\frac{\omega^2(2\varepsilon_{01}\gamma_{32}-\zeta_1^2)\rho_0^4}{32c^2k_0^2\varepsilon_{01}}\left(\cos 4k_0x-i\frac{k_2}{2k_0}\sin 4k_0x\right)\right]e^{ik_2x}, \quad (14)$$

and it follows from the expression for k_2 (which is the wave vector in this case) that the dispersion-law corrections of interest to us vanish here in the considered approximation, just as in the preceding case.

When the wave propagates along the z axis, both solutions of Eq. (9) are characterized by the fact that for them all three components u_i differ from zero. We consider first a wave in which the vector **E** becomes parallel to the x axis as $\rho_0\to 0$. The general form of the corresponding solution of Eq. (9) is

$$u_x=C\left(1+\rho_0^4\sum_{n\geq 1}A_n^{(3)}\cos 4nk_0x\right), \quad u_y=C\rho_0^2\sum_{n\geq 0}B_n^{(3)}\cos(2n+1)2k_0x,$$

$$u_z=iC\rho_0^4\sum_{n\geq 1}C_n^{(3)}\sin 4nk_0x \quad (15)$$

The solution of Eq. (9) with the aid of the expansion in ρ_0 yields in the first-order approximations the result

$$E_x=C\left(1-\frac{\gamma_{31}\rho_0^4}{\varepsilon_{01}}\cos 4k_0x\right)e^{ik_3r}, \quad E_y=C\frac{\omega^2\rho_0^2}{4c^2k_0^2}(\zeta_1+\zeta_2\rho_0^2)\cos 2k_0xe^{ik_3r},$$

$$E_z=-\frac{iC\omega\gamma_{31}\rho_0^4}{4ck_0\varepsilon_{01}^{1/2}}\sin 4k_0xe^{ik_3z}, \quad k_3^2=\frac{\omega^2}{c^2}\left(\bar{\varepsilon}_{xx}+\frac{\omega^2\zeta_1^2\rho_0^4}{8c^2k_0^2}\right), \quad (16)$$

where a bar over a letter means averaging over the superstructure.

For a wave in which the vector **E** becomes parallel to the y axis at $\rho_0\to 0$, the general form of the solution is

$$u_x=C\rho_0^2\sum_{n\geq 0}A_n^{(4)}\cos(2n+1)2k_0x, \quad u_y=C\left(1+\rho_0^4\sum_{n\geq 1}B_n^{(4)}\cos 4nk_0x\right),$$

$$u_z=iC\rho_0^2\sum_{n\geq 0}C_n^{(4)}\sin(2n+1)2k_0x. \quad (17)$$

In the lowest approximations in ρ_0 and d/λ, the field intensity and the wave vector k_4 are given by

$$E_x=-\frac{C\rho_0^2}{\varepsilon_{01}}\left[\zeta_1+\rho_0^2\left(\zeta_1\frac{\gamma_{12}-2\gamma_{11}}{2\varepsilon_{01}}+\zeta_2\right)\right]\cos 2k_0xe^{ik_4z},$$

$$E_y=C\left[1+\frac{\omega^2\rho_0^4}{32c^2k_0^2\varepsilon_{01}}(2\varepsilon_{01}\gamma_{32}-\zeta_1^2)\cos 4k_0x\right]e^{ik_4z},$$

$$E_z=-\frac{iC\omega\varepsilon_{02}^{1/2}\rho_0^2}{4ck_0\varepsilon_{01}}\left\{2\zeta_1+\rho_0^2\left[\zeta_1\left(\frac{\gamma_{12}}{\varepsilon_{02}}+\frac{2\gamma_{11}-3\gamma_{12}}{\varepsilon_{01}}\right)+2\zeta_2\right]\right\}\sin 2k_0xe^{ik_4z}, \quad (18)$$

$$k_4^2=\frac{\omega^2}{c^2}\left[\bar{\varepsilon}_{yy}-\frac{\zeta_1^2\rho_0^4}{2\varepsilon_{01}}\left(1-\frac{\omega^2\varepsilon_{02}\varepsilon_{03}}{4c^2k_0^2\varepsilon_{01}}\right)\right].$$

A similar analysis can be carried out for waves propagating along the y axis. The wave vector is determined in this case, accurate to quantities $\sim\rho_0^8$, by the corresponding components ε_{ik} averaged over the superstructure.

As will be shown below, second-harmonic generation manifests itself most strongly for light waves propagating at an angle to the coordinate axes. Then, bearing in mind the discussion that follows, we consider by way of example a wave with vector k lying in the xz plane:

$$k_x=k\cos\theta, \quad k_z=k\sin\theta.$$

If we choose a wave whose electric field **E** is parallel to the y axis at $\rho_0=0$, the general form of Eq. (9) is then

$$u_x=C\rho_0^2\sum_{n\geq 0}[A_n^{(a)}\cos(2n+1)2k_0x+i\cos\theta(B_n^{(a)}\sin\theta+\rho_0^4C_n^{(a)})\sin(2n+1)2k_0x],$$
$$u_y=C\left[1+\rho_0^4\sum_{n\geq 1}(D_n^{(a)}\cos 4nk_0x+i\cos\theta E_n^{(a)}\sin 4nk_0x)\right], \quad (19)$$
$$u_z=C\sin\theta\rho_0^2\sum_{n\geq 0}[\cos\theta F_n^{(a)}\cos(2n+1)2k_0x+iG_n^{(a)}\sin(2n+1)2k_0x].$$

The field intensity and the wave vector k_a are given, accurate to terms $\sim\rho_0^4$ and ρ_0^6 respectively, by the expressions

$$E_x=-\frac{\zeta_1}{\varepsilon_{01}}\rho_0^2C\left(\cos 2k_0x+i\frac{k_a^3\varepsilon_{03}\sin^2\theta\cos\theta}{4k_0^3\varepsilon_{01}}\sin 2k_0x\right)e^{ik_ar}, \quad E_y=Ce^{ik_ar},$$
$$E_z=\frac{k_a\zeta_1\sin\theta}{2k_0\varepsilon_{01}}\rho_0^2C\left(\frac{k_a}{2k_0}\cos\theta\cos 2k_0x-i\sin 2k_0x\right)e^{ik_ar},$$
$$k_a^2=\frac{\omega^2}{c^2}\left[\varepsilon_{yy}-\frac{\zeta_1^2\rho_0^4}{2\varepsilon_{01}}\left(1-\frac{\omega^2\varepsilon_{02}\varepsilon_{03}\sin^2\theta}{4c^2k_0^2\varepsilon_{01}}\right)\right]. \quad (20)$$

On the basis of the obtained formulas we can immediately point out, for example, the following manifestation of a superstructure: if in the commensurable phase the vector **E** is polarized along one of the principal dielectric axes, then the refractive index is the same for all k perpendicular to the given axis.[16] In the incommensurable phase in a similar situation, the refractive index will depend on the direction of wave propagation. Thus, for a wave polarized on the average along the x (or y) axis and propagating along the z axis, and for a wave polarized along the same axis and propagating along the y axis (or x axis), the refractive indices differ by an amount

$$\sim(\zeta_1\rho_0^2\omega/ck_0)^2\sim(\zeta_1\rho_0^2k/k_0)^2.$$

This follows from (16) and (18), and the dependence of k on the angle θ is seen from (20). A similar effect takes place also in ordinary crystals in the presence of spatial dispersion. In the latter case, this difference of the refractive indices is of the order of $(a/\lambda)^2\sim10^{-6}$. To estimate the order of this difference in the incommensurable phase of ammonium fluoroberyllate, we use the results of birefringence measurements,[17] which show that at the midpoint of the temperature interval of the existence of the incommensurable phase the increments of the birefringence, which can be ascribed to the presence of the superstructure, are $\sim10^{-4}$. This gives for the difference in order of magnitude $(\gamma_{1i}-\gamma_{1k})\rho_0^2$. It is natural to assume that the temperature of the anisotropy of the coefficients γ_{1i} is the same that as ε_{0i}, i.e., $\gamma_{1i}\approx\varepsilon_{0i}A$; hence

$$(\gamma_{1i}-\gamma_{1k})\rho_0^2\approx A\rho_0^2(\varepsilon_{0i}-\varepsilon_{0k}).$$

According to the values of the refractive indices for ammonium fluoroberyllate,[18] $\varepsilon_{0i}-\varepsilon_{0k}\sim10^{-3}$, which yields ultimately for the considered temperatures $\gamma_{1i}\rho_0^2\sim10^{-1}$. The same order of magnitude should be expected for $\xi_1\rho_0^2$ in (6). According to Ref. 2, $k/k_0\sim10^{-1}$ in this case. We can thus expect

$$(\zeta_1\rho_0^2k/k_0)^2\sim10^{-4},$$

and the discussed difference of the refractive indices will be larger by two orders of magnitude than in the commensurable phase. The accuracy of modern methods makes it possible apparently to observe this effect.

The character of the spatial structure of the electromagnetic wave in the incommensurable phase, determined by the functions $u_i(x)$, turns out to be substantial in second-harmonic generation, as will be shown below. In addition, this character can manifest itself in some other phenomena, for example in the scattering of light by defects.

3. REFLECTION OF LIGHT FROM THE SURFACE OF AN INCOMMENSURABLE PHASE

As already noted in the introductory part, the presence of a superstructure in a crystal can influence the reflection of light. When considering problems of this kind, it is necessary to know the boundary conditions for the electromagnetic wave. We shall assume that the structure of the incommensurable phase near the surface of the crystal is the same as in the depth. This assumption is natural, since at the present time there are no data of any specifics of the superstructure near the surface.

Waves incident on a surface perpendicular to the x axis, along which the superstructure is periodic, encounter a homogeneous boundary that does not differ in principle from the boundary of an ordinary crystal. We can therefore impose here the usual boundary conditions. We assume that the wave $E_z^I=C_I\exp(ikx)$ is normally incident on a boundary situated in the $x=x_0$ plane. The wave excites in the crystal a wave $E_z=u_z(x)\exp(ik_1x)$, where u_z is determined by (11), and produces also a reflected wave $E_z^R=C_R\exp(-ikx)$. The conditions for the continuity of the z component of the field **E** and of the y component of the field H at $x=x_0$ yield two relations:

$$C_Ie^{ikx_0}+C_Re^{-ikx_0}=u_z(x_0)e^{ik_1x_0},$$
$$kC_Ie^{ikx_0}-kC_Re^{-ikx_0}=[k_1u_z(x_0)-iu_z'(x_0)]e^{ik_1x_0},$$

which make it possible to find the constant C_R and C (C enters in u_z) as a function of C_I. Solving these equations, we obtain also expressions for the transmitted and reflected waves:

$$E_z=\frac{2ku_z(x)E_z^I(x_0)}{(k_1+k)u_z(x_0)-iu_z'(x_0)}e^{ik_1(x-x_0)},$$
$$E_z^R=\frac{(k-k_1)u_z(x_0)+iu_z'(x_0)}{(k_1+k)u_z(x_0)-iu_z'(x_0)}E_z^I(x_0)e^{-ik(x-x_0)}. \quad (21)$$

At a constant value of u_z, these formulas go over into the Fresnel formulas[16] for normal incidence of light.

At $x=x_0$, the coefficients of proportionality between E_z^I, E_z and E_z^R in (21) are generally speaking complex. Therefore, in contrast to the incidence of light on the medium without a superstructure, the phases of both the transmitted and reflected wave change, but the change of phase of the reflected wave is not equal to π. Using for u_z the approximate expression (12), we obtain, accurate to terms $\sim\rho_0^6$, the reflection coefficient

$$R_1=\frac{|E_z^R|^2}{|E_z^I|^2}=\left[1-\frac{kk_1^3\gamma_{33}\rho_0^4}{2k_0^2(k_1^2-k^2)\varepsilon_{03}}\cos 4k_0x_0\right]\frac{(k_1-k)^2}{(k_1+k)^2}$$

and the change of the phase upon reflection

$$\delta_1=\pi+\frac{kk_1^2\gamma_{33}\rho_0^4}{2k_0(k_1^2-k^2)\varepsilon_{03}}\sin 4k_0x_0.$$

It is assumed that $k_1 > k$; if $k_1 < k$, the term π is missing from δ_1. In addition, the difference $k_1 - k$ is assumed to be not too small.

For a wave incident along the x axis and having a component E_y^I, we obtain similarly on the basis of (14)

$$R_2=\left[1-\frac{kk_2^3(2\varepsilon_{01}\gamma_{32}-\zeta_1^2)\rho_0^4}{4k_0^2(k_2^2-k^2)\varepsilon_{01}\varepsilon_{02}}\cos 4k_0x_0\right]\frac{(k_2-k)^2}{(k_2+k)^2},$$

$$\delta_2=\pi+\frac{kk_2^2(2\varepsilon_{01}\gamma_{32}-\zeta_1^2)\rho_0^4}{4k_0(k_2^2-k^2)\varepsilon_{01}\varepsilon_{02}}\sin 4k_0x_0.$$

The obtained formulas show that if we remove in some manner thin layers of the substance, i.e., if we vary x_0, the reflection coefficients R_1 and R_2 will vary periodically. Since $\delta_1 \neq \delta_2$, if the incident light is polarized in a plane that does not pass through the y and z axes, then the reflected light is polarized eliptically, and the phase difference $\delta_1 - \delta_2$ is also a periodic function of x_0.

Estimates made under the same assumptions as in Sec. 2 yield a value $\sim 10^{-4}$ for the reflection-coefficient correction necessitated by the presence of the superstructure, and yield for $\delta_1 - \delta_2$ a value $\sim 10^{-3}$. Effects of this order were observed at contemporary experimental accuracy.

When the incident light is perpendicular to the x axis, the ordinary Fresnel formulas remain in force, just as for the commensurable phase. The reason is that in this case the components of the field intensity take the form $u(x)\exp\{i(k_y y + k_z z)\}$ and can be averaged over x independently of y or z. It is the obtained expressions of type $C\exp\{i(k_y y + k_z z)\}$ which enter in the boundary conditions that follow from the x-averaged Maxwell's equations, and this leads to the Fresnel formulas. We note that this averaging procedure is meaningless in the case of the boundary conditions for a wave propagating along the x axis. The wave takes then the form $u(x)\exp(ikx)$, it is not periodic in x, and averaging over x does not yield the expression $C\exp(ikx)$; the result of the averaging depends on all the coefficients in (11) or (13), and the size of the averaging interval also plays a definite role.

4. SECOND-HARMONIC GENERATION

As indicated above, second-harmonic generation (SHG) in ammonium fluoroberyllate was observed experimentally,[5] but there is in fact no interpretation of the experimental results in the cited paper. It is therefore of particular interest to consider this question theoretically. The symmetry group of the high-temperature commensurable phase which, as noted in Sec. 1, is also the group of the "averaged" symmetry of the incommensurable phase, excludes SHG, since it contains an inversion, but in the low-temperature commensurable polar phase SHG is, naturally, possible. Yet according to Ref. 5, SHG is observed in the incommensurable phase, and furthermore the generated light, at a given polarization of the fundamental wave, contains field-intensity components both allowed by the symmetry of the polar phase and forbidden by the symmetry of both commensurable phases.

The statements made above with respect to the symmetry-forbiddenness is valid, of course, only if no account is taken of the dependence of the nonlinear susceptibility tensor on the wave vector k. If account is taken, SHG becomes possible in a medium with an inversion center, but the intensity observed in this case is relatively low.[19] In the incommensurable phase one can expect a similar but more pronounced effect not only because of the large period of the superstructure but also because the local symmetry is lower than the average one.

Let us explain the physical nature of this effect. The local SHG is determined by the local values of the tensor of the nonlinear susceptibility χ_{ijk}, whose value averaged over volumes with dimensions exceeding the superstructure period is zero in accordance with Sec. 1. Therefore in the case of a homogeneous exciting field the second harmonic would not be generated. In fact, in a homogeneous field, within the limits of the period $\chi_{ijk}(x)$, each point would correspond to another point that would generate a harmonic of the same amplitude, but with opposite phase. Actually, however, the exciting field is not homogeneous, therefore the waves generated in the indicated points have a phase difference not equal to π, and have different amplitudes, so that there is no complete cancellation. It follows from this also that the amplitude of the generated harmonic should be determined by the inhomogeneity of the field, i.e., it should be proportional to the magnitude of the wave vector.

The intensity of the harmonic, as is well known, depends strongly on the degree of satisfaction of the synchronism condition.[19] The latter means that the spatial periodicity of the "nonlinear source"

$$P_i^{NLS}=\chi_{ijk}E_jE_k$$

should coincide with the length of the normal wave of frequency 2ω. If we disregard the modulation of the amplitude of the fundamental wave at the period of the superstructure, the field of this wave is proportional to $\exp(i\mathbf{k}\cdot\mathbf{r})$, and when the periodicity of $\chi_{ijk}(x)$ is taken into account we see that the periodicity of P_i^{NLS} is determined by a factor of the type $\exp\{2i(\mathbf{k}_0+\mathbf{k})\mathbf{r}\}$. Since $k_0 \gg k$, the periodicities of P_i^{NLS} and of the normal wave differs substantially and satisfaction of the synchronism condition and the incommensurable phase is impossible. Actually, however, the field of the fundamental wave is modulated with the period of the superstructure, and terms of the type const $\cdot\exp(2i\mathbf{k}\cdot\mathbf{r})$ can appear in the nonlinear source, i.e., there is a possibility of satisfying the synchronism condition.

The SHG in the incommensurable phase can, of course, be phenomenologically described by starting with an "averaged" symmetry of the phase, corresponding to the point group D_{2h} in accordance with Sec. 1. The SHG is then characterized by a fourth-rank tensor:

$$\bar{P}_i^{NLS}=\varkappa_{ijkl}k_l\bar{E}_j\bar{E}_k.$$

If we characterize the SHG by an effective tensor of third-rank, in analogy with Ref. 5, then it is defined by the relation

$$\chi_{ijk}^{eff}=\varkappa_{ijkl}k_l,$$

and it is necessary to take into account that its components depend on the direction of the wave vector **k**. From this we find, in particular, that when waves propagate along the crystallographic axes only a longitudinal component of $\overline{P}_i^{NLS}$ is produced. This follows from the form of the fourth-rank tensors for the class D_{2h} and from the transversality of $\overline{\mathbf{E}}$ in this case. Such a nonlinear source cannot effectively excite an electromagnetic wave, and therefore when SHG is considered special interest attaches to the propagation of the waves at an angle to the axes.

In the preceding arguments we did not take into account the presence of a boundary. By virtue of difference between the local symmetry and that averaged over the volume, the symmetry of the boundary layer perpendicular to the x axis does not coincide with the averaged one at distances of the order of d. Therefore the boundary can give rise to harmonic components that are forbidden by the symmetry of the tensor $\varkappa_{ijkl}$, as will be demonstrated explicitly below.

Proceeding to the analytic treatment, we must first clarify the form of the local tensor χ_{ijk}. The nonzero components of this tensor, with an odd number of indices x, are transformed like P_x, while the components with an odd number of indices y are transformed like P_y. The Fourier expansions of these components χ_{ijk} are analogous to the corresponding series (4). The remaining components with odd number of indices z are equal to zero by virtue of the local symmetry.

Among the combinations of the quantities η, ξ, η', ξ', which transform like P_x, there is one second-degree combination $\eta\eta' + \xi\xi'$ and eight combinations of fourth degree. When Eq. (1) is substituted in these combinations, the terms of order ρ_0^2 vanish from $\eta\eta' + \xi\xi'$, while the terms $\sim\rho_0^4$ in all combinations are proportional to $\sin 4k_0x$. Therefore, accurate to terms $\sim\rho_0^6$ we have

$$\chi_{xxx}=h_1\rho_0^4\sin 4k_0x,\quad \chi_{xyy}=h_2\rho_0^4\sin 4k_0x,\quad \chi_{xzz}=h_3\rho_0^4\sin 4k_0x,$$
$$\chi_{yxy}=\chi_{yyx}=h_4\rho_0^4\sin 4k_0x,\quad \chi_{zxz}=\chi_{zzx}=h_5\rho_0^4\sin 4k_0x. \tag{22}$$

There are three combinations of second degree $\eta\xi, \eta\eta' - \xi\xi', \eta'\xi'$ and eight combinations of the fourth degree, which transform like P_y. Taking (1) into account, all of them are proportional, accurate to terms $\sim\rho_0^6$, to $\sin 2k_0x$. Therefore

$$\chi_{yxx}=\rho_0^2(f_1+f_1'\rho_0^2)\sin 2k_0x,\quad \chi_{yyy}=\rho_0^2(f_2+f_2'\rho_0^2)\sin 2k_0x, \tag{23}$$
$$\chi_{xxy}=\chi_{xyx}=\rho_0^2(f_4+f_4'\rho_0^2)\sin 2k_0x,\quad \chi_{zyz}=\chi_{zzy}=\rho_0^2(f_5+f_5'\rho_0^2)\sin 2k_0x.$$

We note that in a polar commensurable phase only components of the type (23) differ from zero.

In the calculations of the SHG we shall use the given-field approximations; it is then necessary to replace E_i in P_i^{NLS} by expression (8) with a given u_i, and the wave equation for the second harmonic[19] takes the form

$$\frac{\partial^2E_i}{\partial x_k^2}-\frac{\partial^2E_k}{\partial x_i\partial x_k}+4\frac{\omega^2}{c^2}\tilde{\varepsilon}_{ik}E_k=-16\pi\frac{\omega^2}{c^2}\chi_{ijk}u_ju_ke^{2ik\mathbf{r}}. \tag{24}$$

Here and below a tilde marks a quantity that corresponds to the frequency 2ω.

We seek a particular solution of Eq. (24) in the form

$$E_i(\mathbf{r})=v_i(x)e^{2ik\mathbf{r}}; \tag{25}$$

and obtain for v_i the equation

$$v_i''-\delta_{i1}v_x''+4ik_xv_i'-2i\delta_{i1}k_kv_k'-2ik_iv_x'-4k^2v_i$$
$$+4k_ik_kv_k+4\omega^2c^{-2}\tilde{\varepsilon}_{ik}(x)v_k=-16\pi\omega^2c^{-2}\chi_{ijk}(x)u_ju_k. \tag{26}$$

By way of example we consider SHG by a wave propagating in the xz plane and have a vector **E** parallel to the y axis at $\rho_0=0$. The solution of the linear wave equation for this case was obtained in Sec. 2. Taking into account the nonzero components of χ_{ijk} we get from (26)

$$-ik_a\sin\theta v_z'-2k_a^2\sin^2\theta v_x+k_a^2\sin 2\theta v_z+2\omega^2c^{-2}(\tilde{\varepsilon}_{xx}v_x$$
$$+\tilde{\varepsilon}_{xy}v_y)=-8\pi\omega^2c^{-2}(\chi_{xxx}u_x^2+\chi_{xyy}u_y^2+\chi_{xzz}u_z^2+2\chi_{xxy}u_xu_y), \tag{27a}$$

$$v_y''+4ik_a\cos\theta v_y'-4k_a^2v_y+4\omega^2c^{-2}(\tilde{\varepsilon}_{yx}v_x+\tilde{\varepsilon}_{yy}v_y)$$
$$=-16\pi\omega^2c^{-2}(\chi_{yxx}u_x^2+\chi_{yyy}u_y^2+\chi_{yzz}u_z^2+2\chi_{yxy}u_xu_y), \tag{27b}$$

$$v_z''+4ik_a\cos\theta v_z'-2ik_a\sin\theta v_x'-4k_a^2\cos^2\theta v_z$$
$$+2k_a^2\sin 2\theta v_x+4\omega^2c^{-2}\tilde{\varepsilon}_{zz}v_z=-32\pi\omega^2c^{-2}(\chi_{zxz}u_xu_z+\chi_{zyz}u_yu_z). \tag{27c}$$

The general form of the functions $\varepsilon_{ik}(x)$ and $\chi_{ijk}(x)$ is determined by series such as (2)–(4). Taking also into account the form of u_i (19), we obtain the general structure of the solution

$$v_x=C^2\rho_0^4\sum_{n\geq 0}(U_n\sin 4nk_0x+i\cos\theta V_n\cos 4nk_0x),$$
$$v_y=C^2\rho_0^2\sum_{n\geq 0}[W_n\sin(2n+1)2k_0x+i\cos\theta X_n\cos(2n+1)2k_0x], \tag{28}$$
$$v_z=\sin\theta C^2\rho_0^4\sum_{n\geq 0}(\cos\theta Y_n\sin 4nk_0x+iZ_n\cos 4nk_0x).$$

We see therefore that averaging over the superstructure does not cause the amplitudes v_x and v_z to vanish, since they contain dc components (at $n=0$); it is precisely for them that we can expect the strongest manifestations of the synchronism conditions.

The concrete form of the solution of Eqs. (27) can be sought, as in Sec. 2, in the form of expansions in ρ_0, taking (22) and (23) into account. Terms of lowest order, $\sim\rho_0^2$, are contained only in the right-hand side of (27b), so that in first-order approximation in ρ_0^2 and in k/k_0, using (20), we have

$$v_y=\frac{4\pi\omega^2f_2}{c^2k_0^2}\rho_0^2C^2\left(\sin 2k_0x+2i\frac{k_a}{k_0}\cos\theta\cos 2k_0x\right). \tag{29}$$

In the next higher approximation, greatest interest attaches to the amplitudes averaged over the superstructure, $\bar{v}_x$ and $\bar{v}_z$, for which we obtain from (27a) and (27c) the equations

$$\left(k_a^2\sin^2\theta-\frac{\omega^2}{c^2}\tilde{\varepsilon}_{01}\right)\bar{v}_x-\frac{k_a^2}{2}\sin 2\theta\bar{v}_z$$
$$=\frac{4\pi i\omega^2k_a^3}{c^2k_0^3\varepsilon_{02}}\cos\theta\rho_0^4C^2\left(\tilde{\zeta}_1f_2-\frac{\varepsilon_{02}\varepsilon_{03}}{4\varepsilon_{01}^2}\zeta_1f_4\sin^2\theta\right), \tag{30}$$
$$\frac{k_a^2}{2}\sin 2\theta\bar{v}_x-\left(k_a^2\cos^2\theta-\frac{\omega^2}{c^2}\tilde{\varepsilon}_{03}\right)\bar{v}_z=\frac{2\pi i\omega^2k_a\zeta_1f_5}{c^2k_0\varepsilon_{01}}\sin\theta\rho_0^4C^2.$$

The solution of these equations (we leave out the inessential terms) is of the form

$$\bar{v}_x=-\pi i\rho_0^4C^2\frac{k_a\cos\theta}{k_0\tilde{\varepsilon}_{01}\tilde{\varepsilon}_{03}}\left[\frac{2\zeta_1f_5\varepsilon_{02}\tilde{k}_b^2}{\varepsilon_{01}(\tilde{k}_b^2-4k_a^2)}\sin^2\theta\right.$$
$$\left.+\frac{\tilde{k}_b^2}{k_0^2}\left(\tilde{\zeta}_1f_2-\frac{\zeta_1f_4\varepsilon_{02}\varepsilon_{03}}{4\varepsilon_{01}^2}\sin^2\theta\right)\cos^2\theta\right], \tag{31}$$
$$\bar{v}_z=\pi i\rho_0^4C^2\frac{\tilde{k}_b^2\zeta_1f_5\varepsilon_{02}\sin\theta}{2k_ak_0\varepsilon_{01}\tilde{\varepsilon}_{01}\tilde{\varepsilon}_{03}}\left[\frac{\tilde{\varepsilon}_{01}\tilde{k}_b^2}{\tilde{\varepsilon}_{03}(\tilde{k}_b^2-4k_a^2)}\cos^2\theta+\sin^2\theta\right],$$

where $\bar{k}_b$ corresponds to the second normal wave frequency 2ω for the same direction of k as for the wave described by (19). Bir virtue of the interrelation of the amplitudes v_i, the small denominator $\bar{k}_b^2-4k_a^2$ appears in the highest-order approximation also in v_y. Denoting the term with this denominator by $\bar{v}_y$, we obtain

$$\bar{v}_y=\frac{\omega^2\tilde{\zeta}_1\rho_0{}^2\bar{v}_x}{c^2k_0{}^2}\left(\cos 2k_0x-2i\frac{k_a}{k_0}\cos\theta\sin 2k_0x\right).$$

The general solution of Eq. (24) is a sum of the obtained particular solution and of the general solution of the homogeneous equation, corresponding to expressions (19) and (20), while the second can be considered similarly. The arbitrary constants that enter in these relations are determined from the boundary conditions for the second-harmonic fields with allowance for the "reflected" wave.[19] If the wave is incident on the boundary $x=x_0$ (see Sec. 3), we have as a result (we write out only the most essential terms)

$$E_x=\frac{k_a}{k_0\varepsilon_{02}{}^2}\tilde{\zeta}_1f_2\rho_0{}^4C^2\mu\Omega_1\exp(i\tilde{\mathbf{k}}_a\mathbf{r})+(\nu_1\bar{v}_x+\nu_2\bar{v}_z)\exp(i\mathbf{k}_b'\mathbf{r})+\bar{v}_x\exp(2i\mathbf{k}_a\mathbf{r}),$$

$$\begin{aligned}E_y=\frac{k_a}{k_0\varepsilon_{02}}f_2\rho_0{}^2C^2\mu\exp(i\tilde{\mathbf{k}}_a\mathbf{r})+\frac{k_a{}^2\tilde{\zeta}_1\rho_0{}^2}{k_0{}^2\varepsilon_{02}}\Omega_2(\nu_1\bar{v}_x+\nu_2\bar{v}_z)\exp(i\mathbf{k}_b'\mathbf{r})\\+\frac{k_a{}^2\rho_0{}^2}{k_0{}^2\varepsilon_{02}}(f_2C^2\Omega_3+\tilde{\zeta}_1\Omega_4\bar{v}_x)\exp(2i\mathbf{k}_a\mathbf{r}),\end{aligned}\tag{32}$$

$$E_z=(\nu_1'\bar{v}_x+\nu_2'\bar{v}_z)\exp(i\mathbf{k}_b'\mathbf{r})+\bar{v}_z\exp(2i\mathbf{k}_a\mathbf{r}).$$

We have introduced here the dimensionless complex quantities

$$\nu_1=-\frac{2\bar{\varepsilon}_{03}\sin\theta\sin\theta_2\exp[i(2k_{ax}-k_{bx}')x_0]}{2\bar{\varepsilon}_{03}\sin\theta\sin\theta_2+\bar{\varepsilon}_{01}(k_ak_x)^{-1}(k_{bx}'k_x+k_R{}^2)\cos\theta_2},$$

$$\nu_1'=-\frac{\bar{\varepsilon}_{01}\cos\theta_2}{\bar{\varepsilon}_{03}\sin\theta_2}\nu_1,$$

$$\nu_2=\frac{\bar{\varepsilon}_{03}\sin\theta_2(2\cos\theta+k_R{}^2k_a{}^{-1}k_x{}^{-1})\exp[i(2k_{ax}-k_{bx}')x_0]}{2\bar{\varepsilon}_{03}\sin\theta\sin\theta_2+\bar{\varepsilon}_{01}(k_ak_x)^{-1}(k_{bx}'k_x+k_R{}^2)\cos\theta_2},$$

$$\nu_2'=-\frac{\bar{\varepsilon}_{01}\cos\theta_2}{\bar{\varepsilon}_{03}\sin\theta_2}\nu_2,$$

$$\mu=\frac{8\pi ik_a}{\tilde{k}_a\cos\theta_1+k_x}\left(\cos 2k_0x_0-i\frac{2k_{ax}-k_x}{2k_0}\sin 2k_0x_0\right)\exp[i(2k_{ax}-\tilde{k}_{ax})x_0],$$

$$\begin{gathered}\Omega_1=-\varepsilon_{02}\bar{\varepsilon}_{01}{}^{-1}\cos 2k_0x,\quad\Omega_2=\cos 2k_0x-ik_{bx}'k_0{}^{-1}\sin 2k_0x,\\\Omega_3=4\pi(\sin 2k_0x+2ik_ak_0{}^{-1}\cos\theta\cos 2k_0x),\\\Omega_4=\cos 2k_0x-2ik_ak_0{}^{-1}\cos\theta\sin 2k_0x,\end{gathered}\tag{33}$$

where θ_1 and θ_2 are the angles that determine the directions of the wave vectors $\tilde{\mathbf{k}}_a$ and $\mathbf{k}_b'$ of the normal waves of frequency 2ω, while $\mathbf{k}_R$ is the wave vector of the reflected harmonic ($k_x=|k_{Rx}|$). All these vectors lie on the xz plane, while the angles θ_1 and θ_2 are obtained from the relation

$$\tilde{k}_a\sin\theta_1=k_b'\sin\theta_2=2k_a\sin\theta.$$

The vector $\mathbf{k}_b'$ differs from $\bar{\mathbf{k}}_b$ in (31), since $\theta_2\neq\theta$.

The appearance of the components $\bar{v}_x$ and $\bar{v}_z$ (31) corresponds to the symmetry of the tensor $\varkappa_{ijkl}$ introduced above, and to the fact that the field E of the fundamental wave is polarized on the average along the y axis. From formulas (31)–(33) it is seen, in particular, that when the waves propagate along the crystal axis ($\sin\theta=0$ or $\cos\theta=0$) the "resonant" terms contained in the denominators $\bar{k}_b^2-4k_a^2$ vanish in accordance with the statements made above.

Equations (30) for the components averaged over the superstructure are similar to the equations that describe SHG in an ordinary crystal. In the latter case the right-hand sides would contain respectively

$$4\pi(\omega/c)^2\chi_{xyy}C_y{}^2,\quad 4\pi(\omega/c)^2\chi_{zyy}C_y{}^2,$$

where C_y is the amplitude of the fundamental wave. We see therefore that if we introduce the effective tensor χ_{ijk}^{eff} for a given direction k, this tensor will have components

$$\chi_{zyy}^{eff}\sim(k/k_0)\rho_0{}^4,\quad\chi_{xyy}^{eff}\sim(k/k_0)^3\rho_0{}^4,$$

which differ in size and depend on the angle θ. However, the effective tensor introduced in this manner does not describe the entire situation. There is also a field component of the harmonic E_y (32) that does not follow from the symmetry of $\varkappa_{ijkl}$, and whose magnitude depends substantially, owing to the presence of μ and Ω_i, on the position of the crystal boundaries relative to the superstructure. We note that the resonant terms in E_x and E_z do not have such a dependence. The resonant factors are contained in the second and third terms of E_y, but they are preceded by a small coefficient (see Sec. 2):

$$(k/k_0)^2\tilde{\zeta}_1\rho_0{}^2\sim10^{-3}.$$

The first and largest term in E_y does not contain a resonant factor, i.e., it is not sensitive to the synchronism condition, and its magnitude is of the order of the amplitude of the reflected wave. We note that surface effects that are not sensitive to the synchronism conditions were noted even in one of the very first studies of SHG in a crystal with an inversion center.[20]

It is not al all trivial that when the fundamental wave propagates perpendicular to the "superstructure axis" (in the yz plane) the qualitative character of the SHG, as shown by a special analysis, remains unchanged. To be sure, the characteristic effects connected with the boundary conditions vanish; in accordance with the symmetry of $\varkappa_{ijkl}$, there only components are $\bar{E}_y$ and $\bar{E}_z$. On the other hand if the wave travels strictly along the y or z axis, then the particular solution (25) yields on the average a longitudinal field, as is seen with expression (28) with $\cos\theta=0$ as an example. Using the boundary conditions (see Sec. 3), we find that in this case there will be neither a reflected harmonic nor one emerging from the crystal.

When the light propagates along the x axis, we see from (32) that at $\theta=0$ there is a transverse component E_y. There are no terms with resonant denominators in this case, and the intensity of the harmonic depends substantially on the position of the boundaries of the crystal relative to the superstructure. To illustrate this, we calculate in this case, on the basis of (32), the Poynting vector averaged over the superstructure for the harmonic. In first-order approximation,

$$\begin{gathered}\bar{S}_x=\omega\tilde{k}_af_2{}^2|\mu|^2\rho_0{}^4C^4/4\pi k_0{}^2\varepsilon_{02},\\\bar{S}_y=\frac{\omega k_a\tilde{\zeta}_1f_2{}^2|\mu|\rho_0{}^6C^4}{k_0{}^2\bar{\varepsilon}_{01}\varepsilon_{02}}\sin[(2k_a-\tilde{k}_a)x-\varphi],\end{gathered}\tag{34}$$

where φ is the argument of μ. As seen from these formulas, both components contain the factor $|\mu|$, which according to (33) is a periodic function of x_0. We note that the Poynting vector is directed at an angle to the z axis, and this angle is a periodic function of x, with a period $2\pi/|2k_a-\tilde{k}_a|$. If it were possible to satisfy the synchronism condition ($2k_a=\tilde{k}_a$), the Poynting vector would have a constant direction making with the x axis an angle that depends on x_0. An additional calculation shows that a fundamental wave with a different polarization (with vector **E** parallel to the z axis, propagating along the x axis, generates a harmonic whose Poynting vector has a form similar to (34), with the argument of the sine function containing $2k_b-\tilde{k}_a$.

Let us estimate the order of magnitude of the component χ_{ijk}^{eff} assuming that in the middle of the temperature interval of the existence of the incommensurable phase the quantities $f_i\rho_0^2$ are of the same order as the corresponding components of the nonlinear susceptibility tensor in the commensurate polar phase χ_{ijk}^{pol}. By way of example we consider the component χ_{zyy}^{eff}, for which we get from (30)

$$\chi_{zyy}^{eff}\sim(k/k_0)(\zeta_1\rho_0^2)(f_5\rho_0^2).$$

At the same numerical estimates as in Sec. 2, we get $\chi_{zyy}^{eff}/\chi_{ijk}^{pol}\sim10^{-2}$. We recall that in contrast to the linear susceptibility, the nonlinear susceptibility of crystals can differ by three orders of magnitude for different substances,[19] and therefore the obtained susceptibility ratio indicates that SHG in the incommensurable phase of ammonium fluoroberyllate is perfectly observable.

A detailed comparison of the results with those of Aleksandrov, Vtyurin, and Shabanov[5] is difficult, since they did not report the details of the experiment. One can note a qualitative agreement between our results and theirs, namely that SHG is observed in the incommensurable phase and there are components χ_{ijk}^{eff} that are forbidden by the symmetries of both commensurable phases, for example χ_{zyy}^{eff}. There are, however, discrepancies between the theory and experiment. The intensity of the generated harmonic in the incommensurable phase, according to our estimates, is 10^{-4} or less of the intensity of the SHG in the polar phase, whereas in Ref. 5 they observed a much higher intensity. This discrepancy can be connected with the fact that we have considered a single-domain incommensurable phase, whereas in the experiment the crystal was apparently multidomain. An analysis of SHG in a multidomain crystal is presented below. In addition, according to Ref. 5 SHG was observed with light propagating along axes that were perpendicular to the axes of the superstructure. On the other hand, according to the foregoing, the harmonic should not be generated in this case. The last discrepancy is possibly due to the preliminary character of the experimental data.

5. SHG IN A MULTIDOMAIN INCOMMENSURABLE PHASE

The thermodynamic potential[8] does not change when the phase of the sines and cosines in (1) is changed. Therefore the incommensurable structure can be broken up into domains that have different values of this phase. This circumstance should greatly influence the SHG, especially when the light propagates along a superstructure axis. In the latter case the SHG takes place in fact on the crystal boundary. It is natural to expect the same role to be played also by the domain walls in a multidomain crystal. At a definite ratio of the phases, a substantial enhancement of the second-harmonic waves generated on domain walls is possible.

We shall assume that the domain walls are perpendicular to the x axis, i.e., they lie in planes $x=x_m$ (we neglect the wall thickness). To obtain the values of the order parameter in each of the domains, x must be replaced in (1) by $x+q_m$. We note first that in first-order approximation we can neglect the influence of the domain structure on the fundamental wave, since the change of its amplitude on passing through the domain wall is of the order of ρ_0^4, as can be verified in analogy with the procedure used in Sec. 3.

For light propagating along the x axis ($\theta=0$), we find from (28) that there is only one component E_y tangential to the domain walls. Using (14) and (29), we find that E_y takes inside the domain with the number m, in the first-order approximation in ρ_0^2, the form

$$E_y=C_{2m-1}e^{i\tilde{k}_2x}+C_{2m}e^{-i\tilde{k}_2x}+F[\sin 2k_0(x+q_m)+2ik_2k_0^{-1}\cos 2k_0(x+q_m)]e^{2ik_2x}, \tag{35}$$

where $F=4\pi k_2^2f_2\rho_0^2C^2/k_0^2\varepsilon_{02}$ and account is taken of the fact that in this case $k_a=k_2$. We note that in the case of the fundamental wave of another polarization E_y also takes the form (35) with k_2 replaced by k_1, f_2 by f_3, and ε_{02} by ε_{03}.

Let the number of domains be n. If C_R and C_T are the amplitudes of the reflected harmonic and that transmitted through crystal, we obtain for the $2n+2$ constants $C_R, C_T, C_1, \ldots, C_{2n}$ the $2n+2$ relations that follow from the continuity of E_y and H_z on the boundaries. It is easy to eliminate from these relations the intermediate constants C_i and obtain for the amplitude of the emerging harmonic, neglecting the terms $\sim k/k_0$,

$$C_T=4ik_0Fe^{i\tilde{k}_2x_0}[(\tilde{k}_2+\tilde{k})^2e^{2i\tilde{k}_2x_0}-(\tilde{k}_2-\tilde{k})^2e^{2i\tilde{k}_2x_n}]^{-1}\times{\sum_{m=0}^{n}}'[\cos 2k_0(x_m+q_{m+1})-\cos 2k_0(x_m+q_m)]\times[\tilde{k}_2\cos\tilde{k}_2(x_m-x_0)-i\tilde{k}\sin\tilde{k}_2(x_m-x_0)]e^{2ik_2x_m}. \tag{36}$$

Here $\tilde{k}$ is the wave vector of the harmonic outside the crystal, x_0 is the position of the "entrance" face of the crystal, the prime on the summation sign denotes that terms containing q_0 and q_{n+1} should be excluded. We note that for the amplitude C_R of the reflected harmonic we obtain an expression similar in structure to (36), therefore its intensity is of the same order as the intensity of the harmonic emerging from the crystal.

To obtain estimates based on (36) it is necessary to make definite assumptions concerning the character of the domain structure. We assume that the dimensions L of the domains are the same and are equal for simplicity to N periods of the superstructure:

$$x_m=x_0+mL=x_0+2\pi mN/k_0.$$

We assume that $q_m=\alpha+m\beta$. Then the sum in (36) breaks up into four sums of the form

$$\sin k_0\beta \sum_{m=0}^{n} \exp\{im[(2k_2 \pm \bar{k}_2)L \pm 2\beta k_0]\}.$$

If the expression in the square brackets is a multiple of 2π, the similar sum is equal to $2n+1$. In this case, i.e., when the unique synchronism conditions

$$(2k_2 \pm \bar{k}_2)L = 2\pi j \mp 2\beta k_0, \quad j=0, \pm 1, \pm 2, \ldots$$

are satisfied, the intensity of the harmonic is proportional to the square of the number of domains, which can be very large. Therefore the dependence of the intensity of the harmonic, for example on the frequency of the light should constitute a set of peaks.

It should be expected that in the case of a random distribution of the thicknesses of the domains and the phases q_m the height of the peaks will decrease somewhat, the width will increase (cf. Ref. 21), and overlap of the peak cannot be excluded. As a net result the general level of SHG in a multidomain incommensurable phase will be much higher than in a single-domain phase. We can similarly explain the appreciable SHG observed in Ref. 5, but an unambiguous interpretation of this experiment is impossible for lack of data on the domain structure of both the incommensurable and the polar phases. We note also that because of the presence of a large number of terms in (36), the position of the crystal boundaries $x = x_0, x_n$ relative to the superstructure influences the SHG much less than in a single-domain crystal.

The authors are grateful to V. V. Lemanov for a discussion of some problems connected with the present study.

[1)]The experimental data[2] pertain to deuterated ammonium fluoroberyllate, but one can expect the substitution of hydrogen for the deuterium to cause no definite changes in the properties.

[2)]We note that in our case, just as in the experimental studies, the axes of the coordinate system were chosen in the same way as in Refs. 13 and 14; if we mark the axes used in Refs. 13 and 14 by primes, then the following correspondence is obtained for the D_{2h}^{16} group: $x=y'$, $y=z'$, and $z=x'$.

[1]S. Tanisaki, J. Phys. Soc. Japan **16**, 579 (1961). S. Hoshino and H. Motegi, Japan J. Appl. Phys. **6**, 708 (1967).

[2]M. Iizumi and K. Gesi, Solid State Commun. **22**, 37 (1977).

[3]M. Iizumi, J. D. Axe, G. Shirane, and K. Shimaoka, Phys. Rev. B15, 4392 (1977).

[4]V. M. Agranovich and V. L. Ginzburg, Kristallooptika s uchetom prostranstvennoĭ dispersii is teoriya ékситonov (Spatial Dispersion in Crystal Optics and the Theory of Excitons), Nauka, 1965 [(Wiley, 1968)].

[5]K. S. Aleksandrov, A. N. Vtyurin, and V. F. Shabanov, Pis'ma Zh. Eksp. Teor. Fiz. **28**, 153 (1978) [JETP Lett. **28**, 143 (1978)].

[6]N. M. Salanskii, M. Sh. Erukhimov, and V. V. Tyurnev, Fiz. Tverd. Tela (Leningrad) **16**, 3676 (1974) [Sov. Phys. Solid State **16**, 2386 (1975)]; M. Sh. Erukhimov and V. V. Tyurnev, *ibid.* **17**, 2440 (1975) [**17**, 1618 (1975)].

[7]I. E. Dzyaloshinskiĭ, Zh. Eksp. Teor. Fiz. **46**, 1420 (1964); **47**, 336, 992 (1964) [Sov. Phys. JETP **19**, 960 (1964); **20**, 223, 665 (1965)]. A. P. Levanyuk and D. G. Sannikov, Fiz. Tverd. Tela (Leningrad) **18**, 423 (1976) [Sov. Phys. Solid State **18**, 245 (1976)].

[9]V. A. Belyaev, V. E. Dmitrienko, and V. P. Orlov, Usp. Fiz. Nauk 127, 221 (1979) [Sov. Phys. Usp. **22**, 63 (1979)].

[10]Y. Ishibashi and V. Dvorak, J. Phys. Soc. Japan **44**, 32 (1978).

[11]H. Shiba and Y. Ishibashi, *ibid.* **44**, 1592 (1978).

[12]A. Onodera and Y. Shiozaki, *ibid.* 42, 1425 (1977).

[13]O. V. Kovalev, Neprivodimye predstavleniya prostvanstvennykh grupp (Irreducible Representations of Space Groups), Izd. AN UkrSSR, Kiev, 1961.

[14]G. Ya. Lyubarskiĭ, Teoriya grupp i ee primenenie v fizike (Group Theory and Its Applications in Physics), Gostekhizdat, 1957.

[15]L. D. Landau and E. M. Lifshitz, Statisticheskaya fizika (Statistical Physics), Part 1, Nauka, 1976 (Pergamon).

[16]L. D. Landau and E. M. Lifshitz, Élektrodinamika sploshnykh sred (Electrodynamics of Continuous Media), Fizmatgiz, 1959 (Pergamon).

[17]A. T. Anistratov and S. V. Mel'nikova, Kristallografiya 18, 1289 (1973) [Sov. Phys. Crystallography **18**, 811 (1974)].

[18]H. E. Swanson, M. C. Morris, E. H. Evans, and L. Ulmer, Natl. Bur. Stds. (US) Monograph, **25**, Sec. 3, 1964.

[19]N. Bloembergen, Nonlinear Optics, Benjamin, 1965.

[20]R. W. Terhune, P. D. Maker, and C. M. Savage, Phys. Rev. Lett. **8**, 404 (1962).

[21]A. S. Chirkin, in: Nelineinaya optika (Nonlinear Optics), Novosibirsk, 1968, p. 202.

Translated by J. G. Adashko