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## CRYSTALS WITH NON-LINEAR POLARIZABILITY

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## INTRODUCTION

THE last few years have been marked by extremely vigorous growth in research in the field of non-linear optics. It stems from the great advances in quantum radiophysics in practical mastery of ever wider regions of the electromagnetic spectrum, starting with the vacuum ultraviolet and proceeding to the far infrared, adjoining the submillimeter range. The existence of powerful coherent-radiation sources has made it possible not only to confirm Vavilov's<sup>[1]</sup> expectations, but also to obtain a vast amount of experimental data. The monographs of Akhmanov and Khokhlov<sup>[2]</sup> and of Bloembergen<sup>[3]</sup> and a large number of journal articles and reviews have been concerned with a preliminary generalization of the latter.

The interaction of time-dependent electromagnetic fields with a medium can be described by the classical thermodynamic approach, using some time-averaged function of the free energy per volume element. This permits one sharply to classify the possible effects involving optically non-linear properties manifested in the media being studied. Such a study has been carried out in<sup>[2,3]</sup> and also by Pershan<sup>[4]</sup> and by Franken and Ward<sup>[5]</sup>, and it has been widely used in the review by Suvorov and Sonin.<sup>[6]</sup> In line with the recent appearance of the above-cited studies, as well as the reviews by Zheludev,<sup>[7]</sup> Akhmanov and Kohhlov,<sup>[8]</sup> Kaminov and Turner,<sup>[9]</sup> Minck, Terhune, and Wang,<sup>[10]</sup> and the monographic handbook by Bechmann and Hearmon,<sup>[11]</sup> it is a propos to devote this article to presenting systematically the existing data on optically non-linear single crystals. I shall use the notation of<sup>[2,3,6-8]</sup>, without repeating, insofar as is possible, the material concerning formal analysis of non-linear interactions of radiation with matter.

In line with this, I shall restrict myself to discussing the results of experimental study of substances in which the following effects have been observed: the linear electrooptic (Pockels) effect, the quadratic electrooptic (Kerr) effect, generation of second harmonics of optical radiation, and parametric generation in the optical range.

The listed effects have been widely applied in practice, serving as the basis of design of many types of devices for control by a radiation beam from optical quantum generators (which I shall call hereinafter LBC (laser-beam control) devices). They are: amplitude, phase, and frequency modulators, optical shutters, discriminators, and beam splitters, devices for smooth (parametric and discrete) tuning of the radiation frequency of lasers, devices for continuous and discrete deviation of a light beam, and many others. In line with the use of passive elements in the overwhelming majority of these devices, I shall devote a certain amount of attention to evaluating the current state of affairs in the problem of developing and studying linear optical mater-

ials having requisite properties, in addition to discussing crystal elements made of active optically non-linear materials. In addition to the characteristics listed above, I shall analyze the existing data on photoelasticity for certain groups of electro-optic crystals, since this property has also begun to be used in practice in developing acoustooptic modulators and light deviators.

As Pockels<sup>[12]</sup> has shown and Nye<sup>[13]</sup> has treated in detail, a linear electrooptic effect can occur in all crystals belonging to the 20 crystal classes having no center of symmetry and capable of showing a piezoelectric effect, the linear electrooptic-effect tensor  $r_{ijk}$  resembling the piezoelectric-effect tensor  $d_{ijk}$  (cf. the table of matrices in<sup>[7]</sup>). Kleinman<sup>[14]</sup> has shown that second-harmonic generation also can occur only in piezoelectric crystals. However, in a non-dissipative, non-dispersive quadratic medium, the number of independent elements of the non-linear polarizability tensor  $\chi_{ijk}^{2\omega}$  is generally reduced from 18 to 10 by limitations imposed by symmetry. As Laizerowicz<sup>[252]</sup> has shown recently, second-harmonic generation is also possible in certain centrosymmetric magnetically-ordered media, in which spin-orbital interactions make probable the formation of an acentric system of dipoles. However, the expected effect must be small, and hence these substances are excluded from consideration.

Since not only solids but also liquids can lack a center of symmetry, Giordmaine<sup>[15]</sup> has made a theoretical analysis of non-linear optical properties in optically-active liquids. He showed that they exhibit a non-linear optical polarization that is quadratic with respect to the optical electric fields, and leads to generation of sum and difference frequencies. An experimental test<sup>[15a]</sup> has confirmed the predictive estimate that the effect is small in comparison with that observed in piezoelectric crystals. Hence I shall not consider problems of optically non-linear liquids in the following presentation.

In line with what I've stated, the effects of interest to us can in principle be tested on all solids having acentric structures, of which more than 2300 are known<sup>[16]</sup> at present. Among them, piezoelectric properties have been established for more than 1300 substances, and about 300 of them show ferro-, antiferro-, and ferrielectricity.<sup>[17-20]</sup> According to the resumes thus far published, electrooptic coefficients have been measured on only 46 substances,<sup>[21]</sup> and optical non-linear properties have been studied on about 30 compounds.<sup>[18]</sup>

As we see from the cited numbers, the extent of study of the substances possessing optically non-linear properties is utterly inadequate to encompass the possible working substances. Essentially only about two percent of the possibly optically non-linear materials have been examined with varying degrees of thoroughness. As we know, with such statistics we evidently cannot say that working substances have already been found and applied in non-linear optics that have the optimum combination of properties. Hence the problem of search-

ing for new working substances considerably surpassing the known ones is extremely pressing.

In developing an approach to solve this very complex problem, the question immediately arises of a preliminary choice of criteria for evaluating the relative potential of various groups of compounds or concrete substances in order to restrict as much as possible the number of substances to be studied experimentally. This is necessary, in view of the extremely inadequate development of a methodology of evaluating the optical non-linearity of substances from the results of tests on easily-attainable finely-crystalline highly-dispersed powders (see, e.g.,<sup>[22]</sup>), rather than from the data of studies performed on precisely-oriented optically-worked plates of rather considerable dimensions (generally of the order of several millimeters) cut from large optically-homogeneous single crystals, the growth of which presents an independent, very complex, cumbersome, and expensive problem.

Unfortunately, there is at present no rigorous microscopic theory of the effects that we are interested in, such that we could achieve a task-oriented planning of structures having the optimal combination of properties by using its methods. The existing thermodynamic and quantum-mechanical theories only let us evaluate the nature of the individual processes which combine to generate the totality of the characteristics inherent in substances showing non-linear polarizability. Thus, for example, Ward and Franken<sup>[23]</sup> have shown that generally three types of transitions contribute to the non-linear component of the polarizability: electronic-electronic, electronic-ionic, and ionic-ionic. For the electronic transitions, they assume transitions between energy levels having wavelengths of radiation shorter than the edge of the absorption band, but longer for ionic transitions. Analysis of the existing experimental data shows that, for example, electronic and electronic-ionic processes predominate in the linear electrooptic effect in one of the most important optically non-linear crystals, KDP. On the other hand, the electronic component of the polarization plays the leading role in the molecular crystal hexamethylenetetramine.<sup>[24,25]</sup> However, we must know the values of the matrix elements even to make such estimates, and this requires a preliminary investigation of the crystal under study with a high quality of measurements. Evidently, at the present state of development of the problem, predictive use of the data discussed above will apparently furnish no heuristic results.

An alternative method of predictive generalization is the semiempirical crystal-chemical method. This is based on determining how the properties being analyzed vary among the members of isomorphous series of similar fundamental structural motif upon successive substitution of selected structural elements. Use of this method has made it possible to classify successfully the entire variety of piezoelectric crystals,<sup>[17,20]</sup> and to formulate clearly the direction of search. Now, the electromechanical couplings are most clearly manifested in piezoelectric crystals, while the contribution of the electronic polarizability to the piezoelectric polarization cannot always be rigorously estimated. Nevertheless, there is a definite correlation between piezoelectric activity and the degree of optical non-linearity.

In particular, this is manifested in the analysis of elastic and photoelastic properties of substances. It therefore seems justified to discuss the known optically non-linear substances as grouped into crystal-chemical families similar to those distinguished in<sup>[20]</sup>.

Furthermore, since the major line of application of non-linear optical properties of substances is in the invention of a variety of LBC devices including the ultraviolet and infrared ranges, we must discuss the list of requirements for working substances for LBC devices arising from the specific features of their application.

To achieve active control, the optical characteristics of the working substances must vary by a given law for a sufficient frequency of the controlling agent. In line with what I have said, possible working substances must show a considerable electrooptic (linear or quadratic), magneto-optic, or elasto-optic effect, or a high quadratic polarizability with the existence of a phase-matching direction. For passive control, they must show a considerable birefringence or rotation of the plane of polarization. The tensor nature of the effects used for control complicates the use of isotropic media such as glasses, while for practical reasons it is not suitable to consider liquids, which also show a large Kerr effect, not to mention gases.

Hence I shall proceed to listing briefly the requirements imposed on crystalline working substances intended for use in LBC devices.

These requirements can be subdivided into two groups (A and B).

A. General requirements for all crystals. They include:

1. The highest attainable optical homogeneity. While in the visible and ultraviolet the crystals must be practically free from dislocations and must match the best optical glass in the amount of absorption and scattering, certain relaxations are permitted in the infrared on homogeneity, owing to the lesser absolute diffraction limitations at longer wavelengths, but not on absorption at the working frequencies.
2. Sufficient hardness for practical purposes, to ensure good workability of the surfaces of the working elements; apparently the microhardness must be  $\geq 120-150 \text{ kg/mm}^2$ , and preferably  $\geq 300-350 \text{ kg/mm}^2$ .
3. Minimal anisotropy of thermal expansion and a minimal variation (and as linear as possible over the working temperature range) of the effective coefficients being used (electro-magneto-piezooptic, etc.).
4. Insolubility in water and ordinary solvents.
5. Good dielectric characteristics, which are maintained at strong fields, and in the range of working frequencies, including microwaves, and in the working range of temperatures.

B. Specific requirements, determined by the concrete conditions of application, in particular:

1. The form and size of the effective linear and quadratic electrooptic coefficients  $r_{ij}$  and  $g_{ij}$ , which determine the optimum orientation of the crystal elements intended for concrete devices based on the Pockels and Kerr effects.
2. The form and size of the effective piezoelectric and elastic coefficients  $d_{ij}$  and  $c_{ij}$ , which determine the optimum orientation and geometry of the crystal elements in devices using the effects of diffraction by

ultrasonic waves and piezooptic resonance.

3. The same features for the piezooptic constants  $\pi_{ij}$  for devices using two-photon interaction to generate hypersonic waves within crystals in order to use these phonon diffraction gratings for UHF modulation and deviation of beams of coherent radiation.

4. The same features for the effective coefficients of the optical non-linearity tensor  $\chi_{ij}$ , together with the dispersion characteristics, for crystalline second- and fourth-harmonic generators with parametric tuning of the emission frequency.

As we see from the above, no requirements have been formulated on the magneto-optic characteristics of possible working substances, owing to the practical non-existence of such at present in the form of crystals of optical quality of the required dimensions.

It now seems possible to proceed to concrete discussion of the existing data, and first of all to summarize what is known on the linear electrooptic effect.

## 1. CRYSTALS POSSESSING A LINEAR ELECTROOPTIC EFFECT

I have compiled Table I, which includes the existing data on the linear electrooptic effect. For convenience in the following discussion, it seems expedient to group the studied substances according to crystal system in the order of decreasing symmetry, and to distinguish crystal-chemical families within these groups, adopting the classification of<sup>[20]</sup>.

**1.1. Cubic Crystals Possessing a Linear Electrooptic Effect.** Among the crystals given in Table I, this group contains 15 crystals of the hexatetrahedral class  $\bar{4}3m-T_d$ , and 13 crystals of the tritetrahedral class  $23-T$ . In the absence of an external electric field, all the listed crystals are optically isotropic, and possess a single effective electrooptic coefficient  $r_{41} = r_{52} = r_{63}$ . This fact, which fundamentally simplifies the design of wide-aperture electrooptic modulators with transverse control, is the reason for the considerable interest that has been shown in searching for and studying such crystals. In using cubic electrooptic crystals in designing various LBC devices, one must consider the following requirements on the orientation of the crystals arising from their symmetry:<sup>[19]</sup> in order to attain the maximum induced birefringence. This is brought about by applying the controlling electric field perpendicular to one of the [100] axes of the cube and to the direction of propagation of the light. In this case, the greatest change in the refractive index amounts to  $\pm n^3 r_{41} E / 2$  (the sign depends on the direction of polarization of the light and its direction of propagation).

In order to obtain phase modulation, one must have the maximum change in the refractive index for the given linear polarization. This is achieved when the directions of the electric field and of the optical polarization are parallel to the [111] axis of the crystal. In this case, the greatest change in the refractive index is  $n^3 r_{41} E / \sqrt{3}$ . The gain over applying the field in the (100) plane is a factor of  $2/\sqrt{3}$ . The direction of propagation of the light must be perpendicular to the direction of the controlling field.

A third rational case is to have the light propagated along the threefold axis [111], with the field applied perpendicular to this direction. This causes a shift in

the refractive index of  $\sqrt{2/3} n^3 r_{41} E$ . When one uses optically-active crystals of class T in designing devices, one must compensate for the natural optical rotation by special design methods, such as using electrodes of special configurations.<sup>[46]</sup> In working with crystals of class T in designing devices, one must compensate for the natural optical rotation by special design methods, such as using electrodes of special configurations.<sup>[46]</sup> In working with crystals of class  $T_d$ , one can rather easily attain light modulation with a single side band and suppression of the carrier,<sup>[93]</sup> as well as smooth shifting of the laser frequency.<sup>[94]</sup> I shall now proceed to discuss cubic electrooptic crystals of class  $T_d$ .

**1.1.1. Hexatetrahedral linear electrooptic crystals.** The known linear electrooptic crystals of class  $\bar{4}3m-T_d$  belong to four structural types: sphalerite, eulytite, sodalite, and hexamethylenetetramine.

**1.1.1.1. The sphalerite structural type** (the cubic modification of zinc sulfide) also covers zinc selenide and telluride, cadmium telluride, halides of copper and silver including cuprous chloride, and gallium phosphide and arsenide. Among these, one can obtain cuprous chloride, sphalerite, stellite, and zinc and cadmium tellurides, and also gallium arsenide in the form of rather strained single crystals of dimensions sufficient for quantitative electrooptic studies. Table II gives some data on the most representative electrooptic crystals having sphalerite-type structures.

A characteristic feature of all the discussed crystals is that their structures contain no light oxygen atoms, which would cause a considerable shift of the absorption edge to longer wavelengths. This allows these compounds to be used as materials for LBC devices in the infrared range including 10.6 microns. At the same time, all the substances of Table II show semiconductor properties to some degree. Consequently, compensatory doping is needed to give them the minimum necessary dielectric properties. The undoped materials show considerable free-carrier absorption, while their high conductivity makes electric control impossible. Unfortunately, doping without impairing the optical homogeneity of the material is possible only within very narrow limits.

Additional technical difficulties that haven't been overcome yet involve the fact that the sphalerite modifications of the discussed substances having the best electrooptic properties are low-temperature forms. Only the hexagonal (wurtzite) modifications crystallize at the melting points for all the compounds listed in Table II except for gallium arsenide, which shows only the cubic structure. The wurtzite-sphalerite polymorphic phase transition in large single crystals practically always leads to complex twinning and great mechanical strain in the monocrystalline regions. Cuprous chloride has shown especial difficulties with forming strained single crystals of the sphalerite modification. People have tried to overcome them by growing single crystals of CuCl from solutions in melts (e.g., in cesium chloride)<sup>[95,96]</sup> and from the vapor below the phase-transition temperature directly as the cubic phase.<sup>[97]</sup> In spite of the rationality of the proposed and applied methods, there is still no technique for reproducible growth of electrooptic single crystals of CuCl. The possibilities of using CuCl crystals in LBC technology are also limited by the fact that they show two-photon excitation

Table I. Crystals showing a linear electrooptic (e.-o.) effect

Crystal		Symmetry	Electrooptic coefficients*	References
Name and formula	Provisional symbol			
Cuprous chloride, CuCl		$\bar{4}3m$	$r_{41} = 18,3$	28, 27
Cuprous bromide, CuBr		$\bar{4}3m$	$r_{41} \approx 2,5$	28
Cuprous bromide-chloride, CuBr <sub>0.7</sub> Cl <sub>0.3</sub>		$\bar{4}3m$	$r_{41} \approx 1$	28
Mayersite, Ag <sub>0.8</sub> Cu <sub>0.2</sub> I		$\bar{4}3m$	$r_{41} \approx 2$	21
Sphalerite, ZnS		$\bar{4}3m$	$r_{41} = 6,0$	29, 30
Stilleite, ZnSe		$\bar{4}3m$	$r_{41} = 6,0$	31-33
Zinc telluride, ZnTe		$\bar{4}3m$	$r_{41} = 13,7$	9, 34
Cadmium telluride, CdTe		$\bar{4}3m$	$r_{41} = 6,7$	255
Gallium arsenide, GaAs		$\bar{4}3m$	$r_{41} = 2-5^{**}$	35-38
Gallium phosphide, GaP		$\bar{4}3m$	$r_{41} = 3,2$	9
Eulytite, Bi <sub>4</sub> Si <sub>3</sub> O <sub>12</sub>		$\bar{4}3m$	$r_{41} \approx 3$	243
Germanoculytite, Bi <sub>4</sub> Ge <sub>3</sub> O <sub>12</sub>		$\bar{4}3m$	$r_{41} = 13$	39
Sodalite, Na <sub>8</sub> [AlSiO <sub>4</sub> ] <sub>6</sub> Cl <sub>2</sub>		$\bar{4}3m$	$r_{41} = 5$	40, 258
Hauynite, Na <sub>8</sub> [SiO <sub>4</sub> ] <sub>2-1</sub> [AlSiO <sub>4</sub> ] <sub>6</sub>		$\bar{4}3m$	$r_{41} \leq 0,1$	9
Hexamethylenetetramine, C <sub>6</sub> H <sub>12</sub> N <sub>4</sub>	HMTA	$\bar{4}3m$	$r_{41} = 22-27$	41-45
Sodium chlorate, NaClO <sub>3</sub>		23	$r_{41} = 1,2$	12
Sodium thioantimonate, Na <sub>3</sub> SbS <sub>4</sub> · 9H <sub>2</sub> O		23	$r_{41} = 2$	46
Ammonium chloride, NH <sub>4</sub> Cl		23	$r_{41} = 4,5^{***}$	47
Molecular compound of ammonium and cuprous chlorides, 2NH <sub>4</sub> Cl · 3CuCl		23	$r_{41} = 2$	21
Langbeinite, K <sub>2</sub> Mg <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>		23	$r_{41} \leq 0,1$	9
Ammonium-manganese langbeinite, (NH <sub>4</sub> ) <sub>2</sub> Mn <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>		23	$r_{41} = 1,6$	48
Ammonium-cadmium langbeinite, (NH <sub>4</sub> ) <sub>2</sub> Cd <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>		23	$r_{41} = 2,1$	48
Thallium-cadmium langbeinite, Tl <sub>2</sub> Cd <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>		23	$r_{41} = 1,8$	254
Silicosillenite, Bi <sub>12</sub> SiO <sub>20</sub>		23	$r_{41} \approx 10$	244
Germanosillenite, Bi <sub>12</sub> GeO <sub>20</sub>		23	$r_{41} = 4^{****}$	49
Sodium uranyl acetate, NaUO <sub>2</sub> (CH <sub>3</sub> COO) <sub>3</sub>		23	$r_{41} = 2,6$	50
Triaminotriethylamine (tren) hydrochloride, N(CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> · HCl) <sub>3</sub>		23	$r_{41} = 5,1$	51, 256
Tren hydrobromide, N(CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> · HBr) <sub>3</sub>		23	$r_{41} = 4,5$	51
Zincite, ZnO		6mm	$r_{33} = 8,4,$ $r_{13} = 4,2^1)$	9
Wurtzite, ZnS		6mm	$r_{33} = 5,6,$ $r_{13} = 2,8$	9
Greenockite, CdS		6mm	$r_{51} = 11,1,$ $r_{33} = 7,2,$ $r_{11} = 3,3$	9, 52
Natrodavyne, Na <sub>6</sub> Ca <sub>2</sub> [(SO <sub>4</sub> ) <sub>2</sub> [AlSiO <sub>4</sub> ] <sub>6</sub> ]		6mm	$r_{\max} = 3$	21
Lithium potassium sulfate, LiKSO <sub>4</sub>		6	$r_{13} - r_{33} = 4,8$	53
Cesium nitrate, CsNO <sub>3</sub>		3m	$r_{22} = 1,3$	245
Lithium niobate, LiNbO <sub>3</sub>	LN	3m	$r_{13} = 25,8,$ $r_{33} = 92,4,$ $r_{42} = 84,$ $r_{22} = 21$	51-57
Lithium tantalate, LiTaO <sub>3</sub>	LT	3m	$r_{13} = 20,7,$ $r_{33} = 91,2$	58
Lithium sodium sulfate, LiNaSO <sub>4</sub>		3m	$r_{22} = 0,06$	53
Tourmaline, Na[LiAl] <sub>3</sub> Al <sub>6</sub> [OH] <sub>1-3</sub> [BO <sub>3</sub> ] <sub>3</sub> [Si <sub>6</sub> O <sub>18</sub> ]		3m	$r_{22} = 0,9$	12
Selenium, Se		32	$r_{41} = 7,5^{**}$	234
Quartz, SiO <sub>2</sub>		32	$r_{11} = 0,8$	53
Potassium dithionate, K <sub>2</sub> S <sub>2</sub> O <sub>6</sub>		32	$r_{11} = 0,8$	53
Strontium dithionate, SrS <sub>2</sub> O <sub>6</sub> · 4H <sub>2</sub> O		32	$r_{11} = 0,1$	53
Cesium tartrate, Cs <sub>2</sub> C <sub>4</sub> H <sub>4</sub> O <sub>6</sub>		32	$r_{11} = 3,0$	53
Molecular compound glucose-sodium bromide, [C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> ] <sub>2</sub> · NaBr · H <sub>2</sub> O		32	$r_{11} = 0,3$	53
Potassium dihydrogen phosphate, KH <sub>2</sub> PO <sub>4</sub>	KDP	$\bar{4}2m$	$r_{63} = 32$ $r_{41} = 26$	62, 65 67-68
Potassium dideuterium phosphate, KD <sub>2</sub> PO <sub>4</sub>	DKDP	$\bar{4}2m$	$r_{63} = 72,$ $r_{41} = 26$	69, 70-72
Rubidium dihydrogen phosphate, RbH <sub>2</sub> PO <sub>4</sub>	RDP	$\bar{4}2m$	$r_{63} = 43$	70, 73
Potassium dihydrogen arsenate, KH <sub>2</sub> AsO <sub>4</sub>	KDA	$\bar{4}2m$	$r_{63} = 33,$ $r_{41} = 38$	62, 70
Rubidium dihydrogen arsenate, RbH <sub>2</sub> AsO <sub>4</sub>	RDA	$\bar{4}2m$	$r_{63} = 39$	70, 73
Cesium dihydrogen arsenate, CsH <sub>2</sub> AsO <sub>4</sub>	CDA	$\bar{4}2m$	$r_{63} = 50$	74
Ammonium dihydrogen phosphate, NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	ADP	$\bar{4}2m$	$r_{63} = 26,$ $r_{41} = 72$	61-67
Ammonium dideuterium phosphate, ND <sub>4</sub> D <sub>2</sub> PO <sub>4</sub>	DADP	$\bar{4}2m$	$r_{63} = 32$	75, 76
Ammonium dihydrogen arsenate, NH <sub>4</sub> H <sub>2</sub> AsO <sub>4</sub>	ADA	$\bar{4}2m$	$r_{63} = 19$	62
Barium titanate, BaTiO <sub>3</sub>	BT	4mm	$r_{13} = 24,$ $r_{33} = 84,$ $r_c = 324$	77-82
Strontium barium niobate, Sr <sub>0.75</sub> Ba <sub>0.25</sub> Nb <sub>2</sub> O <sub>6</sub>	SBN	4mm	$r_{13} = 194,$ $r_{33} = 4020,$ $r_{51} = 126$	246
Pentaerythritol, C[CH <sub>2</sub> OH] <sub>4</sub>	PE	$\bar{4}$	$r_{52} = 4,4^2)$	83
Ammonium oxalate, (NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> · H <sub>2</sub> O	AMO	222	$r_{41} = 680,$ $r_{52} = 980,$ $r_{63} = 750$	248
Rochelle salt, KNaC <sub>4</sub> H <sub>4</sub> O <sub>6</sub> · 4H <sub>2</sub> O	RS	222	$r_{41} = 6,0,$ $r_{52} = 5,1$	84-86

Table I. (Cont'd)

Crystal		Symmetry	Electrooptic coefficients*	References
Name and formula	Provisional symbol			
Tetramethylammonium triiodomercurate, $N(CH_3)_4HgI_3$ Calcium pyroniobate, $Ca_2Nb_2O_7$	TTM	$mm2$	$r_{eff} = n^3 r_{13} - n^3 r_{33} \approx 100$	247
		2	$r_{22} = 1,01,$ $r_{32} = 41$	87
Triglycine sulfate, $(NH_2CH_2COOH)_3H_2SO_4$	TGS	2	at 30° C:	88-92
			$r_x = 125,$ $r_y = 58^3),$ $r_z = 83,$ $r_{22} = 21,6,$ $r_{32} = 40,8$ at 49° C:	
Deuterotriglycine sulfate $(ND_2CH_2COOD)_3D_2SO_4$	DTGS	2	at 40° C:	88-91
			$r_x = 700,$ $r_y = 220,$ $r_z = 530$ at 59° C: $r_x = 94,$ $r_y = 22,$ $r_z = 83$ at 59° C: $r_x = 780,$ $r_y = 155,$ $r_z = 595$	

\*Unless expressly stated, all measured values of  $r_{ij}$  are for  $\lambda = 0.546 \mu$ .  
\*\*Measurements for  $\lambda = 1-10.6 \mu$ .  
\*\*\*Measurements in the non-centrosymmetric phase at  $-196^\circ C$ .  
\*\*\*\*At  $\lambda = 0.66 \mu$ .  
1) At  $\lambda = 0.63 \mu$ .  
2) The  $r_{52}$  values were calculated for a pseudomonoclinic specimen whose symmetry had been reduced by growth stresses.  
3)  $r_x, r_y,$  and  $r_z$  for TGS and DTGS crystals are the coefficients of the linear electrooptic effect under constant mechanical stresses. They are related to the electrooptic coefficients of the primary electrooptic effect by equations taking the symmetry of TGS into account, similar to those discussed in Sec. 1.4.1.2.

caused by the laser beam.<sup>[98,99]</sup>

Although the  $A^{II}B^{VI}$ -type cubic crystals (ZnS, ZnSe, ZnTe, CdTe) show somewhat better dielectric characteristics, it is even more complicated to attain the requisite highly-exact stoichiometry for them than for CuCl, owing to the high volatility of the B component. Growth of relatively perfect crystals of the required modification is made difficult by the high melting points and ease of dissociation. This requires one to crystallize them from the melt at high counterpressures of inert gas.<sup>[100,101]</sup> Additional complications in using zinc sulfide, selenide, and telluride as electrooptic crystals involve the fact that these crystals are classic luminophors and electroluminophors (see, e.g.<sup>[102,103]</sup>). Nevertheless, experimental results have been obtained<sup>[29-34,255]</sup> from individual specimens cut from the rare natural variety of colorless sphalerite, the mineral cleiophane, and also from specimens cut from the untwinned regions of artificial single crystals of zinc selenide and telluride and cadmium telluride, that confirm the possibility of building practical LBC devices when the technical difficulties of getting extended homogeneous single crystals of electrooptic quality have been overcome.

The last of the studied crystals of this type listed in Table II is gallium arsenide. With compensatory doping with Fe and Ni, one can get single crystals of volume resistivities of the order of  $4 \times 10^8$  ohm-cm<sup>[38]</sup> that are transparent over the range 1-15 microns. The large value of the refractive index, together with its insignificant dispersion in the infrared, makes it possible to achieve a value of the product  $n_0^3 r_{41} = 17.7 \times 10^{-7}$  electrostatic units over the range 3.39-10.6 microns. This is about twice the value of  $n_0^3 r_{63} = 9.9 \times 10^{-7}$  electrostatic units for the most widely used modulator crystal KDP in the visible.<sup>[38]</sup> The practical identity of the values of

the dielectric constant of GaAs at low frequencies ( $\epsilon = 11.5$ ) and at UHF ( $\epsilon = 11.2$ ) indicates that one could probably build long modulating elements operating in a running-wave system,<sup>[104]</sup> i.e., with small controlling potentials. Naturally, to do this one needs extended big crystals of considerable dimensions, having the required optical homogeneity and necessary dielectric properties. It is especially important to fulfill the latter condition, not only because of impairments of the optical properties through absorption by free carriers, but also because of the recent discovery in semiconductors of a new type of optical non-linearity. The latter is due to the conduction electrons, and attains a rather high value under infrared power densities that might be actually applied.<sup>[105]</sup>

Single crystals of gallium phosphide, which are more transparent in the near infrared and part of the visible (from 0.6 microns), are considerably harder to grow in the form of relatively large homogeneous single crystals. This also applies to the other  $A^{III}B^V$  cubic semiconductors, which might be of definite interest for electrical purposes, including also the numerous solid solutions. Furthermore, single crystals of the latter could suffer from impaired optical homogeneity.

1.1.1.2. Let us discuss the structural type of eulytite,  $Bi_4(SiO_4)_3$ , (space group  $I43d-T^6$ ). Germanoeulytite, which was studied by Nitsche,<sup>[39]</sup> belongs to this type. The eulytite structure is characterized by isolated  $SiO_4$  tetrahedra octahedrally surrounding Bi ions.<sup>[106]</sup> The preparation is described in<sup>[39]</sup> of single crystals of germanoeulytite by crucible-free pulling from the melt at  $1040^\circ C$ . The crystals have  $n_0 = 2.07$ , and are transparent over the range 0.4-6.0 microns. They have a Mohs hardness of 5-6 and an electrooptic coefficient  $r_{41} = 3.1 \times 10^{-8}$  electrostatic units with  $\epsilon \approx 6$  and

**Table II.** The properties of certain linear cubic electro-optic crystals having sphalerite-type structures

Crystal	CuCl	ZnS	ZnSe	ZnTe	GaAs
Electrooptic coefficient $r_{41} \times 10^8$ , electrostatic units	18.3	6.0	6.0	13.7 **)	2-5 ****)
Refractive index	1.996	3.5 *) 2.37	2.66	11.8 ***) 2.97 ***)	3.60 *****)
Transparency region, $\mu$	0.4-20	0.4-12	0.5-12	0.55-12	3.30
Melting point, °C	422	1850. decomp. 3-4	1100. decomp. 2.5-3.5	1238. decomp. 2.5-3.5	1-15 1238. decomp. 3-4
Mohs hardness	2-2.5				
Electric resistivity, ohm-cm	$10^8$	$10^8$	$10^8$	$10^8$	$10^8$
UHF dielectric constant	8	8.3	8.1	10.1	11.2
UHF dielectric losses	0,001				
Solubility in water	Slight		Insoluble		
References	26-28	29, 30	31-33	9, 34	35-38

Unless expressly stated, all measured values of  $r_{ij}$  and  $n_0$  are for  $\lambda = 0.546 \mu$ .

\*)  $\lambda = 0.400 \mu$   
 \*\*)  $\lambda = 0.54 \mu$   
 \*\*\*)  $\lambda = 0.69 \mu$   
 \*\*\*\*)  $\lambda = 1 - 10,6 \mu$   
 \*\*\*\*\*)  $\lambda = 5 \mu$

$\rho_N \geq 10^{13}$  ohm-cm. The relatively large value of  $n_0$ , together with the likelihood that one can grow large crystals, lets us judge germanoelytite as promising for the near infrared, analogously to gallium arsenide. Germanoelytite is also of considerable interest because of the unusually wide possibilities of replacement of the individual structural elements revealed in a series of studies by the Grenoble school of crystal chemists.<sup>[107,108]</sup> The extreme stability of the eulytite framework permits one to carry out complete or partial substitution of the  $\text{Bi}^{+3}$  ions by the combinations  $[\text{Bi}^{+3} + \text{Pb}^{+2}]$ ,  $\text{Pb}^{+2}$ , and  $[\text{Pb}^{+2} + \text{M}^{+2}]$ , with  $\text{M}^{+2} = \text{Mg}, \text{Ni}, \text{Co}, \text{Cu}, \text{Sr}, \text{Cd}, \text{Mn}, \text{Zn}, \text{or Ca}$ . The  $[\text{SiO}_4]^{-4}$  tetrahedra can be replaced by  $[\text{GeO}_4]^{-4}$ ,  $[\text{PO}_4]^{-3}$ ,  $[\text{AsO}_4]^{-3}$ ,  $[\text{VO}_4]^{-3}$ , and the combinations  $[[\text{PO}_4]^{-3} + [\text{CrO}_4]^{-2}]$  and  $[[\text{PO}_4]^{-3} + [\text{SO}_4]^{-2}]$ . In all, more than 20 compounds isomorphous to eulytite have been synthesized, not to consider the large number of possible isostructural solid solutions. All of this leads us to expect to find substances in this series with better characteristics than the two representatives thus far studied, germanoelytite and eulytite.<sup>[243]</sup>

1.1.1.3. Two of the representatives of the sodalite structural type have been studied: sodalite itself<sup>[40]</sup> and hauynite.<sup>[9]</sup> Hauynite has been shown to have only an extremely weak electrooptic effect ( $r_{41} \leq 0.1 \times 10^{-8}$  electrostatic units), whereas for sodalite  $r_{41} = 13 \times 10^{-8}$  electrostatic units. Colorless sodalite crystals are transparent from 0.3 to 1.7 microns, have  $n_{0,546\mu} = 1.483$ , Mohs hardness 4-5,  $\epsilon = 8.5$ , and  $\tan \delta \approx 0.05$  (at 1 kHz). They are insoluble in water, and stable to 400-500°C. They are obtained artificially by hydrothermal synthesis. Besides hauynite, the sodalite structural type also contains the minerals hackmanite, nose-lite, helvite, genthelvite, and danalite. However, there are no grounds for expecting any of them to show a marked improvement in characteristics over those obtained for sodalite. In conjunction with the lack of natural single crystals of optical quality and the difficulty of synthesis, this does not let us judge this series to be promising.

1.1.1.4. The hexamethylenetetramine (urotropin) structural type. Hexamethylenetetramine (space group  $I\bar{4}3m-T^3$ ) is a typical molecular crystal. Non-centrosymmetrical, almost spherical molecules are arranged at the lattice points, and are close-packed with the high coordination number of 14. The distances between the atomic centers are somewhat greater than the sum of the ionic radii.<sup>[109]</sup> Colorless crystals of hexamethylenetetramine (HMTA) are transparent over the range 0.35-2 microns, have  $n_{0,589\mu} = 1.5911$ ,  $\rho_V \geq 10^{14}$  ohm-cm,  $\epsilon = 3.2$  (at 1 kHz and 24 GHz),  $\tan \delta < 0.001$  up to 24 GHz. The Mohs hardness  $\approx 1$ . The crystals are highly soluble in water, and volatilize at temperatures approaching 100°C. In spite of quite satisfactory electro-optic and optical properties, HMTA crystals seem technically unpromising because of their very slight hardness, easy volatility, and extreme solubility in water. Growth of large unstrained HMTA crystals of optical quality and preparation of precisely-worked elements from them for LBC devices are very difficult. This is indicated by the great spread in the experimental values of  $r_{41}$  and  $V_{\lambda/2}$ <sup>[41-45]</sup> occasioned by the inhomogeneity of the studied specimens.

It is of considerable interest that Hellmeier<sup>[24,25]</sup> has established a purely electronic mechanism of the electrooptic effect in the molecular crystals of HMTA. Consequently, the modulation frequency here should be limited only by the infrared molecular lattice vibrations, with small losses in the UHF. Hellmeier's data lend reason to the hypothesis that it would be expedient to search for new cubic electrooptic crystals among the molecular crystals of complex and element-organic compounds containing structural elements of high electronic polarizability, but having better technological characteristics than HMTA. Some preliminary thoughts on this problem are presented in<sup>[110]</sup>, and are corroborated by the calculations given in<sup>[249]</sup>.

1.1.2. Tritetrahedral linear electrooptic crystals. The practical application of the electrooptic effect in all the 13 known representatives of class 23-T is complicated by the natural optical activity of these substan-

ces. The latter requires one to use special electrode configurations. None of the crystals cited in Table I shows a combination of characteristics that would make it competitive with the other known linear electrooptic materials. However, from the standpoint of crystal chemistry, we can distinguish three structural types of interest for further study: the langbeinite, sillenite, and complex structural types.

**1.1.2.1. Electrooptic crystals belonging to the langbeinite structural type.** The electrooptic characteristics of the three studied representatives are rather poor. However, 25 isomorphous compounds of the type  $\text{Me}_2\text{Me}_2^{*2}[\text{SO}_4]_3$  having the langbeinite structure have been prepared.<sup>[111,112]</sup> Among these, it would seem, we might expect interesting results from the thallium-cadmium and rubidium-cadmium langbeinites. The preparation of these (from melts or solutions) shouldn't involve great difficulty. These crystals are probably transparent in the visible and the near infrared, with a refractive index of about 1.55–1.6, hardness of the order of 3.5, low solubility in water, and melting points above 500°C. For preliminary data on thallium-cadmium langbeinite, see<sup>[254]</sup>.

**1.1.2.2. Electrooptic crystals of the sillenite structural type.** The high-temperature cubic  $\gamma$  modification of bismuth oxide  $\gamma$ - $\text{Bi}_2\text{O}_3$  (sillenite) becomes stable at normal temperatures when small amounts of germanium or titanium ions are introduced into the structural framework. The isostructural compounds germanosillenite  $\text{Bi}_{12}\text{GeO}_{20}$ ,<sup>[113]</sup> titanosillenite  $\text{Bi}_8\text{TiO}_{14}$ ,<sup>[114]</sup> and silicosillenite  $\text{Bi}_{12}\text{SiO}_{20}$ <sup>[244]</sup> are known, and we should expect them to be quite similar in properties. A considerable linear electrooptic effect<sup>[49]</sup> has been found in germanosillenite:  $n_{0r_{41}}^3 = 1.6 \times 10^{-6}$  cm/statvolt at  $\lambda = 0.666$  microns, combined with a large specific rotation (at the maximum at  $0.5 \mu$ , the specific rotation amounts to  $42^\circ/\text{mm}$ ). The crystals show a considerable electromechanical coupling constant  $k_{14} = 30\%$  and a high mechanical Q factor ( $Q_{\text{mech}}$  at 500 MHz amounts to  $127 \times 10^3$  at 296°K and  $27 \times 10^6$  at 4.2°K).<sup>[115]</sup> Similar data have been obtained from silicosillenite. This permits us to assume that isotropic crystals of this structural type may prove to be especially suitable for acoustooptic modulators and deflectors, surpassing in this regard the optically-uniaxial birefringent crystals of lithium niobate and tantalate and lithium gallate. By analogy with the single crystals of layer-type bismuth titanate (see, e.g.<sup>[116]</sup>), sillenite-type crystals should show good dielectric properties ( $\rho_V \geq 10^{13}$  ohm-cm,  $\epsilon \geq 100$ ), a high refractive index ( $n_0 \geq 3$ ), and should be transparent from 0.55–0.6 to 6–8 microns. In conjunction with low melting points ( $\leq 1000^\circ\text{C}$ ), rather great hardness, and insolubility in water, the listed complex of properties leads us to expect the development of linear electrooptic materials of practical interest based on sillenite-type crystals.

**1.1.2.3. Complex and molecular electrooptic crystals of class 23–T.** They include the studied compounds sodium uranyl acetate, sodium thioantimonate enneahydrate (Schlippe's salt), triaminotriethylamine (tren) hydrochloride, and triaminotriethylamine hydrobromide. They are characterized by low dielectric losses in the UHF region, as pointed out by Hellmeier for HMTA, due to the primarily electronic mechanism of polarization.

This is also confirmed by the large piezooptic "stiffness" of tren hydrochloride crystals, for which the value of the effective difference of piezooptic constants  $\pi_{11} - \pi_{12}$  is two orders of magnitude smaller than the values of the piezooptic constants  $\pi_{ij}$  of crystals of the KDP group.<sup>[256]</sup>

Owing to the random choice of the studied crystals, which was occasioned mainly by their availability in the form of specimens of sufficient dimensions, the obtained results cannot be considered optimal. In this regard, it might be of some interest to make an exploratory study of such series of compounds as the complexes of uranyl with the alkali metals and organic ligands, e.g., the uranyl propionates of potassium, ammonium, rubidium, cesium, and thallium, or the sulfide (selenide-telluride)-halides of mercury of the type  $\text{Hg}_3\text{X}_2\text{Y}_2$  (where X = S, Se, Te; Y = Cl, Br). We might expect the representatives of the latter family to show high transparency out to the far infrared, combined with high refractive indices and large specific rotations, apparently with a considerable dispersion.

**1.2. Hexagonal Linear Electrooptic Crystals.** Table I gives the data on four crystals from the dihedral pyramidal class  $6mm-C_{6v}$ , and one from the hexagonal pyramidal class  $6-C_6$ . The three crystals of  $6mm$  symmetry ZnO, ZnS, and CdS belong to the wurtzite structural type. ZnS and CdS crystals can be prepared in the form of rather large boules, fundamentally by a modified Bridgman method under a high counterpressure of inert gas. All that I've said about the preparation of the sphalerite modifications of these substances holds fully for the wurtzite forms. The electrooptic characteristics of these crystals do not surpass the average range, while their practical use is complicated by strongly marked piezoelectric and photoelectric properties, since all the cited compounds are piezoelectric substances having semiconductor properties. Individual attempts have been made in the USSR and the USA to use AIIbVI piezosemiconductors for constructing LBC devices. However, they were motivated mainly by the lack of other electrooptic crystals transparent in the infrared, rather than by especial suitability of cadmium and zinc sulfides. Crystals of zincite, ZnO, can be prepared by different methods, but there has been no way of growing them reproducibly thus far. Natrodavne crystals can be grown by a hydrothermal technique analogous to that for sodalite, but they fall short of the latter in quality.

The last of the crystals under discussion, lithium potassium sulfate, is distinguished by relatively good transmission in the short-wave region of the spectrum, being transparent in the region extending from 2000 Å. The infrared absorption edge is at 4.2 microns.

Among the substances of hexagonal symmetry of fundamental interest in the infrared, I should mention the family of thioperovskites  $\text{BaTiS}_3$ ,  $\text{BaZrS}_3$ ,  $\text{SrTiS}_3$ ,  $\text{BaTiSe}_3$ , and barium trithiocarbonate  $\text{BaCS}_3$ , which have the symmetry  $P6_3mc-C_{6v}^4$ , and also the extensive group of bismuth thiocyanates of the rare earths, having the general formula  $\text{RE}[\text{Bi}(\text{SCN})_6]$ , (RE = Nd, La, Sm, Ce, Pr, Gd, Eu, and Er), and symmetry  $P6_322-D_6^6$ .<sup>[110]</sup> Assuming that these crystals can be successfully synthesized, we can expect a combination of properties showing considerable practical interest. These include good

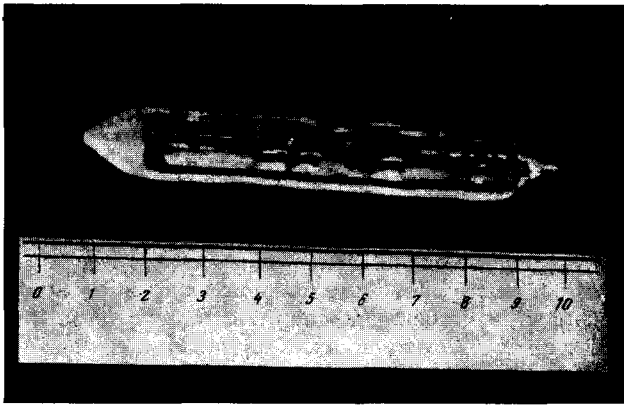


FIG. 1. Single crystal of lithium niobate.

infrared transparency and high refractive indices, and in some cases, a considerable birefringence, which is important in potential non-linear optical applications.

### 1.3. Trigonal Linear Electrooptic Crystals

**1.3.1. Ditrigonal pyramidal linear electrooptic crystals.** Five crystals in Table I belong to the class  $3m-C_{3v}$ . Among these, three are of no interest (lithium sodium sulfate, tourmaline, and cesium nitrate), in distinction from lithium niobate and tantalate (LN and LT).

**1.3.1.1. Lithium niobate crystals.** Lithium niobate crystals, which were first prepared from the melt in the USSR, <sup>[117]</sup> are grown by the Czochralski method as boules of diameters up to 18 mm and lengths up to 80–120 mm (Fig. 1). LN is transparent from 0.35 to 6 microns (Fig. 2). When antireflective coatings are applied, the sum of losses from absorption and reflection in well-annealed specimens can be reduced to values close to those found in standard optical materials. As was shown in <sup>[118]</sup>, the gaps in the region of spectral transparency are due to oxygen defects that can be removed by oxidative annealing, while the absorption band

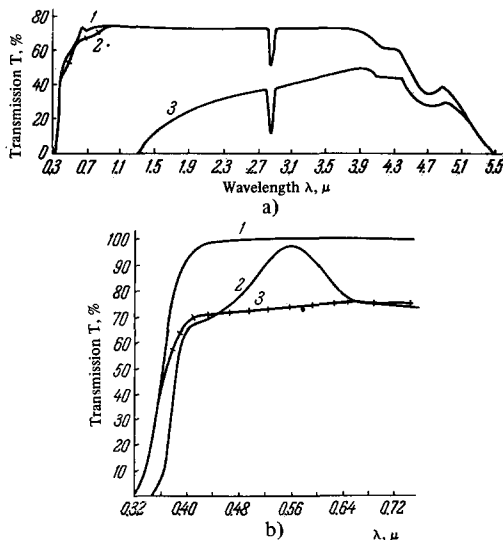


FIG. 2. a) Effect of annealing in hydrogen on the spectral transmission of lithium niobate. Transmission of crystal: 1—before annealing; 2—after annealing 5 min at 500°C; 3—after annealing 15 min at 800°C. b) Transmission of lithium niobate in the ultraviolet and visible: 1—with reflection taken into account ( $t = 4$  mm); 2—for a coated specimen ( $t = 4$  mm); 3—without account taken of reflection ( $t = 4.8$  mm).

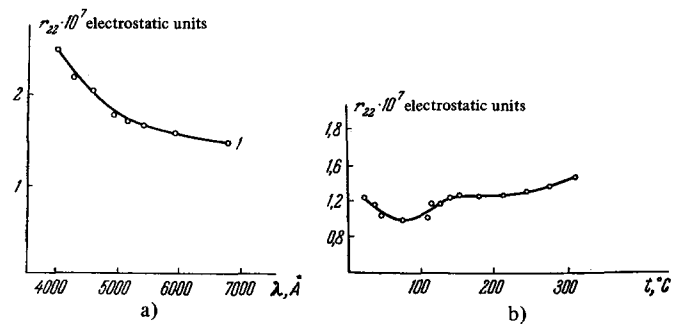


FIG. 3. a) Wavelength-dependence of the electrooptic coefficient  $r_{22}$  of a lithium niobate crystal; b) temperature-dependence of the electrooptic coefficient  $r_{22}$  of a lithium niobate crystal for  $\lambda = 5400$  Å.

at  $2.87 \mu$  apparently involves the technique of preparing the original raw materials. The temperature-dependence of the refractive indices of LN is given in <sup>[119,120]</sup>, and will be discussed in more detail in Sec. 4 of this review.

LN crystals have four independent electrooptic coefficients, and the results of measuring them are given in <sup>[54-57]</sup>. The possibility of transverse control, combined with large absolute values of  $r_{ij}$ , makes it possible to design effective light modulators from LN crystals for the visible and near infrared (up to  $5 \mu$ ). The rather great hardness of LN ( $\approx 5$  Mohs hardness, or  $M_T = 450-500$  kg/mm<sup>2</sup>), together with good workability and insolubility in water, is an additional advantage of LN as a material for electrooptic modulators. In <sup>[54]</sup>, modulators made of LN were studied up to a frequency of 200 MHz, which apparently was not the limiting frequency. The dependence of the electrooptic coefficient  $r_{22}$  on the wavelength of the light and the temperature <sup>[57]</sup> is of interest (Figs. 3a and b). The small anomaly in  $r_{22}$  in the  $150-170^\circ\text{C}$  region correlates well with the data of <sup>[121]</sup>. The dispersion relation  $r_{22}(\lambda)$  (Fig. 3a) is analogous to that found for KTN ( $\text{KTa}_{0.65}\text{Nb}_{0.35}\text{O}_3$ ) crystals, <sup>[122]</sup> as well as for KDP and ADP <sup>[123]</sup> near their intrinsic absorption edges in the ultraviolet. If we assume that the model explaining the nature of the non-linear effects in KDP-type crystals <sup>[23]</sup> is applicable to lithium niobate, then the established rise in the electrooptic coefficient with decreasing wavelength of light indicates that electron-ion processes contribute substantially to the electrooptic properties of LN.

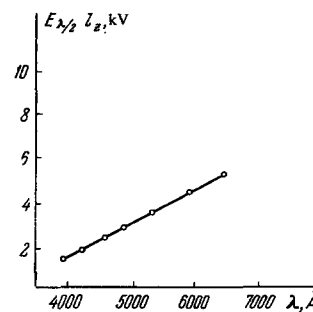


FIG. 4

FIG. 4. Wavelength-dependence of the control voltage for a lithium niobate crystal of unit dimensions.

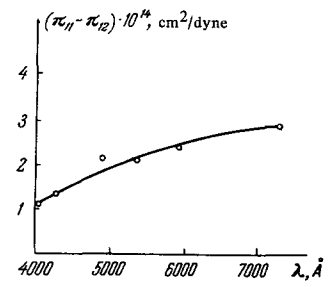


FIG. 5

FIG. 5. Wavelength-dependence of the piezooptic coefficients  $\pi_{11} - \pi_{12}$  of lithium niobate crystals at room temperature.



Figure 4 shows the dispersion relation of the voltage necessary to obtain a half-wave retardation for specimens of unit dimensions. This relation is linear, and the control (half-wave) voltage increases by a factor of five with increase in wavelength from 4000 to 7000 Å.

Figure 5 gives data on the wavelength-dependence of the difference of piezoptic coefficients  $\pi_{11} - \pi_{12}$  of lithium niobate crystals. It is pertinent to note that the measured difference of piezoptic coefficients declines more steeply with decreasing wavelength than in crystals of the KDP group. This apparently involves the greater closeness to the intrinsic absorption edge in the ultraviolet in the case of LN. It is especially necessary to consider the very highly marked piezoelectric properties of LN. They permit one to use these crystals, which are distinguished by a high mechanical Q factor, in modern ultrasonic technology, particularly in transducers, and possibly, in networks of ultrasonic delay lines. According to<sup>[124]</sup>, LN crystals are useful in principle for UHF elastooptic applications. For example, they are four times as efficient as quartz at equal acoustic power. According to the existing data, LN crystals maintain fully satisfactory dielectric characteristics up to temperatures of the order of 300–350°C, with a Curie point near 1200°C (depending on the purity of the original raw material). For data on the dielectric constant and losses in LN crystals, see<sup>[55,117,121,125]</sup>.

1.3.1.2. **Lithium tantalate crystals.** Lithium tantalate,  $\text{LiTaO}_3$  (LT) is a structural analog of lithium niobate (LN), but it differs in having a considerably lower Curie point ( $640 \pm 10^\circ\text{C}$ , as compared with  $1200 \pm 10^\circ\text{C}$  for LN)<sup>[125]</sup> and much lower birefringence.<sup>[126]</sup> This fact complicates its use in non-linear optics (see Chapter 4). The LT crystal resembles LN in its electrooptic characteristics, but according to the data of<sup>[58]</sup> it is apparently more suitable for work in the UHF range. In addition, according to the report<sup>[127]</sup>, LT experiences alterations of the refractive index under laser-beam action with  $\lambda \leq 0.63 \mu$  considerably more rarely than LN crystals do. This indicates a greater probable stability in service for LT crystals. However, owing to the higher melting point ( $\sim 1600^\circ\text{C}$ , as compared with  $1270^\circ\text{C}$ ) than LN and the greater difficulty of preparing pure raw materials, which cost considerably more than those for LN, LT crystals can find wide application only if they also show technical characteristics that would justify the use in LBC devices of a relatively technically intractable and expensive material.

1.3.1.3. **Promising crystals of class 3m.** Mention is made in<sup>[110]</sup> of pyrargyrite  $\text{Ag}_3\text{SbS}_3$ , proustite  $\text{Ag}_3\text{AsS}_3$ , and lithium uranate  $\text{LiUO}_3$ , among other promising crystals. The existing information indicates that crystals of proustite and pyrargyrite can be prepared relatively easily hydrothermally or from the melt. These isostructural crystals are transparent from 0.6 to 13.5 microns (Fig. 6) with a transmission maximum in the range 8.5–12 microns, if we take into account the reflection losses, which amount to 62–65%. It was shown in<sup>[257]</sup> that there is also considerable transmission beyond the absorption band at 13.5–14.5  $\mu$ . The proustite crystal is characterized by large negative birefringence ( $\omega = 2.979$ ,  $\epsilon = 2.711$  in Li light). The Mohs hardness is of the order of 2.5, and the crystals are insoluble in water. Apparently, the optical properties of pyrargyrite

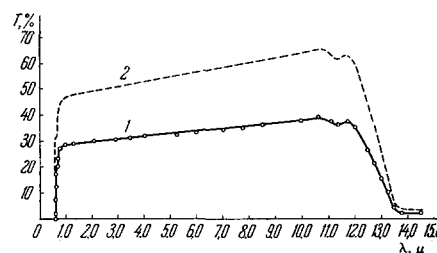


FIG. 6. Spectral transmission (neglecting reflection) of a crystal of proustite  $\text{Ag}_3\text{AsS}_3$  ( $t = 1.72 \text{ mm}$ ) (1) and of pyrargyrite  $\text{Ag}_3\text{SbS}_3$  ( $t = 0.1 \text{ mm}$ ) (2).

resemble those of proustite. Both crystals show a strong piezoeffect, and have rather good dielectric and weak photoelectric properties.<sup>[128]</sup> In addition, a large optical non-linearity has been found in proustite.

In spite of the probability that lithium uranate crystals might show a considerable optical non-linearity because of the crystal-chemical features of their structure, which is isomorphous to lithium niobate,<sup>[129]</sup> they should be less transparent in the infrared (no farther than 6  $\mu$ ), and considerably harder to prepare.

1.3.2. **Trigonal trapezohedral linear electrooptic crystals.** Class 32-D<sub>3</sub> contains six crystals listed in Table I, namely: selenium,  $\alpha$ -quartz, potassium and strontium dithionates, cesium tartrate, the molecular compound glucose-sodium bromide, and also elemental tellurium and selenium. The electrooptic characteristics of all the studied crystals of class 32 do not permit them to compete effectively to any extent with the other known materials. Only tellurium is an exception.<sup>[130]</sup> Tellurium crystals are transparent from 5 to 20 microns and beyond. They show an unusually high birefringence at 10  $\mu$  ( $\omega = 4.8$ ,  $\epsilon = 6.2$ ), and they show high photoelasticity in the infrared. According to the data of<sup>[130]</sup>, tellurium at 10.6  $\mu$  is a considerably better acoustic modulator than quartz at 0.63  $\mu$ , but at frequencies above 300 MHz tellurium shows considerable acoustic losses. Therefore, tellurium modulators can be recommended for work at frequencies below the UHF at room temperature, and possibly for UHF at low temperatures. Owing to the clearly marked semiconductor characteristics of tellurium modulators, one has to use external piezoelectric generators (quartz or monocrystalline cadmium sulfide films), in spite of their considerable piezoelectric effect. Selenium possesses all the defects of tellurium without its merits, and hence it will not be discussed further.

Crystals of the hexathiocyanate complexes of bismuth with the alkali metals might conceivably be of some interest for the infrared. They have the general formula  $\text{NaM}_2[\text{Bi}(\text{SCN})_6]$ , where  $\text{M} = \text{Na}, \text{NH}_4, \text{K}, \text{Rb}, \text{or Cs}$ .<sup>[110]</sup> These compounds crystallize in the space group  $\text{P}312-\text{D}_3$ . If Hellmeier's principle holds true, they might be a material for UHF modulators of infrared radiation, of course, provided that they can be prepared in the form of single crystals of optical quality and dimensions sufficient for use.

#### 1.4. Tetragonal linear electrooptic crystals

1.4.1. **Tetragonal scalenohedral crystals of the  $\text{KH}_2\text{PO}_4$  type ( $42m-\text{D}_{2d}$ ).** Tetragonal scalenohedral crystals of the KDP type are at present the fundamental material for designing and building practically all types

of LBC devices. In all, nine crystals belonging to this family have been studied, and they are listed in Table I. The historically first crystal among them to be used in practice was ammonium dihydrogen phosphate (ADP). This was due to the existence of a technique of growing large ADP crystals of relatively high quality for piezo-technical purposes, which had been developed already at the time of World War II.

Supplanted in hydroacoustics and electroacoustics by the piezoceramics, ADP crystals have enjoyed a "second youth" with the rise of quantum electronics. Up to about 1964, all elements of any considerable size for LBC devices were made only from ADP crystals. However, at about this time, the development of the technique of growing other crystals of this type began to produce results. First there was KDP, and then DKDP, RDP, RDA, and others, brought about by the design of apparatus and technique for growing large, optically homogeneous KDP crystals, which substantially threatened the former monopoly of ADP. [131, 132, 262, 263]

All crystals of the KDP group have  $\bar{4}2m$  symmetry and are piezoelectric at room temperature. At low temperatures, they transform to ferroelectric or antiferroelectric states, forming by this feature two physically isomorphous subgroups. The former, or KDP subgroup, which undergoes ferroelectric ordering below the phase-transition point, contains the crystals KDP,

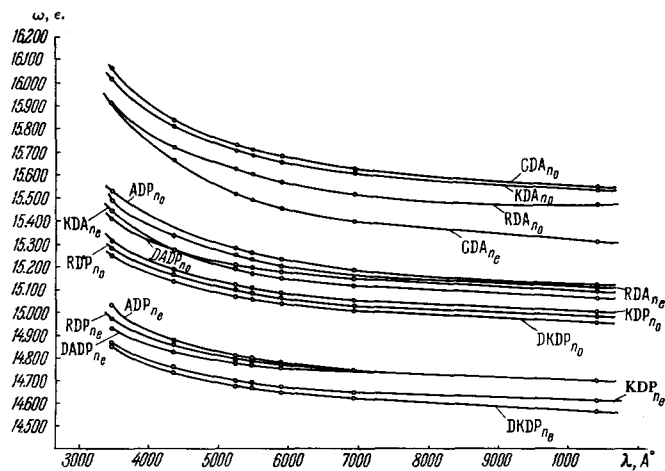


FIG. 7. Wavelength-dependence of the refractive indices of KDP-type crystals.

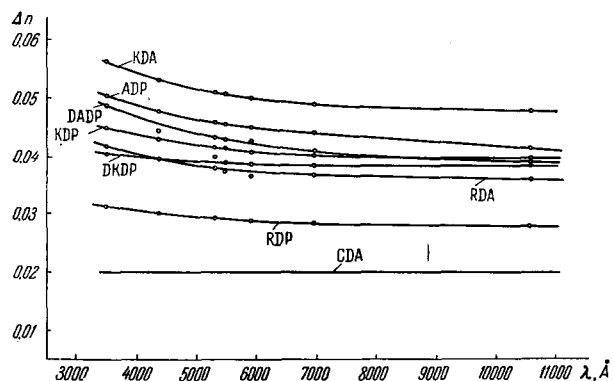


FIG. 8. Wavelength-dependence of the birefringence of KDP-type crystals.

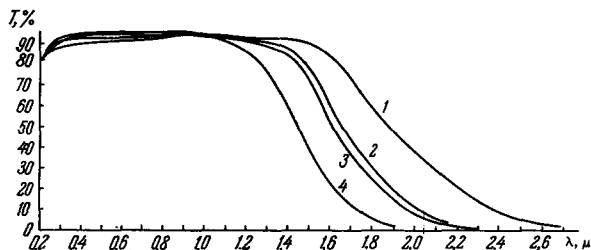


FIG. 9. Spectral transmission of crystals of DKDP and KDP (x-sections). 1—DKDP,  $t = 2$  mm; 2—DKDP,  $t = 8$  mm; 3—KDP,  $t = 2$  mm; 4—KDP,  $t = 8$  mm.

DKDP, KDA, RDA, and CDA. The second subgroup, which goes over into an antiferroelectric phase, contains the crystals ADP, DADP, and ADA. We shall proceed to discuss the properties of these crystals that are of interest to us.

1.4.1.1. The optical properties of KDP-type crystals.

These crystals are optically uniaxial negative. That is,  $\omega > \epsilon$ . Figure 7 shows the dispersion of the refractive indices  $\omega$  and  $\epsilon$  for all the studied phosphates and arsenates. Figure 8 gives the same for the birefringence  $((\omega - \epsilon)$  as a function of  $\lambda$ ). The measurements were made on an IRF-23 with an accuracy of  $\pm 0.0001$  at the wavelengths 4358, 5468, and 5893 Å. The values were extrapolated to other wavelengths by the formula

$$\frac{n^2 + 2}{n^2 - 1} = f \frac{1}{\lambda^2}$$

with an accuracy of  $\pm 0.0004$ . The obtained values for ADP, KDP, and DKDP agreed with those from [133, 134]. For the temperature-dependence of the refractive indices at 4358, 5461, and 5893 Å for KDP crystals from 100° to 300°K, ADP from 150° to 300°K, and DKDP from 180° to 300°K, see [134]. Data are given in [135] on the temperature-dependence of the dispersion of the refractive indices of ADP and KDP, respectively from -196° to +20°C, and to +200°C, over the wavelength range 2500–7500 Å. Figures 9 and 10 give, respectively, the spectral transmission of KDP and DKDP, and the ultraviolet transmission edge of KDP. The studied pure crystals of this group, including RDP, are transparent from the ultraviolet below 2000 Å to 1.5 microns. In DADP, the infrared edge is shifted to longer wavelengths by 500–600 mμ as compared with KDP, and in DKDP by 300–400 mμ. The reflectivity of the phosphates is of the

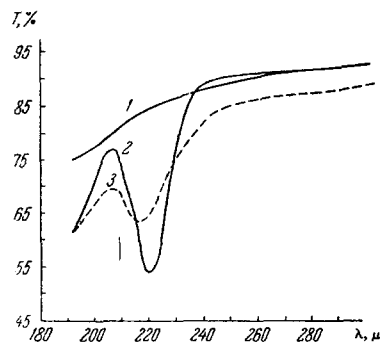


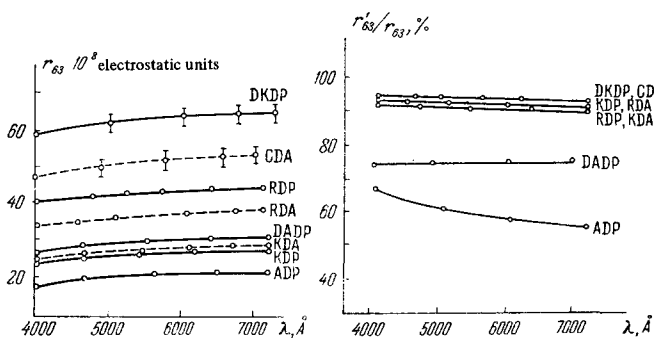
FIG. 10. The ultraviolet transmission limit of KDP crystals of varying origin. 1—a specimen grown by the author's technique,  $t = 6.5$  mm; [131] 2—a NIRFI specimen,  $t = 7.8$  mm; 3—an American specimen,  $t = 4.8$  mm.

**Table III.** Crystal-chemical characteristics of certain KDP-type crystals

Crystal	KDP	RDP	KDA	CDA	
Lattice parameters, Å	<i>a</i>	7.43	7.60	7.65	7.98
	<i>c</i>	6.94	7.32	7.17	7.87
Interatomic distances in the XO <sub>4</sub> group, Å	Cation-O	1.538	1.60	1.74	1.74
	Cation-O'	2.79	2.86	2.86	3.01
Valence angles in the XO <sub>4</sub> group	< OXO	110°34'	116°4'	113°	115.3°
	< OXO'	108°43'	106°48'	104°	98.4°

**Table IV.** Certain elastic properties of a set of KDP-type crystals

Crystal	KDP	DKDP	RDP	KDA	RDA	CDA
<i>C</i> <sub>66</sub> · 10 <sup>-10</sup> dynes/cm <sup>2</sup>	5.95	6.2	3.2	7.4	3.9	1.8
Microhardness <i>h</i> <sub>p</sub> (101), kg/mm <sup>2</sup>	110	122	100	151	105	61



**FIG. 11**

**FIG. 11.** Wavelength-dependence of the electrooptic coefficients *r*<sub>63</sub> of KDP-type crystals.

**FIG. 12**

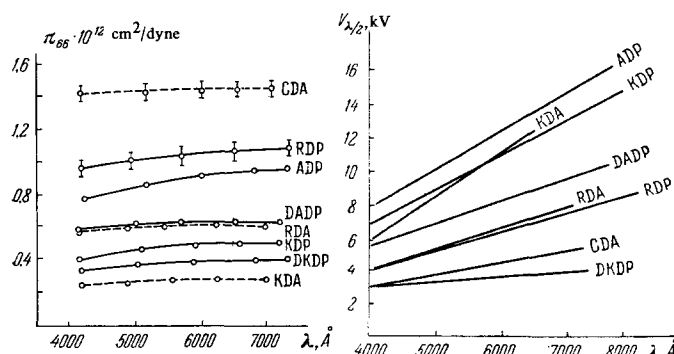
**FIG. 12.** Wavelength-dependence of the ratio *r*'<sub>63</sub>/*r*<sub>63</sub> of the electrooptic coefficients of a mechanically-clamped and a free crystal.

order of *R* ≈ 0.04. The spectra of the arsenates KDA, RDA, and CDA resemble those of the phosphates. The ultraviolet edge occurs at 213–218 mμ for a specimen thickness of 1.5–10 mm, and the reflectivity *R* ≈ 0.045.

1.4.1.2. The electrooptic properties of KDP-type crystals. KDP-type crystals possess two independent coefficients of the linear electrooptic effect, *r*<sub>63</sub> and *r*<sub>41</sub>.<sup>[12]</sup> Since *r*<sub>63</sub> > *r*<sub>41</sub> for all the studied members of the series except ADP, and it is simpler to design LBC devices using *r*<sub>63</sub>, I shall restrict myself to discussing the data on *r*<sub>63</sub>. As we know,<sup>[67]</sup> when the external electric field is directed along the [001] axis of KDP-type crystals, the equation for the overall electrooptic effect has the form

$$r_{63} = r'_{63} + d_{36}P_{66} = r'_{63} + d_{36}c_{66}\pi_{66}$$

Here *r*<sub>63</sub> is the electrooptic coefficient for the mechanically-free crystal, and *r*'<sub>63</sub> is the electrooptic coefficient for the mechanically clamped crystal corresponding to the genuine electrooptic effect, and *d*<sub>36</sub>*c*<sub>66</sub> $\pi$ <sub>66</sub> is the elasto-optic effect, which is determined by the piezo-



**FIG. 13**

**FIG. 13.** Wavelength-dependence of the piezooptic coefficient  $\pi_{66}$  of KDP-type crystals.

**FIG. 14**

**FIG. 14.** Wavelength-dependence of the half-wave voltage *V* <sub>$\lambda/2$</sub>  for KDP-type crystals.

electric modulus *d*<sub>36</sub> and the elasto-optic coefficient *p*<sub>66</sub> or the elastic stiffness constant *c*<sub>66</sub> and the piezooptic coefficient  $\pi_{66}$ . Figures 11–13 give the dispersion relations of the coefficients *r*<sub>63</sub>, *r*'<sub>63</sub>/*r*<sub>63</sub>, and  $\pi_{66}$  for KDP-type crystals. Fig. 14 gives the dispersions of the control voltages *V* <sub>$\lambda/2$</sub>  for the discussed crystals. All the data of Figs. 9–14 are for room temperature. We can draw this conclusion from examining the experimental data: the values of the control voltages decline regularly with increasing cation radius in the physically isomorphous subgroup of phosphates and arsenates of the KDP type. The piezooptic coefficients  $\pi_{66}$  and the electrooptic coefficients *r*<sub>63</sub> show the opposite trend. As was shown in<sup>[136]</sup>, this is due to the strong distortion of the MH<sub>2</sub>XO<sub>4</sub> structure upon cation substitution. This appreciably deforms the XO<sub>4</sub> tetrahedra, owing to the tendency to keep the lengths of the hydrogen bonds invariant upon isomorphous substitution.

Table III, which has been compiled from the data of<sup>[136-138]</sup>, illustrates this.

The increased deformability of the XO<sub>4</sub> anions with increasing cation radius is also distinctly manifested in the regular variation of their elastic properties (see Table IV).

The observed relations indicate that the hydrogen bond does not vary substantially in its nature, and correspondingly in its energy, for the dihydrogen arsenates.

As Figs. 11–13 imply, while the studied properties vary in an analogous way in the physically-isomorphous ADP subgroup, the size of the true electrooptic effect differs markedly in ADP and DADP, being considerably less than in crystals of the KDP subgroup. This fact somewhat complicates the possibilities of practical use of ADP and DADP, and is discussed in detail in<sup>[67,140]</sup>, where it is shown probable that the electrooptic characteristics are altered by the appearance of a new system of strong N–H(D)...O hydrogen bonds in addition to the O–H(D)...O bonds. They also show that the anomalous variations in the electrooptic coefficients above the Curie points are due to dielectric anomalies. In addition, the large electromechanical coupling coefficients of ADP crystals make it possible to design highly-economical narrow-band resonance modulators having *V* <sub>$\lambda/2$</sub>  ≈ 10–15 V,<sup>[259]</sup> e.g., such as are required in auto-

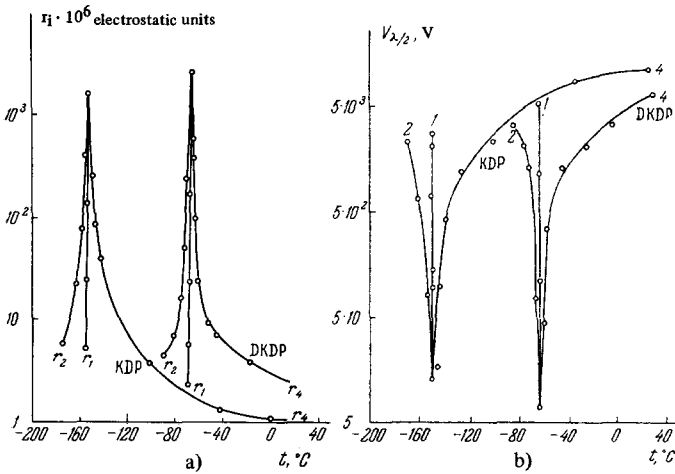


FIG. 15. a) Temperature-dependences of the electrooptic coefficients  $r_i$  for KDP and DKDP crystals:  $r_1 = n_3^3 r_{33} - n_2^3 r_{23}$ ,  $r_2 = n_3^3 r_{33} - n_1^3 r_{13}$ ,  $r_4 = n_0^3 r_{63}$ . b) Temperature-dependences of the half-wave voltages for KDP and DKDP crystals.

matic spectral-ratio pyrometers,<sup>[260]</sup> television color-temperature meters, and automatic plotters of temperature-field isotherms on the surface of a heated body.<sup>[261]</sup>

The sharp rise in the electrooptic coefficients  $r_{63}$  in the tetragonal phases and in  $r_{13}$ ,  $r_{23}$ , and  $r_{33}$  in the orthorhombic phases of KDP and DKDP crystals near the phase-transition point is of considerable interest (Fig. 15a).<sup>[71,72,140]</sup> Figure 15b shows the corresponding variation in the control voltages  $V_{\lambda/2}$ . As these data imply, if one can maintain sufficiently exact cryostatic conditions, use of KDP and DKDP crystals near their phase-transition temperatures ( $-150^\circ$  and  $-52^\circ\text{C}$ ) makes possible the design of very economical LBC devices.

**1.4.2. Other tetragonal crystals showing a linear electrooptic effect.** Table I gives the linear electrooptic effect coefficients for single crystals of barium titanate  $\text{BaTiO}_3$  in the ferroelectric ditetragonal-pyramidal modification. The measurements of American and Soviet researchers<sup>[77-82]</sup> have given well-concordant results. However, in spite of the large values of the electrooptic coefficients and rather wide range of spectral transparency (from 0.45 to 8 microns), the practical application of barium titanate crystals is greatly complicated by the difficulty of growing optically-homogeneous equidimensional crystals of any appreciable size and the very high electromechanical coupling coefficient characteristic of barium titanate (see, e.g.<sup>[139]</sup>). The latter is the reason for the unusually small contribution of the true electrooptic effect to the overall effect. Thus, according to the data of<sup>[77]</sup>,  $r'_C/r_C = 0.22$ , where  $r'_C = r_{33} - (n_a/n_c)^3/r_{13}$ , although  $r'_C$  surpasses  $r_{63}$  of KDP ( $324 \times 10^{-8}$  electrostatic units) in absolute value by a factor of ten. Nevertheless, Kaminow<sup>[81]</sup> was able to build a highly-effective phase modulator for light from a single-domain single-crystal barium titanate rod of dimensions  $0.25 \times 0.34 \times 3.8$  mm. It was tested over the range 5–250 MHz, and showed a power dissipation of less than 215 mW. Preliminary information has appeared very recently on the development of a new, highly effective linear electrooptic crystal having the structure of tetragonal barium titanate: strontium-barium niobate,<sup>[246]</sup> which shows the highest measured

value of  $r_{ij}$  ( $r_{33} = 4020 \times 10^{-8}$  electrostatic units) and the lowest half-wave voltage ( $V_{\lambda/2} = 24$  V at 15 MHz). The technological potential of the SBN crystal cannot yet be judged.

The last tetragonal-tetrahedral linear electrooptic crystal is pentaerythritol,  $\text{C}(\text{CH}_2\text{OH})_4$ .<sup>[83]</sup> Unfortunately, pentaerythritol crystals are not technically amenable, are hard to grow, and show perfect cleavage on [001]. Combined with the small value of the only measured coefficient  $r_{52}$ , which is furthermore ascribed to a symmetry state lowered by growth stresses, we cannot hope to use it. PE crystals are also somewhat inferior to the molecular crystals of HMTA in their spectral transparency.

**1.5. Orthorhombic Electrooptic Crystals.** The most important orthorhombic linear electrooptic crystal is ammonium oxalate  $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$  (AMO).<sup>[248]</sup> Owing to the happy combination of large  $r_{ij}$  and small  $\epsilon_{ij}$ , this water-soluble crystal is distinguished by very small control energies, which open up favorable perspectives for its practical use. Certain complications along this line can arise only from the large birefringence ( $\Delta n_{\text{max}} = 0.15$ ), which in turn facilitates the use of AMO in instruments for deviating laser beams.

Practical use of the crystal tetramethylammonium triiodomercurate (TTM), which has a large static linear electrooptic effect, is complicated by its softness (Mohs hardness  $< 1$ ). Crystals of Rochelle salt are of no practical interest as an electrooptic material. Besides Rochelle salt, which was cited in Table I, the orthorhombic system also contains the orthorhombic pyramidal crystals of antimony sulfoiodide SbSI and compounds isomorphous with it. They exhibit an exceedingly high dependence of the intrinsic absorption edge on the value of the shifting field.<sup>[141]</sup> When a d.c. field of 5000 V/cm is applied along the c axis of a crystal of antimony sulfoiodide, the edge of the intrinsic absorption band is shifted to shorter wavelengths by almost 80 Å. Elucidation of the nature of this anomalous effect, which is due to piezoelectric deformation of the crystal, is the topic of<sup>[142-143]</sup>. According to the data of<sup>[144,145]</sup>, the piezoeffect in antimony sulfoiodide is the largest ever measured. At TC, the electromechanical coupling coefficient  $k_{33}$  is as high as 90%, and  $d_{33} = 10^{-4}$  electrostatic units. In conjunction with strongly-marked ferroelectric properties and photoconductivity, the anomalous characteristics of SbSI crystals listed above demand considerable engineering work to realize its potentialities as a working substance for LBC devices.

**1.6. Monoclinic Linear Electrooptic Crystals.** As we know, non-centrosymmetric monoclinic crystals are optically biaxial, and can have eight (class 2) or ten (class m) independent electrooptic coefficients. This fact not only highly complicates measurement of the coefficients themselves, since by the usual methods one can only measure the differences of certain coefficients, rather than their direct values, but also it hinders their practical application to no lesser degree. Table I gives the results for three monoclinic crystals: calcium pyroniobate,<sup>[87]</sup> triglycine sulfate, and deuterotriglycine sulfate.<sup>[88-92]</sup> Fig. 16 gives the temperature-dependences of the electrooptic coefficients  $r_i$  and of the corresponding control voltages  $V_{\lambda/2}$ <sup>[91]</sup> for triglycine sulfate (TGS) crystals. Here the electrooptic coefficients  $r_i$  describe

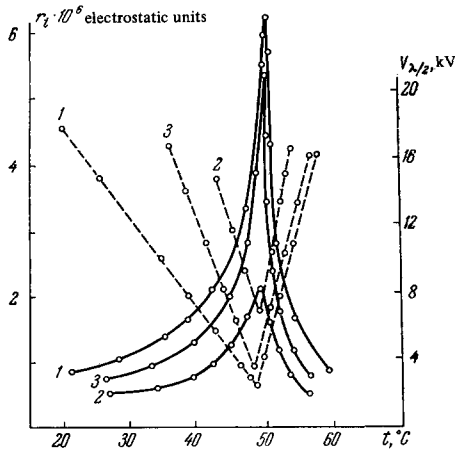


FIG. 16. Temperature-dependences of the electrooptic coefficients  $r_i$  and half-wave voltages  $V_{\lambda/2}$  for TGS crystals.

the linear electrooptic effect at constant mechanical stress, and are related to the electrooptic coefficients of the primary electrooptic effect  $r_i^1$  by equations taking account of the symmetry of TGS, similar to those discussed in Sec. 1.4.1.2. The curves in Fig. 16 have a clearly marked anomaly at the Curie point, indicating that non-linearity of the induced polarization is maintained up to optical frequencies, with a maximum at the Curie point. It was shown in<sup>[91]</sup> that at optical frequencies the anisotropy of the electric polarization and its non-linearity differ in nature from those at low frequencies. At optical frequencies, the quasisymmetric tetrahedral  $SO_4$  ions, whose dipole moments are perpendicular to the ferroelectric axis, are responsible for the polarization. This agrees well with the data of<sup>[146]</sup>. According to<sup>[91]</sup>, the contribution of the primary electrooptic effect to the overall effect in TGS is 90%. This indicates that the linear electrooptic effect in TGS is mainly caused by electronic polarization processes. This correlates with Hellmeier's hypothesis<sup>[24,25]</sup> on the nature of the polarization at optical frequencies in molecular crystals (HMTA), as confirmed also for tren hydrochloride. However, the considerable size of the

dielectric losses in TGS near  $T_C$ , where it becomes electrooptically "soft," prevents us from expecting to design efficient LBC devices based on it. All that has been said about TGS holds also for DTGS, except for a certain broadening of its range of spectral transparency in the infrared (from 1.4 to 1.7  $\mu$ ). Calcium pyroniobate crystals are rather difficult to deal with technically, and show a cleavage that interferes with handling them. Besides the compounds cited in Table I, second-order electrooptic effects (rotations of the optic indicatrix) have been studied in crystals of triglycine selenate and lithium hydrogen selenite, which revealed no technically important characteristics.<sup>[147,148]</sup>

**1.7. Triclinic Linear Electrooptic Crystals.** Apparently, the potassium iodate crystal is triclinic. It has been shown to have considerable optical non-linearity.<sup>[149]</sup> However, the lack of crystals of sufficient dimensions and requisite optical quality prevented making any quantitative electrooptic measurements. Among other triclinic acentric crystals, only sodium hydrogen selenite<sup>[150]</sup> has been studied, the rotation of the optic indicatrix being measured.

**2. CRYSTALS SHOWING A QUADRATIC ELECTROOPTIC EFFECT**

As the reviews<sup>[7,9]</sup> have thoroughly shown, certain of the crystals of the perovskite-type ferroelectrics show a considerable quadratic electrooptic effect in the centrosymmetric paraelectric phase near the Curie point. Table V summarizes the values of the quadratic electrooptic effect coefficients  $g_{ij}$ , as compiled from the data of<sup>[19,151,132,241,242]</sup>.

The results for barium titanate have also been confirmed in<sup>[153]</sup>. For judging the practical applicability of crystals showing an appreciable quadratic electrooptic effect, as compared with linear electrooptic crystals, I have compiled Table VI from the data of<sup>[72,140,154]</sup>.

The data of Table VI are involved in the possibility of using electrooptic crystals as the active elements of systems for deviating light beams, and they show the high values of the characteristics of the paraelectric perovskites (Fig. 17). In their deviating power, the

**Table V. Quadratic electrooptic coefficients of certain perovskites at 6328 Å**

Crystal	$T_C, ^\circ C$	Studied temperature range, $^\circ C$	Refractive index n	Electrooptic coefficients, $10^{10}$ electrostatic units			
				$g_{11}$	$g_{12}$	$g_{11} - g_{12}$	$g_{14}$
BaTiO <sub>3</sub>	128	135-160	2.4	+1.33	-0.11	+1.44	
SrTiO <sub>3</sub>	Low	-269+27	2.38			+1.1	+1.56
KTaO <sub>3</sub>	-269	-271-196	2.24			+1.77	+1.33
KTa <sub>0.85</sub> Nb <sub>0.35</sub> O <sub>3</sub>	10	12+37	2.29	+1.51	-0.42	+1.93	+1.63
PbMg <sub>1/3</sub> Nb <sub>2/3</sub> O <sub>3</sub>	-12	-10 + +25	2.56			+0.17	+0.09

**Table VI. Alterations of the refractive indices of certain crystals when acted on by an external field of 5000 V.**

CuCl at 25 $^\circ$ C	ZnS at 25 $^\circ$ C	SrTiO <sub>3</sub> at -213 $^\circ$ C	BaTiO <sub>3</sub> at 130 $^\circ$ C	KTN at 12 $^\circ$ C	KDP at 25 $^\circ$ C	KDP at -151 $^\circ$ C	DKDP at -51 $^\circ$ C
1.10 <sup>-5</sup>	6.10 <sup>-6</sup>	2.10 <sup>-3</sup>	2.10 <sup>-3</sup>	2.10 <sup>-3</sup>	9.10 <sup>-3</sup>	5.10 <sup>-3</sup>	5.10 <sup>-3</sup>

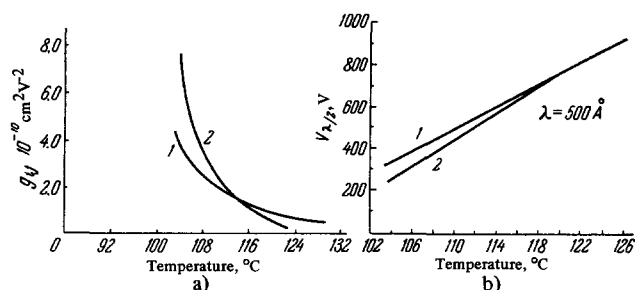


FIG. 17. a) Temperature-dependence of the electrooptic coefficients for BaTiO<sub>3</sub> crystals: 1—field along [110], light along [001]; 2—field along [100], light along [001]. b) Temperature-dependence of the half-wave voltage for BaTiO<sub>3</sub> crystals: 1—field along [110], light along [001]; 2—field along [100], light along [001].

perovskites considerably surpass the usual linear electrooptic crystals, and are practically equivalent to KDP and DKDP near their Curie points. However, use of KDP and DKDP requires more complex cryostating than work with the titanates or KTN, although the perovskites are considerably poorer than the phosphates in optical quality. For judging the comparative characteristics of modulators (light-polarization switches) using various electrooptic crystals, I give the data of Kurtz's calculations<sup>[155]</sup> (Table VII).

In spite of the tempting characteristics of devices that can be realized in principle by using quadratic electrooptic crystals and the relatively best of them, KTN, we must bear in mind that at present the perovskites can be applied at best to prepare single prototypes having considerably poorer properties than the calculated ones used in Tables VI and VII. This involves difficulties not yet overcome in the technique of growing large, optically homogeneous single crystals of the paraelectric perovskites. It was pointed out in<sup>[155]</sup> that the homogeneity of composition of the best specimens of KTN is 100–1000 times poorer than the value taken in calculating Table VII. It was emphasized in<sup>[156]</sup> that the studied crystals of strontium titanate were essentially not cubic over the entire range from  $-264^{\circ}$  to  $+27^{\circ}$  C. Apparently this also involved the optical inhomogeneity of the crystals, and it is confirmed by the author's observations and data<sup>[153]</sup> on barium titanate. In spite of

Table VII. A comparison of KTN with linear electrooptic crystals

Characteristics	LiNbO <sub>3</sub> *)	ZnTe **)	KTN ***)
Dimensions of a modulator element for a discrete-deviation system, cm	2.64×0.5×1	2.64×0.5×1	2.24×0.75×0.8
Reduced half-wave voltage $V_{\lambda/2}$ , V	400	2500	45
Dielectric constant	40	10	14 000
Number of positions in the address system	3.6·10 <sup>4</sup>	3.6·10 <sup>8</sup>	1.0·10 <sup>8</sup>
Speed of addressing, sec/address	10 <sup>-6</sup>	10 <sup>-6</sup>	10 <sup>-6</sup>
Control voltage, V	2000	1250	42
Reactive power, watts	10	10	2.6
Bias voltage, V	0	0	1200
Capacitance, nf	19	4.6	3000

\*)  $\lambda = 5000 \text{ \AA}$ .  
 \*\*)  $\lambda = 6000 \text{ \AA}$ .  
 \*\*\*)  $\lambda = 5000 \text{ \AA}$ , operating in a displacement field of 1200 V.

the fact that the cubic symmetry of the paraelectric ABO<sub>3</sub>-type crystals is reduced to trigonal (3m) or tetragonal (4mm) in the presence of a displacement field, whereas structures of this type show considerable ionic displacement as was shown in<sup>[7]</sup>, the contribution of the true quadratic electrooptic effect to the overall effect is greater than 90%. Apparently this involves the high electronic polarizability of the oxygen [BO<sub>6</sub>] octahedra, which are the fundamental building blocks of this structural type. Unfortunately, all that I have said about the optical homogeneity of the paraelectric perovskites holds, though to a lesser degree, for the growth from the melt of linear electrooptic crystals of the ilmenite and sphalerite structures.

Lead magnesium niobate PbMg<sub>1/3</sub>Nb<sub>2/3</sub>O<sub>3</sub><sup>[240,241]</sup> has relatively better technical characteristics, together with satisfactory electrooptic properties. It has been used to build an efficient light modulator working over the range up to 100 MHz.<sup>[240]</sup> Lead zinc niobate PbZn<sub>1/3</sub>Nb<sub>2/3</sub>O<sub>3</sub> has practically identical properties.<sup>[242]</sup>

The problem was discussed in<sup>[7]</sup> of the size of the coefficients of the quadratic electrooptic effect in non-centrosymmetric crystals, and it was shown for the examples of KDP and Rochelle salt crystals that they might show appreciable quadratic effects. The problem of detecting a Kerr effect in non-centrosymmetric crystals was discussed in detail in<sup>[157-159]</sup>. They showed that in the studied crystals in the physically-isomorphous subgroup KDP, DKDP, and RDP, as well as in ADP and DADP, the values of the quadratic electrooptic coefficients at room temperature are directly proportional to the value of T<sub>C</sub> of the corresponding single crystals in each of the subgroups.<sup>[159]</sup> Except for the paraelectric perovskites, the quadratic electrooptic effect is considerably smaller in all the studied crystals than the linear electrooptic effect whenever the latter is clearly marked.

In conclusion, I shall compare the efficiency of the best of the above-discussed linear and quadratic electrooptic crystals, for which purpose I have compiled Table VIII by the method of<sup>[251]</sup> (from the data of<sup>[251,246,248]</sup>). In estimating the relative qualities of substances included in the table, I had to take into account also their previously-cited technical and service characteristics. Naturally, this also holds for the other LBC materials.

### 3. OPTICALLY NON-LINEAR CRYSTALS

In line with the problem formulated in the introduction, this section will discuss only the data on the characteristics of single crystals having optical non-linear-

Table VIII. A comparison of the control characteristics of the most important electrooptic crystals

Crystal	Dielectric constant $\epsilon$	Control voltage (E, $l/\lambda/2$ , V)	Control energy $\epsilon(E, l)^2/\lambda/2$ , joules/meter
KDP	21	1.9·10 <sup>4</sup>	6.7·10 <sup>-2</sup>
LN	28	2.8·10 <sup>3</sup>	1.9·10 <sup>-3</sup>
LT	43	2.7·10 <sup>3</sup>	2.8·10 <sup>-3</sup>
AMO	7	0.7·10 <sup>3</sup>	2·10 <sup>-5</sup>
SEN	10 <sup>8</sup>	40	1·10 <sup>-5</sup>
KTN	10 <sup>4</sup>	28	7.1·10 <sup>-5</sup>

**Table IX.** Relative values of the components of the non-linear susceptibility tensor  $\chi_{ijk}^{2\omega = \omega + \omega}$ . Voigt's notation is used:  $x = 1, y = 2, z = 3, yz = zy = 4, xz = zx = 5, xy = yx = 6$ . The value of  $\chi_{36}$  for KDP is taken as unity. Its absolute value is  $\chi_{36} = 6 \times 10^{-9}$  electrostatic units. [165]

Crystal			Susceptibility coefficients for second-harmonic generation		References
Name of formula	Provisional symbol	Symmetry	$\lambda = 6943 \text{ \AA}$	$\lambda = 1.06 \text{ \mu}$	
Potassium dihydrogen phosphate, $\text{KH}_2\text{PO}_4$	KDP	$\bar{4}2m$	$\chi_{36} = 1.00$	$\chi_{36} = 1.00$	166
			$\chi_{14} = 0.95$		167
			$\chi_{36} = 1.00$ $\chi_{14} = 0.86$ $\chi_{36} = 1.00$	$\chi_{14} = 1.01$	171, 172
Potassium dideuterium phosphate, $\text{KD}_2\text{PO}_4$	DKDP	$\bar{4}2m$	$\chi_{36} = 1.04$	$\chi_{36} = 0.92$	170
			$\chi_{14} = 0.99$	$\chi_{14} = 0.91$	167
			$\chi_{36} = 0.99$ $\chi_{14} = 0.85$ $\chi_{36} = 0.75$ $\chi_{36} = 1.04$		171, 172
Rubidium dihydrogen phosphate, $\text{RbH}_2\text{PO}_4$	RDP	$\bar{4}2m$			171, 172
Potassium dihydrogen arsenate, $\text{KH}_2\text{AsO}_4$	KDA	$\bar{4}2m$	$\chi_{36} = 1.0$	$\chi_{36} = 1.06$	167
			$\chi_{14} = 0.86$	$\chi_{14} = 1.12$	170
			$\chi_{36} = 0.70$		171, 172
Rubidium dihydrogen arsenate, $\text{RbH}_2\text{AsO}_4$	RDA	$\bar{4}2m$	$\chi_{36} = 0.64$		171, 172
Cesium dihydrogen arsenate, $\text{CsH}_2\text{AsO}_4$	CDA	$\bar{4}2m$	$\chi_{36} = 0.53$		171, 172
Ammonium dihydrogen phosphate, $\text{NH}_4\text{H}_2\text{PO}_4$	ADP	$\bar{4}2m$	$\chi_{36} = 0.93$	$\chi_{14} = 0.89$	166, 167
			$\chi_{36} = 0.99$	$\chi_{14} = 0.98$	
			$\chi_{36} = 1.25$ $\chi_{36} = 1.18$	$\chi_{14} = 1.07$	171, 172
Ammonium dideuterium phosphate, $\text{ND}_4\text{D}_2\text{PO}_4$	DADP	$\bar{4}2m$	$\chi_{36} = 1.10$		171, 172
Gallium phosphide, GaP		$\bar{4}3m$		$\chi_{14} = 175$	170
Gallium arsenide, GaAs		$\bar{4}3m$	$\chi_{14} = 490$	$\chi_{14} = 580$	170
Gallium antimonide, GaSb		$\bar{4}3m$	$\chi_{14} = 400$	$\chi_{14} = 1300$	170
Indium arsenide, InAs		$\bar{4}3m$	$\chi_{14} = 340$	$\chi_{14} = 770$	170
Hexamethylenetetramine, $\text{C}_6\text{H}_{12}\text{N}_4$	HMTA	$\bar{4}3m$	$\chi_{14} = 10$		25
Sodium chlorate, $\text{NaClO}_3$		23	$\chi_{14} = 1.7$		265
Sodium bromate, $\text{NaBrO}_3$		23	$\chi_{14} = 0.6$		265
Zinc oxide, ZnO		$6mm$	$\chi_{24} = 4.7$ $\chi_{32} = 4.0$ $\chi_{33} = 14.3$		170
Cadmium sulfide, CdS		$6mm$	$\chi_{15} = 35$ $\chi_{33} = 63$	$\chi_{33} = 32$	168
Lithium niobate, $\text{LiNbO}_3$	LN	$3m$	$\chi_{22} = 6.3$		119
			$\chi_{31} = 11.9$		173
			$\chi_{33} = 83$		
Lithium tantalate, $\text{LiTaO}_3$	LT	$3m$	$\chi_{22} = 4.3$	$\chi_{31} = 2.6$	119
			$\chi_{33} = 40$		173
Proustite, $\text{Ag}_3\text{AsS}_3$		$3m$	$\chi_{22} = 50$	$\chi_{31} = 30$	250
Potassium dithionate, $\text{K}_2\text{S}_2\text{O}_6$		32	$\chi_{11} = 0.16$		174
Quartz, $\text{SiO}_2$		32	$\chi_{11} = 0.82$		168
Aluminum phosphate, $\text{AlPO}_4$		32	$\chi_{11} = 0.84$		170
Barium titanate, $\text{BaTiO}_3$		$4mm$	$\chi_{15} = 35$ $\chi_{33} = 14$	$\chi_{14} = 37$	168
Hippuric acid, $\text{C}_9\text{H}_9\text{O}_3\text{N}$		222	$\chi_{36} = 6$		175
Ammonium oxalate, $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$	AMO	222	$(\chi_{36} + \chi_{25})/2 \approx 1.6$		264

ity coefficients large enough to permit generation of second harmonics and sum and difference frequencies, parametric frequency tuning, and amplification of laser radiation. The ultraviolet and infrared ranges are included. Certain problems of the theory of these phenomena have been discussed in detail in [160-164], in addition to the reviews. [2-8, 8, 10]

I have compiled Table IX for comparative evaluation of the optical non-linearity coefficients measured up to now.

Among the 24 crystals whose optical non-linearity tensor coefficients have been measured up to now, the crystals of the KDP group and recently lithium niobate have been most widely applied. The huge values of the coefficients for the  $\text{A}^{\text{III}}\text{B}^{\text{V}}$ -type crystals do not result in second-harmonic generation with a large degree of conversion because of the lack of a phase-matching direction and the large absorption of the harmonic wave. The latter factor also excludes practical use of cadmium sulfide and barium titanate crystals for  $\lambda = 6943 \text{ \AA}$ .

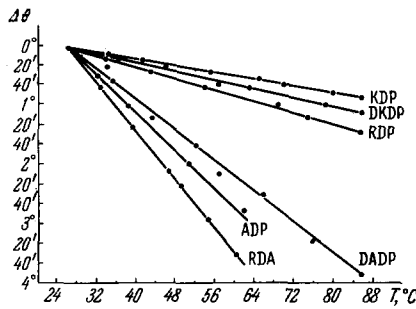


FIG. 18. Temperature-dependence of the deviation from the phase-matching direction (oeo) for  $\lambda = 6943 \text{ \AA}$  at  $25^\circ\text{C}$  for KDP-group crystals.

Thus, the eight KDP-type crystals, lithium niobate and tantalate, proustite, hippuric acid, and ammonium oxalate remain for more detailed study.

I have compiled from the data of [171,172] a summary of the characteristics of the crystals of the KDP group for second-harmonic generation from ruby-laser radiation, with matching of the ordinary ray of the fundamental frequency and the extraordinary ray of the harmonic, at room temperature (Table X).

I have supplemented Table X with Fig. 18 according to the data of [172]. It shows the temperature-dependence of the deviation from the phase-matching direction at  $25^\circ\text{C}$  for crystals of the KDP group. Also, Fig. 19a shows the temperature-dependence of the second-harmonic power in the phase-matching direction for the RDA crystal, and Fig. 19b shows the relative second-harmonic yield in the phase-matching direction (oeo) for  $\lambda = 6943 \text{ \AA}$  for RDA crystals at  $92^\circ\text{C}$  and KDP crystals at  $25^\circ\text{C}$ .

Besides the "classical" optically non-linear crystals KDP and ADP, the cited set of data indicates that RDP and RDA have properties of practical interest. The latter are considerably more efficient at room temperature than KDP because of longer coherence lengths and less critical phase-matching angles. RDA crystals show a very favorable feature: the second harmonic of  $6943 \text{ \AA}$  can be matched in a direction perpendicular to the optic axis at  $92 \pm 1^\circ\text{C}$  by temperature adjustment of the dispersion characteristics. [176] Thus one can achieve very great coherence lengths because of the absence of phase mismatch caused by the natural birefringence, and to enhance the conversion coefficient considerably. According to the data of [177], one can attain  $90^\circ$  phase-

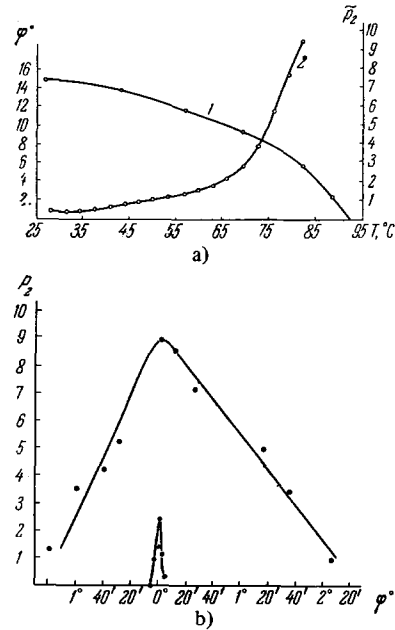


FIG. 19. a) Temperature-dependence of the second-harmonic power in the phase-matching direction (oeo) for  $\lambda = 6943 \text{ \AA}$  for RDA crystals: 1—phase-matching angle, degrees; 2—second-harmonic power (arbitrary units). b) Relative second-harmonic yield in the phase-matching direction (oeo) for  $\lambda = 6943 \text{ \AA}$  for RDA crystals at  $92^\circ\text{C}$  and KDP crystals at  $25^\circ\text{C}$ .

matching in KDP for second-harmonic generation from blue-green argon laser radiation by adjusting the dispersion characteristics with an electric field while working near the Curie temperature in the paraelectric phase. This method is apparently general in nature, and may give results for all crystals of the KDP group, naturally for certain particular frequencies in each individual case.

I must mention the high stability of crystals of the KDP group toward the action of pulsed power intensities when used as materials for electrooptic Q-switched laser shutters. According to the data of [178,179], KDP crystals withstand up to 200–300 megawatts/cm<sup>2</sup>, ADP up to 500 megawatts/cm<sup>2</sup>, and RDP up to 800 megawatts/cm<sup>2</sup>. In converting 1.06- $\mu$  radiation, the conversion coefficient can be as high as 45% under optimal conditions with minimum beam divergence and high crystal quality. [180] The role of the optical homogeneity of the non-linear crystal has been discussed thoroughly in [181], where it was shown that random inhomogeneities in the optically non-linear medium sharply impair the conversion, and the requirement was justified that the crystal should not be disoriented with respect to its optic axis by more than  $5-10'$ . Such rigid requirements are effectively satisfied at present only by crystals of the KDP group, for which a technique has been developed for growing large single crystals (of dimensions up to  $100 \times 100 \times 400 \text{ mm}$ ) of optical quality. [131,262] Fig. 20 shows a view of a KDP crystal.

Hippuric acid [175] is of some interest as an optically non-linear crystal for the visible and near infrared (to  $1.2 \mu$ ). It shows considerable birefringence, but the application of  $90^\circ$  phase-matching is complicated by the fact that it is optically biaxial (symmetry (222)). No method has been developed for growing large crystals

Table X. Certain characteristics of optically non-linear crystals of the KDP group

Characteristic	Crystal					
	KDP	DKDP	RDP	RDA	ADP	DADP
Phase-matching angle for second-harmonic generation from $\lambda = 6943 \text{ \AA}$ for oeo type ( $\theta$ , degrees)	49	52	66	80	48	47
Angular half-width of the phase-matching direction ( $\Delta\theta'$ )	6	5	11	15	6	5
Coherence length in relative units (experimental)	1.0	1.1	2	2.5	0.89	0.92
Second-harmonic power in relative units (experimental)	1	0.4	2.5	1.3	0.88	1.3
Second-harmonic power $P_2$ in relative units (calculated)	1	0.6	6	3.3	1.1	0.95



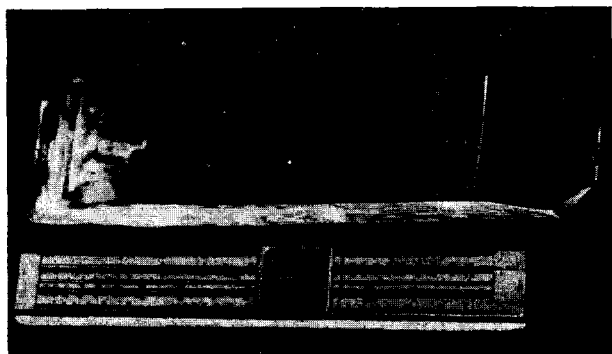


FIG. 20. A single crystal of KDP.

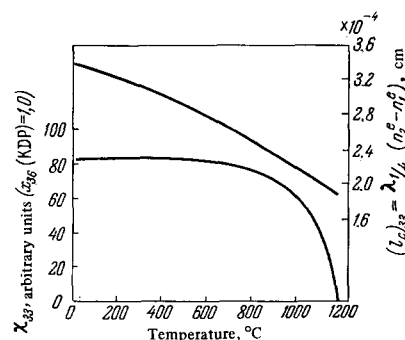


FIG. 21. Temperature-dependence of the non-linearity coefficient  $\chi_{33}$  and the coherence length  $(l_c)_{33}$  for lithium niobate crystals. [119]

of hippuric acid. This is also true of ammonium oxalate.

Proustite<sup>[110,250,257]</sup> is a promising material for a very wide range of wavelengths (0.6–20  $\mu$ ), but it requires the development of a technique of reproducibility growing optically-homogeneous single crystals. Only thereafter can it become widely applied.

A property of proustite-pyrargyrite to be elucidated further is their threshold of light sensitivity, which can restrict their use in working with high-intensity light beams.

3.1. Lithium Niobate Crystals and Other Crystals.

In spite of very high optical non-linearity coefficients, which persist up to the Curie point (Fig. 21), lithium niobate has thus far not shown enough optical homogeneity and stability to the action of pulsed power intensity. Thus, according to the data of<sup>[182]</sup>, when coherent radiation of wavelengths shorter than 1.0  $\mu$  or incoherent visible or ultraviolet radiation acts on lithium niobate crystals, they can show very slowly relaxing fluctuations of the refractive index of as much as  $2 \times 10^{-4}$ . Perhaps this undesired property involves the technique of growing and annealing the LN crystals.<sup>[182]</sup> A fact of considerable interest is that LN crystals show 90° phase-matching, which is observed for 1.06  $\mu$  at 0°C.<sup>[183]</sup>

A 90° phase-matching of LN is described in<sup>[235]</sup> at 1.7  $\mu$  at 74°C, and it was shown possible to convert infrared radiation in the range 1.6–2.6  $\mu$  into visible light, with thermal adjustment of the phase-matching over the temperature range 0–350°C.

LiTaO<sub>3</sub> crystals resemble LN in many ways, but in individual cases they do not show refractive changes upon irradiation.

In addition to quantitative measurements on optically-perfect single crystals, the literature gives data on detection of second harmonics of ruby-laser radiation for a number of piezoelectric crystals,<sup>[184]</sup> and also in studying powders.<sup>[185,186]</sup> The results of<sup>[184,185]</sup> on about 50 substances are given in the review<sup>[61]</sup>. The point of greatest interest in the data of<sup>[186]</sup> is the discovery that powders of crystals of potassium iodate and bromate (KIO<sub>3</sub> and KBrO<sub>3</sub>) give a second-harmonic yield somewhat greater than KDP and ADP, a fact apparently worthy of further study.

In closing this section, it is pertinent to note the very thorough study<sup>[187]</sup> where the phase-matching angles and mismatch gradients were calculated for the crystals of greatest practical importance, KDP, ADP, and LN, for second-harmonic generation from radiation at 11523,

Table XI. Crystals showing optical non-linearity at 10.6  $\mu$ .

Crystal		Non-linear characteristics		
Name of formula	Symmetry	Susceptibility coefficients for second-harmonic generation, $10^7$ electrostatic units	Coherence length (exptl.) $\mu$	Reference
Cuprous chloride, CuCl	$\bar{4}3m$	$\chi_{14} = 0.2 \pm 0.1$	$l_c \geq 100$	266
Gallium arsenide, GaAs	$\bar{4}3m$	$\chi_{14} = 8.8 \pm 3.0$	$l_c = 110 \pm 10$	188–190
Indium arsenide, InAs	$\bar{4}3m$	$\chi_{14} = 1.0 \pm 3.0$	$l_c = 60 \pm 10$	188, 190
Zinc sulfide, ZnS	$\bar{4}3m$	$\chi_{14} = 0.73 \pm 0.2$	$l_c = 53 \pm 0.5$	188–190
Zinc selenide, ZnSe	$\bar{4}3m$	$\chi_{14} = 1.87 \pm 0.2$	$l_c = 126$ (calc.)	190
Zinc telluride, ZnTe	$\bar{4}3m$	$\chi_{14} = 2.2 \pm 0.8$	$l_c = 290 \pm 50$	188, 190
Cadmium telluride, CdTe	$\bar{4}3m$	$\chi_{14} = 4.0 \pm 1.5$	$l_c = 235$ (calc.)	190
Zinc sulfide, ZnS	6mm	$\chi_{33} = 0.89 \pm 0.3$ $\chi_{31} = 0.45 \pm 0.15$ $\chi_{15} = 1.05 \pm 0.3$	$l_{33} = 52 \pm 3$ $l_{31} = 51 \pm 3$ $l_{15} = 53 \pm 3$	199, 190
Cadmium sulfide, CdS	6mm	$\chi_{33} = 1.05 \pm 0.3$ $\chi_{31} = 0.63 \pm 0.15$ $\chi_{15} = 0.69 \pm 0.17$	$l_{33} = 67 \pm 7$ $l_{31} = 50 \pm 5$ $l_{15} = 73 \pm 7$	188, 190
Cadmium selenide, CdSe	6mm	$\chi_{33} = 1.3 \pm 0.3$ $\chi_{31} = 0.68 \pm 0.15$ $\chi_{15} = 0.74 \pm 0.18$	$l_{33} = 120 \pm 10$ $l_{31} = 64 \pm 6$ $l_{15} = 152 \pm 10$	188, 190
Selenium, Se	32	$\chi_{11} = 1.9 \pm 1.0$	By phase-matching	190, 266
Tellurium, Te	32	$\chi_{11} = 127 \pm 20$	By phase-matching	191, 266
Cinnabar, HgS	32	$\chi_{11} = 1.5 \pm 0.3$	By phase-matching	266

10600, 6943, and 6328 Å for 21 cases for KDP, 23 for ADP, and three for LN.

**3.2. Optically Non-linear Crystals for the Far Infra-red.** The invention of powerful gas lasers in the 10.6  $\mu$  range has given rise to a number of studies searching for optically non-linear materials that are transparent in the intermediate and far infrared ranges. Table XI summarizes the published experimental results.

As Table XI indicates, the trigonal single crystals selenium, tellurium, and cinnabar are characterized by the relatively best properties as optically non-linear infrared materials. They possess phase-matching directions that make it possible to enhance the conversion coefficient by accumulation of coherent interaction throughout their length. Apparently the uniaxial piezo- and pyroelectric crystals proustite and pyrargyrite are also quite promising in this regard. It is advantageous to apply anti-reflection coatings to all the cited crystals having high refractive indices because of high reflection losses. It is of considerable interest that parametric amplification has been obtained in tellurium crystals in the far infrared (17.888  $\mu$ ) when pumped at 10.6  $\mu$ .<sup>[192]</sup> Optically non-linear crystals that are transparent in the infrared can also be used to generate difference and sum frequencies,<sup>[193,194]</sup> in analogy to the use of KDP and LN crystals at shorter wavelengths.<sup>[195,196]</sup>

A parametric infrared generator based on selenium has been proposed,<sup>[197]</sup> and it ensures that we can expect results similar to those obtained previously for the near infrared and visible.<sup>[198,199]</sup> Proustite has shown promise when used as a mixer crystal for parametric frequency-raising of an infrared signal to convert it to a frequency in the range of greatest sensitivity of a photomultiplier or photodiode.<sup>[253,257]</sup> In closing this section, I must mention the recent discovery<sup>[200]</sup> of a new type of optical non-linearity in non-centrosymmetric semiconductor single crystals, due to electrons in the conduction band. The obtained preliminary results indicate an extension of the possibilities of parametric conversion, owing to the ease of controlling the conduction electrons by external electric or magnetic fields.

I must mention the publication of some preliminary communications indicating that one can get phase-matching in harmonic generation by using optical rotatory dispersion.<sup>[236]</sup> The optically-active crystals of quartz, potassium lithium sulfate, sodium chlorate, germano- and titanosillenites, and a large number of optically-active organic and complex compounds are worth studying in this respect. Possibly the rotatory dispersion of the latter can be varied by planned modification of the type structure.

The next line along which encouraging experimental results have been noted is the demonstration of second-harmonic generation from the radiation of a pulsed ruby laser in mechanically textured films of liquid crystals of cholesteryl 2-(2-ethoxyethoxy)ethyl carbonate.<sup>[237,268]</sup> The second-harmonic yield was an order of magnitude higher than in quartz, with a greater breadth of the phase-matching direction. Apparently it would be advantageous both to survey the known liquid crystals (see, e.g.<sup>[238]</sup>) and perhaps to synthesize new ones.

A prediction of efficient second-harmonic generation in absorbing media is also of considerable interest.<sup>[201]</sup> According to it, special matrix media containing added

paramagnetic rare-earth ions will probably show optical non-linearity coefficients  $\chi_{ijk}$   $10^3$  times as great as  $\chi_{36}$  of KDP, with absorption coefficients at the working frequencies of less than  $1 \text{ cm}^{-1}$ . A confirmation of the prediction in<sup>[201]</sup> would make it possible to get efficient conversion at low pumping power levels with small crystals and under less critical phase-matching conditions.

#### 4. MAGNETOOPTIC CRYSTALS

In spite of the considerable extent to which magneto-optic phenomena have been studied, surpassing that of electrooptic effects until fairly recently, construction of technical instruments based on magneto-optic crystals for purposes of quantum electronics has not yet been reduced to engineering practice.

The reason for this is the opacity of the substances showing a large Faraday rotation in the range of interest to us, and the rather high magneto-optic "stiffness" of the exceedingly limited number of transparent crystals having Verdet constants of a size adequate for practice.

The relatively best characteristics are shown by chromium tribromide<sup>[202,203]</sup> and europium oxide and sulfide (EuO and EuS).<sup>[204]</sup> They surpass ytterbium iron garnet<sup>[205]</sup> and ytterbium gallium iron garnet.<sup>[206]</sup> Data have recently appeared indicating that it would be advantageous to test in magneto-optic apparatus the transparent ferrimagnetic crystals RbNiF<sub>3</sub><sup>[207]</sup> and Na<sub>3</sub>Fe<sub>3</sub>F<sub>14</sub>,<sup>[208]</sup> which have Curie points of 128° and 193°C, respectively. According to the data of<sup>[209]</sup>, a rotation of 300°/cm at  $\lambda = 0.55 \mu$  is attained in RbNiF<sub>3</sub> at 4.2°K in a saturation field of 5 kOe. These crystals are transparent from 0.4 to 11  $\mu$ . The new ferrimagnetic material TlNiF<sub>3</sub><sup>[239]</sup> having  $T_N = 150^\circ\text{K}$  is a structural analog of RbNiF<sub>3</sub>.

An optical rectifier based on the Faraday effect is described in<sup>[210]</sup>. In developing it, they used diamagnetic lead-cerium glasses, paramagnetic cerium and terbium phosphate glasses, and also terbium aluminum garnet. The maximum value of the Verdet constant (for the latter material) amounted to about 1 min/cm-gauss. Data on the magneto-optic properties of the new transparent compounds europium orthosilicate, fluoride, and selenide are given in<sup>[211]</sup>.

#### 5. BIREFRINGENT CRYSTALS FOR NEW OPTICAL ELECTRONIC ELEMENTS

Problems of creating systems operating in the optical range designed for different purposes have required invention of an entire series of new optical elements, in particular FM-AM converters,<sup>[212,213]</sup> optical discriminators and beam-splitters,<sup>[214]</sup> optical rectifiers,<sup>[215]</sup> demodulators and switches,<sup>[216]</sup> narrow-band filters, including those with rapid tuning of the transmission band,<sup>[217-220]</sup> all varieties of apparatus for deviating a light beam (deflectors and deviators),<sup>[221-227]</sup> light-bunching modulators,<sup>[228]</sup> and many others.

A series of theoretical papers<sup>[229a-C,230]</sup> has appeared in recent years with the fundamental idea of using different optical systems involving birefringent crystals in some form to attain set goals. Among these, the literature has mentioned only the classical materials of

Table XII. Lyot-type birefringent filters for the  $H_{\alpha}$  line with a 1-Å transmission band

Crystal	Thickness of the largest plate, cm	Birefringence	Crystal	Thickness of the largest plate, cm	Birefringence
Quartz . . . .	23.84	0.009	Ammonium oxalate	1.40	0.155
KDP . . . .	5.24	0.041	Calcite . . . .	1.268	0.172
ADP . . . .	4.78	0.045	Potassium nitrate	1.268	0.172
Lithium niobate	2.39	0.09	Guanidinium iodide	1.10	0.96
Triglycine sulfite . . . .	2.15	0.100	Sodium nitrate	0.86	0.251
Matlockite . . . .	1.55	0.139	Rutile . . . .	0.75	0.287
			Calomel . . . .	0.31	0.683

linear optics, calcite and quartz. Here they have often emphasized the impossibility of finding the best engineering solutions for lack of natural crystals having the requisite qualities and dimensions.

Part of the trouble can be eliminated by using the natural birefringence of ADP and KDP crystals. For example, they are used in the design of narrow-band interference-polarization filters.<sup>[217-220]</sup> However, the optical characteristics of KDP and ADP are inadequate for an entire series of purposes. As one of the possible ways of solving this problem, I have proposed<sup>[231, 232, 269]</sup> a program of determining the possibilities of using a number of artificially-grown birefringent crystals in the design of passive elements of optical-electronic systems.

Let us examine Table XII, which gives the values of the calculated thicknesses of the largest plates in Lyot filters for the  $H_{\alpha}$  line with a 1 Å transmission band for a number of promising single crystals.

The existing data permit us to classify the cited crystals according to some characteristics of practical importance in the order of relative decline of the discussed properties, in the following sequences:

1. In the order of birefringence: calomel, rutile, sodium nitrate, etc. (in the opposite order from Table XII).
2. In the order of mastery of the technique of growing large, optically homogeneous crystals: ADP, KDP, TGS, sodium nitrate, quartz, LN, rutile, AMO.
3. In the order of hardness and optical workability: quartz, LN, rutile, calcite, matlockite, KDP, ADP, TGS, AMO, sodium nitrate.
4. In the order of likelihood of developing a technique for preparing single crystals of optical quality (for the substances thus far not yet investigated along this line): AMO, potassium nitrate, LN, guanidinium iodide, rutile, matlockite, calomel.
5. In the order of insolubility in water in the range of thermal stability: quartz, rutile, LN, calcite, calomel, matlockite, potassium nitrate, sodium nitrate, KDP, AMO, guanidinium iodide, TGS, ADP.

Crystals that possibly may be used in the infrared are proustite-pyrargyrite, matlockite, trigonal selenium, tellurium, and cinnabar.

Understandably, the above-discussed list of single crystals that might be applied to prepare birefringent elements for optical electronics is by no means exhaustive. The reason for compiling it was primarily to draw attention to a new set of materials that should be studied thoroughly.

## CONCLUSION

The material that I have presented in this review indicates the great possibilities opened up for non-linear optics by the properties of the crystals having non-linear polarization that have already been studied.

The regularities found in studying the isomorphous series of the phosphates-arsenates, perovskites, and ilmenites have made it possible to reveal more deeply the basis of the optically non-linear properties in the crystal-chemical features of the structures, and they have created a more reliable basis for predictive exploratory studies. These advances could be made in spite of delay in developing a rigorous microscopic theory of optically non-linear phenomena, which has thus far prevented making reliable quantitative calculations. In turn, the development of a phenomenological thermodynamic theory makes it possible to treat the accumulated facts from a unified standpoint (see<sup>[90, 164, 233, 249]</sup>) and facilitates a more rigorous evaluation of them.

I must make special note of the established rationale of applying lattice labilization of ferroelectric single crystals in the paraelectric phase near the phase transition point to create highly efficient LBC devices with small power requirements (e.g., one needs a power  $10^5$  times smaller at  $-151^{\circ}\text{C}$  than at  $+25^{\circ}\text{C}$  to get 100% modulation in KDP crystals).

The existing KDP-type crystals allow one to work down to 2000 Å. Crystals of the Se and Te type cover the range out to 20  $\mu$ . However, further work is needed to search for new working substances having better technological and service characteristics than those discussed in this review.

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<sup>2</sup> S. A. Akhmanov and R. V. Khokhlov, Problemy nelineinoi optiki (Problems of Non-linear Optics), M., VINITI, 1964. [Gordon & Breach, in prep.]

<sup>3</sup> N. Bloembergen, Nonlinear Optics, Benjamin, New York, 1965.

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