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# *SOME NUCLEAR OPTICAL PROPERTIES OF CRYSTALS OF THE KDP GROUP*

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Second harmonic generation by a ruby laser in crystals of the KDP group is investigated. The nonlinearity coefficients $\chi_{36}$, the coherence lengths, and the temperature dependences of the mismatch index were measured. The matching angles were obtained from the experimental values of the refractive indices. The second harmonic power in the matching direction and the thermal dependences of the matching angles were measured.

THE nonlinear optical properties of crystals and particularly their ability to generate a powerful second harmonic of laser emission have recently been the subject of considerable interest. This is due to the significance of such phenomena in the study of the nature of nonlinear electron polarization of crystals, as well as to the possibilities of practical application.

One of the most widely used nonlinear optical crystals is potassium dihydrophosphate $KH_2PO_4$ (KDP), which belongs to the tetragonal-scalenohedral type of symmetry ($\bar{4}2m$) and is optically uniaxial. Second harmonic generation of ruby laser emission was first observed in KDP crystals by Giordmaine [1] in 1962 and was later thoroughly and frequently studied [2–4]. Later, second harmonic generation was observed in crystals of ammonium dihydrophosphate (ADP), which is isomorphic with KDP [5], and in deuterized potassium dihydrophosphate (DKDP) [6]. Miller [7] measured the coefficients of nonlinear polarization $\chi_{36}$ in all these crystals and also in potassium dihydroarsenate (KDA). Nevertheless the nonlinear optical properties of some crystals of the KDP group have not yet been studied, although a large number of crystals with the same structure and similar chemical composition are suitable for the study of the effect of isomorphic substitution on second harmonic generation.

We studied second harmonic generation of ruby laser emission ($\lambda = 6943$ Å) in isomorphic crystals of the KDP group: KDP, ADP, DKDP, deuterized ammonium dihydrophosphate (DADP), rubidium dihydrophosphate (RDP), rubidium and cesium dihydroarsenates (RDA and CDA), and KDA. All measurements were performed under identical experimental conditions.

Relative power in the matching direction and the coefficients of nonlinear polarization $\chi_{36}$ were measured by the standard method [2,3]: a parallel beam of light from a 2—3 kW ruby laser passed through the investigated crystal and through a system of filters to remove the pump lamp radiation and entered the input slit of a monochromator tuned to the second harmonic wavelength ($\lambda = 3472$ Å). A photomultiplier at the output slit of the monochromator generated a signal, proportional to the square of the laser output power, which entered a channel of a DÉSO-1 oscilloscope. A semitransparent plate in front of the investigated crystal directed a portion of the main radiation through a system of filters to a second photomultiplier whose signal entered the second channel of the oscilloscope. The investigated samples, with identical dimensions, were placed in a special thermostat, where they could be rotated in two mutually perpendicular planes; the angles of rotation were read off precision dials (±20″). The temperature in the thermostat was maintained constant by means of a TS-15 water thermostat with an accuracy of ±0.1°C.

The problem of measuring the coefficients of nonlinear polarization was investigated theoretically by Kleinman [8]; Maker et al. [9] provided a convenient practical solution. Generation of the second harmonic in crystals of the KDP group in a direction that is sufficiently far away from the matching direction is described by the following formula, given a suitably selected polarization of the laser beam:

$$P_2 = K\chi_{36}^2 P_1^2 \Delta^{-2} \sin^2(\Delta l/2). \qquad (1)$$

Here $P_1$ and $P_2$ are the fundamental and second harmonic powers respectively, K includes refractive indices, $\Delta = 2\pi(n_2 - n_1)/\lambda_2$, where $\lambda_2$ is the second harmonic wavelength, $n_1$ and $n_2$ are the refractive indices of the fundamental and the second harmonic respectively, and $l$ is the length of path of laser emission in the crystal. The quantity $\Delta n = n_2 - n_1$ is called the mismatch index of the phase velocities of the fundamental and the second harmonic.

It follows from (1) that the intensity of the second harmonic oscillates when the path length of the laser beam in the crystal varies, and that oscillation maxima occur for lengths $l$ that are multiples of a length $l_c$ called the coherence length, i.e., when $l = (2m + 1)l_c$, where $m = 0, 1, 2, \dots$, and

$$l_c = \lambda_2 / 2\Delta n. \tag{2}$$

In the case of the maxima (1) assumes the form

$$P_2 = K' \chi_{36}^2 P_1^2 l_c^2, \tag{3}$$

where K′ differs from K by a constant factor. The coefficient $\chi_{36}$ can be readily obtained from (3).

In [9], to find the maxima of harmonic intensity, the optical path length was varied by varying the angle of incidence of the beam on the crystal. However, this method is applicable only when the quantity $\Delta n$ remains constant while the plate angle varies. A generalization of this method [10] to the case of $\Delta n$ varying with the angle is difficult and introduces a considerable error into the coefficients of nonlinear polarization. In this case it is more convenient to use the temperature, dependence of the harmonic power to find the $\Delta n$ necessary for the computation of the nonlinear polarization coefficient according to (2). The variation of second harmonic generation with temperature is caused by a variation of $\Delta n$, which is equal to

$$d(\Delta n) = \lambda_2 / l \tag{4}$$

for the case of two neighboring maxima (or minima). The mismatch index for any maximum having a number m corresponding to the temperature $t_m$ will then be

$$\Delta n_{t_m} = \Delta n_{t_0} \pm m\lambda_2 / l. \tag{5}$$

Here $\Delta n_{t_0}$ is taken for the maximum at the temperature $t_0$ from which m is reckoned.

We can use (5) to obtain an expression for the mismatch index $\Delta n_t$ for any maximum corresponding to the temperature t:

$$\Delta n_t = \frac{d(\Delta n)\, m}{1 - \sqrt{a}} \tag{6}$$

where m is the number of the maximum, with power $P_{2m}$ reckoned from the maximum corresponding to a temperature t and having a power $P_{2t}$; $a = P_{2t}/P_{2m}$. We assume here that the coefficient of nonlinear polarization does not change with temperature within the temperature interval in question. The assumption is valid for crystals of the KDP group within the temperature interval 20–100°C.

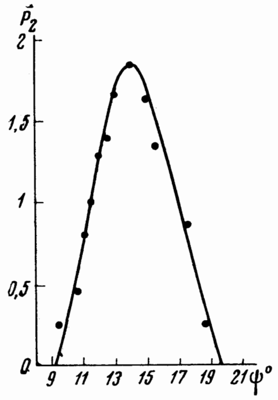

FIG. 1. Second harmonic power (arbitrary units) due to the coefficient $\chi_{36}$ of an ADP crystal as a function of the angle about the Z axis. The crystal is 1.03 mm

The coefficients of nonlinear polarization $\chi_{36}$ of the above crystals of the KDP group were measured by both methods with good agreement between the results. As an example, Fig. 1 shows the second harmonic power due to the coefficient $\chi_{36}$ as a function of the angle of rotation of the ADP plate about the Z axis. Figure 2 shows the harmonic power as a function of temperature for an RDA crystal. Curves analogous to those of Fig. 2 were used to plot the temperature dependence of the mismatch indices in the direction perpendicular to the Z axis.

The quantity $\Delta n$ decreases linearly in some crystals of the KDP group within the given temperature interval, as is shown in Fig. 3. Using this figure we can easily determine the temperatures for which $\Delta n = 0$, i.e., when matching is observed in a direction perpendicular to the Z axis without double refraction. Such a temperature was found for a lithium niobate single crystal [11] where the coherence length is much greater than the thickness of the sample. In all crystals of the KDP group this point lies above their temperature of decomposition, with the exception of RDA crystals, for which this temperature is 92.6°C [12].

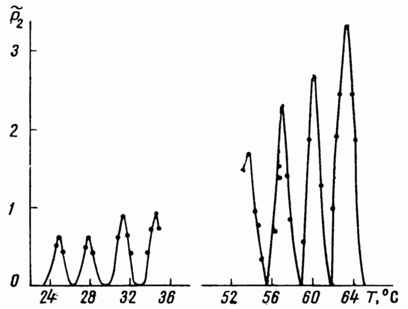

FIG. 2. Second harmonic power (arbitrary units) due to the coefficient $\chi_{36}$ of an RDA crystal as a function of temperature. The crystal is 6.55 mm thick.

Table I

| Crystal | KDP | DKDP | ADP | DADP | RDP | KDA | RDA | CDA |
|---|---|---|---|---|---|---|---|---|
| $l_c$ (exper.), $\mu$ | 9 | 10 | 7,9 | 8,9 | 32,7 | — | 158 | — |
| $l_c$ (calc), $\mu$ | 9,4 | 11,6 | 8,1 | 7.9 | 34 | 13,8 | — | 5,7 |
| $\chi_{36}$ | 1,00 | 0,75 | 1,18 | 1.10 | 1.04 | 0.70 | 0,64 | 0.53 |
| $\delta_{36}$ | 0,52 | 0.40 | 0,55 | 0,54 | 0.51 | 0.23 | 0.23 | 0.17 |

Table I gives the values of the coefficients of nonlinear polarization $\chi_{36}$ of the investigated crystals together with the coherence lengths measured experimentally and calculated from (2). The coefficients of nonlinear polarization are given, as is customary, in relative units, with the coefficient of the KDP crystal taken as 1.00.

The ratio $\chi_{36}/(\chi_{36})$ KDP was calculated from (3). The coefficient $K'$ depends on $n_0^{\omega}$, which is the index of refraction of the ordinary wave having a frequency $\omega$, and on $n_e^{2\omega}$, which is the index of refraction of the extraordinary wave having a frequency $2\omega$; $K'$ also depends on the direction cosines of the intensity vector of the fundamental frequency $\overline{E}_{\omega}$. The refractive indices were determined with an accuracy of ±0.0003, the values of the direction cosines were obtained with an accuracy of ±0.003, and the relative error in $P_2/P_1^2$ obtained by averaging several dozen values was ±12%. These data as well as the explicit form of $K'$[8] were used to obtain $\chi_{36}/(\chi_{36})\text{KDP}$ with a relative error ±15%.

In the case of dihydrophosphates, the coherence lengths determined experimentally were in good agreement with those calculated from the refractive indices. We note that the coherence length in RDA crystals in the direction perpendicular to the Z axis is very large, owing to the smallness of $\Delta n$.

The coefficients of nonlinear polarization $\chi_{36}$, being the components of a tensor of the third rank, are determinate if the field intensity is selected as the independent variable. Thermodynamics of crystals shows that nonlinear optical properties can be described by a number of coefficients that are determinate when other internal and external crystal parameters are selected as the independent variables. Miller[7] suggested the use of the coefficient $\delta_{ij}$ (polarization being the independent variable) and showed that it is almost constant for all the investigated substances. The coefficients $\chi_{ij}$ and $\delta_{ij}$ are related to each other in the following manner (in tensor notation)

$$\chi_{ijk} = \varkappa_{ii}^{2\omega}\varkappa_{jj}^{\omega}\varkappa_{kk}^{\omega}\delta_{ijk}, \tag{7}$$

where $\kappa_{ii}^{2\omega}$, $\kappa_{jj}^{\omega}$, and $\kappa_{kk}^{\omega}$ are the linear susceptibilities of the crystal at frequencies indicated by the superscripts.

The coefficients $\delta_{36}$ calculated by us from refractive indices and determined from (7) are also given in Table I.

Garrett[13] recently showed, using a model of an anharmonic oscillator, that the coefficient $\delta_{ij}$ depends on the microscopic parameters of the crystal in the following manner

$$\delta_{ij} \sim A\omega_0^2/\Pi^{5/2}, \tag{8}$$

where A is a constant, $\omega_0$ is the natural frequency of inelastically bound optical electrons producing dispersion, and $\Pi$ is electron density. Since the electron density is practically the same in all crystals of the KDP group, the difference in the coefficients $\delta_{36}$ is due only to the position of the intrinsic absorption edge of these crystals. In fact, Table I shows that $\delta_{36}$ is larger in ADP than in KDP since the edge of the absorption band of the former is shifted into the ultraviolet region[4].

When deuterium replaces hydrogen in ADP and KDP, the coefficients $\delta_{36}$ are decreased. This effect is particularly strong in DKDP, whose absorption band edge is considerably shifted into the visible region of the spectrum[14]. The low values of $\delta_{36}$ in dihydroarsenates are of interest. Since we know the position of the absorption edge in dihydrophosphate crystals, we can easily deduce from (8) that in arsenates this shift should be ~500—600 Å. An investigation of the position of the absorption edge$^{1)}$ in KDA and RDA crystals compared with KDP and RDP verified this assumption. However, the refractive indices and consequently the linear polarizations at optical frequencies are larger in these crystals than in the phosphates. Therefore the coefficients $\chi_{36}$ of the dihydroarsenates change as a result of two causes: they are increased by the increase in the

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$^{1)}$The absorption spectra of KDA and RDA crystals were obtained by L. M. Guseva. The absorption edge is 2160 Å in a KDA crystal 7 mm thick, and 2140 Å in an RDA crystal 1.45 mm thick.

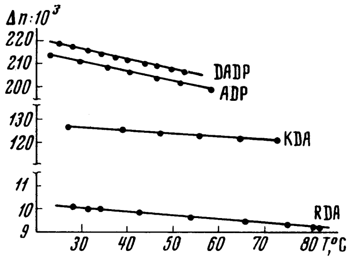

FIG. 3. Temperature dependence of mismatch indices in some crystals of the KDP group.

linear polarization and decreased by the shift in the absorption edge. The second cause is predominant.

It follows from (7) and (8) that the dispersion of nonlinear polarization coefficients differs, depending on the method of approach to the edge of the intrinsic absorption band, i.e., whether the laser frequency is varied leaving the edge of the absorption band without change, or whether the absorption edge alone is varied. In the first case the quantity $\delta_{ij}$ is changed by the change of the product of the susceptibilities, and in the second case both the susceptibility and the natural frequency of absorption $\omega_0$ change.

The experimental refractive indices [3] were used to calculate the matching angles with the Z axis (see Table II). We considered only the matching occurring in the KDP-group crystals when the phase velocities of the ordinary ray of the fundamental frequency and the extraordinary ray of the second harmonic coincide. It should be noted that as the cation radius increases the matching angle increases and there is no matching in CDA crystals.

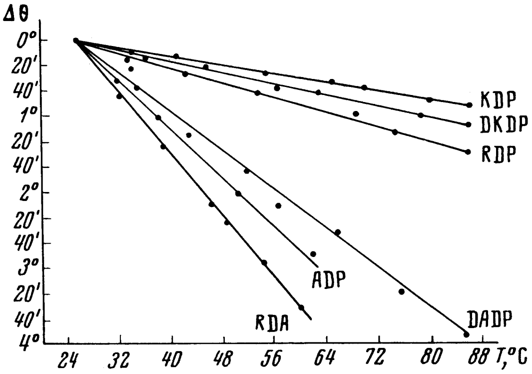

FIG. 4. Temperature dependence of matching directions in crystals of the KDP group (in the KDP crystal the matching angle approaches the Z axis with increasing temperature).

We investigated the second-harmonic power in the matching direction in crystals of the KDP group, with the exception of KDA, whose crystal size prohibits the preparation of oblique slices. The greatest power was found in RDP crystals and the smallest in DKDP crystals, which is in good agreement with the values obtained for the nonlinear coefficients and coherence lengths. Table II gives the relative second harmonic powers in the matching direction (the power for the case of KDP is taken as 1.00), determined experimentally and calculated for samples with thickness $l > l_c$ from the formula

$$P_2 = P_1^2 K_1 \chi_{36}^2 l_c l \sin^2 \theta.$$

Here $K_1$ is a coefficient depending on the refractive indices $n_0^{\omega}$ and $n_e^{2\omega}$, $\theta$ is the matching angle, $l_c$ is a coherence length in the matching direction calculated from the formula [15]

$$l_c = 4\Pi / K\alpha,$$

where $\alpha$ is the divergence of the laser beam, a constant quantity in our experiments

$$K = \frac{\omega n_\omega{}^0}{2c} \sin \beta,$$

and $\beta$ is the angle between the normals and tangents at the point of intersection of the refractive-index surfaces [16].

**Table II**

| Crystal | KDP | DKDP | ADP | DADP | RDP | KDA | RDA |
|---|---|---|---|---|---|---|---|
| Matching angle $\theta^\circ$ | 49 | 52 | 48 | 47 | 66 | 59 | 80 |
| Half-width $\Delta\theta'$ | 6 | 5 | 6 | 5 | 11 | | 15 |
| $l_c$ | 1 | 1,13 | 0,89 | 0,92 | 2 | | 2,5 |
| $\widetilde{P}_2$ (exper.) | 1 | 0,4 | 0.88 | 1,3 | 2,5 | | 1,3 |
| $\widetilde{P}_2$ (calc.) | 1 | 0.6 | 1,2 | 1,1 | 2,4 | | 1,2 |

These values are considered to be in satisfactory agreement. Table II also gives relative values (coherent length in KDP is taken as 1.00) of the coherence lengths of the investigated crystals and of the half-width of the second harmonic power curve in the matching direction.

The temperature dependence of the matching direction in crystals of the KDP group is of importance. Experiments revealed that this dependence is linear within the investigated temperature range (Fig. 4) except for RDA crystals at the temperatures of ~80—90°C, where the considerable nonlinearity in the T-dependence of $\theta$ is due to the fact that $\theta$ is ~90° for RDA.

In conclusion we thank T. A. Regul'skaya for measurements of the refractive indices of the crystals, V. M. Guseva for plotting absorption spectra of the arsenates, V. T. Ovsyannikova and T. P. Kalitina for help in the investigation of generation of the harmonic, and M. F. Koldobskaya, V. P. Popova, V. N. Nepomnyashchaya and L. N. Rashkovich for furnishing the crystals.

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