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Electro-optical properties of gadolinium molybdate

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The temperature dependence of the electro-optical response z_a, z_b and spontaneous birefringence Δn^S_{yz}, Δn^S_{zx} of gadolinium molybdate has been determined at 6328 Å by the static "improved Sénarmont method." A lattice-parameter correction was found to be necessary to obtain the precise values of Δn^S_{yz} and Δn^S_{zx}. The electro-optical responses z_a and z_b are essentially temperature independent except in the vicinity of the transition temperature, and the relation $z_a \simeq -z_b \simeq 1.5 \times 10^{-12}$ m/V was found to hold. The analysis of the electro-optical properties is made in terms of the electro-optical effect caused by polarization and the "structural optical effect" caused by the primary order parameters which belong to a representation at the M point. The spontaneous birefringence was found to be composed of linear and quadratic terms in the spontaneous polarization, and the contributions from both terms are of the same order of magnitude.

I. INTRODUCTION

Gadolinium molybdate, β-$Gd_2(MoO_4)_3$, undergoes a ferroelectric phase transition at about 160 °C with space-group change from D^3_{2d} to C^8_{2v}.[1] The transition is triggered by the condensation of Brillouin-zone boundary phonons.[2] The unusual ferroelectric properties of β-$Gd_2(MoO_4)_3$ have been qualitatively described by the Landau thermodynamics,[3-5] in which the primary order parameters belong to a representation with the momentum $\vec{k}$ at the Brillouin-zone-boundary M point. However, the experimental results previously reported on macroscopic parameters such as polarization and strain are not sufficient to examine whether this type of free-energy expansion well describes the characteristics of the phase transition in gadolinium molybdate. On the other hand, the electro-optical properties clearly reflect the aspect of the zone-boundary phonon condensation. In this respect accurate measurements of the electro-optical properties of gadolinium molybdate are important.

In the present paper, the axes referring to tetragonal coordinates in the high-temperature paraelectric phase are denoted by 1, 2, and 3, and the axes referring to orthorhombic coordinates in the low-temperature ferroelectric phase are denoted by x, y, and z or a, b, and c. The 3 axis is identical to the z axis. The 1 axis and the 2 axis are obtained by rotating the x axis and the y axis around the 3 axis by 45°. All physical quantities are related to the same coordinate system through the whole temperature range.

Nakamura *et al.*[6] first observed the anomalous electro-optical response by experiments with light propagating along the c axis, and the temperature dependence of the spontaneous birefringence Δn^S_{xy} and the electro-optical response z_{63} have been studied by many authors.[7-10] These properties were understood by means of the Landau free-energy expansion.[8,10] Smith *et al.*[11] measured the temperature dependence of $z_a = -(\delta n_{yz} - \Delta n^S_{yz})/n_0^3 E_3$ at 6328 Å, where n_0 is the refractive index of the ordinary ray. In the present paper, the suffix a stands for the axis along which light propagates in the electro-optical measurements. The quantity z_a is identical to $\frac{1}{2} r_c$ in the literature.[11] The results of Smith and Burns[11] showed a peak at about 160 °C. Since the magnitude of δn_{yz} and δn_{zx} is very high (about 10^2 times as high as for δn_{xy}), in order to obtain a phase difference $\phi = 2\pi d \delta n_{zx}/\lambda$ lower than π it is necessary to prepare a very thin crystal, $d < 8 \mu m$, which is impossible to attain with the usual technique of sample preparation. It was pointed out by Anistratov *et al.*[12] that even with thick samples the determination of the change in δn_{ij} with temperature is feasible, if the change in phase difference is followed starting from a certain temperature. Hence let us call this method the "improved Sénarmont method." Anistratov *et al.* measured the temperature dependence of the birefringence δn_{yz}, δn_{zx} under a static electric field $E_3 = 3$ kV/cm in the neighborhood of the transition point T_{tr}. The change in δn_{yz}, δn_{zx} in the neighborhood of T_{tr} is less than about one percent of these absolute values. Measurement by the improved Sénarmont method gives the relative change of δn_{ij} with an accuracy of $(10^{-3}$–$10^{-4})$%.

On the other hand, Anistratov's measurements of δn_{yz}, δn_{zx} are made on one specimen with the same optical geometry by interchanging the a axis and the b axis under the electric field E_3. In the measurements of δn_{yz} and δn_{zx}, $(\delta n_{yz} - \delta n_{zx})/\delta n_{yz}$ is of the same order of magnitude as $(a_0 - b_0)/b_0$ (a_0 and b_0 are the lattice parameters along the a and b axes, respectively), and $[\delta n_{yz}(T) - \delta n_{yz}(T_c)]/$

$\delta n_{yz}(T)$ is of the same order of magnitude as $[a_0(T)-a_0(T_c)]/a_0(T)$. Therefore the lattice-parameter corrections for switching the axes and thermal expansion are necessary to obtain the precise values of Δn^S_{yz} and Δn^S_{zx}. On the other hand, in the measurement of δn_{xy} on a c plate (parallel to a and b axes), $[\delta n_{xy}(T)-\delta n_{xy}(T_c)]/\delta n_{xy}(T)$ is much larger than $[c(T)-c(T_c)]/c(T)$, as confirmed by experiments. Note that $\delta n_{yz}(T)$ is about one hundred times as large as $\delta n_{xy}(T)$, and $[\delta n_{xy}(T)-\delta n_{xy}(T_c)]$ and $[\delta n_{yz}(T)-\delta n_{yz}(T_c)]$ are of the same order of magnitude. In the measurements of δn_{xy} on c plates, it was shown that the lattice-parameter correction is not necessary.[13]

In Sec. II we report on the measured temperature dependence of the electro-optical response z_a, z_b and spontaneous birefringence Δn^S_{yz}, Δn^S_{zx} in the range 20–200 °C, with

$$z_a=-(\delta n_{yz}-\Delta n^S_{yz})/n_0^3E_3\ ,$$

$$z_b=-(\delta n_{zx}-\Delta n^S_{zx})/n_0^3E_3\ .$$

In Sec. III we analyze the electro-optical properties in terms of the electro-optical effect caused by polarization and the structural-optical effect caused by the primary-order parameters.

II. EXPERIMENTAL

A. Temperature dependence and dispersion relation of spontaneous birefringence Δn^S_{yz}

The absolute value of Δn^S_{yz} at 6328 Å has been determined as a function of temperature by the method described below. By this method, the order-of-magnitude change in Δn^S_{yz} from room temperature to a somewhat higher temperature than the transition temperature T_{tr}, as well as the dispersion relation of the spontaneous birefringence Δn^S_{yz} were obtained.

When the crystal is placed between crossed polarizers, extinction occurs at λ_m, with

$$\Delta n^S_{yz}d=m\lambda_m\quad (m\ \text{integer})$$

(d is thickness of the sample along the light-propagation direction). A power monochromator (Shimadzu–Bausch & Lomb) was used as a light source to determine λ_m. The sample used was an a plate with thickness 243 μm. The thickness was accurately determined from the width of an existing right-angle prismatic domain with c axis in the plane of the plate.[14]

Nomura *et al.*[13] measured the dispersion of the refractive index n_a, n_b, and n_c by the minimum-deviation method on a prism made of gadolinium molybdate. The values of m were obtained by comparison of $m\lambda_m/d$ with the calculated Δn^S_{ij} from Nomura's data and an unambiguous determination of the m values has been feasible. The results are shown in Figs. 1(a) and 1(b). The observed dispersion of Δn^S_{yz} was well fitted by Cauchy's relation

$$\Delta n^S_{yz}=4.607\times10^{-2}+2.344\times10^{3}\times\lambda^{-2}\quad \text{for } 25\,^\circ\text{C}\ ,$$

$$\Delta n^S_{zx}=4.588\times10^{-2}+2.325\times10^{3}\times\lambda^{-2}\quad \text{for } 184\,^\circ\text{C}\ ,$$

by a least-mean-square procedure.

The change in Δn^S_{yz} at 6328 Å from 25 to 184 °C is found to be about 2%.

B. Accurate measurement of the temperature dependence of the spontaneous birefringence Δn^S_{yz} and Δ^S_{zx}.

According to the measurements in Sec. II A, the change in Δn^S_{yz} is about 2%. We made high-accuracy measurements of the relative change in Δn^S_{yz} and Δn^S_{zx} using the Sénarmont method by use of a Faraday cell, as described in the previous paper.[10]

A sample is first kept at a temperature at which

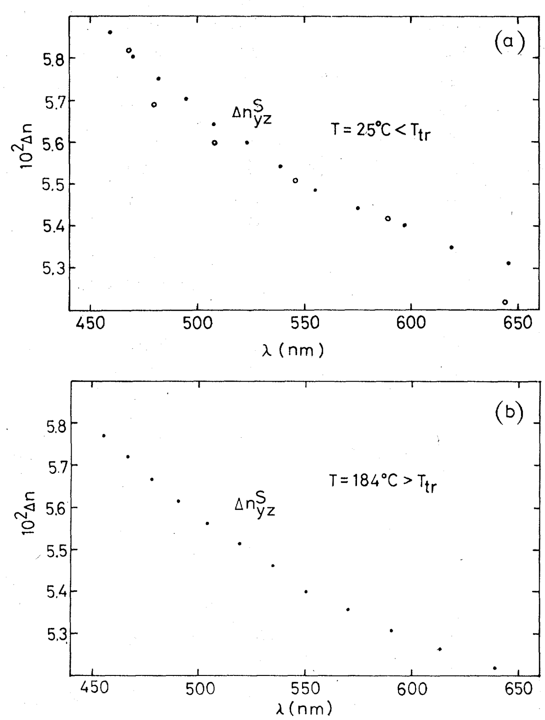

FIG. 1. (a) Dispersion curve of the spontaneous birefringence Δn^S_{yz} at room temperature. Open circles indicate the values by Nomura *et al.* Closed circles indicate the values by the authors. (b) Dispersion curves of the birefringence Δn^S_{yz} at a temperature above T_{tr}.

the birefringence is known from the experiment in Sec. II A, and the extinction is attained at the Sénarmont alignment. This can be done since $\Delta n^S_{yz}, \Delta n^S_{zx}$ and the thickness are known from the experiment in Sec. II A, although $d\Delta n/\lambda$ is much larger than unity. Then the temperature is changed, and the extinction position is determined. The increment of Δn in changing temperature can be obtained from the angle of rotation of the analyzer.

The sample is the same as that used in the experiments described in Sec. II A. The gold electrode of elongated rectangular shape evaporated at about 150 °C so that the electric field is applied along the c axis. To measure δn_{yz} and δn_{zx} the directions of light propagation are parallel to the a and b axes, respectively. In gadolinium molybdate, the a and b axes can be interchanged by the reversal of P_z. Measurements of δn_{yz} and δn_{zx} were made with the same alignment by using this interchange. Before the measurements an electric field E_3 of about 3.5 kV/cm was applied at a higher temperature above T_{tr} and cooled slowly down to room temperature. When the applied field is reversed, the resultant polarization is reversed. We measured the temperature dependence of Δn^S_{yz} and Δn^S_{zx} at $E_3 = 0$. While the temperature of the sample changed the $E_3 = 3.5$ kV/cm was applied, and once the temperature was controlled within $\pm 10^{-2}$ °C accuracy, E_3 was removed and the measurement was made. The results for Δn^S_{yz} and Δn^S_{zx} are shown in Fig. 2. They are in agreement with Anistratov's data which were confined to the neighborhood of T_{tr}.

Since the Sénarmont method measures the phase difference $\theta = \delta n_{yz} d/\lambda$ or $\theta = \delta n_{zx} d/\lambda$, if δn_{yx} or δn_{zx} is large, a change in d causes a large change in θ. Since δn_{yz} or δn_{zx} is about 10^2 times as large as δn_{xy}, thermal expansion and interchanging x and y cause a considerable amount of change in θ. Thus, the

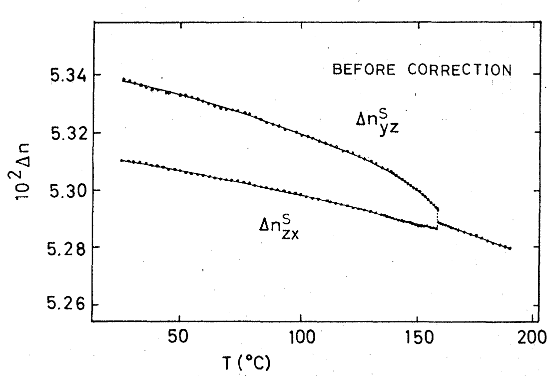

FIG. 2. Temperature dependence of the spontaneous birefringence Δn^S_{yz}, Δn^S_{zx} at 6328 Å before lattice-parameter correction.

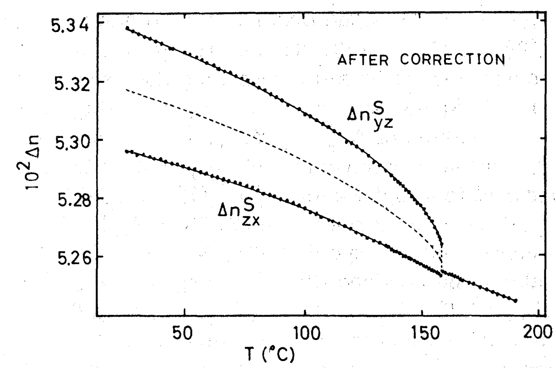

FIG. 3. Temperature dependence of the spontaneous birefringence Δn^S_{yz}, Δn^S_{zx} at 6328 Å after lattice-parameter correction. The dotted line indicates the mean values of Δn^S_{yz} and Δn^S_{zx}.

lattice-parameter[15] correction causes considerable change in the curves, as shown in Fig. 3. The quantity $\Delta n^S_{xy} = \Delta n^S_{yz} - \Delta n^S_{zx}$ is shown in Fig. 4. The temperature dependence of Δn^S_{xy} is in good agreement within experimental accuracy with the results of experiments using light propagating along the c axis. The crosses in Fig. 4 show the data obtained in our previous work.[10] The absolute values of Δn^S_{yz} and Δn^S_{zx} are as large as about 10^2 times the value of Δn^S_{xy} (where $\Delta n^S_{xy} = 4.0 \times 10^{-4}$ at 20 °C). However, the changes in Δn^S_{yz} and Δn^S_{zx} in the range from 20 to 200° C are of the same order of magnitude as for Δn^S_{xy}.

C. Measurements of electro-optical response z_a and z_b

Another thicker a plate was prepared to increase the electrically induced birefringence. It is about six times as thick as the sample used in Sec. II B.

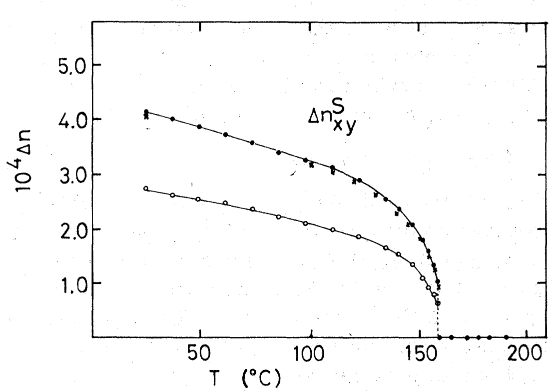

FIG. 4. Temperature dependence of the spontaneous birefringence $\Delta n^S_{xy} = \Delta n^S_{yz} - \Delta n^S_{zx}$ calculated from Δn^S_{yz} and Δn^S_{zx}. Open circles are values before lattice-parameter correction. Closed circles are values after the correction. Crosses are the values in our previous paper.

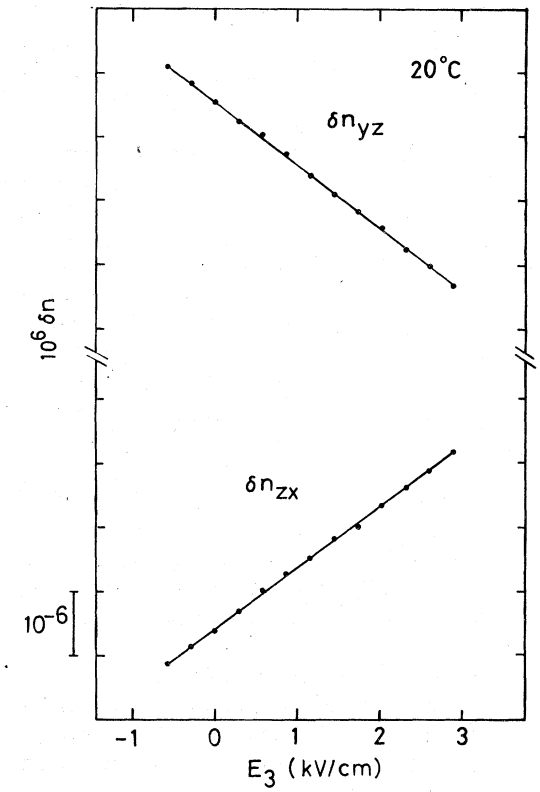

FIG. 5. Electric-field E_3 dependence of the birefringence δn_{yz}, δn_{zx} at 20 °C. Here, the positive direction of E_3 is taken to be the positive direction of P_z.

The distance between electrodes along the c axis is the same as the sample used in Sec. II B.

When the electric field is applied at room temperature, the birefringence $\delta n_{yz}, \delta n_{zx}$ shifts as shown in Fig. 5. Here, the direction of the electric field is taken to be the positive direction of P_z.

The quantities z_a and z_b can be found from the slope of the δn_{ij} vs. E_3 curves,

$$z_a = -(\delta n_{yz} - \Delta n^S_{yz})/n_0^3 E_3 ,$$
$$z_b = -(\delta n_{zx} - \Delta n^S_{zx})/n_0^3 E_3 .$$

The relations between z_a, z_b, and z_{ij}, determined from point-group symmetry for gadolinium molybdate, are shown in Table I. The temperature dependence of z_a and z_b is shown in Fig. 6. It holds numerically, $z_a \simeq -z_b \simeq 1.5 \times 10^{-12}$ m/V, except in the vicinity of T_{tr}. Our result at z_a is in contradiction with Smith's data[11] in the neighborhood of T_{tr}.

TABLE I. Relation between z_a, z_b and the electro-optical coefficients z_{ij}.

	z_a	z_b
$T > T_{tr}$	$\frac{1}{2} z_{63}$	$-\frac{1}{2} z_{63}$
$T < T_{tr}$	$\frac{1}{2}\left[z_{23} - \left(\frac{n_e}{n_0}\right)^3 z_{33}\right]$	$\frac{1}{2}\left[z_{13} - \left(\frac{n_e}{n_0}\right)^3 z_{33}\right]$

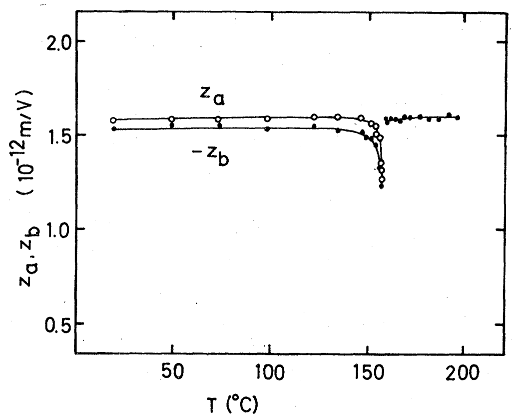

FIG. 6. Temperature dependence of the electro-optical response z_a, z_b and 6328 Å.

III. DISCUSSION

The electro-optical properties are represented by the optical impermittivity $B_{ij} = \partial E_i / \partial D_j$. From symmetry, the change in B_{ij} in the presence of polarization P_z and order parameters q_1, q_2 is expanded as

$$\begin{aligned} B_1 &= 1/n_o^2 + g_{13} P_z^2 + \omega_{13} q_1^2 q_2^2 + \gamma_{13} q_1 q_2 P_z , \\ B_2 &= 1/n_o^2 + g_{13} P_z^2 + \omega_{13} q_1^2 q_2^2 + \gamma_{13} q_1 q_2 P_z , \\ B_3 &= 1/n_e^2 + g_{33} P_z^2 + \omega_{33} q_1^2 q_2^2 + \gamma_{33} q_1 q_2 P_z , \\ B_4 &= 0, \quad B_5 = 0, \quad B_6 = r_{63} P_z + \omega_1 q_1 q_2 , \end{aligned} \tag{1}$$

in the high-symmetry-phase coördinates, where n_o and n_e stand for the refractive index of ordinary and extraordinary rays, respectively. The terms $\omega_{ij} q_1^2 q_2^2$ and $\omega_1 q_1 q_2$ give the dependence of the optical-impermittivity-tensor component on the soft-mode coordinate, which should be called the "structural optical effect."

Now we define the quantities

$$\delta n_{xy} = n_x - n_y \ (>0) , \quad \delta n_{yz} = n_z - n_y \ (>0) , \quad \delta n_{zx} = n_z - n_x \ (>0) , \tag{2}$$

which are calculated to be

$$-\delta n_{xy}/n_o^3 = r_{63} P_z + \omega_1 q_1 q_2 , \tag{3}$$

$$-\delta n_{yz}/n_o^3 = -(n_e - n_o)/n_o^3 + \tfrac{1}{2} r_{63} P_z + \tfrac{1}{2}\omega_1 q_1 q_2 + \tfrac{1}{4} g P_z^2 + \tfrac{1}{4}\omega_2 q_1^2 q_2^2 + \tfrac{1}{4}\gamma q_1 q_2 P_z , \tag{4}$$

$$-\delta n_{zx}/n_o^3 = -(n_e - n_o)/n_o^3 - \tfrac{1}{2} r_{63} P_z - \tfrac{1}{2}\omega_1 q_1 q_2 + \tfrac{1}{4} g P_z^2 + \tfrac{1}{4}\omega_2 q_1^2 q_2^2 + \tfrac{1}{4}\gamma q_1 q_2 P_z , \tag{5}$$

where

$$g=2[g_{13}-(n_e/n_o)^3 g_{33}]\ ,$$

$$\omega_2=2[\omega_{13}-(n_e/n_o)^3\omega_{33}]\ ,$$

$$\gamma=2[\gamma_{13}-(n_e/n_o)^3\gamma_{33}]\ .$$

Put

$$P_z=P_z^S+P_z^i\ , \quad (6)$$

$$q=q^S+q^i\ , \quad (7)$$

where P_z^S and q^S are the values at $E_3=0$. Making a substitution in the same manner as in Eqs. (6) and (7),

$$\delta n_j=\Delta n_j^S+\delta n_j^i\ . \quad (8)$$

By substituting Eqs. (A4) and (A5) into Eqs. (4) and (5), respectively, and taking terms up to quadratic order in P_z^S and only linear terms in P_z^i in the expansion, we have

$$\frac{-\Delta n_{yz}^S}{n_o^3}=-\frac{n_e-n_o}{n_o^3}+\frac{1}{2}\left(r_{63}-\frac{\kappa\omega_1}{\mu}\right)P_z^S + \frac{1}{4}\left(g-\frac{\kappa\gamma}{\mu}+\frac{\kappa^2\omega_2}{\mu^2}\right)(P_z^S)^2\ , \quad (9)$$

$$\frac{-\Delta n_{zx}^S}{n_o^3}=-\frac{n_e-n_o}{n_o^3}-\frac{1}{2}\left(r_{63}-\frac{\kappa\omega_1}{\mu}\right)P_z^S + \frac{1}{4}\left(g-\frac{\kappa\gamma}{\mu}+\frac{\kappa^2\omega_2}{\mu}\right)(P_z^S)^2\ , \quad (10)$$

$$z_a=\frac{1}{2\kappa}\left(r_{63}-\frac{\mu^2\omega_1}{\beta\mu-8\kappa\xi P_z^S}\right) + \frac{1}{4\kappa}\left(2g-\frac{\kappa\gamma}{\mu}+\frac{\mu(2\kappa\omega_2-\gamma\mu)}{\beta\mu-8\kappa\xi P_z^S}\right)P_z^S\ , \quad (11)$$

$$-z_b=\frac{1}{2\kappa}\left(r_{63}-\frac{\mu^2\omega_1}{\beta\mu-8\kappa\xi P_z^S}\right) - \frac{1}{4\kappa}\left(2g-\frac{\kappa\gamma}{\mu}+\frac{\mu(2\kappa\omega_2-\gamma\mu)}{\beta\mu-8\kappa\xi P_z^S}\right)P_z^S\ . \quad (12)$$

Since the high-symmetry phase of gadolinium molybdate belongs to a piezoelectric point group, both the electro-optical effect and the structural-optical effect includes the linear and quadratic terms in P_z and q_1q_2, respectively. Therefore, the spontaneous birefringence $\Delta n_{yz}^S, \Delta n_{zx}^S$ contains both linear and quadratic terms in P_z^S in the low-temperature phase. Assuming the term n_e-n_o in Eqs. (9) and (10) to be linearly dependent on temperature throughout the whole temperature range, the temperature dependence of Δn_{yz}^S and Δn_{zx}^S is qualitatively explained by Eqs. (9) and (10). The mean value of Δn_{yz}^S and Δn_{zx}^S which is shown in Fig. 3 by a dotted curve gives the quadratic effect, because

$$-\frac{1}{2}\ \frac{\Delta n_{yz}^S+\Delta n_{zx}^S}{n_0^3}=-\frac{n_e-n_0}{n_0^3} + \frac{1}{4}\left(g-\frac{\kappa\gamma}{\mu}+\frac{\kappa^2\omega_2}{\mu^2}\right)(P_z^S)^2\ . \quad (13)$$

In Eq. (13), $(P_z^S)^2$ was observed to be proportional to $(T_1-T)^{2/3}$,[16] and if Eq. (13) is correct, the quantity $[\frac{1}{2}(\Delta n_{yz}^S+\Delta n_{zx}^S)+(n_e-n_0)]^{3/2}$ should be linear to (T_1-T). The observed values versus T curve is approximated by a linear relation in the neighborhood of T_{tr}. The difference between Δn_{yz}^S and Δn_{zx}^S gives the linear effect, as shown in Fig. 4,

$$-\frac{\Delta n_{yz}^S-\Delta n_{zx}^S}{n_0^3}=\frac{-\Delta n_{xy}^S}{n_0^3}=\left(r_{63}-\frac{\kappa\omega_1}{\mu}\right)P_z^S\ . \quad (14)$$

Equation (14) was shown to be correct in our previous paper.[10] From Fig. 3, the term in P_z^S and the term in $(P_z^S)^2$ in Eqs. (9) and (10) are of the same order of magnitude. The present experiment clarified that both effects certainly exist and that these two terms are of the same order of magnitude.

As to the electro-optical response, the temperature dependence of z_a and z_b is qualitatively explained by Eqs. (11) and (12). The quantity (z_a-z_b) is equal to z_{63} which can be measured with a c plate, that is,

$$z_a-z_b=z_{63}=\frac{1}{\kappa}\left(r_{63}-\frac{\mu^2\omega_1}{\beta\mu-8\kappa\xi P_z^S}\right)\ . \quad (15)$$

Observed values of (z_a-z_b) as a function of temperature are in good agreement with those of z_{63} measured by the present authors using the static method[10] and those by Fousek and Koňák using the dynamical method.[8]

On the other hand, from Eqs. (11) and (12),

$$z_a+z_b=\frac{1}{2\kappa}\left(2g-\frac{\kappa\gamma}{\mu}+\frac{\mu(2\kappa\omega_2-\gamma\mu)}{\beta\mu-8\kappa\xi P_z^S}\right)P_z^S\ . \quad (16)$$

This quantity is small and of the order of magnitude of the experimental accuracy, but still it is detectable and its existence is seen from Fig. 6.

The electro-optical response z_a, z_b is essentially given by the term [Eqs. (11) and (12)],

$$\frac{1}{2\kappa}\left(r_{63}-\frac{\mu^2\omega_1}{\beta\mu-8\kappa\xi P_z^S}\right)\ ,$$

and it holds, $z_a\simeq -z_b\simeq\frac{1}{2}z_{63}=1.5\times10^{-12}$ m/V.

IV. CONCLUSIONS

Here we report on the temperature dependence of the electro-optical response z_a, z_b and spontaneous birefringence $\Delta n_{yz}^S, \Delta n_{zx}^S$ of β-gadolinium molybdate in the range from 20 to 200° C. Measurements were made at 6328 Å by the static "improved Sénarmont method." The absolute values of Δn_{yz}^S and Δn_{zx}^S are about 10^2 times as large as the values of Δn_{xy}^S. However, the changes in Δn_{yz}^S and Δn_{zx}^S in the present range of measurements are of the same order of magnitude as for Δn_{xy}^S. It is pointed out that the lattice-parameter correction is necessary to obtain precise values of Δn_{yz}^S and Δn_{zx}^S. The electro-optical response z_a, z_b is essentially temperature independent except in the vicinity of the transition temperature, and the relation $z_a \simeq -z_b \simeq 1.5 \times 10^{-12}$ m/V has been found to hold.

We have analyzed the electro-optical properties in terms of the electro-optical effect caused by polarization and the "structural-optical effect" caused by the primary-order parameters which belong to a representation with the momentum $\vec{k}$ at the Brillouin-zone-boundary M point. The spontaneous birefringence $\Delta n_{yz}^S, \Delta n_{zx}^S$ was found to be composed of linear and quadratic terms in the spontaneous polarization, and the contributions from both terms are of the same order of magnitude. The electro-optical response z_a, z_b is essentially given by the term in Eqs. (11) and (12),

$$(1/2\kappa)[r_{63} - \mu^2\omega_1/(\beta\mu - 8\kappa\xi P_z^S)] ,$$

and it holds, $z_a \simeq -z_b \simeq \frac{1}{2} z_{63} = 1.5 \times 10^{-12}$ m/V.

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APPENDIX

Calculations of the temperature dependence of the spontaneous quantities P_z^S, q_1^S, q_2^S and electrically induced quantities P_z^i, q_1^i, q_2^i are shown. The simplified Gibbs function is given by[8]

$$G = \tfrac{1}{2}\alpha_0(T - T_0)(q_1^2 + q_2^2) + \tfrac{1}{4}\beta_1(q_1^4 + q_2^4) + \tfrac{1}{2}\beta_2 q_1^2 q_2^2 + \tfrac{1}{6}\xi(q_1^2 + q_2^2)^3 + \tfrac{1}{2}\kappa P_z^2 + \mu P_z q_1 q_2 . \tag{A1}$$

The equilibrium conditions are

$$\frac{\partial G}{\partial q_i} = 0 \quad (i = 1, 2) , \tag{A2}$$

$$\frac{\partial G}{\partial P_z} = E_3 . \tag{A3}$$

Equations (A2) and (A3) have two solutions $q_1 = \pm q_2$ for zero as well as nonzero E_3.[8] $q_1 = \pm q_2$ corresponds to domains with $\mp P_z$. We take the solution $q_1 = q_2 \equiv q$. Substituting Eqs. (6) and (7) into Eqs. (A2) and (A3) and taking only linear terms in P_z^i and q^i,

$$(q^S)^2 = -(\kappa/\mu)P_z^S , \tag{A4}$$

$$q^i = -\{\mu q^S / [2\beta(q^S)^2 + 16\xi(q^S)^4]\} P_z^i , \tag{A5}$$

$$[q^S(T)]^2 - \tfrac{2}{3}[q^S(T_c)]^2 = [(\alpha_0/4\xi)(T_1 - T)]^{1/2} , \tag{A6}$$

where

$$T_1 = T_0 + (1/16\alpha_0\xi)(\mu^2/\kappa - \beta)^2 ,$$

$$\beta = \beta_1 + \beta_2 .$$

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