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# Intensity-Induced Changes in Optical Polarizations in Glasses*

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Using a single-mode ruby laser we have made the first measurements of intensity-induced changes of the optical polarization (ellipse rotation) in solids, viz., fused quartz and Schott BK-7 and SF-7 glasses for which we have obtained the nonlinear susceptibility values $c_{1221}(-\omega, \omega, \omega, -\omega) = 1.5$, 2.3, and $9.9\times10^{-15}$ esu, respectively. These values are accurate to within 10% relative to the value for liquid $CS_2$, which we used for calibration and determined from other experiments to be $37.8\times10^{-14}$ esu to within 2%. We also show theoretically that a comparison of these values with electric-field-induced birefringence (Kerr) data can determine uniquely the fractional contribution to both of purely electronic nonlinearities. Existing Kerr data are only accurate enough at present for us to conclude that the electronic nonlinearities might dominate our effect.

## I. INTRODUCTION

A strong, elliptically polarized, optical beam induces an optical anisotropy in any normally isotropic medium through which it passes, and undergoes thereby a change in its state of polarization. Maker *et al.* first predicted and observed the intensity-induced rotation of the polarization ellipse of a plane wave by monitoring the polarization of an elliptically polarized ruby laser giant pulse after it had traversed a liquid-filled absorption cell.[1] Here we report the first measurements of this intensity-induced ellipse rotation in solids, viz., fused quartz, BK-7 borosilicate crown (BSC) glass, and SF-7 dense flint glass. Being around 10% absolute accuracy, these constitute the most accurate measurements of any nonlinear coefficients for glasses to date.

As we show in Sec. II, both this effect of "ellipse rotation" and also the electric-field-induced birefringence (Kerr effect) depend on the (one) nonlinear electronic polarizability parameter, and also, but in different ways, on another parameter that measures certain contributions of local nuclear redistribution to the effects. Hence, these two experiments jointly offer a unique possibility of distinguishing between the two underlying physical mechanisms unambiguously in glasses and liquids. Of all other nonlinear optical effects observed in glasses only the purely electronic process of third-harmonic generation (THG) depends on no other independent parameters than the two involved in these two effects. Wang and Baardsen have measured THG in borosilicate crown glass,[2] and their result is consistent with ours for BK-7 glass. The great difficulty in calibrating this effect led them to estimate their absolute accuracy to be a factor of 3. So there is little significance in the comparison.

Maker and Terhune have observed three-wave mixing (TWM) in fused quartz, BSC glass and in liquids and crystals.[3] They argued that, because no variation in the effect with frequency is observed in the glasses, it is probably purely electronic in origin. This interpretation of their data is not inconsistent with our results, but their experimental uncertainties were too large to confirm this conclusion by comparison with ours. The many other nonlinear optical effects that have been observed in glasses clearly involve index coefficients and physical mechanisms independent of those of interest here.

In Sec. III we describe our experimental results and the experimental means we have developed to overcome some of the difficulties that have arisen in the previous ellipse-rotation studies on liquids. When in the discussion of Sec. IV we use the theory of Sec. II to compare our experimental results with the Kerr data of Duguay and Hansen on fused quartz and BK-7,[4,5] we find that the electronic contribution to either effect is not negligible, but the uncertainties in the Kerr data leave the possibility that the nuclear contribution may or may not be significant. Other evidence is discussed which suggests that the nuclear contribution cannot yet be ruled insignificant. Implications of our measurements to other nonlinear optical effects are also discussed in Sec. IV.

## II. RELATION BETWEEN ELLIPSE ROTATION AND KERR EFFECTS

In order to establish the desired relations between certain nonlinear susceptibility coefficients for isotropic media, we use the fact that the nonlinear polarization density $\vec{P}^{NL}(\vec{r}, t)$, third order in the electric field, may be separated into two parts. First, there is an "electronic" part $\vec{P}_e(\vec{r}, t)$, which results from a distortion of the electron orbits about the nuclei, considered fixed in a typical spatial configuration. This polarization responds so quickly in transparent media (within several electronic cycles) that we may consider the response to be instantaneous for the electromagnetic fields of interest. Therefore, it may be expressed in the form

$$\vec{P}_e(\vec{r}, t) = \tfrac{1}{2}\sigma\, \vec{E}(\vec{r}, t) \cdot \vec{E}(\vec{r}, t)\vec{E}(\vec{r}, t) \tag{1}$$

for an isotropic material. This term alone would be responsible for third-harmonic generation. The electronic nonlinear susceptibility coefficient $\sigma$ exhibits dispersion which is small at the optical frequencies we employ and which we correct for when necessary. Evidently $\sigma$ is independent of temperature at fixed density, but it varies with temperature at fixed pressure in a way not yet understood.

The remaining part of $\vec{P}^{NL}$ is a nuclear part $\vec{P}_n(\vec{r}, t)$, which is due to the linear response of the electronic currents about nuclear arrangements whose statistical probabilities are altered slightly in order to lower the average field-crystal interaction energy. When (as here) the medium has no absorption near field frequencies and has negligible dispersion, the instantaneous fluctuation in this interaction energy density in a small volume (compared to a wavelength) about $\vec{r}$ may be written

$$-\vec{E}(\vec{r}, t) \cdot \delta\overleftrightarrow{\epsilon}(\vec{r}, t) \cdot \vec{E}(\vec{r}, t)/8\pi ,$$

where $\delta\overleftrightarrow{\epsilon}$ is the deviation from its average of the dielectric permittivity tensor appropriate to the nuclear placements in the neighborhood of $\vec{r}$ at time $t$. Since $\vec{P}_n(\vec{r}, t)$ equals $\delta\overleftrightarrow{\epsilon} \cdot \vec{E}(\vec{r}, t)/4\pi$ averaged with a weighting function (i.e., density matrix) expanded to first order in the above interaction energy, it is easy to see that, for isotropic media, $\vec{P}_n$ must be of the form

$$\vec{P}_n(\vec{r}, t) = \vec{E}(\vec{r}, t) \int a(t-s)E^2(\vec{r}, s)ds + \int \vec{E}(\vec{r}, t) \cdot \vec{E}(\vec{r}, s)b(t-s)\vec{E}(\vec{r}, s)ds . \tag{2}$$

Here the scalars $a(t)$ and $b(t)$ are nuclear response functions for the "isotropic" and "anisotropic" parts of the nonlinear polarization, respectively, formed from the appropriate two-time correlations of components of $\delta\overleftrightarrow{\epsilon}$. It is often useful to think of these functions as weighted sums over normal modes (of the nuclear motions) of the mode coordinates, temporal response functions. The characteristic decay times in these response functions, and hence in $a(t)$ and $b(t)$, are several orders of magnitude longer than those for electronic nonlinearities. Also $a$ and $b$ are temperature dependent at fixed density. However, no predictions of the temperature dependence for specific glasses is yet available, and so there is no known way of distinguishing nuclear and electronic contributions to nonlinear optical effects in glasses by observing their temperature variations.

Substituting into Eqs. (1) and (2) the specific forms of $\vec{E}(\vec{r}, t)$ used in observing various nonlinear effects, we now proceed to solve Maxwell's equations to see what combinations of the infinitude of parameters contained in $a(t)$ and $b(t)$ describe the ellipse rotation and Kerr effects.

### Intensity-Induced Rotation of the Polarization Ellipse

To analyze this effect, we assume that there is propagating in the medium a $z$-directed monochromatic plane wave of frequency $\omega$ composed of right and left circularly polarized waves having complex vector amplitudes $(\hat{x} \pm i\hat{y})E_\pm/\sqrt{2}$ and propagating with wave vectors $\vec{k}_+$ and $\vec{k}_-$, respectively. Substituting such a field in Eqs. (1) and (2), one finds directly that Maxwell's equations are satisfied at the frequency $\omega$ if

$$\left(\frac{ck_\pm}{n\omega}\right)^2 = 1 + \pi[(\sigma + 2\alpha + \beta)E^2 + (\sigma + 2\beta)|E_\mp|^2]/n^2 , \tag{3}$$

where $E^2 \equiv |E_+|^2 + |E_-|^2$ is the time average of $2\vec{E} \cdot \vec{E}$, $\alpha \equiv \int a(s)ds$, $\beta \equiv \int b(s)ds$, and $n$ is the (linear) refractive index at $\omega$. We have neglected the terms which are proportional to the Fourier transforms of $a(t)$ and $b(t)$ at $2\omega$, because the nuclear response at this frequency is extremely small. According to Eq. (3) the axes of the polarization ellipse rotate by an angle $\theta$ over a distance $z$ so that a fraction

$$F(z) = (\sin 2\phi \sin\theta)^2 \tag{4a}$$

of the field at $z$ becomes orthogonally polarized to the field at $z = 0$; here $\tan\phi \equiv |E_+/E_-|$ and $\theta = \frac{1}{2}(k_+ - k_-)z$. In our experiments $|k_+ - k_-| \ll n\omega/c$, whence

$$\theta = \pi\omega z E^2 (4nc)^{-1}(\sigma + 2\beta)\cos 2\phi . \tag{4b}$$

If focusing is weak enough so that no further self-focusing due to nonlinear effects occurs, then we expect geometrical optics to be valid. In this case the ellipse-rotation angle may be computed for each ray by substituting $\int_{z_1}^{z_2} E^2(z)dz$ for $E^2 z$ in Eq. (4b); here the integral is taken along the ray path. If this integral is calculated along an axial ray through the focus of an ideal Gaussian beam, then

$$\int_{-\infty}^{\infty} E^2(z)dz = 8\pi\omega P/c^2, \tag{4c}$$

where $P$ is the total power in the beam. We shall allow our nonlinear samples to completely encompass a focal region so as to take advantage of the independence of $\theta$ on beam geometry indicated here. We will ensure that self-focusing and nonlinear absorption effects are negligible by confining measurements to low-enough powers that the $\theta \propto E^2$ dependence of Eq. (4b) is observed.

In terms of the "$B$" coefficient defined by Maker *et al.*,[1] in their original description of ellipse rotation, and in terms of the appropriate commonly used "$c$-coefficients" defined by Maker and Terhune,[3] we have

$$\sigma + 2\beta = 4\text{``}B\text{''} = 24c_{1221}(-\omega, \omega, \omega, -\omega). \qquad (5)$$

### Kerr Effect

In an isotropic material a test beam $\vec{E}_\omega(\vec{r}, t)$ of frequency $\omega$ will exhibit birefringence in the presence of a strong beam $\vec{E}_\nu(\vec{r}, t)$ of frequency $\nu$. This "electric-field-induced birefringence" is called the "ac Kerr effect" when $\nu$ is an optical frequency, and called the "dc Kerr effect" when $\nu$ is a radio frequency or lower. Both cases are described by a Kerr constant $B$, defined by

$$B = \frac{\omega(\delta n_\parallel - \delta n_\perp)}{2\pi c \langle E_j^2 \rangle_{\text{av}}} , \qquad (6)$$

where $\delta n_\parallel - \delta n_\perp$ is the difference between the induced changes in the refractive index parallel and perpendicular to the direction of $\vec{E}_\nu$ whose mean square value in time is $\langle E_\nu^2 \rangle_{\text{av}}$. Again using the forms of Eqs. (1) and (2) in Maxwell's equations, we come directly to values for the desired index changes (second order in $E_\nu$) that yield

$$B = \omega(\sigma + \beta)/(nc), \qquad (7)$$

provided that $b(t)$ has no appreciable Fourier component at $2\nu$ and $|\omega - \nu|$, as is the case in the experimental works we will cite. In terms of the appropriate $c$ coefficients,

$$\sigma + \beta = 12[c_{1212}(-\omega, \omega, \nu, -\nu) + c_{1221}(-\omega, \omega, \nu, -\nu)].$$

From Eqs. (4) and (7) come the important consequence that (small-angle) ellipse rotation measures $\sigma + 2\beta$, while the Kerr effect measures $\sigma + \beta$, and together the effects yield the electronic parameter $\sigma$ and the nuclear parameter $\beta$ separately.

## III. EXPERIMENT

The first measurements by Maker *et al.*[1] of ellipse-rotation coefficients, which (like subsequent measurements) were done in liquids, depended on an estimate of the beam profile for a weakly focused multimode beam. Wang,[6] and McWane and Sealer,[7] found by repeating the measurements with more carefully controlled unfocused (but multimode) beams that the earlier estimates had yielded coefficients about an order of magnitude too small. In the present measurements on glasses we have attempted to avoid some of the earlier difficulties in several ways. First, we have employed a single (transverse and longitudinal) mode beam, calibrated by measuring the ellipse rotation of $CS_2$, whose $\sigma + 2\beta$ value we are able to determine to within 2% from other experiments. We have also used strong-enough focusing of the beam into the sample so as to ensure that the entire ellipse rotation takes place within the focal volume and to take advantage of the resulting independence of the ellipse-rotation angle on sample and focal dimensions. This arrangement also allows the optical intensity at the entrance and exit air-glass interfaces to be much lower for a given ellipse-rotation angle, thus eliminating the danger of a nondamaging absorbing plasma forming at the entrance face. As a result we have obtained reproducible results, for all glasses studied, while using different focal-length lenses and samples, and also after using both passive and active $Q$-spoiling techniques.

The experimental configuration is shown in Fig. 1. The laser is a water-cooled room-temperature ruby laser $Q$-switched with a dye of cryptocyanine in acetone. Mode selection is performed by aperturing the $\frac{9}{16}$-in.-diam × 4-in.-long ruby to give a 3-mm output spot employing a sapphire etalon as the output reflector. The laser output is 0.05 $J$ in a 20-nsec pulse under a single-mode operation. Power monitoring of the laser output is performed via a beam splitter (BS) which directs a portion of the beam to an ITT FW 114A S-20 biplanar photodiode. The rest of the beam is coupled through a Rochon prism (P-1) to define its plane of polarization prior to its introduction into the fresnel rhomb (R-1) which is oriented so as to produce an elliptically polarized input of desired eccentricity. The beam is then focused into the sample centrally by lens (L-1) and then recollimated by lens (L-2). A second Fresnel rhomb (R-2) is oriented parallel to

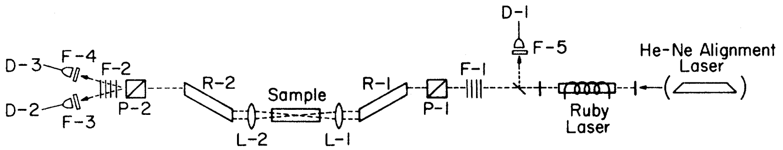

FIG. 1. Schematic diagram of the experimental arrangement used to observe ellipse rotation. BS is the beam splitter; P − 1 is the Rochon prism; P − 2 is the Wollaston prism; F - 1 and F − 2 are the Schott neutral density stacks totaling n.d. = 4.0; F − 3, F − 4, and F − 5 are the 6943-Å spike filters; D − 1, D − 2, and D − 3 are the ITT FW114A biplanar photodiodes; R − 1 and R − 2 are the Fresnel rhombs; and L − 1 and L − 2 are the lenses (10–15-cm focal length).

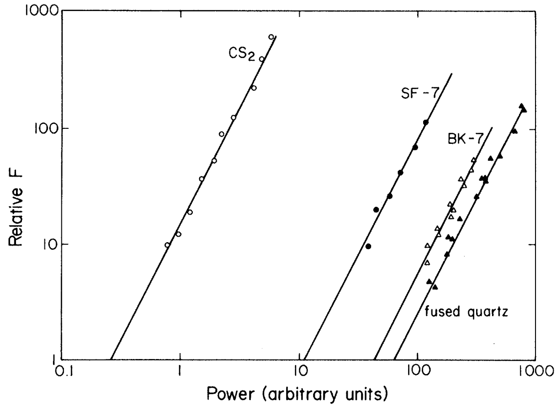

FIG. 2. Graph of intensity-induced polarization change as measured by relative $F$ vs optical beam power for fused quartz, BK-7 and SF-7 glass, and $CS_2$. Unit abscissa corresponds approximately to an absolute $P = 0.6$ kW and the ordinate 10 corresponds to an angular ellipse rotation of $\theta \simeq 2°$, both of which are cross-sectional averages of uncertain precision. [From Eq. (4) it is noted that for each ray $F \propto \theta^2$ for small $\theta$.]

R-1 so as to produce a linearly polarized output in the absence of ellipse rotation. This is followed by a Wollaston prism (P-2) oriented to direct a maximum "transmitted" signal into D-3 and a minimum "nulled" signal into D-2 in the absence of ellipse rotation.

The laser power delivered to the sample is adjusted by moving the Schott high-power neutral density filters from neutral density stack F-1 to F-2, thus ensuring a constant reference power level into the diodes in the absence of a nonlinearity. Any rotation of the polarization ellipse during propagation through the sample thus reveals itself as a relative increase in the "nulled" signal. Monitoring of the transmitted beam in D-3 reveals any induced changes in the transmission path or changes in the spatial profile of the laser. A He-Ne laser operating at 6328 Å and adjusted collinearly with the ruby laser beam was used continuously to ensure proper alignment of the system. The result of a typical run of the three glasses and liquid $CS_2$ is shown in Fig. 2. The fraction $F$ of orthogonal polarization is plotted versus input laser power $P$, and exhibits the $P^2$ dependence of Eq. (4). Clearly, this could not result if self-focusing or absorptive nonlinear effects, which would alter the assumed beam shape in a power-dependent way, were occurring to a significant degree.

In this study, as in the Kerr-effect measurements, liquid carbon disulphide ($CS_2$) was chosen as the standard to which measurements of ellipse rotation in fused quartz and Schott BK-7 and SF-7 glasses were compared. The absolute value of the dc Kerr constant of $CS_2$ is the best known of any substance and has been determined in a recent very accurate measurement by Volkova *et al.* to be $(3494 \pm 4) \times 10^{-10}$ esu at 546 nm and 23 °C.[8] Using the variation of this "constant" with wavelength measured by McComb,[9] we obtain for it the value $(253 \pm 5) \times 10^{-9}$ esu at 694 nm and 23 °C. Mayer[10] and Hauchecorne *et al.*[11] have found that $\sigma$ is unobservable in $CS_2$ by a sensitive method (second-harmonic generation in the presence of a static field) that clearly would observe it directly. One can conclude from their data that $\sigma < 0.01\beta$ and so from Eqs. (5) and (7) we conclude that for $CS_2$, $\frac{1}{24}(\sigma + 2\beta) = c_{1221}(-\omega, \omega, \omega, -\omega) = (37.8 \pm 0.7) \times 10^{-14}$ esu at 694 nm and 23 °C.[12] Because the dielectric constant of $CS_2$ is equal to the square of the refractive index (at 6943 Å and 23 °C) to within less than 0.5% we feel we can neglect dispersion corrections in inferring the ellipse-rotation constant from the dc Kerr constant.

The results of interpreting our $F$-vs-$P$ observations with Eq. (4) are summarized in Table I along with ac Kerr, three-wave mixing data, and the linear refractive indices used in data reduction. The coefficients listed have been chosen so that they would all be equal to $c_{1221} = \frac{1}{24}\sigma$ if nuclear motions and dispersion could be neglected. Fortunately for our purposes, $CS_2$ was also used to calibrate the ac Kerr effect observations. Although the three-wave mixing effect depends in a different way (signified by $\delta$) on $a(t)$ and $b(t)$, we have listed its measured values also, these being the most accurate of other existing related data.

## IV. DISCUSSION

It is evident from their definitions in Sec. II that both $\sigma$ and $\beta$ must be positive in order that the electronic and nuclear distortions lower the field-sample interaction energy. Therefore, comparing our results with the Kerr data from Table I indicates that the electronic contribution to either effect is not negligible, but that the nuclear contribution may be. However, we hesitate to conjecture from these results that the relative nuclear contribution is in fact negligible, mainly for the following reason. As is the case for liquids, there is a rigorous connection between the Fourier transforms at frequency $\omega$ of the nuclear correlation functions $a(t)$ and $b(t)$ and the intensity of light scattered at a frequency shift $\Delta\omega$ from glasses.[15] This means, for one thing, that the nuclear contribution $\beta$ to the ellipse rotation and Kerr effects could be found independently from the depolarized light-scattering intensity (just as for liquids[16]). Although the absolute intensity of the depolarized scattering from a glass has not yet been calibrated, it is known to be roughly as large as that from some liquids in which nuclear contributions to the Kerr effect are known to be important.[17]

The nuclear motions which cause electrostriction

TABLE I. Results of ellipse-rotation (ER) measurement on glasses tabulated with ac Kerr and three-wave mixing (TWM) data for comparison (all in units $10^{15}$ esu).

| Material | $\frac{1}{24}(\sigma+2\beta)$ from ER[a] | $\frac{1}{24}(\sigma+\beta)$ from ac Kerr[b] | $\frac{1}{24}(\sigma+\delta)$ from TWM | $n_{6943\text{Å}}$ |
|---|---|---|---|---|
| Fused quartz | 1.5(1.5) | 1.7(9) | 2.0(4)[c]<br>1.75[d] | 1.455 |
| BK-7 | 2.3(2) | 2.6(9) | 3.8(8)[c] | 1.513 |
| SF-7 | 9.9(10) | ··· | ··· | 1.631 |
| LaSF-7 | ··· | 13.3(40) | ··· | 1.91 |
| $CS_2$ | 378(7) | 189(4) | ··· | 1.62 |

[a] The uncertainties in the last digit relative to $CS_2$ are given in the parentheses. The absolute uncertainty in the value for $CS_2$ is given.

[b] The data are taken from Refs. 4 and 5 with the uncertainty in the last digit relative to $CS_2$ given in parentheses. The absolute uncertainty for errors in the $CS_2$ value are quoted as obtained from the literature cited in the text.

[c] The data are taken from Ref. 3 and are normalized to the value for the resonant Raman cross section for benzene at 992 $cm^{-1}$ obtained in the two independent studies of Refs. 13 and 14; $c_{111}(-\omega,-\Delta,\ \omega,\ \omega,\ \Delta-\omega)=(35\pm7)\times10^{-14}$ esu. The uncertainties in the last digit relative to this value are quoted in parentheses.

[d] This value was given in Ref. (11) where the authors also discussed at length the difficulties in calibrating the value and assigning limits of error to it.

and which appear in the isotropic $a(t)$ term of Eq. (2) are well known to be important to self-focusing in glasses. It is instructive to estimate for comparison the electronic contribution to the commonly used nonlinear index $n_2$ for linearly polarized light, assuming that all of our ellipse-rotation results were electronic. From Eq. (3) one has immediately that $n_2=\pi(\frac{3}{2}\sigma+2\beta+2\alpha)/n$ in general, and $n_2=3\pi\sigma/(2n)$ for purely electronic effects. With our results in Table I this would give $n_2=1.2$, 1.7, and $6.9\times10^{-13}$ esu, for fused quartz, BK-7, and SF-7 glasses respectively. These values alone imply critical powers for the electronic self-focusing of a Gaussian beam in an infinite medium from around 0.25 to 1.5 MW, close to what is expected from transient electrostriction and to what is commonly observed.

If the nonlinear medium were not isotropic then the relations we derived in Sec. II and all of the foregoing discussion and interpretation which derived from them would not apply. The strain birefringence that can be observed in some glass samples indicates that anisotropic regions may exist within glass samples. We have determined that such inhomogeneities did not contribute to our results (to within our stated errors) from the following observations. First, the strain birefringence was too small to be observable in our samples which produced extinction of ~$10^{-3}$ between crossed polarizers. More important, our results were reproducible (within the stated errors) when the samples were rotated about the beam axis and when different samples of the same glass were employed.

In summary, we have demonstrated here that intensity-induced index changes for a monochromatic beam can be seen and measured in glasses, and with an absolute accuracy (~ 10%) that makes quantitative interpretation useful. We have shown that comparison of these effects with the electric-field-induced birefringence (Kerr) effect in the same glass can yield a unique determination of the relative contributions of electronic and nuclear mechanisms to these effects, and that existing Kerr data indicate that electronic mechanisms must be important in the glasses which we have studied.

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electronic, then we would replace the values in the first column of Table I by 1.43, 2.2, 9.4, and 360, respectively, from top to bottom. This alteration would not change appreciably any of our other conclusions.

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PHYSICAL REVIEW B VOLUME 5, NUMBER 2 15 JANUARY 1972

# Polarization of Luminescence in NaCl : $Pb^{2+}$ and KCl : $Pb^{2+}$ †

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The polarized luminescence of $Pb^{2+}$ impurity-vacancy complexes in NaCl and KCl induced by excitation with polarized light has been studied. A single emission band at 340 nm of predominantly tetragonal symmetry was found in KCl : Pb; this emission decreased and shifted in wavelength during aging. Three emission bands were found in NaCl : Pb at 315, 380, and 460 nm. The 315-nm emission was at its maximum intensity after quenching and the 380-nm band was the first to appear upon aging with the 460-nm band appearing later. The 315-nm emission was found to originate from centers of both tetragonal and orthorhombic symmetry. Both the 380- and 460-nm bands are due to centers of trigonal symmetry. We have assigned the 340-nm band in quenched KCl and the 315-nm band in NaCl to isolated Pb-vacancy dipoles. We conclude that in KCl the vacancies are predominantly next-nearest neighbors to the impurity while in NaCl both nearest- and next-nearest-neighbor sites are comparable. The 380-nm emission band appears to be due to trimers of dipoles in a hexagon arrangement in {111} plane in agreement with the model of Dryden and Harvey. That the origin of the 460-nm band is due to higher aggregates is not well established.

## I. INTRODUCTION

The state of dispersion of divalent impurities in the alkali halides has been of considerable interest in color-center research.[1] At ordinary temperatures these impurities are bound to the charge-compensating vacancies forming dipolar complexes, and the role of the vacancies in the observed properties of the complexes is not yet fully understood. This is particularly true regarding the aggregation of impurities. Cook and Dryden[2] first measured the aggregation of divalent impurity-cation vacancy complexes by observing the kinetics of the decay of dielectric loss. They observed an initial third-order reaction and proposed that three dipoles combine simultaneously forming a trimer of dipoles in a hexagonal arrangement in the {111} plane as the first stage of aggregation. They postulated that further aggregation consists of the addition of dipoles, two at a time, to the trimers forming pentamers, heptamers, etc. all in the {111} plane.

It has long been known that the luminescent emission of the Pb ions in the alkali halides is sensitive to the state of dispersion of the ions.[3] In general $s^2$-configuration ions, such as $Pb^{2+}$, exhibit three characteristic absorption bands in the ultraviolet designated *A*, *B*, and *C* in the order of increasing energy.[4] Seitz[5] has attributed these to the intraionic transitions $s^2 \rightarrow sp$, or $a_{1g}^2 \rightarrow a_{1g} t_{1u}$ in the molecular-orbital description of Sugano.[6] The *C* band corresponds to the dipole-allowed transition $^1S_0 \rightarrow {}^1P_1 \times (A_{1g} \rightarrow T_{1u})$; the *B* band corresponds to the vibration-induced transition $^1S_0 \rightarrow {}^3P_2 (A_{1g} \rightarrow E_u,\ T_{2u})$; and the *A* band corresponds to the spin-orbit-allowed transition $^1S_0 \rightarrow {}^3P_1 (A_{1g} \rightarrow T_{1u})$. Excitation in the $Pb^{2+}$-*A* band leads to a 340-nm emission in KCl and three emission bands in NaCl at 315, 380, and 460 nm. The 340-nm band in KCl and the 315-nm band in NaCl are at a maximum upon quenching with the 380- and 460-nm bands in NaCl appearing successively upon aging. Dryden and Harvey[7] assigned these emission bands to particular aggregates in NaCl by comparing their decay and growth with the expected behavior of monomers, trimers, pentamers, etc. according to the Cook and Dryden model.[2] They assigned the 315-nm band to monomers, the 380-nm band to trimers and the 460-nm band to heptamers. None of the emission bands could be correlated with the expected behavior of pentamers.

The polarization properties of the emission bands of the $s^2$ ions have also received considerable attention. Klick and Compton[8] first measured the polarization of the luminescence of KCl : Tl at low tem-