Photoelectric domain structure in ruby: Studies with electric-field modulation of photon echo

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Electric-field-modulated two-pulse photon-echo experiments were performed in heavily doped ruby crystals containing photoinduced domains possessing internal electric fields. The photon-echo modulation patterns are sensitive to the photoelectric domain structure in the crystals. Studies as a function of the relative orientation of the optical excitation beam and the crystal axes make it possible to obtain information about the size and shape of the domains. The domains occur in sheets oriented perpendicular to the c axis and are about 20 μm in thickness.

I. INTRODUCTION

Intense optical excitation of heavily doped ($>0.2\%$) ruby, Al_2O_3:Cr^{3+}, at low temperatures results in the creation of a high (10^5-10^6 V/cm) internal electric field, which is parallel to the trigonal c axis.[1] Such an effect is quite unusual for a centrosymmetric crystal. In noncentrosymmetric materials, internal electric fields can give rise to strong photorefractive effects, which have important applications. The presence of this electric field in ruby is observed via the "pseudo-Stark" effect in which a doublet splitting of the zero-phonon spectral lines of Cr^{3+} is observed. The pseudo-Stark splitting results from the opposite linear shifts of the energy levels of the Cr^{3+} ions occupying the two different polar site positions (A,B) in the centrosymmetric (D_{3d})Al_2O_3 lattice.[2]

Previous experiments in which an additional external electric field was applied to the sample[3] have shown that the photoinduced electric field occurs in domains of two types in which the internal field is of opposite sign (see Fig. 1). Within each domain the internal field has the same absolute value and is very uniform. The field within the domains results from photoinduced space charges, which are localized at their borders. Each type of domain produces an identical pseudo-Stark doublet in the R-line spectrum. Whereas in the (+) domains the A (B) sites will correspond to the lower (higher) energy transition, in the ($-$) domains the A (B) sites have their relative energies reversed and will correspond to the higher (lower) transition energy in the doublet.

The mechanisms responsible for the creation of the electric field are well understood and involve the electrical instability due to negative absolute photoconductivity.[3-5] However, attempts to visualize the domain structure and to determine the shape and size of the domains and/or of the domain walls have been unsuccessful, in part because in centrosymmetric systems such as Al_2O_3 the linear electrooptical effect is absent and thus visualization via photorefraction is not possible. While other techniques to reveal the domain structure in bulk crystals have also failed, the observation of a photoinduced pseudo-Stark splitting in the spectra of ruby powders indicates that the domains can be as small as a few microns. Other indirect results such as the fact that the field within the domains is highly homogeneous indicates that the domains must be larger than some tens of nanometers.

In the present study we apply optical coherent transient techniques to examine the size and geometry of the photoinduced domains. Modulations in the intensity of the two-pulse photon echo produced by pulsed electric fields are used to provide information on the size and shape of the domains.

Photon-echo modulation spectroscopy allows for the high-resolution measurement of small spectral line splittings that fall within the inhomogeneous linewidth and are not accessible with conventional spectroscopy.[6,7] In the absence of an external pulsed electric field, all excited ions simultaneously rephase at a time 2τ, where τ is the time between echo preparation pulses, generating the coherent pulse of radiation referred to as the photon echo. Ruby contains two electric-field inequivalent

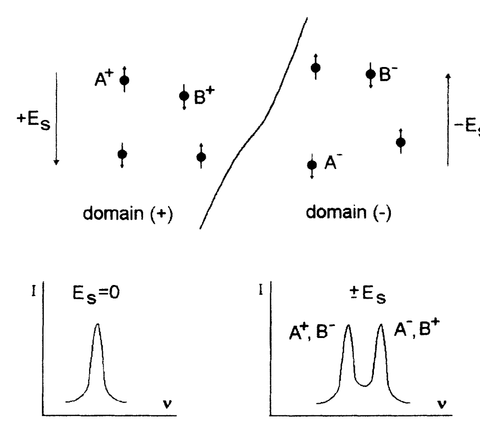

FIG. 1. Cr^{3+} ions in A and B crystal C_3 sites in (+) and ($-$) photoelectric domains and the R-line spectra in an unirradiated ($E_s=0$) sample and in an Ar-ion-laser-irradiated sample ($\pm E_s$).

groups of Cr^{3+} ions, labeled A and B, whose transition energies are oppositely shifted by an electric field $\mathbf{E}\|c$. As the timing of an external electric-field pulse is scanned across the echo-pulse sequence, a modulation of the echo intensity occurs due to the opposite phase shifts produced for the two groups of ions, which causes an interference between the radiation of the two groups at the moment when each group rephases among themselves. In the absence of an internal electric field, E_s, the A and B groups are homogeneously distributed. The echo intensity will be modulated according to the expression

$$I = I_0 \cos^2[2\pi(d\nu/dE)(E_0 \Delta t)] \ , \tag{1}$$

where $d\nu/dE$ is the Stark shift of the echo-producing ions, E_0 is the amplitude of the applied electric field and Δt is the time difference between the duration of the electric-field pulse, which occurs between the echo preparation pulses and the duration between the second preparation pulse and the echo formation.[6] Modulations of the intensity will occur as the effective electric pulse area $E_0 \Delta t$ is changed by scanning the electric-field pulse relative to the echo pulse sequence.

As shown in Fig. 1, in the presence of E_s only the A sites in the (+) domains and B sites in the (−) domains are resonant with one another and can both be excited by the resonant radiation field of the echo-producing light pulses. These two groups of ions are now spatially separated from one another by distances corresponding to the domain size. The amplitude of the echo intensity modulations will depend on the shape and size of the domains and the direction of the beam of optical pulses with respect to this domain structure. In the present work, observation of modulations of the echo produced by Cr^{3+} ions in the photoelectric domains as a function of the size, position and orientation of the optical excitation beam relative to the c axis provide new information on the structure of the domains.

II. EXPERIMENTS

The measurements were made at $T = 1.5$ K with 0.4 wt. % Cr_2O_3 ruby crystals. The regions containing the photoelectric domain structure were produced in 0.4-mm-thick samples by Ar^+ laser irradiation (beam diameter ~ 1 mm, $P \sim 1$ W). The irradiation times was several hours in order to produce the most uniform field in domains over the whole irradiated spot. The resulting electric field in the domains was $E_s \cong 350$ kV/cm.

The pulses for the photon echo were obtained with a pulsed tunable dye laser, pumped with two synchronized Nd:YAG lasers, operating in their second harmonic. The pulse separation between the Nd:YAG lasers was set at $\tau = 100$ ns. The laser was tuned to the R_1 ($^4A_2$-E) transition of the Cr^{3+} ions and was focused to a spot size of about 100 μm in diameter. The echo measurements were made in a magnetic field $H = 30$ kOe, $H \perp c$, in order to increase the dephasing time T_2 and make the echo observation possible. In heavily doped ruby T_2 is very short due to dephasing produced by interactions between the magnetic moments of the closely spaced Cr^{3+} ions.

The external electric field pulses $E\|c$, $E = 50$ V/cm, pulse duration $\Delta t = \tau = 100$ ns, were applied to the sample with the help of metal electrodes. The experiment was made in two geometries—with the laser beam propagation vector $\mathbf{k}\|c$ and $\mathbf{k}\perp c$ [see Figs. 2(a) and 2(b)]. For the $\mathbf{k}\perp c$ geometry the sample was placed between the electrodes and the light entered and exited the sample between the electrodes. For the $\mathbf{k}\|c$ beam geometry, the laser beam entered the sample through a pair of pinholes situated opposite one another in each of the electrodes. The distance between the electrodes (5 mm) was made significantly larger than the pinhole size (1 mm) and sample thickness (0.4 mm) in order to make the field more uniform.

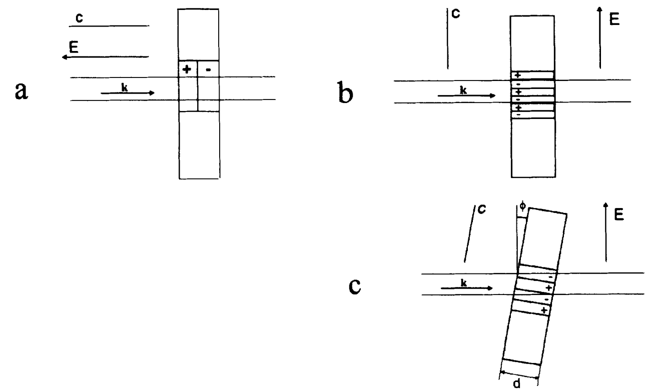

FIG. 2. Geometries of the photon-echo modulation experiment containing photoelectric domain structures: (a) laser beam parallel to the c axis ($\mathbf{k}\|c$), (b) laser beam perpendicular to c axis ($\mathbf{k}\perp c$), and (c) sample tilted by a small angle ϕ relative to $\mathbf{k}\perp c$ orientation.

The echo intensity was measured as the electric-field pulse was scanned in time with the help of programmable delay (as in Ref. 6). The sequence of electric field and laser pulses is shown in the inset in Fig. 3. The scanning range began such that the electric-field pulse ended before the first optical preparation pulse and extended to a time in which its turn on was beyond the occurrence of the echo, ensuring that data was taken where the pulse was effectively absent. The data for each temporal position of the electric field pulse, T, was averaged for 100 laser pulses. In addition, the temporal scan was repeated 2–3 times to generate a number of echo modulation data patterns. These were then averaged to produce the data reported here. Because there is a background signal, which must be subtracted in order to obtain the actual echo intensity, the external magnetic field was decreased to $H = 18$ kOe during the first and last few data points. At this field, for $\tau = 100$ ns, the echo intensity falls to zero because of the rapid decrease of T_2 with a reduction in H,[8] making it possible to obtain the background level. All modulation data is shown with this background subtracted.

III. RESULTS

The results of the experiment for the laser beam oriented with $\mathbf{k}\perp c$ and $\mathbf{E}\|c$ in a "fresh" sample in which $E_s = 0$ are shown in Fig. 3(a). The modulation pattern is quite similar to that obtained for alexandrite.[6] The period of

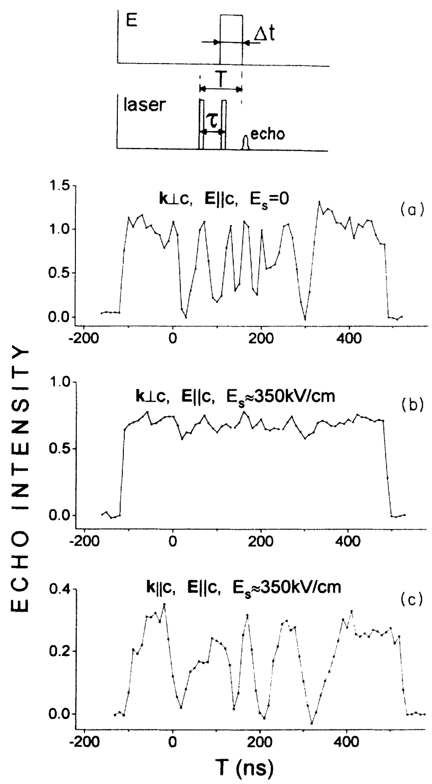

FIG. 3. Echo-modulation patterns for (a) unirradiated sample $\mathbf{k}\perp c$, (b) Ar-ion-laser-irradiated sample containing photoelectric domains $\mathbf{k}\perp c$, and (c) Ar-ion-laser-irradiated sample containing photoelectric domains $\mathbf{k}\|c$. The inset shows the echo and electric field pulse sequence.

modulations is consistent with the known[9] splitting of the R lines in the external electric field. We find a value of $d\nu/dE \cong 0.15\pm0.02$ MHz/V cm^{-1} compared to the previously measured value of 0.12 MHz/V cm^{-1}.[9] The different value for $d\nu/dE$ obtained from the echo modulation pattern is probably due to the uncertainty in estimating the pulse area of the short electric-field pulse. The depth of the modulation pattern is close to 100%.

In Fig. 3(b) the typical modulation pattern obtained in the crystal volume containing the photoelectric domains is shown for $\mathbf{k}\perp c$. The laser was tuned into one of the pseudo-Stark components of the R_1 line, split by the internal photoinduced domain field E_s. The positions of the maxima and the minima in the modulation pattern are the same as for the unirradiated sample, but the depth of the modulations is greatly reduced relative to those in Fig. 3(a). It was also observed that the depth of the modulations is very sensitive to the position of the beam inside the domain structure and the modulation depth typically was found to vary over the range between 15% and 80%. An identical result was obtained when the laser was tuned to the other Stark component.

Also shown in Fig. 3(c) are the modulations in the echo, which are observed from an area of the crystal containing the photoinduced domains for $\mathbf{k}\|c$ and $\mathbf{E}\|c$. The depth of the modulations is again nearly 100%, as found for the unirradiated sample, and the modulation depth was independent of the beam position on the sample. Thus, it was observed that the echo-modulation patterns are sensitive to the creation of the domain structure and the experimental geometry.

IV. DISCUSSION

The sensitivity of the echo-modulation patterns to the creation of the domain structure and to the experimental geometry suggests that it must contain information on the domain structure. Consider the generation of an echo in the sample containing the photoelectric domains. The dye laser is tuned into resonance with one of the components of the R_1 line, split by the photoinduced electric field of the domains. Each component includes the contribution of different groups of ions: one component is due to A ions in the $(+)$ domains and B ions in the $(-)$ domains and the other to B ions in $(+)$ domains and A ions in $(-)$ domains (see Fig. 1). We shall mark these groups of ions A^+, B^-, A^-, and B^+. When the laser is resonant with one of the split R_1 components, two groups of ions are excited by the laser, e.g., A^+ and B^-. In the absence of the external electric field both groups give equal in-phase contributions to the echo signal. When the external electric-field pulse is applied, the contributions of A^+ and B^- ions to the echo become out of phase and the final echo intensity is determined by the interference of these two contributions. As the A^+ and B^- ions belong to different domains, they are separated spatially and the resulting echo intensity may depend on the domain geometry.

We first examine the case for $\mathbf{k}\|c$, where 100% modulations are observed. Since the modulation pattern is independent of laser position, we conclude either that the cross sectional area of the domains intercepted by the laser beam is much smaller or is much larger than the laser beam area. Consider the situation in which the cross-sectional area of the domains is large compared to the focused laser beam so that the laser beam passes through the $(+)$ and $(-)$ domains one after another [see Fig. 2(a)]. The echoes generated by the A^+ and B^- ions will follow the same path and, since their initial phases are determined by the same laser pulse the echo modulations will be the same as if the A^+ and B^- ions are mixed in the same sample volume. If the beam paths through the $(+)$ and $(-)$ domains are equal, 100% modulations will be observed. This is in agreement with the theoretical expectation[3,4] that for $\mathbf{k}\|c$

$$\sum_i E_s^i x_i = 0 ,$$

where $E_s^i = \pm E_s$ is the photoinduced electric field in domain i and x_i is the domain length along the c axis. This condition leads to the absence of a voltage between the ends of the irradiated sample. Thus the observation of 100% modulations for $\mathbf{k}\|c$ implies zero voltage across the sample as expected. If the domains are much smaller than the laser beam area, it is as if the A^+ and B^- ions are microscopically mixed so that 100% modulations are again expected.

The more informative experiment is conducted in the **k**⊥c geometry. Indeed, the sensitivity of the echo-modulation pattern to the beam position suggests that the domain sizes cannot be very small in comparison to the beam diameter. The observation of modulation amplitudes as low as ~20% suggests that in the plane ⊥c the domains stretch from one sample surface to the other. In this case we can consider dividing the optical beam into a set of parallel beam segments, each passing through a different domain as in Fig. 2(b). Coherently prepared ions within each beam segment rephase at time 2τ. However, the contribution from ions in different beam segments no longer interfere with one another, since they travel different optical paths. Therefore, the echo intensity modulations disappear. It therefore follows from the symmetry of the crystal (D_{3d}, containing a trigonal c axis) and of the experimental geometry that the domains must be flat in order for the observed strong reduction of the echo modulation depth to occur. Only in such a geometry can the low modulation depth be achieved because here the echoes generated in different domains are spatially separated over the total optical path length in the sample. Of course there always must be some residual echo modulations due to the interference of echoes generated by the ions situated within an optical wavelength of the domain walls.

In order to verify the suggested picture of flat domains perpendicular to the c axis, an additional experiment was performed. The dependence of echo modulation patterns on the angle ϕ between **k** and the direction ⊥ to c for small angles ($\phi \sim 1°$) were studied. The results are shown in Fig. 4. The echo-modulation pattern is very sensitive to ϕ. For values of $\phi > 4°$ the 100% modulation depth is fully restored. From these observations the domain thickness may be roughly estimated. The 50% modulation depth is achieved when the sample is tilted by $\phi = 1.5°$ relative to the position with minimal modulations. If the domain structure is treated as a pile of flat domains stretching across the whole irradiated sample volume, it follows from simple geometric considerations [see Fig. 2(c)] that the domain thickness is $x = 2d \sin\phi = \sim 20$ μm (the sample thickness for these experiments was $d \sim 400$ μm).

The above estimation of the domain thickness means that for **k**⊥c about five domains lie within the dye-laser beam in the echo experiment. The A^+ and B^- Cr^{3+} ions close to the domain walls, within a distance of about an optical wavelength λ, must give a contribution to the modulation (of the order of relative volume of the regions adjacent to the domain walls), and thus the modulations may not be less than about a few percent.

For the optical geometry **k**⊥c the echo signal is expected to have spatial structure. This structure can be described as the Fraunhofer diffraction pattern of a multislit transmission grating. The echo signal from each domain has an additional phase shift caused by the pulsed electric field: contributions from the (+) domains have a positive phase shift and those from the (−) domains have an equivalent negative phase shift. In such a situation, the echo signal in the far field will have a spatial structure consisting of interference fringes. For

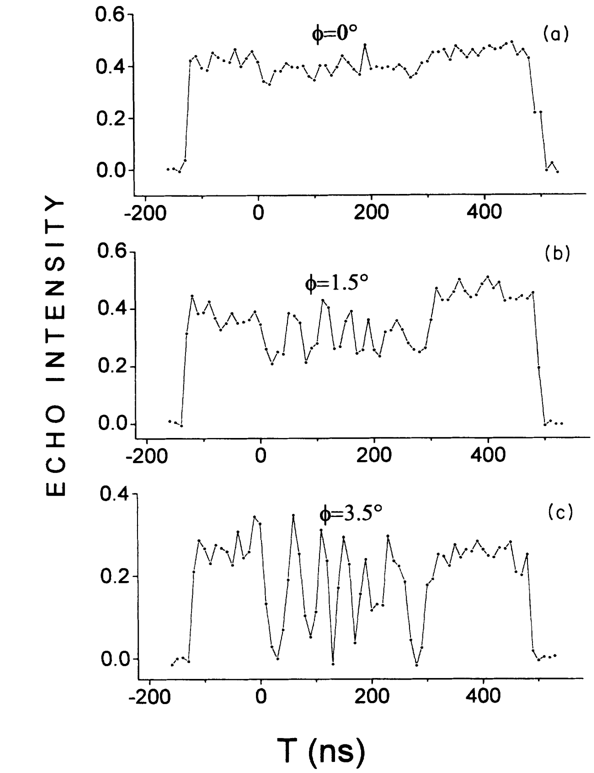

FIG. 4. Echo-modulation patterns for an Ar-ion-laser-irradiated sample containing photoelectric domains. The sample is tilted relative to the **k**⊥c orientation [see Fig. 2(c)]: (a) $\phi = 0°$, (b) $\phi = 1.5°$, and (c) $\phi = 3.5°$.

domains ("slits") of thickness ~20 μm the fringes will be much narrower than the light spot containing the echo signal. Scanning the electric-field pulse through the echo-pulse sequence will produce changes in the relative phases of the two types of domains, which will result in shifts of the interference fringes within the echo spot, but not in changes of the integrated signal intensity. It is estimated that these fringe shifts will give only small modulations of the echo pattern. Observation of the structure within the echo spot would be quite difficult given the weakness of the echo signal and the small separation between the interference fringes and the likely case that the domains are not all of the same thickness. This experiment was not attempted.

The suggested domain structure is consistent with all of the previously known properties of the domains[3] and the current theory.[4] The flat layered domain structure makes it easy to explain the highly uniform field in the domains (the pseudo-Stark doublet components are not broader than the initial spectral line). Taking into account the relatively large (~20 μm) domain thickness, it is expected that the contributions of ions near the domain walls to the fluorescence spectrum will be negligible. The observation of photoelectric domain structure in 10-μm ruby powders[10] suggests that the shape and size of the domains may be different and may be sensitive to the sample geometry caused by the diameter of the Ar-laser beam used for preparation of the domains and the sample shape and size. In these experiments the sample thickness and the irradiated spot size were nearly as large as possible. The thickness was limited by the large *U*-band absorption, which would attenuate the beam in a thick sample and the beam diameter was made sufficiently small so as to provide adequate laser power to produce the photoinduced domains.

V. CONCLUSIONS

Photon-echo modulation techniques have been successfully applied to probing the geometry of otherwise invisible photoelectric domains in ruby crystals. The domain structure consists of flat domains perpendicular to the *c* axis with a thickness of about 20 μm. These results suggest the possibility of applying coherent transient spectroscopy techniques to studies of spatial structures in other doped insulators such as domains in ferroelectric materials.

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