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Optical Behavior of Domains in KH_2PO_4†

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Below the Curie temperature, KH_2PO_4 is found to act as a layered dielectric waveguide for light propagating along the polar axis. Each thin ($3\times10^{-4}-10\times10^{-4}$ cm) domain is a waveguide for light polarized along its "slow" direction. The domain walls are parallel to one tetragonal axis and the polar axis and are continuous through the whole crystal. A collimated beam is diffracted at the exit face of the KH_2PO_4 crystal. Both regular (ordered) and irregular diffraction patterns were observed. When the incident light was plane polarized, the regular diffraction pattern consisted of even and odd orders (spots) which were in general plane polarized in different directions. These propagation effects are explained in terms of the domain structure.

INTRODUCTION

THE ferroelectric behavior of KH_2PO_4, KDP, was first noted in 1935[1] and has been studied extensively since then.[2] The tetragonal form of the crystal undergoes a phase change as the temperature is lowered to the Curie point $T_c \simeq 120°K$, which is accompanied by the appearance of spontaneous polarization and shear strain which lowers the crystal symmetry to orthorhombic. The optical behavior of this material above T_c and as a single domain below T_c has been carefully examined by Zwicker and Scherrer.[3] Above T_c, KDP is uniaxial but shows a large, electric-field-dependent birefringence which is linear with the polarization (or strain) induced by the field. Below T_c, the crystal is biaxial and has a large "spontaneous" birefringence which has the same dependence on the polarization or strain. When Zwicker and Scherrer removed the dc bias field below T_c, the linear, "spontaneous" birefringence disappeared presumably due to the formation of equal volumes of oppositely polarized domains such that the linear effects would cancel.

The existence of domains in KDP was demonstrated by x-ray measurements.[4] Kanzig[5] predicted that the domain structure should have a layer-like structure with the domain walls containing the polar axis and one of the tetragonal axes. Kanzig estimated a layer thickness of the order of 10^{-4} cm. Mitsui and Furuichi[6] observed a gross domain pattern with a polarizing microscope and barely resolved a minute crack-like structure, thickness $\approx 10^{-3}$ cm, parallel to the tetragonal axis which they assumed was the basic domain pattern. Hill and Ichiki[7] deduced a domain thickness of 4×10^{-4} cm on the basis of microwave loss measurements and Oettel[8] has recently reported the optical observation of thin-layered domains of about the same thickness.

We report here the observation of a thin, regular, layered domain pattern in KDP and some interesting optical properties which result from this structure.

OBSERVATIONS

The experiment consisted of transmitting a collimated light beam through a KDP crystal and observing both an image of the transmitted beam and the exit face of the crystal as a function of temperature. The crystal, usually a 1.25-cm cube cut with the tetragonal axes parallel to the cube edges, was mounted in a glass Dewar which had flat input and output windows. The crystal temperature was measured by a thermocouple and was readily controllable in the neighborhood of T_c.

Above T_c, the crystal was transparent and transmitted an undistorted beam. With a He-Ne gas laser operating at 6328 Å, as the source of the beam, the transmitted beam image was a spot as shown in Fig. 1(a). As the temperature was lowered through T_c, the beam image abruptly became a line parallel to one of the tetragonal axes, Fig. 1(b), or a sequence of spots along the same direction, Fig. 1(c).

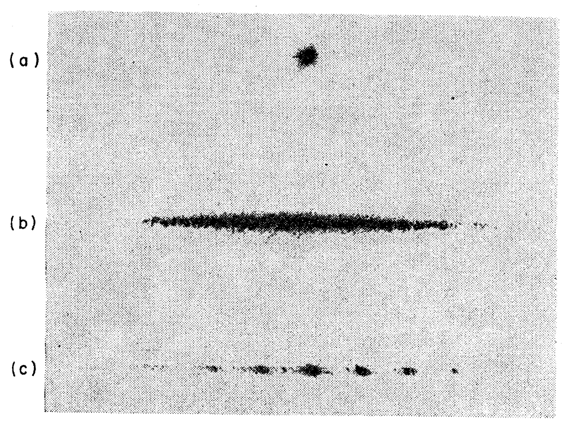

FIG. 1. Intensity distribution of light beam transmitted along polar axis of KH_2PO_4. Viewed 8 cm beyond crystal. (a) Temperature $T>T_c$, Curie temperature. (b) $T<T_c$ domains of nonregular thicknesses. (c) $T<T_c$ domains of equal thickness.

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[1] G. Busch and P. Scherrer, Naturwiss. **23**, 737 (1935).
[2] F. Jona and G. Shirane, *Ferroelectric Crystals* (The Macmillan Company, New York, 1962), Chap. III.
[3] B. Zwicker and P. Sherrer, Helv. Phys. Acta **17**, 346 (1944).
[4] M. de Quervain, Helv. Phys. Acta **17**, 509 (1944); A. R. Ubbelhode and I. Woodward, Nature **156**, 20 (1945).
[5] W. Kanzig, *Solid State Physics*, edited by F. Seitz and P. Turnbull (Academic Press Inc., New York, 1957), Vol. 4, pp. 99–116.
[6] T. Mitsui and J. Furuichi, Phys. Rev. **90**, 193 (1953).
[7] R. M. Hill and S. Ichiki, Phys. Rev. **132**, 1603 (1963).
[8] R. E. Oettel, Bull. Am. Phys. Soc. **9**, 215 (1964), and (private communication).

Microscopic examination of the crystal in transmitted light revealed a thin layer pattern, Fig. 2. These layers were parallel to one or the other of the tetragonal axes but perpendicular to the direction defined by the beam image. The beam, at the exit face of the crystal, had the same size as the beam at the input face and, except for the resolvable layer pattern, it was indistinguishable from Fig. 1(a). This leads one to guess that the images shown in Figs. 1(b) and 1(c) are diffraction patterns produced by the layered domain structure. This concept was strengthened by observing that the layers are quite regular when an ordered pattern, Fig. 1(c), is observed, and that the layer thickness t is related to the angular separation of the spots by the usual grating law, $n\lambda = t \sin\theta$. t was observed to be typically 6×10^{-4} cm.

The layer boundaries appeared to act as reflectors for the transmitted radiation. This was seen most clearly by illuminating a portion of the crystal which contained layers along one tetragonal axis in one region and along the orthogonal axis in a neighboring region.

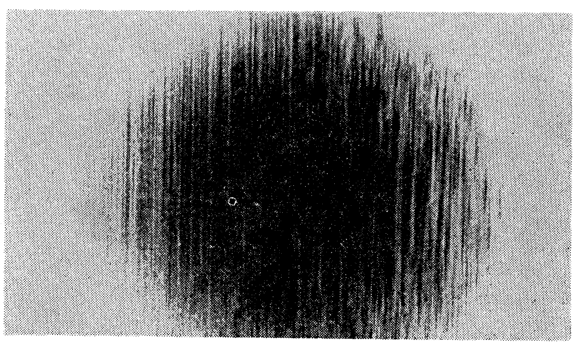

FIG. 2. Magnified image of crystal face in transmitted light. $T<T_c$.

As the crystal was rotated slightly about one of the tetragonal axes, the beam moved with the moving layer boundaries, but remained stationary in the region where the layer boundaries were perpendicular to the rotation axis. It was possible to completely separate a circular beam which had part of the beam in each region.

The polarization properties of the ordered diffraction pattern, Fig. 1(c), were quite unusual. The expected behavior for a biaxial crystal would show a transmitted beam that was linearly polarized only when the incident beam was polarized along one of the orthorhombic crystal axes. For any other incident polarization, the transmitted beam should be elliptically polarized unless the crystal is just long enough to act as a half- or full-wave plate. We found, however, that the ordered diffraction pattern was polarized for all directions of the incident polarization and, in general, the even and odd orders were polarized along different directions.

Figure 3(a) shows schematically the observations when the incident polarization was along the orthorhombic or tetragonal crystal axes. As expected, for

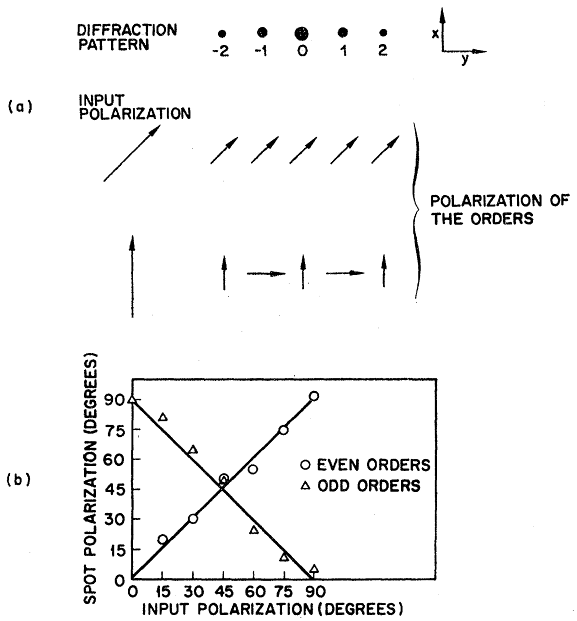

FIG. 3. Diffraction pattern and polarization of the orders. (a) Diffraction pattern with the observed polarization for different input polarizations. (b) Polarization of even and odd orders as a function of input polarization.

light polarized along the orthrohombic axis, i.e., at 45° to the layer boundary, all of the diffraction orders, or spots, were polarized along the incident direction. However, when the incident light was polarized along a tetragonal axis, perpendicular or parallel to the domain wall, the even orders [labeled in Fig. 3(a)] were polarized parallel and odd orders perpendicular to the incident light. For arbitrary incident polarization, the even and odd orders were polarized as shown in Fig. 3(b). The even orders continued to be polarized parallel to the incident direction while the plane of polarization of the odd orders rotated in the opposite sense.

DISCUSSION

These observations can be explained by noting that domains of opposite polarization are crystallographically and optically inequivalent. Above T_c KDP is tetragonal, symmetry $\bar{4}2m$, with axes $x=y\neq z$. The crystal is uniaxial with the optic axis parallel to z. At T_c the symmetry is lowered to orthorhombic, mm, by the appearance of a spontaneous strain x_y. The orthorhombic axes, a and b, are in the x, y plane but are at 45° to x and y. c is parallel to z. The important feature is that the shear for a domain polarized positively along z is in the opposite sense the shear for a domain polarized negatively along z.[9] Therefore, a and b are interchanged for the two senses of dipolar polarization. In addition, the optical index ellipsoid is rotated by nearly 90° around c for the two cases.[3] This is shown

[9] A. Von Arx and W. Bantle, Helv. Phys. Acta **17**, 298 (1944).

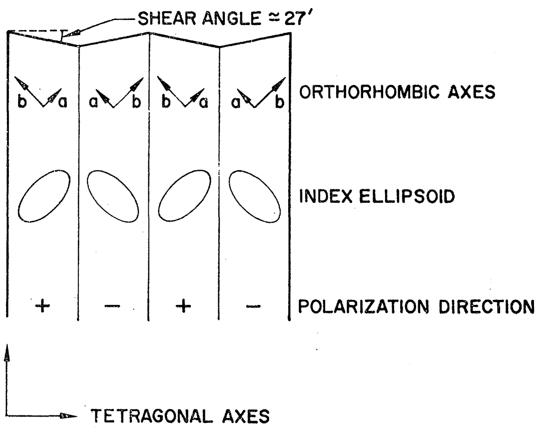

FIG. 4. Domain pattern showing alternating shear strain, orthorhombic directions, orientation of index ellipsoids and dipole polarization directions.

schematically in Fig. 4. For the multidomain crystal below T_c, this inequivalence leads to the observed propagation anomalies.

For light propagating along c, there is now a "slow" wave polarized along a and a "fast" wave polarized along b. However, the a direction in one domain is the b direction for the domains on either side. Since the measured[3] relative index difference, $(n_a-n_b)/n_b$, is

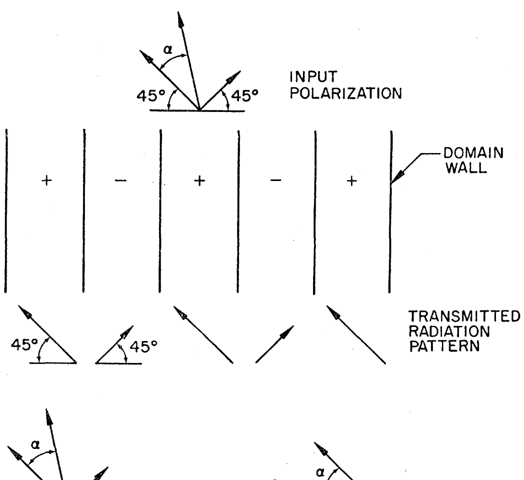

FIG. 5. Domain pattern showing direction and amplitude of transmitted radiation for an arbitrary input polarization. Also shows direction and phases of radiation contributing to even and odd diffraction orders.

about 0.01, the slow wave in any domain is trapped by total internal reflection, as long as the angle between c and the direction of propagation is less than the critical angle, 8–10°. That part of the light incident on a domain which is polarized along b, the fast wave, is multiply refracted and scattered by the many domain walls and is essentially lost to the beam.

The crystal thus acts as a layered dielectric waveguide, with each domain transmitting only light polarized along its a axis, which is at 45° to the domain boundary and 90° to the a axis of its two neighboring domains. A part of the energy of any beam incident along c on a multidomain crystal is trapped by the layer structure. The amplitude of the slow wave trapped in each domain is determined by the polarization of the incident light, as shown in Fig. 5. For light incident with its polarization at 45° to a domain wall, every other domain will transmit trapped radiation. This gives rise to a diffraction pattern with a slit separation of $2t$ with each order polarized in the same direction as the incident light. For light incident with arbitrary polarization, each domain transmits its slow wave with an amplitude determined by the angle α between a and the input polarization, Fig. 4. This gives rise to a diffraction pattern for which the even orders are the sum of the in-phase components of neighboring domains and the odd orders are the sum of the 180° out-of-phase components of neighboring domains. Thus, the even orders are polarized with the incident radiation while the odd orders are polarized along a direction which is the reflection of the incident direction about an a axis, as observed.

We can also propagate parallel to the domain walls in the x, y plane. Since this direction is at 45° to the orthorhombic axes, there should be no index difference in neighboring domains and no diffraction pattern. Propagation in this direction not only failed to show diffraction but no evidence for domain walls could be found, indicating that the domain wall is too thin to be resolved.

In summary, we observe KDP to possess a thin ($3\text{–}10\times10^{-4}$ cm) layered domain structure. For light propagating along the polar axis, the crystal behaves as a layered dielectric waveguide, with each domain transmitting its "slow wave". When the thickness of the layers is constant, the resulting ordered diffraction pattern has even and odd orders which are, in general, polarized in different directions.

ACKNOWLEDGMENTS

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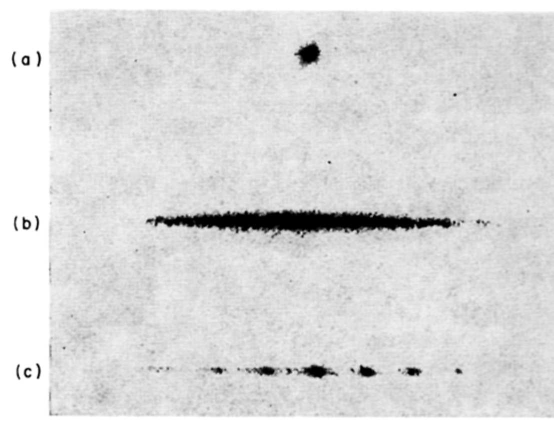

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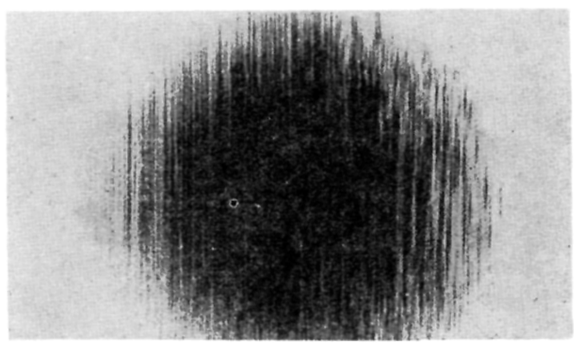

FIG. 2. Magnified image of crystal face in transmitted light. $T < T_c$.