

for AuFe, we conclude that the s - d and other scattering contributions are of equal magnitude. However, the variation of $\Gamma(\vec{k})$ over the various belly orbits obtained from their model is greater than we predict from consideration of the s - d term Γ_{sd} alone. Since the model of Ref. 22 is purely heuristic, we cannot resolve this discrepancy, without further study of the anisotropy contained in the

ordinary scattering, as described in (2).

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Optical Anisotropy of Silicon Single Crystals*

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The birefringence of Si single crystal was measured for He-Ne laser light of wavelength $\lambda = 1.15 \mu$ propagating along $\langle 110 \rangle$ directions, and found to be $\Delta n = n_{\langle 110 \rangle} - n_{\langle 100 \rangle} = (5.04 \pm 0.12) \times 10^{-6}$. For $\langle 100 \rangle$ and $\langle 111 \rangle$ directions of propagation, no birefringence was observed. The magnitude and symmetry of the observed optical response as well as the spectral dependence of birefringence are in good agreement with the theory of spatial dispersion in cubic crystals.

INTRODUCTION

According to classical crystal optics which neglects spatial dispersion and takes into account only dipole-type transitions, cubic crystals should be optically isotropic.¹ Lorentz indicated the possibility of optical anisotropy in cubic crystals if one considers the polarization in a given point to be dependent not only on the value of the local field at that point but also on its value in the close neigh-

borhood, i. e., polarization being not only frequency but also wave vector dependent. On the Lorentz calculation, the birefringence is a maximum for the cubic crystal for light propagation along $\langle 110 \rangle$ directions and takes the value²

$$\Delta n = 0.44\pi\bar{n}(\bar{n}^2 - 1)^2(a/\lambda)^2, \quad (1)$$

where a is the characteristic dimension of the order of the molecule size or interatomic distance, λ is the wavelength, and \bar{n} is the mean of the mea-

sured refractive index (birefringence is supposed to be small).

Optical anisotropy in cubic crystals may also result from the presence of quadrupole transitions. This possibility was investigated by Hellwege for the case of transitions in $3d$ shells in transition-metal ions.³ It was shown that the absorption coefficient in cubic crystals may be directional dependent. The absorption coefficient is polarization independent and is a maximum either for $\langle 100 \rangle$ or $\langle 111 \rangle$ directions of light propagation, according to the symmetry of wave functions of initial and final state of the ion under consideration. On the other hand, for $\langle 110 \rangle$ directions of light propagation, the value of the absorption coefficient was found to depend on the polarization of the incident light.

The detailed macroscopic theory of the optical properties of crystals with higher-order effects taken into consideration is given by Agranovich and Ginzburg.⁴ The dielectric tensor of a crystal $\epsilon_{ij}(\omega, \vec{k})$ is considered not only frequency but also wave vector dependent. It is shown that in the macroscopic approach this dependence not only accounts for the spatial dispersion in the case of dipole transitions, but also for the effect of quadrupole transitions with the exception of the very narrow region near the line center. The dielectric tensor is expanded and only the lowest terms in \vec{k} are retained. In the case of crystals with an inversion center, we have

$$\epsilon_{ij}(\omega, \vec{k}) = \epsilon_{ij}(\omega) + \alpha_{ijlm}(\omega) k_l k_m, \quad (2a)$$

where repeating subscripts denote the usual summations. The number of independent components of the fourth-rank tensor α_{ijlm} is limited by the symmetry; in the case of silicon with O_h symmetry, this tensor is determined by three scalars. Quite analogously, we can expand the inverse dielectric tensor

$$\epsilon_{ij}^{-1}(\omega, \vec{k}) = \epsilon_{ij}^{-1}(\omega) + \beta_{ijlm}(\omega) k_l k_m. \quad (2b)$$

The limitations of these expansions are discussed in Ref. 4; as shown in detail, the use of (2) in wave equations for dielectric media gives different values of the refractive index for different propagation directions. For $\langle 100 \rangle$ and $\langle 111 \rangle$ directions of light propagation, the refractive index is independent of the orientation of the plane of polarization, while for $\langle 110 \rangle$ directions, the birefringence is a maximum and has the value

$$\Delta n = \frac{1}{2} [\beta_{xyxy} + \frac{1}{2} (\beta_{xyxy} - \beta_{xxxx})] n^5 \omega^2 / c^2, \quad (3)$$

where β_{ijkl} are the constants in the expansion (2b) and n is the refractive index without taking into account the spatial dispersion. Here we denote $\Delta n = n_s - n_p = n_{\langle 110 \rangle} - n_{\langle 100 \rangle}$, and the condition $4\epsilon_0^2 \beta_{ijkl} \omega^2 / c^2 \ll 1$ has been used to derive (3) from Eqs. (8, 7) and (8, 8) of Ref. 4. The x , y , and z axes corre-

spond naturally to the fourfold cubic axes.

Consideration of the higher-order effects in crystal optics leads to the existence of more than one wave of the same frequency but of different propagation properties even in cubic crystals. This possibility was first pointed out by Pekar⁵ and Ginzburg.⁶ The former introduced the differential relation between the polarization and electric field in the crystal, while the latter has discussed the \vec{k} dependence of dielectric constant in the form (2).⁻

In spite of the fact that a quite solid theoretical basis for understanding the influence of the higher-order effects in crystal optics has already been laid, the experimental evidence is still sparse and sometimes even contradictory. The first experimental observation of quadrupole transitions in the solid state has been made for Cu_2O hydrogenlike exciton series absorption line with $n=1$ by Gross and Kaplyanskii.⁷ The corresponding theory for this case was given by Cherepanov and Galishev.⁸ The optical anisotropy caused by the presence of quadrupole transitions in Ni ions was observed in cubic Ni-I boracite, where both birefringence and dichroisms were found.⁹ Similar, but three orders of magnitude smaller, effects were observed with Co-I cubic boracite.¹⁰

The concept of \vec{k} dependence of the refractive index was used by Hopfield and Thomas¹¹ for the explanation of the spectral dependence of the reflection curve of CdS crystals in the region of exciton absorption, and later by Reynolds *et al.*¹² in the description of interference fringes in emission and transmission spectra of thin CdS platelets at low temperatures. An attempt to reveal the new waves experimentally was made by Brodin and Pekar¹³ and Gorban and Timofeev,¹⁴ who measured the thickness dependence of the absorption coefficient in exciton lines in anthracene and cuprous oxide crystals, respectively, and explained the observed oscillations in the absorption coefficient as arising from the interference of two waves propagating through crystal.

A detailed analysis of most of the experimental investigations to date on higher-order effects in crystal optics is given in Ref. 4. While the presence of quadrupole transitions has already been unmistakably established, the experiments dealing with the influence of the spatial dispersion in the case of dipole transitions are not so straightforward. We undertook, therefore, a direct measurement of the birefringence in simple cubic crystals as suggested in Refs. 2 and 4.

Whatever the values of β are, the birefringence due to the spatial dispersion will be more easily observed in materials with high refractive index as can be seen from Eqs. (3) and (1). Recently, Lopez and Kornreich¹⁵ observed the directional dependence of photoconductivity in homopolar cubic semicon-

ductors. They do not connect their observations with the optical anisotropy of these crystals; we consider nonetheless this question worthy of further investigation. Therefore, the exact measurement of the birefringence of silicon single crystals for different directions of light propagation was carried out. As far as we know no positive results of the direct measurements of the birefringence of cubic crystals due to spatial dispersion has been reported. Even if the expected effect is small it is not lacking in practical importance as silicon is commonly used as an optical material in the infra-red region.

EXPERIMENTAL

All measurements were performed on two low-dislocation density silicon single crystals with resistivity larger than 200 Ω cm (intrinsic *p*-type conductivity). Crystals had the form of rectangular bars, one limited by (110), ($\bar{1}\bar{1}0$), and (001) planes and the second by two (111) planes and four planes of general orientation. The dimensions were 5.794 \times 6.721 \times 22.001 mm and 5.743 \times 7.585 \times 24.168 mm, $\langle 110 \rangle$ and $\langle 111 \rangle$ directions being parallel to the longest sides. All six faces of both crystals were polished so that the measurements might be performed in all three mutually perpendicular directions.

The experimental arrangement is shown in Fig. 1. The He-Ne laser beam of $\lambda = 1.15 \mu$ (1 mW) was chopped and passed through a polarizer, sample, compensator, and analyzer consecutively. A PbS photocell was used as the detector and connected with a preamplifier and lock-in amplifier. The sample was mounted on a rotatory table with its axis parallel to the beam so that it was possible to measure the retardation for different angles between the plane of polarization and the fourfold cubic axis of crystal. The retardation was compensated by a Soleil-Babinet compensator; the detec-

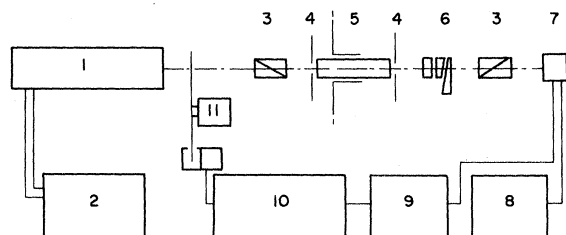


FIG. 1. Experimental arrangement for the birefringence measurements: 1, 2 are the laser with the power supply; 3 is the polarizer and analyzer; 4 is the stops; 5 is the sample on the rotatory table; 6 is the Soleil-Babinet compensator; 7 is the PbS photocell; 8 is the stabilized voltage supply; 9, 10 are the preamplifier and lock-in amplifier; and 11 is the chopper with source of reference signal.

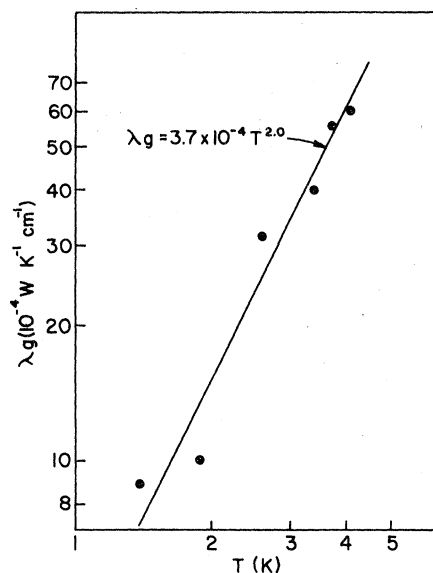


FIG. 2. Indicatrix of the light intensity passing through crossed nicols as a function of the angle between [100] axis and plane of polarization.

tion system was then used as a null instrument. Care was taken to see that the beam did not touch the edge of the sample, and no phase change due to stray internal reflection occurred.

In addition to the above-described measurements, the variation of the intensity of light transmitted along the [110] direction of the sample between crossed nicols, with the angle between the polarization plane and the $\langle 100 \rangle$ direction was also measured. In this arrangement, if the retardation is small, the transmitted intensity is proportional to the square of the birefringence:

$$I/I_0 = \frac{1}{2} (kd\Delta n)^2 \sin^2(2\theta), \quad (4)$$

where d is the path length of the ray in the birefringent medium. Δn is the birefringence for given direction of propagation and \vec{k} is the wave vector.

The variation of the intensity of light passing through the silicon sample along the [110] direction is given in Fig. 2. Pronounced extinction occurs when the plane of polarization is either perpendicular to or coincides with $\langle 100 \rangle$ directions. Similar behavior can be observed for all directions of the light propagations other than $\langle 100 \rangle$ and $\langle 111 \rangle$ directions. For these special directions, no retardation occurs and there is no dependence of light propagation on the orientation of the plane of polarization, in full accord with the spatial dispersion theory.

The slight nonzero value of the light intensity for these extinction directions apparent in Fig. 2 may be caused either by the small misalignment of the sample or an additional strain birefringence overlapping the birefringence due to the spatial dispersion. Also small depolarizing effects on the polished front and back surfaces may to some extent

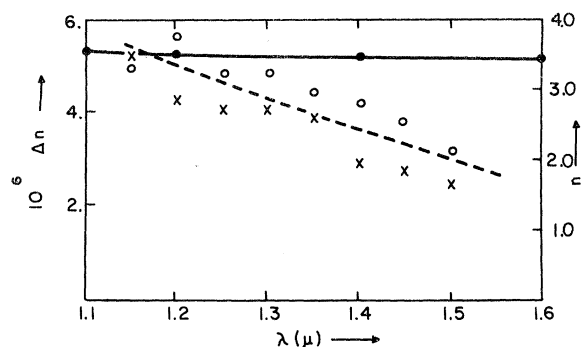


FIG. 3. Dispersion of birefringence (dashed line) and refractive index (solid line). Open circle is for the angle between [100] and polarization plane equal $+45^\circ$. Cross is for an angle equal to -45° . The value of refractive index was taken from Ref. 17.

contribute to this residual intensity.

The maximum value of birefringence for light propagating along the [110] direction was found¹⁶ to be $\Delta n = n_{(110)} - n_{(100)} = (5.04 \pm 0.12) \times 10^{-6}$. The errors in these measurements are due mainly to the differences found in different sites on the crystals or for different direction of light propagation. Such differences may be due either to the misalignment of the crystal, the error in orientation (we estimated it from the Laue pictures to be 2–3%), or to the small strain birefringence superimposed on the birefringence due to spatial dispersion. The error in individual measurements for given direction and orientation was less than 1%.

The dispersion of birefringence observed for propagation of light along $\langle 110 \rangle$ orientations is given in Fig. 3 for two different orientations of the crystal. In these measurements, a tungsten filament lamp with a Bausch and Lomb grating monochromator and suitable collimator lenses was used as the light source; the remainder of the arrangement was the same as shown in Fig. 1. Even though the errors in these measurements were greater than those with the laser as the light source, the trend of the dispersion is unmistakably clear. All measurements reported here were performed at room temperature. A change of temperature of the

sample $\pm 40^\circ\text{C}$ above and below the room temperature did not cause a noticeable change in the birefringence within the limits of experimental error.

The birefringence in silicon due to spatial dispersion and the directional dependence (Fig. 2) can also easily be demonstrated visually with the help of a silicon sample at least 2 cm long, a He-Ne 1.15- μ (1-mW) laser, a pair of polaroid sheets, and a Kodak infrared phosphor screen.

DISCUSSION

The orientation and the order of magnitude of the observed birefringence agree with the predictions of the theory of spatial dispersion.^{2,4} The origin of the birefringence as due to strain is excluded by the fact that $\langle 100 \rangle$ and $\langle 111 \rangle$ directions are propagation directions of zero retardation, irrespective of the state of polarization of the incident light; in case strain were present, such a behavior cannot be expected for *both* these directions. Further, the value of birefringence has the expected order of magnitude. If we use the Lorentz formula (1), we obtain for the critical dimension the value $a = 1.01 \times 10^{-8}$ cm, close to the nearest-neighbor distance in silicon.

The slope of the birefringence curve as a function of wavelength in Fig. 3 is also much steeper than that of the refractive index (solid line) and, in fact, has the value expected from Eqs. (1) and (3). Indeed, if we consider the values of β_{ijkl} in (3) as frequency independent, then from the known values of refractive index we can easily show that the value of Δn at $\lambda = 1.45\mu$ should be approximately one-half of its value at 1.15μ , in full agreement with the data in Fig. 3.

In comparison with the optical anisotropy of cubic boracites,^{9,10} no apparent dichroism was observed in Si up to $\lambda = 1.08\mu$. This fact agrees with the assignment of different origin of the anisotropy in silicon crystals.

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¹We do not consider the gyrotropy which exists in crystals with structures that do not possess a center of inversion.

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Differential Electroabsorption*

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Differential-electroabsorption spectra are calculated, using the Elliott theory of optical absorption by excitons, and are compared with experiments by Frova *et al.* at the direct (M_0) edge of Ge. The theory does not fit the data for any reasonable set of values of ϵ_0 , μ^* , E_{gap} , Γ , $\langle c | \hat{e} \cdot \vec{p} | v \rangle$, and applied electric field strength. The discrepancies between theory and experiment can be understood qualitatively as due to nonuniformities in the applied electric field. The physics of electroabsorption is discussed with particular attention paid to the effects of excitons (i.e., the final-state Coulomb interaction) on both quasibound and continuum states of the electron-hole pair. In general, exciton theory predicts three phenomena omitted by the one-electron theory: (i) The excitons enhance the amplitude of the differential absorption both below and above the direct bandgap; (ii) the excitons increase the period of spectral oscillations of the electroabsorption signal above that predicted by Franz-Keldysh theory; and (iii) the first negative peak in the electroabsorption spectrum is due to the broadened zero-field bound-state excitons. The electron-hole interaction is responsible for a differential absorption which is both qualitatively and quantitatively different from that predicted by one-electron Franz-Keldysh theory—even when the applied electric field is so large that the discrete excitons are completely ionized.

I. INTRODUCTION

In recent years, the lock-in amplifier has revolutionized solid-state spectroscopy—giving rise to thermal modulation, strain modulation, wavelength modulation, polarization modulation, and electric field modulation as techniques for probing the changes in the optical properties of solids due to applied fields.¹ Of the various differential spectroscopies, electric field modulation often gives the sharpest signals—suggesting that it may provide the best test for a theory of differential spectra.²

Until now, most theories³ of electroabsorption and electoreflexion have assumed (i) the validity of the effective-mass approximation, (ii) the applicability of one-electron theory, (iii) that the line-widths of the observed spectra are adequately described by a single energy-independent broadening parameter Γ , and (iv) that the experimental data with which the theories are compared are uniform-field data.

These theories have been successful in describing

the *signatures* of electoreflexion and electroabsorption data at M_0 and M_1 critical points in transition-band structures; that is, the theories have succeeded in giving *qualitative* fits to the line shapes, and therefore have led to the determination of the *energies* and the *types* of the various critical points in transition-band structures.

Still, there are no *quantitative* fits to the line shapes of the data; and there is some reason to suspect that the best fits to date may have tended to obscure real discrepancies between theory and experiment, by permitting the fitting parameters to assume unrealistic values.

It is generally believed that many of the discrepancies between existing theories and data can be attributed to the failure of the one-electron approximation and that exciton effects (i.e., correlations in the motions of electron and hole due to final-state interaction) are important. A number of attempts^{4–7} have been made to develop a theory which includes exciton effects, with significant contributions made by Duke and Alferieff,⁴ Ralph,⁵ and Blosssey.⁶ How-