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Nonlinear Piezo-Optic Behavior of Sphalerite (α-ZnS)†

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The variation of the refractive index of sphalerite with pressure to 7 kbar has been determined by an interferometric method. The refractive index decreases with increasing pressure, as was predicted earlier. Above 3 kbar the change in refractive index is found to be nonlinear with respect to both stress *and* strain, thus demonstrating that Pockels's linear elasto- and piezo-optic equations have to be extended.

THE recent measurements[1,2,3] on the variation of the refractive index of solids as a function of pressure up to fairly high stress levels have indicated departures from the Pockels's[4] linear laws of photoelasticity, namely, that the change in refractive index Δn is linearly related to the stress applied σ and to the strain produced. It was found that both in the crystalline media and in glasses, the above law is valid only at low stress levels, where the infinitesimal deformation laws are valid. But at high stress levels involving finite elastic deformations the observed Δn in glasses[1] was significantly higher than that predicted by the linear relation between Δn and σ; and in the case of crystalline media[2,3] it was significantly lower. However, in all cases Δn was found to be linearly related to the Lagrangian strain η, computed using the nonlinear theory of elasticity, even though the total volume strain involved in the cases of vitreous silica and RbCl[3] were as high as 2% and 3.2%, respectively. Thus it appeared that the strain is a more fundamental parameter, from the theoretical point of view as well as the extensive range over which the linear laws seem to be valid. Of course there is no *a priori* reason to expect such a linear relation to be valid universally. In fact it is shown in this article that this linear relation between Δn versus η fails even at fairly low strain in the case of sphalerite (α-ZnS) and that one must take into account higher order strain-optical coefficients to explain the behavior.

Good-optical-quality near-colorless single crystals of the mineral sphalerite were obtained from Juan Montal,[5] Spain and a spectrochemical analysis revealed the following impurities: Cd, 0.2–0.5%; Fe, 100–300 parts per million (ppm); Cu, 20 ppm; Mg, 5–20 ppm; Al, 10 ppm; Mn, 1–10 ppm. The variation of the refractive index with hydrostatic pressure to 7 kbar was determined by an interferometric method described elsewhere[6] in detail. Due allowance for the change in thickness of the sample was made by using (i) the data of Bridgman[7] on compressibility of α-ZnS and its variation with pressure, (ii) recent similar data of Cline and Stephans,[8] and (iii) the second-order elastic-constant data of Bhagavantam and Suryanarayana.[9] The volume strain computed from the data of Bridgman differs from the data of Cline and Stephans and Bhagavantam and Suryanarayana by 3.5% and 7%, respectively, at the maximum pressure investigated. However, since this does not in any way alter the trend of the final results nor the conclusions derived from them, in what follows the data derived from Bridgman's values alone are given.

Figure 1 represents the results obtained between Δn and stress as well as strain. Since the stress-strain relation is essentially linear in the range investigated, both are presented in the same graph. Since about sixty fringes were observed to shift with each specimen, only representative points have been plotted in the figure. It is seen that the refractive index of α-ZnS decreases under hydrostatic pressure, as predicted by Ramaseshan *et al.*[10] Further, it is obvious that Δn varies nonlinearly

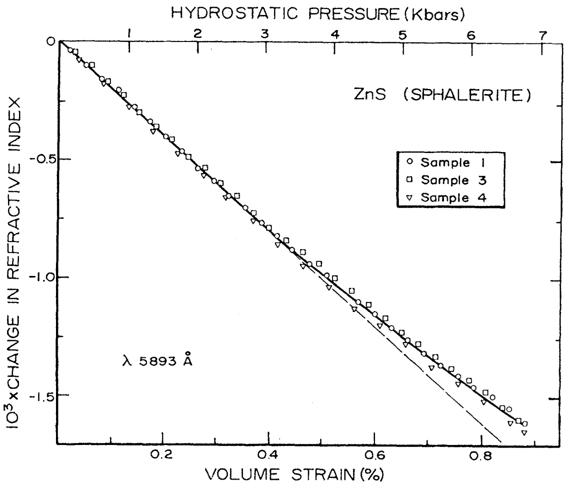

FIG. 1. Variation of refractive index of sphalerite (α-ZnS) with pressure and volume strain. $T=22°\mathrm{C}$.

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both with stress *and* strain beyond about 3 kbar (0.4% volume strain). This is the first time that such a nonlinear behavior with strain has been observed for any material. Since the number of fringes shifted on increasing the pressure matched exactly to the number shifted on the release of pressure to within a fraction of a fringe, it is concluded that the above phenomenon is noticed in the elastic region.

Recently[11] Pockels' piezo- and elasto-optic equations have been extended to take into account such nonlinear effects. It was shown that for a cubic crystal under hydrostatic stress Δn is given by

$$\begin{aligned}\Delta n &= (n^3/2)[(p_{11}+2p_{12})\eta+(p_{111}+4p_{112}+2p_{122}+2p_{123})\eta^2],\\ &=A\eta+B\eta^2,\end{aligned}$$

where η is the Lagrangian strain and p_{ij} and p_{ijk} are the first- and second-order elasto-optic coefficients. By using the data on all three specimens and the relation $\Delta V/V_0=3\eta(1+\frac{1}{2}\eta)$, the constants A and B were determined by least-squares fit and found to have the values 0.666±0.001 and 34.6±0.6, respectively.

The initial slope of $\rho dn/d\rho$ for α-ZnS for λ5893 was found to have a value 0.200. The interpretation of these results in terms of strain-polarizability constant, etc. will be dealt with elsewhere along with similar results on other cubic crystals.

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Matrix Elements for the Indirect Piezoabsorption Coefficient in Silicon*

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Relative matrix elements are calculated for the absorption coefficient in the indirect-absorption-edge region for uniaxially stressed silicon. The calculations are for ⟨100⟩, ⟨110⟩, and ⟨111⟩ stress, for all possible phonons, for all independent polarization directions of the light, and through all relevant intermediate states. The results are compared with experiments and interpreted to show that the deformation potential b is negative and that several intermediate states must participate in the transition, resulting in interference effects.

INTRODUCTION

SEVERAL investigators[1–3] have recently measured the polarization dependence of the indirect absorption edge of germanium and silicon under uniaxial stress. The polarization dependence is the result of the stress induced splitting of the initially fourfold-degenerate valence band into two doubly degenerate levels and of the breaking of the equivalence of the various valleys in the conduction band for certain stress directions. To compare the experimental results with theory, one must calculate the matrix elements for this indirect absorption for the various possible transitions. It is the purpose of this paper to present a calculation of these matrix elements for all allowed transitions through the various possible intermediate states in silicon.

METHOD AND RESULTS

The final state for the electron is in one of the six conduction-band valleys along the ⟨100⟩ directions in silicon, which will no longer necessarily be equivalent after the application of uniaxial stress. We call the particular final state under consideration $\psi_f=\Delta_f{}^1\Delta_k{}^6$ since the space symmetry is Δ_1 and the spin degeneracy is Δ_6. The index f labels the particular ⟨100⟩ valley under consideration. The initial states may be labeled by ψ_m where $m=\pm\frac{1}{2}, \pm\frac{3}{2}$ for the four states. The form of ψ_m will depend on the direction of stress. For ⟨100⟩ stress we still label the states $\pm\frac{3}{2}, \pm\frac{1}{2}$ although the states are not necessarily eigenfunctions of J_z. The intermediate state is $\Gamma_j{}^i\Gamma_{k'}{}^6$, where Γ^i is the space symmetry of the intermediate state, and Γ^6 is the spin degeneracy. We neglect spin-orbit effects in the intermediate state, as well as stress-induced level splitting since this will only affect the energy denominator and therefore have a relatively smaller effect on the matrix elements.

The matrix element for the indirect transition[4] is

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