

## Faraday Rotation in the Absorption Edge of Amorphous Selenium

J. Mort and H. Scher

*Xerox Research Laboratories, Xerox Square, Rochester, New York 14603*

(Received 28 August 1970)

The Faraday rotation in amorphous Se has been measured with an ac technique between 1.1 and  $0.64\ \mu$  ( $1.127 - 1.94\ \text{eV}$ ). The results are compared with a theoretical dispersion formula based on the Tauc model of optical absorption in an amorphous semiconductor. A key feature of the model is a description of the violation of the  $k$ -conservation rule, induced by the disorder of the amorphous state, with a single parameter  $z$ . For  $z=0$  the dispersion formula reduces to the standard one for direct transitions, and for  $z>1$  it reduces to the form for indirect transitions. A satisfactory fit is obtained with  $z=0.2$ , which indicates a range of local order about half that in amorphous Ge. The gap energy obtained in the fit is  $E_g=2.13\ \text{eV}$ . This value is interpreted as further evidence for a two mechanism absorption in the absorption edge in amorphous Se. One is due to localized-molecular states and the other to delocalized bandlike states. The present experiments have allowed an optical resolution of these two absorption mechanisms, because of the different magneto-optical properties of the associated states.

### I. INTRODUCTION

There has been a recent upsurge in interest in the optical, electrical, and photoconductive properties of amorphous solids, particularly in the way these properties are influenced by the electronic energy structure of the disordered solid state.<sup>1</sup> From the point of view of detailed reproducible optical and charge transport properties, amorphous selenium is the best-characterized amorphous material. Its optical absorption exhibits a long-wavelength edge and an absorption coefficient which reaches high values and extends for an appreciable energy range.<sup>2</sup> These properties are consistent with transitions involving one energy band of substantial width. On the other hand, the small slope of the absorption edge suggests that the optical transitions are not between sharply defined energy bands. Measurements of the quantum efficiency for the photogeneration of electrons and holes as a function of photon energy by Hartke and Regensburger were interpreted by them as evidence that the optical properties of amorphous selenium arise from two different types of optical transitions.<sup>2</sup> One type, assumed to have unit quantum efficiency, was interpreted as direct allowed transitions between valence and conduction bands separated by an energy gap of  $2.53\ \text{eV}$ . The other type of optical transition, assumed to occur with zero quantum efficiency, was attributed to intrinsic excitonlike absorption. This would suggest that one-electron tail states, which have been postulated to extend into the forbidden gap because of the disordered nature of an amorphous material, do not play a significant role in determining the optical properties of amorphous selenium. Recent studies of the photoemission of hot carriers from metals into amorphous selenium also led to the conclusion that the nonphotoconducting absorption in this material arose from localized

excitonic-type transitions.<sup>3</sup> Indeed, it was pointed out that the nonphotoconducting absorption found in single crystals of orthorhombic sulfur meant that such absorption is not a unique characteristic of the amorphous state. A common feature of amorphous Se and orthorhombic sulfur is that they both possess molecular species consisting of eight-membered rings. The fact that amorphous Se consists of a large number of  $\text{Se}_8$  rings and disordered Se chains was established by the infrared and Raman studies of Lucovsky *et al.*<sup>4</sup>

A recent analysis by Lucovsky<sup>5</sup> of the temperature dependence of the quantum efficiency of the photoconductivity and its relationship to the temperature dependence of the absorption edge has further elucidated the nature of the two types of absorptive transitions. His analysis indicates that all the properties of the quantum efficiency can be associated with a bandlike edge and that the localized absorption is compatible with a photoconducting loss. This work stresses the distinctions between the two absorption processes. Theoretical results by Chen<sup>6</sup> support this conclusion. Nevertheless, despite the growing evidence that the absorption edge in amorphous Se was the sum of two absorption processes, all attempts to detect any structure in the optical absorption at high and low temperatures were unsuccessful.<sup>7</sup>

Since the Faraday effect is directly proportional to the dispersion of a material, it represents a method of obtaining the differential of the absorption curve. It was hoped that this might reveal some weak structure not directly observable in absorption. In addition, Faraday rotation has been widely used to study the nature of interband electronic transitions at the band edges of conventional valence semiconductors for which general theories have been developed. In this paper a general theory of

the interband Faraday rotation is presented in which the results for direct and indirect transitions for single-crystal semiconductors emerge as a special case. The theory can accommodate varying degrees of disorder and is used to analyze the experimental data for amorphous selenium. Measurements of the Faraday rotation in amorphous Se have been reported by Gobrecht *et al.*<sup>8</sup> and by Garben and Seliger.<sup>9</sup> These measurements spanned a limited range of photon energies, particularly in the region of most interest at higher photon energies; a sensitivity of about  $0.1^\circ$  was the limiting factor. In addition these earlier results were interpreted in a classical effective-mass approximation which, as will be indicated later, is probably not appropriate to disordered materials.

In Sec. II of this paper the experimental technique will be described and the results presented. In Sec. III a theory, developed for the Faraday rotation in disordered systems, will be presented and in Sec. IV the significance of the results will be discussed.

## II. EXPERIMENTAL TECHNIQUE AND RESULTS

Faraday rotation is the rotation of the plane of polarization of a plane-polarized light wave upon traversing an optical medium in the direction of an applied magnetic field. The amount of rotation depends upon the difference in phase of the two circularly polarized components of the plane-polarized wave after traversing the medium. The Faraday angle  $\theta$  is given by

$$\theta = (\omega/2c)(N_r - N_l)l, \quad (1)$$

where  $\omega$  is the angular frequency of the light,  $N_r$  and  $N_l$  the index of refraction for right and left circularly polarized components, respectively,  $l$  the sample thickness, and  $c$  the velocity of light. If the energy shift between the right and left refractive indices is small, as is usually the case, then

$$\theta = \frac{\omega l}{2c} \frac{dn}{dE} \Delta E, \quad (2)$$

where  $\Delta E$  is, equivalently, the Zeeman splitting  $\gamma H$ , where  $\gamma$  is the effective gyromagnetic factor. The amount of rotation is, therefore, proportional to the sample thickness. However, as the photon energy increases the optical density of the sample increases and since the measurement technique uses the transmitted light, the signal level decreases rapidly and approaches the noise level. There is thus a conflicting requirement between having a sample thin enough to transmit sufficient light and yet thick enough to exhibit detectable rotation. Operationally, a maximum value of  $\alpha l$  is  $\approx 1.0$ , where  $\alpha$  is the absorption coefficient. In the vicinity of the absorption edge,  $\alpha$  increases faster as a function of  $E$  than  $\theta$  so that the Faraday rotation cannot be measured over the entire range of photon ener-

gies with a sample of one thickness. In order to make measurements as far into the absorption edge as possible, a very sensitive means for measuring the Faraday angle is required in order to use thin samples. In the present experiments the minimum value of  $l$  was  $7 \mu$ . This meant that the deepest penetration attained into the absorption edge region was the photon energy at which  $\alpha = 1400 \text{ cm}^{-1}$ , i.e.,  $\hbar\omega \approx 2 \text{ eV}$ .

A dynamic rather than the usual static technique was employed and a schematic of the apparatus is shown in Fig. 1. Monochromatic linearly polarized light traveling parallel to the magnetic field was incident on the sample. The transmitted light passed through a polarizer rotating at 95 Hz onto a photomultiplier. This gave an alternating 190-Hz signal, the phase of which was determined by the polarization of the transmitted light. A fixed reference phase was obtained by analyzing a reference beam with a second polarizer mounted on the same rotating shaft as the first. These two signals were amplified and compared in phase with an amplitude-independent phase computer. By integrating the output from the phase computer, rotations could be measured to about  $0.015^\circ$ . The advantages of this technique have been discussed previously<sup>10</sup> and they need not be restated here.

The amorphous-selenium samples were made by the vacuum deposition of high-purity selenium onto thin quartz slides held at a temperature of  $55^\circ \text{C}$ . Since quartz gives a measurable Faraday rotation in the visible spectrum, thin slides were used to minimize this substrate effect. Although the rotation in quartz, over the range of energies studied, is essentially constant, this background rotation has been subtracted from the total rotation in the data presented. The range of photon energies studied is from 1.1 to 1.95 eV with a range of Se sample thicknesses from 7.0 to  $325 \mu$ . Figure 2 shows a recorder trace of the output from the phase computer. The deflections represent rotations in opposite directions of  $1.4 \text{ deg}$  and correspond to reversed magnetic field configurations. In order

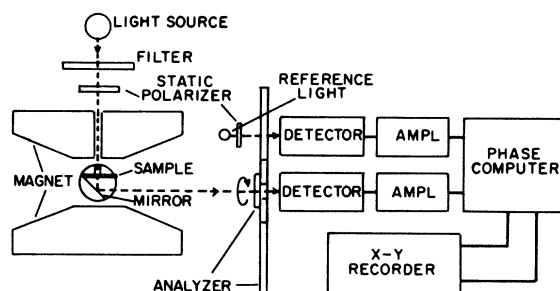


FIG. 1. Schematic diagram of apparatus used to observe the Faraday rotation.

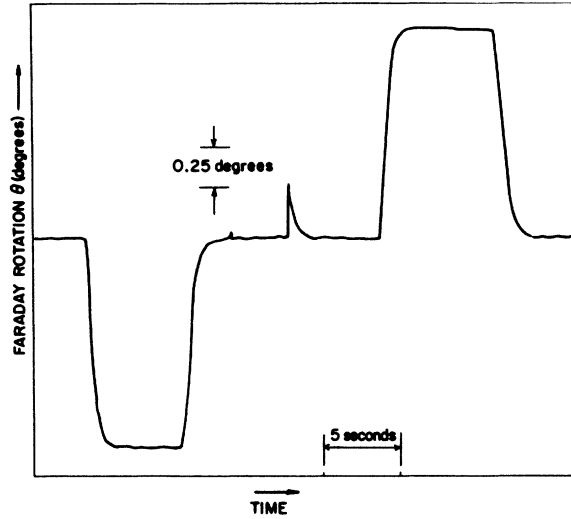


FIG. 2. Recorder trace of Faraday rotation in an amorphous Se sample 325  $\mu$  thick. The photon energy is 1.55 eV and the magnetic field is 15 kG. The two deflections correspond to the magnetic field being applied in opposite directions.

to compare theory and experiment it is convenient to define a Verdet constant  $V$ , i. e., the Faraday rotation per unit magnetic field and thickness. This can only be done if over the range of magnetic fields (up to 15 kG in this work) and sample thicknesses used, the rotation varies linearly with magnetic field and sample thickness. Figure 3 substantiates the linear dependence of  $\theta$  in these two parameters. The resultant spectral dependence of  $n\theta/d$  ( $n$  is the wavelength dependent refractive index of selenium) in the absorption edge of amorphous selenium is given in Fig. 4. The results are a composite from several different samples. For a given thickness  $n\theta/d$  increases rapidly with photon energy so that the error becomes smaller; however, when, for signal reasons it is necessary to switch to a smaller thickness the error initially increases again.

### III. THEORY

We herein develop a general theory of interband Faraday rotation appropriate to the case of an amorphous semiconductor. Based on the general relation Eq. (2), a natural starting point for a calculation of Faraday rotation is a consideration of the index of refraction  $n(E)$  as a function of photon energy or equivalently, frequency. The dispersion is associated with the interband transitions and is contained in the Kramers-Kronig relation

$$n(\omega) - \kappa^{1/2} \approx \frac{1}{\pi \epsilon_0 \kappa^{1/2}} P \int_0^\infty \frac{\omega' \epsilon_2(\omega') d\omega'}{\omega'^2 - \omega^2}, \quad (3)$$

where  $\kappa$  is the dielectric constant and  $\epsilon_2(\omega)$  is the imaginary (absorptive) part of the complex dielec-

tric function. It has been assumed in Eq. (3) that the index of refraction varies slowly with  $\omega$  in the region where  $\epsilon_2(\omega)$  is large.

In general  $\epsilon_2(\omega)$ , in a one-electron formulation, is a superposition of all allowed transitions at the fixed  $\omega$  weighted by the matrix element for each transition

$$\epsilon_2(\omega) = \left( \frac{2\pi e}{m\omega} \right)^2 \frac{2}{(2\pi)^3} \frac{1}{B} \int_{BZ} d^3k d^3k' F(\mathbf{k}, \mathbf{k}') \times \delta(E_c(\mathbf{k}') - E_v(\mathbf{k}) - \hbar\omega). \quad (4)$$

In Eq. (4),  $B$  is the volume of the Brillouin zone (BZ),  $E_c$  and  $E_v$  are the energies of states labeled by  $k'$  and  $k$  in the conduction and valence bands, respectively, and  $F(k, k')$  is proportional to the square of the transition matrix element. In a crystal,  $F(k, k')$  reduces to  $B |p_{vc}|^2 \delta(k - k')$ , where  $p_{vc}$  is the ( $k$ -independent) momentum matrix element between the conduction and valence bands; this results in an  $\epsilon_2(\omega)$  which corresponds to the usual formula for absorption via direct transitions.

In an amorphous semiconductor, owing to the lack of long-range order,  $k$  can no longer be considered a good quantum number. In their model for absorption in an amorphous semiconductor Tauc *et al.*<sup>11</sup> considered the effects of the breakdown in the  $k$ -selection rule. Their main results are (i) the delta function in  $F(k, k')$  is broadened and (ii) the broadening is characterized by a single parameter if the valence- and conduction-band wave functions in the amorphous material can be considered as linear combinations of the crystal wave functions

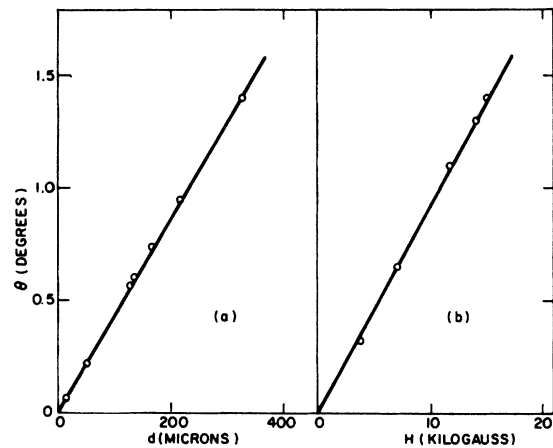


FIG. 3. (a) Faraday rotation angle  $\theta$  as a function of sample thickness. The photon energy is 1.55 eV and the magnetic field 15 kG. (b) Faraday rotation angle  $\theta$  as a function of magnetic field. Sample is 325  $\mu$  thick and the photon energy is 1.55 eV.

of the same bands. Explicit in (ii) is the assumption that when the perturbation corresponding to the transition from the crystalline to the amorphous state is switched on, the number of states in the valence and conduction band do not change. This assumption leads to the simplification that  $F(k, k')$  obeys the Véllicky sum rule<sup>11</sup>

$$\int_{\text{BZ}} d^3k d^3k' F(\mathbf{k}, \mathbf{k}') = B^2 |p_{vc}|^2. \quad (5)$$

It is the sum rule restriction on  $F(k, k')$  that enables

$$\begin{aligned} \theta = K \frac{3}{x^2} & \left[ - \left( 1 + \frac{1}{2z^2} \right) [2(1+z^2)^{1/2} - (1-x+z^2)^{1/2} - (1+x+z^2)^{1/2}] \right. \\ & \left. + \left( \frac{1}{2z^3} \right) \left( 2 \sinh^{-1} z - (1-x) \sinh^{-1} \frac{z}{(1-x)^{1/2}} - (1+x) \sinh^{-1} \frac{z}{(1+x)^{1/2}} \right) \right], \end{aligned} \quad (6)$$

where  $x = \omega/\omega_g$ ,  $\omega_g$  is the gap frequency,  $z = \frac{1}{2}(3\pi^2 B_0)^{1/3} [(m_c + m_v)\omega_g/2\hbar]^{-1/2}$ , and  $K = (\gamma H/4c) \times [\kappa^{1/2} e^2 (2\mu)^{3/2} |p_{vc}|^2] / (8m^2 \hbar^5/2\pi \omega_g^3/2\epsilon)$ .

The main difference between Eq. (6) and other dispersion formulas, which contain the energy gap and the scaling factor as adjustable parameters, is the parameter  $z$  which characterizes the disorder. In the limit  $z \rightarrow 0$ ,

$$\begin{aligned} \theta \simeq K(1/x) & [(1-x)^{-1/2} - (1+x)^{-1/2} \\ & - (4/x)(2 - (1-x)^{1/2} - (1+x)^{1/2})], \end{aligned} \quad (7)$$

one recovers the standard form for  $\theta$  for direct transitions between two simple bands, derived by Kolodziejczak, Lax, and Nishina (KLN).<sup>12</sup> As  $x \rightarrow 1$ ,  $\theta \sim (1-x)^{-1/2}$ . This singularity is related to the  $k$ -selection rule and the sharp edge for the absorption,<sup>13</sup> i.e.,

$$\alpha(E) = 0 \text{ for } E < E_g, \quad \alpha(E) \propto (E - E_g)^{1/2} \text{ for } E > E_g.$$

For  $z > 1$  (i.e.,  $B_0 \rightarrow B$ )

$$\begin{aligned} \theta \simeq (3K/4z^3) & \{ (1/x^2) \ln(1-x^2) \\ & + (1/x) \ln[(1+x)/(1-x)] - 1 \}, \end{aligned} \quad (8)$$

which has the form of the KLN<sup>12</sup> expression for indirect transitions. The only difference between Eq. (8) and the KLN result is in the proportionality constant; to obtain  $3K/4z^3$  one must replace the matrix element  $|M_{kk'}|^2$  of KLN, which is a product of a momentum matrix and a phonon matrix, by  $|p_{vc}|^2/B$ .

Thus, depending on the value of  $z$ , Eq. (6) incorporates both the direct transition form (with the rapid rise near  $x=1$ ) and the indirect transition form. If we set  $x=1$  in Eq. (6), then  $\theta \simeq z^{-1}$  (for  $z < 1$ ), thus the over-all "steepness" of the shape of  $\theta$  as a function of  $x$  depends on the value of  $z$ . The smearing of the absorption edge and/or the selection rule eliminates the singularity. For  $x \ll 1$ ,

one to characterize the broadening by a single parameter. In the simple case where  $F(k, k')$  is a constant  $F_0$  in a certain part  $B_0$  of the BZ centered at  $k-k'=0$ , and zero in the rest, then Eq. (5) determines  $F_0$  to be  $B |p_{vc}|^2/B_0$ . The single parameter, therefore, is  $B_0$  the volume in  $k$  space within which the disorder induces transitions. If we use this simple form for  $F(k, k')$  and insert it into Eq. (4) and substitute the result into Eqs. (2) and (3) we develop the following expression for the Faraday rotation:

$\theta \simeq x^2 C(z)$ , which is the well-known limiting form for  $\theta$ , except in this case the coefficient depends on  $z$ .

In the Tauc model, the states near the bottom of the conduction band and the top of the valence band are considered bandlike or quasilocalized. The application of these results to Se will be considered in Sec. IV.

#### IV. ANALYSIS OF EXPERIMENTAL RESULTS AND DISCUSSION

Interband Faraday rotation, unlike that for free carriers, is not generally useful for determining carrier effective masses. A detailed knowledge of the matrix element for the transitions involved is always required, together with the gyromagnetic ratios of carriers in both conduction and valence bands. Therefore at best such a procedure can lead to an estimate of the reduced effective mass of electrons and holes. In the face of these considerable requirements, together with the additional uncertainty as to the range of validity of the band model for amorphous materials, it was considered inappropriate to attempt an estimate of effective masses from the data. A more useful and productive avenue appeared to be the utilization of the Faraday rotation as a means of elucidating the nature of the transitions which constitute the absorption edge in amorphous Se.

Attempts were first made to fit the data to the theories of KLN<sup>12</sup> for the Faraday rotation for indirect and direct band gaps. The fit with the function for an indirect band gap was completely unsatisfactory. A better fit was achieved using the direct transition dispersion function as seen in Fig. 4(a) but a much better fit was realized with a combination of direct and indirect transitions, Fig. 4(b). This fit, however, gave an indirect band gap which was larger than that obtained for the direct gap.

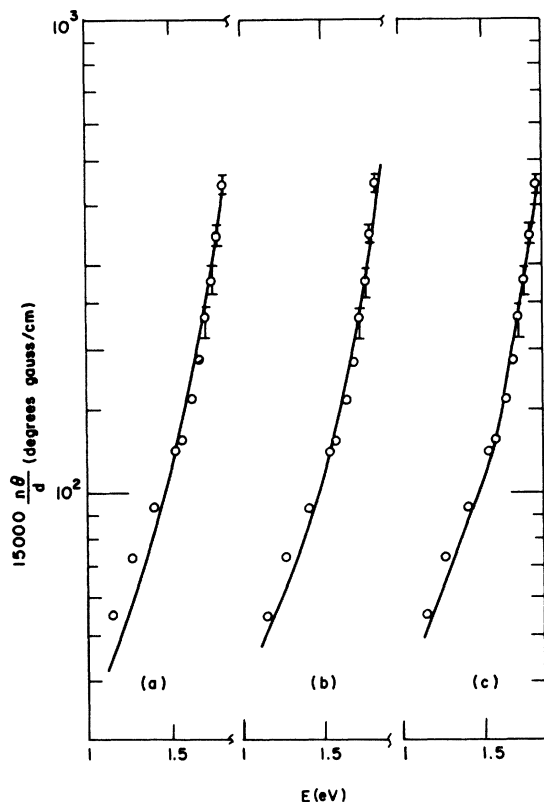


FIG. 4.  $15000n\theta/d$  as a function of photon energy fitted with (a) direct transition dispersion formula, (b) combination of direct and indirect dispersion formulas, and (c) dispersion formula for amorphous materials (see text).

Despite the quantitative fit there was no obvious physical justification for it. A direct band gap which is smaller than the indirect gap should dominate by itself the dispersion in the absorption edge. The inference drawn was that the transitions are basically direct in nature but possess to a detectable degree some indirect character (which may be termed nondirect). Precisely these characteristics have been attributed to transitions in amorphous solids by Tauc *et al.*<sup>11</sup> (as discussed in Sec. III). The transitions can be considered as modified direct transitions in which, because of the disordered state of the solid, the usual conservation of the  $k$ -selection rule is relaxed for a limited range of energies. The theoretical description of the Faraday rotation under these more generalized conditions given in Sec. III was therefore developed.

As discussed in Sec. III the main difference between the dispersion formula, Eq. (6), based on the Tauc model, and the standard ones, Eq. (7) and (8), is the inclusion of the parameter  $z$  which characterizes the breakdown in the  $k$ -selection rule. The analysis of the experimental results establishes the

extent of the nonconservation of  $k$  in amorphous Se.

The data was fitted to Eq. (6) and the best value obtained for  $z$  is 0.2. The fit as seen in Fig. 4(c) is comparable to that obtained with the combined direct and indirect functions, Fig. 4(b), but with a much firmer justification in physical terms. Using reasonable values of the masses  $[(m_c + m_v)/m_e \approx 1.8]$  based on trigonal Se, the value obtained for  $z$  translates into a  $B_0 \approx 8 \times 10^{21} \text{ cm}^{-3}$ , which is an order of magnitude larger than the value obtained<sup>11</sup> for amorphous Ge from optical absorption studies. Thus the local order corresponds to nearly eight nearest neighbors, about half the degree of local order estimated for amorphous Ge. Although amorphous Se exclusively contains Se atoms bonded to two nearest neighbors, it does have two varieties of molecular species.<sup>4</sup> So, besides the positional disorder present in amorphous Ge there is, in addition, a form of compositional disorder. A correspondingly smaller short-range order is therefore reasonable.

The band gap obtained with the fit to Eq. (6) is 2.13 eV. This value is remarkably close to the value of the photoinjection band gap reported by Mort and Lakatos.<sup>3</sup> They inferred that the nonphotoconducting absorption edge in amorphous Se is not due to one-electron tail states but rather that it arises from correlated excitonic-type states. It was pointed out that this is consistent with the fact that, since a comparable nonphotoconducting absorption process occurs in orthorhombic sulfur single crystals, such nonphotoconducting processes could not be considered characteristic of the amorphous state. The fact that both orthorhombic sulfur and amorphous Se contain eight-membered rings suggest that intramolecular electronic transitions with in these molecules could explain the existence of very strong nonphotoconducting absorption. Chen<sup>6</sup> recently has shown that there are two manifolds of excited states associated with a molecular solid based on the  $\text{Se}_8$  ( $\text{S}_8$ ) ring molecule. The states in the low-lying manifold are localized – the transfer integral vanishes owing to the symmetry of the states. The higher-lying states are delocalized (finite transfer integral) and constitute the basis for the bands. The photoinjection and Faraday rotation results together suggest that the energy of 2.13 eV corresponds to the onset of the quasilocalized one-electron tail states<sup>2,3</sup> which ultimately become conduction band states at higher energies.<sup>14</sup>

Further, Lucovsky<sup>5</sup> has shown that the temperature dependence of this edge accounts for the temperature dependence of the quantum efficiency and the localized absorption is therefore consistent with a photoconducting loss.

The Faraday rotation thus appears to be determined only by the dispersion of the conductionlike states (the type of states described by the Tauc model) and the dispersion due to the highly localized

intramolecular  $\text{Se}_8$  transitions plays only a negligible role. It is assumed that these latter transitions contribute a small  $\omega^2$  term at low energies. As seen in Fig. 4(c) such a term would improve the fit in the low-energy region. As an aside, the fit in Fig. 4(a) would not be materially improved at low energies by an  $\omega^2$  term.

Since the absorption coefficient at 2.13 eV is already  $\approx 10^4 \text{ cm}^{-1}$ , this must be associated with the intramolecular transitions. Paradoxically, it appears that highly allowed transitions occur which only contribute in a negligible way to the Faraday rotation. Equation (2) shows that the Faraday rotation is directly proportional to the dispersion  $dn/dE$  and the Zeeman splitting  $\Delta E$ . Plausibility arguments on two levels of sophistication can be advanced to show that the Zeeman splitting,  $\Delta E$ , is expected to be much smaller for the localized transitions than for the delocalized transitions in the absorption edge. One can argue intuitively, for example, that the highly localized intramolecular transitions will be much less perturbed by an externally applied magnetic field (large effective mass) than the highly delocalized states found at the absorption edge. A more quantitative argument has been pointed out by Chen.<sup>6</sup> To zeroth order, the fact that  $\text{Se}_8$  ring forms a stable molecule means

that there is no orbital degeneracy and therefore no net angular momentum. Any degeneracy which might occur would be removed by Jahn-Teller distortion. All these considerations lead to the conclusion that two distinct and unrelated absorption processes occur in the absorption edge of amorphous Se. There is strong nonphotoconducting absorption arising from intramolecular transitions within  $\text{Se}_8$  molecules and interband transitions smeared out by possible band-tailing effects arising from the amorphous state. The different magneto-optical properties of localized molecular states and delocalized band states have allowed the optical resolution of the absorption edge of amorphous Se into its constituent parts.

The theory presented here, as it turns out, applies well to Se. Since it is mainly the delocalized states that make the significant contribution to the Faraday rotation, and especially since the band tailing is comparatively small, the underlying Tauc model is most appropriate for the description of these states.

#### ACKNOWLEDGMENT

The authors wish to acknowledge very useful discussions with Dr. I. Chen, Dr. G. Lucovsky, and Dr. R. Zallen. They also wish to thank A. Ciuffini for the preparation of the Se films.

<sup>1</sup>J. Stuke, *J. Non-Cryst. Solids* **4**, 1 (1970).

<sup>2</sup>J. L. Hartke and P. J. Regensburger, *Phys. Rev.* **139**, A970 (1965).

<sup>3</sup>J. Mort and A. I. Lakatos, *J. Non-Cryst. Solids* **4**, 129 (1970).

<sup>4</sup>G. Lucovsky, A. Mooradian, W. Taylor, G. B. Wright, and R. C. Keezer, *Solid State Commun.* **5**, 113 (1967).

<sup>5</sup>G. Lucovsky, in *Proceedings of the Tenth International Conference of the Physics of Semiconductors*, Boston, 1970 (unpublished).

<sup>6</sup>I. Chen, *Phys. Rev. B* **2**, 1053 (1970); **2**, 1060 (1970); and (private communication).

<sup>7</sup>S. Tutihasi (private communication).

<sup>8</sup>H. Gobrecht, A. Tausend, and I. Bach, *Z. Physik* **166**, 76 (1962).

<sup>9</sup>B. Garben and H. Seliger, *Phys. Status Solidi* **29**, K27 (1968).

<sup>10</sup>J. Mort, F. Luty, and F. C. Brown, *Phys. Rev.* **137**, A566 (1965).

<sup>11</sup>J. Tauc, R. Grigorovici, and A. Vancu, *Phys. Status Solidi* **15**, 627 (1966); J. Tauc, *Optical Properties of Solids*, edited by F. Abeles (North-Holland, Amsterdam, 1970).

<sup>12</sup>J. Kolodziejczak, B. Lax, and Y. Nishina, *Phys. Rev.* **128**, 2655 (1962).

<sup>13</sup>F. Stern, *Phys. Rev.* **133**, A1653 (1964).

<sup>14</sup>It is interesting to note that J. M. Caywood and C. A. Mead, *J. Phys. Chem. Solids* **31**, 903 (1970), have found that the threshold for photoconducting absorption in  $\alpha$ -monoclinic Se (a molecular solid composed of  $\text{Se}_8$  rings) is 2.1 eV.