

## Constant-dipole-matrix-element model for Faraday rotation in amorphous semiconductors

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A model is presented which describes the interband Faraday rotation in amorphous semiconductors by means of a constant dipole matrix element. The model is applied to *a*-Se, *a*-As<sub>2</sub>Se<sub>3</sub>, and *a*-As<sub>2</sub>S<sub>3</sub>. The parameters which fit the Faraday rotation data and those which describe the corresponding behavior of optical absorption at higher photon energies are more consistent than was the case with earlier descriptions in the constant-momentum-matrix-element model. The energy parameters which are obtained are discussed in terms of the corresponding mobility and crystalline band gaps.

Faraday rotation (FR) is the rotation of the plane of polarization of a polarized electromagnetic wave in a material under the influence of a longitudinal magnetic field. Interband FR in amorphous semiconductors has been discussed in the literature for a number of materials.<sup>1-6</sup> Unlike crystalline semiconductors where the effect can be attributed primarily to direct transitions between extended states in valence and conduction bands, it is not clear which process determines the effect in amorphous materials. In a recent paper<sup>6</sup> the problem was analyzed and it was shown that the FR formula for direct transitions in crystals may also be applied to glasses if a correlation between states in valence and conduction bands is assumed. The energy gap  $E_g^{\text{FR}}$ , which can be determined from FR measurements as a function of frequency, is the lowest energy of the contributing transitions. As only transitions between extended states are involved, it is reasonable to compare  $E_g^{\text{FR}}$  with the mobility gap  $E_g^{\mu}$  which can be defined as the distance between the edges  $E_c$  and  $E_v$  of extended states in conduction and valence bands.

Until now all formulas describing FR as a function of the frequency  $\omega$ , for the crystalline as well as for the amorphous state, have been derived under the assumption that the momentum matrix element is constant, independent of the transition energy. We will call this the constant-momentum-matrix (CMM) model in what follows. In this paper we present a constant-dipole-matrix (CDM) model and we show that the energy gap  $E_g^{\text{FR}}$  which is then obtained is in better agreement with the energy gaps associated with the optical absorption at the corresponding energies.

Faraday rotation at photon energies below the energy gap is directly related to other optical effects such as dispersion of the refractive index and absorption at higher energies. The absorption may be described by  $\epsilon_2$ , the imaginary part of the complex dielectric function  $\epsilon = \epsilon_1 + i\epsilon_2$ . Kramers-Kronig transformations allow  $\epsilon_1$  to be calculated from  $\epsilon_2$ . From  $\epsilon_1$ , in turn, the refractive index  $n$  may be determined and thus the FR angle  $\theta$  through the Becquerel relation  $\theta \propto \omega dn/d\omega$  for diamagnetic materials. The result for  $\omega < \omega_g$  may be written as follows:

$$n\theta(\omega) = (\text{const})\omega^2 \int_{\omega_g}^{\infty} \frac{\omega' \epsilon_2(\omega') d\omega'}{(\omega'^2 - \omega^2)^2} \quad (1)$$

with  $\hbar\omega_g = E_g^{\text{FR}}$ ;  $\omega$  is the measurement frequency. From the fact that FR in amorphous materials can be described by a dispersion equation for direct transitions in crystals, it then follows in the CMM model that for amorphous solids at higher frequencies  $\epsilon_2$  has to obey the corresponding equation

$$\epsilon_2(\hbar\omega)^2 = (\text{const})(\hbar\omega - E_g)^p \quad (2)$$

with  $p = \frac{1}{2}$ . This relation was verified by Young<sup>7</sup> for *a*-As<sub>2</sub>S<sub>3</sub> and by Van den Keybus *et al.*<sup>5</sup> for *a*-As<sub>2</sub>Se<sub>3</sub>. Other authors<sup>8,9</sup> have nevertheless found that a squared power law ( $p=2$  instead of  $p=\frac{1}{2}$ ) could describe their data for *a*-As<sub>2</sub>Se<sub>3</sub> up to  $\sim 3$  eV. To complicate matters further, some authors<sup>9,10</sup> obtained a  $p=1$  behavior from *a*-Se samples. Absorption according to Eq. (2) with  $p=1$  was in fact predicted in the CMM model by Tripathi *et al.*<sup>11</sup> for strongly disordered materials. Since there is a corresponding FR expression for every absorption formula, CMM model calculations have not been able to provide a unified picture for amorphous semiconductors.

However, a reevaluation of the absorption data can be carried out within the framework of a recent development in the theory of optical absorption. Cody<sup>12</sup> suggested that, for *a*-Si:H, not the momentum matrix element, but the dipole matrix element must be held constant in the absorption process. This hypothesis was supported by the experimental work of Jackson *et al.*<sup>13</sup> and generalized to all amorphous semiconductors by Cohen *et al.*<sup>14</sup> In the expression for  $\epsilon_2$  as a function of energy  $E$  in the one-electron approximation,

$$\epsilon_2(E) = (\text{const}) \sum_{i,f} |P_{vc}|^2 \delta(E_{c,f} - E_{v,i} - E),$$

the transition probability or momentum matrix element  $|P_{vc}|^2$  between states in the valence band ( $v$ ) and conduction band ( $c$ ) is in that case proportional to the square of the energy:  $(\hbar\omega)^2$ . An absorption law of the form of Eq. (2) in the CMM model is consequently transformed into

$$\varepsilon_2 = (\text{const})(\hbar\omega - E_g)^p \quad (3)$$

in the CDM model.<sup>12</sup> Through the use of Eq. (1) the corresponding expression for FR can then be derived for any choice of  $p$ .

In order to evaluate experimental data for  $a$ -Se,  $a$ -As<sub>2</sub>Se<sub>3</sub>, and  $a$ -As<sub>2</sub>S<sub>3</sub>, we will need expressions for (at least) the  $p = \frac{1}{2}$  and  $p = 1$  cases in the CMM model. For the CDM model, on the other hand, we will show that satisfactory results are obtained with just the  $p = \frac{1}{2}$  expressions. With CMM and  $p = 1$ , FR is given by

$$n\theta = \frac{\text{const}}{x^2} [(1+x/2)\ln(1+x) + (1-x/2)\ln(1-x)] \quad (4)$$

with  $x = \omega/\omega_g = \hbar\omega/E_g^{\text{FR}}$ . The  $p = \frac{1}{2}$  case of the CMM model gives the well-known FR formula derived by Koldziejczak *et al.*<sup>15</sup> for direct transitions in crystalline semiconductors:

$$n\theta = \frac{\text{const}}{x} \left[ (1+x)^{-1/2} - (1-x)^{-1/2} + \frac{4}{x} [2 - (1-x)^{1/2} - (1+x)^{1/2}] \right]. \quad (5)$$

In the CDM model, for transitions between correlated states, we use Eq. (3) with  $p = \frac{1}{2}$  for absorption and

$$n\theta = (\text{const})x[(1+x)^{-1/2} - (1-x)^{-1/2}] \quad (6)$$

for Faraday rotation.

Let us now compare these theoretical expressions to experimental data from vitreous chalcogenide semiconductors. Experimental procedures have been described before.<sup>4</sup> We measured in bulk samples with thicknesses  $d = 0.41$  mm for  $a$ -Se and 0.33 mm for  $a$ -As<sub>2</sub>Se<sub>3</sub>. For  $a$ -As<sub>2</sub>S<sub>3</sub> we refer to the results of Van den Keybus *et al.*<sup>4</sup> We used the frequency range where the product of  $\alpha$ , the absorption coefficient, and the thickness  $d$  is smaller than 0.1, such that the influence of possible internal reflections shows up only in the proportionality constant and not in  $E_g^{\text{FR}}$ . An example of a  $\theta(\omega)$  curve is given in Fig. 1. Such curves were analyzed with formulas for the various choices of  $p$  in both the CMM and the CDM model. Criteria for a good fit were (1) constancy of  $E_g^{\text{FR}}$  in different parts of the frequency region and (2) low root-mean-square (rms) values for the statistical errors. For  $a$ -Se and the CMM model these criteria were best fulfilled by Eq. (4) with  $\Delta_{\text{rms}} = 3 \times 10^{-3}$  deg/T mm and  $E_g^{\text{FR}} = 2.22$  eV. Literature<sup>16</sup> data of  $\varepsilon_2$  were fitted to Eq. (2) with  $p = 1$  and give  $E_g = 2.06$  eV. In the CDM model the best fit ( $\Delta_{\text{rms}} = 2 \times 10^{-3}$  deg/T mm) of the FR was with Eq. (6):  $E_g^{\text{FR}} = 2.11$  eV. At the same time the corresponding Eq. (3) with  $p = \frac{1}{2}$  fits the  $\varepsilon_2$  data, as is shown in Fig. 2, with  $E_g = 2.12$  eV. In the CDM model there is not only a (slightly) better fitting quality for FR but also a good correspondence between absorption and FR behavior. The value of 2.11 eV is in agreement with the 2.13 eV found by Mort and Scher<sup>2</sup> by FR experiments on thin films of  $a$ -Se. However, this agreement is fortuitous. The three-parameter formula of these authors does not fit our measurements on bulk  $a$ -Se, while their thin-film results

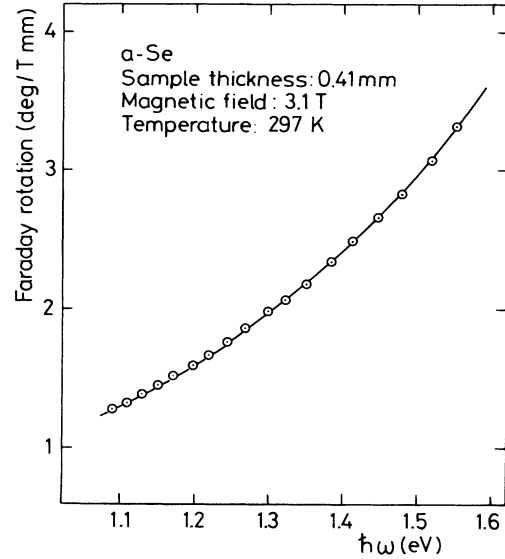


FIG. 1. Faraday rotation as a function of photon energy in  $a$ -Se. The curve corresponds to Eq. (6) with  $E_g^{\text{FR}} = \hbar\omega_g = 2.11$  eV.

should have been corrected for internal reflections. The energy parameter  $E_g^{\text{FR}} = 2.11$  eV also corresponds to  $E_g^\mu = 2.1$  eV, proposed by Davis<sup>10</sup> and Mott<sup>17</sup> as the mobility gap of  $a$ -Se. The energy gap, as determined with Eq. (6), is the lowest energy difference between the correlated extended states involved in the FR and may indeed coincide with  $E_g^\mu$ .

An analogous analysis has been made for our measure-

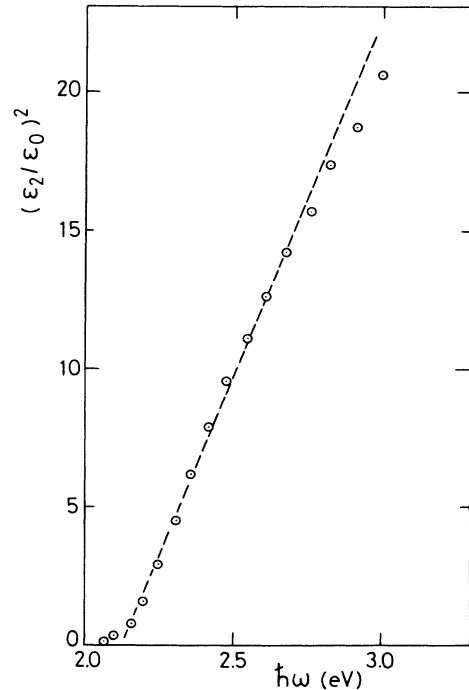


FIG. 2.  $\varepsilon_2$  data of Ref. 16 in the energy range 2–3 eV;  $\varepsilon_0$  is the permittivity of vacuum. The line represents Eq. (3) with  $p = \frac{1}{2}$  and  $E_g = 2.12$  eV.

ments on the FR of  $a\text{-As}_2\text{Se}_3$  and for the  $\varepsilon_2$  data, based on Shaw *et al.*<sup>18</sup> combined with refractive-index data from reflectivity measurements by Zallen *et al.*<sup>19</sup> Both sets of data are best fitted in the CDM model with Eq. (3) with  $p = \frac{1}{2}$  and Eq. (6):  $E_g = 2.15$  eV and  $E_g^{\text{FR}} = 2.06$  eV. In the CMM model the corresponding Eq. (2) with  $p = \frac{1}{2}$  fits the data with parameters  $E_g = 2.50$  eV and  $E_g^{\text{FR}} = 2.35$  eV. Again the consistency of results is improved by the CDM model. A similar study is also possible for  $a\text{-As}_2\text{S}_3$  with FR data from Van den Keybus *et al.*,<sup>4</sup>  $\varepsilon_2$  data from Young,<sup>7</sup> and refractive indices from Zallen *et al.*<sup>19</sup> In the CDM model the results are  $E_g = 2.90$  eV and  $E_g^{\text{FR}} = 2.87$  eV, compared with 3.40 and 3.2 eV in the CMM model with Eq. (2) with  $p = \frac{1}{2}$  and Eq. (5). It may be noted that  $E_g^{\text{FR}}$  values for  $a\text{-As}_2\text{Se}_3$  and  $a\text{-As}_2\text{S}_3$  coincide with the lowest direct band gaps of their crystalline counterparts: 2.05 eV (Ref. 20) for  $c\text{-As}_2\text{Se}_3$  and 2.85 eV (Ref. 21) for  $c\text{-As}_2\text{S}_3$  (extrapolated values at 300 K). For  $a\text{-Se}$  the  $E_g^{\text{FR}}$  value of 2.11 eV lies roughly midway between the direct gap of trigonal  $c\text{-Se}$  [1.95 eV (Ref. 22)] and the 2.25-eV gap, identified in  $\alpha$  monoclinic selenium.<sup>23</sup> Whereas  $E_g^{\text{FR}}$  of  $a\text{-Se}$  is comparable to the mobility gap  $E_g^\mu$ , such correspondence is not obvious for  $a\text{-As}_2\text{Se}_3$  and  $a\text{-As}_2\text{S}_3$ . With the Fermi level in the middle of the gap,  $E_g^\mu$  is twice the activation energy  $\Delta E_\sigma$  for electrical transport in the bands. Literature provides us with many different values for  $\Delta E_\sigma$ , the most probable being about 0.9 eV (Refs. 24–26) for  $a\text{-As}_2\text{Se}_3$  and 1.15 eV (Refs. 26 and 27) for

$a\text{-As}_2\text{S}_3$ . In each of these cases  $E_g^{\text{FR}}$  is larger than  $2\Delta E_\sigma$ . As  $a\text{-As}_2\text{Se}_3$  and  $a\text{-As}_2\text{S}_3$  are  $p$ -type semiconductors, this discrepancy may partly be explained by a slight shift of the Fermi level towards the valence band so that  $E_g^\mu > 2\Delta E_\sigma$ . There may also be a remnant of the  $k$  selection rule, leading to a (small) difference between an indirect gap as the smallest energy distance between extended states (the mobility gap for electrical transport), and a direct gap for optical transitions. Such a remnant of the  $k$  selection rule could correspond to the medium-range order observed in some of the chalcogenide glasses.<sup>28</sup>

The main conclusion of this paper is that FR and the related absorption at higher energies may be described in a more consistent way in a constant-dipole-matrix-element model than in the constant-momentum-matrix-element model. In the CDM  $a\text{-Se}$  obeys the same equations for absorption and FR as  $a\text{-As}_2\text{Se}_3$  and  $a\text{-As}_2\text{S}_3$ ; this is not the case in the CMM model. In  $a\text{-Se}$ ,  $E_g^{\text{FR}}$  coincides with the mobility gap. This coincidence is expected when no distinction must be made between direct and indirect transitions. With a remnant of the  $k$  selection rule the direct transition between extended states in valence and conduction bands involved in the FR may have a larger gap value than the indirect gap which governs electrical transport.

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