

Optical Absorption Coefficient of Pyrite (FeS₂)

Mario Birkholz
 Ingenieurbüro für Solartechnik
 Offenbacher Str. 7, D - 1000 Berlin 33
 Tel.: ++49 - 30 - 822 44 94

ABSTRACT. The thickness of a light-absorbing *p-n* junctions is determined by two requirements: (i) the system has to separate charges via an extended space charge region and (ii) it must absorb a high enough portion of the solar spectrum. Except for very few materials, the second criteria causes most junctions to be thicker than they had to with respect to the first criteria. Semiconducting iron-pyrite, FeS₂, however, has an extraordinary high absorption coefficient of more than $2 \times 10^5 \text{ cm}^{-1}$ in the visible range and would make possible ultrathin solar cells. A physical explanation is put forward to understand the high transition probability for electrons from the valence to the conduction band. It is argued in terms of Stark-effect perturbation theory, that electronic transitions from iron- to sulfur-states are enhanced by the crystal electric field, that acts at the sulfur-position and was recently found to amount to $2.2 \times 10^{10} \text{ Vm}^{-1}$. The field is due to the special symmetry of the S-lattice site and, therefore, by regarding lattice site symmetries one may be led to other high-absorbing materials.

1. INTRODUCTION

How thin may a solar cell be? Which thickness is necessary at least for the system to separate charge carriers? The answer to these questions simply is: for a typical *p-n* junction it has to be thicker than the depletion layer, which amounts to ca. 5000 Å for silicon solar cells [1]. The law of Lambert-Beer

$$I(d) = I_0 \exp(-Kd) \quad (1)$$

describes, which intensity $I(d)$ passes through the solar cell with thickness d and absorption coefficient K when the cell's surface is radiated perpendicularly by a beam of light of intensity I_0 . For silicon, $K = 10^3 \text{ cm}^{-1}$ at 1.5 eV [1], so a Si-solar cell of 5000 Å is roughly estimated to absorb only 5 % of the solar spectrum. If production costs of photovoltaic devices should be reduced, materials with high K -values have to be used. This motivates the recent research efforts on a-Si:H, GaAs, CuInSe₂, CuInS₂ and others, although they still would have larger thicknesses than necessary from the considerations made above.

The situation is different for semiconducting iron-pyrite cubic FeS₂, which has an absorption coefficient [2-4] as large as $K \geq 2 \times 10^5 \text{ cm}^{-1}$ for $\hbar\omega \geq 1.3 \text{ eV}$ so a thin pyrite film with $d = 2000 \text{ Å}$ would absorb more than 98 % of the solar spectrum. A thinner solar cell material is hardly thinkable, because any smaller thickness would come in conflict with the extension of the depletion layer. Concerning the thickness of solar cells, pyrite,

therefore, would aim at the ultimate limit of photovoltaic devices, see Fig. 1. Also because of its non-toxic constituents the material seems attractive for solar cell applications. This paper puts forward an explanation of the physical cause of the high absorption coefficient that is based on the enhancement of electronic transitions by an electrical field as it occurs in the crystal lattice.

The considerations are based on a recent work about the crystal energy of pyrite [5], which has shown that a non-vanishing crystal electric field $E(u)$ occurs at the sulfur-lattice site (abbreviated by the sulfur positional parameter u). The field is due to the non-centrosymmetric charge configuration around the S-lattice site of point group symmetry C_3 (Schönflies notation). The crystal electrical field causes the S-ion to become polarized. Its calculation yielded $E(u) = 2.2 \times 10^{10}$ volts per meter, whereas the induced sulfur dipole strength was found to amount to $12.3 \times 10^{-30} \text{ Cm}$ being twice as strong as the dipole moment of the water molecule. It is the basic approach of this work, that electronic transitions from iron- to sulfur-states are enhanced by the crystal electric field.

The enhancement of electronic transitions by electric fields is well known within the framework of experimental and theoretical atomic physics from the so-called Stark-effect [6,7], although its significance is usually studied for the splitting of emission lines. The techniques used in the following are based upon the tools developed for this effect. No rigorous band-structure calculation will be done, but the physical basis of the high optical absorption coefficient will be motivated. Some simplifying assumptions have to be made, which will be mentioned for each. It is not the aim of this work to calculate the absorption coefficient explicitly, but to obtain an enhancement factor $\nu(E)$, which is the ratio of transition probabilities between the relevant electronic levels with and without an electric field acting at the position of the S-ion.

The absorption coefficient $K(\omega)$ is coupled with the frequency ω of the electromagnetic wave by

$$K(\omega) = \frac{\omega}{c} \epsilon_2(\omega) \quad (2)$$

with c standing for the velocity of light (SI-units are used through all the text). For transversal polarized light with its electrical field vector E_0 along the z -axis and with wavelength λ

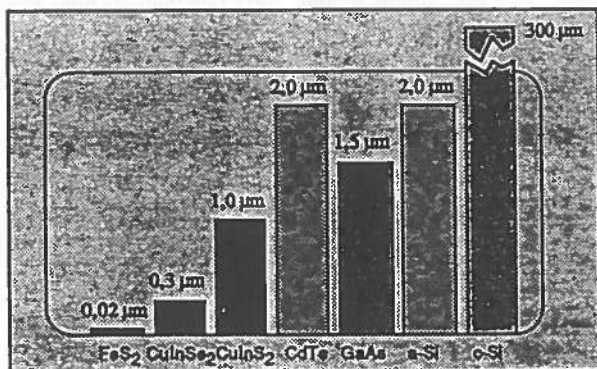


Figure 1: Thicknesses of today and possible future solar cells.

larger than atomic dimensions (optical case) it holds [8]

$$\epsilon_2(\omega) = \frac{\pi e^2}{\epsilon_0 V} \sum |z_{ij}|^2 \{ \delta(\hbar\omega - (E_j - E_i)) - \delta(\hbar\omega + (E_j - E_i)) \} \quad (3)$$

with e , ϵ_0 and \hbar having their usual meaning and V is the volume of the crystallographic unit cell. For cubic pyrite $V = a^3$ with the cell edge as measured [9] to be $a = 5.4187\Omega(6)$ Å. δ should symbolize the delta-function, indicating that an electronic transition only occurs, if the energy of the radiation fits into the energy difference between the ground and the excited state, being E_i and E_j , respectively. $|z_{ij}|$ stands for the transition matrix element $\langle \psi_j | z | \psi_i \rangle$ between the two electronic states with wave functions ψ_j and ψ_i . For an intrinsic or weakly doped semiconductor, $\hbar\omega$ has to be larger than the band gap energy E_g , of course. E_g has been determined to be ≈ 0.9 eV for pyrite, although it must be mentioned that different values have been measured by different authors. A compilation of E_g -values is given in Ref. [10]. The special form of eq. (3) would allow for the incorporation of lattice vibrations with impuls vectors k by writing $E_i(k)$ etc. No consensus has been achieved, however, on the mechanism of the optical transition in pyrite, i. e. whether it is a direct or an indirect transition [10]. The usual plotting procedures of (absorptivity $\times \hbar\omega$)ⁿ versus energy, $\hbar\omega$, with $n = 2$ and $1/2$ seem not to be adequate for deciding this question [11], because these procedures were developed for parabolic bands [1], whereas the valence and conduction band in pyrite were found by band structure calculations to be rather flat than parabolic [12-14].

2. THE ENHANCEMENT-FACTOR

According to experimental [1,15,16] and theoretical [12-14] investigations the fundamental optical absorption in pyrite is due to transitions from Fe3d-levels (t_{2g}) to mixed Fe- and S-states (Fe3d e_g and S3sp³). The composition of the valence and the conduction band from atomic orbitals is visualized in Fig. 2. Atomic orbitals are indexed by their corresponding quantum numbers in the usual $n\ell m$ -notation. For electronic transitions in atoms and ions the selection rules $\Delta\ell = \pm 1$ and $\Delta m = 0$ have to be fulfilled for the quantum number of angular momentum ℓ and the magnetic quantum number m , respectively. Although for solids these rules are not of such a general validity as for atoms we will take them as a starting point for this investigation - to start with something at all. The transitions allowed by these rules have been marked by arrows in fig. 2. According to it, the charge transfer transition from $|Fe321\rangle$ - to $|S311\rangle$ -levels would account for the optical absorption. Usually, the optical absorption of pyrite is assumed to be due to electronic excitations from Fe- t_{2g} - to e_g -levels. However, it is the matrix element $T = \langle Fe321 | z | S311 \rangle$ that will be investigated here.

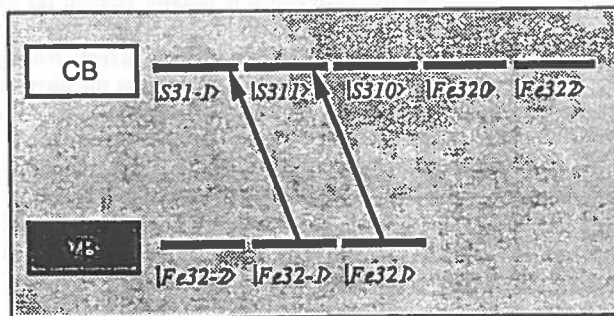


Figure 2: Scheme of the composition of bands in pyrite. The valence band (VB) is a linear combination of filled Fe- t_{2g} -states while the conduction band (CB) consists of empty Fe- e_g - and antibonding S-3p-levels. Arrows should indicate electronic interband transitions following the usual atomic selection rules for the azimuthal and magnetic quantum number $\Delta\ell = \pm 1$ and $\Delta m = 0$.

The following calculations will proceed in two steps. First, the wave functions of Fe²⁺ and S⁻ will be presented. Those of sulfur will also be given under the influence of an external electric field. Second, the enhancement factor ν is calculated, which is the ratio of the transition matrix element with and without the field, $\nu = T(E(u)) / T(0)$. It describes how the absorption between iron- and sulfur-states is enhanced by turning on the crystal electric field that acts at the S-site. The first step is formulated in separate coordinates for each ion and a necessary transformation of the sulfur's wave function to parabolic coordinates is done. The second step evaluates a two-center integral and is formulated for both ions in a common system of spheroidal coordinates. To avoid confusion, the reader is pleased, to follow the choice of coordinates carefully.

The wave functions of iron and sulfur are assumed to be hydrogen-like. This is done, because (i) it was not possible to find second-order Stark-effect wave functions for the S-ion and (ii) this study should only motivate the enhancement of the transition by the electric field instead of giving an analytic expression of the absorption coefficient. In the usual spherical coordinate system of each atom (r_F, θ_F, φ_F) and (r_S, θ_S, φ_S) the hydronic wave functions are written as

$$|Fe321\rangle = \left[\frac{1}{3a_F^3\pi} \right]^{1/2} \left[\frac{r_F}{a_F} \right]^2 \exp\left[-\frac{r_F}{a_F} + i\varphi_F\right] \cos\theta_F \sin\theta_F \quad (4a)$$

$$|S311\rangle = \left[\frac{1}{3a_S^3\pi} \right]^{1/2} \left[2 - \frac{r_S}{a_S} \right] \frac{r_S}{a_S} \exp\left[-\frac{r_S}{a_S} + i\varphi_S\right] \sin\theta_S \quad (4b)$$

which differ from the normal hydronic one only by the occurrence of the unit lengths a_F and a_S instead of Bohr's radius a_0 . For them it holds

$$a_F = \frac{3a_0}{Z'_{Fe}} \quad a_S = \frac{3a_0}{Z'_S} \quad (5a,b)$$

with Z' being the effective nuclear charge acting at the valence electrons of each atom.

To find the wave functions of sulfur-atoms in an electrical field, it will be assumed that the crystal electric field acting on the charge distribution of the sulfur-ion can be replaced by an homogenous field with a strength as at its center, $E(u) = 2.2 \times 10^{10}$ Vm⁻¹. With this assumption the tools developed for the calculation of the Stark effect can be applied to the problem (see most textbooks on quantum mechanics about the general solution of Schrödinger's equation with an extra electric field as perturbation). In an homogenous electrical field the operator of angular momentum ℓ^2 does not commute with the Hamiltonian of the system because space is no longer isotropic, only the magnetic quantum number m remains a constant of motion. Instead of n , ℓ and m the new quantum numbers are n_1 , n_2 and m , with $n = n_1 + n_2 + m + \ell$, and wave functions are now written as $|n_1 n_2 m\rangle$ -symbols. Putting the direction of the electric field along the z-axis, atomic or ionic wave functions are most adequately written in parabolic coordinates

$$\xi = r_S + r_S \cos\theta_S, \quad \eta = r_S - r_S \cos\theta_S, \quad \varphi = \varphi_S \quad (6)$$

(the index S has now been omitted for parabolic coordinates, because they are reserved for the sulfurs' wave function exclusively). The parabolic wave functions can be shown to develop from spherical ones. For the relevant case $n = 3$ the $|S311\rangle$ -state ($n\ell m$ -notation) splits into the new $|S101\rangle$ - and $|S011\rangle$ -wave functions ($n_1 n_2 m$ -notation), being of the form

$$|S101\rangle = \left[\frac{\xi\eta}{a_-^3\pi} \right]^{1/2} \left(2 - \frac{\xi}{a_-} \right) \exp\left[-\frac{\xi + \eta}{2a_-} + i\varphi\right] \quad (7a)$$

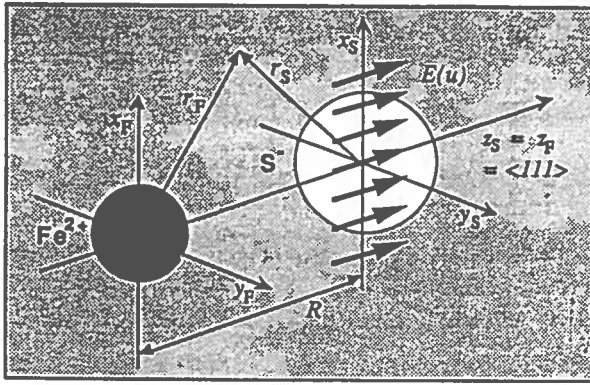


Figure 3: Common iron- and sulfur-coordinate systems for the evaluation of the two-center integrals in eq. (16) and (21). Black and white spheres should represent Fe^{2+} - and S^- -ions.

$$|S011\rangle = \left[\frac{\xi\eta}{a_+^3\pi} \right]^{1/2} \left(2 - \frac{\eta}{a_+} \right) \exp\left[-\frac{\xi + \eta}{2a_+} + i\varphi \right] \quad (7b)$$

for which the meaning of a and a_+ is to explain now.

The perturbation theory of the Stark-effect is different from the usual one. Instead of writing the wave function of the perturbed problem as a linear combination of unperturbed states, the radial coordinate is upset by a factor including the perturbation, i. e. the electric field $E(u)$. It is shown in Ref. [17] that the perturbed wave function in second order theory has the parabolic form as above with the unit length of the atom (a_S in the case considered here) multiplied by a factor $1/k$ being dependent on n_1, n_2 and m as

$$k = \left[1 - 3En^3(n_1 - n_2) + \frac{E^3}{8}n^6(17n^2 - 3(n_1 - n_2)^2 - 9m^2 + 19) \right]^{1/2} \quad (8)$$

and the electric field strength E must be specified in units of $e/(4\pi\epsilon_0 a_S^2)$. This leads for the case of quantum numbers $n=3$, $(n_1 n_2 m) = (101)$ and $(n_1 n_2 m) = (011)$ to

$$k_{\pm} = \sqrt{1 \pm 81E + 14580E^2} \quad (9)$$

$|S101\rangle$ and $|S011\rangle$ may be rewritten in spherical coordinates by doing the inverse transformation of (6) and one obtains:

$$|S101\rangle = \left[\frac{1}{a_+^3\pi} \right]^{1/2} \left(2 - \frac{r_S}{a_+} (1 + \cos\theta_S) \right) \frac{r_S}{a_+} \exp\left[-\frac{r_S}{a_+} + i\varphi_S \right] \sin\theta_S$$

$$|S011\rangle = \left[\frac{1}{a_+^3\pi} \right]^{1/2} \left(2 - \frac{r_S}{a_+} (1 - \cos\theta_S) \right) \frac{r_S}{a_+} \exp\left[-\frac{r_S}{a_+} + i\varphi_S \right] \sin\theta_S \quad (10a,b)$$

These are the new wave functions of the $|S311\rangle$ -state in an electric field $E(u)$. The field dependence is hidden within the unit lengths $a_+ = a_S/k_+$ and $a_- = a_S/k_-$. Qualitatively, the Stark-effect may be understood as causing the atom to swell in the electric field. The normalisation factor of the wave functions in (10) is upset by the swelling factor k_{\pm} as contained in a_{\pm} . It has been mentioned above that the electric field causes the $|S311\rangle$ -state to split into two new terms, which can now be seen easily. For the case of $E(u) = 0$ we have $a_+ = a_- = a_S$ and the enhancement factor is defined as

$$v = \frac{\langle Fe321|z|S101\rangle + \langle Fe321|z|S011\rangle}{2\langle Fe321|z|S311\rangle} \quad (11)$$

The first and second order terms of perturbation theory can be clearly recognized to occur as powers of the field strength

in eq. (8) defining k_{\pm} . Furthermore, one may learn from eq. (8) for what strengthes of the electrical field second order perturbation theory may give reliable results: this is the case, if k does not deviate too strong from unity. For instance, if the electrical field strenght $E(u)$ in units of $4\pi\epsilon_0 e/a_S^2$ equals 0.008, k_{\pm} deviate already by 0.61 und 0.13 from 1 and the formulae (10) is probably beyond the range of validity for the approach of a small perturbation of the system. The formula might be better substituted by higher order perturbation theory or even a solution of the wave equation that holds for the full Hamiltonian.

Now, the wave function for the Fe- and for the perturbed S-ion have been given in separate coordinate systems. We come to the second part, i. e. the evaluation of the transition matrix element between $|Fe321\rangle$ - and $|S311\rangle$ -states, which will be done in a common coordinate system, see figure 3. There are three special directions: (i) the iron-sulfur distance R , (ii) the direction of the crystal electric field $E(u)$ and (iii) the plane of oscillation of the electromagnetic wave amplitude E_0 . First, the transition propability $T(0)$ without a crystal electric field will be evaluated. The wave functions of both atoms in a common system are expressed in spheroidal coordinates λ, μ and φ , for an introduction see for instance Ref. [18]. If the z-axes of both atomic systems are oriented along R , see figure 3, they depend on the spherical coordinates of the atoms as

$$\lambda = \frac{r_S + r_F}{R} \quad \mu = \frac{r_S - r_F}{R} \quad \varphi = \varphi_S = \varphi_F \quad (12)$$

With this choice of a common z-axis the coordinate frames of Fe- and S-atoms are aligned into the same direction, which may be recognized for instance to be the case for the iron at (000) and the sulfur-ion at (uuu) . This causes also $E(u)$ to be oriented along the z-axis and R to become equal $\sqrt{3}au = 3.613$ Å. The selection of this special Fe-S-pair is not assumed to have much influence on the enhancement factor v , but it leads to a significant simplification for the geometry of the problem. The cartesian coordinates of the separate atoms are then related to the common system as $x_S = x_F = x$, $y_S = y_F = y$, $z_S = z + R/2$ and $z_F = z - R/2$. To transform the wave functions as given in (4a) and (10) into the common system of coordinates, the formulas

$$x = \frac{R \cos\varphi}{2} \sqrt{(\lambda^2 - 1)(1 - \mu^2)} \quad y = \frac{R \sin\varphi}{2} \sqrt{(\lambda^2 - 1)(1 - \mu^2)}$$

$$z = \frac{R \lambda \mu}{2} \quad (13a-c)$$

have to be used. To write down the transition matrix element $T(0)$ only the amplitude E_0 of the electromagnetic wave has to be given. For full generality we will assume it to be arbitrarily oriented in space and its potential Φ ($E_0 = -\text{grad}\Phi$) is expressed as

$$\Phi = -E_{01}x - E_{02}y - E_{03}z \quad ; \quad E_0 = \sqrt{E_{01}^2 + E_{02}^2 + E_{03}^2} \quad (14)$$

which may also be given in spheroidal coordinates by applying eqs. (13a-c). With the volume element

$$dV = \frac{R^3}{8} (\lambda^2 - \mu^2) d\lambda d\mu d\varphi \quad (15)$$

the transition matrix element finally becomes

$$T(0) = \frac{R^7}{96 a_F^{7/2} a_S^{7/2} \pi} \int_1^{\infty} d\lambda \int_{-1}^1 d\mu \int_0^{2\pi} d\varphi \left[\frac{\Phi}{E_0} C(p) e^{-\alpha\lambda} e^{-\beta\mu} \right] \quad (16)$$

where the abbreviations

$$\alpha = \frac{R a_F + a_S}{2 a_F a_S} \quad \beta = \frac{R a_F - a_S}{2 a_F a_S} \quad (17)$$

$$C(p) = (\lambda^2 - 1)(1 - \mu^2)(\lambda\mu - 1)(1 - p(\lambda + \mu))(\lambda^2 - \mu^2) \quad (18)$$

and $p = R/4a_S$ have been introduced. The φ -integration causes the E_{01x} - and E_{02y} -terms to cancel, so only $2\pi E_{03z}/E_0 = \pi E_{03}R\lambda\mu/E_0$ survives. We conclude, only electrical field components along the direction of R will lead to electronic transitions from the iron- to sulfur-states. We now face the problem of integrating the integral kernel over λ and μ , which can be best achieved by developing the mixed product into sums of powers of λ and μ . It yields:

$$\begin{aligned} C(p)\lambda\mu &= f_1(\mu)(p\lambda^6 - \lambda^5 - p\lambda^4 + \lambda^3) \\ &+ f_2(\mu)(\lambda^6 - p\lambda^7 + 2p\lambda^5 - \lambda^4 - p\lambda^3) \\ &+ f_3(\mu)(\lambda^3 - p\lambda^6 + p\lambda^2 - \lambda) \\ &+ f_4(\mu)(p\lambda^5 - \lambda^4 - 2p\lambda^3 + \lambda^2 + p\lambda) \\ &+ f_5(\mu)(p\lambda^4 - p\lambda^2) \end{aligned} \quad (19)$$

where the abbreviation $f_m(\mu) = (1-\mu^2)\mu^m$ was used. One obtains five products of two integrals, each of them to be done over λ or μ . This can be evaluated with the usual method developed elsewhere (see for instance Ref. [19]). With

$$\int_{-1}^1 (1-\mu^2)\mu^m e^{-\beta\mu} d\mu = \frac{2(2+m)!}{\beta^{2+m}} \left(\frac{\sinh \beta}{\beta} \cdot \cosh \beta \right) \quad (20)$$

the μ -integration may be done analytically. In principle, this would also be possible for the λ -integration, but because this would lead to a sum of 40 terms the problem was solved with the use of numerical methods, i. e. λ -integrations were done with the help of a computer-procedure.

With the notation developed before and equation (11) the enhancement factor now becomes the ratio of the integrals

$$v = \frac{\int d\lambda \int d\mu [k_+^{1/2} \lambda \mu C(p_+) e^{-\alpha_+ \lambda} e^{-\beta_+ \mu} + k_-^{1/2} \lambda \mu C(p_-) e^{-\alpha_- \lambda} e^{-\beta_- \mu}]}{2 \int d\lambda \int d\mu [\lambda \mu C(p) e^{-\alpha \lambda} e^{-\beta \mu}]} \quad (21)$$

where indices + or - mean, that a_+ and a_- have to be inserted instead of a_S in the defining formulas (17) and (18). As the absorption coefficient itself, v can be seen to be not dependent upon the amplitude of the light wave, E_0 , but it depends upon the strength of the crystal electric field $E(u)$.

3. RESULTS AND DISCUSSION

In figure 4 the function $v(E)$ according to eq. (21) is shown for some reliable choices of a_S and a_F . The functions can all be seen to increase strongly on the scale of field strengths $E(u)$ investigated here. It was argued, that the crystal electric field actually existent at the sulfur-lattice site is larger than the range of validity of second-order perturbation theory. Therefore, it can only be used to predict trends and $v(E)$ is only given for a limited range of $E(u)$ -values. This was necessary, because the analytical form of eq. (21) gave meaningless results beyond this region. It can be seen for all values of parameters a_S and a_F that the crystal electric field enhances the electronic transition from Fe- to S-levels by orders of magnitudes. It was the aim of this work to show this tendency.

Because of group-theoretical reasons crystal electric fields will not occur on sites with T_d -symmetry, as in crystalline silicon, III-V- or II-VI-compounds with zinkblende-structure. They may appear, however, on other sites than the S-position in the pyrite lattice, for instance at the chalcogen-position in chalcopyrites as CuInSe_2 , CuInS_2 etc. of point group symmetry C_2 . Also in a-Si:H electrical fields of varying strength will probably occur. So one may recognize, that crystallographic lattice sites of non-inversional symmetry cause generally enhanced electronic transitions. This hypothesis, however, needs more intense studies to be confirmed.

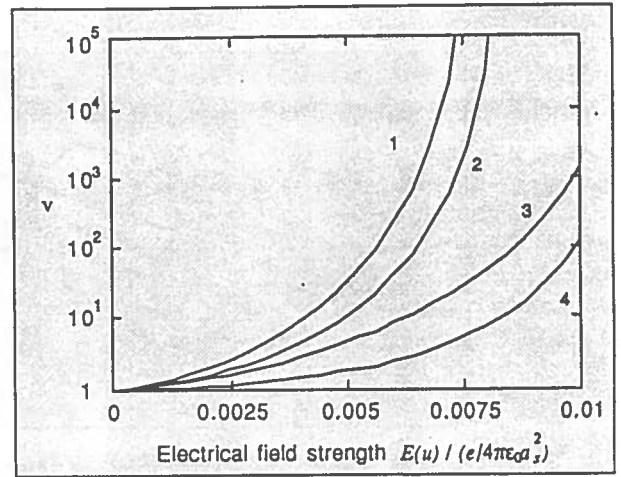


Figure 4: Enhancement factor v for some reliable choices of a_F and a_S (1) 0.5, 0.8 (2) 0.3, 0.5 (3) 0.4, 0.8 (4) 0.2, 0.4 (in Å). The transition from Fe3d to S3p-levels can be seen to increase with the strength of the crystal electric field. The actual field $E(u)$ is even stronger than 0.01 and second order perturbation theory can only be used to predict trends.

In conclusion, the enhancement of electronic transitions by $E(u)$ has been justified in a simplified model by second-order Stark-effect perturbation theory. A two-center integral showed the charge transfer from Fe3d- to S3p-levels to increase with increasing field strength. Crystal electric fields at certain lattice sites may be a common feature of materials with high absorption coefficients. If this can be generally corroborated in subsequent work, it would allow for searching other well-suited materials for solar cell applications by regarding structural properties.

4. REFERENCES

- [1] A. L. Fahrenbruch and R. H. Bube, *Fundamentals of Solar Cells* (Academic Press, New York, 1983), p. 269, 48-53.
- [2] K. Sato, *J. Phys. Soc. Jap.* **53**, 1617 (1984).
- [3] A. Ennaoui, S. Fiechter, H. Goslowsky and H. Tributsch, *J. Electrochem. Soc.* **132**, 1579 (1985).
- [4] S. Bausch, *et al.*, *Appl. Phys. Lett.* **57**, 25 (1990).
- [5] M. Birkholz, *J. Phys.: Condens. Matter* **4**, 6227 (1992).
- [6] J. Stark and H. Kirschbaum, *Ann. Phys.* **43**, 991 (1914).
- [7] J. Stark, *Ann. Phys.* **48**, 210 (1915).
- [8] H. Ibach and H. Lüth, *Festkörperphysik* (Springer, Berlin, 1990), p. 269.
- [9] M. Birkholz, S. Fiechter, A. Hartmann and H. Tributsch, *Phys. Rev. B* **43**, 11926 (1991).
- [10] I. J. Ferrer, D. M. Nevskaja, C. d. l. Haeras and C. Sanchez, *Solid State Comm.* **74**, 913 (1990).
- [11] M. Birkholz, D. Lichtenberger, C. Höpfner and S. Fiechter, *Sol. Energy Mat. and Sol. Cells* **27**, 243 (1992).
- [12] M. A. Khan, *J. Phys. C* **9**, 81 (1976).
- [13] S. Lauer, A. X. Trautwein and F. E. Harris, *Phys. Rev. B* **29**, 6774 (1984).
- [14] W. Folkerts, G. A. Sawatzky, C. Haas, R. A. d. Groot and F. U. Hillebrecht, *J. Phys. C* **20**, 4135 (1987).
- [15] T. A. Bither, R. J. Bouchard, W. H. Cloud, P. C. Donohue and W. J. Siemons, *Inorg. Chem.* **7**, 2208 (1968).
- [16] A. Ennaoui, S. Fiechter, W. Jaegermann and H. Tributsch, *J. Electrochem. Soc.* **133**, 97 (1986).
- [17] L. D. Landau and E. M. Lifschitz, *Quantenmechanik* (Akademie-Verlag, Berlin, 1971), §§ 76-77.
- [18] J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill, New York, 1963), Sect. 1.1 & App. 1.
- [19] H. Bruss, *Integraltafeln zur Quantenchemie* (Springer-Verlag, Berlin, 1956), Sect. 1.4.