Large Local-Field Corrections in Optical Rotatory Power of Quartz and Selenium

Lars Jönsson,[1] Zachary H. Levine,[1,2] and John W. Wilkins[1]

[1]*Department of Physics, Ohio State University, 174 West 18th Avenue, Columbus, Ohio 43210-1106*
[2]*Building 221/A253, National Institute of Standards and Technology, Gaithersburg, Maryland 20899*
(Received 22 March 1995)

We show that local fields can increase the rotatory power ρ of nonconductors by a factor of 10—in contrast to the typical 10% effect in other properties. We present calculations for quartz and Se, and a general method to estimate the size of local-field corrections. Notably, only scalar local fields are needed despite the vector character of light. A self-energy-corrected local-density band structure yields corrections to ρ of a *factor* of $+7$ in quartz and -4 in Se. These values are 30% above experiment for quartz, and, for one sign choice, within the 50% error bars for Se.

PACS numbers: 78.20.Ek, 78.20.Bh

As linearly polarized light travels along the optic axis in a quartz crystal, the plane of polarization rotates by an angle proportional to the propagated distance. This optical rotation is due to a crystal structure in which the SiO_2 units are arranged in helices along the c axis (optic axis) of a hexagonal lattice [1]. Because of the helical structure, left and right circularly polarized light have different refractive indices (n_L, n_R), which results in a rotation of polarization for linearly polarized light. This phenomenon is described by the optical rotatory power $\rho = \omega(n_L - n_R)/2c$, where ω is the light angular frequency and c is the speed of light in vacuum. Many different materials exhibit optical rotation, but among crystalline materials α-quartz in the most carefully studied. For a recent discussion of stress-induced optical rotation in semiconductors see Ref. [2].

Recently, Zhong *et al.* [3] calculated the optical rotatory power for α-quartz and selenium. Their results are too small compared to experiment by a factor of 5 in α-quartz [4] and two (in absolute value) in Se [5–7]. In this Letter we show that these differences are due to very large local-field corrections (caused by the microscopic variation of the electric field), and we predict a change of sign in Se (see Table I). The local-field correction is a factor of $+7$ in α-quartz and -4 in Se, which is a factor of 10–100 larger than typical local-field effects in other properties, e.g., dielectric constant ε and second-order susceptibility $\chi^{(2)}$.

Following Zhong *et al.,* we use a self-energy-corrected, time-dependent local-density approximation (TDLDA) [3], but extended to include local-field corrections. A crucial observation is that one can use a combined vector-scalar theory in which the macroscopic field is given by a vector potential and the local fields by a scalar potential [8]. This approximation is of second order in the ratio of the lattice parameter and the wavelength. This key simplification avoids the use of a vector based density-functional theory, which would require a *vector* exchange-correction potential [9] rather than the familiar, and known, scalar potential. Our results for the rotatory

power are the first for which local-field corrections have been calculated for a vector property of light. Further, the use of scalar local fields permits simple general estimates of the size of local-field corrections.

The *ab initio* method of using local-density approximation (LDA) excited states in a linear-response theory [10] of optical properties for semiconductors, implemented using pseudopotentials and plane waves, typically gives (5–20)% agreement with experiment (in the long-wavelength limit; excluding excitonic effects). However, this accuracy requires an explicit correction of the band gap [11], since the gap is usually 1–2 eV too small in LDA [12]. The correction we use is a rigid shift Δ of all the conduction band energies relative to the valence band energies [13]. Zhong *et al.* [3] calculated ε and $\chi^{(2)}$ for α-quartz and Se with $\Delta = 1.8$ eV for quartz and $\Delta = 1.1$ eV for Se, obtained by fitting to the optical absorption edge in Se and to ε in α-quartz, where the edge is ill-defined. All their results were in good agreement with experiment, and the local-field corrections were of order 10%. TDLDA seems to work well for both materials.

The optical rotatory power is related to the optical activity tensor η, defined by

$$4\pi \delta J_i = (\omega^2/c)[(\varepsilon_{ij} - \delta_{ij})A_j + i\eta_{ilj}q_l A_j], \quad (1)$$

where we describe the polarization in terms of the induced current $\delta\mathbf{J}$ and the total, macroscopic electric field by the vector potential $\mathbf{A}$; ε is the dielectric matrix and $\mathbf{q}$ is the wave vector. In the uniaxial crystals α-quartz and trigonal selenium (point group 32), the rotatory power is given by the tensor component η_{231} (3 = optical axis): $\rho = \omega^2 \eta_{231}/2c^2$.

TABLE I. Optical rotatory power $\rho/(\hbar\omega)^2$ in deg/[mm (eV)^2] of α-quartz and selenium in the zero-frequency limit.

	α-quartz	Selenium
No local fields	0.7	21
With local fields	5.6	-55
Experiment	4.6 ± 0.1	$\pm 56 \pm 30$

0031-9007/96/76(8)/1372(4)$06.00

To obtain η, we need the induced current to first order both in $\mathbf{A}$ and $\mathbf{q}$. For independent electrons, linear-response theory (TDLDA) yields

$$\delta \mathbf{J} = \sum_{v,c,\mathbf{k},\pm} \frac{\langle v, \mathbf{k} + \mathbf{q} | \mathbf{A} \cdot \mathbf{J}_\mathbf{k}/c - e\phi(\mathbf{r})|c,\mathbf{k}\rangle \langle c, \mathbf{k}|\mathbf{J}_\mathbf{k}|v, \mathbf{k} + \mathbf{q}\rangle}{\epsilon_{v,\mathbf{k}+\mathbf{q}} - \epsilon_{c,\mathbf{k}} \pm \omega}, \tag{2}$$

where $\mathbf{J}_\mathbf{k}$ is the current operator, and $|v, \mathbf{k}\rangle$ and $|c, \mathbf{k}\rangle$ are the periodic part of the valence- and conduction-band wave functions, with energies $\epsilon_{v,\mathbf{k}} = \epsilon_{v,\mathbf{k}}^{\mathrm{LDA}}$ and $\epsilon_{c,\mathbf{k}} = \epsilon_{c,\mathbf{k}}^{\mathrm{LDA}} + \Delta$, respectively. The microscopic scalar potential ϕ is a sum of the Coulomb interaction and the LDA exchange-correlation potential ($\mathbf{G}$ is a reciprocal lattice vector):

$$\phi_\mathbf{G} = \frac{4\pi \delta n_\mathbf{G}}{|\mathbf{q} + \mathbf{G}|^2} + \sum_{\mathbf{G}'} \left. \frac{\delta v_{\mathrm{xc}}}{\delta n}\right|_{\mathbf{G}'} \delta n_{\mathbf{G}-\mathbf{G}'}. \tag{3}$$

Here $\mathbf{G} \neq 0$ since ϕ represents only local fields [14]. The induced charge density δn is again given by linear-response theory. All fields and densities are assumed to vary as $\exp(\mathbf{q} \cdot \mathbf{r} - i\omega t)$ times a function with the periodicity of the lattice. Note that, with our choice of gauge, $\mathbf{A}$ and $\delta \mathbf{J}$ are macroscopic ($\mathbf{G} = 0$), while ϕ and δn are microscopic ($\mathbf{G} \neq 0$). In our calculations we expand to first order in q and take the zero-frequency limit.

Figure 1 shows the calculated and experimental results [4] for the rotatory power of α-quartz. The data are plotted as $\rho/(\hbar\omega)^2$ as a function of $(\hbar\omega)^2$, which in accordance with the coupled-oscillator model [15] gives a slow variation with ω. The dip at the lowest experimental frequency is probably due to an additional screening by phonons [16], which we do not include. The theoretical curve with no local-field corrections is due to Zhong *et al.*, while the arrow marks our zero-frequency value 5.6 deg/[mm (eV)^2] (with $\Delta = 1.8$ eV). With $\Delta = 0$ (LDA), we obtain $\rho/(\hbar\omega)^2 = 6.8$ deg/[mm (eV)^2]. In light of the usually moderate local-field corrections in other optical properties the effect here is remarkable. The

correction is about a factor of 7. The remaining difference between theory and experiment can be attributed to the inaccuracy of TDLDA. The local fields make up the physics missing in the results of Zhong *et al.* This conclusion should hold at finite frequencies too, since local-field corrections generally show weak frequency dispersion [11,17].

The other independent component η_{321} of α-quartz has also been measured [18,19]. The situation is similar to that for the rotatory power; the local-field correction is 10 times the value given by Zhong *et al.* At $\omega = 0$, we obtain $\eta_{321} = 4.8$ pm, while Zhong *et al.* obtained $\eta_{321} = 0.46$ pm. The experimental values fall in the range 3–4 pm at zero frequency.

For selenium, the theoretical and experimental values [5–7] for the rotatory power are shown in Fig. 2. Here the local-field correction is negative and larger than the uncorrected response, so we predict a change of sign. The experiments do not give the sign for Se, but if we use the negative sign for the experiments our value at $\omega = 0$ falls within the error bars of a zero-frequency extrapolation of the data of Adams and Haas [5] and Henrion and Eckart [7]. (The cause for the strong low-frequency dispersion in the data of Day [6] and the kink in the data by Adams and Haas are unknown [3].) In the LDA ($\Delta = 0$), we obtain $\rho/(\hbar\omega)^2 = -131$ deg/[mm (eV)^2], compared to -55 deg/[mm (eV)^2] with $\Delta = 1.1$ eV. Therefore, due to the sensitivity to Δ, the close agreement with experiment

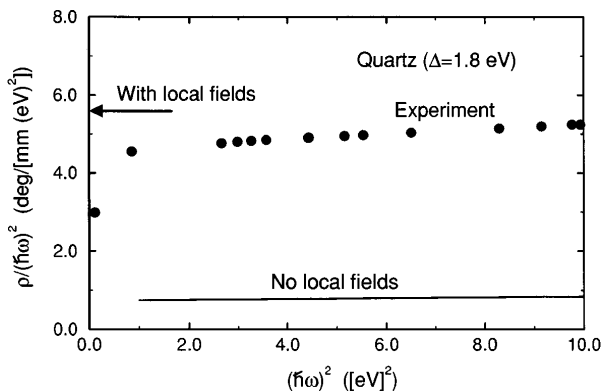FIG. 1. Optical rotatory power $[\rho/(\hbar\omega)^2]$ for α-quartz. The arrow indicates the zero-frequency value of the present work. The curve without local-field corrections is from Zhong *et al.* (Ref. [3]). The experimental points (dots) are from Ref. [4].

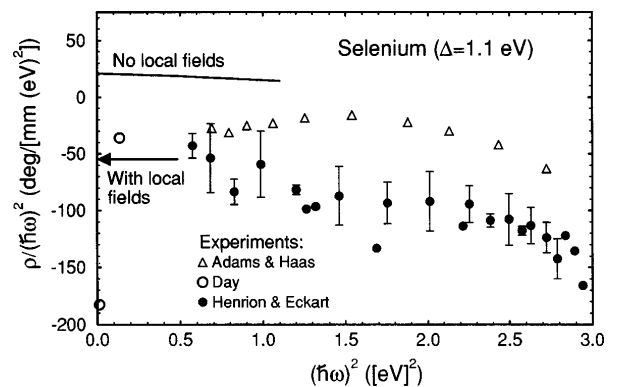

FIG. 2. Optical rotatory power $[\rho/(\hbar\omega)^2]$ for trigonal Se, with notation as in Fig. 1. The experiments do not give the sign of ρ, but we use negative values for comparison with our calculation. The error bars for Henrion and Eckart [7] show the total variation due to sample thickness in both positive and negative crystals. Day [6] estimates an error of ± 5 deg/mm, while Adams and Haas [5] mentions a variation of $\pm 30\%$ at $\hbar\omega = 1.09$ eV.

is probably accidental. However, the calculation is good enough to determine the sign and the order of magnitude. An experimental verification of the sign would prove the importance of the local fields in Se.

The large local-field corrections can be understood by considering the order of magnitude of the relevant response functions. Generally, we can define linear response functions that connect the charge and current densities with the scalar and vector potentials:

$$\delta n = \chi^{nj} \cdot \mathbf{A} + \chi^{nn}\phi, \quad \delta \mathbf{J} = \chi^{jj} \cdot \mathbf{A} + \chi^{jn}\phi. \tag{4}$$

As in Eqs. (2) and (3), $\mathbf{A}$ and $\delta \mathbf{J}$ are macroscopic ($\mathbf{G} = 0$), while ϕ and δn are microscopic ($G \neq 0$). Therefore, a j superscript also indicates that $\mathbf{G} = 0$, while an n superscript indicates that $\mathbf{G} \neq 0$. The potential ϕ is given by Eq. (3), which we write as $\phi = V\delta n$. Eliminating ϕ, the effective current-current response is

$$\delta \mathbf{J} = \chi^{jj} \cdot \mathbf{A} + \chi^{jn}(1 - V\chi^{nn})^{-1}V\chi^{nj} \cdot \mathbf{A}. \tag{5}$$

The relative local-field correction is then the ratio of the second and first term.

To estimate the size of the local-field correction, we shall use only the Coulomb part $V_{\mathbf{G}} = 4\pi/|\mathbf{q} + \mathbf{G}|^2$ of the electron-electron interaction. The potential ϕ is then equal to the electrical potential, and we can relate all the response functions to the susceptibility χ, defined by $\mathbf{P}_{\mathbf{G}} = \sum_{\mathbf{G}'} \chi_{\mathbf{G}\mathbf{G}'} \cdot \mathbf{E}_{\mathbf{G}'}$, where $\mathbf{P}$ is the polarization density and $\mathbf{E}$ is the electric field. The definitions ($\mathbf{G} \neq 0$) $\delta \mathbf{J}_0 = \partial \mathbf{P}_0/\partial t$, $\delta n_{\mathbf{G}} = -\nabla \cdot \mathbf{P}_{\mathbf{G}}$, $\mathbf{E}_0 = -\partial \mathbf{A}_0/c\partial t$, and $\mathbf{E}_{\mathbf{G}} = -\nabla\phi_{\mathbf{G}}$, with $\nabla \rightarrow i(\mathbf{q} + \mathbf{G})$, yield the relations [20]

$$\chi^{jj}_{00} = (1/c)\omega^2\chi_{00}, \quad \chi^{nn}_{\mathbf{G}\mathbf{G}'} = -(\mathbf{q} + \mathbf{G}) \cdot \chi_{\mathbf{G}\mathbf{G}'} \cdot (\mathbf{q} + \mathbf{G}'), \tag{6}$$

$$\chi^{nj}_{\mathbf{G}0} = (1/c)\omega(\mathbf{q} + \mathbf{G}) \cdot \chi_{\mathbf{G}0}, \quad \chi^{jn}_{0\mathbf{G}'} = -\omega\chi_{0\mathbf{G}'} \cdot (\mathbf{q} + \mathbf{G}').$$

There is one-to-one correspondence between a j superscript and a ω factor and between an n superscript and a $\mathbf{q} + \mathbf{G}$ multiplication. Below we abandon the explicit vector notation (i.e., $\chi_{\mathbf{G}\mathbf{G}'} \rightarrow \chi$), disregard angular factors, and focus on orders of magnitude.

A comparison with Eq. (1) shows that if we take $q = 0$ in Eq. (5) we obtain the local-field correction to the susceptibility $\varepsilon - 1$. With $q = 0$ in Eq. (6) we obtain the ratio between the local-field correction to the macroscopic response

$$\frac{\chi^{jn}V\chi^{nj}}{\chi^{jj}(1 - V\chi^{nn})} \simeq -\frac{4\pi\chi}{1 + 4\pi\chi} \equiv -\frac{\varepsilon - 1}{\varepsilon}, \tag{7}$$

which indicates that the local-field correction is negative and smaller than the macroscopic response. This conclusion is in reasonable agreement with the typical -10% correction for the dielectric constant. A similar result can be obtained for the second-harmonic coefficient.

For the rotatory power, we need the first-order terms in the q expansion of Eq. (5):

$$\delta \mathbf{J}^{[1]} = \chi^{jj[1]} \cdot \mathbf{A} + \chi^{jn[1]}[1 - (V\chi^{nn})^{[0]}]^{-1}(V\chi^{nj})^{[0]} \cdot \mathbf{A}$$

$$+ \chi^{jn[0]}[1 - (V\chi^{nn})^{[0]}]^{-1}(V\chi^{nj})^{[1]} \cdot \mathbf{A}$$

$$+ \chi^{jn[0]}(V\chi^{nn})^{[1]}[1 - (V\chi^{nn})^{[0]}]^{-2}(V\chi^{nj})^{[0]} \cdot \mathbf{A}, \tag{8}$$

where the extra superscript represents the order in q. The corresponding equation to zeroth order is given by the earlier Eq. (5) with superscript [0] on all response functions.

The relative size of the local-field correction is the ratio of the three last terms and the first term in Eq. (8). If we now form the ratio R of the *relative* local-field corrections to the first- and zeroth-order response, most of the factors with superscript [0] cancel:

$$R = \frac{\chi^{jj[0]}}{\chi^{jj[1]}}\left[\frac{\chi^{jn[1]}}{\chi^{jn[0]}} + \frac{(V\chi^{nj})^{[1]}}{(V\chi^{nj})^{[10]}} + \frac{(V\chi^{nn})^{[1]}}{1 - (V\chi^{nn})^{[0]}}\right]. \tag{9}$$

With the definitions $\varepsilon \equiv 1 + 4\pi\chi^{[0]}$ and $q\eta \equiv 4\pi\chi^{[1]}$ [Eq. (1)], the first factor in Eq. (9) is

$$\chi^{jj[0]}/\chi^{jj[1]} = \chi^{[0]}/\chi^{[1]} = (\varepsilon - 1)/q\eta. \tag{10}$$

Note that the values *without local-field corrections* should be used for ε and η.

A first-order expansion in q of χ^{jn} in Eq. (6), gives the first term in brackets in Eq. (9):

$$\chi^{jn[1]}/\chi^{jn[0]} = (\chi^{[1]}\overline{G} + \chi^{[0]}q)/\chi^{[0]}\overline{G}$$

$$= (\chi^{[1]}/\chi^{[0]} + q/\overline{G}), \tag{11}$$

where the average $\overline{G}$ is a typical reciprocal lattice vector in the Fourier expansion of the charge density. The length scale associated with the local fields is the size of the bonds in the material, so we can also write $\overline{G} = 2\pi/b$, where b is a typical bond length.

The product of Eqs. (10) and (11) yields a contribution to R of $1 + (\varepsilon - 1)/\overline{G}\eta$. The two other terms in Eq. (9) are more complex due to the potential V, and we skip the details. All terms are either of order 1 or $(\varepsilon - 1)/\overline{G}\eta$. In total, we obtain

$$R \simeq 3 + 8(\varepsilon - 1)/\overline{G}\eta \simeq 3 + b(\varepsilon - 1)/\eta. \tag{12}$$

The values for η_{231} and ε (ordinary) without local-field corrections are for α-quartz $\eta_{231} = 0.94$ pm $= 0.018$ a.u. and $\varepsilon = 2.4$, and for Se $\eta_{231} = 28$ pm $= 0.53$ a.u. and $\varepsilon = 9.0$ [3]. A bond length of one atomic unit yields $b(\varepsilon - 1)/\eta = 78$ for α-quartz and $b(\varepsilon - 1)/\eta = 15$ for Se. We infer from these values that R is of order 10–100. A local-field correction of 10% for ε then yields a correction to the rotatory power of a factor of 1–10 [21].

This estimate agrees very well with the corrections of a factor of 7 and 4 for α-quartz and Se (Table I).

In conclusion, we have shown both by calculations for α-quartz and selenium and by general estimates that the local-field correction to the optical rotatory power is very large compared to the typical correction in other optical properties. These calculations are the first in which local-field corrections have been calculated for a vector property of light. Since only scalar local fields are important [8], TDLDA can be used also for vector properties of light. In α-quartz, the local fields increase the rotatory power by a factor 7, and in selenium the rotatory power changes sign due to a correction of a factor of -4. We have also shown that it is possible, by general estimates of the size of the different linear response functions, to obtain order of magnitude estimates of the size of local-field corrections.

[1] J. F. Nye, *Physical Properties of Crystals* (Clarendon, Oxford, 1989).

[2] P. Etchegoin and M. Cardona, Solid State Commun. **82**, 655 (1992).

[3] H. Zhong, Z. H. Levine, D. C. Allan, and J. W. Wilkins, Phys. Rev. B **48**, 1384 (1993); Phys. Rev. Lett. **69**, 379 (1992); **70**, 1032(E) (1993).

[4] A. Carvallo, C. R. Acad. Sci. **126**, 728 (1898); cited in D. E. Gray, *American Institute of Physics Handbook* (McGraw-Hill, New York, 1963), 2nd ed., pp. 6–26.

[5] J. E. Adams and W. Haas, in *The Physics of Selenium and Tellurium,* edited by W. C. Cooper (Pergamon, New York, 1969), p. 293.

[6] G. W. Day, Appl. Phys. Lett. **18**, 347 (1971).

[7] W. Henrion and F. Eckart, Z. Naturforsch. **19A**, 1024 (1964).

[8] W. L. Mochan and R. G. Barrera, Phys. Rev. B **32**, 4984 (1985). Formally, local fields can be described by a complete vector theory [22–24].

[9] G. Vignale and M. Rasolt, Phys. Rev. Lett. **59**, 2360 (1987); G. Vignale, M. Rasolt, and D. J. W. Geldart, Phys. Rev. B **37**, 2502 (1988).

[10] A. Zangwill and P. Soven, Phys. Rev. A **21**, 1561 (1980).

[11] Z. H. Levine and D. C. Allan, Phys. Rev. B **43**, 4187 (1991).

[12] R. O. Jones and O. Gunnarsson, Rev. Mod. Phys. **61**, 689 (1989).

[13] Z. H. Levine and D. C. Allan, Phys. Rev. Lett. **63**, 1719 (1989).

[14] The $\mathbf{G} = 0$ exchange-correlation potential can be disregarded, since it yields only q^2 corrections [11].

[15] S. Chandrasekhar, Proc. Indian Acad. Sci., Sect. A **37**, 468 (1953).

[16] F. Gervais and B. Piriou, Phys. Rev. B **11**, 3944 (1975).

[17] Z. H. Levine, Phys. Rev. B **49**, 4532 (1994).

[18] J. Kobayashi, T. Takahashi, T. Hosokawa, and Y. Ueso, J. Appl. Phys. **49**, 809 (1978).

[19] A. F. Konstatinova, N. R. Ivanov, and B. N. Grechushnikov, Kristallografiya **14**, 283 (1969) [Sov. Phys. Crystallogr. **14**, 222 (1969)].

[20] The response functions are tensors, but we use scalar notation for simplicity.

[21] Based on a Lorentz-type (ionic) local-field correction, a similar result was found in J. Jerphagnon and D. S. Chemla, J. Chem. Phys. **65**, 1522 (1976).

[22] D. Adler, Phys. Rev. **126**, 413 (1962).

[23] A. S. Pine, Phys. Rev. **139**, A901 (1965).

[24] S. T. Chui, H. Ma, R. V. Kasowski, and W. Y. Hsu, Phys. Rev. B **47**, 6293 (1993).