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OPTICAL PROPERTIES OF *C*2/*c* PYROXENES: A POINT-DIPOLE EXPLANATION

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ABSTRACT

Using point-dipole theory (Abbott 1993, 1994a, b), electronic polarizabilities (α_p) were determined for various *M1*, *M2* and *T* cations, bridging (Ob) and non-bridging (Onb) oxygen atoms in thirteen *C*2/*c* pyroxenes. Because the number of variable polarizabilities (5) exceeds the number of constraints (4) on the optical properties (α, β, γ, Z^c, for a given wavelength of incident light), there are an infinite number of solutions (combinations of calculated values for α_p) for each of which the discrepancy (expressed as a least-squares residual, *R*) between calculated and observed optical properties is a minimum. In order to find the correct solution for each clinopyroxene, solutions were determined for several fixed values of $\alpha_p(T)$. For each fixed value of $\alpha_p(T)$, the solution is unique, within the limits of precision of the least-squares procedure. Unrealistic solutions were then rejected. For a particular clinopyroxene, solutions proved to be similar and reasonable wherever the final (minimum) value for *R* is very small. For each clinopyroxene, the best solution (set of α_p values) was taken to be the one giving the smallest possible *R*-value. The calculations show the following: (1) For an element present in more than one structure, α_p can vary considerably from one structure to another in ways that are not clearly related to chemical composition or structure; thus calculated values for $\alpha_p(T)$ range from 0.105 to 0.40 Å^3, those for α_p(Ca), from 0.25 to 1.03 Å^3, those for α_p(Ob), from 1.16 to 1.55 Å^3, and those for α_p(Onb), from 1.29 to 1.60 Å^3. (2) For each structure, the sum of the calculated α_p values for one unit cell is consistently less by the same amount (approximately 5%) than the sum of α_p values calculated from the Lorentz–Lorenz formula using the observed indices of refraction. (3) The optic-axial half-angle, V_γ, decreases with increasing $\alpha_p(T)$, from V_γ = 64°, $\alpha_p(T)$ = 0.105 Å^3 in kosmochlor to V_γ = 27°, $\alpha_p(T)$ = 0.40 Å^3 in subsilicic titanoan aluminian diopside. The relationship is well defined but distinctly nonlinear. (4) The relationship between extinction angle Z^c and the ratio α_p(Ob)/α_p(Onb) is approximately linear, Z^$c = -350\ \alpha_p$(Ob)/α_p(Onb) + 420, (Z^c in °; + in obtuse a^c), such that Z^c increases with decreasing α_p(Ob)/α_p(Onb).

Keywords: optical properties, clinopyroxenes, point-dipole theory, electronic polarizabilities.

SOMMAIRE

La méthode des dipoles ponctuels (Abbott 1993, 1994a, b) a permis de déterminer les polarisabilités électroniques de divers cations *M*1, *M*2 et *T*, et des atomes d'oxygène partagés (Ob) ou non (Onb) entre tétraèdres dans treize pyroxènes *C*2/*c*. Le nombre de polarisabilités variables (5) dépasse le nombre (4) de contraintes imposées par les propriétés optiques (α, β, γ, Z^c, pour un longueur d'onde donnée de la lumière incidente); il existe donc un nombre infini de solutions (combinaisons de valeurs calculées de α_p), et dans chaque cas, le décalage entre propriétés optiques calculées et observées, tel qu'exprimé par un résidu *R* obtenu par moindres carrés, est minimal. Afin de trouver la solution correcte pour chaque clinopyroxène, des solutions ont été déterminées pour plusieurs valeurs fixes de $\alpha_p(T)$. Dans chaque cas, la solution est unique, compte tenu de la précision de la méthode des moindres carrés. Les solutions improbables ont ensuite été rejetées. Pour un clinopyroxène donné, les solutions se ressemblent et sont raisonnables dans tous les cas où la valeur de *R* est très faible. Pour chaque clinopyroxène, la meilleure solution (ensemble de valeurs de α_p) est celle qui mène à la plus faible valeur de *R* possible. Les calculs démontrent les points suivants: (1) Pour un élément présent dans plus d'une structure, α_p peut varier beaucoup d'une structure à l'autre, de façons qui ne sont pas clairement dépendantes de la composition chimique ou la structure. Ainsi, les valeurs calculées de $\alpha_p(T)$ vont de 0.105 à 0.40 Å^3, celles de α_p(Ca), de 0.25 à 1.03 Å^3, celles de α_p(Ob), de 1.16 à 1.55 Å^3, et celles de α_p(Onb), de 1.29 à 1.60 Å^3. (2) Dans le cas de chaque structure, la somme des valeurs calculées de α_p pour la maille élémentaire est systématiquement moins élevée par le même facteur (environ 5%) que la somme des valeurs de α_p calculée par la formule Lorentz–Lorenz, fondée sur les indices de réfraction observés. (3) La moitié de l'angle optique, V_γ, diminue avec augmentation de $\alpha_p(T)$, de V_γ = 64°, $\alpha_p(T)$ = 0.105 dans le cas du kosmochlor à V_γ = 27°, $\alpha_p(T)$ = 0.40 dans le diopside subsiliceux titanifère et alumineux. La relation est bien définie, mais définitivement non linéaire. (4) La relation entre l'angle d'extinction Z^c et le rapport α_p(Ob)/α_p(Onb) est sensiblement linéaire, Z^$c = -350\alpha_p$(Ob)/α_p(Onb) + 420 (Z^c en °, + dans l'angle obtus a^c), de sorte que Z^c augmente à mesure que diminue α_p(Ob)/α_p(Onb).

(Traduit par la Rédaction)

Mots-clés: propriétés optiques, clinopyroxènes, théorie des dipoles ponctuels, polarisabilités électroniques.

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INTRODUCTION

Recent advances in point-dipole theory (Abbott 1993, 1994a, b) offer a more complete understanding of the relationship between optical properties and atomic structure. With a knowledge of individual electronic polarizabilities, α_p, the extended theory has been used to calculate not only the principal indices of refraction for a given wavelength of light, but also the orientation of the optical indicatrix in monoclinic and triclinic minerals. The calculations show that point-dipole theory correctly predicts the orientation of the optical indicatrix, where the orientation is not otherwise fully constrained by symmetry. The theory can also be used to calculate electronic polarizabilities by searching for the set of polarizabilities that give the smallest discrepancy between observed and calculated optical properties. The number of electronic polarizabilities that can be determined in this way is limited to the number of parameters needed to describe the optical properties. For example, in the triclinic system, it is necessary to specify six parameters to fully describe the optical properties (*i.e.*, the optical indicatrix) for a given wavelength of incident light, and hence there are six degrees of freedom. Three of the degrees of freedom are the magnitudes of the principal indices of refraction α, β, γ; the remaining three degrees of freedom relate to the orientation of the indicatrix. Hence, as many as six electronic polarizabilities can be defined and calculated. In the monoclinic system, there are four degrees of freedom, three for the principal indices of refraction, and only one for the orientation of the indicatrix. Hence, four polarizabilities can be defined and calculated. In the higher-symmetry systems, there are three or fewer degrees of freedom; hence three or fewer electronic polarizabilities can be calculated.

This study addresses the optical properties of *C2/c* pyroxenes, and derives electronic polarizabilities for the constituent atomic species. The goal is to discover the reason for variations in the optical properties as a function of the composition of the pyroxene, specifically with regard to the magnitudes of the principal indices of refraction and the extinction angle (Z^c). The specific objectives are as follows: (1) for each composition, determine the electronic polarizabilities of the constituent atom species, (2) analyze the variation in α_p(O) as a function of coordination, and *M1*, *M2*, and *T* site occupancy, and (3) from the point-dipole approach, interpret the reasons for variations in the optical properties of the *C2/c* pyroxenes.

TABLE 1. *C2/c* PYROXENES USED IN THE INVESTIGATION

	Variety. $M2(M2)[T]O_6$	α	β	γ	Z^c (°)	V_γ (°)[1]	References[2]
	M2 = Ca						
1.	Diopside. $Ca(Mg)[Si_2]O_6$	1.664	1.672	1.694	38	31.4	(1) [9]
2.	Hedenbergite. $Ca(Fe)[Si_2]O_6$	1.732	1.739	1.753	48	32.2	(1) [10]
3.	Johannsenite. $Ca(Mn)[Si_2]O_6$	1.699	1.710	1.725	48	40.9	(2) [9]
4.	$CaAl_2SiO_6$ (CaTs). $Ca(Al)[AlSi]O_6$	1.709	1.714	1.730	30.5	29.4	(3) [9][3] [11][4]
5.	Essenite[5]	1.795	1.815	1.825	-9	55.1	(4) [4]
6.	STAD[6]	1.747	1.750	1.762	58	26.7	(5) [5]
7.	SAFD[7]	1.725	1.732	1.745	35	36.5	(6) [6]
	M2 = Na						
8.	Jadeite, $Na(Al)[Si_2]O_6$	1.654	1.659	1.667	29	38.5	(1) [10]
9.	Aegirine. $Na(Fe^{3+})[Si_2]O_6$	1.776	1.820	1.836	100	59.5	(1) [9]
10.	Kosmochlor, $Na(Cr)[Si_2]O_6$	1.766	1.778	1.781	98	63.6	(1) [9]
11.	Jervisite. $Na(Sc)[Si_2]O_6$	1.683	1.715	1.724	98	62.5	(7) [12]
	M2 = Li						
12.	Spodumene. $Li(Al)[Si_2]O_6$	1.656	1.663	1.671	20	43.3	(1) [9]
13.	$LiScSi_2O_6$. $Li(Sc)[Si_2]O_6$	1.702	1.710	1.716	127	49.3	(8) [12]

1. Calculated from observed α, β, γ.
2. References. ( ) = structure determination. [ ] = optical properties:
   (1) Cameron *et al.* (1973). (2) Freed & Peacor (1967). (3) Okamura *et al.* (1974).
   (4) [4] Cosca & Peacor (1987). (5) [5] Dowty & Clarke (1973). (6) [6] Peacor (1967).
   (7) Hawthorne & Grundy (1973). (8) Hawthorne & Grundy (1977). [9] Deer *et al.* (1978).
   [10] Phillips & Griffen (1981). [11] Hay (1966). [12] Ito & Frondel (1968).
3. Z^c extrapolated from $CaTs_{40}Di_{60}$ (Z^c = 35°) and Di_{100} (Z^c = 38°).
4. α, β, γ.
5. $Ca(Fe^{3+}_{.72}Mg_{.16}Al_{.04}Ti_{.03}Fe^{2+}_{.02})[Al\ Si]O_6$
6. Subsilicic titanoan aluminian diopside. $Ca(Mg_{.39}Ti^{3+}_{.35}Ti^{4+}_{.13}Al_{.13})[Al_{.74}Si_{1.26}]O_6$
7. Subsilicic aluminian ferrian diopside, $Ca(Mg_{.57}Al_{.17}Fe^{3+}_{.16}Fe^{2+}_{.06}Ti_{.07})[Al_{.5}Si_{1.5}]O_6$

CLINOPYROXENES USED IN STUDY

Calculations were done on the clinopyroxenes described in Table 1. For the purpose of this work, a clinopyroxene can be used only if both a structure refinement and experimentally determined optical properties are available. Ideally, the optical properties and structural data should pertain to the same specimen, but this was possible only for esseneite, subsilicic titanoan aluminian diopside (STAD), and subsilicic aluminian ferrian diopside (SAFD). However, being complex solid-solutions, these are the three compositions for which correspondence between structural data and optical properties is most critical. The other clinopyroxenes used here are end-member (or near end-member) compositions, and the optical properties should be appropriate for the structures. The CaTs pyroxene ($CaAl_2SiO_6$) presented a problem insofar as an extinction angle (Z^c) has not been determined experimentally. The angle reported in Table 1 was extrapolated from end-member diopside (Z^c = 31.4°) and synthetic $CaTs_{40}Di_{60}$ (Z^c = 35°). With regard to the optical properties, it should be noted that the Z vibration direction is in the obtuse angle a^c for all compositions except esseneite. In Table 1, the extinction angle, Z^c, is given as positive where Z is in the obtuse angle a^c, and negative where Z is outside the obtuse angle a^c (esseneite).

METHODOLOGY

If the electronic polarizabilities of the atoms composing a crystal are known, the optical properties can be calculated for a given wavelength of incident light (Abbott 1993, 1994a, b). In this study and in Abbott (1994a, b), electronic polarizabilities were determined by searching for the set of electronic polarizabilities giving the smallest discrepancy between the observed and calculated optical properties. The basic strategy was pioneered by Pohl (1978), Pohl *et al.* (1978), Pohl & Rath (1979) and Lager *et al.* (1987). However, in these early studies, only three (or fewer) independently variable electronic polarizabilities were considered. The theory did not recognize that, in the monoclinic and triclinic systems, respectively, one and three additional parameters are needed to account for the orientation of the optical indicatrix.

This section explains the methodology of the application of the point-dipole theory to crystals, and to *C*2/*c* pyroxenes in particular: (1) A brief review of the theory is given, as extended by Abbott (1993, 1994a, b), (2) a description of the least-squares procedure used to calculate the best set of electronic polarizabilities is outlined, and (3) a description of the strategy is discussed to overcome the special problem of too many potentially variable electronic polarizabilities in clinopyroxenes.

Point-dipole theory

For a given frequency of light, the principal indices of refraction of an anisotropic crystal can be calculated from the structure and the electronic polarizabilities of the constituent species (Abbott 1993, 1994a, b, Pohl 1978, Pohl & Rath 1979, Lager *et al.* 1987). According to the point dipole-theory as extended by Abbott (1993, 1994a, b), relations among structure, electronic polarizability, and refraction of light can be summarized in four equations. The first equation (Cummins *et al.* 1976, Pohl 1978) gives the local electric field, F(k), at site k as a function of the local electric fields at all sites, k′, in the unit cell,

$$\mathbf{F}(\mathrm{k}) = \mathbf{E} + (1/V)\Sigma_{\mathrm{k}'}\, \mathrm{L}(\mathrm{kk}')\, \alpha_{\mathrm{p}}(\mathrm{k}')\, \mathbf{F}(\mathrm{k}'). \qquad (1)$$

Vector **E** is the macroscopic (externally applied) electric field, L(kk′) is the Lorentz-factor tensor for the pair k–k′, $\alpha_p(k')$ is the electronic polarizability of species k′, and *V* is the volume of the unit cell. The macroscopic electric field, **E**, is equated with the plane of polarization of the incident light. The Lorentz factor tensors, L(kk′), were calculated using the method of Cummins *et al.* (1976). For a given set of electronic polarizabilities, $\alpha_p(k')$, equation (1) forms a system of linear equations solvable for the individual local electric fields, **F**(k).

The dielectric susceptibility tensor, χ, is then obtained from the local electric fields (Pohl 1978):

$$\chi\mathbf{E} = (1/V)\Sigma_{\mathrm{k}}\, \alpha_{\mathrm{p}}(\mathrm{k})\, \mathbf{F}(\mathrm{k}) \qquad (2)$$

Referred to a Cartesian basis, **x** (column matrix of coordinate variables *x*, *y*, *z*), the coefficients of the dielectric susceptibility tensor describe the surface of an ellipsoid,

$$\mathbf{x}^{\mathrm{T}}\, \chi\, \mathbf{x} = 1. \qquad (3)$$

The principal axes of the ellipsoid are parallel to the principal axes of the optical indicatrix. The directions of the principal axes and their magnitudes (eigenvectors and eigenvalues, respectively) are found by diagonalizing the dielectric susceptibility tensor (*e.g.*, Julian & Bloss 1987). The principal indices of refraction are related to the corresponding eigenvalues, χ_{ii},

$$n_{\mathrm{i}} = (\chi_{\mathrm{ii}} + 1)^{1/2}, \qquad (4)$$

where values of n_i (i = 1, 2, 3) correspond to indices of refraction α, β, and γ. The quantity $\chi_{ii} + 1$ is the familiar dielectric constant. All calculations were done for the D wavelength (λ_D = 5893 Å). A computer program, OPT, was written in TURBO PASCAL by the author to do the calculations; this program is available upon request.

Least-squares procedure

As noted above, the dielectric susceptibility tensor,

$$\chi = \begin{vmatrix} \chi_{11} & \chi_{12} & \chi_{13} \\ \chi_{21} & \chi_{22} & \chi_{23} \\ \chi_{31} & \chi_{32} & \chi_{33} \end{vmatrix}, \qquad (5)$$

contains a complete description of the optical indicatrix (*i.e.*, α, β, γ, and the orientation of the indicatrix) for a given wavelength of incident light. The tensor is symmetrical ($\chi_{ij} = \chi_{ji}$, where j ≠ i), such that the maximum number of independently variable tensor elements is six. In the triclinic system, there are no special constraints on the values for χ_{ij}, and hence there are six variables. In the monoclinic system (*b* axis unique), the tensor elements are subject to the constraint $\chi_{12} = \chi_{23} = 0$, leaving four independent variables. In the orthorhombic system, off-diagonal elements are zero, leaving three variables. In the tetragonal, hexagonal, and trigonal systems, off-diagonal elements are zero, and $\chi_{11} = \chi_{22}$, leaving two independent variables. In the cubic system, all off-diagonal elements are zero, $\chi_{11} = \chi_{22} = \chi_{33}$, and hence there is one independent variable.

A second computer program, OPTRFN, was written by the author to determine the set of electronic polarizabilities giving the smallest discrepancy between observed and calculated optical properties. The strategy is much the same as that used by Lager *et al.* (1987) for the same purpose, except that OPTRFN incorporates non-zero, off-diagonal elements of the dielectric susceptibility tensor.

The best set of values for the electronic polarizabilities was determined by least squares, by minimizing the function,

$$R = [\Sigma_{i=1,3}\, \Sigma_{j=i,3}\, (\chi_{ij,obs} - \chi_{ij,calc})^2 / \Sigma_{i=1,3}\Sigma_{j=i,3}\, \chi_{ij,obs}{}^2]^{1/2}, \qquad (6)$$

TABLE 2. CALCULATED ELECTRONIC POLARIZABILITIES (Å³) FOR CLINOPYROXENES

	$\alpha_p(M1)$	$\alpha_p(M2)$	$\alpha_p(T)$	$\alpha_p(\mathrm{Onb})^1$	$\alpha_p(\mathrm{Ob})^1$	R^2
M2 = Ca						
Diopside	0.30	1.03	0.27	1.24	1.37	0.00118
Hedenbergite	0.68	0.86	0.31	1.33	1.45	0.00341
Johannsenite	0.964	0.842	0.26	1.33	1.46	0.00494
CaTs	0.246	0.61	0.39	1.28	1.36	0.00068
Essenite	1.22	0.75	0.19	1.36	1.60	0.00367
STAD	0.699	0.248	0.40	1.37	1.455	0.00263
SAFD	0.66	0.79	0.24	1.36	1.48	0.00256
M2 = Na						
Jadeite	0.42	0.28	0.225	1.18	1.285	0.00380
Aegirine	1.13	0.15	0.19	1.45	1.31	0.00576
Kosmochlor	0.585	0.095	0.105	1.54	1.475	0.00328
Jervisite	0.881	0.0	0.125	1.545	1.315	0.00353
M2 = Li						
Spodumene	0.38	0.20	0.26	1.16	1.24	0.00505
Synthetic $\mathrm{LiScSi_2O_6}$	0.865	0.034	0.19	1.45	1.29	0.00407

1. Onb = O1, O2. Ob = O3.
2. $R = [\Sigma_{i=1,3} \Sigma_{j=i,3} (\chi_{ij,obs} - \chi_{ij,calc})^2 / \Sigma_{i=1,3} \Sigma_{j=i,3} \chi_{ij,obs}^2]^{1/2}$, where $\chi_{ij,obs}$, $\chi_{ij,calc}$ are elements of the observed and calculated dielectric susceptibility tensors.

where $\chi_{ij,obs}$ and $\chi_{ij,calc}$ are elements of the observed and calculated dielectric susceptibility tensors. The observed dielectric tensor was calculated from experimentally determined optical properties (Table 1). The calculated dielectric susceptibility tensor was determined by the methods outlined above in the program OPT, which in large part is incorporated into OPTRFN.

Typically, minimum values for *R* (Table 2) were less than 0.006, indicating excellent agreement between observed and calculated optical properties. For minimum values of *R* less than this value, the observed (Table 1) and calculated principal indices of refraction usually match to within ± 0.001. Extinctions angles (Z^c) were found to be less accurate, but usually within ± 10°. The extinction angle is sensitive to very small variations in electronic polarizabilities.

The problem of indeterminacy

In a *C*2/*c* pyroxene, there are six independent sites (*M1*, *M2*, *T*, O1, O2, O3), hence six potentially variable electronic polarizabilities, exceeding by two the four parameters (α, β, γ, Z^c) that describe the optical properties; the system of equations is therefore indeterminate. In order to circumvent this problem, three strategies were tried: (1) one may impose interdependency of the electron polarizabilities assigned to two or more of the sites; (2) one may hold $\alpha_p(T)$ constant; (3) one can reject unreasonable sets of calculated polarizabilities.

In preliminary calculations, the O1, O2 and O3 sites were grouped together such that all oxygen atoms were assigned the same electronic polarizability, which reduces the number of variables to four. Final values of *R* were found to be unacceptably high, indicating that this is not an appropriate approximation. Neither the indices of refraction nor the extinction angle were accurately reproduced, and calculated values of α_p were not similar to values reported elsewhere (*e.g.*, Pohl 1978, Pohl & Rath 1979, Lager *et al.* 1987, Jaffe 1988).

In the next stage of calculations, oxygen atoms were classified according to two types, bridging (Ob = O3) and nonbridging (Onb = O1, O2), which leaves five variable electronic polarizabilities. In other studies, the electronic polarizability of Si was found to be negligible (Lager *et al.* 1987, Pohl *et al.* 1978) or very small (Lasaga & Cygan 1982). Assuming $\alpha_p(T) = 0$, calculations with four variable electronic polarizabilities, $\alpha_p(M1)$, $\alpha_p(M2)$, $\alpha_p(\mathrm{Ob})$, and $\alpha_p(\mathrm{Onb})$, did not give satisfactory results, which indicates the existence of electronic polarizability at the *T*-site, *i.e.*, $\alpha_p(T) > 0$. It seems clear that the optical properties of *C*2/*c* pyroxenes cannot be explained with fewer than five electronic polarizabilities.

With five potentially variable electronic polarizabilities in a monoclinic crystal, there are an infinite number of possible solutions, only one of which can be correct. By solution is meant a set of calculated α_p values. Fortunately, not all solutions are reasonable. Some solutions may be rejected simply because they do not reproduce the observed optical properties accurately (high *R*). For other solutions, in order to achieve a satisfactory match between calculated and observed optical properties, one or more of the electronic polarizabilities may have an unrealistic value. On the other hand, a whole range of possible solutions may be similar and have comparably small values for *R*, in which case the correct solution might reasonably be expected to be encompassed by the range. Within this framework, for each of the clinopyroxenes, up to thirty solutions were determined for up to 12 different (fixed) values of $\alpha_p(T)$. Thus in each calculation, only four electronic polarizabilities were allowed to vary: $\alpha_p(M1)$, $\alpha_p(M2)$, $\alpha_p(\mathrm{Onb})$ and $\alpha_p(\mathrm{Ob})$. For each fixed value of $\alpha_p(T)$, the calculation was done several times with different starting values for the variable polarizabilities. Ideally, for a given value of $\alpha_p(T)$, the solution (set of α_p values) is unique, but because limits are imposed on the precision in the least-squares procedure, different solutions are obtained, depending on (1) the preset increment, Δ, by which α_p values are varied, and (2) the starting values for the variable polarizabilities. In most of the calculations, the final Δ was set at 0.01 Å³, but in some cases, the final Δ was set as low as 0.001 Å³. In general, solutions were not improved significantly by using a value of Δ less than 0.01 Å³. Indeed, given the presumed uncertainty in observed optical properties, there is little justification for using a Δ value less than 0.01 Å³.

As an example, all solutions for diopside with $R < 0.01$ are given in Figure 1. Typically, for a particular clinopyroxene (*e.g.*, Fig. 1), values for $\alpha_p(\mathrm{Onb})$, $\alpha_p(\mathrm{Ob})$ and $\alpha_p(M1)$ do not vary significantly from one solution to the next. Thus, values for

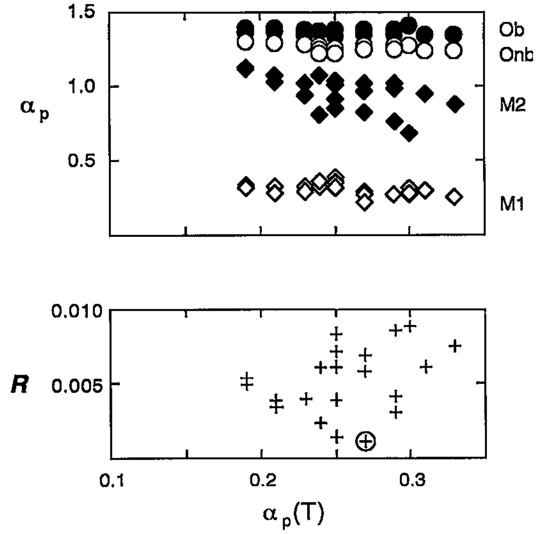

FIG. 1. Diopside. Solutions [$\alpha_p(M1)$, $\alpha_p(M2)$, α_p(Onb), α_p(Ob)] and final R-values, calculated for various fixed values of $\alpha_p(T)$. The circled value for R corresponds to the solution reported in Table 2.

α_p(Onb), α_p(Ob) and $\alpha_p(M1)$ do not depend significantly on the value for $\alpha_p(T)$; changing $\alpha_p(T)$ is compensated mainly by changes in $\alpha_p(M2)$. Once a solution was obtained, all of the α_p values, including $\alpha_p(T)$, were allowed to vary; however, $\alpha_p(T)$ did not vary significantly within the limits of precision of the refinement. This shows that the final value for R represents at least a local minimum (*within the limits of precision of the refinement*). For a particular clinopyroxene, solutions proved to be similar if the final values for R were small, $R < 0.01$ (*e.g.*, Fig. 1). For each clinopyroxene, the best, representative solution (set of α_p values, Table 2) was taken to be the one giving the smallest R.

The reader should note that the final value for R would equal zero only fortuitously for at least two reasons. Ultimately, (1) calculated α_p values and correct α_p values may differ within the preset limits of precision. Much more importantly, however, (2) point-dipole theory itself is an approximation, as the electronic polarizability of an atom is assumed to be isotropic, *i.e.*, the same with respect all other atoms coordinated to it. There is no reason to believe that this should generally be the case. That such a close match can be achieved between calculated and observed optical properties is quite remarkable, and, while acknowledging deficiencies, serves to validate the utility of the theory.

RESULTS AND DISCUSSION

The "best" calculated electronic polarizabilities and minimum values for R are presented in Table 2. Values for R in the range from 0.00118 (diopside) to 0.00576 (aegirine) indicate that for each of the compositions, the discrepancy between observed and calculated optical properties is very small, in most cases within the presumed uncertainty in the observed optical properties.

For a particular element (*e.g.*, Ca at $M2$, Table 2), the electronic polarizability can vary considerably from one clinopyroxene to another, presumably depending on the elements occupying other sites. This kind of variation has been noted in other mineral groups (Pohl 1978, Pohl *et al.* 1978, Pohl & Rath 1979, Lager *et al.* 1987, Abbott 1994a, b). In the case of Ca, all but one value for α_p(Ca) is in the range from 0.61 Å^3 to 1.03 Å^3. However, even the one outlying value, α_p(Ca) = 0.248 Å^3 (STAD), is within the range of values reported elsewhere, from as low as α_p(Ca) = 0.159 Å^3 in calcite (Pohl & Rath 1979) to as high as α_p(Ca) = 1.66 Å^3 (an average based on silicate minerals, Lasaga & Cygan 1982). Other values near the low end of the range for Ca have been reported for anhydrite and hemihydrite (both 0.383 Å^3: Lager *et al.* 1987) and aragonite (0.413 Å^3: Pohl 1978). Consequently, electronic polarizabilities (*e.g.*, Lasaga & Cygan 1982) are only approximately transferable, even among minerals belonging to the same structural group (*e.g.*, $C2/c$ pyroxenes). With regard to the cation site-occupancies, trends in electronic polarizabilities are not easily discerned. The calculated polarizabilities (Table 2) were examined from many perspectives, but only four noteworthy relations were identified. The polarizabilities are presented with an open invitation (dare I say, challenge) to the reader to speculate on the underlying causes for the relations described below. Possibly involved are one or more of the following: (1) distortion of the coordination polyhedra, (2) mean bond-length, (3) bond-strength considerations, and (4) inductive charge-transfer.

Relation 1

The Lorentz–Lorenz formula (Bloss 1971, Lasaga & Cygan 1982, Eggleton 1991, Arndt 1994),

$$K_{L-L} = \alpha_{p,\text{total}} = (3V_{\text{cell}}/4\pi)(n^2 - 1)/(n^2 + 2), \quad (7)$$

wherein $n = (\alpha + \beta + \gamma)/3$ and V_{cell} = cell volume, provides an independent check on the total electronic polarizability, $\alpha_{p,\text{total}}$, defined as the sum over the unit cell of the electronic polarizabilities. Table 3 and Figure 2 compare total electronic polarizabilities derived from the Lorentz–Lorenz formula and total electronic polarizabilities, K_{P-D}, summed from the electronic polarizabilities reported in Table 2. Total

TABLE 3. TOTAL ELECTRONIC POLARIZABILITIES, COMPARISON WITH LORENTZ-LORENZ CONSTANT

	n^1	$V_{cell}{}^2$	$K_{L\text{-}L}{}^{2,3}$ -	$K_{P\text{-}D}{}^{2,4}$	= Diff.^{2}
M2 = Ca					
Diopside	1.677	438.6	39.43	38.28	1.15
Hedenbergite	1.743	450.6	43.52	41.52	2.00
Johannsenite	1.711	466.0	43.18	41.92	1.26
CaTs	1.718	421.4	39.65	37.90	1.75
Essenite	1.812	446.2	46.04	43.96	2.08
STAD	1.753	447.7	43.68	41.56	2.12
SAFD	1.734	446.2	43.09	41.32	1.77
M2 = Na					
Jadeite	1.660	401.8	35.41	33.72	1.69
Aegirine	1.811	429.1	44.23	40.32	3.91
Kosmochlor	1.775	420.0	41.87	40.00	1.87
Jervisite	1.707	455.3	40.51	39.76	0.75
M2 = Li					
Spodumene	1.663	389.0	34.41	33.00	1.41
$LiScSi_2O_6$	1.709	441.0	41.09	38.63	2.46

1. $n = (\alpha+\beta+\gamma)/3$, from observed indices of refraction. 2. Units, Å^3.
3. Lorentz-Lorenz formula, $K_{L\text{-}L} = \alpha_{p,total} = (3V_{cell}/4\pi)(n^2-1)/(n^2+2)$.
4. For *C2/c* pyroxene, $K_{P\text{-}D} = 4\,[\,\alpha_p(M1)+\alpha_p(M2)+2\alpha_p(T)+4\alpha_p(Onb)+2\alpha_p(Ob)]$, where α_p values are from Table 2.

electronic polarizabilities based on point-dipole calculations, $K_{P\text{-}D}$, are consistently about 5% lower than those predicted by the Lorentz–Lorenz formula. Distributed evenly over the contents of the unit cell for a clinopyroxene, the discrepancy is approximately 0.05 Å^3 per atom site. Strictly, the Lorentz–Lorenz equation (7) pertains to cubic crystals and amorphous substances, and does not take into account steric effects associated with the overlap of electron density of neighboring atoms (Eggleton 1991, Arndt 1994). In other words, the Lorentz–Lorenz formula doesn't take covalency into account. Modified to account for covalency (Eggleton 1991, Arndt 1994), the Lorentz–Lorenz equation predicts higher total electronic polarizabilities, and even greater discrepancy with $K_{P\text{-}D}$ summed from electronic polarizabilities in Table 2. Covalency tends to increase electronic polarizability. Thus, total electronic polarizabilities ($K_{P\text{-}D}$) summed from values in Table 2, though close to the 100% ionic approximation for cubic crystals (equation 7), are actually beyond the range bounded by values consistent with 100% ionic bonding and 100% covalent bonding. Acknowledging some covalency in silicate minerals, the discrepancy is all the more significant, and serves to emphasize the uncertainty in applying the Lorentz–Lorenz equation (modified to account for covalency or otherwise) to anisotropic crystals.

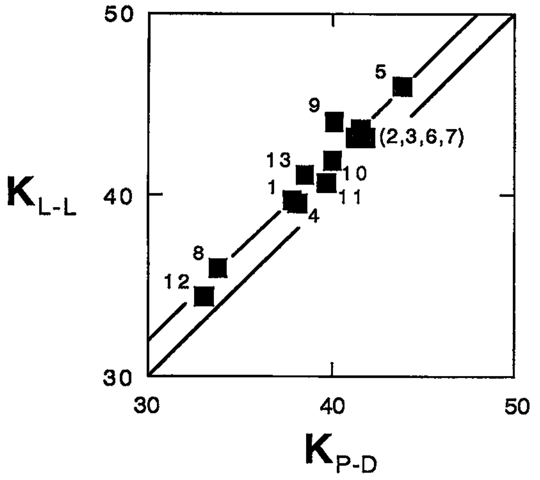

FIG. 2. Total electronic polarizability from the Lorentz–Lorenz formula, $K_{L\text{-}L} = \alpha_{p,total} = (3V_{cell}/4\pi)(n^2 - 1)/(n^2 + 2)$, compared with the total electronic polarizability from values calculated here (Table 2), $K_{P\text{-}D} = 4\,[\alpha_p(M1) + \alpha_p(M2) + 2\alpha_p(T) + 4\alpha_p(Onb) + 2\alpha_p(Ob)]$, based on point-dipole theory. Data points are numbered according to listing in Table 1.

Relation 2

Values for α_p(Onb) and α_p(Ob) (Table 2) vary within limits that are generally consistent with values reported elsewhere for α_p(O) in other minerals (Abbott 1993, 1994a, b, Pohl 1978, Pohl & Rath 1979, Lager *et al.* 1987, Jaffe 1988). Both α_p(Onb) and α_p(Ob) increase with increasing mean index of refraction, which generally reflects the increasing number of electrons in the unit cell (*i.e.*, sum of atomic numbers; essentially the mass density). Thus the range of $K_{P\text{-}D}$ (or $K_{L\text{-}L}$) values in Table 3 (or Fig. 2) reflects an increase not just in the sum of the electronic polarizabilities of the cations, but also an increase in the electronic polarizability of oxygen. As the density of the clinopyroxene increases by substitution of cations of progressively higher atomic number at *M1* and *M2*, a progressively larger share of the total electronic polarizability becomes associated with oxygen. In simple terms, the electronic polarizability of an oxygen atom depends significantly on the atomic numbers of the cations coordinated to the oxygen. This emphasizes why electronic polarizabilities for individual atoms are not additive, and further indicates why electronic polarizabilities for "oxide" components are approximately additive. Electronic polarizabilities for components expressed as oxides incorporate two contributions, one from the cation(s) and one from the oxygen atom(s), in proportions that approximately reflect the combined effect in a crystal containing the oxide component. The proven success of various methods of predicting mean index of refraction from composition, density and tabulated optical constants for oxide components (*e.g.*, Bloss 1971, Jaffe 1988, Mandarino 1976, 1978, 1979, 1981, Eggleton 1991) depend inherently on this relationship. Thus, a set of universally additive optical constants for individual elements is not possible without taking into account

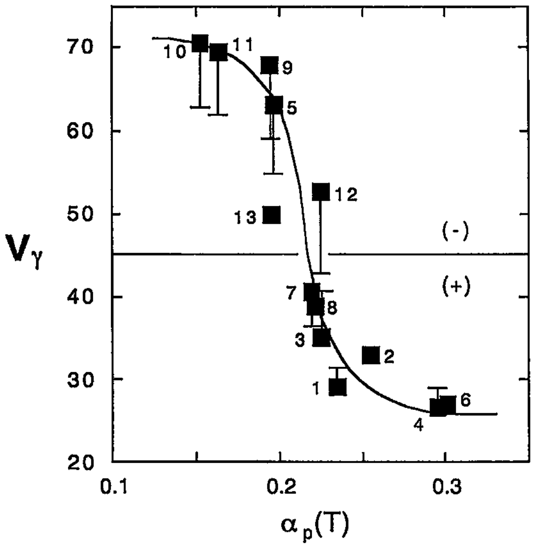

FIG. 3. Optical axial half-angle, V_γ (in degrees), *versus* $\alpha_p(T)$ (in Å^3) from Table 2. The filled squares are for half-angles calculated in this study from point-dipole theory. The short horizontal bars are for observed half-angles from Table 1. Where an observed half-angle, V_γ, is not indicated, the calculated half-angle and the observed half-angle (Table 1) are nearly the same. The horizontal line separates optically negative (–) clinopyroxenes, $V_\gamma > 45°$, from optically positive (+) clinopyroxenes, $V_\gamma < 45°$. Data points are numbered according to listing in Table 1.

the coordination of both cations and anions. For illuminating expositions of this problem, the reader is referred to Eggleton (1991) and Jaffe (1988).

Relation 3

The strategy for determing electronic polarizabilities emphasizes the effect of varying $\alpha_p(T)$. During the course of doing the calculations, a relationship (Fig. 3) between $\alpha_p(T)$ and the optical axial half-angle, V_γ, became evident. The half-angle, V_γ, decreases with increasing $\alpha_p(T)$, from $V_\gamma = 64°$, $\alpha_p(T) = 0.105$ Å^3 in kosmochlor to $V_\gamma = 27°$, $\alpha_p(T) = 0.40$ Å^3 in subsilicic titanoan aluminian diopside. The relationship is well defined but distinctly nonlinear; the reason for the relationship is not obvious, but is reported here as an interesting observation.

Relation 4

Figure 4 indicates that the extinction angle *Z^c* is determined mainly by the ratio $\alpha_p(\mathrm{Ob})/\alpha_p(\mathrm{Onb})$, and the relationship is approximately linear: $Z\wedge c = -350\ \alpha_p(\mathrm{Ob})/\alpha_p(\mathrm{Onb}) + 420$. The nonbridging oxygen atom O2 is strongly undersaturated in the sense of Pauling's second rule, regardless of pyroxene composition. Sums of Pauling bond-strengths reaching the O2 site vary from 1.58 *e* in diopside to 1.75 *e* in CaTs. The bridging O3 atom is oversaturated regardless of composition. Sums of Pauling bond-strengths reaching the O3 site vary from 2.25 *e* in CaTs and jadeite to

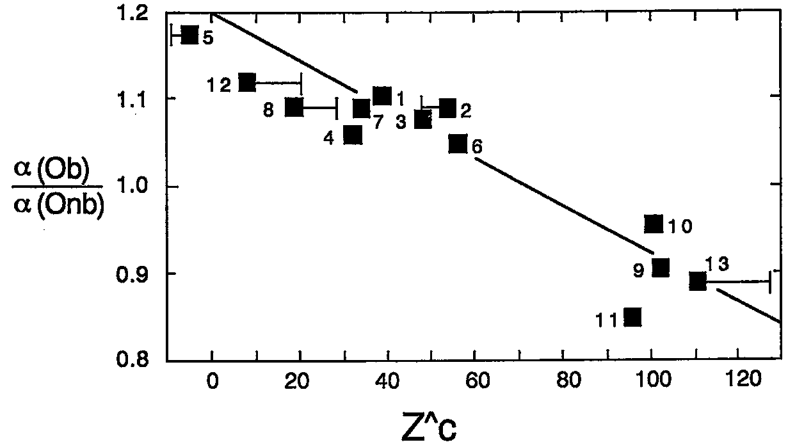

FIG. 4. Ratio of $\alpha_p(\mathrm{Ob})/\alpha_p(\mathrm{Onb})$ *versus* extinction angle, *Z^c* (in degrees). The filled squares are for extinction angles, *Z^c*, calculated in this study from point-dipole theory. The short vertical bars are for observed extinction angles from Table 1. Where an observed extinction angle is not indicated for a particular clinopyroxene, the calculated extinction angle (from point-dipole theory) and the observed extinction angle (Table 1) are nearly the same. Data points are numbered according to listing in Table 1.

2.50 *e* in diopside. The relationships in Figure 4 are consistent with transfer of electron density so as to better satisfy the bond-strength requirements of the O2 and O3 oxygen atoms. To increase the α_p(Ob)/α_p(Onb) ratio (and hence decrease Z^c), the desired transfer of electron density would be toward the O2 oxygen atoms and away from the O3 oxygen atom. A trivalent transition-series cation (Sc, Cr, Fe) at *M1*, coupled with a monovalent cation (Na, Li) at *M2*, produces a low α_p(Ob)/α_p(Onb) value and high extinction angles. Ca at *M2*, regardless of the *M1* site occupancy, or Al at *M1*, regardless of *M2* or *T* site occupancy, produces a high α_p(Ob)/α_p(Onb) value and, consequently, a lower extinction angle.

CONCLUSIONS

Electronic polarizabilities were determined for the constituent atoms of a wide range of compositions of *C2/c* pyroxene. The calculations show the following:

1. For an element present in more than one structure, α_p can vary considerably from one structure to another, in ways that are not clearly related to chemical or structural variations.

2. For each structure, the total electronic polarizability, K_{P-D}, summed from calculated values of α_p (Table 2), is consistently less by approximately 5% than the sum of α_p values, K_{L-L}, calculated from the Lorentz–Lorenz relation with observed indices of refraction. The discrepancy is ascribed to inadequacy of the Lorentz–Lorenz relationship to account for anisotropy and for covalency.

3. The behavior of α_p(Onb) and α_p(Ob) indicates that the electronic polarizability of oxygen depends very much on the atomic number of the cations coordinated to the oxygen, thus providing a reason for the non-transferability of electronic polarizabilities.

4. The value of the optic axial half-angle, V_γ, depends on $\alpha_p(T)$. The relationship is well defined but distinctly nonlinear, such that V_γ decreases with increasing $\alpha_p(T)$.

5. The extinction angle Z^c depends on the ratio of α_p(Ob)/α_p(Onb). The relationship is approximately linear, $Z\wedge c = -350\ \alpha_p(\mathrm{Ob})/\alpha_p(\mathrm{Onb}) + 420$. The cause is not obvious, but possibly involves inductive transfer of electron density from O3 atom to the O2 atom.

The calculated electronic polarizabilities (Table 2) may soon make possible reasonably accurate predictions of the optical properties of hypothetical compositions of clinopyroxene, and optical properties of clinopyroxenes at high temperatures and high pressures (see Arndt 1994). Electronic polarizabilities can be a useful guide to covalent bonding in minerals (Lasaga & Cygan 1982, Jaffe 1988, Eggleton 1991).

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