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A NOTE ON THE STRAIN-DEPENDENCE OF REFRACTIVE INDEX IN CRYSTALS

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The refractive index of a substance is closely related to the atomic property of polarizability. In any study of the strain-dependence of refractive index, one must ultimately consider the strain-dependence of the polarizability. In a previous paper (1) this author presented a mathematical expression governing polarizability. Subsequently, it was discovered that the expression could be simplified, and that it then became nearly identical to the result obtained by earlier authors. Here, the mathematical simplification is presented, and a few comments on the physical significance of the result are offered.

Polarizability is fundamentally a measure of the distortion produced in the electron distribution within the refracting substance by the incident light wave. Formally, polarizability may be defined by the relation

$$E' = -\tfrac{1}{2}\alpha F^2.$$

Here, E' is the increment to the steady-state energy of the system. This increment is due to the interaction of the electrons and the electric field associated with the light wave. The field strength is F, the polarizability is α. The relation is valid for static fields and for alternating fields (light), so long as the frequency is below the value necessary to excite the electrons to a more nearly permanent higher energy state; i.e., below an absorption band.

Polarizability may be approximately calculated from a knowledge of the electron distribution. The formula given below relates the polarizability of a single bonding electron to its wave function; this is the mathematical expression mentioned in the first paragraph. The formula was derived in a dissertation (2).

$$\alpha = -\frac{8\pi^2 me^2}{h^2}\,\frac{\left[\int\int\int_{-\infty}^{+\infty} \psi^2 z^2 dxdydz\right]^2}{\int \psi z \dfrac{\partial\psi}{\partial z}\, dxdydz}. \qquad (1)$$

As written here, a minus sign appears before the right side; an error was made in the original derivation. Also, the more conventional ψ has been used for the electron distribution function, instead of ϕ. The proton mass is m; the electron charge is e; Planck's constant is h.

The denominator may be integrated by parts. We have the formula

$$\int udv = uv - \int vdu.$$

We substitute as follows:

$$u = z \qquad dv = \psi \frac{\partial \psi}{\partial z} dz$$

$$du = dz \qquad = \psi d\psi - \psi \frac{\partial \psi}{\partial x} dx - \psi \frac{\partial \psi}{\partial y} dy.$$

We at first integrate with respect to z, while we hold x and y constant.

$$dv = \psi d\psi \quad \text{or} \quad v = \frac{\psi^2}{2} + C$$

We then obtain the relation:

$$\iiint_{-\infty}^{+\infty} \psi z \frac{\partial \psi}{\partial z} dxdydz = \iint_{-\infty}^{+\infty} \left[\frac{\psi^2}{2} z \right]_{-\infty}^{+\infty} dxdy - \frac{1}{2} \iiint_{-\infty}^{+\infty} \psi^2 dxdydz.$$

The first term on the right vanishes, since ψ^2 varies essentially as $\exp(-\sqrt{x^2+y^2+z^2})$ and thus goes to zero much faster than z tends to infinity. The second term is simply $-[(\frac{1}{2}) \cdot 1]$ or $-\frac{1}{2}$, because ψ was assumed normalized in the original derivation.

Returning to equation (1), we obtain a new result:

$$\alpha = \frac{16\pi^2 me^2}{h^2} \left[\iiint_{-\infty}^{+\infty} \psi^2 z^2 dxdydz \right]^2.$$

This integral represents the second moment of the electronic charge distribution, again of a single electron. Since we have assumed a normalized ψ, the integral also represents the mean square deviation of the electron from its average position, i.e., $\overline{(z-\bar{z})^2}$.

The quantity $16\pi^2 me^2/h^2$ is equal to $4/a_0$, where a_0 is the Bohr radius for a hydrogen atom in the ground state. We may then substitute and obtain the new relation:

$$\alpha = \frac{4}{a_0} [\overline{(z - \bar{z})^2}]^2 \tag{2}$$

This is now similar to the expression given by Hirschfelder (3), based on work by Hylleraas (4), Hasse (5), and Kirkwood (6), which is:

$$\alpha = \frac{4N}{a_0} [\overline{(z - \bar{z})^2} - (N - 1)\overline{(z_1 - \bar{z})(z_2 - \bar{z})}]^2. \tag{3}$$

The total number of electrons considered is N. The term in z_1 and z_2 represents the mean correlation between two electrons. If we consider only one electron, equation (3) reduces to equation (2).

Abbott and Bolton (7) have observed that polarizability may be proportional to the fourth power of a linear dimension. This may be seen from equation (2) if it is assumed that it is possible to expand or contract a bound electron's wave function uniformly. It might be expected that bonding electrons in a covalent crystal would approximate such behavior. A covalent electron circulates around at least two nuclei, so its wave function is more directly affected by any change in internuclear spacing. We would not expect any simple first-order effect in ionic crystals. In the idealized, simplified covalent crystal, a reduction in internuclear spacing, perhaps caused by externally applied stress, would lead to a rapid reduction in polarizability.

Polarizability is commonly related to refractive index by the somewhat empirical Lorentz-Lorenz formula

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi L}{3M} \alpha\rho.$$

Here, L is Avogadro's number, ρ is density, and M is the molecular weight associated with the unit for which α is defined. This formula, as well as that of Drude and of Kurz and Ward, contains a term in $\alpha\rho$. A third power dependence of α upon a linear dimension, i.e., an inverse first power dependence upon density, would lead to no change in refractive index upon compression of the substance. A fourth power dependence would lead to a reduction in the index upon compression.

In equation (3), the correlation terms in z_1, z_2 are of significance because of the mutual repulsion of electrons. These terms would become more significant as the interatomic distance is reduced. As a qualitative estimate, one might expect that repulsion between electrons would tend to prevent proportional collapse of the wave function with reduction in internuclear spacing. This would mean that polarizability would not decline in accord with the fourth power of the internuclear spacing. It is inadvisable, however, to draw any conclusions from this crude reasoning. The actual disposition of electronic wave functions and dependent properties is often entirely nonintuitive.

No rigorous calculations of the strain-dependence of polarizability have been made for any system more complex than the hydrogen molecule. Furthermore, experimental determinations of $\partial n/\partial\rho$ for such simple covalent crystals as diamond are too inaccurate to establish with certainty even the sign of the change.

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BERTRANDITE FROM MICA CREEK, QUEENSLAND

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Bertrandite, $Be_4(OH)_2Si_2O_7$, a mineral whose occurrence in Australia has not previously been recorded, has been observed in a beryl-bearing pegmatite from the Mica Creek area, near Mt. Isa, Queensland. Specimens of this pegmatite were submitted to the Mineragraphic Investigations section of the Commonwealth Scientific and Industrial Research Organization by Mr. A. K. Denmead, Chief Geologist of the Queensland Geological Survey. An analysis of one of the specimens was reported as follows:

SiO_2	54.9
Al_2O_3	17.7
Fe_2O_3	2.6
BeO	13.1
MgO	0.9
CaO	—
K_2O	3.9
H_2O^+	5.2
H_2O^-	0.2
Total	98.5 wt. per cent

The analyzed specimen is a micaceous pseudomorph after beryl, but, despite the extensive alteration, the analysis shows 13.1 per cent BeO, compared with 13.4 per cent BeO previously found for unaltered beryl from the same locality. The other specimens are mostly composed of massive mica, without apparent beryl, and such material has been reported to assay up to 14.1 per cent BeO.

Examination of thin sections has shown that the specimens consist of bertrandite, residual beryl, abundant fine-grained mica, quartz, albite, and limonitic material. Bertrandite contains 42.0 per cent BeO, which explains the high BeO contents reported in the analyses.