able on compressibilities, it is a a similar relationship is true for silicate minerals data are availauartz, but the compressibility of entical to that for α quartz (both is only 30% greater than that of a t 600°C); also, the compressistalline and glassy diabase are ntical at 25°C [Birch, 1966]. No γ data are available for diopside ss, so that in the following treateen necessary to use the crystal es for these minerals under the at they do not differ significantly es for the glasses.

TIVE INDEX CALCULATIONS

o dielectric theory, the refractive molar volume (V) of a condensed related by a general molar refrac-

$$= V/[\beta + 4\pi/(n^2 - 1)]$$
 (2)

etually the sum of the individual zabilities of the constituent ions their mole fractions and is concesses in which the polarizabilities ge [*Ritland*, 1955]. The 'overlap ter β is a measure of the nearesteraction field and must be determentally; the limiting values of β /3. In the case of point dipoles in a rbic lattice the nearest-neighbor innishes and only the 'distant-neighntz field is effective; $\beta = 4\pi/3$ and fraction law can be written

$$= V(n^{2} - 1)/(n^{2} + 2)$$
(3)

Lorentz-Lorenz refraction equation 6]. When large deformable ions are here is an 'overlap' nearest-neighbor osite sign, which reduces the polariaction; when this field equals the d, $\beta = 0$, and the refraction law ply

$$R_{\rm D} = V(n^2 - 1) \tag{4}$$

te Drude refraction equation. (R_{LL} $4\pi/3$ and 4π times the R defined 2.) Equations 3 and 4 are discussed and Gurney [1940] and Ritland o show that they are limiting laws

PERMANENT COMPRESSION OF SILICATE GLASSES

for the refractive index-volume correlation for a given substance. Anderson and Schreiber [1965] have shown that a plot of mean refractive index versus uncompressed density for silicates of different composition also obeys equation 2, with a value of β close to zero; this does not require, however, that β have such a value, or be the same, for compression of the individual silicate phases.

Since the values of β for diopside and albite glass are not known, calculations for these glasses were made by using both equation 3 and equation 4 as limiting laws for the n-V relation. For SiO₂ glass, however, the value of β can be evaluated from the recent precise data of Arndt and Stöffler [1968] on n and ρ (density) of permanently densified silica glass obtained at pressures and temperatures to 60 kb and 700°C. They observed an approximately linear relationship over their entire range of densities ($\rho = 2.200$ to 2.526); their data on 120 samples give a least-squares relationship $n = 0.196\rho + 1.026$ (J. Arndt, personal communication). (The older data of Cohen and Roy [1962] on eleven samples give the same relationship.) Using their data with equation 2 gives the overlap field parameter as

β (SiO₂ glass) = 1.37

which reproduces the index values to four decimal places over the range $\rho = 2.2$ to 2.6. *Ritland* [1955] obtained $\beta = 0.5$ for a borosilicate glass, in changing the density by heat treatments. (It should be noted that literature statements that the molar refraction of SiO₂ glass changes with compression [*Cohen and Roy*, 1961, 1962, 1965; *Vedam et al.*, 1966] are based on *defining* the molar refraction according to equation 3 or 4, i.e. for an a priori assumption as to the value of β , which, in fact, does not match the data at zero pressure.)

Compressibility Data

The compressibility parameters have been evaluated in the usual form

$$\Delta V/V_0 = -(aP - bP^2)$$

(5)

where $\Delta V = V - V_{\circ}$ and the compressibility (referred to V_{\circ}) is $\kappa = a - 2bP$. For diopside the data of Bridgman on $\Delta V/V_{\circ}$ at 25°C and 0-40 kb [*Birch*, 1966] were plotted as ($\Delta V/V_{\circ}$) (1/P) versus P and found to be linear; a and b were obtained by the least-squares method. For albite the data of Yoder at 25°C and 2–10 kb, as tabulated by Birch, were converted to the a and b form in equation 4.

SiO₂ data are available for the glass over a range of temperature. Both *a* and *b* were plotted versus t (°C), and it was found that the data fall into two groups, each of which gives a highly linear plot for each parameter. The first group includes the data of *Birch and Law* [1935] and *Birch and Dow* [1936], who measured linear compression from 0 to 10 kb at temperatures up to 390°C. A least-squares fit to their data gives

$$10^6 a = 2.58 - 3.8 \times 10^{-4} t \tag{6}$$

$$10^{12}b = -34.1 + 6.7 \times 10^{-2}t \tag{7}$$

with units of $t^{\circ}C$ and κ in reciprocal bars and with the values from the original references (the data from these two papers are incorrectly referenced in Birch [1966]). Older data by Adams and Gibson, and Bridgman, measured at room temperature (cited by Birch and Law [1935]) agree with the more recent values of Reitzel et al. [1957], who obtained similar linear relationships by linear compression in the range 0-4 kb, 22°-259°C. Reitzel et al. obtained coefficients of 2.695 and -5.0×10^{-4} for the a equation, and -22.7 and $+4.2 \times 10^{-2}$ for the b equation. Both sets of data show the parameter b changing sign with temperature, at 510° (Birch) and 540°C (Reitzel); κ increases with pressure below this temperature and decreases with pressure at higher temperatures. Also, both sets of data show that the compressibility decreases with increasing temperature, in contrast to the normal effect. The differences between the two sets of data are not significant in the present calculations, and the data of Birch and co-workers, as given by equations 6 and 7, were used for extrapolation to higher temperatures (600°C) to obtain the 0- to 10-kb range compressibility coefficients.

To calculate $\Delta V/V_{\circ}$ at pressures above the measurement range, the quadratic equation (5) can be extrapolated. Generally, however, a better extrapolation for crystalline compounds (e.g., quartz) and metals is obtained from the Murnaghan logarithmic equation [Anderson, 1966], which can be written in terms of the

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