

Density and Refractive Index Hysteresis in Compressed Silicate Glasses

H. CRAIG¹

*Physikalisches Institut, Universität Bern
Bern, Switzerland*

The increased refractive index of diopside and albite glass, quenched from liquidus temperatures at pressures to 50 kb, can be accurately calculated from compressibility data on the crystals at 25°C and the Lorentz-Lorenz refraction law. The results indicate that the pressure effect is locked in by 'configurational trapping' on cooling through the glass point, but thermal relaxation takes place with the thermal expansion coefficient characteristic of the applied pressure. The resulting permanent compression is therefore that predicted at 25°C and load pressure. Permanent compression of glasses at temperatures below the glass point should be that predicted at load pressure and (1) 25°C, if temperature is released before pressure, or (2) run temperature, if pressure is released before temperature, because thermal relaxation then takes place with the low-pressure thermal expansion coefficient. For SiO₂ the glass compressibility is known as a function of temperature, and the overlap field parameter ($\beta = 1.37$) can be established from other data. Refractive indices of SiO₂ glass compressed at various P and T with varying quenching cycles are consistent with the values calculated for permanent compression when $T > \sim 500^\circ\text{C}$. At lower temperatures the compression is partly elastic and the resultant indices are thus lower than expected. In all these glasses, configurational trapping of pressure deformation is adequate to explain the permanent compression. The direct relationship of permanent compression with compressibility shows that the model of H. M. Cohen and R. Roy (1961, 1965), based on second-order structural changes at high P followed by elastic decompression, is not necessary to explain any of the existing data.

INTRODUCTION

Bridgman and Simon [1953] discovered that glasses display imperfect volume elasticity at large hydrostatic pressures and suffer permanent changes in density proportional, within limits, to the applied pressure. Because crystalline inorganic solids exhibit perfect elasticity, this effect was quite unexpected, and Bridgman and Simon established several important characteristics of the behavior of compressed glasses: (1) SiO₂ glass at room temperature has an elastic limit that must be exceeded before permanent deformation occurs; (2) both the elastic limit and the permanent compressibility decrease progressively when ions such as sodium are added to SiO₂; (3) the permanent compressibility of SiO₂ is greater at higher temperature; and (4) the density increase is

achieved by folding up the vitreous network of the glass so that the Si-O bond angles are altered although the nearest neighbor Si-O distances appear to remain unchanged. The folded structures are mechanically stable at room temperature, but the original density can be restored by annealing at high temperatures. The annealing effect is similar, though opposite in sign, to the increase of density observed in annealing rapidly chilled glasses at ordinary pressure. Bridgman and Simon therefore suggested that there exists an equilibrium configuration for a glass at any temperature and that both high- and low-density metastable states, characterized by the trapping of displaced atoms behind relatively strong potential barriers, can exist.

Cohen and Roy [1961] showed that the permanent densification of SiO₂ and other glasses is accompanied by an increased refractive index, which they found to be continuously proportional to pressure at temperatures greater than 500°C. At room temperature they found a threshold pressure of about 20 kb for SiO₂ glass,

¹ On leave from University of California at San Diego, La Jolla, California, to which the author has now returned.

eresis in

77

quenched from liquidus tem-
n compressibility data on the
alts indicate that the pressure
h the glass point, but thermal
characteristic of the applied
t predicted at 25°C and load
ow the glass point should be
s released before pressure, or
e, because thermal relaxation
cient. For SiO₂ the glass com-
lap field parameter ($\beta = 1.37$)
glass compressed at various P
dues calculated for permanent
mpression is partly elastic and
e glasses, configurational trap-
ment compression. The direct
ows that the model of H. M.
ral changes at high P followed
existing data.

olding up the vitreous network of
that the Si-O bond angles are
ugh the nearest neighbor Si-O dis-
t to remain unchanged. The folded
e mechanically stable at room tem-
t the original density can be re-
nealing at high temperatures. The
ect is similar, though opposite in
increase of density observed in
apidly chilled glasses at ordinary
idgman and Simon therefore sug-
there exists an equilibrium con-
or a glass at any temperature and
high- and low-density metastable
eterized by the trapping of displaced
ad relatively strong potential bar-
ist.

d Roy [1961] showed that the per-
sification of SiO₂ and other glasses
ied by an increased refractive index.
found to be continuously propor-
ressure at temperatures greater than
room temperature they found a
ressure of about 20 kb for SiO₂ glass.

considerably lower than the value reported by
Bridgman and Simon.

Boyd and England [1963] have observed
similar increases in the refractive indices of
glasses of albite (NaAlSi₃O₈) and diopside
(CaMgSi₂O₆) quenched from above the liquidus
at high pressures; their experiments were done
with a solid pressure-medium apparatus in
which samples could be rapidly quenched to low
temperatures at pressure [Boyd and England,
1960]. They found a continuous increase of
refractive index with applied pressures of up
to 50 kb. These experiments are similar to the
experiments of Tammann [1933, p. 66 ff.], who
supercooled liquids at different pressures and
observed glasses with different volumes when
the pressures were released. That is, the ob-
served increase in refractive index of a glass
reflects, at least to some extent, the density
increase due to the permanent compressibility.
A large body of theoretical and experimental
work on glasses has developed since Tammann's
work, but no quantitative discussion of the
effects of permanent compression on density
and refractive index of glasses has been at-
tempted. In this paper I describe a very simple
model that reproduces the observations on
albite, diopside, and quartz glass with remark-
able success.

THERMODYNAMIC CONSIDERATIONS

In applying the normal thermal and mechan-
ical coefficients to thermodynamic calculations
on glasses, it must be recognized that these
coefficients are not uniquely defined, since a
glass, by definition, is not a stable thermo-
dynamic phase in internal equilibrium. Rigor-
ously defined, a glass is a supercooled disordered
phase in which the configurational contributions
to its properties have been frozen out at a
higher temperature [Jones and Simon, 1949;
Davies and Jones, 1953; Stevels, 1962]. Thus
we can describe volume changes by the usual
equation

$$d \ln V = \alpha dT' - \kappa dP \quad (1)$$

where α is the thermal expansion coefficient and
 κ is compressibility. The values of α and κ will,
however, normally vary somewhat with the
history of the glass even at temperatures at
which vibrational contributions dominate the
configurational effects. At higher temperatures

at which configurational changes can occur, e.g.
during a thermal process, the coefficients will
also vary with the rate at which the process is
carried out.

Tammann [1933] showed that the configura-
tional quenching that produces a glass occurs
at a viscosity of 10¹³ poises in all glass-forming
substances; this viscosity is encountered at a
characteristic transformation temperature or
'glass point' at which the viscous relaxation time
is of the order of minutes or less and second-
order transitions occur. A schematic illustra-
tion of the effects on compressibility and vol-
ume, which are of particular concern in the
discussion to follow, is shown in Figure 1. In
all glasses the compressibility and heat capa-
city decrease rapidly on cooling through the
glass point; the thermal expansion coefficient
shows a similar discontinuity but can increase
or decrease [Davies and Jones, 1953]. As the
liquid supercools below T_M , however, the volume,
entropy, and other state functions are contin-
uous across T_M and T_G ; between these tem-
peratures the liquid is a metastable, equilibrium
phase, but below T_G the glass is an unstable
phase because it retains the high-temperature
configuration frozen in at T_G . The dashed lines

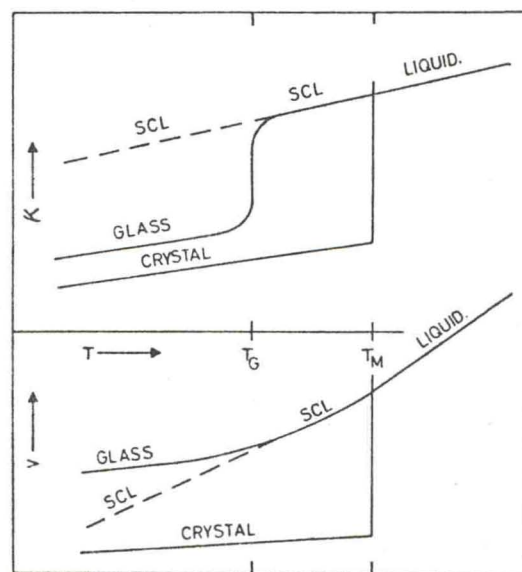


Fig. 1. Variation of compressibility and volume
with temperature in crystal, liquid, and super-
cooled liquid (SCL). T_M is the melting point and
 T_G is the glass point.

in Figure 1 show the equilibrium paths of supercooled liquid below T_g ; this liquid continues to maintain internal equilibrium and is metastable relative to the solid. At normal pressure the volume of the glass is greater than that of the supercooled liquid, and at constant temperature all fluctuations will tend to decrease the volume (and increase the compressibility) to those of the supercooled liquid phase at the same temperature. On the other hand, if the glass is rapidly compressed, the volume can be made less than that of the supercooled liquid, and, on release of pressure, fluctuations will tend to increase it irreversibly toward the liquid volume at a rate dependent on temperature. The equilibrium configuration suggested by Bridgman and Simon, which can be approached from both high- and low-density states, thus corresponds to the supercooled liquid at the same temperature.

The temperature T_g is to some extent a function of the cooling rate, so that the compressibility, thermal expansion, and volume of the glass will vary somewhat depending on the conditions under which the glass is formed and on the extent to which the glass has been annealed. For borosilicate and lime glasses and normal silicates, such as diopside and albite, T_g is about 550°C, but for SiO₂ glass it is 1200°C. In addition, T_g is a function of pressure because it actually defines a viscosity. If the temperature and pressure dependence of viscosity are assumed to be of the form $\exp(E/RT)$ and $\exp(AP)$, respectively, and if the crude estimates of $E = 100$ kcal/mole and $A = 10^{-4}$ bar⁻¹ [Clark, 1966] are used, then dT/dP for constant viscosity is about 1°C/kb as the approximate P - T slope of T_g . Thus, in the measurements of Boyd and England on diopside and albite at pressures up to 50 kb T_g remains well below the liquidus at all pressures and increases by only some 50°C at the highest pressures.

The compressibility variation shown in Figure 1 indicates that κ for the glass is much closer to the value for the crystal than to the equilibrium value of the supercooled liquid. This relationship is observed for α and heat capacity [Davies and Jones, 1953, pp. 378-379]; it reflects the loss of the configurational contribution to the liquid coefficients and the fact that the remaining contribution is principally vibrational in both glass and crystal. Although very few

data are available on compressibilities, it is a fair guess that a similar relationship is true for κ . For natural silicate minerals data are available only for quartz, but the compressibility of SiO₂ glass is identical to that for α quartz (both at 25°C) and is only 30% greater than that of β quartz (both at 600°C); also, the compressibilities of crystalline and glassy diopside are essentially identical at 25°C [Birch, 1966]. No compressibility data are available for diopside and albite glass, so that in the following treatment it has been necessary to use the crystal compressibilities for these minerals under the assumption that they do not differ significantly from the values for the glasses.

REFRACTIVE INDEX CALCULATIONS

According to dielectric theory, the refractive index (n) and molar volume (V) of a condensed phase can be related by a general molar refraction function

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

where R is actually the sum of the individual molar polarizabilities of the constituent ions multiplied by their mole fractions and is constant for processes in which the polarizabilities do not change [Ritland, 1955]. The 'overlap field' parameter β is a measure of the nearest-neighbor interaction field and must be determined experimentally; the limiting values of β are 0 and $4\pi/3$. In the case of point dipoles in a random or cubic lattice the nearest-neighbor interaction vanishes and only the 'distant-neighbor' or Lorentz field is effective; $\beta = 4\pi/3$ and the molar refraction law can be written

$$R_{LL} = V(n^2 - 1)/(n^2 + 2) \quad (3)$$

which is the Lorentz-Lorenz refraction equation [Brown, 1956]. When large deformable ions are considered, there is an 'overlap' nearest-neighbor field of opposite sign, which reduces the polarization interaction; when this field equals the Lorentz field, $\beta = 0$, and the refraction law becomes simply

$$R_D = V(n^2 - 1) \quad (4)$$

which is the Drude refraction equation. (R_{LL} and R_D are $4\pi/3$ and 4π times the R defined in equation 2.) Equations 3 and 4 are discussed by Mott and Gurney [1940] and Ritland [1955], who show that they are limiting laws

for the
a given
[1965]
fractiv
silicate
equatio
this d
such a
of the
Sing
glass
glasses
equatio
tion. I
can be
of A
(densi
obtain
and 7
linear
densit
120 s
 $n =$
munie
Rog
relativ
gives

which
decim
Ritlan
cate
treat
stater
glas
Rog
are 0
cordin
assum
does

The
CRAIG

where
the
the
0.40

able on compressibilities, it is a similar relationship is true for silicate minerals data are available for quartz, but the compressibility of quartz is only 30% greater than that of glass at 600°C; also, the compressibilities of crystalline and glassy diopside are identical at 25°C [Birch, 1966]. No data are available for diopside glasses, so that in the following treatment it is necessary to use the crystal data for these minerals under the assumption that they do not differ significantly from the glasses.

REFRACTIVE INDEX CALCULATIONS

From dielectric theory, the refractive index n is related to the molar volume (V) of a condensed material by a general molar refrac-

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

where β is actually the sum of the individual polarizabilities of the constituent ions weighted by their mole fractions and is a measure of the polarizability of the material [Ritland, 1955]. The 'overlap' parameter β is a measure of the nearest-neighbor interaction field and must be determined experimentally; the limiting values of β are $4\pi/3$. In the case of point dipoles in a cubic lattice the nearest-neighbor interaction vanishes and only the 'distant-neighbor' field is effective; $\beta = 4\pi/3$ and the Lorentz-Lorenz law can be written

$$n^2 = V(n^2 - 1)/(n^2 + 2) \quad (3)$$

the Lorentz-Lorenz refraction equation [6]. When large deformable ions are present there is an 'overlap' nearest-neighbor interaction, which reduces the polarizability; when this field equals the distant-neighbor field, $\beta = 0$, and the refraction law reduces to the Drude equation.

$$R_D = V(n^2 - 1) \quad (4)$$

the Drude refraction equation. (R_D is $4\pi/3$ and 4π times the R defined by equation 2.) Equations 3 and 4 are discussed by Gurney [1940] and Ritland [1955] to show that they are limiting laws

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 SiO_2 glass, however, the value of β can be evaluated from the recent precise data of Arndt and Stöfler [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

$$\beta(\text{SiO}_2 \text{ glass}) = 1.37$$

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 SiO_2 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

$$\Delta V/V_0 = -(aP - bP^2) \quad (5)$$

where $\Delta V = V - V_0$ and the compressibility (referred to V_0) is $\kappa = a - 2bP$. For diopside the data of Bridgman on $\Delta V/V_0$ at 25°C and 0-40 kb [Birch, 1966] were plotted as $(\Delta V/V_0)$

($1/P$) 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.

SiO_2 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

$$10^6 a = 2.58 - 3.8 \times 10^{-4} t \quad (6)$$

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

with units of t in °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 $\Delta V/V_0$ 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

TABLE 1. Compressibility Parameters ($\kappa = \text{bar}^{-1}$) and Calculated Volume and Refractive Index Effects at 50 kb

Substance	$10^4 a$	$10^{12} b$	Calculated: 50 kb		
			$(\Delta V/V_0), \%$	$(\Delta n/n_0), \%$	$(\Delta n/n_0)$
Diopside, 25°C (0-40 kb, 25°C)*	0.92	+3.0	-4.0 ^{a,b}	2.0 ^c	-2.0
Albite, 25°C (2-10 kb, 25°C)*	2.11	+21.6	-7.2 ^a	3.0 ^c	-2.4
SiO ₂ glass, 25°C (0-98 kb, 25°C)*	...	...	-13.6 ^d	4.7 ^e	-2.9
SiO ₂ glass, 600°C (0-10 kb, 11-390°C)*	2.35	+6.1	-10.4 ^{a,b}	3.4 ^e	-3.0

* P and T range of compressibility measurements.^a Murnaghan equation.^b Quadratic equation.^c Lorentz-Lorenz equation.^d Measured at 49 kb [Bridgman, 1948].^e Equation 2, $\beta = 1.37$.

measured quadratic parameters as

$$\ln \left(\frac{V}{V_0} \right) = \frac{-\ln \{1 + [(2b/a^2) - 1]aP\}}{[(2b/a^2) - 1]} \quad (8)$$

Both equations were used to extrapolate the albite volume compression above 10 kb. For diopside in the extrapolation range 40-50 kb, the volume compressions calculated from (5) and (8) do not differ significantly.

At room temperature neither the quadratic nor the Murnaghan equation gives a correct extrapolation of the SiO₂ glass compression above 10 kb, as can be seen by comparing the volumes extrapolated by using the quadratic parameters with the volume compression measured by Bridgman [1948] from 0 to 100 kb. The volumes extrapolated with (5) and (8) go to zero at $P = 140$ and 36 kb, respectively, whereas the volume compression measured by Bridgman is only 20.2% at 98 kb. That is, the compressibility of SiO₂ glass at room temperature increases with pressure up to about 35 kb, and beyond this pressure it decreases as in a normal substance. This effect was measured by Bridgman several times. For the calculations at room temperature, the volume compression data measured by Bridgman [1948] from 0 to 100 kb were therefore used. For the high-temperature calculations, however, no data on SiO₂ glass are

available above 10 kb, and it was necessary to use the high-temperature quadratic parameters, extrapolated (to 600°C) from equations 6 and 7, for extrapolation to pressures above 10 kb with equations 5 and 8. Since the initial compressibility decreases with pressure in the normal manner above 510°C, as shown by (7), the high-pressure extrapolation at 600°C should be adequate, and, in fact, both the quadratic and the Murnaghan equations give essentially identical volume compression along the 600°C isotherm.

The compressibility parameters used for the three minerals at the indicated temperatures are given in Table 1, together with the magnitude of the calculated volume and refractive index variations at 50 kb. The fractional volume change is seen to be of the order of 2 to 3 times the fractional index change for all three substances and at both temperatures for SiO₂.

CALCULATIONS FOR DIOPSIDE AND ALBITE

The refractive index was calculated as a function of pressure by using the Lorentz-Lorenz equation (3) and the V/V_0 values from both the quadratic and the Murnaghan equations, under the assumption of constant molar refractivity. (The quadratic and Murnaghan equations give identical results for diopside over

lated Volume and Refractive Index

Calculated: 50 kb

%	$(\Delta n/n_0)$, %	$(\Delta V/V_0)$
		$(\Delta n/n_0)$
b	2.0 ^c	-2.0
	3.0 ^c	-2.4
	4.7 ^c	-2.9
b	3.4 ^c	-3.0

above 10 kb, and it was necessary to high-temperature quadratic parameters, (to 600°C) from equations 6 and extrapolation to pressures above 10 kb equations 5 and 8. Since the initial compressibility decreases with pressure in the manner above 510°C, as shown by (7), pressure extrapolation at 600°C should be made, and, in fact, both the quadratic and Murnaghan equations give essentially the same volume compression along the 600°C

compressibility parameters used for the minerals at the indicated temperatures are in Table 1, together with the magnitude of the calculated volume and refractive index at 50 kb. The fractional volume change is seen to be of the order of 2 to 3 percent and the fractional index change for all three minerals and at both temperatures for SiO_2 .

CALCULATIONS FOR DIOPSIDE AND ALBITE

The refractive index was calculated as a function of pressure by using the Lorentz-Lorenz equation (3) and the V/V_0 values from both the quadratic and the Murnaghan equations, under the assumption of constant molar refraction. (The quadratic and Murnaghan equations give identical results for diopside over

the small extrapolation range above 40 kb but deviate considerably for albite at high pressures.)

It should be noted that the *only* input data are the compressibility parameters a and b (Table 1) and the values of n_0 (the index of the original uncompressed glass). The values of n_0 measured by Boyd and England on the glass used for their compression runs are 1.488 for albite glass and 1.604 for diopside glass (they give 1.603 in text and 1.605 in their Figure 7; the average has been used). The calculated values of n_{LL} from 0 to 50 kb are shown in Figure 2, together with all measured values by Boyd and England [1963]. The errors shown on the measured data are their uncertainty limits of ± 0.002 on the indices and $\pm 5\%$ on (load) pressure.

The fit of the calculated indices to the measurements is remarkably good, even for albite for which the compressibility parameter are measured only to 10 kb (solid part of the calculated curve). Although both compressibility equations (equations 5 and 8) fit the albite data surprisingly well, the Murnaghan equation is clearly superior, as would be expected from the comparisons given by Anderson [1966]. The average deviation of the measured points from the calculated curves is ± 0.0010 for diopside and ± 0.0018 for albite, and some of the deviation is clearly due to scatter in the observations, especially for the albite data, which will not fit any smooth curve exactly. The indices calculated from the Drude equation are lower for both substances; the differences increase with pressure and reach 0.01 at 50 kb. Indices calculated for the empirical refraction laws of Gladstone and Dale and of Allen [Anderson and Schreiber, 1965] were found to be the same for both laws and to be close to the mean of n_{LL} and n_D at each pressure, in agreement with the fact that the latter two indices are calculated from the limiting refraction laws. It is possible that β is actually somewhat less than the Lorentz-Lorenz value of $4\pi/3$, as the compressibility data used are for the crystalline phase and are thus close to, but lower limits for, the glass compressibilities (Figure 1). If the glass compressibilities are significantly greater, the calculated indices would be increased so that the curve from the Drude equation would approach the observations. To raise the calculated Drude curve to match the Lorentz-Lorenz

curve for diopside in Figure 1, the compressibility must be increased by 50%. However, this question cannot be decided until compressibility and density data for the glasses are actually measured over a range of pressure. What is important is that the crystal compressibilities are *lower limits* and the n_{LL} curve is an *upper limit* for any compressibility, so that improvements in the data will not change the fact that the observations can be fit by a molar refraction law (always under the assumption that the refraction itself remains constant, which is reasonable on the basis of the structural observations of Bridgman and Simon).

INTERPRETATION OF DIOPSIDE-ALBITE RESULTS

The diopside-albite glass measurements are by far the most carefully controlled experimental data available. According to Boyd and England [1963], the albite glass samples were prepared chemically by two different methods and carefully dried at high temperatures; the diopside glass used was also synthetic and was dried even more stringently. The albite samples were

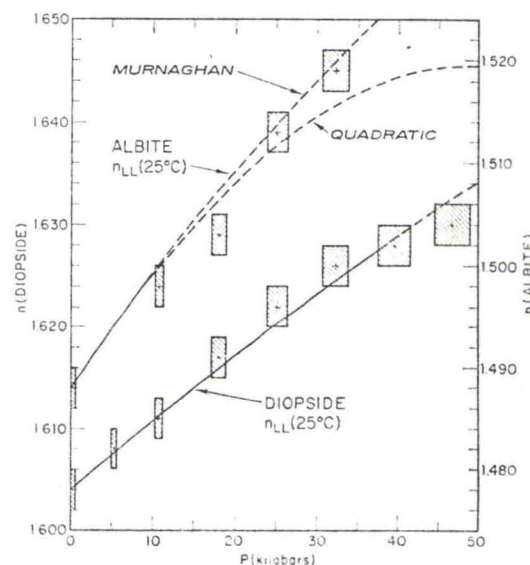


Fig. 2. Refractive indices of albite and diopside glass quenched from liquidus temperatures at the indicated pressures. The data of Boyd and England [1963] are shown by rectangles with dimensions according to their estimated precision. The curves are calculated from compressibilities that have been measured over the pressure range corresponding to the solid parts of curve and extrapolated into the dashed parts.

brought to pressure and temperature through both the solid and the liquid fields, and diopside samples were brought up to temperature at pressure through the crystalline field. All samples were temperature-quenched at pressures; with their apparatus, which has water cooling, the furnace temperature can be dropped to less than 500°C within 5 seconds [Boyd and England, 1960]. The glasses are quenched under pressure from above the liquidus (temperatures of 1100°–1850°C in their experiments), and the uniform relationships obtained from glasses of different history show that a highly reproducible effect is being observed.

If we assume that the agreement of calculated and measured effects shown in Figure 2 is not a coincidence, we must then ask why the quenched glasses are matched by the curve calculated for 25°C. The straightforward answer is that the total pressure effect is 'locked' into the glass, but the thermal effect is relieved during temperature release at load pressure. We know from equation 1 that $(\partial\alpha/\partial P) = -(\partial\kappa/\partial T)$, so that the volume change in taking an equilibrium phase from temperature and pressure T, P , to 25°, P , is the same as that along the path $(T, P), (T, 1 \text{ bar}), (25^\circ, 1 \text{ bar}), (25^\circ, P)$. This means that, if the pressure effect at T, P , is locked in, the pressure dependence of α is

such that samples quenched from a series of T, P , states will, in a P - V diagram, plot on a curve with an origin corresponding to V_0 (25°, 1 bar) and a slope proportional to the compressibility at 25°. The pressure effect is presumably locked in when the glass cools through the glass point; below this temperature the glass is no longer an equilibrium phase, but the approach to configurational equilibrium is so slow that volume effects can be discussed in terms of the usual parameters. However, small deviations due to slight variations of α and κ with cooling rate should occur, so that the relationship cannot be expected to be as exact as for an equilibrium phase.

It is worth noting that the fit observed in Figure 2 requires that not only the compressibility, but also its pressure dependence, be approximately correct. In fact, one sees that, although the curves fit the points with very small mean deviations, the slope in the diopside curve is not quite correct, especially at high pressures. With the same assumptions used previously, the calculation could be reversed to calculate the compressibility parameters from the observed indices. Carrying this through shows that a plot of $[f(n) - f(n_0)]/f(n)P$ versus P , where $f(n)$ is the Lorentz-Lorenz index function $(n^2 - 1)/(n^2 + 2)$, is linear except for a large deviation of the point at 10.8 kb. The intercept and slope of the plot give effective values of $10^6 a = 1.08$, $10^{12} b = 7.4$, and a calculated curve with a mean deviation of only 0.0005 in n , which indicates an effective compressibility very similar to that of the crystal but with a somewhat higher initial value and a greater pressure dependence. Both these differences are in the direction expected, but, more importantly, the improved fit shows that the observed indices are very consistent with the type of pressure dependence shown by normal substances, i.e. compressibility decreasing with increasing pressure.²

² Note added in press. F. R. Boyd has pointed out to me that in his experiments the quench is not absolutely isobaric; the actual load pressure at the glass point is somewhat lower than the nominal run pressure because of the rapid thermal contraction. He suggests that a fluid liquid, such as diopside at 1700°C, might record this pressure change, which would also account for the slight deviations of the 40- to 50-kb diopside points in Figure 2.

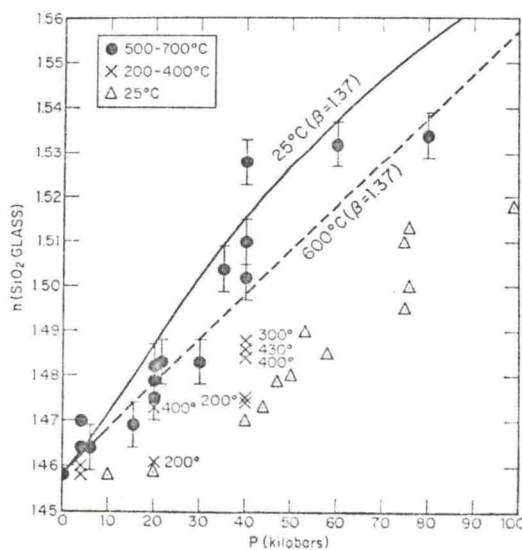


Fig. 3. Refractive indices of SiO_2 glass compressed at the indicated temperatures and pressures.

CALCULATIONS FOR SiO_2 GLASS

The refractive indices were calculated at 25° and 600°C for compression to 100 kb, for comparison with the measurements of *Cohen and Roy* [1961, 1965] and *Roy and Cohen* [1961], which were made along these two isotherms. The resulting n - P curves are shown in Figure 3 together with the measured data; additional measurements reported by *Cohen and Roy* [1961, Figure 2] at a few temperatures between their two isotherms are also plotted. The 25°C curve is based on the direct 0- to 100-kb volume compression measurements of *Bridgman* [1948], and the 600°C curve is based on the high-temperature quadratic parameters as described earlier, extrapolated above 10 kb by means of the Murnaghan equation. The quadratic equation gives essentially identical results. In both cases the high-pressure index is calculated from the index of the uncompressed glass, $n_0 = 1.458$ given by *Cohen and Roy*, by using equation 2 with $\beta = 1.37$. It should be noted that the SiO_2 glass compressibility decreases with increasing temperature, so that the 600°C curve falls below the 25°C curve, in contrast to the relationship in normal glasses. At the glass point, however, κ must increase markedly with temperature, and so there is a minimum compressibility at something like 800°–900°C and above 1200°C the curves will lie above the 25° curve in Figure 3.

Calculations were also made for the limiting equations (equations 3 and 4). An indication of the maximum range can be seen from the values at 50 kb, 600°C; $n_{LL} = 1.521$, $n_D = 1.502$, whereas $n = 1.508$ for $\beta = 1.37$ and is thus intermediate with a value proportional to the ratio of β to the maximum value $4\pi/3$.

The SiO_2 results show several marked features: (1) samples compressed at 500°–700°C plot generally in the range of the two isothermal curves; (2) samples compressed at 25°C have indices far lower than expected from the compressibility data; (3) samples compressed at intermediate temperatures have indices between the 25° and 600°C data and are considerably lower than the predicted values (which would lie between the 25° and 600°C isotherms).

The low-temperature data in Figure 3 are consistent with the observation of *Bridgman and Simon* [1953] that SiO_2 glass has a thresh-

old pressure or elastic limit that must be exceeded for permanent compression; the data of *Cohen and Roy* indicate this limit is about 20 kb at room temperature, and, as they noted, it disappears at temperatures of 500°C or higher. *Anderson* [1956] studied the compression of borosilicate glass in the range 4–7 kb, 100°–300°C, and showed that both reversible and irreversible volume changes, which he called densification and compaction, occur at these temperatures. SiO_2 glass showed no permanent compression at these pressures and temperatures. The data in Figure 3 are quite consistent with his results and indicate that at temperatures of 200°C and less SiO_2 glass is almost totally elastic at all pressures, so that even above the threshold pressure the permanent compression obtained is only a fraction of the actual volume change given by the compressibility. At 300°–400°C, the glass is partly elastic, so that at 40 kb the permanent compression is about half the total volume change corresponding to the compressibility. Both the elastic limit and the fraction of the deformation that is elastic or reversible decrease with increasing temperature and vanish at about 500°C. Accordingly, the discussion of the temperature-refractive index relationship is limited to temperatures above 500°C in the range in which the elasticity effects have vanished.

HIGH-TEMPERATURE SiO_2 DATA (500–700°C)

All data points in Figure 3 were picked off the plots of *Cohen and Roy* [1961] and *Roy and Cohen* [1961] and Figure 1 of *Cohen and Roy* [1965] as no tabulations have been published; the indicated precision is about ± 0.005 in the index and is estimated to be ± 10 kb in pressure [*Cohen and Roy*, 1965]. Some of the scatter in the index data is evidently due to their use of powdered glass samples with subsequent inhomogeneity. The large uncertainties in the data, coupled with the relatively close spacing of the two isotherms, makes it impossible to match the data to one or the other of the two isotherms, and, in fact, it appears that a scatter of points between the two isotherms should be expected because of variations in the quenching procedures. The quenching techniques used by *Cohen and Roy* [1961] are not described in their paper, but *Mackenzie* [1963, footnote 5] refers to a preprint of *Cohen and*

amples quenched from a series of will, in a P - V diagram, plot on a origin corresponding to V_0 (25°, a slope proportional to the constant 25°. The pressure effect is predicted in when the glass cools through; below this temperature the is no longer an equilibrium phase, but a transition to configurational equilibrium is possible. Volume effects can be discussed in terms of usual parameters. However, small variations of α and κ with pressure should occur, so that the fit cannot be expected to be as exact as for an equilibrium phase.

In noting that the fit observed in Figure 3 requires that not only the compressibility but also its pressure dependence, be correctly predicted, one sees that the calculated curves fit the points with very small deviations, the slope in the diopside plot is quite correct, especially at high pressures. With the same assumptions used in the calculation could be reversed to determine the compressibility parameters from the indices. Carrying this through a plot of $[f(n) - f(n_0)] / f(n) P$ where $f(n)$ is the Lorentz-Lorenz index $(n^2 - 1)/(n^2 + 2)$, is linear except for a deviation of the point at 10.8 kb. The intercept and slope of the plot give effective values of $10^6 a = 1.08$, $10^{12} b = 7.4$, and a curve with a mean deviation of only 0.001, which indicates an effective compressibility very similar to that of the crystal but with a somewhat higher initial value and a less pressure dependence. Both these differences are in the direction expected, but, more importantly, the improved fit shows that the indices are very consistent with the pressure dependence shown by normal glasses, i.e. compressibility decreasing with pressure.²

ded in press. F. R. Boyd has pointed out that in his experiments the quench is not exactly isobaric; the actual load pressure at the glass point is somewhat lower than the pressure because of the rapid thermal contraction. He suggests that a fluid liquid, such as water at 1700°C, might record this pressure drop which would also account for the slight deviation of the 40- to 50-kb diopside points in

^a Non drawn.
et al., 1983).
refracted
quench
in a by
showed
glass w
Lorentz
ment 10
60-10 k
in Fig.

trajectory to room temperature and pressure via the equilibrium supercooled phase, and A^* can be returned to A or by heating the liquid via D^* at then compressing it. The density with pressure and temperature are 1 to the equilibrium-phase κ and α 25°C and T , and at 1 bar and P . A^* is a reversible cycle involving of a glass instead of the supercooled points B and C will scatter some-ordinate during a number of cycles variations in rates of cooling or heat-cycle is drawn for a 'normal' silicate (side-albite).

consider the diopside-albite experiment which temperature is quenched at the liquid is at A^* (T , P) and is to point B (25°, P) with ΔV proportional to the thermal expansion coefficient at temperature drops through the glass the volume (density, refractive index) to 25°C and pressure P is at point B , via the reversible thermal. The potential energy barrier is now or pressure relaxation at low temperature that pressure release is irreversible properties at point B are locked in to. Thus, any point on any trajectory any T and P , will, in this process, ally to the 25° trajectory $C-B$ and $C-B$ at the pressure at which temperature was quenched. As discussed in the the diopside-albite results, this follows the equality $(\partial\alpha/\partial P) = -(\partial\kappa/\partial T)$. $A^*-B-C-D^*-A^*$ is drawn for normal cases in which $\alpha_p < \alpha_0$ and $\kappa_T > \kappa_{\infty}$. release from above the glass point only result in an equilibrium trajectory A^*-D^* down the isotherm, with subthermal relaxation to point C , the uncompressed glass. If the pressure is at a high temperature below the glass pressure effect may be locked in with thermal contraction at 1 bar. This is shown in Figure 4 by the area $C-D$. O_2 glass, in which $C-B$ is now assumed 25°C compression slope for the glass compressed glass sample at 600°C is at below the glass point T_g (as, for example, reached by cooling at pressure from us). When the pressure is released,

the pressure deformation is trapped by viscosity, as configurational changes are required for pressure relaxation. However, thermal relaxation is dominantly a vibrational effect and occurs with the α value characteristic of ambient pressure, in this case α_0 . The trajectory is $E-F$, this difference being equal to $D-C$, and the points from compression along an isotherm $D-E$ will plot on the isotherm $C-F$ with a slope given by κ at the isotherm temperature. (At 600°C, however, the difference $C-D$ is only 0.1% on density, so that the difference between the two lines cannot actually be observed.) For normal silicates, the trajectory $C-F$ would, of course, lie above $C-B$ because of the higher compressibility at higher temperature.

At still lower temperatures it is evident from Figure 3 that SiO_2 glass is partly elastic, with some rebound along $D-E$ on decompression; subsequent cooling then produces a trajectory from C below $C-F$ as is observed. Although shear effects may be involved in the degree of elasticity observed, Cohen and Roy [1965, Figure 6 and Table 2] observed quite similar effects in hydrostatic compression in argon up to 10 kb. Samples compressed at 600°C and above scatter between the 25° and 600°C isotherms in Figure 3 (the quenching cycle is not described), whereas partial or total elasticity was observed at lower temperatures.³

Cohen and Roy [1961, 1965] have proposed that the densification of glass is independent of the compressibility and involves an irreversible, second-order structural change at high pressure, followed by completely elastic volume relaxation of the new phase. It is evident, however, that the relationships between densification and compressibility shown in Figures 2 and 3 are incompatible with such a model. Configurational

trapping of pressure deformation is clearly adequate to explain the permanent compression of the glasses studied here.

Recent work dealing with pressure effects on refractive index in elastic compression [Waxler and Weir, 1965, and references therein] has dealt with some substances in which the molar polarizabilities actually change with pressure, so that R in (2) cannot be considered constant. Discussions of possible effects of this type in glasses [Waxler and Weir, 1965; Vedam et al., 1966] have, so far, been confined to models based on the Lorentz-Lorenz or Drude law, rather than on equation 2, which allows an intermediate overlap field. It is clear that the more general refraction model given by equation 2 should be used as the basis for further studies of polarizability changes. Fortunately, pressure effects on polarizability do not seem to be important in the glasses studied here.

This study was originally undertaken in the hope that meteoritic glasses might yield some information on conditions under which they were quenched. Although the results indicate this is unlikely, it should be of interest to study the quenching conditions in tektites. By simply heating tektite samples above the glass point and cooling, and comparing the refractive index before and after, it would be possible to see if a pressure deformation has been trapped in the glass; if so, measurement of the compressibility as a function of temperature might yield some interesting information.

Note added in press. In the *Annual Report of the Geophysical Laboratory for 1967-68*, E. C. Chao and P. M. Bell have recently reported data on refractive index as a function of pressure to 50 kb, for three feldspar glasses quenched at pressure. The n - P relation for oligoclase (An_{25}) is given exactly by the Lorentz-Lorenz law, using the crystal compressibility, and the relationship for orthoclase is given exactly by the Drude law; compressibility data for their third glass were not available. The oligoclase curve is essentially linear, and it seems clear that with very precise data a plagioclase glass of some composition can be found that will give a precisely linear curve and should be most useful for an experimental barometer. Measurement of the actual feldspar glass compressibilities, together with the n - P curves, would provide very interesting data on

³ Note added in press. G. J. Wasserburg has drawn my attention to two papers by Kennedy et al. [1961, 1962] in which permanent increases in refractive index were observed in SiO_2 glass quenched under hydrostatic pressures up to 10 kb in a hydrothermal system. Kennedy et al. [1962] showed that the refractive index of the quenched glass was approximately given by the Lorentz-Lorenz equation and attributed this to a permanent 'set' in the high-pressure density. Their data (0-10 kb) fit the 25°C, $\beta = 1.37$, calculated curve in Figure 3 very closely.

the effect of composition on the overlap field in feldspars.

Acknowledgments. Dr. J. Arndt of Tübingen kindly provided me with copies of several important papers that I had not seen and helpful discussions of his work on SiO_2 . Dr. F. R. Boyd contributed very helpful comments in reviewing the manuscript. I am most grateful to Drs. P. Eberhardt and H. Oeschger at the University of Bern for their assistance and hospitality.

REFERENCES

- Anderson, O. L., Effect of pressure on glass structure, *J. Appl. Phys.*, **27**, 943-949, 1956.
- Anderson, O. L., The use of ultrasonic measurements under modest pressure to estimate compression at high pressure, *J. Phys. Chem. Solids*, **27**, 547-565, 1966.
- Anderson, O. L., and E. Schreiber, The relation between refractive index and density of minerals related to the earth's mantle, *J. Geophys. Res.*, **70**, 1463-1471, 1965.
- Arndt, J., and D. Stöffler, Evidence of quasi-crystalline atomic arrangements in silica glass densified at very high pressures, *Naturwiss.*, **55**, 226-227, 1968.
- Birch, F., Compressibility; Elastic constants, in *Handbook of Physical Constants*, edited by S. P. Clark, *Geol. Soc. Am. Mem.*, **97**, 97-173, 1966.
- Birch, F., and R. B. Dow, Compressibility of rocks and glasses at high temperatures and pressures: Seismological application, *Bull. Geol. Soc. Am.*, **47**, 1235-1255, 1936.
- Birch, F., and R. R. Law, Measurement of compressibility at high pressures and high temperatures, *Bull. Geol. Soc. Am.*, **46**, 1219-1250, 1935.
- Boyd, F. R., and J. L. England, Apparatus for phase-equilibrium measurements at pressures up to 50 kilobars and temperatures up to 1750°C, *J. Geophys. Res.*, **65**, 741-748, 1960.
- Boyd, F. R., and J. L. England, Effect of pressure on the melting of diopside, $\text{CaMgSi}_2\text{O}_6$, and albite, $\text{NaAlSi}_3\text{O}_8$, in the range up to 50 kilobars, *J. Geophys. Res.*, **68**, 311-323, 1963.
- Bridgman, P. W., The compression of 39 substances to 100,000 kg/cm², *Proc. Am. Acad. Arts Sci.*, **76**, 55-70, 1948.
- Bridgman, P. W., and I. Simon, Effects of very high pressures on glass, *J. Appl. Phys.*, **24**, 405-413, 1953.
- Brown, W. F., Dielectrics, in *Encyclopedia of Physics*, edited by S. Flugge, vol. 17, pp. 114-119, Springer-Verlag, Berlin, 1956.
- Clark, S. P., Viscosity, in *Handbook of Physical Constants*, edited by S. P. Clark, *Geol. Soc. Am. Mem.*, **97**, 291-298, 1966.
- Cohen, H. M., and R. Roy, Effects of ultrahigh pressures on glass, *J. Am. Ceram. Soc.*, **44**, 523-524, 1961.
- Cohen, H. M., and R. Roy, Reply to "Comments on 'Effects of ultrahigh pressures on glass,'" *J. Am. Ceram. Soc.*, **45**, 398-399, 1962.
- Cohen, H. M., and R. Roy, Densification of glass at very high pressure, *Phys. Chem. Glasses*, **6**, 149-161, 1965.
- Davies, R. O., and G. O. Jones, Thermodynamic and kinetic properties of glasses, *Advan. Phys.*, **2**, 370-410, 1953.
- Jones, F. O., and F. E. Simon, What is a glass?, *Endeavour*, **8**, 175-181, 1949.
- Kennedy, G. C., G. J. Wasserburg, H. C. Heard, and R. C. Newton, The upper three-phase region in the system $\text{SiO}_2\text{-H}_2\text{O}$, in *Progress in Very High Pressure Research*, edited by F. P. Bundy, W. R. Hibbard, and H. M. Strong, pp. 28-45, John Wiley, New York, 1961.
- Kennedy, G. C., G. J. Wasserburg, H. C. Heard, and R. C. Newton, The upper three-phase region in the system $\text{SiO}_2\text{-H}_2\text{O}$, *Am. J. Sci.*, **260**, 501-521, 1962.
- Mackenzie, J. D., High-pressure effects on oxide glasses, **2**, Subsequent heat treatment, *J. Am. Ceram. Soc.*, **46**, 470-476, 1963.
- Mott, N. F., and R. W. Gurney, *Electronic Processes in Ionic Crystals*, pp. 13-19, Clarendon Press, Oxford, 1940.
- Reitzel, J., I. Simon, and J. Walker, New methods for measuring linear compressibility of solids, *Rev. Sci. Instr.*, **28**, 828-829, 1957.
- Ritland, H. N., Relation between refractive index and density for a glass at constant temperature, *J. Am. Ceram. Soc.*, **38**, 86-88, 1955.
- Roy, R., and H. M. Cohen, Effects of high pressure on glass: A possible piezometer for the 100-kilobar region, *Nature*, **190**, 798-799, 1931.
- Stevens, J. M., The structure and physical properties of glass, in *Encyclopedia of Physics*, edited by S. Flugge, vol. 13, pp. 510-645, Springer-Verlag, Berlin, 1962.
- Tammann, G., *Der Glaszustand*, Voss, Leipzig, 1933.
- Vedam, K., E. D. Schmidt, and R. Roy, Non-linear variation of refractive index of vitreous silica with pressure to 7 kilobars, *J. Am. Ceram. Soc.*, **49**, 531-535, 1966.
- Waxler, R. M., and C. E. Weir, Effect of hydrostatic pressure on the refractive indices of some solids, *J. Res. NBS*, **69A**, 325-333, 1965.

(Received December 12, 1968;
revised June 13, 1969.)