Infrared absorption spectra of sodium silicate glasses at high pressures*

John R. Ferraro
Argonne National Laboratory, Argonne, Illinois 60439

Murli H. Manghnani
Hawaii Institute of Geophysics, University of Hawaii, Honolulu, Hawaii 96822
(Received 15 May 1972; in final form 13 July 1972)

Infrared absorption spectra of 12 sodium silicate glasses of varying composition (10 to 45 mole% Na_2O) are examined at varying pressures to 58.8 kbar. The pressure dependences of all the infrared absorption frequencies studied are found to be positive. Grüneisen γ's are evaluated from the pressure dependence of the infrared vibrations and elastic parameters. The results are compared with those obtained from previous high-pressure studies of α-quartz and several other silicate glasses.

INTRODUCTION

Physical properties such as elastic moduli and mechanical strength of silicate glasses are related to the density of the Si-O-Si bridges in the random-network structure of glasses.[1] The addition of Na_2O as a network modifier causes a breakdown of some of the Si-O-Si bridges and the formation of weaker Si-O-Na bridges and some terminal Si-O bonds—in proportion to the amount of Na_2O added. Further, some of the Si-O-Si bridges between the SiO_4 tetrahedra may be stretched to accommodate the sodium ion in the network. As a result, the elastic moduli and strength of Na_2O-SiO_2 glasses decrease with an increase in the Na_2O content.[1,2]

Several infrared investigations have been conducted on sodium silicate glasses.[3-9] Hanna and co-workers[3,4] have examined the infrared absorption spectra from 2500 to 50 cm^{-1} at ambient pressure, and others[5-9] have investigated the infrared reflectance spectra of the glasses. However, the pressure dependence of the infrared spectra of such glasses has not been investigated. This paper reports on a high-pressure study of the infrared spectra of 12 sodium silicate glasses from 1600 to 80 cm^{-1}. The mode Grüneisen parameters, γ_i, are calculated from the pressure dependence of all of the infrared vibration mode frequencies examined, and the values compared with the high-temperature limit of $\bar{\gamma}_{th}$, γ_{HT} arrived at from the pressure coefficients of the elastic parameters. The results are correlated with previous pressure studies on α-quartz and several other silicate glasses.[10]

EXPERIMENTAL METHODS

Eight sodium silicate glasses (K nomenclature) from the National Bureau of Standards and four (JRS nomenclature) from Sweet and White[6] at Pennsylvania State University were used in this study. Table I lists the chemical composition of the glasses in mole%.

The specimens were crushed in a ball mill finely powdered by extensive grinding in an agate mortar. The midinfrared sbsorption spectra at ambient conditions were obtained using KBr pellets and employing a Beckman IR-12 spectrophotometer. The spectra from 650 to 80 cm^{-1} were obtained with polyethylene pellets using a Perkin-Elmer Model No. 301 spectrophotometer. The region from 166 to 80 cm^{-1} was also checked with heavy concentrations of the glasses in Nujol. The instruments were calibrated in the midinfrared region with polystyrene film; and at frequencies <650 cm^{-1} with water vapor, the Hg emission lines and with low-frequency absorptions of solid HgO.

For the high-pressure measurements in regions of 333 to 80 cm^{-1} we used an opposed diamond cell linked with the Perkin-Elmer No. 301 spectrophotometer equipped with a 6×beam condenser.[11] Midinfrared studies at high pressures were made with a Beckman IR-12 spectrophotometer equipped with a 6×beam condenser.[12] The powdered sample was loaded in the cell, and the pressure alternately increased and decreased to distribute the material evenly between the anvils. During the pressure cycling, the sample was observed with a microscope. A description of the pressure cell and the method used in pressure calibration has been previously reported.[11-12]

TABLE I. Composition of Na_2O-SiO_2 glasses.

| Sample No. | mole % | | Ratio |
	SiO_2	Na_2O	SiO_2/Na_2O
K-110	90	10	9.0
K-111	85	15	5.7
K-112	80	20	4.0
K-113	75	25	3.0
K-114	70	30	2.3
K-115	65	35	1.9
K-116	60	40	1.5
K-117	55	45	1.2
JRS-2	66.9	33.1	2.0
JRS-3	64.5	35.5	1.8
JRS-4	60.4	39.6	1.5
JRS-5	72.5	27.5	2.6

TABLE II. Sodium silicate glasses. Observed infrared absorptions at ambient pressure (cm^{-1}). Abbreviations: s = strong; m = medium; v = very; b = broad; w = weak.

Glass (mole % Na_2O)	ν			
α quartz(0)	1082(vs)[a]		783(m) 800(m)	459(s)
Fused silica(0)	1087(vs)		815(m)	475(s)
(10)	1085[a](vs, b)		787(m)	460(s)
(15)	1075[b](vs, b)		785(m)	461(s)
(20)	1065(vs, b)	965(sh)	775(m)	462(s)
(25)	1065(vs)	975(vs)	765(m)	462(s)
(27.5)	1075(vs)	960(vs)	765(m)	458(s)
(30)	1070(vs)	960(vs)	760(m)	460(s)
(33.1)	1075(vs)	940(vs)	760(m)	460(s)
(35)	1070(vs)	940(vs)	755(m)	458(s)
(35.5)	1075(vs)	940(vs)	760(w)	458(s)
(39.6)	1060(vs)	930(vs)	745(w)	461(s)
(40)	1060(vs)	935(vs)	750(w)	460(s)
(45)	1040(vs)	935(vs)	730(w)	468(s)

[a]Asymmetric on high- and low-frequency sides of band.
[b]Very weak shoulder 980 cm^{-1}, 1220 cm^{-1}.

RESULTS AND DISCUSSION

A. Infrared absorption spectra at varying pressures

Table II lists the infrared absorption bands at ambient pressure for the sodium silicate glasses under study, and Fig. 1 displays several typical spectra. Figure 2 illustrates the effects of adding Na_2O to silica on the various absorptions between 1400—350 cm^{-1}. The increasing content of Na_2O causes a decrease in frequency of the three absorptions at ~1100, ~960, and ~790 cm^{-1}, and an increase for the ~460-cm^{-1} absorption. It is of interest to note that as the Na_2O content increases, the ~790-cm^{-1} band shifts toward a lower frequency than that found in α-quartz, and the intensity is considerably reduced. Since the number of Si-O-Si bridging units in the network decreases with an increase in the Na_2O content, it is expected that a decrease in intensity of this absorption would also occur. The low-frequency shift of the remaining Si-O-Si bridging units is consistent with a stretching of the Si-O bond as Na_2O enters the network. The ambient-pressure results are substantially in agreement with the reflectance work of Sweet and White[6] and the absorption studies of Hanna and Su.[3,4]

Although it is recognized that it may be incorrect to characterize an absorption band by a particular type of vibration in an amorphous material such as glass,[13] we find it convenient for purposes of the discussion in this paper to indicate that the four modes of vibration on interest may involve the following motions:

(a) ~1100 cm^{-1}, Si-O stretching within the tetrahedra;[6,14]
(b) ~960 cm^{-1}, Si-O terminal, nonbridged stretching;[6]
(c) ~790 cm^{-1}, Si-O-Si bridged stretching between tetrahedra; (d) ~460-cm^{-1}, bending modes involving Si-O-Si and O-Si-O. It should be emphasized that more definitive assignments for fused and crystalline silica have now been made.[13,15—19]

Under conditions of our experiments no significant absorptions were found lower than the broad band at ~460 cm^{-1}. Our measurements were carried out to 80 cm^{-1}. The pressure experiment is essentially a thin-film measurement, and under these conditions the glasses appeared to be transparent. When the glasses were measured in the far-infrared region as thick glasses, some weak absorptions were noted.

Table III presents the pressure dependence for the four main vibration modes, in terms of $d\nu_i/dP$, for the sodium silicate glasses. It is observed that $d\nu_i/dP$ values for all the absorption bands are higher than those for α-quartz and other silicate glasses.[10] Figure 3 presents typical infrared spectra (sample K-116) under high pressures. With an increase in pressure, frequencies of the three bands shift toward higher frequencies.
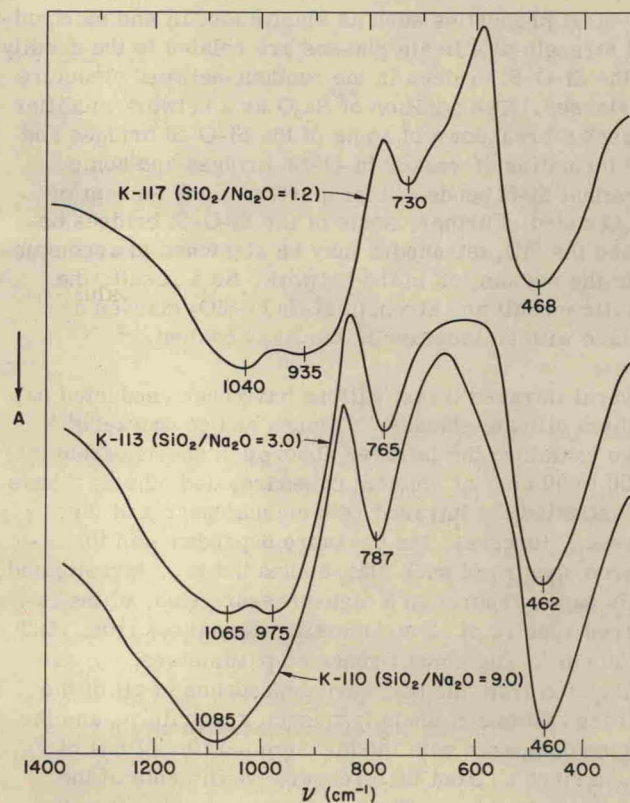
FIG. 1. Spectra (1400—350 cm^{-1}) of several sodium glasses at varying concentrations of SiO_2/Na_2O at ambient pressure.
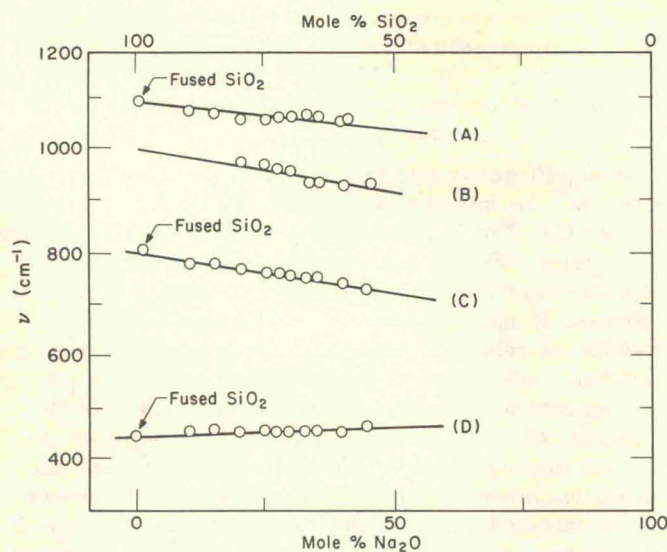
FIG. 2. (A) Plot of tetrahedra SiO stretching vibration vs mole% of Na_2O. (B) Plot of terminal SiO stretching vibration vs mole% of Na_2O. (C) Plot of SiOSi stretching vibration vs mole% of Na_2O. (D) Plot of bending vibrations vs mole% of Na_2O.

In pressure studies made on α-quartz, fused silica, Vycor, and Pyrex glasses, the pseudolatticelike Si stretching mode at ~800 cm⁻¹ was found to be most pressure dependent.[10] For the sodium silicate glasses, all of the vibration modes studied are pressure sensitive, especially the tetrahedral Si-O stretching (~1100 cm⁻¹) and the bridging Si-O-Si stretching (~790 cm⁻¹) modes, and the terminal Si-O stretching (~960 cm⁻¹) mode. The effect of Na_2O on $d\nu_i/dP$ appears to be greater than the effect of B_2O_3 on $d\nu_i/dP$ in Vycor and Pyrex glasses. Differences between the effects of B_2O_3 and Na_2O on $d\nu_i/dP$ in silicate glasses are not unexpected since B_2O_3 is a glass former and strengthens the glass (e.g., elastic moduli increase as B_2O_3 increases),[1,2] whereas Na_2O is a glass modifier and weakens the glass.

The mode Grüneisen γ, γ_i, in Table III are evaluated from the relation

$$\gamma_i = \frac{K_T}{\nu_i}\left(\frac{d\nu_i}{dP}\right), \quad (1)$$

where K_T is the isothermal bulk modulus.

Whenever comparisons are possible, the sodium silicate glasses demonstrate γ_i values which are higher than those calculated for α-quartz and other silicate glasses,[10] and in every case are positive. The α-quartz and fused silica glass demonstrate negative γ_i values for some modes and also show anomalous thermal expansion and elastic behavior.[10,19] The positive γ_i values for the sodium silicate glasses are consistent with the effects of network filling agents such as Na_2O in diminishing these anomalies.[20] The higher ionic character of the sodium silicate glasses is also contributory to the higher sensitivity to pressure as opposed to the pure silicate glasses or those incorporating the more covalent boron atoms into the glass framework.[1,21,22]

Contrary to what was found for α-quartz and other silicate glasses,[10] even the modes involving the motions of the atoms within the SiO_4 tetrahedra in the sodium silicate glasses are significantly pressure sensitive. Thus, with an increase in pressure, the sodium silicate glasses demonstrate compression along the intertetrahedral linkages, but in addition some distortions of the individual tetrahedra[20] must occur. This difference from α-quartz and related nonmodified silicate glasses must relate to the insertion of the modifying sodium ions in the interstices of the glasses.

B. Thermal expansion and the Grüneisen parameters

The observed negative thermal expansion coefficients, α_v, at $T < 200\,°K$ for fused silica and Pyrex and the effects of diminishing this anomaly by the addition of a network filling agent such as Na_2O is of considerable interest.[23,24] The coefficient, α_v, is related to $\bar{\gamma}_{th}$ through the relation

$$\bar{\gamma}_{th} = \alpha_v K_s / \rho C_v, \quad (2)$$

where K_s is the adiabatic bulk modulus, ρ and C_v are density and specific heat at constant volume. $\bar{\gamma}_{th}$ is also related to γ_i and C_{v_i} by the relationship

$$\bar{\gamma}_{th} = \sum_{i=1}^{3n} \gamma_i C_{v_i} \Big/ \sum_{i=1}^{3n} C_{v_i}, \quad (3)$$

TABLE III. Mode Grüneisen parameters calculated for various sodium silicate glasses.

| Glass (mole % Na_2O)	ν_i (cm⁻¹)	$d\nu_i/dp$ (cm⁻¹/kbar)	χ (kbar⁻¹)	Calculated γ_i
α-quartz(0)	783 800	0.14	0.00267	0.07
Fused silica(0)	815	0.17	0.00302	0.07
Vycor(0)	814	0.22	0.00382	0.07
Pyrex(4)	812	0.27	0.00289	0.12
(10)	787	0.64	0.00295	0.28
(25)	765	0.50	0.00270	0.24
(35)	755	0.48	0.00252	0.25
(35.5)	760	0.50	0.00253	0.26
(40)	750	0.50	0.00251	0.27
(45)	730	0.56	0.00232	0.33
α-quartz(0)	1082	−0.07	0.00267	−0.02
(10)	1085	0.46	0.00295	0.14
(25)	1065	0.45	0.00270	0.16
(35)	1070	0.48	0.00252	0.18
(35.5)	1075	0.50	0.00253	0.18
(40)	1060	0.42	0.00251	0.16
(45)	1040	0.42	0.00232	0.17
(25)	975	0.45	0.00267	0.17
(35)	940	0.35	0.00252	0.15
(35.5)	940	0.50	0.00253	0.21
(40)	935	0.40	0.00251	0.17
(45)	935	0.45	0.00232	0.21
α-quartz(0)	459	0.09	0.00267	0.07
Fused silica(0)	475	−0.07	0.00302	−0.05
(10)	460	0.19	0.00295	0.14
(25)	462	0.13	0.00270	0.10
(35)	458	0.16	0.00252	0.14
(35.5)	458	0.21	0.00253	0.18
(40)	460	0.13	0.00251	0.11
(45)	468	0.19	0.00232	0.18
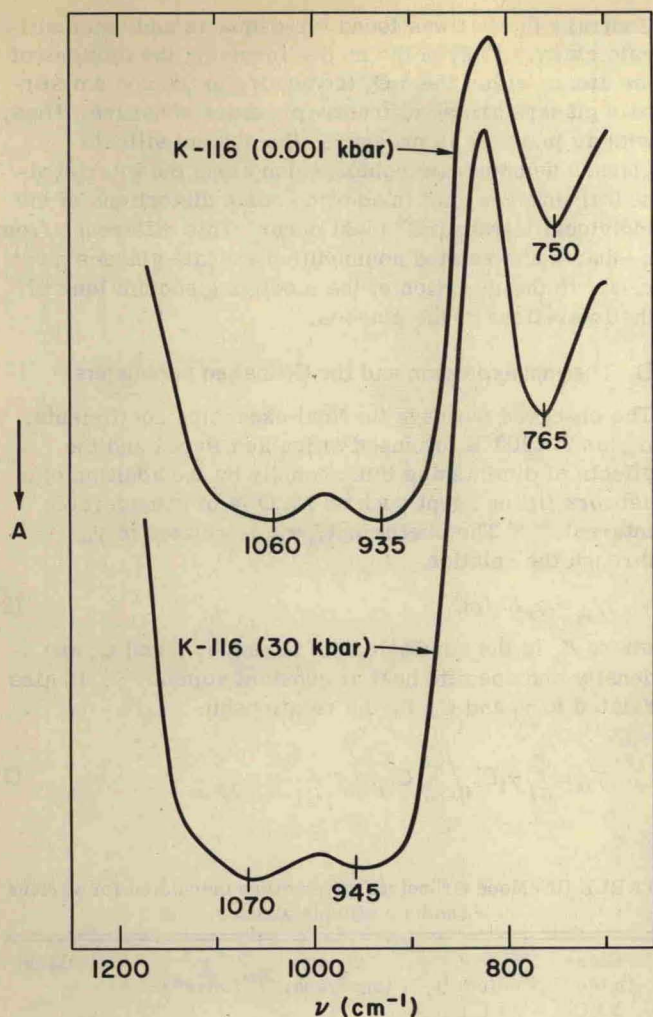
FIG. 3. Spectra of the K-116 glass at varying pressures from 1200—700 cm^{-1}.

where γ_i is defined by Eq. (1) and C_v is the specific-heat contribution for each vibrational mode to the total Einstein specific heat.

Since the thermal expansion data were obtained at room temperature and above, we will consider only the high-temperature limit of $\bar{\gamma}_{th}$ designated as γ_{HT}. γ_{HT} may be calculated from the pressure derivatives of the elastic parameters, assuming only the acoustic modes contributing to γ;

$$\gamma_{HT} = \tfrac{1}{3}(\gamma_p + 2\gamma_s), \tag{4}$$

where

$$\gamma_s = \frac{1}{3} + K_T \left(\frac{\partial \ln v_s}{\partial \ln P}\right)_T \tag{5}$$

and

$$\gamma_p = \frac{1}{3} + K_T \left(\frac{\partial \ln v_p}{\partial P}\right)_T. \tag{6}$$

Here γ_p and γ_s are the γ contributions to the compressional and shear-wave propagation, and v_p and v_s represent, respectively, compressional and shear acoustic wave velocities.[25,26]

Table IV shows a comparison of $\bar{\gamma}_{th}$ and γ_{HT} for the sodium silicate glasses at 298 °K. The values for α-quartz, fused silica, Vycor, and Pyrex are also included. We have no ready explanation for the observed differences in the $\bar{\gamma}_{th}$ and γ_{HT} values.

It is significant to note that as the Na$_2$O content increases, the optical γ_i values are observed to increase (Table III). The $\bar{\gamma}_{th}$ parameter increases slightly, but the γ_{HT} values increase significantly, and are much more sensitive to compositional changes occurring in the glasses. It may also be observed that the negative γ_{HT} values are related to the anomalous behavior in α-quartz and fused silica, for as Na$_2$O enters the glass, γ_{HT} becomes increasingly more positive and the anomaly decreases. Since Raman-active modes have not been examined under pressure, definite conclusions were not possible. However, the positive pressure dependences of the infrared-active modes examined, correlated with the absence of any negative thermal expansion observed for sodium silicate glasses.

SUMMARY

Infrared absorption spectra of sodium silicate glasses vary systematically with composition and pressure. The following findings are noteworthy:

(i) The strong broad band at ~1100 cm^{-1} due to Si-O stretching within the tetrahedron splits; the frequencies of both of the resultant bands decrease with substitution of Na$_2$O in the structure. With an increase in pressure these bands show a shift toward higher frequency.

(ii) The frequency and intensity of the bridging Si-O-Si stretching mode at ~790 cm^{-1} decreases with an increase in Na$_2$O content. The frequency was found to increase with pressure.

(iii) The low-frequency band, due to Si-O-Si and O-Si-O bending modes, slightly increases in frequency with Na$_2$O content, and with increasing pressure.

(iv) All values of $d\nu_i/dP$ for the four optical vibrational modes examined are positive.

TABLE IV. Thermal and elastic data and the Grüneisen parameter values for the Na$_2$O-SiO$_2$ glasses.

(mole % Na$_2$O)	$\bar{\gamma}_{th}$	γ_{HT}
(10)	0.003	−1.35
(15)	0.004	−0.84
(20)	0.006	−0.31
(25)	0.007	−0.17
(27.5)	0.008	0.32
(30)	0.008	0.49
(33.1)	0.009	0.68
(35)	0.011	0.71
(35.5)	0.010	0.74
(39.6)	0.011	0.93
(40)	0.012	1.03
(45)	0.013	1.08
α-quartz(0)	0.69[a]	· · ·
Fused silica(0)	0.04	−2.32
Vycor(0)	0.04	−1.80
Pyrex(4)	0.22	−1.80

[a]N. Soga, J. Geophys. Res. 72, 4227 (1967).

(v) The γ_i's calculated from $d\nu_i/dP$ are higher than those for α-quartz and high-silica glasses, reflecting the increase in ionic character of the glasses as the Na_2O content increases.

(vi) As the Na_2O content is increased in the sodium glasses, the value of γ_{HT} increases significantly, correlating with an absence of negative thermal expansion in these glasses.

ACKNOWLEDGMENT

*Based on work performed under the auspices of the U. S. Atomic Energy Commission.
[1] R. J. Charles, *Progress in Ceramic Science* (Pergamon, New York, 1961), Vol. I.
[2] M. H. Manghnani (unpublished).
[3] R. Hanna, J. Phys. Chem. **69**, 3846 (1965).
[4] R. Hanna and G.-J. Su, J. Amer. Ceram. Soc. **47**, 597 (1964).
[5] D. Crozier and R. W. Douglas, Phys. Chem. Glasses **6**, 240 (1965).
[6] J. R. Sweet and W. B. White, Phys. Chem. Glasses **10**, 246 (1969).
[7] P. E. Jellyman and J. P. Proctor, J. Soc. Glass Technol. **39**, 173 (1955).
[8] V. A. Florinskaya, *The Structure of Glass* (Consultants Bureau, New York, 1960), p. 154.
[9] I. Simon and H. O. McMahon, J. Amer. Ceram. Soc. **36**, 160 (1953).
[10] J. R. Ferraro and M. H. Manghnani, J. Phys. Chem. Glasses (to be published).
[11] J. R. Ferraro, S. S. Mitra, and C. Postmus, Inorg. Nucl. Chem. Lett. **2**, 269 (1966).
[12] C. Postmus, S. S. Mitra, and J. R. Ferraro, Inorg. Nucl. Chem. Lett. **4**, 55 (1966).
[13] N. F. Borrelli and G.-J. Su, Mater. Res. Bull. **3**, 181 (1968).
[14] E. R. Lippincott, R. Van Valkenburg, A. Wier, and C. E. Bunting, J. Res. Nat. Bur. Stand. **61**, 61 (1958).
[15] R. J. Bell, M. E. Bird, and P. Dean, Proc. Phys. Soc. Lond. **1**, 299 (1968).
[16] P. H. Gaskell, Phys. Chem. Glasses **8**, 69 (1967).
[17] J. Bock and G. -J. Su, J. Amer. Ceramic Soc. **53**, 69 (1970).
[18] M. Blackman, Proc. Phys. Soc. Lond. **70**, 827 (1957).
[19] A. Bienenstock and G. Burley, J. Phys. Chem. Solids **24**, 1271 (1963).
[20] H. T. Smyth, J. Amer. Ceram. Soc. **42**, 276 (1959).
[21] J. Zarzycki, *Chemical and Mechanical Behavior of Inorganic Materials* edited by A. W. Searcy, D. V. Ragone, and V. Columbo (Interscience, New York, 1970), pp. 443–474.
[22] B. E. Warren, J. Appl. Phys. **8**, 645 (1937).
[23] O. L. Anderson and G. J. Dienes, *Noncrystalline Solids* (Wiley, New York, 1960), p. 449.
[24] G. K. White, Cryogenics 4, 2 (1964).
[25] T. H. K. Barron, Phil. Mag. **46**, 720 (1955).
[26] D. E. Schuele and C. S. Smith, J. Phys. Chem. Solids **25**, 801 (1964).