Optical Phonons in Amorphous Silicon Oxides. I. Calculation of the Density of States and Interpretation of LO-TO Splittings of Amorphous Sio2

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Optical Phonons in Amorphous Silicon Oxides

I. Calculation of the Density of States and Interpretation of LO–TO Splittings of Amorphous SiO₂

By

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Until now there exists no calculation of the phonon density of states of amorphous SiO_2 and related materials, which could interpret the experimentally detected splittings between longitudinal and transverse modes in their optical phonon spectra. This problem is solved by taking into account the influence of the vibrationally induced polarization on the motion of atoms. A simple model for the description of this polarization in non-crystalline SiO_2 is developed and used for the calculation of the density of states of LO and TO phonons in the framework of a coherent potential approximation for structurally disordered systems. This new method leads also to the determination of the IR response function and to simple analytical expressions for the microscopic parameters of the model, i.e. the bond angle at the oxygen atom and transverse dynamic effective charges. The values of these parameters are determined from IR transmission spectra of thin SiO_2 layers prepared with the help of different methods. The calculated density of states and IR response function are in good agreement with corresponding experimental results.

Bis heute existiert keine Berechnung der Phononenzustandsdichte des amorphen SiO_2 und von ähnlichen Materialien, die in der Lage wäre, die experimentell nachgewiesenen Aufspaltungen zwischen longitudinalen und transversalen Moden in ihren optischen Phononenspektren zu interpretieren. Dieses Problem wird durch Berücksichtigung des Einflusses der schwingungsinduzierten Polarisation auf die Atombewegung gelöst. Es wird ein einfaches Modell für die Beschreibung dieser Polarisation im nichtkristallinen SiO_2 entwickelt und zur Berechnung der Zustandsdichte von LO- und TO-Phononen in einer kohärenten Potentialapproximation für strukturell ungeordnete Systeme verwendet. Diese neue Methode führt auch zur Ermittlung der IR-Responsefunktion sowie auf einfache analytische Ausdrücke für die mikroskopischen Parameter des Modells, d. h. den Bindungswinkel am Sauerstoffatom und transversale dynamische effektive Ladungen. Die Werte dieser Parameter werden aus IR-Transmissionsspektren dünner SiO_2-Schichten, die mit Hilfe unterschiedlicher Methoden präpariert worden sind, bestimmt. Die berechnete Zustandsdichte und IR-Responsefunktion stimmen gut mit entsprechenden experimentellen Ergebnissen überein.

1. Introduction

Additional features in the neighbourhood of the peaks of transverse optical (TO) modes in Raman spectra of glassy SiO_2 and GeO_2 have led Galeener and Lucovsky [1] to the prediction of the existence of LO–TO splittings in these and related materials. This prediction was experimentally proved in glassy SiO_2 by hyper-Raman studies [2] and in thin SiO_2 films by IR measurements at oblique incidence [3]. With the help of the latter method LO–TO splittings were detected for the first time even in the complicated geometrically and chemically disordered material SiO_x [4]. The experimentally determined mode splittings of non-crystalline SiO_2 are similar to those found for crystalline forms of SiO_2 [5, 6]. However, until now phonon spectra of non-crystalline SiO_2 were calculated only by consideration of short-range forces [7 to 9]. Therefore, these

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calculations are not able to reproduce the experimentally detected splittings. Generally, the parameters of the short-range potential are chosen in such way, that the calculated IR response function agrees with the experimental absorption spectrum [9]. Therefore, the phonon density of states (DOS) calculated with such short-range potentials contains only contributions of TO phonons. This approach is also used here for the calculation of the contribution of the TO phonons to the total DOS. The contribution of the LO phonons must be calculated with the help of another set of equations of motion, which take into account additional Coulomb forces. As in crystals these forces depend on the dynamic effective charges of the atomic constituents of the ionic material considered.

Our method leads to analytical relations connecting the various LO and TO phonon frequencies, which are determined experimentally, with the parameters of the short-range potential, the angle of the oxygen bridge, and transverse dynamic effective charges. With the help of the IR experiments mentioned above [3, 4] we have determined the values of these parameters for different amorphous SiO_2 forms. They are used for the calculation of the DOS and of the IR response function. The results of these calculations are in good agreement with known experimental spectra [10, 11].

The paper is organized in the following way. In Section 2 the equations of motion are described. Vibrational Green functions and theoretical phonon spectra of non-crystalline SiO_2 are derived in Section 3. Section 4 involves the interpretation of IR transmission spectra of differently prepared SiO_2 layers. Some conclusions are drawn in Section 5.

2. Equations of Motion for Non-Crystalline SiO₂

It is well known that the chemical bonds of SiO_2 in its various structural forms are partially (about 50%) ionic [12]. Therefor e,also non-crystalline SiO_2 has to be considered as a polar solid, in which optical vibrations are associated with strong electrical moments. In the approximation of long waves [13], which is most suitable in the case of amorphous solids, these moments p_j and the effective electric field E_{eff} acting on an ion can be described by the relations

$$M_j \ddot{u}_j = - \sum_i \frac{\partial V_{ij}}{\partial u_i} + \hat{Z}_j E_{eff}(R_j) \tag{1}$$

and

$$p_j = \hat{Z}_j u_j + \alpha_j E_{eff}(R_j) , \tag{2}$$

where M_j, u_j, $\hat{Z}_j$, R_j, and α_j is the mass, the displacement vector, the matrix of the so-called Szigeti charge, the equilibrium position, and the polarizability of the j-th atom, respectively. The short-range potential connecting the atoms i and j is denoted by V_{ij}. The vibrationally induced moments p_j lead to the polarization P, which is related to the total electric field E by the equation

$$P = (\varepsilon - 1) \varepsilon_v E \tag{3}$$

in the case of an infinite large solid. In the SI system ε_v and ε is the absolute dielectric constant of the vacuum and the relative dielectric function of the material considered, respectively. Using the basic equations of electrostatics, the Clausius-Mosotti equation for the description of the atomic polarizabilities, and the Lorentz approximation [13] the equations (2) and (3) lead to the effective field

$$E_{eff}^{LO}(R_j) = - \frac{2(\varepsilon_\infty + 2)}{9\varepsilon_v \varepsilon_\infty \Omega_N} \sum_{i=1}^{N} \hat{Z}_i u_i \tag{4}$$
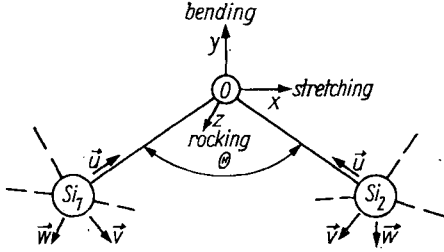
Fig. 1. Si–O–Si bonding unit with the bond angle θ and atomic displacements forming for each atom a set of Cartesian axes. The displacements x, y, u, and v are in the plane of the two Si–O bonds. The type of oxygen motion is denoted

in the case of LO phonons and to

$$E_{\text{eff}}^{\text{TO}}(\boldsymbol{R_j}) = \frac{\varepsilon_\infty + 2}{9\varepsilon_\gamma \Omega_N} \sum_{i=1}^{N} \hat{Z}_i \boldsymbol{u}_i \tag{5}$$

in the case of TO phonons, where ε_∞ means the static electronic dielectric constant. In crystals the electrically neutral volume Ω_N contains N ions (among them the j-th ion) and has to be identified with a unit cell. Which volume must be chosen in the case of an amorphous solid? Let us consider the polarization from the position of the j-th ion. If there exists any short-range order, then the polarization acting on the j-th ion does not vanish. Because of the absence of a long- (or intermediate-) range order this polarization may be regarded as to be caused only by the neighbouring moments. Therefore, in an amorphous material with preserved short-range order the extension of the electrically neutral volume must be comparable with the scale of the short-range order around the ion considered. The number N of the ions in this volume depends on j and may have values of a rational number. This is consistent with the distribution of the valence electrons of the atomic neighbours of the constituent j in their chemical bonds. In the case of an oxygen atom in amorphous SiO_2 we choose the volume $\Omega_{N(O)}$ in such a way that it contains the O atom considered and a quarter of each neighbouring Si atom. This means that the volume $\Omega_{N(Si)}$ with an Si atom in its center must contain one half of each of the four neighbouring O atoms. Therefore, in harmonic approximation with a short-range Born potential [14]

$$V_{ij} = \frac{\alpha - \beta}{2} \left[\frac{(\boldsymbol{u}_i - \boldsymbol{u}_j)(\boldsymbol{R}_i - \boldsymbol{R}_j)}{\sqrt{(\boldsymbol{R}_i - \boldsymbol{R}_j)^2}} \right]^2 + \frac{\beta}{2}(\boldsymbol{u}_i - \boldsymbol{u}_j)^2 , \tag{6}$$

the appropriate force constants α and β of which enable the evaluation of corresponding TO frequencies, the motion of the atomic constituents of an Si–O–Si bridge with the angle θ is described by the equations

$$m\omega^2 x = (2\alpha s^2 + 2\beta c^2) x - \alpha s u_1 + \alpha s u_2 - \beta c v_1 + \beta c v_2 , \tag{7}$$

$$m\omega^2 y = (2\alpha c^2 + 2\beta s^2) y - \alpha c u_1 - \alpha c u_2 + \beta s v_1 + \beta s v_2 , \tag{8}$$

$$m\omega^2 z = 2\beta z - \beta w_1 - \beta w_2 , \tag{9}$$

$$M\omega^2 u_1 = \alpha u_1 - \alpha s x - \alpha c y , \tag{10}$$

$$M\omega^2 v_1 = \beta v_1 - \beta c x + \beta s y , \tag{11}$$

and

$$M\omega^2 w_1 = \beta w_1 - \beta z \tag{12}$$

in the case of TO phonons and by the equations

$$m\omega^2 x = 2(\alpha s^2 + \beta c^2 + \gamma^{SS})\, x - \left(\alpha s + \gamma^{SiS}\frac{s}{2}\right) u_1 + \left(\alpha s + \gamma^{SiS}\frac{s}{2}\right) u_2 -$$

$$- \left(\beta c + \gamma^{SiS}\frac{c}{2}\right) v_1 + \left(\beta c + \gamma^{SiS}\frac{c}{2}\right) v_2 , \tag{13}$$

$$m\omega^2 y = 2(\alpha c^2 + \beta s^2 + \gamma^{BB})\, y - \left(\alpha c + \gamma^{SiB}\frac{c}{2}\right) u_1 - \left(\alpha c + \gamma^{SiB}\frac{c}{2}\right) u_2 +$$

$$+ \left(\beta s + \gamma^{SiB}\frac{s}{2}\right) v_1 + \left(\beta s + \gamma^{SiB}\frac{s}{2}\right) v_2 , \tag{14}$$

$$m\omega^2 z = 2(\beta + \gamma^{RR})\, z - \left(\beta + \frac{\gamma^{SiR}}{2}\right) w_1 - \left(\beta + \frac{\gamma^{SiR}}{2}\right) w_2 , \tag{15}$$

$$M\omega^2 u_1 = \left(\alpha + \frac{\gamma^{SiSi}}{4}\right) u_1 - \left(\alpha + \frac{\gamma^{SiS}}{2}\right) sx - \left(\alpha + \frac{\gamma^{SiB}}{2}\right) cy , \tag{16}$$

$$M\omega^2 v_1 = \left(\beta + \frac{\gamma^{SiSi}}{4}\right) v_1 - \left(\beta + \frac{\gamma^{SiS}}{2}\right) cx + \left(\beta + \frac{\gamma^{SiB}}{2}\right) sy , \tag{17}$$

and

$$M\omega^2 w_1 = \left(\beta + \frac{\gamma^{SiSi}}{4}\right) w_1 - \left(\beta + \frac{\gamma^{SiR}}{2}\right) z \tag{18}$$

in the case of LO phonons. The atomic displacements x, y, z, u_1, v_1, w_1, u_2, v_2, and w_2 of the oxygen atom with mass m and the two Si atoms of mass M are defined in Fig. 1. The symbols s and c denote the quantities $\sin\theta/2$ and $\cos\theta/2$, respectively, and ω means the frequency. The Coulomb force constants γ depend on the elements of the matrix of the transverse dynamic effective charges

$$\hat{Z}_j^T = \left(\frac{\varepsilon_\infty + 2}{3}\right) \hat{Z}_j \tag{19}$$

in the following way:

$$\gamma^{SS} = C(Z_{OS}^T)^2 , \tag{20}$$

$$\gamma^{BB} = C(Z_{OB}^T)^2 , \tag{21}$$

$$\gamma^{RR} = C(Z_{OR}^T)^2 , \tag{22}$$

$$\gamma^{SiSi} = C(Z_{Si}^T)^2 , \tag{23}$$

$$\gamma^{SiS} = -CZ_{Si}^T Z_{OS}^T , \tag{24}$$

$$\gamma^{SiB} = -CZ_{Si}^T Z_{OB}^T , \tag{25}$$

$$\gamma^{SiR} = -CZ_{Si}^T Z_{OR}^T , \tag{26}$$

where the factor

$$C = \varrho_M [\varepsilon_\infty \varepsilon_v (2m + M)]^{-1} \tag{27}$$

depends on the mass density ϱ_M of the non-crystalline SiO_2 form considered. The transverse effective charges Z_{OS}^T, Z_{OB}^T, Z_{OR}^T, and Z_{Si}^T are related to the oxygen stretching, oxygen bending, oxygen rocking and the silicon motion, respectively (cf. Fig. 1). The equations (7) to (18) are the basis for our further calculations.

3. Vibrational Green Functions and Theoretical Phonon Spectra of Amorphous SiO₂

For the evaluation of the vibrational (displacement–displacement) Green function we use a coherent potential approximation for structurally disordered systems. The usefulness of this approximation for the application to vibrational properties was demonstrated for amorphous silicon by Thorpe [15]. This convenient method bases on the neglect of all harmonic interactions between second nearest and more distant neighbours. With the same method Kulas and Thorpe [8] have calculated the DOS of an SiO₂ model with straight Si–O–Si bridges ($\theta = 180°$). Since they did not take into account the vibrationally induced polarization, this DOS is representative only for the so-called bare (or center) modes of the polar solid SiO₂ [16, 17]. In the case of an electrically neutral volume $\Omega_{N(j)}$ containing only the valence electrons of the neighbours of the atom j (and of course of the atom j itsself) Thorpe's method can be used also for the calculation of the Green function for LO phonon-like excitations of amorphous SiO₂, as will be demonstrated in the following.

With the help of (7) to (9) and (14) to (16) we eliminate x, y, and z in (10) to (12) and (16) to (18), respectively. Then, the motions of the Si atoms of the Si–O–Si bridge are coupled by frequency-dependent effective force constants, which are different for TO and LO phonons. The next step in the calculation of the DOS is a transformation of the displacements of the Si atoms (see Fig. 2). The new displacements are equivalent to those used for amorphous silicon and the hypothetical SiO₂ model with straight Si–O–Si bridges [8, 15]. The transformation leads to simplified equations for the elements of the vibrational Green function of the effective Si₅ cluster now considered, whose atoms are connected by the above mentioned effective force constants. Because of the local displacement coordinates used these effective force constants are equal for all the four oxygen bridges. Furthermore, we neglect the weak coupling between displacements of neighbouring Si atoms, which are orthogonal to each other. Upon each surface atom j of the cluster the additional potential

$$V_j^S = \tfrac{1}{2} \left[\alpha'(u_{j_s}^*)^2 + \beta'(v_j^*)^2 + \delta'(w_j)^2 \right] \tag{28}$$

is imposed. The parameters α', β', and δ' are frequency-dependent functions determined by the condition that the mean-square displacement of each surface atom must be equal to the mean-square displacement of the interior Si atom for each frequency. In terms of Green functions this condition has to be written as

$$3G_{\mathrm{Si}} = G_{11}^{u^*u^*} + G_{11}^{v^*v^*} + G_{11}^{ww} = \tfrac{1}{4} \sum_{j=2}^{5} \left(G_{jj}^{u^*u^*} + G_{jj}^{v^*v^*} + G_{jj}^{ww} \right) , \tag{29}$$

where $G_{jj}^{u^*u^*}$, $G_{jj}^{v^*v^*}$, and G_{jj}^{ww} ($j = 1, \dots , 5$) are the diagonal elements of the vibrational Green function. The index j stands for the numbers of the Si atoms of the Si₅ cluster with the atom $j = 1$ in its center. The upper indices designate the kind of motion. The symmetry of the problem is also taken into account in (29).
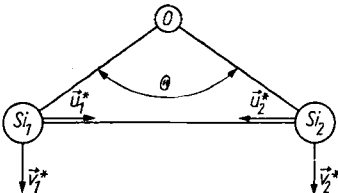

Fig. 2. Transformed displacements u^* and v^* of the Si atoms in the bonding plane of an Si–O–Si bridge
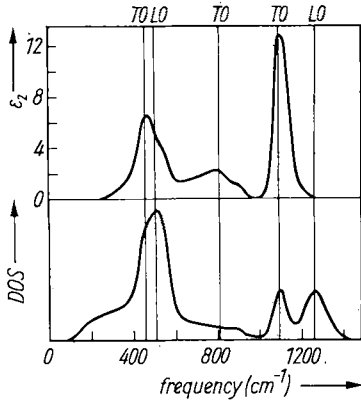
Fig. 3. Imaginary part ε_2 (in absolute units) of the IR dielectric function and the density of states (DOS) (in arb. units) calculated for SiO_2 with an oxygen bond angle $\theta = \equiv 150°$ after a broadening by 75 cm^{-1}. The other parameters are given in the text. The vertical lines mark the positions of the LO and TO frequencies of the SiO_2 layer prepared by thermal oxidation in dry atmosphere

After some algebraic manipulations we get for the evaluation of $G_{Si}(\omega)$ in the case of TO phonons the equation

$$[M\omega^2 - \tfrac{4}{3}(D_{11}^{uu} + D_{11}^{vv} + D_{11}^{ww})]\,G_{Si} + 1 = \tfrac{2}{3}\,\{[1 + (2D_{12}^{u^*u^*}G_{Si})^2]^{1/2} +$$

$$+ [1 + (2D_{12}^{v^*v^*}G_{Si})^2]^{1/2} + [1 + (2D_{12}^{ww}G_{Si})^2]^{1/2}\} \tag{30}$$

with the abbreviations

$$D_{11}^{uu} = \alpha + \frac{(\alpha s)^2}{N_x} + \frac{(\alpha c)^2}{N_y}, \tag{31}$$

$$D_{11}^{vv} = \beta + \frac{(\beta c)^2}{N_x} + \frac{(\beta s)^2}{N_y}, \tag{32}$$

$$D_{11}^{ww} = \beta + \frac{\beta^2}{N_z}, \tag{33}$$

$$D_{12}^{u^*u^*} = s^2\left(-\frac{(\alpha s)^2}{N_x} + \frac{(\alpha c)^2}{N_y}\right) - 2\alpha\beta s^2 c^2\left(\frac{1}{N_x} + \frac{1}{N_y}\right) + c^2\left(-\frac{(\beta c)^2}{N_x} + \frac{(\beta s)^2}{N_y}\right), \tag{34}$$

$$D_{12}^{v^*v^*} = c^2\left(-\frac{(\alpha s)^2}{N_x} + \frac{(\alpha c)^2}{N_y}\right) + 2\alpha\beta s^2 c^2\left(\frac{1}{N_x} + \frac{1}{N_y}\right) + s^2\left(-\frac{(\beta c)^2}{N_x} + \frac{(\beta s)^2}{N_y}\right), \tag{35}$$

$$D_{12}^{ww} = \frac{\beta^2}{N_z}, \tag{36}$$

where

$$N_x = m\omega^2 - 2\alpha s^2 - 2\beta c^2\,, \tag{37}$$

$$N_y = m\omega^2 - 2\alpha c^2 - 2\beta s^2\,, \tag{38}$$

$$N_z = m\omega^2 - 2\beta\,. \tag{39}$$

An analogous equation was obtained for $G_{Si}(\omega)$ in the case of LO phonons.

If we put the functions $G_{Si}(\omega)$, $\alpha'(\omega)$, $\beta'(\omega)$, and $\delta'(\omega)$ into the system of motional equations for the Si–O–Si bridge (on the "surface atoms" of which the potential (28) acts) we get for the oxygen motions in the case of TO modes the system

$$\text{Im } G_{00}^{zz} = \text{Im }\left\{\frac{1}{2N_x}\left[M\omega^2 - \frac{4}{3}(\alpha + 2\beta)\right]G_{Si}\right\}, \tag{40}$$

$$\operatorname{Im} G_{00}^{yy} = \operatorname{Im} \left\{ \frac{1}{2N_y} \left[M\omega^2 - \frac{4}{3}(\alpha + 2\beta) \right] G_{\text{Si}} \right\}, \tag{41}$$

$$\operatorname{Im} G_{00}^{zz} = \operatorname{Im} \left\{ \frac{1}{2N_z} \left[M\omega^2 - \frac{4}{3}(\alpha - 2\beta) \right] G_{\text{Si}} \right\}, \tag{42}$$

and an analogous system for the case of LO phonons. Additionally, the relation

$$\gamma^{\text{SiSi}} = \tfrac{2}{3}(\gamma^{\text{SiS}} + \gamma^{\text{SiB}} + \gamma^{\text{SiR}}) \tag{43}$$

is obtained as a result of the condition of translational invariance of the motional equations in the case of LO phonons. The non-diagonal parts of the vibrational Green function, which correspond to correlations of Si and O motions, can be calculated in a similar manner. The non-diagonal parts for the case of TO phonons are besides the diagonal parts neccessary for the evaluation of the IR response function [9, 18]. The DOS is calculated with the help of the diagonal parts of the vibrational Green functions for TO *and* LO phonons. In the case of TO phonons we have to take into account their twofold degeneracy.

The theoretical IR response function $\varepsilon_2(\omega)$ and the total DOS for amorphous SiO$_2$ with $\theta = 150°$ are shown in Fig. 3 after a broadening by 75 cm^{-1}. The calculations were performed with the help of the model parameters $\alpha = 600$ N/m, $\beta = 100$ N/m, $Z_{\text{Si}}^{\text{T}} = 2.57$, $Z_{\text{OS}}^{\text{T}} = -2.40$, $Z_{\text{OR}}^{\text{T}} = -0.83$ (in units of the elementary charge) and the material constants $\varrho_M = 2.2$ g cm^{-3} and $\varepsilon_\infty = 2.14$ [12]. The values of the model parameters were obtained comparing our experimental IR data of a thermally grown oxide [3, 19] with our theoretical results in a manner that will be used in the next section for the interpretation of further experimental IR spectra.

4. Interpretation of IR Transmission Spectra of Differently Prepared SiO₂ Layers

One of the advantages of the method developed here is the possibility of getting analytical relations between experimental peak positions and the microscopic parameters of the model, i.e. force constants, bonding angles, and transverse effective charges. The peak positions in the theoretical spectra are defined by the positions of δ-functions in the unbroadened DOS. They are given by the following expressions for the frequencies in the stretching, bending, and rocking motion of oxygen and in the motion of Si atoms:

$$\omega_{\text{TO}}^{\text{OS}} = \left[\frac{2}{m}(\alpha s^2 + \beta c^2) \right]^{1/2}, \tag{44}$$

$$\omega_{\text{LO}}^{\text{OS}} = \left[\frac{2}{m}(\alpha s^2 + \beta c^2 + \gamma^{\text{SS}}) \right]^{1/2}, \tag{45}$$

$$\omega_{\text{TO}}^{\text{OB}} = \left[\frac{2}{m}(\alpha c^2 + \beta s^2) \right]^{1/2}, \tag{46}$$

$$\omega_{\text{LO}}^{\text{OB}} = \left[\frac{2}{m}(\alpha c^2 + \beta s^2 + \gamma^{\text{BB}}) \right]^{1/2}, \tag{47}$$

$$\omega_{\text{TO}}^{\text{OR}} = \left(\frac{2}{m}\beta \right)^{1/2}, \tag{48}$$

$$\omega_{\text{LO}}^{\text{OR}} = \left[\frac{2}{m}(\beta + \gamma^{\text{RR}}) \right]^{1/2}, \tag{49}$$

$$\omega_{\text{TO}}^{\text{Si}} \approx \left[\frac{4}{3M}\left(\alpha + 2\beta\right)\right]^{1/2}, \tag{50}$$

$$\omega_{\text{LO}}^{\text{Si}} \approx \left[\frac{4}{3M}\left(\alpha + 2\beta + \frac{3}{4}\gamma^{\text{SiSi}}\right)\right]^{1/2}. \tag{51}$$

The last two relations are valid for the case that $\omega_{\text{TO}}^{\text{Si}}$ (or $\omega_{\text{LO}}^{\text{Si}}$) is located in the center of a broad gap between $\omega_{\text{TO}}^{\text{OB}}$ (or $\omega_{\text{LO}}^{\text{OB}}$) and $\omega_{\text{TO}}^{\text{OS}}$ (or $\omega_{\text{LO}}^{\text{OS}}$).

We find meaningful model parameters only by the identification of the theoretical phonon frequencies with the experimental ones shown in Table 1. If we know the most frequent value of θ of an SiO_2 form from other experiments we are able to determine the force constants α and β without use of the approximate relation (50). Then, because of the very small changes of the Si–O distances in different SiO_2 forms [12] these values α and β can be used for the evaluation of θ of other SiO_2 forms by a corresponding interpretation of their IR spectra. Such oxygen bridge angles derived (with the help of the force constants mentioned above using (44)) from the experimental spectra shown in Fig. 4 are listed in Table 1. There are also tabulated the θ-values which were evaluated from the transmission spectra by means of (44), (48), and (50).

The IR transmission spectra $T_{||}$ recorded at oblique incidence of radiation polarized in the plane of incidence show according to the Berreman effect [20] LO–TO splittings of the characteristic transmission minima. From the well-resolved splittings of the minima of the stretching and the rocking modes of oxygen we get with the help of (44), (45) and (48), (49) the transverse effective charges Z_{OS}^{T} and Z_{OR}^{T}, respectively [4]. The values of these charges found for the different SiO_2 layers investigated are also given in Table 1. Since the Si–O distance remains almost unchanged by the oxygen rocking motion the charge Z_{OR}^{T} must be equal to the static effective charge Z_{O}^{S}. This

Table 1

Vibrational frequencies of the oxygen stretching (OS), silicon (Si), and oxygen rocking (OR) mode in cm^{-1}, values of the most frequent angle θ of an Si–O–Si bridge, transverse dynamic effective charges Z_{OS}^{T} and Z_{OR}^{T} (in units of the elementary charge) of the stretching and rocking motion of oxygen, respectively, derived with the help of (44), (45), (48), and (49) from the IR transmission spectra shown in Fig. 4 for four differently prepared SiO_2 layers

oxide	a	b	c	d
$\omega_{\text{LO}}^{\text{OS}}$	1256	1255	1250	1255
$\omega_{\text{TO}}^{\text{OS}}$	1084	1088	1080	1090
$\omega_{\text{TO}}^{\text{Si}}$	812	810	812	812
$\omega_{\text{LO}}^{\text{OR}}$	506	507	507	506
$\omega_{\text{TO}}^{\text{OR}}$	458	458	458	464
θ*)	145°	146.5°	143.5°	147.5°
θ**)	139°	141.5°	137.5°	142.5°
Z_{OS}^{T}	−2.52	−2.48	−2.50	−2.47
Z_{OR}^{T}	−0.85	−0.86	−0.82	−0.80

*) Determined with the help of the assumed force constant $\alpha = 600$ N/m and $\beta = 100$ N/m by use of (44).

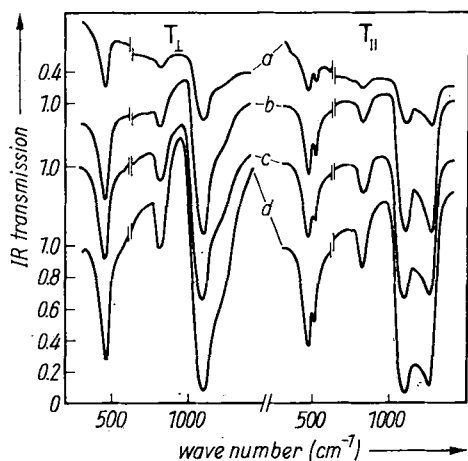**) Evaluated by means of (44), (48), and (50).

Fig. 4. IR transmission (in relative units) for oblique incidence of radiation (the angle of incidence is 55°) for different forms of amorphous SiO_2. The incident radiation is polarized in the plane of incidence $(T_{||})$ and perpendicular to the plane of incidence $(T_\perp)$, respectively. The SiO_2 layers with a thickness of approximately 1 μm were prepared by chemical vapour deposition (a), dry thermal oxidation (b), sputtering in a high frequency field (c), and thermal oxidation in water steam (d). The contributions of their Si substrates to the transmission are eliminated with the help of the transmission spectra of an identical substrate without any oxygen layer. At 630 cm^{-1}a grating change is indicated

condition is fulfilled by the derived values of Z_{OR}^T, since the relation $-1.02 \leq Z_O^S \leq$ ≤ -0.71 (in units of the elementary charge) is valid. The limits in this relation are given by the lowest and the highest value of the charges Z_O^S resulting from various theoretical methods [21 to 23]. The value $Z_{OS}^T = -2.74$ calculated by Pantelides and Harrison [23] for α-quartz with the help of a bond-orbital model is comparable with the values of Z_{OS}^T derived in this work.

5. Conclusions

Besides the above mentioned qualitative statements the microscopic parameters, which were derived for different forms of amorphous SiO_2, demonstrate a new possibility of classification of these SiO_2 forms. The theoretical considerations can be applied also to other amorphous AX_2 materials, if there exists a corresponding short-range order. The great advantage of the method developed here is that it leads for the first time to a calculation of TO *and* LO features of the optical phonon spectra of non-crystalline SiO_2.

Keeping in mind the suppositions used in Section 1, our results lead to the following model for the structure of amorphous SiO_2. In amorphous SiO_2 some kind of long-range order must exist, which could be described by very large unit cells with dimensions much greater than the interatomic distances. In the case of long waves the effects of the surely existing details of randomness inside these cells can be considered in a manner similar to the approximation for the vibrational induced polarization. A model of such large unit cells in form of cubic blocks was used by Sekimoto and Matsubara [24] for their theoretical investigations of the nature of TO and LO vibrational modes in glassy dielectrics.

In a subsequent paper [25] we will apply our theory to the complicated geometrically and chemically disordered material SiO_x $(0 < x < 2)$, for which we have detected LO–TO splittings, too [4].

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