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1993 J. Phys.: Condens. Matter 5 867

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Local s, p and d charge distributions and x-ray emission bands of SiO₂: α -quartz and stishovite

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Received 23 March 1992, in final form 27 April 1992

Abstract. An experimental and theoretical study of the electronic structure and the x-ray Si K and Si L emission bands of 4:2-coordinated α -quartz and 6:3-coordinated stishovite is presented. The nature of atomic states participating in the x-ray valence band spectra is identified. In particular the long-standing controversy about the role of Si 3d-like states is analysed; evidently, Si 3d-like electrons essentially contribute to the intensity of Si L emission bands. We have calculated the total density of states, the local partial densities of states, the ratios of the s, p and d charge components inside silicon and oxygen sited spheres, and the Si K and Si L emission bands. There is good agreement between our measured and calculated spectra. Reasons are given why in contrast with the Si K emission bands the Si L emission bands are insensitive to the local crystal structure of α -quartz and stishovite.

1. Introduction

Crystalline silicon dioxide (c-SiO₂) occurs in various polymorphs (quartz, tridymite, cristobalite, coesite and stishovite), and silicon dioxide also exists in the vitreous state (amorphous SiO₂ (a-SiO₂)). The complex Si–O bonding and the electronic structure of c-SiO₂ and vitreous SiO₂ have been persistently studied for more than 20 years, theoretically [1–12] and experimentally applying different techniques such as x-ray spectroscopy [13–20] and photoelectron spectroscopy (UPS and XPS) [20–24]. At present there is a general consensus as far as the description of the electronic structures of these materials is concerned. However, the understanding of the Si L emission band of SiO₂ compounds is still unsatisfactory.

The Si L emission band has been measured for several c-SiO₂ and a-SiO₂ compounds [17–20]. The spectrum exhibits a characteristic double-peak shape. The interpretation of the Si L emission bands is linked with the controversy about Si d-like states in the valence bands (vbs) of SiO₂, the so-called d controversy [15, 26]. The aim of this paper is to explain the origin of this controversy and to elucidate this long-standing problem.

All polymorphs of c-SiO₂—except stishovite—and vitreous silica have similar structures. The basic structural units are SiO₄ tetrahedra and the different structures result from different geometrical arrangement of the tetrahedra [18, 27]. Only in quartz have the Si–O bond length and the Si–O–Si bonding angle well defined values.

The same also holds for stishovite whose structure, however, differs significantly from that of quartz. We therefore shall confine ourselves to studying the electronic structure of α -quartz and stishovite.

α -quartz is formed by regular tetrahedra, each silicon atom being surrounded by four oxygen atoms, and each oxygen atom having two silicon neighbours (hexagonal 4:2 coordination). The Si–O distance is 1.61 Å. Stishovite has tetragonal 6:3 coordination. Each silicon atom is surrounded by six oxygen atoms, forming a slightly distorted octahedron. The oxygen atoms have three neighbouring silicon atoms lying in a plane and forming an isosceles triangle. The Si–O distance varies from 1.75 to 1.81 Å [10]. In view of these structural differences it is not surprising that the Si K emission bands of α -quartz and stishovite which reflect the local silicon-centred p character of the valence electrons differ significantly. (The Si K emission bands of other SiO₂ polymorphs consisting of SiO₄ structural units are qualitatively very similar to that of α -quartz [18].) On the other hand, the Si L emission bands of several SiO₂ polymorphs including the structurally different stishovite are very similar in shape and exhibit a spectrum with two characteristic peaks [17, 18]. This gives rise to the question why the Si L emission bands do not react to different local structures as the Si K emission bands do.

2. Calculations

The silicon oxides crystallize in open structures and therefore for the calculation of their electronic states the symmetry unbiased plane-wave expansion of wavefunctions is the most suitable. The form of the potential and the electronic charge density is completely general and without any shape approximations. Self-consistent pseudopotential calculations for silicon dioxides have been described in several recent papers [12, 25, 28–30] and, because we use the same formalism, we shall outline only the major steps of our computations.

For generating the pseudopotentials we applied the phase shift technique described elsewhere [31]. The oxygen pseudopotential was generated from the atomic $2s^2 2p^4$ ground-state configuration; the oxygen d component was neglected. For silicon, not only the s and p but also the d components were included. Self-consistency was performed using the structures of α -quartz and stishovite and the experimental lattice constants. The semilocal form of the pseudopotential was used and plane waves up to an energy cut-off of 30 Ryd were included in the basis set. For the calculations of the local partial densities of states (PDOSS) the wavefunctions were projected into Gaussian s, p and d orbitals centred on the oxygen and silicon atoms. In the Gaussian factor $\exp(-\alpha r^2)$ for α the values 1.5 and 1.0 were chosen for oxygen and silicon orbitals, respectively.

In figure 1 and figure 2 the calculated total densities of states (TDOS) and PDOSS of α -quartz and stishovite, respectively, are shown. The theoretical curves have been convoluted with a Gaussian broadening function with a full width at half-maximum (FWHM) of 0.5 eV. The resulting TDOS for α -quartz is in very good agreement with the calculations of Binggeli *et al* [25], and it reflects quite well all the features and the energy of a recent UPS spectrum obtained by Sferco *et al* [24] and Binggeli *et al* [25].

For the interpretation of x-ray emission bands a very important point in question is the charge-density distribution and its s-, p- and d-like character. Therefore we

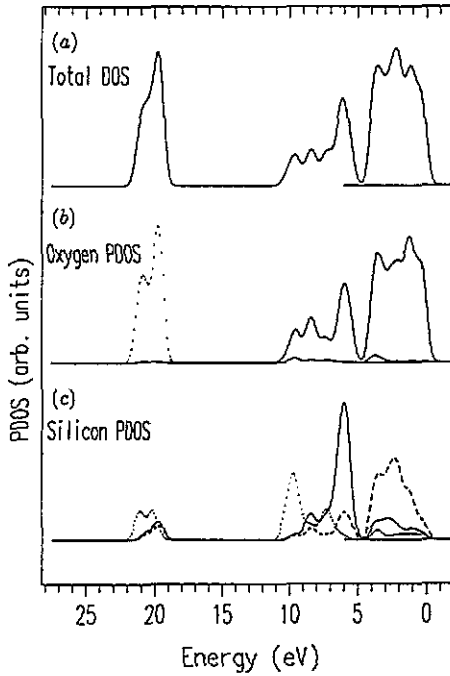


Figure 1. DOS curves for α -quartz. (a) TDOS. (b) Oxygen PDOS; —, p-like DOS; ·····, s-like DOS. (c) Silicon PDOS: —, p-like DOS; ·····, s-like DOS; - - -, d-like DOS. The zero of the energy scale relates to the top of the vb.

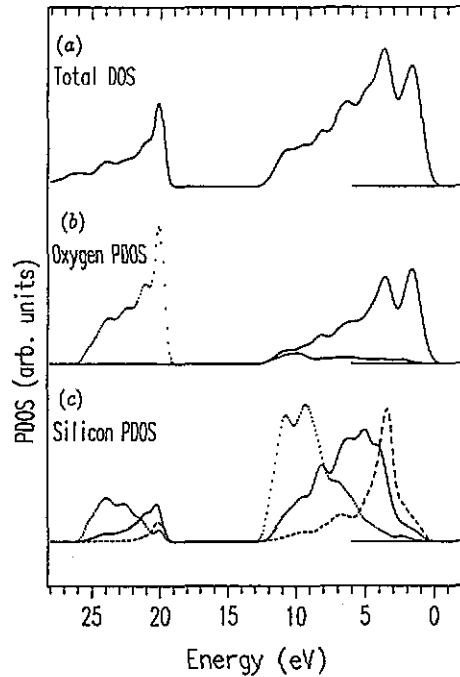


Figure 2. DOS curves for stishovite. (a) TDOS. (b) Oxygen PDOS; —, p-like DOS; ·····, s-like DOS. (c) Silicon PDOS: —, p-like DOS; ·····, s-like DOS; - - -, d-like DOS. The zero of the energy scale relates to the top of the vb.

have performed a real-space integration of the charge densities obtained from the self-consistent band-structure calculations. Using the spherical-wave expansion of plane waves we decomposed the total charge inside spheres of radius R centred at the position of an atom into s, p and d charge components. The resulting ratios of the charge components referring to the s components are presented in table 1. For comparison the corresponding decomposition for c-Si is included. The oxygen d charge component is very small (less than 8% of the s components for all given radii) and therefore is omitted in table 1.

Table 1. Ratios of the s, p and d charge components inside silicon and oxygen sited spheres of radius R for α -quartz, stishovite and c-Si.

Radius R (au) (1 au = 0.53 Å)	α -quartz		Stishovite		c-Si sp:d
	Silicon site sp:d	Oxygen site sp	Silicon site sp:d	Oxygen site sp	
1.6	1:1.52:0.59	1:1.92	1:1.40:0.60	1:1.95	1:1.32:0.07
1.8	1:1.60:0.72	1:2.16	1:1.43:0.72	1:2.18	1:1.39:0.08
2.0	1:1.70:0.88	1:2.45	1:1.47:0.87	1:2.46	1:1.47:0.10
2.5	1:2.00:1.43	1:2.64	1:1.83:1.39	1:2.61	1:1.72:0.18

The values in table 1 show several essential facts.

(i) The magnitudes of the ratio of p to s and its evolution with R of charges on oxygen are almost the same for α -quartz and stishovite. The small differences are within the accuracy of computations.

(ii) The same outcome as in (i) holds also for the ratio of d to s for silicon sited charges.

(iii) The ratio of p to s for silicon sited charges decreases in the order α -quartz, stishovite and c-Si.

(iv) For c-Si the ratio of d to s of charges is much smaller than for α -quartz and stishovite.

As a consequence of the Si–O bonds we observe a significantly different s–p–d composition of silicon sited electrons in α -quartz and stishovite than in c-Si or a free silicon atom. In addition the electrons are strongly localized on the oxygen atoms. For example, in α -quartz spheres centred on silicon and oxygen and having a radius of half the Si–O distance contain 0.8 and 4.6 electrons, respectively. Very similar values are obtained for stishovite. That valence electrons in silicon dioxides are mainly localized around the oxygen atoms is nicely demonstrated by a contour plot of the valence pseudo-charge densities in cristobalite published recently by Allan and Teter [28]. The fact that the valence electrons of α -quartz and of stishovite are localized on the oxygen atoms is accordingly reflected in the close similarity of the oxygen PDOS with the TDOS shown in figures 1 and 2.

Besides the TDOS and PDOS we have also calculated the Si K and Si L emission bands of α -quartz and stishovite. In the pseudopotential approach the valence wavefunctions $\Psi_v(\mathbf{k}, \mathbf{r})$ are without a nodal structure in the core region of the atoms. To obtain the matrix elements of the x-ray core–valence transitions we split the dipole transition matrix element into its radial and angular parts in the following way:

$$\langle \Psi_c(\mathbf{k}, \mathbf{r}) | e \cdot \mathbf{r} | \Psi_v(\mathbf{k}, \mathbf{r}) \rangle = \langle \Psi_c | r | \Psi_v \rangle_{\text{rad}} \langle \Psi_c | e \cdot \mathbf{r} / r | \Psi_v \rangle_{\text{ang}}$$

where e is the polarization vector. The angular part is fully determined by the bond symmetry in the solid and is adequately calculated by the pseudo-wavefunctions $\Psi_v(\mathbf{k}, \mathbf{r})$. The core states O 1s, Si 1s and Si 2p are localized in the core region of the atoms. Therefore the wavefunctions $\Psi(\mathbf{k}, \mathbf{r})$ are almost dispersionless and the radial integral is evaluated within the core region of the atoms. In view of the frozen-core approximation forming the basis of the pseudopotential approach the wavefunctions of the valence electrons have a frozen atomic character in the core region. The radial part of the matrix element $\langle \Psi_c | r | \Psi_v \rangle_{\text{rad}}$ therefore can be approximated by atomic calculations if we take into account the charge redistribution and the new s–p–d configuration created by the bonds. To study the influence of various quantities on this approximation we have calculated the radial matrix elements for several configurations and ionicities of the silicon atom. The matrix elements were also calculated directly for the resulting s, p and d charge densities in α -quartz and stishovite using the phase shift technique which allows recovery of the nodal structure of wavefunctions in the core region [32]. We have found that

(i) the ratio of the transition matrix elements $\langle 2p|r|3s \rangle / \langle 2p|r|3d \rangle$ which determines the relative intensities of features in the Si L emission bands is more sensitive to the ionicity than to the s–p–d configuration of the silicon atom,

(ii) its value is well established within the limits of plausible ionicities and configurations of the silicon atom in the Si–O bonds and

(iii) this value in any case is calculated with an accuracy better than 10%.

A thorough analysis of the s to d ratio of the transition probabilities and the Si d -like PDOS leads to the conclusion that Si d -like valence electrons significantly contribute to the Si L emission bands of α -quartz and stishovite, and of other silicon dioxides.

The same techniques and approximations were also applied to calculate the Si L emission bands of c -Si and c -SiC and very good quantitative agreement with experiment was found.

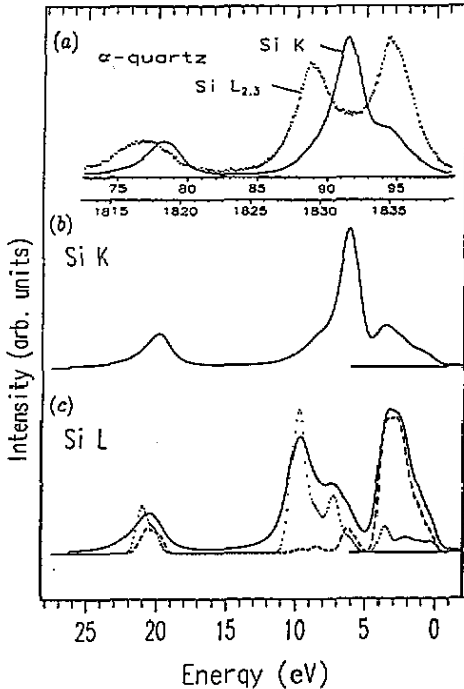


Figure 3. α -quartz. (a) Measured Si K and Si L emission bands [17]. (b) Calculated Si K emission band. (c) Calculated Si L emission band (—) and separation into the s contribution (.....) and the d contribution (---).

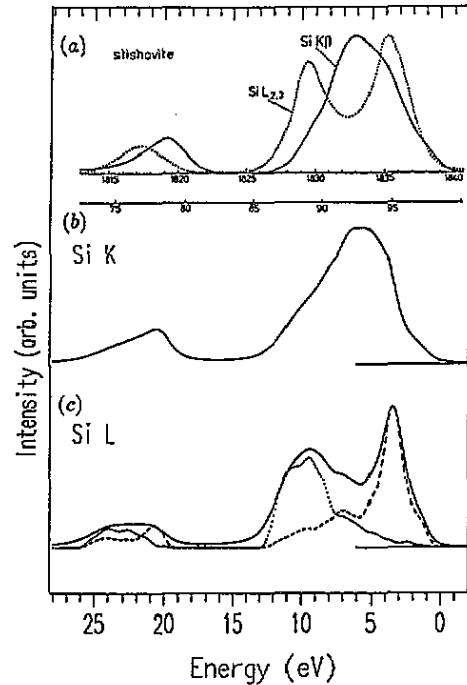


Figure 4. Stishovite. (a) Measured Si K and Si L emission bands [17]. (b) Calculated Si K emission band. (c) Calculated Si L emission band (—) and separation into the s contribution (.....) and the d contribution (---).

The calculated Si K and Si L emission bands of α -quartz and stishovite are presented in figures 3 and 4, respectively. For comparison with experiment the theoretical curves have been convoluted with a Lorentzian function whose FWHM $w(E)$ varies according to $w(E) = w_c + w(E/w_B)^2$ [33, 34] where E is the energy measured from the top of the VB with width w_B , w is a parameter which takes into account the lifetime of holes in the VB and is assumed to be 1 eV [34], and w_c corresponds to the lifetime of the core holes and for the Si K and Si L emission bands the values 0.5 and 0.3, respectively, were used. Apparatus broadening was not accounted for. In the case of the Si L emission bands the s - and d -like components of the bands are shown. The sum of the s and d component is not equal to the Si L emission band because all three curves were convoluted separately. The value $w = 0$ was used for s and d components to magnify the details in them.

All experimental Si K and Si L emission bands displayed in this work are taken from [17]. We have also calculated the O K emission bands of both compounds and

for α -quartz there is good agreement with experiment [35]. These results are not required for further discussion and are therefore not presented here.

3. Discussion of x-ray emission bands

As figure 3 shows, there is very good overall agreement of the calculated with the measured Si K and Si L emission bands; this holds for the width of the emission bands too. In the calculated spectra, features are more pronounced than in the measured spectra although a smearing function has been applied. In the calculated Si L emission band the energy separation of the two peaks is larger by 0.6–0.8 eV than in the experiment (about 6 eV). Moreover the valley between the two peaks is deeper. At about 7 eV there is a feature which is not visible in the measured spectrum, indicated only by the asymmetry of the left peak.

The distances between the maximum of the Si K emission band and the O 2s-derived line at about 20 eV are the same in theory and experiment. In the calculated Si L emission band this line is located at a higher binding energy by about 1 eV, in excellent agreement with experiment. Also for stishovite (figure 4) there is very good agreement with respect to shapes and band widths between the calculated and measured Si K and Si L emission bands. For the Si K emission band the theory reflects the asymmetry of the main peak, the changes in slope at about 4 and about 2 eV, and the weak shoulder at about 10 eV. For the calculated Si L emission band the energy separation of the two peaks is the same as in experiment. The peak at about 9 eV, however, is broader than in the measured spectrum. In particular there is a large contribution to intensity at about 11 eV while the intensity of the measured spectrum rapidly decreases.

It is interesting to note that even the asymmetry of the O 2s-derived line in the Si K emission band is reflected in the calculated spectrum. In stishovite the energy spacing between the O 2s-derived lines in the Si K and Si L emission bands is about 2 eV, and larger than in α -quartz. This larger spacing and the larger width of O 2s-derived states are also reflected in the calculated spectra.

The good agreement of the theoretical and experimental results enables us to clarify the so-called d-orbital controversy over silicon dioxide (see, e.g., [26]). For more than 20 years the question has been discussed whether or not in Si–O compounds Si 3d electrons do exist and participate in bonding. In view of our results the question usually is incorrectly asked; there are in fact two questions which should be answered. The answer to the first question of whether Si 3d-like valence electrons significantly contribute to the intensity of the Si L emission band of SiO₂ is yes; the answer to the second, very similar question of whether Si 3d-like valence electrons significantly participate in the bonding of SiO₂ is no.

The first answer is based on our calculations of the Si L emission bands of α -quartz and stishovite (lowest curves in figures 3 and 4). The calculated Si L emission bands are decomposed in their s and d constituents, and the curves show clearly that, in the upper part of the VB (0–6 eV), d-like electrons and, in the lower part of the VB, s-like electrons do contribute to the Si L emission band. Obviously the peak in the measured Si L emission bands of α -quartz and stishovite at a photon energy of about 95 eV is predominantly due to Si d-like electrons.

The key to understanding the second answer is the distribution of valence charge between the silicon and oxygen atoms. The short Si–O distances, the large difference

between the sizes of Si and O atoms and the high electronegativity of O atoms lead to localization of the valence electrons on the oxygen atoms. The bonding states in α -quartz and stishovite form VBS with high binding energies having predominantly O s, p and Si s, p character. The non-bonding states which form the upper VBS with low binding energies have mainly O p and Si p, d character. According to the concentration of electrons on the oxygen sites (4.6 electrons compared with 0.8 electrons on the silicon sites) the PDOSs are much higher for the oxygen site than for the silicon site. The small amount of silicon sited states and the non-bonding character of Si d-like states are the reasons why Si 3d electrons do not play a significant role in bonding. As a consequence, Si 3d states are not sensitive to the various structure configurations of silicon dioxides and, because Si s states have a spherical and therefore structurally insensitive symmetry, the Si L emission bands of all SiO_2 compounds show qualitatively the same shapes. In contrast, the Si K emission bands reflect the structurally sensitive Si p-like bonding electrons, and this is the reason why the Si K emission bands of α -quartz and stishovite are completely different.

4. Conclusions

In conclusion we wish to point out that x-ray emission spectroscopy is a local-orbital-sensitive probe for studying the electronic structure of solids. The density of valence electrons is low in the vicinity of silicon atoms in Si-O compounds or—more generally—in the vicinity of the electropositive element in ionic compounds. Therefore the charge redistribution caused by bonding significantly rearranges the local s-p-d configuration of electrons on the electropositive element, while redistribution affects the rearrangement on the electronegative atom (oxygen in our case) only to a slight extent. Thus, although the absolute amount of charge on the electropositive element (silicon) is small, the relative changes may be quite large and lead to significant changes in the (Si K and Si L) x-ray emission bands. Consequently the x-ray emission bands of the electropositive constituent of a compound yield a very sensitive response to changes in chemical bonding and provide experimental data which are difficult to obtain, if at all, by other experimental techniques, e.g. UPS and XPS.

Acknowledgments

We thank Leibniz-Rechenzentrum der Bayerischen Akademie der Wissenschaften, München, for generously putting computer time at our disposal. AŠ is greatly indebted to Deutsche Forschungsgemeinschaft for financial support.

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