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p → p-like transitions at the silicon L_{2,3}-edges of silicates

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Abstract. — We provide evidence for the existence of p → p-like transitions at the silicon L_{2,3}-edges of common silicates. This arises due to the local, tetrahedral potential at the silicon site imposed by the nearest neighbour atoms leading to a loss of inversion symmetry. In order to successfully describe the resultant electron energy loss near-edge structure (ELNES) in such environments, we show that the consideration of such effects is extremely important.

Introduction.

With recent advances in instrumentation and a gradual improvement in theoretical modelling procedures, the study of near-edge structure measured using electron energy loss spectroscopy (EELS) has developed into a powerful tool for the investigation of the local geometrical and electronic structure around a particular atomic species in the solid state [1, 2]. Since the technique is performed in a transmission electron microscope this may be combined with the benefits of a spatial resolution of the order of nanometres in both analysis and image formation.

Normally the structure observed on a core-loss edge is interpreted in terms of a local density of states (DOS) projected from the particular atomic site in question [3], which may be modified by creation of the core hole and interactions in the final state. If the scattered electrons are collected over a small range of collection semi-angles (i.e. in the limit $q \rightarrow 0$, where q is the momentum transfer upon excitation) then it has been shown that the dipole selection rules apply to the various transitions, the results being identical to those obtained using X-ray absorption spectroscopy (XAS) [4]. Normally this is quoted as the change in orbital angular momentum, $\Delta l = \pm 1$, with $\Delta l = +1$ predominating. Thus at a K-edge (transitions from the 1s level) we would expect electrons to be excited to predominantly p-like final states, while an L_{2,3}-edge (transitions from the 2p level) probes mainly the unoccupied d-like states, with some contribution from s-like states. However, our studies indicate that this is a misleading interpretation of the dipole selection rules for L_{2,3}-excitations. Firstly, the $\Delta l = -1$ channel is not always negligible as has been shown by a

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number of studies [5, 6]. Secondly, it is the purpose of this work to show that, in certain situations, transitions apparently corresponding to $\Delta l = 0$ contribute significantly to core-loss edges in which the initial state has a value of $l = 1$.

The selection rules.

To understand the correct form of the dipole selection rule it is instructive to follow through the mathematics. There are a number of different frameworks within which it is possible to derive essentially the same result and the interested reader is referred to references [7, 8] for these alternative pictures. Here we consider photon absorption, although it is also possible to derive the same result in terms of the impact of high energy incident electrons. The starting point is Fermi's golden rule which states that the probability of a one electron transition from an initial state, ψ_i , to a final state, ψ_f , is given by

$$R_{i \rightarrow f} \propto |M_{\hat{n}}|^2 \rho(E) \quad (1)$$

Here $\rho(E)$ is the density of states and $M_{\hat{n}}$ is the matrix element of the dipole operator, $M = \epsilon \cdot r$ which contains the various selection rules

$$M_{\hat{n}} = \langle \psi_f | M | \psi_i \rangle \quad (2)$$

It is possible to expand M in terms of spherical harmonic functions $Y_{lm}(\theta, \phi)$ and in the case of the dipole operator we only need consider $l = 1$ and $m = 0, \pm 1$.

$$M = \epsilon \cdot r = \sqrt{(4\pi/3)} \left\{ \epsilon_z Y_{10} + \left(1/\sqrt{2}\right) (-\epsilon_x + i\epsilon_y) Y_{11} + \left(1/\sqrt{2}\right) (\epsilon_x + i\epsilon_y) Y_{1-1} \right\} \quad (3)$$

where ϵ is the polarization vector of the photon with components ϵ_x, ϵ_y and ϵ_z . Similarly assuming ψ_i and ψ_f can be written in terms of single electron hydrogen-like orbitals with well defined values of n, l and m (subscripted i for the initial state and f for the final state) - it is possible to arrive at an expression for the dipole matrix element in terms of radial and angular parts. The dipole operator separates out with the angular part of the expression which is given by

$$\int Y_{l_f m_f}^* \epsilon \cdot r Y_{l_i m_i} \delta\Omega \quad (4)$$

Substituting equation (3) into equation (4) gives an expression consisting of a sum of integrals of the form,

$$\int Y_{l_f m_f}^* Y_{1m} Y_{l_i m_i} \delta\Omega \quad (5)$$

where $m = 0, \pm 1$. The product of two spherical harmonics may be written as a sum of spherical harmonics. More explicitly,

$$Y_{l_1 m_1} Y_{l_2 m_2} = \sum_{L=|l_1-l_2|}^{|l_1+l_2|} C(L, m_1 + m_2, l_1, l_2, m_1, m_2) Y_{L, m_1+m_2} \quad (6)$$

where the coefficients C are the Clebsch-Gordan coefficients. Employing the identity in equation (6) in equation (5) gives an expression

$$C(l_i + 1, m + m_i) \int Y_{l_f m_f}^* Y_{l_i+1, m_i+m} \delta\Omega + C(l_i, m + m_i) \int Y_{l_f m_f}^* Y_{l_i, m_i+m} \delta\Omega \\ + C(l_i - 1, m + m_i) \int Y_{l_f m_f}^* Y_{l_i-1, m_i+m} \delta\Omega \quad (7)$$

where we have used the general abbreviation $C(l_i + 1, m + m_i) = C(l_i + 1, m + m_i, l, l_i, m, m_i)$ for the various Clebsch-Gordan coefficients. The spherical harmonics are mutually orthogonal so for the sum of the three integrals to be non-zero, l_f must equal either $l_i + 1$ or $l_i - 1$. This may be expressed in the form

$$\Delta l = l_f - l_i = 0, \pm 1. \quad (8)$$

Another constraint which also follows from the orthogonality properties is that l_f and l_i cannot be both zero (i.e. and s → s transition is forbidden).

A further constraint is that the transition matrix element, given in equation (3) must be totally symmetrical under the symmetry operations of the system. Consider the inversion operation, $\mathbf{r} \rightarrow -\mathbf{r}$, present in centrosymmetric systems such as atoms. The parity of the spherical harmonic Y_{lm} is given by

$$Y_{lm}(\pi - \theta, \pi + \phi) = (-1)^l Y_{lm}(\theta, \phi) \quad (9)$$

Thus a s-like wavefunction has even parity, p-like odd and d-like even etc. For the integrand in equation (5) to be invariant under inversion symmetry, it follows that

$$1 = (-1)^{l_f + l_i + 1} \quad (10)$$

Hence the transition $\Delta l = 0$ is forbidden in centrosymmetric systems. This is known as the Laporte or parity selection rule which only allows transitions involving a change in parity. Thus we may conclude that the dipole selection rule for atomic transitions is $\Delta l = \pm 1$.

Considering now molecular systems, the simplest procedure is to analyse equation (2) in terms of group theory. In a given molecular symmetry both the initial and final states will transform from atomic states to various symmetry species. If the integral in equation (2) is a basis for the totally symmetric one-dimensional irreducible representation of the molecular symmetry group then it will be non-zero and the transition will be dipole allowed.

Using this method it is possible to compare the dipole allowed transitions in two differing symmetries: octahedral and tetrahedral (centrosymmetric and non-centrosymmetric respectively). If the initial state is a p orbital ($l = 1$) then in octahedral symmetry this transforms as t_{1u} . The final states for which the transition matrix element is non-zero are a_{1g} (s-like), t_{2g} and e_g (both d-like); i.e. $\Delta l = \pm 1$. In tetrahedral symmetry, the initial p state transforms as t_2 and the dipole allowed final states are a_1 (s-like), e (d-like) and t_2 (d-like and p-like). Thus transitions to p-like final states are dipole allowed and we have an apparent violation of the selection rule $\Delta l = \pm 1$. The reason for this lies in the fact that in T_d symmetry both the p_x, p_y, p_z and d_{xy}, d_{xz}, d_{yz} orbitals transform as t_2 and as a consequence of this p-d mixing occurs giving p orbitals with some d character and vice versa. The true wavefunctions of both the initial and final states cannot have a definite parity and must consist of some mixture of orbitals of different parity. Therefore the parity selection rule prohibiting $\Delta l = 0$ transitions is not strictly applicable. A formally less correct explanation for this behaviour is to imagine that in a system which possesses no inversion symmetry we no longer have the constraint imposed by the Laporte selection rule (Eq. (10)) and transitions apparently corresponding to $\Delta l = 0$ will be observed.

Discussion.

As an example of these effects, we now discuss the silicon L_{2,3}-edge of silicates. The initial state is a silicon 2p level ($l = 1$) so, on the basis of the selection rules we would expect the excited electron to probe both s-like and d-like final states. In the absence of the Laporte selection rule, transitions to p-like final states also have to be considered.

In α -SiO₂ silicon is tetrahedrally co-ordinated to oxygen. The tetrahedron is slightly distorted from perfect T_d symmetry, however, this does not affect our subsequent arguments. In stishovite, a rare, high density form of silica, the oxygen nearest neighbours form a (slightly distorted) octahedron around the silicon atoms in the structure. Figure 1a shows the Si L_{2,3}-edge of α -SiO₂, while figure 1b shows the Si L_{2,3}-edge of stishovite measured by Brytov and Romashchenko [9] using the photoelectron quantum yield technique. Both spectra show four major features which we have labelled A-D.

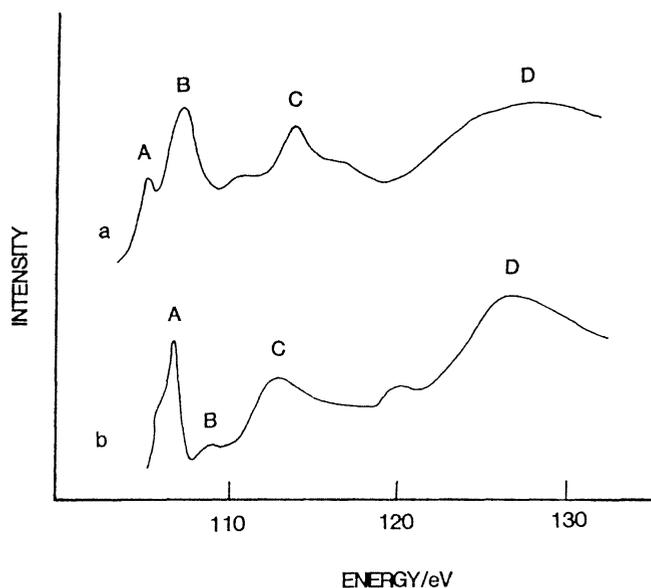


Fig. 1. — Experimental silicon L_{2,3}-edge in (a) α -SiO₂, which contains tetrahedral SiO₄ units and (b) stishovite which contains octahedral SiO₆ units [9]. Note the diminution of peak B in the octahedral case.

Previous studies have shown that particularly in the case of insulators, the effect of the core hole potential combined with the presence of strong scatterers in the first coordination shell can lead to the effective localization of the final density of states within this first shell [2, 5]. In other words, much of the gross structure in the near-edge region arises from multiple elastic scattering of the excited electron within a “molecular unit” surrounding the atom undergoing excitation. In such cases, it is possible to describe the majority of features in terms of transitions to specific molecular orbitals (MOs) formed from the interaction of atomic orbitals on the central atom with those on the surrounding ligands. In a recent paper we assigned the feature A, B, C and D in figure 1a to transitions to predominantly 6a₁ (s-like), 6t₂ (p-like), 2e and 7t₂ (both d-like) MOs respectively [10]. This was based on the results of previous molecular orbital calculations on SiO₄⁴⁻ clusters [11] and extensive experimental investigations [12, 13] together with the results of our own multiple scattering (MS) calculations. A MO calculation for SiO₆⁸⁻ [14] allows us to assign the various features present in figure 1b. Peaks A and B then correspond to transitions to 7a_{1g} (s-like) and 7t_{1u} (p-like) MOs respectively, while peaks C and D are associated with t_{2g} and e_g (both d-like) MOs.

Comparison of figures 1a and 1b indicates that on going from tetrahedral to octahedral coordination the relative intensity of peak B, the feature associated with p → p-like transitions, decreases

markedly. This is in agreement with the operation of the Laporte selection rule in O_h symmetry. The small, yet significant, intensity present in peak B of the stishovite Si L_{2,3} spectrum is presumably due to the transition being “slightly allowed” via vibronic coupling or small distortions from perfect O_h symmetry.

Further evidence for the existence of p → p-like transitions at the Si L_{2,3}-edge of tetrahedrally coordinated silicon may be derived from the results of our theoretical MS calculations obtained using the computer code of Vvedensky *et al.* [15]. Employing a cluster consisting of a single shell of tetrahedrally coordinated oxygen atoms surrounding a central sp³-hybridized silicon atom plus core hole (empirically simulated by use of the (Z + 1)* approximation for this atom [16]), we obtain the results shown in figures 2a-c. Figure 2a shows the contribution of transitions to both s- and d-like final states (these have been calculated separately and simply added according to the formula given by Schaich [17]). To achieve satisfactory agreement with experiment (Fig. 1a), primarily in the relative intensity of peak B, it is necessary to include the contribution of transitions to p-like final states shown in figure 2b. This is due to the non-overlapping, muffin tin form of the potential used to determine the scattering phase shifts and atomic matrix elements for the MS calculation which assumes spherical symmetry. The effects of d-p mixing due to the lack of inversion symmetry are therefore not explicitly included. Figure 2c shows an arbitrary linear combination of the curves in figures 2a and 2b which clearly models the major features observed experimentally. Increasing the number of shells used in the calculation indicates that the s- and d-like unoccupied DOS is largely confined within the first shell of oxygen atoms. The p-like DOS, however, is much more spatially delocalized and may be influenced by outer lying shells. In the case of the silicates zircon and forsterite we have shown that this effect leads to the appearance of further structure in peak B which may also extend into peak C [10, 18]. Fujikawa [19] has also attempted to model the Si L_{2,3} near-edge structure in α-SiO₂ using MS theory. Considering only transitions to d- and s-like final states within a three shell (Si₅O₁₆) cluster, he achieved relatively poor agreement especially within the first 5-10 eV from the edge onset which we attribute to the lack of inclusion of p → p-like transitions.

An alternative picture of the near-edge transitions observed in the different silicon environments may be derived in terms of hybridization of the various atomic orbitals. In tetrahedral coordination the silicon 3s and 3p orbitals combine to form an sp³ hybrid, forming final states which will have mixed s and p character and hence, to some extent, allow p → p-like transitions. Also the possibility of sd³ hybridization or a combination of both sp³ and sd³ will tend to blur the distinction between p- and d-like final states. A synergistic effect arises because of the shorter bond length present in tetrahedral coordination (as opposed to octahedral) which will lead to an increased overlap between the silicon 3d and/or 3s orbitals and the oxygen 2p orbitals. Therefore there is an increased probability of probing states with considerable ligand p character. From the latter argument it follows that the intensity of these transitions should depend on the size of the molecular cage defined by the nearest neighbour oxygen ligands, increasing as the bond length decreases. At this point it is interesting to speculate as to whether the scattering power of the confining ligand cage (as defined by the electronegativity of the ligand) is related to the observation of p → p-like transitions. The observations of Waki and Hirai [20] on the Si L_{2,3}-edges of a variety of species suggest that as the electronegativity of the tetrahedrally coordinated ligand decreases (e.g. the progression F, O, N, Si) the relative intensity of peak B (representing p-like final states) also decreases. Thus it appears that we require strong scatterers in the first co-ordination shell if we are to induce a local, non-centrosymmetric potential which will lead to an apparent violation of the Laporte selection rule.

The effects we describe here are, in principle, analogous to the observation of ls → 3d pre-edge transitions at the metal K-edges of 3d transition metal compounds measured using XAS [21, 22]. In perfect O_h symmetry the Laporte selection rule forbids the transition from the ls (a_{1g})

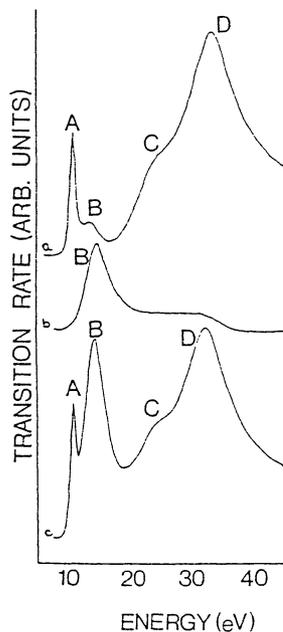


Fig. 2. — Multiple scattering calculations for an SiO_4 cluster with inclusion of the core hole. Transitions to (a) d- and s-like final states and (b) p-like final states. (c) Arbitrary linear combination of curves 2a and 2b which models experimental data shown in figure 1a.

level to the t_{2g} and e_g final states which consist of predominantly metal 3d character hybridized with some ligand p character. However, as the symmetry is lowered, increased transition metal 3d-4p orbital mixing together with stronger metal 3d-ligand 2p overlap results in the transition becoming progressively “more allowed”. In T_d symmetry the presence of this intense pre-edge feature serves as a fingerprint for the tetrahedral environment of the transition metal atom [23]. A further example of these effects may be found in the optical or ultraviolet $d \rightarrow d$ transitions observed in non-centrosymmetric transition metal complexes [24].

Auerhammer and Rez [25] have demonstrated the importance of monopole transitions (i.e. $s \rightarrow s$, $p \rightarrow p$ etc.) at large momentum transfers. These effects arise since we are now outside the region where the dipole approximation is valid and we have to consider corrections (both monopole and quadrupole) to equation (3). More specifically, in the case of the Si $L_{2,3}$ -edge of hexagonal SiC, they have shown that the relative intensity of the peak due to p-like final states increases as the momentum transfer increases. Their findings do not contradict our work, however, we would like to stress the importance of $p \rightarrow p$ -like transitions even at small momentum transfers, i.e. within the dipole regime.

Finally we wish to point out that spectra from other tetrahedrally coordinated metal cations, such as aluminium and magnesium, should also exhibit these effects. Indeed, the Al $L_{2,3}$ -ELNES of amorphous alumina (which contains predominantly tetrahedral AlO_4 units) has a very similar form to the Si $L_{2,3}$ -ELNES of α - SiO_2 (Fig. 1a) [9]. This is to be expected since the unoccupied MO structure of the isoelectronic clusters AlO_4^{5-} and SiO_4^{4-} are very similar [11]. Initial MS calculations on an AlO_4 cluster also suggest that transitions to p-like final states must be included in order to model the experimental spectrum. Further work is in progress to resolve this point.

Conclusions.

We have provided substantial evidence for existence of $p \rightarrow p$ -like transitions at the $L_{2,3}$ -edges of tetrahedrally co-ordinated silicon compounds in addition to the contribution from d- and s-like final states. This arises due to the breakdown of the Laporte selection rule in non-centrosymmetric environments due to significant mixing of p and d atomic orbitals. In principle, these effects should also be observed at the $L_{2,3}$ -edges of other elements.

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