INTRODUCTION

Silica is an important material from both the geological and the materials science points of view. Amorphous SiO$_2$ is vital to the electronics and glass industries, and crystalline varieties are important as precision oscillators and dielectric materials. Hence, considerable effort has been devoted to the study of this material. The bonding and valence bands of $\alpha$-quartz are well understood from band-structure (Chelikowsky and Schlüter 1977; Xu and Ching 1991; Simunek et al. 1993; Di Pomponio et al. 1995) and molecular-orbital (Tossell 1973, 1975) calculations. These calculations were used to interpret X-ray photoelectron and emission spectra (XPS and XES) from $\alpha$-quartz (e.g., Tossell 1975; Simunek et al. 1993). The conduction-band structure is not nearly as well understood. This lack of understanding is in part caused by the theoretical limitations in modeling the higher-lying conduction-band states and, up to now, experimental difficulties in probing these states at high-energy resolution.

Electron energy-loss (EELS) spectroscopy is efficient for studying unoccupied states because inner-shell electrons are excited into unoccupied states in the conduction band. Because the inner-shell states have well-defined energy and angular momentum, EELS probes the variation in the angular-momentum-resolved density of conduction-band states at a particular atomic site weighted by an appropriate squared matrix element. The matrix element represents the probability of a transition from the initial state in the inner-shell level to a final state in the conduction band. When the dipole approximation is used for the evaluation of the matrix elements, dipole selection rules apply, and the angular and energy dependence of scattering for cubic materials is described by the double differential cross section (Weng et al. 1989)

$$\frac{d^2\sigma}{dE d\Omega} = \frac{4\gamma^2}{a_0^2 q^2} \left[ |m_{l\pm1}|^2 \rho_{l\pm1}(E) + |m_{l-1}|^2 \rho_{l-1}(E) \right]$$

where $\rho_{l\pm1}(E)$ is the localized density of states, with angular momentum quantum number $l$ at energy $E$, $\gamma = (1-v^2/c^2)^{1/2}$ is the relativistic correction, $m_{l\pm1}$ are the matrix elements to states of angular momentum $l \pm 1$, $a_0 = 0.529 \times 10^{-10}$ m is the Bohr radius, and $q$ is the momentum transfer.

ABSTRACT

High-resolution core-loss and low-loss spectra of $\alpha$-quartz were acquired by electron energy-loss spectroscopy (EELS) with a transmission electron microscope (TEM). Spectra contain the Si L$_1$, L$_{2,3}$, K, and O K core-loss edges, and the surface and bulk low-loss spectra. The core-loss edges represent the atom-projected partial densities of states of the excited atoms and provide information on the unoccupied s, p, and d states as a function of energy above the edge onset. The band structure and total density of states were calculated for $\alpha$-quartz using a self-consistent pseudopotential method. Projected local densities of Si and O s, p, and d states (LDOS) were calculated and compared with the EELS core-loss edges. These LDOS successfully reproduce the dominant Si and O core-loss edge shapes up to ca. 15 eV above the conduction-band onset. In addition, the calculations provide evidence for considerable charge transfer from Si to O and suggest a marked ionicity of the Si-O bond. The experimental and calculated data indicate that O 2p-Si d $\pi$-type bonding is minimal. The low-loss spectra exhibit four peaks that are assigned to transitions from maxima in the valence-band density of states to the conduction band. A band gap of 9.65 eV is measured from the low-loss spectrum. The structures of the surface low-loss spectrum are reproduced by the joint density of states derived from the band-structure calculation. This study provides a detailed description of the unoccupied DOS of $\alpha$-quartz by comparing the core-loss edges and low-loss spectrum, on a relative energy scale and relating the spectral features to the atom- and angular-momentum-resolved components of a pseudopotential band-structure calculation.

Bonding in alpha-quartz (SiO$_2$): A view of the unoccupied states

LAURENCE A.J. GARVIE,1,* PETER REZ,2 JOSE R. ALVAREZ,2 PETER R. BUSECK,1,3 ALAN J. CRAVEN,4 AND RIK BRYDSON5

1Department of Geology, Arizona State University, Tempe 85287, U.S.A.
2Department of Physics, Arizona State University, Tempe 85287, U.S.A.
3Department of Chemistry/Biochemistry, Arizona State University, Tempe 85287, U.S.A.
4Department of Physics and Astronomy, University of Glasgow, Glasgow G12 8QQ, U.K.
5Department of Materials, School of Process, Environmental and Materials Engineering, University of Leeds, Leeds LS2 9JT, U.K.