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Reflectivity, Resonance Raman Scattering, and Energy Level Structure in Ti_2O_3

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In order to gain information concerning the energy level structure and electron–phonon interaction in Ti_2O_3, both of which are crucial for a full understanding of the nature of the SCM (Semiconductor to metal) transition in this material, we have investigated the tensorial properties of the reflectivity as well as resonance Raman scattering in this material. The results of this experiment have confirmed the energy level structure proposed by several theoretical works.

The optical reflectivity at room temperature of Ti_2O_3 utilizing polarized light parallel and perpendicular to the c axis was investigated in the range 0.5–5 eV by means of a rotating light pipe reflectometer. Scouler and Raccah have previously made similar measurements using unpolarized light. In the range 0.5–2.2 eV there is a strong peak for both polarization directions, the magnitude being somewhat larger for $E\|c$ axis. There are minima in both curves at about 2.2 eV. A pronounced peak at 2.9 eV is observed for $\mathbf{E}\|c$ axis, while for $\mathbf{E}\|a$ axis only a small shoulder is seen in the region 2.2–3.0 eV. For $\mathbf{E}\|a$ axis a doublet is observed at about 4.5 eV, while for $\mathbf{E}\|c$ axis there is no structure in this region.

These results have been interpreted in terms of the energy level scheme of Goodenough and energy bond calculation by Weger and co-workers. Group theoretical considerations indicate that along the line Γ–A–T (c axis) a_{1g}–a_{1g} dipole transitions are allowed only for $E\|c$ axis while a_{1g}–e_g transitions occur only for $E\|c$ axis. The weak polarization dependence of the large structure below 2.2 eV suggests that the electronic states involved contain large admixtures of a_{1g} and e_g electronic states. The band calculations of Nebenzahl and Weger show that along the ξ direction, there is a strong admixture of a_{1g} and e_g states which originate from the bonding a_{1g} and lowest lying e_g^{π} states at Γ, i.e., those states involved in the SCM transition. The strong polarization dependence of the 2.9 eV optical structure suggests predominantly $a_{1g} \rightarrow a_{1g}$ with a weak admixture of e_g and hence corresponds to a_{1g} bonding to antibonding transition. Since the 4.5 eV doublet is seen only for $E\|a$ axis it corresponds to $a_{1g} \rightarrow e_g$ transitions thus suggesting an assignment to transitions between the a_{1g} ground state and the e_g^{σ} bonding and antibonding levels.

We have also investigated the spectral dependence of the first order Stokes Raman scattering cross section of the A_{1g} and E_g phonon modes in the energy range 1.8–2.7 eV. It has been demonstrated that inelastic light scattering by phonons in a solid can be described by a phenomenological formalism similar to that of modulation spectroscopy. The resonance Raman results have been interpreted in terms of the modulation of the tensorial properties of the measured reflectivity. In addition the modulation-like nature of the resonance Raman scattering has brought forth a structure at 2.3 eV not seen in the reflectivity. This peak has been assigned to the a_{1g} bonding $\rightarrow e_g^{\pi}$ antibonding transition.

The results of this experiment have provided the first experimental confirmation of the energy level structure proposed by several authors in which the e_g^{π} levels occur between the bonding and antibonding a_{1g} states (2.9 eV) with the e_g^{σ} levels above these at an energy of 4.5 eV above the lowest a_{1g} bonding level.