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Effects of Uniaxial Stress on the Raman Frequencies of Ti_2O_3 and Al_2O_3

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In recent years there has been considerable interest in the subject of the semiconductor-to-metal transition in materials in which the *d*-electrons interaction plays a significant role such as Ti_2O_3. In order to gain further insight into the behavior of the *d* electrons and the electron–phonon interaction we have utilized the technique of uniaxial stress which has been developed into a powerful method for investigating the bond-stretching and bond-bending interactions between atoms. In particular we have investigated the effects of large static compressive stresses on the phonon frequencies of the A_{1g} and E_g modes of Ti_2O_3. In addition we have also studied for comparison Al_2O_3, which has the same crystal structure as Ti_2O_3 but no *d* electrons. Of particular interest is the response of the A_{1g} modes, which are directly related to the behavior of the *d* electrons. The stress-induced splittings and/or shifts of the frequency of these phonons has been investigated for stress along various crystallographic direction.

For $X \| c$ axis only shifts (no splittings) occur since the symmetry of the crystal is not modified by the applied stress. We observed a large effect on the low frequency A_{1g} mode of Ti_2O_3. A hardening of about 9 cm^{-1} for a stress of 10^{10} dyn cm^{-2} was found compared to 1.5 cm^{-1} for the same mode and stress in Al_2O_3. This effect can be understood in terms of an increase in the *d*-electrons bonding energy when the *c*/*a* ratio is decreased by the applied stress.

For stresses perpendicular to the *c* axis the symmetry of the crystal is lowered and splittings of the doubly degenerate E_g modes should occur. Although this effect is observed in the case of the Al_2O_3, no splitting of any of the E_g modes of Ti_2O_3 has been detected. It should be pointed out that a similar situation (i.e., no E_g mode spitting) has been observed for NbO_2, another material in which there is *d*-electron pairing. Although the above results for the E_g modes of Ti_2O_3 are not completely understood at this time they strongly suggest that the highly polarizable *d* electrons are rearranging themselves to compensate for the change in crystal symmetry so that no splitting occurs.