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Effects of differential stress on the structure and Raman spectra of calcite from first-principles calculations

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Abstract

Differential stresses are expected to influence the properties of minerals. The structural and Raman vibrational properties of calcite under hydrostatic and differential stresses were studied using a first-principles method based on density functional theory. Our results show that the density of calcite increases or decreases under different differential stress, relative to its value under hydrostatic pressure. The calculated effects of differential stress on bond lengths are nominal. As pressure increases, the frequencies of all Raman modes increase, with their pressure derivatives slightly depending on the differential stress. The state of stress influences the Raman modes by shifting their frequencies to either higher or lower values relative to the corresponding hydrostatic results. In particular, the largest and smallest frequency shifts were predicted for E_g-156 and A_{1g}-1086 modes, respectively, when the additional stress was applied along the *a*-axis. Visualization of atomic motions associated with Raman modes suggests that the differential stress-induced shifts in Raman frequencies are controlled by out-of-plane vibrations of atoms. The stress estimated on the basis of the experimentally measured shift of the Raman frequency of calcite sample gathered from the Wuchuan earthquake fault by applying our calculated $d\nu_i/dP$ value of A_{1g}-1085 mode is 785 MPa, which appears to be comparable to the stress inferred at the Wuchuan earthquake focus. Thus, the first-principles simulations and Raman spectroscopy experiments together may help us in elucidating the state of stress in the Earth's interior.

Keywords: Differential stress, structure, Raman vibrational properties, calcite, first-principles