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

Lei Liu1,*, Chaojia Lv1, Chunqiang Zhuang2, Li Yi1, Hong Liu1, and Jianguo Du1

1Key Laboratory of Earthquake Prediction, Institute of Earthquake Science, China Earthquake Administration, No.63 Fuxing Road, Haidian District, Beijing, China
2Institute of Microstructure and Properties of Advanced Materials, Beijing University of Technology, 100 Pingleyuan, Chaoyang District, Beijing, 100124, China

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�-156 and A肥料-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 dv/dP value of A肥料-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

INTRODUCTION

Differential stress exists in the Earth’s interior. It can be produced by tectonic compression or by deep fluid movement, particularly at plate boundaries or minerals’ grain boundaries, thereby possibly driving plate tectonics and causing earthquakes. The effects of differential stress on the properties of minerals are shown or expected to be substantial (Demouchy et al. 2011; Sato et al. 2013; Liu et al. 2014). Therefore, the state of differential stress in the Earth’s interior, particularly its distribution in space and its time-dependent evolution, is a fundamental issue in geoscience. However, this issue has yet to be fully understood (Solberg et al. 1978; Kidder 2012).

Calcite is one of the most abundant minerals in the Earth’s continental crust. Understanding its structural, spectral, and mechanical properties under differential stress is important for understanding the mechanical behavior of rock and the state of stress in the deep Earth. The X-ray diffusive and Raman spectral detection have been widely used to determine the crystal structure and Raman spectrum of minerals. In particular, laser Raman spectroscopic analysis of minerals (such as quartz) allows us to investigate the pressure conditions in metamorphic rocks (Enami et al. 2007). As an important rock-forming mineral, calcite is usually abundant in fault and tectonic boundaries. So, if we quantify how the crystal structure and Raman frequencies of calcite behave under different stress conditions, we can infer the state of stress of fault or tectonic boundaries by measuring the structure and/or Raman spectrum of calcite gathered from the sites. Several investigations of the stress state of the Earth’s interior have been reported (Enami et al. 2007), by focusing on the relationship between pressure and Raman frequency shift of minerals (Liu and Mernagh 1990; Dean et al. 1982; Prencipe et al. 2004; Schmidt and Ziemann 2000). In general, these investigations have been performed under hydrostatic pressure.

However, determining the complex microstructures of multiple mineral phases in mineral assemblages and rocks under non-hydrostatic stress or differential stress represents a formidable challenge. For example, the questions of what non-hydrostatic stresses can be developed and how much of the differential stress state can be preserved remain unanswered (Weathers et al. 1979; Christie and Ord 1980; Demouchy et al. 2011; Angel et al. 2014). At present, quantitatively investigating the effects of differential stress on the structure and Raman spectrum is difficult by experiments. Alternatively, the first-principles methods can be used to accurately calculate various properties of minerals at the atomic scale (Gillan et al. 2006; Jahn and Kowalski 2014), including the state of differential stress and its effects (Parrinello and Rahman 1982; Liu et al. 2014). Here, we investigated the structure and Raman spectra of calcite from first-principles calculations to quantify the effects of differential stress on these properties.