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High-temperature and high-pressure Raman spectra of $Fo_{89}Fa_{11}$ and $Fo_{58}Fa_{42}$ olivines: Iron effect on thermodynamic properties

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Abstract

The intrinsic anharmonicity plays an important role in the thermodynamic properties of minerals at the high-temperature conditions of the mantle. To investigate the effect of iron on the thermodynamic properties of olivine, the most abundant mineral in the upper mantle, we collected in situ high-temperature and high-pressure Raman spectra of natural $Fo_{89}Fa_{11}$ and synthetic $Fo_{58}Fa_{42}$ samples. $Fo_{58}Fa_{42}$ dissociates to enstatite + quartz + Fe_2O_3(+Fe) at 893 K. All the Raman-active modes systematically shift to lower frequencies at elevated temperatures, whereas to higher frequencies with increasing pressure. The A_g mode at ~960 cm^{-1} is more sensitive to the variations of temperature and pressure than other internal modes. The crystal-field splitting of the vibrational energy states becomes slightly weakened at high temperatures but strengthened at elevated pressures. We calculated the isobaric (γ_{iP}) and isothermal (γ_{iT}) mode Grüneisen parameters for these olivine samples. The intrinsic anharmonic parameters (a_i) are negative for both the lattice and internal vibrations, and our calculations indicate that the intrinsic anharmonicity makes positive contributions to the thermodynamic properties of olivine at high temperatures, such as the internal energy (U), heat capacities (C_V and C_P), and entropy (S). Iron incorporation further increases the magnitudes of these anharmonic contributions. In addition, the Fe effect on the intrinsic anharmonicity may also apply to other thermodynamic properties in olivine, such as equations of state and equilibrium isotopic fractionations, which are important in constraining physical and chemical properties of the upper mantle.

Keywords: Olivine, in situ high-temperature Raman, high-pressure Raman, Grüneisen parameter, intrinsic anharmonicity, thermodynamic properties