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Phonon anomalies and structural transition in spin ice $Dy_2Ti_2O_7$: a simultaneous pressure-dependent and temperature-dependent Raman study

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We revisit the assignment of Raman phonons of rare-earth titanates by performing Raman measurements on single crystals of O^{18} isotope-rich spin ice $Dy_2Ti_2O_7^{18}$ and nonmagnetic $Lu_2Ti_2O_7^{18}$ pyrochlores and compare the results with their O^{16} counterparts. We show that the low-wavenumber Raman modes below 250 cm^{-1} are not due to oxygen vibrations. A mode near 200 cm^{-1}, commonly assigned as F_{2g} phonon, which shows highly anomalous temperature dependence, is now assigned to a disorder-induced Raman active mode involving Ti^{4+} vibrations. Moreover, we address here the origin of the 'new' Raman mode, observed below $T_C \sim 110$ K in $Dy_2Ti_2O_7$, through a simultaneous pressure-dependent and temperature-dependent Raman study. Our study confirms the 'new' mode to be a phonon mode. We find that $dT_C/dP = +5.9$ K/GPa. Temperature dependence of other phonons has also been studied at various pressures up to ~8 GPa. We find that pressure suppresses the anomalous temperature dependence. The role of the inherent vacant sites present in the pyrochlore structure in the anomalous temperature dependence is also discussed.

Keywords: geometrically frustrated pyrochlore; low-temperature and high-pressure physics; Raman spectroscopy; phonon anharmonicity; crystal field transition

Introduction

Spins in geometrically frustrated insulating pyrochlore titanates ($A_2Ti_2O_7$) are known to show complex magnetic ground states, such as spin liquid, spin glass, and spin ice.[1–3] The spin ice is the magnetic pyrochlores in which the spin orientations are analogous to the arrangement of the protons in the hexagonal phase of water ice.[4–6] The presence of competing dipolar and antiferromagnetic exchange interactions in these systems do not allow long-range correlations among the spins. However, the 'ice rule' governs the ground state by ensuring 'two spins in and two spins out' configuration on every tetrahedron formed by the rare-earth ions.[3] Among all the rare-earth titanates ($A_2Ti_2O_7$, A = rare earth), only $Ho_2Ti_2O_7$[4] and $Dy_2Ti_2O_7$[5] exhibit the spin ice ground state at very low temperatures, called dipolar spin ice, because the ferromagnetic dipolar interactions between the rare-earth ions are stronger than the near-neighbor antiferromagnetic exchange interactions.[4,5] Recent reports on the presence of magnetic monopoles in $Dy_2Ti_2O_7$[7] and of a magnetic Coulomb phase in $Ho_2Ti_2O_7$[8] have made these compounds even more exciting.

In recent years, phonons of pyrochlores, specially the rare-earth titanates ($A_2Ti_2O_7$), have been studied to reveal structural phase transitions under high pressure[9–14] and temperature-dependent phonon anomalies.[12,15–19] The origin of anomalous temperature dependence of the wavenumber of phonon (i.e. phonon wavenumber decreases on decreasing temperature) in these compounds has been attributed to strong phonon–phonon anharmonic interactions[12,15–17] and not to the spin–phonon coupling as was proposed[18] earlier. We have recently shown[17,19] that the phonon near 200 cm^{-1} shows an enormous anomaly, namely a decrease in wavenumber by ~20% when the temperature is reduced from 300 to 10 K, whereas the anomalous decrease of the other phonon wavenumbers are within 1%–2%. In order to understand the reason for the highly anomalous behavior of the ~200 cm^{-1} mode (and also the other modes), a clear understanding of the phonons and their assignments is needed. In literature, the ~200 cm^{-1} mode has been associated with the F_{2g} phonon involving the O'_{8b} vibrations.[12,15–17,20,21] We recall that in pyrochlores, all the six Raman active modes ($A_{1g} + E_g + 4F_{2g}$) predicted by group theory are due to the vibrations of oxygen atoms only. Since the F_{2g} mode near 200 cm^{-1} is unusually anomalous in comparison to the other oxygen vibrations, a question arises on its origin, thus motivating the present study. As all the Raman active modes are due to oxygen vibrations only, we have replaced O^{16} by O^{18} isotope in spin ice $Dy_2Ti_2O_7$ and nonmagnetic $Lu_2Ti_2O_7$ and compared their phonon wavenumbers. We show that the phonons with

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