

Raman spectroscopy of Fe₂O₃ to 62 GPa

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ABSTRACT

Raman spectra of Fe₂O₃ were measured to 62 GPa in a diamond anvil cell. All group theoretically predicted Raman-active phonon modes were detected to 54 GPa. In addition, some high-pressure spectra show an IR-active E_u mode (~ 660 cm⁻¹), possibly induced by surface defects or stress. This mode is related by a factor of two to a mode at 1320 cm⁻¹. The assignment of the 1320 cm⁻¹ mode has been controversial (two-magnon scattering or two-phonon scattering), and our observation supports the phonon assignment. All Raman-active phonons show nonlinear pressure-induced shifts. The mode Grüneisen parameters and their logarithmic volume dependences for two low-frequency phonons, A_{1g} and E_g , become negative and infinite, respectively, near 50 GPa as a result of the instability of the corundum structure at this pressure. Using the observed Raman-active phonons together with acoustic phonons previously measured by ultrasonics, and Kieffer's model, we calculate the phonon contribution to the thermodynamic parameters of hematite. Comparison with experimentally measured values allows an estimation of an upper bound to the magnon contribution to the heat capacity at ambient pressure. This increases continuously above the Morin temperature and reaches a maximum at the Néel temperature ($\sim 37\%$). The Raman spectra change dramatically at pressures greater than 54 GPa as indicated by the appearance of new peaks and a significant increase in background. Although direct structural analysis is not possible due to the low signal-to-background ratio and the lack of polarization information, we were able to examine the consistency of our Raman observation with the corundum-to-perovskite phase transformation using the results for an analog system: MgSiO₃ ilmenite (ordered corundum type) and perovskite. This analysis shows that observed new features in Fe₂O₃ Raman spectra may not be consistent with the GdFeO₃ perovskite structure.