Raman spectroscopy of Fe$_2$O$_3$ to 62 GPa

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ABSTRACT

Raman spectra of Fe$_2$O$_3$ 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 $E_g$ mode ($\sim$660 cm$^{-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$37%). The Raman spectra change dramatically at pressures greater than 54 GPa as indicated by the appearance of new peaks and a significant increase in background. Although direct structural analysis is not possible due to the low signal-to-background ratio and the lack of polarization information, we were able to examine the consistency of our Raman observation with the corundum-to-perovskite phase transformation using the results for an analog system: MgSiO$_3$ ilmenite (ordered corundum type) and perovskite. This analysis shows that observed new features in Fe$_2$O$_3$ Raman spectra may not be consistent with the GdFeO$_3$ perovskite structure.

INTRODUCTION

Fe$_2$O$_3$ crystallizes in the corundum ($\alpha$-Al$_2$O$_3$) structure at ambient conditions ($\alpha$-Fe$_2$O$_3$, hematite). It is antiferromagnetic below the Morin temperature ($T_M = 250$ K) and weakly ferromagnetic between 250 K and the Néel temperature ($T_N = 950$ K) as a result of spin canting. Due to its relatively simple structure and magnetic ordering, hematite has attracted much interest from theorists (e.g., Catti et al. 1995; Punkkinen et al. 1999) and experimentalists (e.g., McQueen and Marsh 1966; Beattie and Gilson 1970; Goto et al. 1982; Yagi and Akimoto 1982; Suzuki et al. 1985; Knittle and Jeanloz 1986; Olsen et al. 1991; Pasternak et al. 1999).

The Raman spectrum of Fe$_2$O$_3$ has been measured at both ambient (Hart et al. 1975; Martin et al. 1977; McCarty 1988) and high pressure (Massey et al. 1990a). These studies are in general agreement on the phonon modes but there is controversy over whether the Raman signature at 1320 cm$^{-1}$ originates from two-magnon or two-phonon scattering. Hart et al. (1975) assigned this mode as two-magnon scattering. This idea was supported by Martin et al. (1977) who measured its temperature dependence. However, McCarty (1988) reported that this feature is still observed above the Néel temperature and is related to an IR-active mode in the Fe$_{x}$Cr$_{2-x}$O$_3$ solid solution system. Massey et al. (1990a) performed in situ high-pressure Raman experiments to 23 GPa. Using the pressure-induced Raman shift, they showed that the Grüneisen parameter of this line is much lower than the expected value for a magnon ($\approx$3.3) based on Bloch’s hypothesis (Bloch 1966). To resolve this question, we have measured the pressure dependence of the 660 cm$^{-1}$ IR-active mode that may be related to the 1320 cm$^{-1}$ mode. 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: MgSiO$_3$ ilmenite (ordered corundum type) and perovskite. This analysis shows that observed new features in Fe$_2$O$_3$ Raman spectra may not be consistent with the GdFeO$_3$ perovskite structure.

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