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Variable-temperature ^{27}Al and ^{29}Si NMR studies of synthetic forsterite and Fe-bearing Dora Maira pyrope garnet: Temperature dependence and mechanisms of paramagnetically shifted peaks

Aaron C. Palke* and Jonathan F. Stebbins

Department of Geological and Environmental Sciences, Stanford University, Stanford, California 94305-2115, U.S.A.

Abstract

We present variable-temperature (VT, 31 to 204 °C) ^{29}Si magic angle spinning NMR (MAS-NMR) spectra of a synthetic forsterite containing dilute paramagnetic impurities and ^{27}Al and ^{29}Si spectra of two iron-bearing natural pyrope garnet specimens from the Dora Maira ultrahigh-pressure metamorphism locality. Previous NMR studies of these materials reported multiple "anomalous" resonances outside the range of expected frequencies. It has been hypothesized that these peaks were caused by interactions between paramagnetic centers and the resonating nuclei. Our VT MAS-NMR study shows a linear relationship between peak position and inverse temperature for the "anomalous" resonances, confirming their assignment as paramagnetic shifts. A detailed analysis of the peaks in the pyropes indicates that the "anomalous" resonances are caused by a combination of the Fermi contact and pseudocontact interactions. The paramagnetic shifts in the ^{29}Si spectra are likely caused by Fe^{2+} in the first, second, and third nearest dodecahedral sites while those in the ^{27}Al spectra are likely caused by one or two Fe^{2+} in the first shell dodecahedral site.

Keywords: NMR spectroscopy, forsterite, pyrope, Dora Maira, paramagnetic shifts