INTRODUCTION

It has long been known that small amounts of hydrogen can be incorporated into nominally anhydrous minerals, NAMs (Griggs 1967; Wilkins and Sabine 1973). Whereas structurally incorporated hydrogen can be identified by IR spectroscopy (Beran and Putnis 1983; Aines and Rossman 1984a; Freund and Oberheuser 1986; Rossman 1988), for most NAMs it is not clear how the hydrogen atoms are incorporated into the structure. This is a result of the difficult localization of the small amounts of hydrogen incorporated into phases stable at the temperatures and pressures prevalent in the mantle. In addition, the energetics of the incorporation of hydrogen in NAMs is not well understood, as calorimetric experiments to study these problems are exceedingly difficult.

The changes of the structure and physical properties of NAMs due to the incorporation of hydrogen are of great technological relevance, as it is the cause of hydrolytic weakening in quartz (Griggs 1967). They are also of considerable interest in the Earth sciences, as NAMs may introduce significant amounts of "water" into the Earth’s mantle, which would significantly change the physical properties of the mantle. In addition, the energetics of the incorporation of hydrogen in NAMs is not well understood, as calorimetric experiments to study these problems are exceedingly difficult.

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The substitution of SiO$_4$ by O$_4$H$_4$ has been called the hydrogarnet substitution, and it has been proposed that it is an effective mechanism of incorporating H into the garnet structure. However, in contrast to grossular, it has not yet been possible to introduce more than very small amounts of hydrogen into garnets belonging to the pyralspite group, and the amounts of hydrogen in natural pyralspite garnets are minute (Wilkins and Sabine 1973; Aines and Rossman 1984b). From infrared spectroscopic studies it now seems clear that there are several sites which hydrogen can occupy in pyralspite garnets, and the hydrogarnet substitution is probably only one of several possible mechanisms for hydrogen incorporation. It would therefore be of interest to establish why the hydrogarnet substitution in pyrope is energetically less favorable than in grossular.

To understand the implications of the presence of hydrogenated garnets in the mantle, it is of interest to understand their properties at high pressures. Olijnik et al. (1991) used energy-dispersive X-ray diffraction to study compression of synthetic katoite in a diamond anvil cell up to 42 GPa. A Birch-Murnaghan fit gave a bulk modulus, $K_T = 66 \pm 4$ GPa, and its pressure derivative, $K' = 4.1 \pm 0.5$ (Olijnik et al. 1991). The low bulk modulus of katoite compared with that of grossular, $K_T = 168$ GPa, was attributed mainly to the high compressibility of the O$_4$H$_4$-tetrahedra. The hydrogarnet substitution also expands CaO$_8$-dodecahedra and makes them more compliant, which contributes as a “second-order” effect to the softening of katoite (Olijnik et al. 1991).

Lager and Von Dreele (1996) refined the crystal structure of katoite up to 9 GPa using neutron powder diffraction. Their results, however, are not completely consistent with the earlier observations. Interatomic distances in the structure reported by Lager and Von Dreele (1996) at ambient conditions differ...