Thermal, compositional, and compressional demagnetization of cementite

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ABSTRACT

The 1 bar Curie temperature, $T_C$, at which cementite (anthropogenic form of the mineral cohenite, nominally Fe$_3$C) abruptly loses ferromagnetism, is found to be sensitive to small deviations from the stoichiometric cementite composition. Stoichiometric Fe$_3$C begins to lose magnetic susceptibility at 187 °C. The $T_C$ of ferromagnetic loss in cementite falls by about 13–14 °C, in either compositional direction, to the limits at either Fe-saturation or graphite-saturation. Formation of C vacancies in, or C stuffings into, Fe$_3$C produces non-stoichiometry, disrupts and weakens the Fe magnetic ordering, and produces excess configurational entropy that is proportional to the disproportion magnitude. C-excess (~0.6 at% C) at graphite-saturation is less than the C-deficiency at Fe-saturation (~2.6 at% C), so the rate at which Curie $T_C$ drops with cementite C% variation is asymmetric about the stoichiometric composition, being steeper on the C-excess side. This asymmetry reflects the higher excess configurational entropy (and consequently greater weakening of Fe magnetic ordering) generated by C excesses than by C vacancies.

The application of ~6 GPa pressure to stoichiometric Fe$_3$C leads to a drop in $T_C$, of more than 160 °C, to below room $T$. This large drop in $T_C$ with pressure is shown by loss of ferromagnetism in a specimen compressed in a multi-anvil device at room $T$. Densely sampled synchrotron XRD cell volumes through the transition pressure interval at room $T$ show that there is also a small drop in compressibility near 6 GPa for non-stoichiometric cementites. C-rich cementite retains its magnetism to ~1 GPa higher $P$ than C-poor cementite. The drop in $T_C$ with pressure for stoichiometric cementite was tracked in an externally heated diamond-anvil cell by the jump in thermal expansion experienced when cementite loses its magnetostriiction above $T_C$ (Wood et al. 2004; Litasov et al. 2013). $T_C$ drops parabolically with pressure, as do the Invar alloys (Leger et al. 1972; Winterrose et al. 2009). Both high $T$ and $P$ favor the magnetically disordered (Curie) paramagnetic over the ferromagnetic form of cementite. The observed large positive change in thermal expansion and small negative change in compressibility at the $T_C$ transition give a good quantitative account of the negative $dT_C/dP$ slope mapped by the ferro-paramagnetic phase stability boundary through Ehrenfest’s (1933) second relation.

Our observations of cementite demagnetization at $P$~6 GPa, room $T$ confirm the synchrotron Mössbauer work of Gao et al. (2008). The demagnetization pressures based upon experiment are lower than those estimated from existing theoretical treatments by about an order of magnitude. Stability calculations for carbide in the mantle and core are influenced by the choice among ferromagnetic, paramagnetic, and non-magnetic equations of state. Because the ferromagnetic phase is more compressible, the calculated $P$-$T$ range for cementite stability would be too large under the assumption of ferromagnetism persisting to higher pressures than shown here experimentally. Our results diminish the theoretical $P$-$T$ range of cementite stability.

Keywords: Cementite, magnetism, Curie temperature, composition, pressure, stability

INTRODUCTION

There has been a recent resurgence of interest in the carbide minerals (Wood 1993; Scott et al. 2001; Li et al. 2002; Vòcadlo et al. 2002; Lin et al. 2004; Gao et al., 2008, 2011; Dasgupta and Walker 2008; Lord et al. 2009; Dasgupta et al. 2009; Nakajima et al. 2009, 2011; Dasgupta and Hirschmann 2010; Ono and Mibe 2010; Mookherjee et al. 2011; Mookherjee et al. 2011; Buono 2011; Buono et al. 2013; Dasgupta 2013; Walker et al. 2013; Chen et al. 2012, 2014; Litasov et al. 2013, 2015) such as cementite as mantle and core constituents in the Earth. Assessing the potential for these minerals to be stable at depth requires extrapolation of density to mantle and core pressures. Any changes in the magnetic state of the material will affect this extrapolation and so needs to be well documented. Existing studies show large discrepancies in the pressure of demagnetization in cementite,