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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_3C) abruptly loses ferromagnetism, is found to be sensitive to small deviations from the stoichiometric cementite composition. Stoichiometric Fe_3C 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_3C produces non-stoichiometry, disrupts and weakens the Fe magnetic ordering, and produces excess configurational entropy that is proportional to the disruption 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_3C 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 magnetostriction 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