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Translation interface modulation in NC-pyrrhotites: Direct imaging by TEM and a model toward understanding partially disordered structural states

Dennis Harries,* Kilian Pollok, and Falko Langenhorst†

Bayerisches Geoinstitut, University of Bayreuth, D-95440 Bayreuth, Germany

Abstract

The crystallographic complexity of "hexagonal" or "intermediate" pyrrhotites ($Fe_{1-x}S$ with $0.125 > x > 0.080$) is a long-standing and challenging problem. Integral (e.g., 5C) and non-integral NC type structures found within this group at ambient temperatures are characterized by sharp but complicated electron diffraction patterns, which were found to be interpretable in terms of a translation interface modulation (TIM) superstructure. Transmission electron microscopy (TEM) dark-field images obtained using superstructure reflections show dense arrangements of stripes, which can be interpreted as arrays of closely spaced anti-phase domain boundaries (APB). The displacement vector at the interface is **R** = 1/8[001] of a metrically hexagonal 4C superstructure cell and the involved translations are solely confined to the Fe sublattice. The vacancy arrangement of the APB-free monoclinic 4C-pyrrhotite serves as a base of the TIM superstructure and therefore NC structures can be regarded as two super-imposed ordering phenomena relating to the arrangements of individual vacancies and APBs, respectively. APBs are chemically non-conservative and govern the higher Fe/S ratios of intermediate NC-pyrrhotites. If oriented strictly parallel to (001) the APBs can be regarded as completely filled Fe double layers within the 4C stacking sequence. However, direct imaging of APBs shows waviness and variable disorder on mesoscopic scales, yielding essentially aperiodic structures. A high degree of self-organization among APBs has been observed within apparent diffusion profiles around exsolved troilite lamellae and along interfaces with 4C-pyrrhotite, where complicated eightfold node arrangements occur. Our TEM observations indicate that all NC-type pyrrhotites can be treated by the TIM approach and that the concepts of polytypism and polysomatism in pyrrhotite are not fully capable in representing the observed structural complexities.

Keywords: Pyrrhotite, modulated structure, anti-phase boundary, TEM, electron diffraction