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

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ABSTRACT

The crystallographic complexity of “hexagonal” or “intermediate” pyrrhotites (Fe_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

INTRODUCTION

Pyrrhotite comes a close second after pyrite among the most abundant iron sulfides in ore deposits and crustal rocks. Its NiAs-derivative structure contains sequences of hexagonal close-packed S atom layers stacked in alternation with layers of Fe atoms in octahedral coordination. Non-stoichiometric compositions arise from the presence of vacancies within Fe layers and span the range between ~47 to 50 at% Fe (Fe_x S_y to FeS), whereas most structural complexity occurs in the narrow compositional range between 47 to 48 at% Fe. At temperatures below 300 °C various superstructures are observed in this range due to vacancy ordering among and within Fe layers, resulting in a complicated subsolidus phase diagram (Desborough and Carpenter 1965; Kissin and Scott 1972, 1982; Nakazawa and Morimoto 1970). A recent review on structural and magnetic phase transitions is given by Wang and Salveson (2005). At ambient temperatures, there are three members of the pyrrhotite family being found in nature: troilite (2C-pyrrhotite, FeS, antiferromagnetic), 4C-pyrrhotite (Fe_x S_y, ferrimagnetic), and NC-pyrrhotite (in-between FeS and Fe_x S_y, antiferromagnetic). Here pyrrhotite prefixes indicate the superstructure lattice repeat along the axis of layer stacking relative to the e-axis periodicity of the NiAs substructure (Morimoto et al. 1970), and the latter two types correspond to the more traditional “monoclinic” and “hexagonal” (or “intermediate”) pyrrhotite designations, respectively. Unlike the well-known 2C and 4C structures, the NC-type pyrrhotites form a structurally diverse group with widely variable N, values, among which the special cases Fe_S10 (5C), Fe_11S12 (6C), and Fe_{10}S_{11} (11C or 5.5C without considering sulfur layer stacking) have been proposed as stable phases at room temperature (Morimoto et al. 1970; Nakazawa and Morimoto 1970). Besides these integral NC-pyrrhotites it is established that NC-pyrrhotites exist in which the apparent superstructure periodicity is related to the e-axis repeat of the NiAs substructure in a non-integral manner. Reported N, values range between 4.2 to 6.6 (Morimoto et al. 1975a, 1975b; Pósfai et al. 2000; Yamamoto and Nakazawa 1982). Over the last decades, the stability relations of integral and non-integral superstructures have been a matter of debate, although it seems that studies preferentially focused on the structural and physical properties of the integral types. Alongside conceptual problems regarding the crystallographic description of non-integral superstructures, observations on synthetic and natural pyrrhotites at ambient temperatures face difficulties due to slow ordering kinetics, pronounced phase heterogeneity, and a high, but often subtle,