XXI Brazilian Meeting on Inorganic Chemistry
X Brazilian Meeting on Rare Earths
III Workshop on Theoretical Bioinorganic Chemistry
Belo Horizonte, September 12 - 15th 2024

From troilite to pyrrhotite: the effect of Fe vacancies on the electronic properties.

Edson F.S. Junior [1*], Tercio P.F. Xisto [1] and Hélio A. Duarte[1]

[1] *GPQIT, Department of Chemistry, Federal University of Minas Gerais, Belo Horizonte, Brazil*
E-mail: edsonferfis@gmail.com

Thematic Area: Materials Chemistry and Catalysis

Keywords: Trolite, vacancy, surface

Troilite (FeS) is a stoichiometric sulfide mineral in the pyrrhotite group. This group includes several materials with compositions ranging from stoichiometric troilite to non-stoichiometric monoclinic pyrrhotite (Fe_7S_8). Monoclinic pyrrhotite, the most abundant and stable mineral in this group, is characterized by a high number of structural vacancies. These vacancies might increase the system's conformational and vibrational entropy, potentially enhancing its stability [1].

The energy of vacancy formation was estimated using Plane-Wave Density Functional Theory (DFT/plane waves) as implemented in the Quantum Espresso package. Ultrasoft pseudopotentials and the GGA PBE exchange-correlation functional, along with Hubbard correction (GGA + U), were utilized. A 2 × 1 × 1 supercell of the troilite unit cell, containing 48 atoms (24 Fe and 24 S), was used as the initial structure. The iron vacancy formation energy varies from 9.460 eV/atom to 9.731 eV/atom with the increase of vacancy concentration from one to six. The cohesive energy of troilite with respect to the concentration of vacancies shows a linear trend, demonstrating that the formation of a vacancy is not affected by the presence of other vacancies.

The density of states (DOS) changes near the Fermi level with the increase in vacancy concentration. In the process of vacancy formation, troilite, a semiconductor material with a calculated band gap of 0.12 eV, becomes a conductor due to the appearance of electronic states inside the band gap [2]. The vacancy formation in troilite approximates its electronic properties to those of monoclinic pyrrhotite, a conductive and non-stoichiometric variation of pyrrhotite.

The thermodynamics analysis of the Fe vacancy formation on troilite will be also discussed aiming to shed light on the stability of the monoclinic pyrrhotite as the most abundant pyrrhotite structures in the nature.

Acknowledgments: CNPq. Based Mineral High-Performance Materials and Processes Network–RENOVAMin (Proc. RED-00102-16)

References

[1] LUCAS, M. S. et al. Effects of vacancies on phonon entropy of B 2 FeAl. **Physical Review B—Condensed Matter and Materials Physics**, v. 80, n. 21, p. 214303, 2009.
[2] RICCI, Fabio; BOUSQUET, Eric. Unveiling the room-temperature magnetoelectricity of troilite FeS. **Physical Review Letters**, v. 116, n. 22, p. 227601, 2016.