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The crystal-structure and vacancy distribution in 6*C* pyrrhotite

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ABSTRACT

The crystal structure of a 6*C* pyrrhotite from Mponeng Mine, South Africa, has been refined using starting atomic parameters postulated by Koto et al. (1975). This pyrrhotite is monoclinic and is described in the non-standard space group *Fd*, so that the metrically orthorhombic unit-cell shape is preserved. The cell symmetry is monoclinic with dimensions $a = 6.897(2)$, $b = 11.954(3)$, $c = 34.521(7)$, and with $\beta = 90.003(4)°$. The structure has been refined with anisotropic displacement parameters to $R = 0.029$ using 1493 observable reflections with $I > 2\sigma(I)$ and $R = 0.034$ for all 1800 reflections. The internal R_{int} is 0.023 for the symmetrically equivalent reflection data. The composition of the crystal, as determined by electron microprobe analysis is $Fe_{10.91}Ni_{0.05}S_{12}$.

The crystal structure resembles that of the 5*C* pyrrhotite in that the atomic positions of the Fe and S atoms are arranged in a very similar fashion, the only real difference being the arrangement of partially occupied iron sites. The coordination of the iron atoms is octahedral and short Fe-Fe distances along the *c*-axis are also encountered in this structure.

The vacancy distribution is similar to that postulated by Koto et al. (1975) and is characterized by the stacking of two approximately half-occupied sites, followed by an essentially fully occupied layer. This is however a simplification and results in a composition that is too metal-rich. Two other slightly defect sites with occupancies of 0.90 and 0.87 are also present in the structure, and all layers contain both fully occupied and partially occupied sites. Refinement of the occupancies of all these sites gives rise to an atomic distribution that resembles the measured composition most closely, and is refined as $Fe_{10.99}S_{12}$.

The powder diffraction pattern of this structure is compared to the very similar pattern of the 5*C* structure. The crystal structure is also given in the more conventional *Cc* setting so as to be compatible with the available crystallographic software that cannot normally accommodate the *Fd* space group.

Keywords: Pyrrhotite-6*C*, crystal structure, non-stoichiometry, iron sulfide, superstructure