

LETTERS

Surface reconstruction and As-polymerization at fractured loellingite (FeAs₂) surfaces

H.W. NESBITT,^{1,*} I. UHLIG,² AND R. SZARGAN²

¹Department of Earth Sciences, University of Western Ontario, London, Ontario N6A 5B7, Canada

²Wilhelm-Ostwald-Institut, Fakultät für Chemie und Mineralogie, Universität Leipzig, Linnéstrasse 2, D-O4103, Germany

ABSTRACT

Synchrotron Radiation X-ray Photoelectron Spectroscopy (SRXPS) and conventional X-ray Photoelectron Spectroscopy (XPS) of pristine (unreacted) loellingite fracture surfaces reveal two distinct contributions to the As 3*d* spectrum. One is derived from As atoms of the bulk phase (fully coordinated As atoms) and the other is derived from polymeric As species located on fracture surfaces. Surface polymerization reactions probably proceed in response to fracture whereby As dimers at the surface react to produce surface tetramers and possibly surface heptamers. Trimeric and pentameric species may form where As-As bond scission occurs during fracture.

The (001) surface of loellingite is autocompensated and unlikely to undergo reconstruction. The (010) and (100) surfaces are, however, arsenic-terminated and uncompensated, and surface reconstruction is expected. The short “*c*” dimension of the loellingite unit cell is critically important to surface polymerization because arsenic dimers on (100) and (010) surfaces are separated by 2.88 Å (normal to *c*) which is only 16% greater than the As-As bond length. Because of the short distance, adjacent surface dimers likely tilt toward each other and bond to produce surface tetramers. This should introduce minimal strain and eliminate high-energy dangling bonds thus stabilizing the surface. The polymerization reaction also explains the absence of surface (core-level-shifted) As dimeric and monomeric signals such as observed on pyrite surfaces.