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### *Synchrotron charge density studies of chemical bonding in the polymorphs of FeS<sub>2</sub>*

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The experimental charge density (CD) distributions in both polymorphs of the photovoltaic compound iron-disulphide (FeS<sub>2</sub>; cubic pyrite and orthorhombic marcasite) will be described.[1] The CDs are determined by multipole modelling using synchrotron X-ray diffraction data collected at 10 K on extremely small single crystals (<10 μm) thus minimizing the influence of systematic errors such as absorption, extinction and TDS, and exploiting experiences gained from our recent synchrotron studies of CoSb<sub>3</sub>. [2] The analysis of the charge density in both polymorphs of FeS<sub>2</sub> provides an opportunity to see how the different geometries affect local atomic properties, such as 2-center chemical bonding, atomic charges and d-orbital populations. In particular, the data and the resulting multipole models enable us to link the atomic-centered view that emerges from the multipole analysis with the band structure approach. This is carried out by combination with results from periodic calculations on the compounds in the experimental geometries using WIEN2k, thereby providing unambiguous answers to a number of unsolved issues regarding the nature of the bonding in FeS<sub>2</sub>. The chemical bonding will be characterized by topological analyses showing that the Fe-S bonds are polar covalent bonds, with only minor charge accumulation but significantly negative energy densities at the bond critical points. Using the IAM as reference, density is found to accumulate in-between the atoms, supporting a partial covalent bonding description. The homopolar covalent S-S interaction is seemingly stronger in pyrite than in marcasite, determined not only from the shorter distance but also from all topological indicators. Integrated atomic (Bader) charges show significantly smaller values than those estimation based on crystal-field theory of Fe<sup>2+</sup>, S<sup>-1</sup>. In connection with this, the experimentally derived d-orbital populations on Fe are found to deviate from the commonly assumed full t<sub>2g</sub> set, empty e<sub>g</sub> set, and they fit very well with the theoretical individual atomic orbitals projected density of states showing a higher d<sub>xy</sub> participation in the valence band in marcasite compared with pyrite. Thus, the differences between the two polymorphic compounds are directly reflected in their valence density distributions and d-orbital populations.

[1] Schmøkel, M. S.; Bjerg, L.; Cenedese, S.; et al., *B. B., Chem. Sci.* 2014, doi: 10.1039/C3SC52977K, [2] Schmøkel, M. S.; Bjerg, L.; Overgaard, J.; et al., *Angew. Chem. Int. Ed. Engl.* 2013, 52 (5), 1503-6

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