Scientific report to ESRF

EXAFS study on an electronic transition in SnO

Eran Sterer, Asaf Pesah, Aviva Melchior, Carlo Marini

Experiment HS-4380, June 10-14, 2010 (12 shifts)

Some years ago we have found that tin monoxide (SnO) undergoes a pressure induced insulator-metal transition at ~4GPa [1]. Wang et al. [2] show IR data supporting this transition. Their study also shows that there is no crystallographic phase transition in SnO at that pressure. Hence this transition is purely electronic. However our electrical resistance measurements (figure 1) persistently showed a hysteresis around 4 GPa, which is highly unusual for an electronic transition in a non-magnetic system. In SnO, the Sn atom has a sterically active lone pair of electrons (to be discussed in some detail later) that causes it to shift from its 'natural' position in the unit cell. SnO is tetragonal from STP to >20GPa. The Sn atom is located at (0, 1/2, z) in the unit cell, with z changing from ~0.235 at STP to ~0.27 at 10GPa, as found by Wang et al. using XRD, and also by Giefers et al. [3] using EXAFS. Our proposal was to repeat these EXAFS measurements with small steps, going up and down with pressure between 2 to 7GPa, and carefully look for hysteresis in z, which according to these researchers gets the higher symmetry value of z=0.25 at ~5GPa.
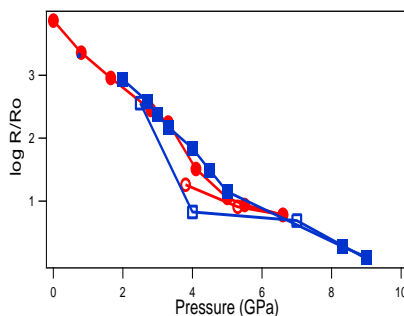

Figure 1: Hysteresis in the electrical resistance of SnO vs. pressure. Full and empty symbols are upstroke and downstroke respectively. Different colors refer to different runs.

We have collected EXAFS data using the BM23 beamline with radiation energy corresponding to Sn K edge (29.2KeV). The raw data was collected for several hours at each pressure point, both upon pressure upstroke and downstroke. The pressure was achieved using a large volume (Paris-Edinburgh) press, and calibrated with an internal calibrant (X-ray diffraction on W wire and BN).

SnO belongs to the IV-VI group of monochalcogenides. As in the prototype GeS and other members of this group, they exhibit a sterically active lone pair of electrons [4]. This lone pair is directly related to the cation (2+) valence in this compound, where in most other compounds it has (4+) valence. This asymmetric electronic lobe protrudes from the Sn atom towards the centre

of the unit cell and pushes the cations towards the oxygen layers at the bottom and top of the unit cell, as seen in figure 2 below.
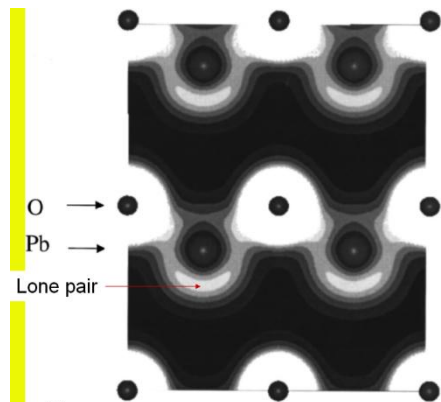

Figure 2: Taken from Watson et al.[7], DFT calculation gives the (2D) electronic density at the (011) plane of a crystal of PbO (ana analog material to SnO) and demonstrates the steric position of the lone pair.

This lone pair is not only a product of the s and p valence electrons of the cation as assumed in the past, but rather a hybridization of those s and p electrons with the 2p electrons of the oxygen [4,5]. Our careful EXAFS study yielded a considerably valuable data about the position of the cation in the unit cell, as shown in figures 3, 4.
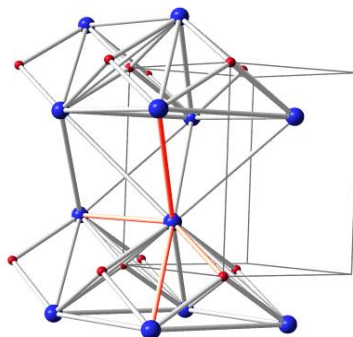

Figure 3: SnO unit cell (Tetragonal) with Sn atoms in blue and oxygens in red. There are 4 interatomic distances denoted by red bars going out of one Sn atom. Sn-Sn1 denotes the distance to a neighboring atom on a lower horizontal plane. Sn-Sn2 denotes the distance to a neighboring atom on an upper horizontal plane. Sn-Sn3 denotes the distance to a neighboring atom on the same horizontal plane. Sn-O denotes the distance to a nearest oxygen atom (there are 4 of them) on a slightly lower plane.

The raw data was processed and interpreted, to give the following results of interatomic distances in the SnO lattice vs. pressure. Although no crystallographic symmetry change is apparent at this pressure range, and thus no first order phase transition exists to justify a hysteresis, still one can clearly see from the processed data (especially for the Sn-Sn2 and Sn-O distances vs. Pressure) that a hysteresis of the steric position of the Sn atom in the unit cell vs. pressure clearly exists, as can be seen from the graphs below. In order to justify this hysteretic behavior we can invoke a technical issue. In the pressure range explored the system undergoes a insulator to metal transition (IMT), which give rise to a small discontinuity around 4 GPa in the Resitivity curves (see fig. 1) only when the pressure is decreased. The behavior of bond distances (R) from EXAFS analysis show important similarities with Resistance plot, showing anomalies around 4Gpa in the downstroke run.
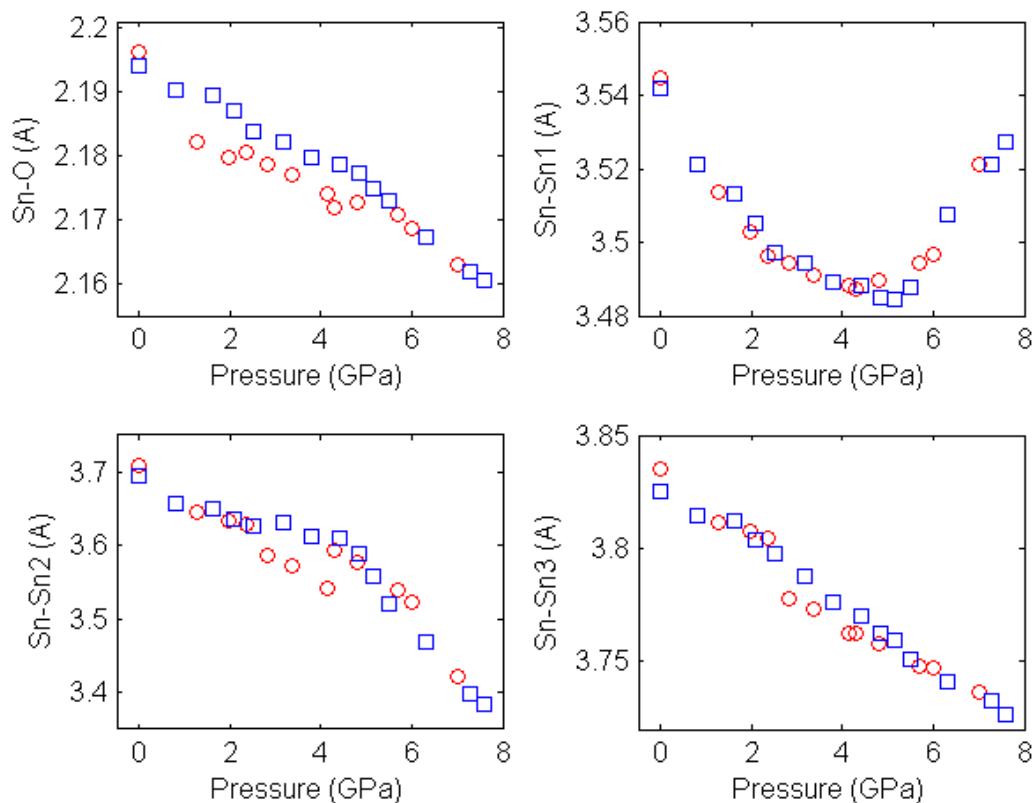

Figure 4: red circles – upstroke, blue squares- downstroke.

Because of MIT indeed the electronic density of the states (DOS) changes as well as the Fermi level. This should result in a shift of the edge (quantifiable approximately with the value of the insulating gap), which is not observed in our XANES spectra because of 1s core hole width (around 30 eV for Sn). Nevertheless these changes in DOS are responsible for small changes of

ΔE parameter of the theory model. In our analysis ΔE is assumed as constant for all the pressure. This means that experimental changes in ΔE affect R values determination, because of the high correlation between these two parameters in the fitting. In other words the hysteretic behaviour of R (particularly strong for the first shell) can be considered as an a posteriori demonstration of the IMT. Comparison on the data with theory could help realize a deeper understanding of the exact mechanism of metallization in SnO. For example the electron distribution in SnO was investigated using DFT methods on the litharge structure and on the idealized CsCl structure [7]. The electronic density of states derived there for ambient pressure could be derived for higher pressures and compared to our measured spectra.

References

1. E. Sterer, Ph. D. dissertation, Scool of Physics and Astromony, Tel-Aviv University (1995) [in Hebrew].
2. X. Wang et al., Physica Status Solidi b **241**(14), 3168-3178 (2004).
3. H. Giefers et al., Physica Scripta T **115**, 538-540, (2005).
4. G. W. Watson and S. C. Parker, J. Phys. Chem. B **103**, 1258-1262 (1999).
5. U. V. Waghmare et al., Phys. Rev. B **67**, 125111 (2003).
6. A. L. Ankudinov, B. Ravel, J. J. Rehr, and S. D. Conradson, Phys. Rev. B **58** (12), 7565-7576 (1998).
7. G. W. Watson, J. Chem. Phys. **114**(2), 758-763 (2001).