X-ray and Neutron Scattering Studies of Lattice Dynamics Near the Metal-Insulator Transition in VO_2

J. D. Budai*[1]

[1]Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

Vanadium dioxide exhibits a well-studied, but poorly-understood, metal-insulator transition (MIT) just above room temperature. On cooling, the conductivity decreases by four orders of magnitude, and concurrently the lattice structure changes from tetragonal (rutile) to monoclinic. The long-debated origins of this MIT have focused on the competing roles of electronic (Mott) versus lattice (Peierls) correlations. An important missing piece of the VO_2 puzzle is the role of lattice dynamics. Early calculations suggested the presence of a soft-mode lattice instability at the tetragonal R-point. However, experimental VO_2 phonon dispersion curves have not been measured using conventional, single-crystal inelastic neutron scattering due to the incoherent neutron scattering cross-section of V atoms.

To help understand this MIT, we have used a synergistic suite of x-ray and neutron scattering techniques for a comprehensive determination of changes in S(Q,E) across the transition1. The Q-integrated phonon density of states (PDOS) using the neutron ARCS/SNS spectrometer revealed that the spectrum is considerably softer in the rutile metal than in the insulator. Importantly, the spectra enabled the first direct measurement of the change in vibrational entropy at the MIT, showing that phonons provide the dominant entropy contribution stabilizing the metallic phase. Further, x-ray thermal diffuse scattering at the APS identified the rutile soft-phonon wavevectors as strong sheets of {111} scattering. Finally, we performed inelastic x-ray scattering measurements at the APS HERIX beamline to obtain the first experimental determination of individual VO_2 dispersions and energy linewidths (phonon lifetimes). The early proposals of a soft mode transition at the R-point are incorrect. Instead, our Q- and E-resolved IXS dispersions revealed low-energy, strongly damped anharmonic transverse acoustic (TA) phonons across a broad range of reciprocal space. These short-lived, low-energy phonons are responsible for thermodynamically stabilizing the metallic phase at high temperatures. Comparing measurements with ab initio molecular dynamics calculations, we find very good agreement. These first-principles calculations reveal that increased occupation of particular vanadium orbitals triggers the Peierls instability, lowering the energy and opening the insulating bandgap.

J. D. Budai, J. Hong et al, Nature 515, 535 (2014).

Research supported by DOE Office of Basic Energy Sciences, Materials Sciences and Engineering Division. APS and SNS facilities supported by DOE-BES.

*Corresponding author: budaijd@ornl.gov