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Correlating inhomogeneity in anionic electron density with hydrogen incorporation in Y_5Si_3 electrides

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Electrides are a unique class of ionic materials in which the anions are loosely bonded electrons that are localized at interstitial sites. These anionic electrons form distinct electronic bands close to Fermi level and are believed to have tremendous potential for improved catalytic activity, superconductivity, hydrogen storage, etc. Till now, these materials have been characterized only with macroscopic experiments. The discovery of one- and two-dimensional (1D/2D) electrides in the last decade, wherein the anionic electrons are confined to a 1D channel or a 2D layer, has necessitated microscopic characterization of these materials. Differential phase contrast (DPC) scanning transmission electron microscopy (STEM) has been used to map local electric fields and charge densities at sub-Å spatial resolution [1, 2]. Such unprecedented spatial resolution can be leveraged to map the localized anionic electron density in 1D and 2D electrides. Recent DPC STEM measurements on Y_5Si_3, a 1D electride, have demonstrated sub-Å resolution in mapping the anionic electron density [3]. The excellent spatial resolution has enabled the authors to also observe inhomogeneity in the anionic electron densities at different interstitial sites. Density functional theory simulations show the incorporation of hydrogen impurities at the anionic electron sites to be responsible for the observed inhomogeneity. However, the presence of hydrogen incorporation at the anionic electron sites has not yet been confirmed experimentally, and their role in tuning band structures in Y_5Si_3 remains unclear. Vibrational electron energy-loss spectroscopy (EELS) has demonstrated good sensitivity for the detection of hydrogen species [4] and has shown nanometer to atomic spatial resolution depending on whether the dipole or impact component of electron scattering is recorded [5, 6]. In this paper, we employ vibrational EELS to study the incorporation of hydrogen impurities at the anionic electron sites in Y_5Si_3.

A polycrystalline Y_5Si_3 ingot was prepared by directly arc-melting high-purity yttrium (99.99% pure; AMES) and Si (99.9999% pure; Alfa Aesar) elements with mole ratio of 5:3 [7]. The ingot was ground in a He-filled glovebox and a powder TEM specimen was prepared. DPC STEM data was acquired using an aberration-corrected Nion UltraSTEM100, operated at 100 kV, using a Nion 2020 Ronchigram camera with a Hamamatsu ORCA CMOS sensor. Vibrational STEM EELS data was recorded with a monochromated, aberration-corrected Nion UltraSTEM100, operated at 30 kV. The probe convergence semi-angle was 27 mrad, while the spectrometer collection semi-angle was 25 mrad. A dispersion on 0.2 meV/channel was used to record all spectra. The energy-resolution during the monochromated experiment was ~6 meV.

Fig. 1a shows an atomic resolution HAADF image of the Y_5Si_3 specimen in the [001] projection. The brightest spots represent double Y atomic columns while the less-bright spots represent single Y atomic columns. The hexagonal ring formed by the single Y atomic columns defines the anionic electron column. Fig. 1b shows the projected charge density map of the same area as the HAADF image. An inconsistent profile is observed across different anionic electron sites. Density functional theory simulations show the incorporation of hydrogen impurities in some of the anionic electron columns to be responsible for the observed inconsistency. Aloof beam vibrational EELS measurements were made to detect the presence of hydrogen impurities in the specimen. Fig. 2a shows a monochromated HAADF image of a Y_5Si_3 nanoparticle cluster and the relative position of the probe. Fig. 2b is the background-subtracted aloof-beam vibrational energy-loss spectrum from the cluster showing two strong and broad peaks between 30 and 80 meV, and between 100 and 150 meV. Preliminary inelastic neutron scattering simulations of the vibrational spectrum (not shown) suggest that these

vibrational features might be associated with the presence of hydrogen impurities in Y_5Si_3. Further vibrational EELS measurements will be presented along with simulations to accurately interpret the experimental spectra.

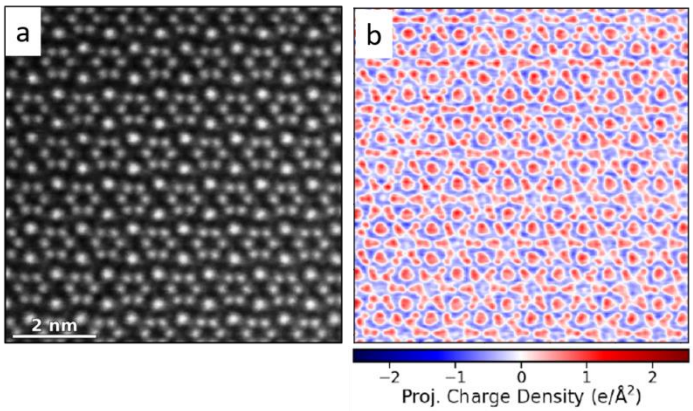

Figure 1. a) Atomic resolution HAADF image of Y5Si3. The hexagonal ring created by the single Y atomic columns defines the anionic electron column. b) Projected charge density map derived from the divergence of center-of-mass shifts due to beam interaction with positive and negative charge densities in the specimen.

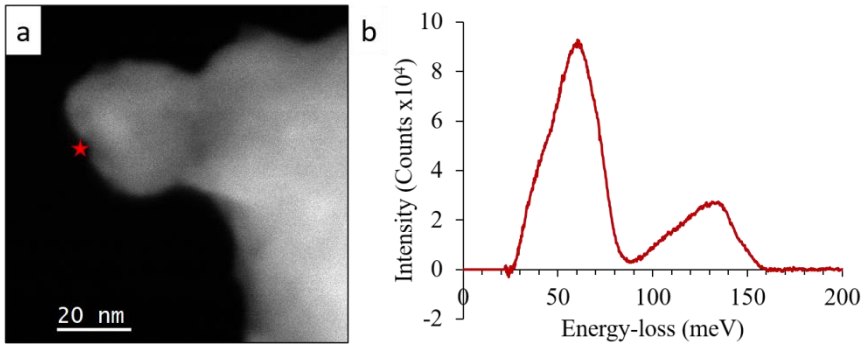

Figure 2. a) Monochromated HAADF image of a cluster of Y5Si3 nanoparticles showing the probe position relative to the specimen. Impact parameter = 4 nm. b) Background-subtracted aloof-beam vibrational energy-loss spectrum from the Y5Si3 cluster showing two strong and broad peaks between 30 and 80 meV and 100 and 150 meV. A power law background subtraction model was employed.

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