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Report:

This experiment aimed at investigating the effects of anisotropic confinement of atomic vibrations in iron nanowires. Although in the past few years an increasing number of nuclear inelastic scattering (NIS) studies have dealt with iron systems of reduced dimensions, i.e. confined in one (thin films) or three (isolated clusters and nanoparticles) dimensions (D), no study on 2D confined systems (such as nanowires) had been reported. Such 2D-confined systems are of great interest – both fundamentally and in term of applications – due to their strong anisotropy. In particular, the vibrational properties along the nanowire axis are expected to differ from those in the nanowire cross-section. Since in NIS only phonons with a component of their wavevector parallel to the x-ray beam are measured, one can therefore measure two different phonon density of states (PDOS) for such a system, which is quite unique and makes the NIS technique the method of choice for such an anisotropy study.

A set of samples consisting of arrays of ^{57}Fe-enriched iron nanowires (NWs) with diameter 18 to 100 nm embedded in an alumina matrix were prepared by electrodeposition into alumina membrane templates. We have performed NIS experiments at the 14.4 keV resonance of ^{57}Fe, using both grazing incidence and transmission geometries, so that the x-ray beam could be aligned either perpendicular or parallel to the NWs long axis (Fig.1).

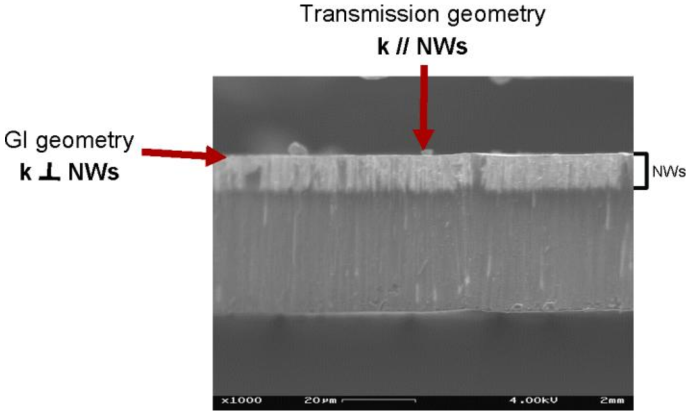

Figure 1: Scanning Electron Microscope image of one NWs array, with indication of the two measurement directions.

Three samples with NW diameters 18, 21 and 100 nm were measured at room temperature in both geometries. Each energy scan of 40 minutes was repeated on average 10 times to obtain good statistics, except for the intermediate diameter sample (21 nm) in transmission geometry for which it was not possible due to time limitations. Note that the experiment was carried out in hybrid mode.

The projected PDOS were extracted for the measured NIS spectra using the DOS program. The main differences observed are located in the low energy part of the PDOS. The two projected PDOS for the samples with the smallest and largest diameters are presented in Fig 2 a) and b), respectively. While the PDOS of the NWs with diameter 18 nm show a clear anisotropy, the vibrational properties of those with diameter 100 nm are found to be isotropic. Note that all NWs PDOS, independently from the direction, show a significant excess of low energy modes, i.e. a clear lattice softening compared to bulk iron.

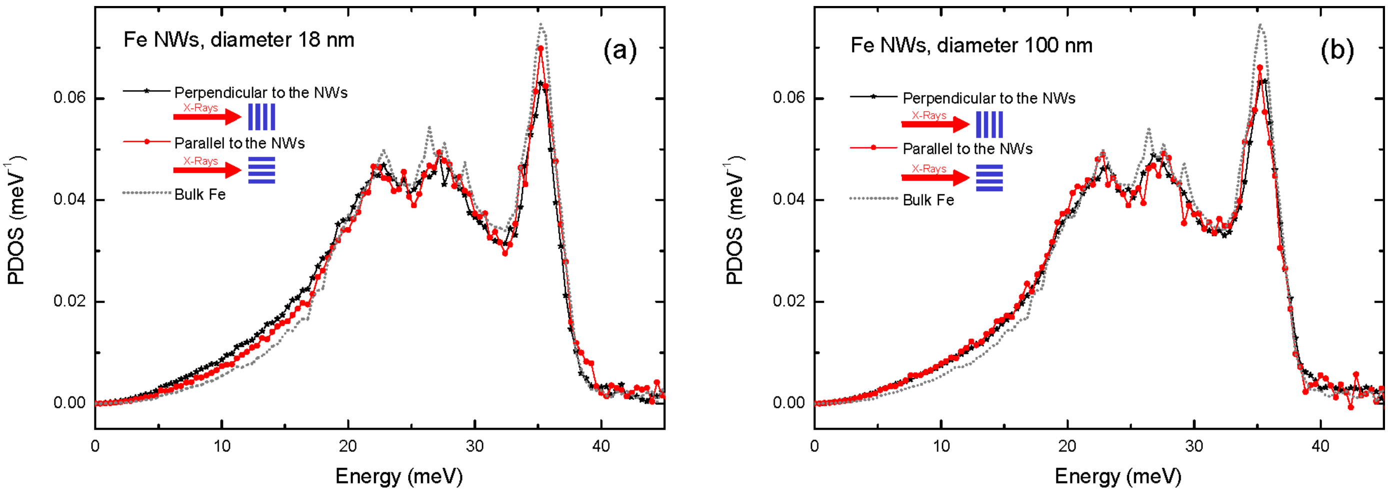

Figure 2: Projected PDOS of iron NWs embedded in an alumina matrix in the directions parallel and perpendicular to the NWs long axis. (a) For NWs with diameter 18 nm; (b) For NWs with diameter 100 nm.

The difference in anisotropy of the vibrational properties of iron NWs depending on their diameter is also clearly seen in the low energy parts of the corresponding double-log plots and reduced PDOS (not shown here for clarity reasons), from which the low energy behavior has been investigated in more details. Whereas none of the NWs samples' vibrational properties show a 3D Debye behavior in their cross-section, in their long axis the PDOS of the small diameter NWs closely follows Debye's law (PDOS ~E^n with n=2), which is not the case for the NWs with large diameter. Interestingly, the coefficient n was shown to reflect the difference in anisotropy observed in the PDOS with similar reduced (n~1.7) value for the sample with NW diameter 100 nm and significantly different values for samples of small diameter depending on the direction i.e. parallel or perpendicularly to the NWs long axis (n_{par}~1.9-2.0 while n_{perp}~1.6-1.7). The sound velocities extracted for the NWs with diameter 18 and 21 nm (parallel direction) amount to about 3050 m/s, which is significantly lower than the value of 3400 m/s extracted for bulk iron. Other extracted parameters such as the mean force constant and the mean atomic displacement confirm the lattice softening.

The NWs samples studied by NIS were characterized by XRD and Mössbauer spectroscopy. XRD measurements have shown that the samples with small and large diameters are structurally significantly different in terms of texture, crystallite size and shape and that the observed difference in vibrational anisotropy can be correlated with differences in structural anisotropy. The composition of the NWs determined by Mössbauer spectroscopy showed the presence of a constant fraction attributed to iron atoms in grain boundaries and a small contribution from oxides, whose nature and quantity depends on the NWs diameter.

The different possible contributors to the differences observed in the vibrational properties, i.e. the grain size and shape, the grain boundaries (fraction and nature), oxides, the surrounding glassy alumina matrix have been considered and correlated with the results of the above mentionned structural characterizations. Additionally, a TEM characterization allowing to visualise grains and grains boundaries in the different NWs samples is planned. The data analysis is now finished and a manuscript is being written to publish the results.