Large anisotropic conductance and band gap fluctuations in nearly-round-shape Bismuth nanoparticles

Ori Cheshnovsky

School of Chemistry, Tel Aviv University, Tel Aviv 69978, Israel

Unlike their bulk counterpart, nanoparticles often show spontaneous fluctuations in their crystal structure at constant temperature. This phenomenon takes place whenever the net gain in the surface energy of the particles outweighs the energy cost of internal strain. The configurational space is then densely populated due to shallow free-energy barriers between structural local minima. Here we report that in the case of bismuth (Bi) nanoparticles (BiNPs), due to the high anisotropy of the mass tensor of their charge carriers, structural fluctuations result in substantial dynamic changes in their electronic and conductance properties. Transmission electron microscopy (TEM) is used to probe the stochastic dynamic structural fluctuations of selected BiNPs. The related fluctuations in the electronic band structure and conductance properties are studied by scanning tunneling spectroscopy (STM) and are shown to be temperature dependent. Continuous probing of the conductance of individual BiNPs reveals corresponding dynamic fluctuations (as high as 1eV) in their apparent band gap. At 80K, upon freezing of structural fluctuations, conductance anisotropy in BiNPs is detected as band gap variations as a function of tip position above individual particles.

We have also tested the role of the capping agents on these dynamics. Bismuth nanoparticles, protected by two types of capping ligands, 1-dodecanethiol and ethylene di-amine tetra-acetate (EDTA) were probed by TEM and STM at 80K and 300K. We show that the different capping ligands dramatically alter the mechanism of structural dynamics in these particles. This finding suggests that molecular control of structural and consequently electronic switching in anisotropic nano-systems is feasible.

BiNPs offer a unique system to explore anisotropy in zero-dimension conductors as well as the dynamic nature of nanoparticles.