Direct Observation of Pressure-induced Metal-to-semiconductor Transition in Lithium

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Lithium (Li) is the typical and simple metallic element whose physical properties can be explained within the nearly free-electron model. In the empirical expectation, the electronic state of Li becomes more-free electron like – more metallic - under compression due to the increase of the electronic density of states. However, Li does not stay simple metal. It has been theoretically predicted that atoms form pairs under compression and Li transits from metal to semiconductor. Previous X-ray diffraction experiments have confirmed that the crystal lattice structure indeed deforms from highly-symmetric compact structures to complex ones, indicating the strong deviation from nearly free electron model. For the purpose to examine whether high pressure can really drive metallic Li to semiconductor, the electrical resistance measurements under high-pressure and low-temperature have been performed using diamond anvil cells(Fig.1). The significant increase of the electrical resistivity with increasing applied pressure was observed. Above 80 GPa (1 GPa = 10,000 atmospheric pressure), the electrical resistance shows abrupt increase and its temperature dependence changes from positive to metal; the slopes of resistance vs. temperature curve are positive in metals and negative in semiconductors (Fig.2). This work provides the concrete evidence of pressure-induced metal to semiconductor transition in Li. The metallic reflection of Li was significantly lost above 80 GPa (Fig.3), supporting the results of electrical resistance measurements. This is the first experimental observation of the pressure induced metal to semiconductor transition in Li.

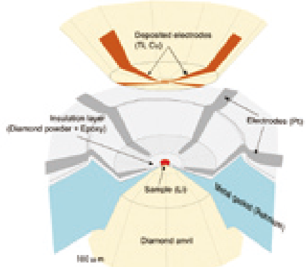

Fig. 1 Experimental set-ups for electrical resistance measurements in a diamond anvil cell. Sample is placed in the center of gasket made of the mixture of diamond powder and epoxy and compressed with two diamond anvils. Electrical resistance is measured with deposited micro-electrodes on the surface of an anvil.

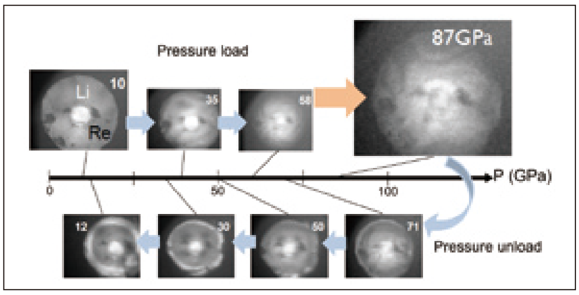

Fig. 3 Photo images of compressed lithium. Li is on the center of metal gasket and shows shiny metallic reflection below near 70 GPa. Above 80 GPa, its metallic reflection is significantly lost. When pressure is released, metallic reflection is recovered. Figure reproduced from Nature, 458(12), 186-189. (2009).

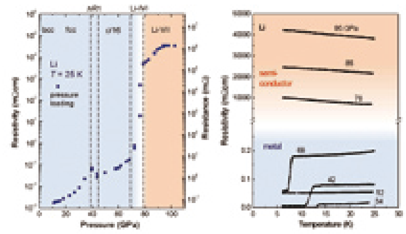

Fig. 2 Pressure and temperature dependence of the electrical resistivity of Li. Lithium is metal in the pressure region shown with blue color and transits to a semiconductor in red region above 80 GPa. Figure reproduced from Nature, 458(12), 186-189. (2009).

Molecular Hula Hoop

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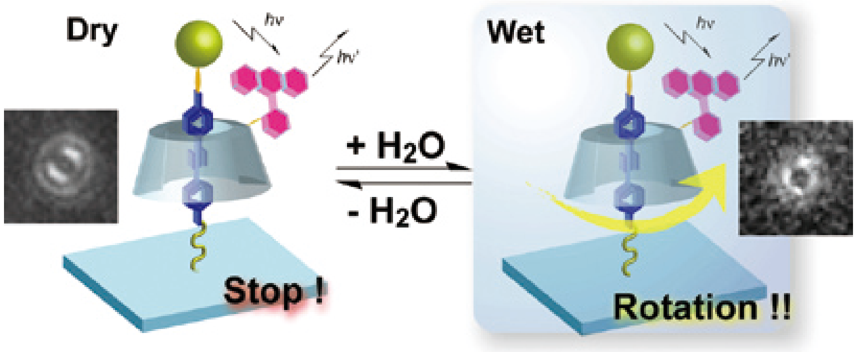
Biological molecular motors such as muscle fibers, flagella and cilia are precisely designed in nature, and are reminiscent of microscale electronic and mechanical devices. Inspired by direct observations of rotary molecular motor systems, some researchers have tried to directly observe artificial molecular motors. On the contrary, even smaller artificial molecular motors are extremely difficult to see, and thus, additional visualization techniques are necessary to observe rotational behavior. We were able to get “snapshots” of individual molecular rotors caught in motion. As the subject of their study we chose a rotaxane. This is a two-part molecular system: A rod-shaped molecule is threaded by a second, ring-shaped molecule while a stopper at the end of the rod prevents the ring from coming off. The researchers attached one end of the rod to a glass support. Herein we observe a single rotaxane molecule based on α-cyclodextrin (α-CD) attached to a fluorescence probe on glass substrates and estimate the rotary movement of α-CD as a rotor, which was measured by total internal reflection fluorescence microscopy (TIRFM).

To observe the rotation of the ring around the rod, the researchers used a microscopic technique called defocused wide-field total internal reflection fluorescence microscopy. This gave snapshots of individual rotaxane molecules in the form of emission patterns. The emission transition dipole orientation of a single chromophore molecule is determined by the characteristic emission intensity distribution. Herein, we observe the rotary movement of α-CD on rotaxane by measuring the emission dipole orientation of the chromophores.

This makes it possible to calculate the orientation of the cuff, which remains constant for every snapshot. However, if the rotor is rotating, the emission pattern does not reveal the spatial orientation of the probe. We showed that the rotor of the rotaxane does not rotate if the sample is dry. However, when it is wet they can see very rapid rotational and vibrational motion. The cuff rotates faster than the time required to snap a picture: the rotational speed is thus over 360° in 300 milliseconds.



Molecular Hula Hoop: The rotary movement of a chromophore-modified α-cyclodextrin (α-CD) was studied in a rotaxane structure attached to a glass substrate. The rotary movement of the α-CD was demonstrated by defocused wide-field imaging with total internal reflection fluorescence microscopy. The motion of the α-CD is suspended in the dry state, whereas a fast rotary movement/rotary vibration is observed in the wet state.