Experimental Report

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Proposal:	**7-03-123**	**Council:**	10/2012
Title:	Ionic diffusion in intercalated fullerides by high resolution neutronspectroscopy		

This proposal is a new proposal

Researh Area: Materials

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Samples: LI4C60 (Lithium intercalated fulleride)

Instrument	Req. Days	All. Days	From	To
IN11	10	9	28/05/2013	06/06/2013

Abstract:

An extraordinary superionic conductivity has been observed in the polymeric phase of the intercalated fulleride Li4C60, due to bulk Li+ ions mobility, which can move through the interstitial voids of the monoclinic lattice. Although extensive investigations of the structural, dynamical and superionic conductivity properties have been performed, a clear picture of the Li+ ions motions inside the polymer is still missing. Here we propose to investigate the slow dynamics of Lithia in the polymeric phase of Li4C60 by means of high resolution neutron spectroscopy, using the spin-echo IN11 spectrometer at the ILL, from room temperature to 500K. From the temperature and Q-dependence of the I(Q,t), we expect to get more information about the energy activation barriers and the mechanism of diffusive processes.

Experimental report: Ionic diffusion in intercalated fullerides by high resolution neutron spectroscopy

There is currently a big interest in the development of new solid state ionic conductors for ion batteries and electrochemical devices. The application of solid electrolytes is currently limited because they attain practically useful conductivities only at 50°-80°C, not competitive with respect to organic liquid electrolytes. Superionic conductivity is solid-state phase is usually observed in strongly disordered compounds characterized by intrinsically large concentration of ions and unoccupied interstitial sites, which originate from defects and imperfect stoichiometry, among which the ions can diffuse. However, we recently observed an exceptionally high ionic conductivity (10-2 S/cm at room temperature) in an ordered crystalline phase of Li-intercalated fulleride Li_4C_{60} [1]. This material is therefore not only of pure scientific interest but may also open new possibilities to the applications of intercalated fullerides in the field on ion batteries.

Structural studies showed that at room conditions Li_4C_{60} fulleride adopts a 2D monoclinic polymer structure, comprising two types of differently bonded fullerene chains running perpendicular to each other in the *ab* basal plane [2]. Despite its quite packed structure, Li^+ ions can easily overcome a relatively low activation energy barrier ($\Lambda E_a \cong 200$meV) and jump from one site to the other in the interstitial voids of C_{60} lattice. The crystal lattice has two tetrahedral and one octahedral interstitial voids which can easily accommodate Li^+ ions. DC-measurements on polymeric Li_4C_{60} showed that above 130K the conductivity increases following an Arrhenius law and we attributed this effect to long-range 3D diffusion of Lithium atoms between different allowed positions in the lattice, with a correlation time in the range of ms. Lithium mobility was observed also with ^{7}Li-NMR [1]. The activated-like temperature dependence of the correlation time probed by NMR has been ascribed to Li^+ local motions inside the octahedral sites instead and we estimated to fall in the time window of IN11, ranging from RT to 500K.
Above 620K, a 2D polymer-to-monomer phase transition occurs and the highest temperature phase recovers the fcc symmetry, typical of pure C_{60}. However little is known about the precise diffusion path of Li^+ in the polymeric phase and for this reason we wanted to profit from high resolution neutron spectroscopy measurement to further investigate the diffusion mechanism.

We have investigated the polymeric phase of Li_4C_{60} using the IN11 spin-echo spectrometer. The instrument set-up was IN11C and the incident wavelength 5.5Å, providing an accessible dynamical range of 5ps-1.3ns. About 485mg of sample (crystalline powder) were put in a flat Al cell, with In o-ring and Cd mask. Sample handling and cell filling were done in inert atmosphere (glove box) in order to prevent any possible oxygen contamination. Three different detector position (2θ=20°-55°-95°) allow to cover a Q range from 0.1 to 1.87$Å^{-1}$.
We measured at different temperature from 400K to 530K, with the angle detector mostly centered at 95° and 20°. This corresponds to a Q-range of approximately 1.47-1.87 $Å^{-1}$ and 0.1-0.69 $Å^{-1}$, respectively. However, due to the small Li cross section and the high crystallinity of the compound, in the whole Q-range the incoherent signal is strongly dominated by the coherent one.
We collected a measurement at 4K as resolution function in the data analysis, in order to obtain the normalized intermediate scattering function $S(Q,t)$.
Changing either temperature or Q-range, we didn't observe any evident evolution of the signal $S(Q,t)/ S(Q,0)$.

[1] Riccò M. et al. PRL 102, 145901 (2009)
[2] Margadonna S. et al., JACS, 126, 15032-15033 (2004)