ESRF	**Experiment title:** **Electronic density of Li_xNiO_2 by Compton scattering**	**Experiment number:** HE 573
Beamline: ID 15B	**Date of experiment:** from: 02/28/99 7:00 to: 03/07/99 7:00	**Date of report:** 08/30/99
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Report:

Compton scattering measurements have been demonstrated to provide an accurate check of valence electron densities. Furthermore, the insensitivity of inelastic scattering to crystalline defects makes this method well adapted to study bonds in solids, particularly with the poor order of synthetic materials. The modification of the electronic density due to intercalation/desintercalation of Li in $LiNiO_2$ is the goal of experiments HE388 and HE573.

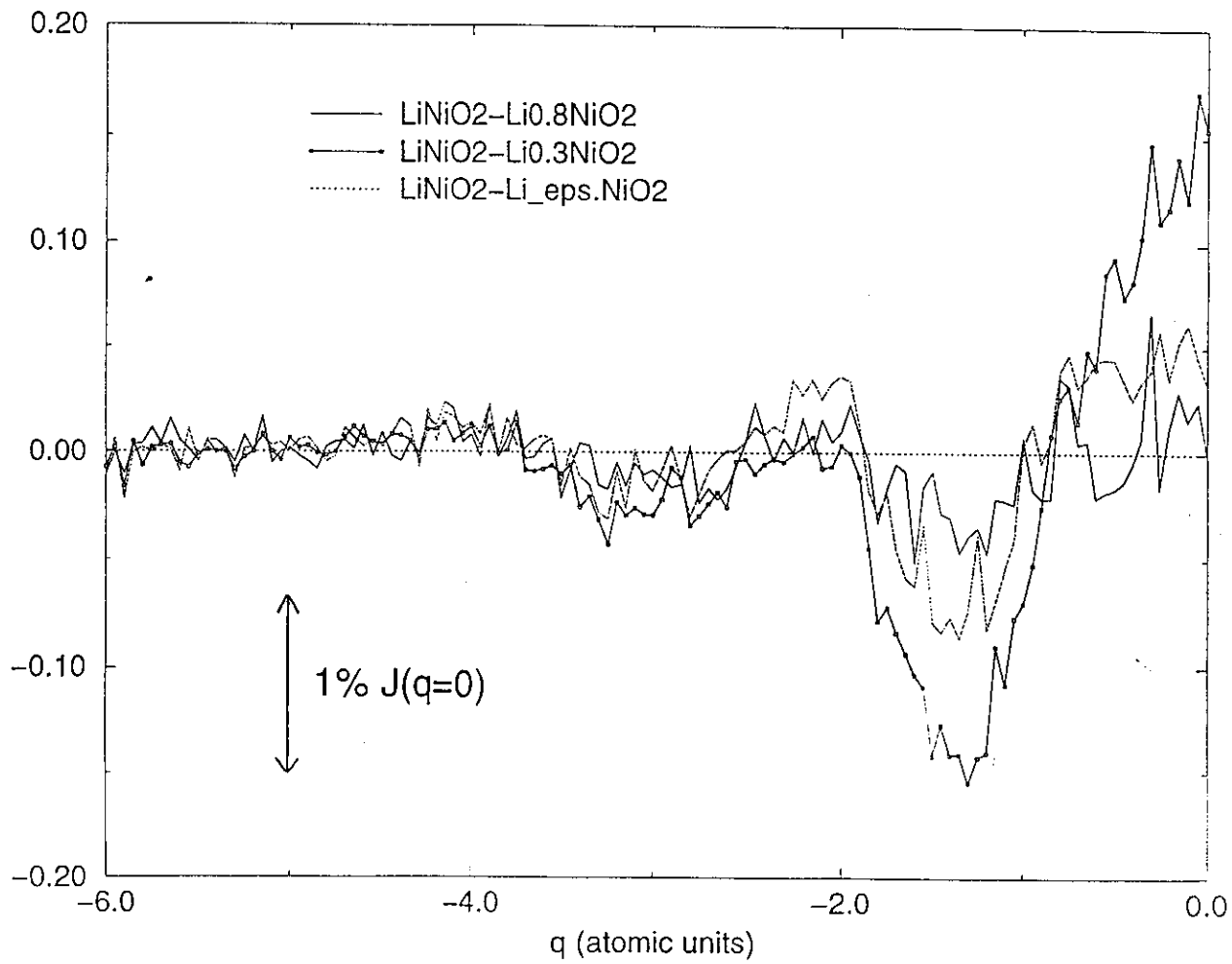
Li_xNiO_2 has a lamellar structure, where layers rich in Ni alternate with layers rich in Li. Both Ni and Li are in an octahedral coordination, surrounded by oxygen atoms.
Stœchiometric $LiNiO_2$ has never been synthetized : a few Ni atoms (at least 2%) always remain in Li layers, leading to the real formula $Li_{0.98}Ni_{1.02}O_2$. This non-stœchiometry strongly affects the magnetic properties of the material.
Upon desintercalation, Li atoms are removed from the structure, leaving vacancies. On the whole range of Li content, the material undergoes very few cristallographic modifications, the rhomboedral cell being only slightly distorted. Even in $Li_\varepsilon Ni_{1.02}O_2$ ($\varepsilon \approx 0.02$), the structure is stable at least in large domains of the crystallographic structure.
From an electronic point of view, adding an atom of Li is like bringing an extra electron into the NiO_6 octahedra.
Intuitively, one can say that in $LiNiO_2$ Ni is oxydized in Ni^{3+}, while the hypothetical (well represented by $Li_\varepsilon Ni_{1.02}O_2$) NiO_2 contains Ni^{4+} (neglecting clusters containing Ni^{2+}, due to

non- stœchiometry). Yet it has been seen that the extra electron brought by Li^+ is delocalized over both Ni and O in the NiO_6 octahedra.

The mixing of nickel d orbitals with oxygen p orbitals in octahedral symmetry lead to the formation of t_{2g} and e_g states. NiO_2 is in the electronic configuration $t_{2g}^6\ e_g^0$, and $LiNiO_2$ is $t_{2g}^6\ e_g^1$; thus NiO_2 is a « full band » insulator, while the insulating character of $LiNiO_2$ is due to both magnetic exchange and Jahn-Teller effect.

Therefore, we await distorsions of the electronic density due mainly to the modification of Jahn-Teller effect and changes in band filling. We followed this modification as a function of Li content by measuring Compton profiles (beamline ID15B) of $Li_{0.98}Ni_{1.02}O_2$, $Li_{0.63}Ni_{1.02}O_2$ (HE388), $Li_{0.8}Ni_{1.02}O_2$, $Li_{0.5}Ni_{1.02}O_2$, $Li_{0.3}Ni_{1.02}O_2$, $Li_\varepsilon Ni_{1.02}O_2$ with $\varepsilon \approx 0.02$ (HE573).

On the figure below are shown the differences between the $LiNiO_2$ Compton profile taken as a reference and respectively $Li_{0.8}Ni_{1.02}O_2$, $Li_{0.3}Ni_{1.02}O_2$ and $Li_\varepsilon Ni_{1.02}O_2$. We can notice that even a lack of 0.2 electrons over 15 electrons of valence and conduction is evidenced in the profile difference $LiNiO_2$ - $Li_{0.8}Ni_{1.02}O_2$.



The interpretation of Compton profiles requires calculation of the electronic wave functions. We are performing these calculations using *ab initio* pseudo potential techniques in the local density approximation, including spin polarization (LSDA formalism) for the magnetic compound $LiNiO_2$.