Annihilation of antiferromagnetic order in $LiCoO_2$ by excess Li

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Among several layered cobalt dioxides with the CoO_2 plane, in which Co ions form a two-dimensional triangular lattice, $LiCoO_2$ has attracted much attention, because of its reversible Li^+ deintercalation/intercalation. Indeed, this is the basic principle behind the operation of the Li-ion batteries. Therefore, a huge number of work was performed for investigating its structural and electrochemical properties, although its magnetic nature has been little studied. This is because $LiCoO_2$ was believed to lack magnetic transitions in the whole T range; that is, magnetic susceptibility measurements, x-ray photoelectron spectroscopic analysis and band-structural calculations confirmed that the Co^{3+} ions are in a low-spin state (t_{2g}^6) with S=0 at ambient T, implying that the low-spin state is the most stable at low T. Nevertheless, our recent μ^+SR experiments on $LiCoO_2$ [1,2] have clearly demonstrated the formation of static antiferromagnetic (AF) order below 30 K (=T_N), although the volume fraction of the AF ordered phase is estimated as ∼10%. Since the results using the samples from two different sources are in good agreement with that of the first sample, the AF order is thought to be an intrinsic behavior of $LiCoO_2$.

A Li-excess phase (i.e., $Li_{1+x}Co_{1-x}O_{2-x}$) has been recently prepared by a conventional technique. Because of the oxygen vacancies, Co^{3+} ions in an intermediate-spin state with S=1 ($t_{2g}^5 e_g^1$) are present in square-based pyramids of the Li-excess phase [3]. The AF order at low T would be, thus, explained by the excess Li ions and/or the presence of the CoO_5 pyramids. In order to elucidate the effect of the excess Li^+ ions on the microscopic magnetic nature of $LiCoO_2$, we have measured μ^+SR spectra on both stoichiometric and Li-excess samples down to 1.8 K. As a result, we have found the existence of the AF phase in the stoichiometric samples as reported in the past work and the absence of it in the Li-excess sample. This clearly confirms the origin of the AF order as a spin/charge fluctuation on the triangular lattice of stoichiometric $LiCoO_2$.

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[2] K Mukai et al., Phys. Rev. Lett. 99 (2007) 087601.
[3] S Levasseur et al., Chem. Mater. 15 (2003) 348.