Magnetic phase diagram of Li[$Mg_x Mn_{2-x}$]O_4 spinel

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In the cubic $(Li)_{8a}[Li_x Mn_{2-x}]_{16d}O_4$ (LLMO) spinel lattice, where $8a$ represents the tetrahedral site and $16d$ the octahedral site, four $16d$-site-ions form a tetrahedron, indicating the existence of three-dimensional (3D) geometrical frustration for Mn ions with an antiferromagnetic (AF) interaction. For the stoichiometric LLMO (Li[Mn_2]O_4), the amount of Mn^{3+} (S=2) is equivalent to that of Mn^{4+} (S=3/2). As a result, charge-ordering of Mn^{3+} and Mn^{4+} occurs below 280 K, at which a cubic phase transforms into an orthorhombic phase due to a cooperative Jahn-Teller distortion [1]. Very recently, we clarified the magnetic phase diagram of LLMO in the whole x range from 0 to the solubility limit of Li^+ at the $16d$ site (x_{cr}=1/3) by μ^+SR and susceptibility measurements [2]. That is, as x increases from 0, T_N (~60 K) reduces very rapidly down to 27 K even for the x=0.02 sample. Since the excess Li^+ annihilates the long-range AF order and takes the system into a spin-glass-like state, T_N is eventually T_f for $x \geq 0.02$. The magnitude of T_f decreases slowly with further increasing x, but the end member (Li[$Li^+_{1/3}Mn^{4+}_{5/3}$]O_4) shows static ferromagnetic (FM) order below ~20 K (=T_C) [3], while the Li-deficient spinel Li_0[Mn^{4+}_2]O_4 is antiferromagnet with T_N=32 K. This suggests that the magnetic nature of LLMO is likely to be determined not only by the average Mn valence but also by the occupancy of Mn^{4+} ions at the $16d$ site ($z_{16d}(Mn^{4+})$).

In order to elucidate the effects of $z_{16d}(Mn^{4+})$ on magnetism of the spinels, we have thus made a systematic μ^+SR experiment on the Li[$Mg^{2+}_x Mn^{3+}_{1-2x} Mn^{4+}_{1+x}$]$O_4$ spinel with x=1/8, 1/4, 3/8, and 1/2. Interestingly, all the Mg-doped samples are found to enter into a static FM ordered phase below ~30 K; more correctly, T_C ~30 K for the x=1/8 sample and ~20 K for x=1/2. This would imply the significant role of $z_{16d}(Mn^{4+})$ on FM order, although we should also note the effect of other parameters, such as, oxygen deficiency and/or cation distribution.

[1] J Sugiyama et al., J. Phys.: Condensed Matter 7 (1995) 9755.
[2] J Sugiyama et al., Phys. Rev. B 75 (2007) 174424.
[3] K Mukai et al., in the Proceedings of the 14th. Int. Symposium on Intercalation Compounds (Seoul, Korea, 2007) p. 236.