ESR STUDY OF LAYERED AND POROUS Na_xMnO_2 COMPOUNDS

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Introduction

Layered and porous manganese oxides have been lately intensively studied due to their possible applications including ion/molecular sieves, catalysis reactions and as anode materials in rechargeable lithium batteries [1]. In fact, $Na_{0.44}MnO_2$ with a tunnel structure was recently suggested as a highly perspective material for Li-batteries [2]. Larger sodium ions were used to stabilize the structure and later fully exchanged by lithium. This structure demonstrated a remarkable ability to cycle lithium with almost no perceptible loss of capacity. Although electrochemical characterization is fundamental, detailed studies of electronic properties are perhaps even more important in the process of electrode optimization.

Results and Discussion

In our study, we focus on several different Na_xMnO_2 structures potentially important for lithium intercalation. In contrast to the porous $Na_{0.44}MnO_2$ compound, the α-$NaMnO_2$ and β-$NaMnO_2$ structures are planar, with the former being characterized by perfectly planar layers of edge shared MnO_6 octahedra and the latter by zig-zag layers. We present the results of the local-probe electron spin resonance (ESR) measurements, obtained in X-band ($\nu = 9.5$ GHz) and in high magnetic field ($\nu = 221$ GHz). The latter measurements were performed at NHMFL on a 17 T superconducting magnet and the spectrometer working in the transmission mode. The X-band ESR measurements show several distinct ESR signals in all three compounds [Fig. 1(a)]. The dominant component is rather broad, which unfortunately makes the analysis reliable only at high temperatures. High-field measurements are therefore instrumental. The high-field spectra are found to be broadened with respect to X-band by a factor of 1.3-1.5. The monotonic broadening with decreasing temperature [Fig 1(c)] is expected for $Na_{0.44}MnO_2$, which undergoes a transition to a long-range magnetically ordered state below 25 K. However, similar behavior is found also in both layered compounds.

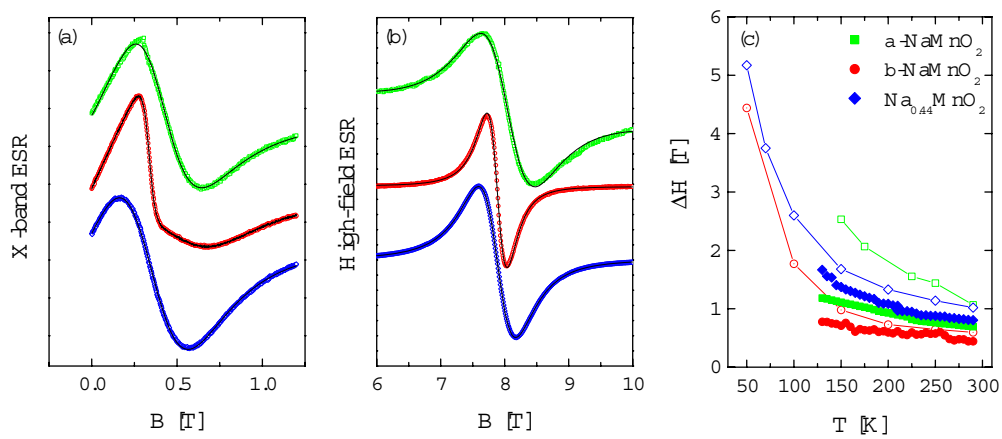

Figure 1. (a) X-band and (b) high-field ESR spectra of Na_xMnO_2 compounds with fits given by solid lines. The temperature dependence of the ESR linewidth measured in X-band (solid symbols) and in high magnetic field (open symbols).

Conclusions

The observed ESR spectra are rather broad, which corresponds to significant magnetic anisotropy at magnetic manganese sites. Despite different crystal structures, all the three investigated samples exhibit ESR signals with similar temperature dependence, speaking in favor of electronic correlations developing in a similar way.

References

[1] Feng, Q., *et al.*, J. Mater. Chem., **9**, 319 (1999).
[2] Armstrong, A.R., *et al.*, J. Mater. Chem., **8**, 255 (1998).