COMMENTS

Comment on "Effect of Chromium Substitution on the Lattice Vibration of Spinel Lithium Manganate: A New Interpretation of the Raman Spectrum of LiMn₂O₄"

Annalisa Paolone,*,†,‡ Andrea Sacchetti,†,§
Paolo Postorino,†,§ and Rosario Cantelli†,‡

*Dipartimento di Fisica, Università di Roma "La Sapienza",
Piazzale A. Moro 5, I-00185 Roma, Italy, Laboratorio
Regionale SUPERMAT, INFM, Via S. Allende, I-84081
Baronissi, Italy, and COHERENTIA, INFM,
Unità di Roma, Italy*

In a recent paper by Hwang et al.[1] the effects of the chromium substitution in spinel lithium manganate (LiMn$_{2-x}$Cr$_x$O$_4$ $0 \leq x \leq 0.5$) have been investigated by means of X-ray absorption spectroscopy (XAS) and micro-Raman spectroscopy. The most evident result, which consistently emerges from X-ray absorption near-edge spectroscopy and extended X-ray absorption fine structure spectroscopy (EXAFS) analysis, is that a tetragonal distortion of the MnO$_6$ octahedra is present and well detectable in the pure sample ($x = 0$) and it is progressively reduced by Cr substitution. The authors, exploiting the XAS results, propose a new interpretation of the Raman spectrum and claim that a simpler analysis of the intensity of the two main spectral features they observed in the Raman spectra enables direct information on the extent of tetragonal distortion to be obtained. In particular, they ascribe the observed peaks at 580 and 620 cm^{-1} to A$_{1g}$ modes for regular Mn^{4+}O$_6$ octahedra and tetragonally distorted Mn^{3+}O$_6$ octahedra, respectively.

In the present comment we want to show that, although the arguments discussed in ref 1 for the above assignment could appear rather reasonable, the Raman spectra themselves are strongly affected by a severe experimental artifact. In fact, using laser sources coupled to highly focusing optics, it is very easy to convey a high photon flux on a small portion of the sample which causes a remarkable local heating for strongly absorbing specimens. Even though the authors were aware of laser-induced sample heating and made use of low-power laser light for their experiment, the resulting power density on the sample surface was still too high (around 500 kW/cm^2, i.e., 5 mW focused over 1 μm^2). Indeed, in a recent paper,[2] exploiting the Stokes−antiStokes ratio, we have estimated that a LiMn$_2$O$_4$ sample can locally reach a temperature as high as 1500 K under about the same power density, I_0, used in ref 1. Such a high-temperature induces a local chemical decomposition with severe effects on the Raman spectrum. Indeed, it is well-known that LiMn$_2$O$_4$
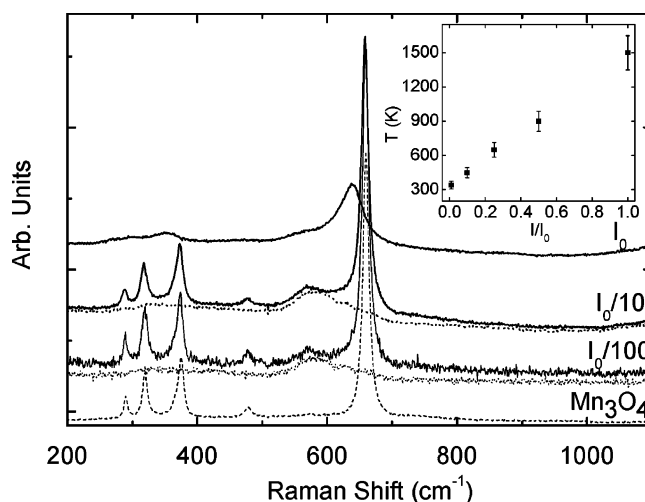
* Corresponding author. Tel: +39-06-49914400, fax: +39-06-4957697, e-mail: Annalisa.Paolone@roma1.infn.it.
† Università di Roma "La Sapienza".
‡ Laboratorio Regionale SUPERMAT, INFM.
§ COHERENTIA, INFM.

Figure 1. Raman spectra of LiMn$_2$O$_4$ measured with different power density (reported on the right). Sequentially the spectra are collected increasing (dotted lines) the power density from I_0/100 up to I_0 and then decreasing the power density (solid lines) down to I_0/100. For comparison the spectrum of Mn$_3$O$_4$ is reported (dashed line). The inset shows the temperature of the sample obtained by the relative intensity of the Stokes−antiStokes lines as a function of the laser power (from ref 2).

undergoes an irreversible phase transformation above ∼850 °C.[3] The effect of thermal decomposition is shown quite clearly by the series of Raman spectra of LiMn$_2$O$_4$ collected as a function of the laser intensity from the same microscopic portion of the sample.[2] Raman spectra collected on a cycle starting from a power density of about 5 kW/cm^2 and reaching the maximum of 500 kW/cm^2, are shown in Figure 1. Following the sequential evolution of the Raman spectrum from the lowest to the highest power density, significant modifications of the spectral shape are apparent. This effect is largely magnified when looking at the spectra collected on decreasing from the highest to the lowest power density. In particular, the comparison between the initial and the final spectra collected at the same power density clearly shows that irreversible chemical decomposition has occurred. It is worth noticing that the spectrum collected at the highest power density is quite similar to that shown in ref 1 for the same sample.

These results show that the true Raman spectrum of LiMn$_2$O$_4$ consists of a broad peak at around 580 cm^{-1}, with poorly defined features between 300 and 450 cm^{-1}, whereas the intense peak around 640 cm^{-1} originates from the products of the thermal decomposition. In Figure 1 we reported for comparison the Raman spectrum of Mn$_3$O$_4$, as this compound is obtained from LiMn$_2$O$_4$ on heating above 1060 °C.[3] It is well evident that the spectrum of LiMn$_2$O$_4$ measured with I_0/100 after exposing the sample to the maximum laser power is very similar to the spectrum of Mn$_3$O$_4$. In the measurement collected at the highest laser power, the position of the phonon of Mn$_3$O$_4$ is displaced toward lower energies, as usually observed on heating the sample. The resemblance of the spectrum measured with $I = I_0$ and that of ref 1 suggests that the latter is measured with a local

T of about 1500 K. It must be pointed out that similar decomposition effect can be found in the great majority of papers on the Raman spectrum of $LiMn_2O_4$ (for details see ref 2).

The phonon structures we ascribe to $LiMn_2O_4$ are in good agreement with the results of a computer simulation reported in ref 4. There, it was shown that Raman-active peaks are expected within the 350−460 cm^{-1} range and at 597 cm^{-1}, whereas at 633 cm^{-1} only an infrared-active phonon peak is predicted. It is worth noticing that also the Raman spectra of $LiMn_2O_4$ reported in ref 4 are affected by the same artifact as that of ref 1. Therefore, the authors of ref 4 should consider that the two highest Raman active phonons are located at 590 and 625 cm^{-1}, instead of being almost degenerate at around 590 cm^{-1}, as their own theoretical calculations predict.

We want to point out that the decomposition effect we describe is extremely local, so that only the small volume impinged by the laser beam is affected. For this reason experimental techniques, which investigate much larger volumes, such as usual chemical analysis or XRD, cannot provide evidence of the laser-induced decomposition of the sample. Moreover, the degradation process is very fast: in our experience, only few seconds of laser irradiation can be sufficient to produce a stable chemical decomposition of the sample. After that, the Raman spectrum of the decomposition products shows a good reproducibility on a very long time scale.

A feature of the Raman spectra of $LiMn_{2-x}Cr_xO_4$ which was underlined in ref 1 is the variation of the relative intensity, $R(580/620)$, of the phonons at 580 and 620 cm^{-1} as a function of Cr doping. According to the authors this is an additional proof of the link of these lines to the regular and distorted MnO_6 octahedra. In view of the results we obtained on $LiMn_2O_4$, the dependence of $R(580/620)$ can be explained differently. For instance, this effect could be ascribed to a progressive Cr-doping induced reduction of the thermal decomposition due to an increased thermal stability or to a shift of the electronic absorption band which reduces the absorption at laser frequency in Cr-doped compounds. Moreover, since in ref 2 Mn_3O_4 has been suggested among the products of thermal decomposition and possibly responsible for the deceptive peak at high-frequency, it could also be conjectured that, on increasing the doping, fewer Mn atoms are available to form Mn_3O_4, leading to a reduction of the intensity of the spectral feature at 625 cm^{-1}.

As to the phonon frequencies, it was shown that while the frequency of the phonon centered at around 580 cm^{-1} decreases by 20 cm^{-1} from $x = 0$ to $x = 0.5$, the position of the phonon at 625 cm^{-1} does not practically change, even for high doping levels. This different doping-dependence appears unlikely since all the Raman active modes are mainly linked to the motion of oxygen and lithium ions. We thus suggest that the phonon at 580 cm^{-1}, with its frequency slightly dependent on x, is a true phonon of $LiMn_2O_4$, while the line at 625 cm^{-1} arises from thermal decomposition products. Moreover, the frequency of the Raman mode of $Li_2Mn_2O_4$, which has only Mn^{3+} ions, is much lower than that of the phonon mode attributed to the same

vibration in $LiMn_2O_4$ (605 cm^{-1} versus 625 cm^{-1}, as stated in ref 1). In our opinion, the above arguments are a further proof that the line at 625 cm^{-1} is due to products of the thermal decomposition and cannot be ascribed to intrinsic properties of the samples.

For all the reasons here reported, we strongly believe that the new interpretation of the Raman spectra reported in ref 1 is completely disguised by the occurrence of laser-induced thermal decomposition of the samples.

Finally, we briefly comment on the interpretation of the X-ray absorption measurements. According to us, there is not a general agreement on the physical picture of the structure of $LiMn_2O_4$. Indeed this compound presents a first-order phase transition around room temperature, which from the first structural study was attributed to a cooperative Jahn−Teller effect.[5,6] More recent studies ascribed the phase transition to a charge ordering process, showing the absence of a J−T distortion of the octahedra above room temperature.[7,8] In this context the analysis of the first EXAFS measurements[9] on $LiMn_2O_4$ based on the model with Jahn−Teller distortions, showed that better fits to the data at 300 and 370 K were obtained using two different Mn−O distances with respect to the case of a single Mn−O distance, as in ref 1. However, a more recent EXAFS study[10] pointed out that the local environments of Mn ions observed by EXAFS are consistent with the occurrence of two different Mn−O bond lengths at low temperature, while above room temperature a better fit of the data is obtained considering just one single Mn−O distance, so that no evidence of Jahn−Teller distortions is obtained in this work.

In conclusion, although a comparative Raman and XAS study would certainly lead to a deeper knowledge of the microscopic mechanism at work in these systems, there is a clear need to apply appropriate experimental precautions and to give an interpretation of the results properly exploiting previous works in the field.

References and Notes

(1) Hwang, S.-J.; Park, D.-H.; Choy, J.-H.; Campet, G. *J. Phys. Chem. B* **2004**, *108*, 12713.

(2) Paolone, A.; Sacchetti, A.; Corridoni, T.; Postorino, P.; Cantelli, R.; Rousse, G.; Masquelier, C. *Solid State Ionics* **2004**, *170*, 135.

(3) See, for example, Tacheray, M. M.; Masueto, M. F.; Dees, D. W.; Vissers, D. R. *Mater. Res. Bull* **1996**, *31*, 133. Tacheray, M. M. *Prog. Solid State Chem.* **1997**, *25*, 1. Yamada, A.; Miura, K.; Hinokuma, K.; Tanaka, M. *J. Electrochem. Soc.* **1995**, *142*, 2149. Massarotti, V.; Capsoni, D.; Bini, M. *Solid State Commun.* **2002**, *122*, 317.

(4) Ammundsen, B.; Burns, G. R.; Saiful Islam, M.; Kanoh, H.; Rozière, J. *J. Phys. Chem. B* **1999**, *103*, 5175.

(5) Yamada, A.; Miura, K.; Hinokuma, K.; Tanaka, M. *J. Electrochem. Soc.* **1995**, *142*, 2149.

(6) Yamada, A.; Tanaka, M. *Mater. Res. Bull.* **1995**, *30*, 715.

(7) Rodriguez-Carvajal, J.; Rousse, G.; Masquelier, C.; Hervieu, M. *Phys. Rev. Lett.* **1998**, *81*, 4660.

(8) Rousse, G.; Masquelier, C.; Rodriguez-Carvajal, J.; Hervieu, M. *Electrochem. Solid State Lett.* **1999**, *2*, 6.

(9) Yamaguchi, H.; Yamada, A.; Uwe, H. *Phys. Rev. B* **1998**, *58*, 8.

(10) Paolone, A.; Castellano, C.; Cantelli, R.; Rousse, G.; Masquelier, C. *Phys. Rev. B* **2003**, *68*, 014108.