Local structure and polaron formation in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$

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Abstract

The local structure of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ is determined from pair-distribution function (PDF) analysis of pulsed neutron diffraction. We have compared the effect on the local structure of crossing the metal–insulator transition as a function of temperature and composition. Crossing the metal–insulator boundary at low temperature by varying the composition yields similar distortions to those seen in the temperature dependence indicating the presence of polarons in the insulating phase which disappear in the metallic phase. © 1998 Published by Elsevier Science B.V. All rights reserved.

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The magnetoresistant properties of the lanthanum manganites have created much interest in these materials [1,2]. Millis and others [3,4] have argued that lattice polarons forming at the metal–insulator (MI) transition are necessary to explain the change in resistivity. Therefore, an understanding of the structure of these compounds can help answer questions regarding the nature of electronic transport in different regions of the phase diagram. Several papers have reported structural distortions due to polarons [5,6] above the metal–insulator transition temperature ($T_{\text{mi}}$). We have studied the structure of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ for $x = 0.12$ and $0.21$ from pair-distribution functions (PDF) obtained from pulsed neutron powder diffraction collected at the Manuel Lujan, Jr., Neutron Scattering Center (MLNSC). The data are Fourier transformed to give the real-space density using the method given in Ref. [7]. Sample preparation and characterization are described elsewhere [5].

At $x = 0.21$, $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ is a paramagnetic insulator above $T_{\text{mi}}$, (about 190 K), and a ferromagnetic metal below. At $x = 0.12$, there is no MI transition and the material is always insulating. By comparing changes in PDFs, we wish to determine whether the underdoped material contains polarons and how the local structure changes when the phase-boundary line is crossed.

Fig. 1 shows a comparison of PDFs from the $x = 0.12$ and $0.21$ samples at high, panel (a), and low, panel (b), temperature. The high-temperature ($T = 220$ K) PDFs appear almost identical. This suggests that the underdoped material has polarons...
at high temperature since we know they exist in the x = 0.21 structure above 190 K \[5\]. Difference curves are plotted below the data with dashed lines indicating uncertainties at the 2σ level. Structural changes, on going from x = 0.12 to x = 0.21 at high temperature, are on the level of the noise and are not significant.

In contrast, the 10 K structures show larger differences. Peaks in the x = 0.21 PDF are sharper and taller, indicating less disorder in the metallic state. This can be explained if small polarons, present in the insulating phase at both temperatures, disappear in the metallic regime.

We examine this hypothesis by comparing changes in PDFs as a function of temperature and composition. Fig. 2 shows two pairs of differences between samples which have crossed the MI boundary: triangles crossing as a function of composition \([x = 0.12] - (x = 0.21)\] at 10 K and solid line crossing as a function of temperature for \(x = 0.21\). The changes are large compared to the random errors and strongly correlated over a wide range of \(r\). There is no reason for the increase in doping to have a similar effect on the structure as a decrease in temperature. The only thing these difference curves have in common is that they were both produced by crossing from the insulating to the metallic phase, albeit via different paths. This is strong evidence that polarons exist in the under-doped material at low temperature and disappear as the MI transition is crossed.

In contrast, panel (b) shows the same low-temperature difference plotted again as triangles, but
the solid line now shows the difference between the \( x = 0.12 \) and 0.21 materials at 220 K. At this temperature, both samples are insulating. In this case the change between PDFs is much smaller and does not correlate as well with the low-temperature structure change. This shows that the differences between the structures of the two compositions at low temperature cannot be explained by the chemical substitution alone. These conclusions will be further discussed elsewhere \[8\].

These results point out that for low-doped compounds the division of the phase diagram between metallic and insulating phases also separates two different local structures. The insulating phase is identified by local distortions caused by polarons which are not seen in the metallic phase.

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References