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Magnetic-field Modulation Experiments on Colossal Magnetoresistance samples: First results

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Recently we have observed a small change in the width, σ , of the Mn-O pair distribution function when a 1T magnetic field is applied. To improve our sensitivity to magnetic-field-induced changes, we have developed a magnetic field modulation technique. At each X-ray energy we collect two data points, one with field on and the other with field off; as a result we collect two scans simultaneously. The difference in these two traces provides a measure of the magnetic-field-induced change. The results for the modulation measurements will be compared to the earlier work using static magnetic fields.

1. Introduction

The Ca substituted manganites ($\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$) have been intensively studied in recent years, because of the unusual coupling between transport phenomena, the magnetization, and the lattice in these systems (Jonker & van Santen, 1950; Schiffer *et al.*, 1995). For Ca concentrations between roughly 20 and 50% these materials exhibit a very large negative magnetoresistance and are thus referred to as Colossal magnetoresistive materials (CMR) (Jin *et al.*, 1994; Kusters *et al.*, 1989). The basic coupling mechanism between charge and spin is assumed to be the double exchange model (DE) (Zener, 1951) but modified by a large lattice effect (Röder *et al.*, 1996; Millis *et al.*, 1996) which amplifies the CMR. At low temperatures these CMR systems are ferromagnetic (FM) metals while above the magnetic transition temperature they become paramagnetic semiconductors (some refer to them as insulators).

Recent local structure measurements have shown that there is an increasing lattice distortion as T approaches T_c from below (Billinge *et al.*, 1996; Booth *et al.*, 1996; Booth *et al.*, 1998a; Booth *et al.*, 1998b; Subías *et al.*, 1997; Subías *et al.*, 1998). Above T_c the lattice disorder changes slowly. This distortion is attributed to the formation of polarons.

In our EXAFS studies (Booth *et al.*, 1998a; Booth *et al.*, 1998b; Cao *et al.*, 2000b) we have shown that there is a relationship between the change in the width of the Mn-O pair distribution width $\sigma(T)$ (the Debye-Waller factor), and the sample magnetization, $M(T)$, that is similar for all CMR samples we have studied. Specifically, $\ln(\Delta\sigma^2(T)) = A M(T)/M_o + B$, where $\Delta\sigma^2$ is the decrease in σ^2 associated with a decrease in the number of polarons as T is lowered below T_c (see ref. onlinecitebooth98b), and M_o is the saturation magnetization. However, the measurements of both $\sigma(T)$ and $M(T)$ were carried out in low or zero magnetic field; consequently each data point on plots of $\ln \Delta\sigma^2$ vs M/M_o is also at a different temperature.

These results imply that near the transition temperature, T_c , the local structure should be magnetic field dependent; also the transition moves to higher temperature with increasing B-field (Pissas *et al.*, 1997). In the DE model, the presence of FM-ordered local magnetic moments enhances transport and increases the hopping rate between sites. In the metallic state below T_c , the hopping rate is assumed to be so fast that the lattice does not have time to respond, and local distortions are reduced as observed in XAFS. Close to T_c the application of a magnetic field increases the magnetization, and hence promotes faster hopping. This in turn implies reduced local distortions, with no change in temperature.

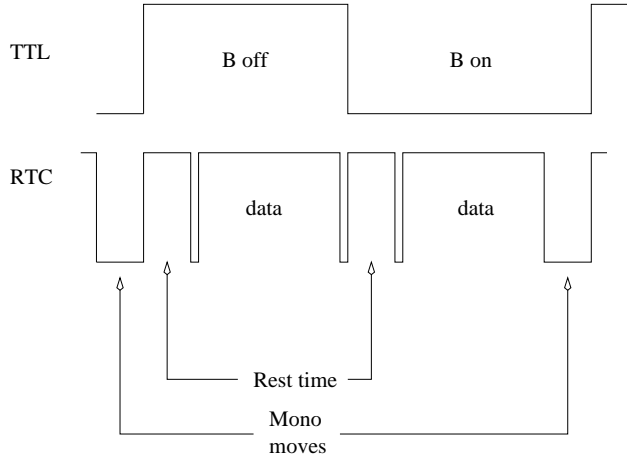
Recently we have investigated the magnetic field dependence to verify this expectation and shown that in a 1 T field there is in fact a small reduction of the local distortions (Cao *et al.*, 2000a). However the effect is small so one cannot investigate any field or field-orientation dependence. The problem is in large part due to small instrumental drift which limits the change in amplitude that can reproducibly be measured in XAFS when scans are an hour apart.

To improve our ability to see small amplitude changes we have developed a magnetic field modulation method for which the drift between corresponding data points (between field on and field off) are of order seconds. This should greatly improve our ability to observe small changes. Here we report our first observations using this technique. We recognise that some hysteresis and time dependent remnant magnetization effects could be present - the present experiments observe changes for field changes occurring on 1-2 second time scales.

2. Experimental Details

The transmission XAFS experiments were carried out on beamline 10-2 at the Stanford Synchrotron Radiation Laboratory (SSRL) using a modified version of the XAS data collection program. A magnetic field up to 1 T was applied using a small electromagnet that could be pulsed on in less than 1 sec. and off in about 1 sec (drops to 5% of maximum field in one second).

The XAS program was modified to collect two data points at each energy; one to correspond to field on and the other to field off. In this way two traces are collected nearly simultaneously - one with a magnetic field on and the other the field off. The difference of these two files provides a measure of any structural change that is induced by the magnetic field. A sketch of the timing pulses is shown in Fig. 1. The usual monochromator rest time was also used to allow the field to reach its new value each time a new pulse was applied to the power supply; it was set to 1 sec. Gate pulses (almost a square wave) were obtained from the XAS program to switch the magnetic field on and off.

**Figure 1**

The timing pulses for the field-modulation experiment. The lower trace shows the real time clock (RTC) pulses for the computer, showing the rest time, data collection time and monochromator move time. The upper trace shows the TTL output that turns the magnetic field on and off. For the data reported here, the rest time was 1 sec and the data collection time (same for each field configuration at a given energy) increased from 1-5 sec over the scan.

3. Data analysis and Results

In Fig. 2 we plot the k -space difference file for a 30% Ca CMR sample at the transition temperature (260K) for a field modulation between 0 and 1T (lower trace). Although noisy there is clearly an oscillatory XAFS signal present. At temperatures well above or well below T_c , the difference file is essentially flat - no obvious XAFS oscillation is present. This verifies directly in a single scan the results of the earlier static field measurements which involved averaging over several scans for each field configuration.

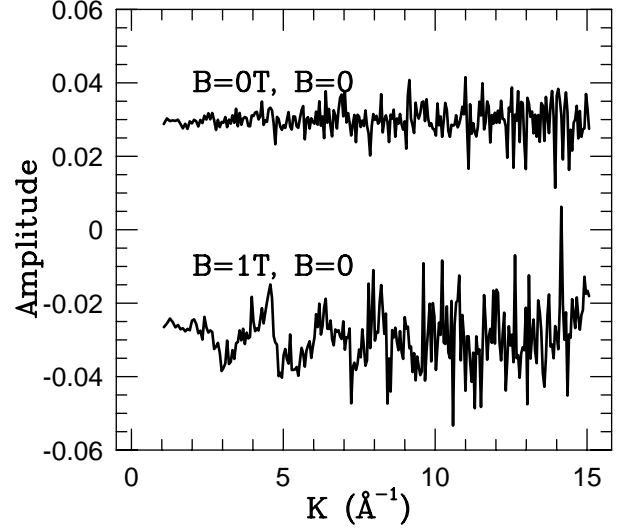
In Fig. 3 we plot the Fourier transform (FT) of the extracted XAFS oscillations from the difference file for three temperatures, 315 K, 260 K and 35 K. The data at 260 K clearly show a peak which corresponds to the Mn-O peak (1.5 Å) while the data at high and low temperature have low amplitudes. If the main change in the local structure is an effective change in the pair distribution width, σ , then the XAFS oscillations in the difference data for a given atom pair should correspond to the derivative of the XAFS equation with respect to σ

$$k\chi(k) = \sum_i \frac{N_i S_0^2 e^{-2k^2\sigma_i^2}}{R_i^2} \sin(2kR_i + \Phi_i) = \sum_i k\chi_i, \quad (1)$$

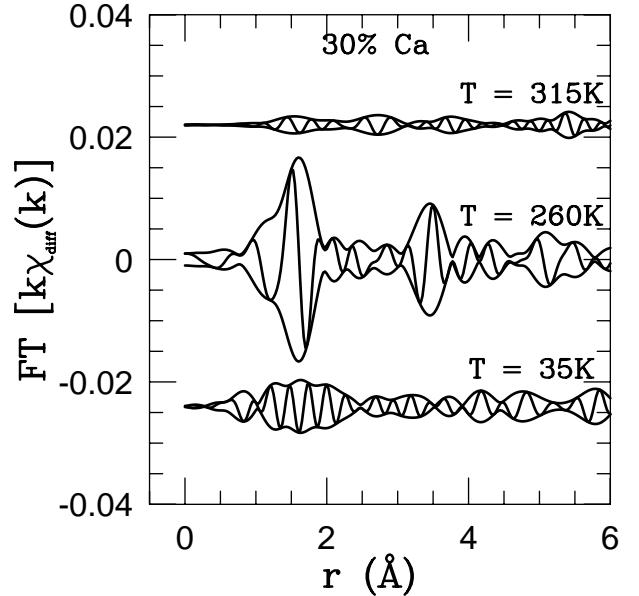
and

$$k \frac{d\chi_i}{d\sigma_i} = \frac{N_i S_0^2 e^{-2k^2\sigma_i^2} (-4k^2\sigma_i)}{R_i^2} \sin(2kR_i + \Phi_i) \quad (2)$$

where N_i is the number of atoms in shell i , S_0^2 is an amplitude reduction factor, which corrects for many-body effects, R_i is the average distance for atoms in shell i to the center atom and Φ_i is the total phase shift in the central and backscattering process.

**Figure 2**

Plots of $k\chi_{diff}$ for the difference file at $T=T_c=260$ K. The upper trace shows data collected in this mode, but with $B=0$ in both channels. Lower trace shows the difference field for field switching between 0 and 1 Tesla.

**Figure 3**

FT scans for the difference data at 315 K, 260 K and 35 K. The amplitude is low at 35 and 315 K indicating little change in structure with B-field modulation. However, well defined peaks are observed at 260 K (T_c) for the first and third neighbors (peaks at 1.5 and 3.5 Å). FT range: 3.5-13.5 Å⁻¹, with a Gaussian broadening of 0.3 Å⁻¹.

Since the main σ_i dependence occurs in the exponential term $e^{-2k^2\sigma_i^2}$, the derivative $k \cdot d\chi_i/d\sigma_i$ is proportional to $k^3\chi_i$, and the phase of the signal in either k - or r -space

should be essentially the same as the regular $k^3\chi$ XAFS data at zero field. To verify this we compare in Fig. 4 the back-transforms for the Mn-O peak (0.9-2.0Å), for $k\chi_{diff}(k)$ (multiplied by 3650) and $k^3\chi(k)$ for a single scan. The large factor is expected; the difference data is about 0.03 of the original data and the additional k^2 factor provides roughly another factor of 100. This plot also shows that there is a small phase shift which is consistent with an expected small change in the average bond length(Booth *et al.*, 1998*b*).

These results also provide a bonus - if a particular peak does not have an associated change in local distortion, then that peak in the r-space data will not be present in the difference data. That is the case in Fig. 3. The second and third peaks in a normal FT plot correspond to Mn-La/Ca and Mn-Mn (and Mn-O-Mn) atom pairs in these materials; they partially overlap in a normal XAFS FT. In the FT of the difference file the contribution for Mn-La/Ca at 3 Å is very small, consistent with our earlier result(Booth *et al.*, 1998*b*) that σ^2 for the Mn-La/Ca peak increases only as little through the transition temperature. In the difference data this result is clear without any analysis.

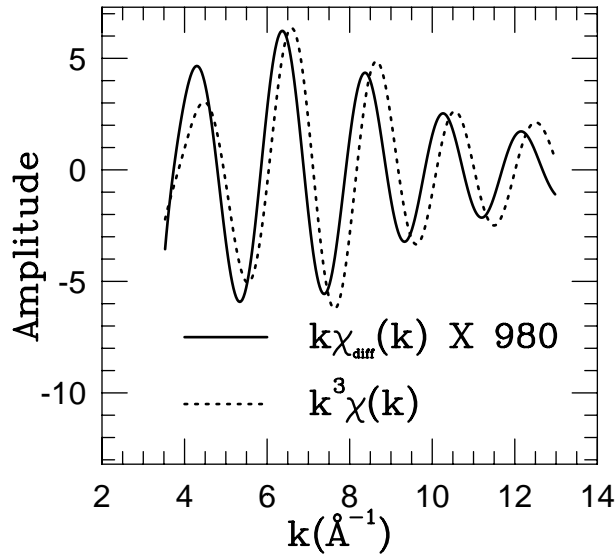


Figure 4

A comparison of the back transforms for the first neighbor (Mn-O) peak for $k\chi_{diff}(k)$ and $k^3\chi(k)$; r-space range, 0.9-2.0 Å. The difference plot $k\chi_{diff}(k)$, has been multiplied by 3650. This figure shows that the decay of the oscillations of the difference data is essentially identical to a $k^3\chi(k)$ plot as predicted from the derivative.

The static field measurements also suggested that there is a small anisotropy in the changes of the local distortions when a magnetic field is applied. The improved sensitivity using the modulation technique should allow us to investigate this possibility.

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