^{139}La NMR detection of ferromagnetic clusters far above the Curie temperature in $La_{0.7}Ca_{0.3}Fe_{0.09}Mn_{0.91}O_3$ spin-glass manganite

2007 J. Phys.: Condens. Matter 19 226209

(http://iopscience.iop.org/0953-8984/19/22/226209)

IOP PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **19** (2007) 226209 (6pp) doi:10.1088/0953-8984/19/22/226209

^{139}La NMR detection of ferromagnetic clusters far above the Curie temperature in $La_{0.7}Ca_{0.3}Fe_{0.09}Mn_{0.91}O_3$ spin-glass manganite

Vladimir V Matveev[1], Eero Ylinen[2], Vasilii S Zakhvalinskii[2,3] and Reino Laiho[2]

[1] Department of Quantum Magnetic Phenomena, V A Fock Institute of Physics, St-Petersburg State University, 198504 St-Petersburg, Russia
[2] Wihuri Physical Laboratory, Department of Physics, University of Turku, FI-20014 Turku, Finland
[3] Physics Department, Belgorod State University, Russia

E-mail: vmatveev@esr.phys.spbu.ru and reino.laiho@utu.fi

Received 14 February 2007, in final form 4 April 2007
Published 8 May 2007
Online at stacks.iop.org/JPhysCM/19/226209

Abstract

The dependence of the ^{139}La nuclear magnetic resonance (NMR) spin-echo signal on temperature and on the power of the applied radio-frequency pulse is investigated in zero applied magnetic field in $La_{0.7}Ca_{0.3}Fe_{0.09}Mn_{0.91}O_3$ (LCFMO) with Curie temperature (T_C) of about 125 K. Plots of the spin-echo signal versus the NMR pulse power reveal two maxima, out of which the high-power component is observed up to temperatures above T_C. It is also found that while the temperature dependence of the NMR signal amplitude follows the value of static magnetization $M(T)$, the NMR frequency, which is related to the local field at La positions, decreases only slowly and the ^{139}La NMR signal is preserved at least to 220 K. These results confirm the existence of large ferromagnetic clusters with long life-times above T_C in LCFMO.

1. Introduction

According to a common point of view, the substituted manganites are intrinsically inhomogeneous, containing a number of nanoscale parts such as droplets, domains, clusters, polarons etc [1]. Various theoretical models and experimental results have been proposed for explanation of the origin of the clusters, their size, magnetic properties and other parameters [1–4]. For example, the reported size of the inhomogeneities varies between 1 nm [2] and 500 nm [3] and no magnetic correlations were found in the $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) system [4]. Only a few experimental methods, such as small angle neutron scattering (SANS), transmission electron microscopy (TEM) and scanning tunnelling microscopy (STM) [5] allow direct detection of nanosize inhomogeneities or clusters in solids. Zero field nuclear magnetic resonance (ZF NMR) is a variant of NMR techniques for investigation of the magnetically ordered state without applying an external magnetic field due to the presence of a

strong local field, mainly hyperfine in origin. ZF NMR is a probe for any atom with unpaired electrons keeping the orientation of their magnetic moment (spin) during a time-period much longer than the nuclear relaxation time, i.e. this method can be applied for investigation of magnetically ordered states or long living magnetic clusters. Thus detection of ZF NMR for ^{139}La or some other nucleus of nonmagnetic atoms can be used for unambiguous confirmation of ferromagnetic (FM) order as the local hyperfine field at the ^{139}La nucleus is a sum of transferred fields from the nearest manganese ions and decreases close to zero if those atoms have antiferromagnetic (AF) order.

In addition to the spectrum and its centre frequency, corresponding to the magnitude of the field, another parameter, dependence of the NMR signal intensity on the amplitude of the applied radio-frequency pulse, reflects local magnetic properties of the material, namely the so-called enhancement factor, depending on the magnetic and crystalline structure and existence and mobility of domain walls (DW).

The ZF NMR technique is widely used for investigation of local structure and magnetic properties of various magnetics including the substituted manganites (see [6–13] and references therein). In particular, this technique was used in order to detect FM clusters in AF surroundings in manganites [10–13]. However, only a few attempts were made to detect FM clusters above the bulk Curie temperature T_C, i.e. in the paramagnetic phase using ^{55}Mn NMR [14, 15]. In a few spin-glass systems, clusters were observed [14] but on the other hand no ^{55}Mn NMR signal above T_C was detected for either $La_{0.7}Ca_{0.3}MnO_3$ [14] or for iron substituted $La_{0.7}Ca_{0.3}Fe_{0.03}Mn_{0.97}O_3$ [15]. However, as can be concluded from current models [1–3, 16], inhomogeneities above T_C may have a key role in explaining the physical origin of the CMR (colossal magnetoresistance) effect.

As found in measurements of the magnetization, $M(T)$, in $La_{0.7}Ca_{0.3}Fe_{0.09}Mn_{0.91}O_3$ (LCFMO) [17], partial substitution of manganese by iron in $La_{0.7}Ca_{0.3}MnO_3$ (LCMO) leads to a decrease of T_C and transforms the material to a cluster-glass like state. In particular for LCFMO, T_C decreased from 258 K down to 125 K. In this paper we report the existence of long-living FM clusters far above T_C in LCFMO, as observed by ZF ^{139}La NMR measurements.

2. Experimental procedures

The $La_{0.7}Ca_{0.3}Fe_{0.09}Mn_{0.91}O_3$ sample used in this work has been described earlier [17]. In order to avoid possible ageing effects, x-ray diffraction measurements were repeated and according to them the sample was of single-phase, keeping its structure as was described before [17].

Experiments were carried out with the Bruker MSL300 pulsed NMR spectrometer. ^{139}La NMR signals were detected in zero external magnetic field by the spin-echo method using a conventional $p1$–τ–$p2$ sequence with $p2 = 2p1$, a $p1$ pulse length of 0.8 μs and τ between 20 and 40 μs. A spin-echo spectrum was obtained as a frequency dependence of the echo amplitude. The resonance circuit was tuned at every frequency. The sensitivity of the spectrometer was calibrated at different frequencies by using a proton sample and a Bruker electromagnet. The ringing of the $p1$ pulse was cancelled by subtracting the signal without the $p2$ pulse, and the ringing of the $p2$ pulse by phase cycling.

3. Experimental results

In figure 1 a few ^{139}La ZF NMR spin-echo spectra are shown at different temperatures. The most important feature of these spectra is that the lanthanum NMR signal does not disappear at $T_C = 125$ K but remains detectable at least up to 220 K. One may expect that the spin-echo signal would be present up to $T_C = 258$ K of undoped $La_{0.7}Ca_{0.3}MnO_3$ [17], but unfortunately above 220 K the NMR signal became practically impossible to detect due to the extremely low

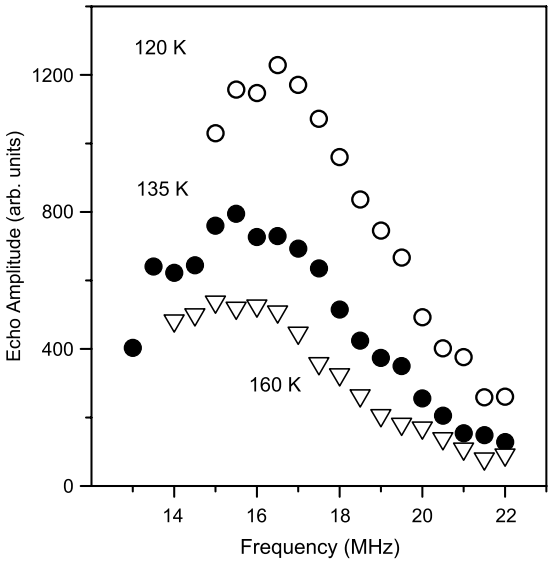

Figure 1. Frequency dependence of the ^{139}La ZF NMR spin-echo signal observed for $La_{0.7}Ca_{0.3}Fe_{0.09}Mn_{0.91}O_3$ at $T = 120$, 135, and 160 K.

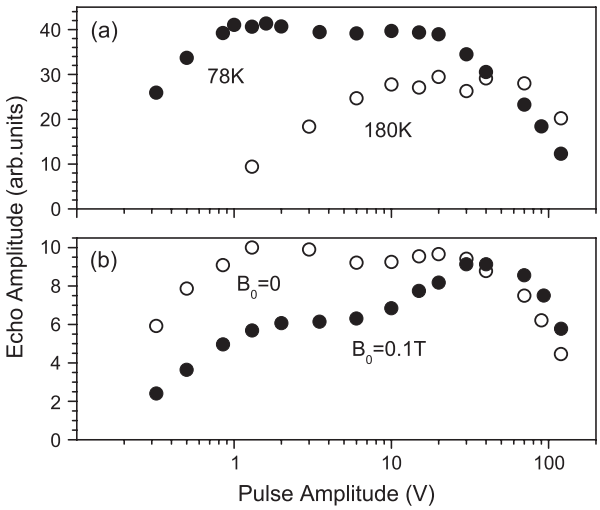

Figure 2. Power dependence of the ^{139}La spin-echo signal for $La_{0.7}Ca_{0.3}Fe_{0.09}Mn_{0.91}O_3$. The data in the upper panel give the signal amplitude in zero field below (78 K) and above (180 K) the Curie temperature $T_C = 125$ K. In the lower panel the amplitudes of the spin-echo signal are given at 4.2 K in zero field and in the applied field $B_0 = 0.1$ T.

signal intensity. The centre frequency of the spectrum in figure 1 is shifted to lower frequencies only slightly when the temperature is increased, while the intensity of the signal decreases strongly. In addition to the frequency dependence, we measured at different temperatures the dependence of the amplitude of the spin-echo signal, A, on the amplitude of the applied radio-frequency pulse, p.

The results in figure 2 show the existence of two maxima in this dependence observed in zero applied field at 4.2 and 78 K. However, at 180 K the shape of this curve is quite different

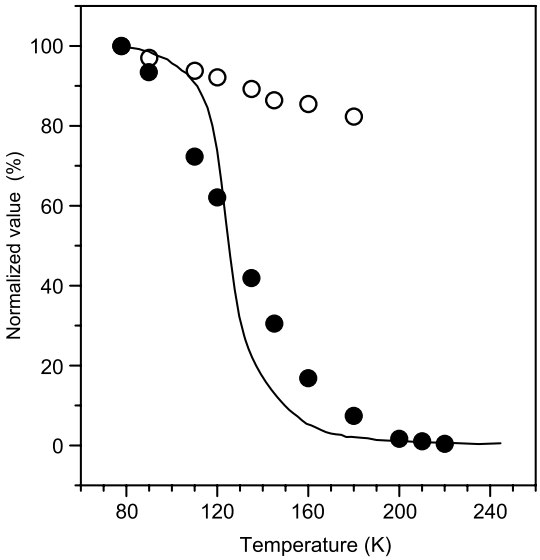

Figure 3. Temperature dependence of ^{139}La spin-echo ZF NMR signal amplitude, A (closed circles), the central frequency of the NMR spin-echo spectrum, f_0 (open circles), proportional to the magnetization m of a cluster, and the bulk magnetization, $M(T)$ (solid curve), all three parameters being normalized against their values at 78 K. The value of A is additionally corrected taking into account the $1/T$ dependence of the nuclear magnetization.

because the low-power part disappears. In figure 3 the NMR data are compared with the results of the static magnetization measured in the same sample [17].

4. Discussion

Observation of the NMR signal up to at least $T/T_C = 1.8$ in figure 3 means that ferromagnetic short-range cluster-glass like order in our LCFMO sample is preserved far above T_C. Therefore, our results give direct experimental confirmation of FM clusters in the LCFMO sample. This observation supports strongly the interpretation of the data of magnetization measurements in the same sample analysed on the basis of a cluster-glass model [17].

In relation to the lifetime of clusters, it is necessary to emphasize that the observation of spin-echo requires a local field where the nuclear magnetization develops in a time longer than the spin–lattice relaxation time T_1 which, in any case, is not shorter than the spin–spin relaxation time T_2. For the ^{139}La NMR signal T_2 is about 1 ms at 180 K and this means that the clusters have a long lifetime—not less than a few milliseconds—pertaining to quasistatic agglomerations which cannot be identified as dynamical quasi-particles or polarons.[4]

It is evident that the existence of two maxima in the dependence of the spin-echo signal amplitude on the applied pulse amplitude in figure 2 corresponds to two lanthanum positions with different magnetic properties. As these positions are not distinguishable by frequency but have strongly different dependence on the pulse amplitude, $A(p)$, it is reasonable to ascribe

[4] One should emphasize that sometimes the lifetime of the clusters is compared with the Larmor frequency of the nucleus investigated—(see, e.g. [14]) but this is misleading as evident from comparison with Mössbauer spectroscopy. The well known characteristic time of Mössbauer experiments, 10^{-8} s [18], corresponds exactly to the natural lifetime of the excited state (natural relaxation time in Mössbauer spectroscopy) and is much longer than 10^{-19} s, which one could calculate according to the inverse energy of the Mössbauer transition, 14 keV [18].

them to nuclei at domain walls (DW) and to those locating within domains of the sample. In order to check this assumption we measured the A versus p at 4.2 K under a weak external magnetic field of 0.1 T. Application of the magnetic field was found to decrease significantly the low-power peak of the curve in figure 2 but did not influence its high-power part. This confirms that the low-power maximum is caused by the nuclei at DW. Preserving of the domain signal at 180 K as shown by open circles in figure 2 means the formation of single-domain FM clusters above $T_C = 125$ K in the sample.

As the clusters are single-domain magnetic particles, their size should be limited between a dimension defined by the 'absolute quantum limit of magnetism', QLM, and the size of the largest magnetic domain. Unfortunately, as far as we know both values are not known exactly for the manganites. As to magnetic domain size, there are estimations between 20 nm [19] and a few micrometres [20] depending on the grain size of the material investigated. Also, regarding the estimation of QLM, its value is of the order of 1 nm [21]. This means that the reported size of the inhomogeneities, varying between 1 nm [2] and 500 nm [3], could agree with our NMR data but we are unable to quote the exact cluster size at the moment.

The central frequency f_0 of the NMR spectrum decreases slowly with increasing temperature. The signal intensity A at the same time displays a fast decrease, reflecting the relative part of the material in the cluster state,

$$A \propto N_{cl} \cdot V_{cl}, \tag{1}$$

where N_{cl} is the number of clusters and V_{cl} is their average volume. Both values in the right side of (1) may be temperature dependent. As far as A follows the magnetization curve when the temperature is increased, one can conclude that the $M(T)$ curve reflects more or less the number of lanthanum ions in the clusters.

5. Conclusion

Summarizing, we have observed for the first time the ZF ^{139}La NMR spin-echo signal far above T_C in $La_{0.7}Ca_{0.3}Fe_{0.09}Mn_{0.91}O_3$. This signal can be connected to FM clusters in the paramagnetic phase, giving direct experimental confirmation for the existence of a cluster-glass like state in the substance. These clusters have lifetimes, not less than a few milliseconds and cannot be identified as quasi-particles including magnetic polarons.

Acknowledgments

We acknowledge Dr Petriina Paturi for carrying out the x-ray diffraction measurements. VVM also gratefully acknowledges the Wihuri foundation and University of Turku for financial support for his research visits.

References

[1] Dagotto E 2003 *Nanoscale Phase Separation and Colossal Magneto-Resistance: The Physics of Manganites and Related Compounds* (Berlin: Springer)
[2] De Teresa J M, Ibarra M R, Algarabel P A, Ritter C, Marquina C, Blasco J, García J, del Moral A and Arnold Z 1997 *Nature* **386** 256
[3] Uehara M, Mori S, Chen C H and Cheong S-W 1999 *Nature* **399** 560
[4] Viret M, Glättli H, Fermon C, de Leon-Guevara A M and Revcolevschi A 1998 *Europhys. Lett.* **42** 301
[5] Renner Ch, Aeppli G, Kim B-G, Soh Y-A and Cheong S-W 2002 *Nature* **416** 518
[6] Kubo T, Goto T, Koshiba T, Takeda K and Awaga K 2002 *Phys. Rev.* B **65** 224425

[7] Inomata K, Okamura S, Miyazaki A, Kikuchi M, Tezuka N, Wojcik M and Jedryka E 2006 *J. Phys. D: Appl. Phys.* **39** 816
[8] Matveev V V, Baranov D A, Yurkov G Yu, Akatiev N G, Dotsenko I P and Gubin S P 2006 *Chem. Phys. Lett.* **422** 402
[9] Pleshakov I V and Matveev V V 2004 *J. Phys.: Condens. Matter* **16** 1725
[10] Papavassiliou G, Pissas M, Belesi M, Fardis M, Dolinsek J, Dimitropoulos C and Ansermet J P 2003 *Phys. Rev. Lett.* **91** 147205
[11] Papavassiliou G, Pissas M, Diamantopoulos G, Belesi M, Fardis M, Stamopoulos D, Kontos A G, Hennion M, Dolinsek J, Ansermet J-Ph and Dimitropoulos C 2006 *Phys. Rev. Lett.* **96** 097201
[12] Kawasaki Y, Minami T, Kishimoto Y, Ohno T, Zenmyo K, Kubo H, Nakajima T and Ueda Y 2006 *Phys. Rev. Lett.* **96** 037202
[13] Shimizu K, Qin Y and Tyson T A 2006 *Phys. Rev.* B **73** 174420
[14] Kapusta Cz, Riedi P C, Kocemba W, Tomka G J, Ibarra M R, De Teresa J M, Viret M and Coey J M D 1999 *J. Phys.: Condens. Matter* **11** 4079
[15] Przewoźnik J, Kapusta Cz, Żukrowski J, Krop K, Sikora M, Rybicki D, Zając D, Oates C J and Riedi P C 2006 *Phys. Status Solidi* b **243** 259
[16] Ibarra M R, Zhao G-M, De Teresa J M, García-Landa B, Arnold Z, Marquina C, Algarabel P A, Keller H and Ritter C 1998 *Phys. Rev.* B **57** 7446
[17] Laiho R, Lisunov K G, Lähderanta E, Salminen J and Zakhvalinskii V S 2002 *J. Magn. Magn. Mater.* **250** 267
[18] *Chemical Applications of Mössbauer Spectroscopy* 1968 (London: Academic)
[19] Mori S, Shoji R, Yamamoto N, Asaka T, Matsui Y, Machida A, Moritomo Y and Katsufuji T 2003 *Phys. Rev.* B **67** 012403
[20] Das A, Sahana M, Yusuf S M, Madhav Rao L, Shivakumara C and Hegde M S 2000 *Mater. Res. Bull.* **35** 651
[21] Vonsovsky S V 1974 *Magnetism* vol 2 (New York: Wiley)