EUROPHYSICS LETTERS 1 June 2005

Europhys. Lett., **70** (5), pp. 677–683 (2005)
DOI: 10.1209/epl/i2004-10519-4

Observation of magnetic excitons in $LaCoO_3$

S. R. Giblin[1], I. Terry[1], S. J. Clark[1], T. Prokscha[2], D. Prabhakaran[3], A. T. Boothroyd[3], J. Wu[4] and C. Leighton[4]

[1] *Department of Physics, University of Durham - South Road, Durham, DH1 3LE, UK*
[2] *Laboratory for Muon Spin Spectroscopy, Paul Scherrer Institut CH-5332, Villigen, PSI, Switzerland*
[3] *Department of Physics, University of Oxford - Oxford, OX1 3PU, UK*
[4] *Department of Chemical Engineering and Materials Science, University of Minnesota 421 Washington Ave SE, Minneapolis 55455, USA*

received 25 November 2004; accepted in final form 14 April 2005
published online 4 May 2005

PACS. 76.75.+i – Muon spin rotation and relaxation.
PACS. 75.30.Hx – Magnetic impurity interactions.

Abstract. – An impurity-driven magnetic phase transition has been investigated in $LaCoO_3$ at temperatures below that of the thermally induced spin state transition of the Co^{3+} ion. We have discovered a saturating component of the magnetisation, which we attribute to previously unobserved interactions between magnetic excitons. These conclusions are confirmed by muon spin spectroscopy which indicates an ordering temperature of 50 K in both the transverse and zero-field configurations. Low-energy muon measurements demonstrate that the magnetic behaviour is independent of implantation energy and hence a property of the bulk of the material. The magnetic exciton formation is attributed to the interaction between electrons bound at oxygen vacancies and neighbouring cobalt ions, and is proposed as the precursor to the magneto-electronic phase separation recently observed in doped lanthanum cobaltite.

Introduction. – $LaCoO_3$ is unique among the $LaMO_3$ family (where M is a transition metal element) as it undergoes a thermally driven spin state transition. This occurs because the crystal-field splitting of the *d*-levels of the Co^{3+} ions is only slightly greater than Hund's exchange energy, leading to a situation where a small input of thermal energy can lead to the occupation of a higher spin state. Explicitly, a transition from a Co^{3+} low spin (LS) $S = 0$, ${t_{2g}}^6{e_g}^0$, state to an intermediate spin (IS) $S = 1$, ${t_{2g}}^5{e_g}^1$, state occurs at around 90 K, although the exact nature of the transition is still a matter of some contention [1–9]. However, the low-temperature ($T < 35$ K) magnetic properties of $LaCoO_3$ are usually dominated by a Curie-like magnetic susceptibility, which is generally acknowledged to be related to defects. In particular, this "Curie tail" has been ascribed to paramagnetic impurities, ferromagnetic regions at the surface [10], and also to the formation of high spin ($S = 16$) magnetic polarons in $LaCoO_3$ [1]. Nagaev *et al.* [11] have also proposed that the paramagnetic centres responsible for the Curie tail are magnetic polarons, although strictly they should be labeled "magnetic excitons". In this model localized holes (electrons) bound to cobalt ions or oxygen interstitials

(vacancies) induce LS to high-spin ($S = 2$) transitions in neighboring Co^{3+} ions leaving the remaining cobalt ions in the LS ground state. The radius of a magnetic exciton will extend over several unit cells, creating spin clusters of $S = 10$ to 15 which are dilute within the solid. The creation of the spin clusters is independent of the thermally excited LS-IS transition. Moreover, Nagaev *et al.* [11] have predicted that magnetic exciton formation is the precursor for magneto-electronic phase separation at high hole (electron) densities. Such a phase separation has been observed in $LaCoO_3$ doped with divalent cations such as Sr [12, 13] and Ca [14]. The nature of a magnetic polaron or exciton implies that it may be most easily observed in a system displaying a diamagnetic ground state, making $LaCoO_3$ an ideal candidate to study such an defect-driven magnetic state. In this letter we report the first measurements, to our knowledge, of the low-temperature muon-spin spectrum of $LaCoO_3$. This technique is sensitive to local magnetism, and so can in principle probe localized entities such as magnetic polarons. We argue that the observed magnetic response from $LaCoO_3$ is consistent with the formation of magnetic excitons. The existence of magnetic excitons in $LaCoO_3$ could well be related to the formation of magnetic polarons in other families of oxide materials.

Bulk Muon Spin Rotation or Relaxation (μSR) experiments were performed at the PSI in Switzerland upon the instrument Dolly. μSR is well suited to the exploration of local magnetic correlations as the spatial sensitivity of the probe decreases rapidly, giving an effective sampling radius of 20 Å. The energy of the incoming muons (4 MeV) means a bulk implantation depth of approximately 0.5 mm. We have also utilised the Low Energy Muon (LEM) beamline at the PSI [15], enabling depth profiling (from 20 nm to 160 nm) of the muon spin relaxation. Knowledge of the muon stopping site is required to fully understand the relaxation of the muons. We have made *ab initio* electronic structure calculations to obtain the position of the muon at the time of its decay, using the CASTEP density functional theory code [16] to examine the electron density. A detailed discussion of CASTEP as a tool to describe muon implantation will be given elsewhere. Complementary bulk magnetic measurements were performed using a Quantum Design MPMS SQUID magnetometer, all measurements were performed whilst warming from 2 K–300 K in fields up to 50 kOe. Measurements have been carried out on both polycrystalline and single-crystal samples, fabricated by a solid-state reaction [13] and floating zone furnace methods, respectively. Iodometric titration measurements on the polycrystal sample reveal a formula unit of $LaCoO_{2.98\pm0.02}$, indicating a slight oxygen deficiency.

Bulk μSR measurements. – To our knowledge, μSR has not been used to observe a pure LS (where $S = 0$) to IS transition, where the contribution to the muon relaxation is from one source: the valence electrons of the cobalt ions. Previous measurements have concentrated upon Spin-Peierls [17, 18] or Spin Crossover [19, 20] materials. For the present case of $LaCoO_3$, our calculations predict that the fractional co-ordinates of the implanted muon within a rhombohedral $1 \times 1 \times 2$ unit cell is $[0.405, 0.463, 0.530]$. This corresponds to a neutral position away from the atoms, meaning that any nuclear spin component will be dominated by the valence electron contribution from cobalt ions. Note that the muons will be influenced by the behaviour of more than one cobalt ion. Our bulk μSR measurements were performed on a single-crystal sample and initially made in a 100 Oe Transverse Field (TF). The data were fitted over the entire temperature range using a relaxation function of the form

$$G_x(t) = A^s_{tf} \exp\left[-\left(\lambda^s_{tf} t\right)^2\right] \cos(2\pi\nu_\mu t) + A^f_{tf} \exp\left[-\left(\sigma^f_{tf} t\right)^2\right], \tag{1}$$

where A^s_{tf} and A^f_{tf} are the initial asymmetries of, respectively, the oscillatory and Gaussian components, where s and f are for slow and fast relaxing components. λ^s_{tf} and σ^f_{tf} are the depolarisation rates for the two separate decays and υ_μ is the muon precession frequency,

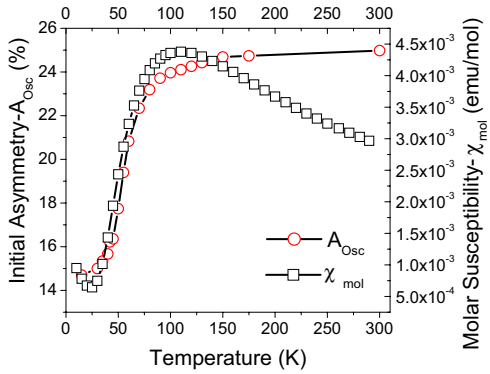

Fig. 1

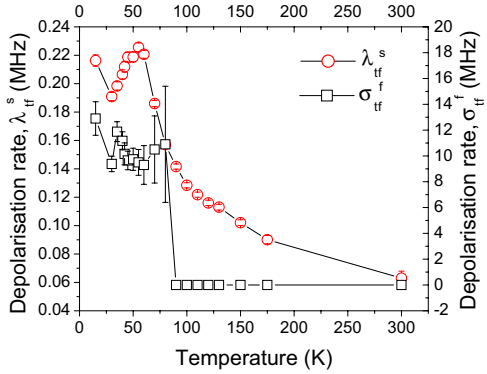

Fig. 2

Fig. 1 – The initial asymmetry, A^s_{tf} of the TF μSR is shown. The LS-IS spin transition is clearly visible. The molar susceptibility measured at 50 kOe of the single crystal is also shown for comparison.

Fig. 2 – Temperature dependence of the depolarisation (λ^s_{tf}) rate of the TF data, showing clear evidence for a magnetic ordering at 50 K in the LS state. A Gaussian (σ^f_{tf}) contribution is apparent below 90 K.

which is dependent upon the externally applied field; no other function was required to fit the TF data. The temperature dependence of the fitting parameters A^s_{tf}, λ^s_{tf} and σ^f_{tf} are shown in figs. 1 and 2. Above 90 K, only the first term in eq. (1) is required to fit the muon spin relaxation data; below 90 K, both terms in eq. (1) are required. The initial asymmetry (A^s_{tf}) of the oscillating decay shows evidence for a strong dephasing upon reducing temperature (fig. 1), coincident with the LS-IS transition as demonstrated by the 50 kOe Field Cooled (FC) and measured, molar susceptibility also shown in fig. 1.

The drop in the initial asymmetry with decreasing temperature is accompanied by the appearance of the second Gaussian component, σ^f_{tf}, of the muon spin relaxation as illustrated in fig. 2. This suggests that the LS-IS is observed in A^f_{tf} because a fraction of the muons are now relaxing in a magnetic region of the material that only exists when the material enters the LS state. Also shown in fig. 2 is the depolarisation rate λ^s_{tf} as a function of temperature. The peak in λ^s_{tf} indicates magnetic ordering at 50 K, below the LS-IS transition. Previous measurements have revealed that the thermal expansion coefficient increases dramatically around 50 K [4], although the heat capacity [21] does not show a similar evolution. The change in expansion coefficient was interpreted as evidence for thermally induced spin transition within the Co *d*-levels. We believe this an unlikely cause of the observed peak in λ^s_{tf} as any effect of thermal expansion would also be observed in σ^f_{tf}.

To clarify the origin of the observed magnetic ordering, we have also carried out Zero Field (ZF) μSR at temperatures representative of the three different magnetic regimes of this material; i) above the 90 K spin state transition, ii) near the magnetic ordering transition at 55 K and iii) in the impurity "paramagnetic tail" at 35 K. The raw data are shown in fig. 3 and a clear change in the initial asymmetry is seen to take place upon reducing temperature. The muon spin relaxation curves were fitted with a function of the form:

$$G_z(t) = A^s_{zf} \exp\left[-\left(\lambda^s_{zf} t\right)^{\beta}\right] + A^f_{zf} \exp\left[-\left(\sigma^f_{zf} t\right)^2\right] \qquad (2)$$

which represents a superposition of Gaussian and stretched exponential relaxations. Here A

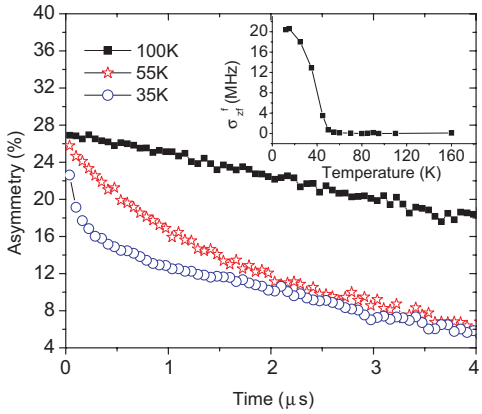

Fig. 3

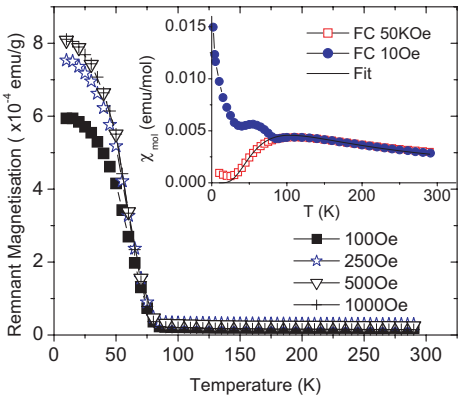

Fig. 4

Fig. 3 – ZF μSR data is shown at 100 K, 55 K and 35 K, representing the different magnetic regions. The inset shows the Gaussian relaxation (σ_{zf}^{f}), which begins at 45 K in the paramagnetic tail.

Fig. 4 – Evidence for saturating magnetic exciton behaviour is shown. $LaCoO_3$ was cooled in various magnetic fields until 50 K and then zero-field cooled and measured in the remnant field, with saturation occuring at 500 Oe. A clear sign of remnance in the LS region is observed. The inset shows the effect of measuring the molar susceptibilities of the sample at 50 kOe (open squares) and 10 Oe (closed circles).

represents the initial asymmetries of the relative relaxations, σ_{zf}^{f} is the depolarisation rate for the Gaussian relaxation and λ_{zf}^{s} represents the depolarisation for the stretched exponential, where β is the exponent.

When in the IS phase (i)), where the majority of Co^{3+} ions have a spin state of 1, we find that the relaxation is fitted best with the first term of eq. (2), with $\beta = 2$, *i.e.* a Gaussian relaxation. When in the LS state (ii)) we find that the data is again best fitted with only the stretched exponential function, but now with $\beta = 0.5$, indicative of a dilute spin system with a single relaxation time τ [22]. We find a depolarization rate that tracks the TF data, with a 50 K peak at 0.52 MHz. The inclusion of the extra Gaussian component in $G_z(t)$ is only relevant when the first component indicates ordering and the paramagnetic tail in the magnetic susceptibility becomes dominant in the temperature region below 45 K (iii)). This can clearly be seen in the inset of fig. 3, where the temperature dependence of the depolarization rate of the muons, σ_{zf}^{f} (from the fast relaxation term in eq. (2)), shows a sharp increase at 45 K. We have applied longitudinal fields up to 4900 Oe at 35 K and 55 K, and for both temperature regions we failed to fully decouple the relaxation, which is an indication of dynamic random local fields.

We have observed the LS-IS transition at 90 K with TF μSR and have detected magnetic ordering at 50 K in TF and ZF μSR data. The observed relaxations cannot be explained by thermal expansion as already discussed and they are not due to muonium formation, as the TF measurements did not demonstrate the characteristic precession frequencies for paramagnetic muonium. Moreover, we observed two different relaxations below 90 K in both ZF and TF techniques which suggest the presence of Co ions with $S > 0$. It is generally accepted that pure $LaCoO_3$ is expected to produce an $S = 0$ ground state, therefore we would expect the magnetic fraction of the material to become more dilute below 90 K. We believe that our results can only be understood by considering the possibility of defect-induced magnetism within $LaCoO_3$.

Bulk magnetic measurements. – We carried out d.c. magnetic susceptibility measurements of single-crystal and polycrystalline $LaCoO_3$ to investigate the defect-related magnetism within the material. Measurements made at 50 kOe reproduce earlier results reported in the literature [2, 4] with the LS-IS transition upon warming, along with a Curie tail. This is demonstrated in the inset of fig. 4 which shows the single-crystal response when Field Cooled (FC), demonstrating the spin transition beginning around 90 K along with the low-temperature Curie tail. Also shown is a fit to the 50 kOe measured data as described by Zobel *et al.* [4] confirming a LS-IS transition, as opposed to a LS-HS. Thus by employing the same measurment protocol as others we can reproduce the published data with both our polycrystalline and single-crystal samples. Significantly, the published magnetic data have always been taken with a large measuring field, typically 10 kOe or 50 kOe; consequently, any small-defect–related features have been swamped by the bulk response to this high measuring field. A much lower measuring field of 10 Oe (fig. 4 inset, closed symbols) produces a dramatically different temperature-dependent susceptibility. This initial measurement shows evidence for a saturating component around 50 K, with the large paramagnetic Curie-like dependence dominating below 35 K.

Further investigation of the saturating component has been made with a different measurement protocol involving field-cooling the samples to 50 K in various applied magnetic fields, then cooling from 50 K to the base temperature in the remnant field, typically 0.5 Oe. The resulting susceptibility was recorded upon warming in the remnant field. This cooling protocol was designed to saturate the interacting component as observed in the μSR, whilst eliminating the paramagnetic tail. The results are shown in fig. 4 for cooling to 50 K in fields of 100 Oe, 250 Oe, 500 Oe and 1000 Oe. Clearly, the sample is showing remnant and saturating behaviour (with respect to both field and temperature), with no change in the remnant magnetisation being detected above a cooling field of 500 Oe. Note that the remnant magnetisation of this extra magnetic component is very small and is easily swamped by the paramagnetic Curie tail at modest measuring fields. No previous results have ever observed a remnant component of the magnetisation. Indeed, isothermal magnetisation loops down to 10 K and up to 50 kOe demonstrate that the material appears to be paramagnetic. The thermally induced LS-IS transition cannot directly account for the remnant behaviour [4] and suggests the defect-induced magnetism to be the cause. The SQUID magnetic measurements were performed upon both single and polycrystalline samples providing the same result.

Low-energy muon results, a depth profile. – The identity of the defects dominating the μSR and low-field magnetic susceptibility may be the same as those responsible for the well-known Curie tail, *i.e.* paramagnetic impurities, ferromagnetic regions in the surface or magnetic polarons/excitons. To address this issue we decided to probe muon spin relaxation rate as a function of depth (20 nm to 160 nm) with the LEM beamline at PSI. The object of this work was to distinguish between bulk and surface contributions to the μSR. A large polycrystalline sample was used because of the greatly reduced muon flux. We reproduced the 100 Oe TF bulk μSR data at a depth of 50 nm, confirming the bulk behaviour. We then performed depth profiles at temperatures of 20 K, 50 K and 130 K. The results at 50 K are shown in fig. 5. The main figure shows the depolarisation rate at various depths, and one can clearly see that it remains constant (within the error bars) over the entire depth range. The constant depolarisation is a feature of all the temperatures that we investigated, implying that the surface behaves in the same way as the bulk. The inset of fig. 5 shows the asymmetry for the energy scan at 50 K. The drop around 50 nm can be partially explained by the reflection probabilities at low energies [23]. Given the density of our material, we expect the asymmetry to drop by approximately 10 percent, but we observe a drop at all temperatures of over 20 percent. One

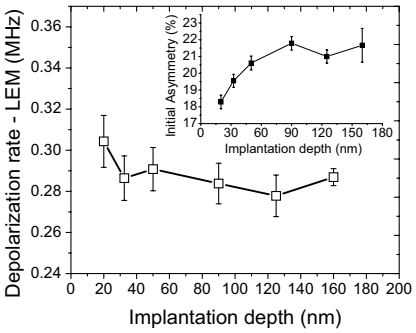

Fig. 5 – LEM data representing a depth profile from 20 nm to 160 nm at 50 K showing no relaxation change with depth. The inset shows the drop of the initial asymmetry over the same range of implantation depths, due to the reflection of muons.

possible explanation is that an increase in the reflection probability is due to some $LaCoO_3$ surface-related effect although this appears to have no impact on the bulk magnetic properties of the material as the asymmetry drop is temperature independent. The exact nature of the asymmetry drop requires further investigation. Thus we have shown that muon depolarization occurs throughout the material and rules out ferromagnetic surface regions as the cause of the low-temperature μSR and low-field magnetic susceptibility.

Discussion. – Oxygen non-stoichiometry is the dominant source of defects in $LaCoO_3$ and are likely to effect the magnetism through the formation of magnetic excitons [11]. In this scenario, once the Co ions start falling into their LS state below 90 K an exciton can form if an oxygen vacancy is contained in the unit cell and the neighbouring Co ions are also in a LS state. The formation of excitons appears to occur under two distinct processes. The excitons can either interact, leading to magnetic remnance or just exist as high-susceptibility large-spin regions. Such a model would explain the two separate relaxations observed by the TF μSR measurement (fig. 2), showing an ordering as one approaches 50 K (interacting excitons) and another stable component indicative of paramagnetic excitons that are polarised by the external field. The ZF μSR experiment is able to distinguish between the two senarios due to the difference in field distribution. It can be shown that [22] $\lambda = \pi c^2 \gamma_\mu \langle \Delta B^2 \rangle \tau$, where ΔB is the width of field distribution, τ the correlation time and c is the fraction of the ions in a non-zero spin state for a dilute system. The stretched exponential function (slow component, λ_{zf}^s) therefore has a maximum as the field distribution peaks due to the interacting excitons. However, the non-interacting (paramagnetic) species are expected to freeze out as their fluctuation time becomes large with respect to the muon time window. These independent relaxations are indistinguishable above 50 K in the ZF configuration. When performing TF measurements, the non-interacting species are frozen out by the applied external field when the excitons form at 90 K leading to the saturated σ_{tf}^f. The oxygen-vacancy-induced magnetic exciton model can also explain the d.c. magnetic susceptibility data. Applying the measuring protocol as described in the text produces remnant behaviour as shown in fig. 4. Above the ordering temperature (50 K), a small amount of net magnetic moment remains due to the polarisation of the exctions. However once the surrounding ions are excited into the IS state the exciton will no longer exist and the contribution to the moment will be paramagnetic in nature.

In summary, this letter has described the low-temperature magnetic properties of single-crystal and polycrystalline $LaCoO_3$ probed by μSR spectroscopy. We see evidence for the

$S = 0$ to $S = 1$ (LS to IS) spin transition, along with a further magnetic ordering at $T_c = 50\,\mathrm{K}$ in the LS diamagnetic phase. Our results indicate that the low-temperature magnetic ordering is associated with interacting magnetic excitons, formed as a result of the presence of oxygen vacancies. ZF muon spin relaxation measurements indicate the presence of dynamic relaxations below 90 K, and confirm the existence of the magnetic ordering below 50 K observed in the TF muon measurements. The presence of this phase was confirmed by magnetization measurements. Low-energy muon relaxation measurements have also demonstrated that the surface of the sample plays no significant role in the low-temperature impurity-driven magnetic properties of $LaCoO_3$. Therefore, we have clear evidence supporting the idea of magnetic phase separation in lanthanum cobaltite at low temperatures, which we attribute to oxygen-vacancy-induced magnetic excitons and that may be the precursor of charge and magnetic phase separation that is observed when the material is doped with strontium or calcium.

* * *

This work was partially supported by the NMI 13 European access program and SRG would like thank EPSRC for financial support. μSR experimetns were performed at the Swiss Muon Source, PSI, Villigen, Switzerland. We would like to thank D. HERLACH, E. MORENZONI, R. SCHEUERMANN and A. SUTER for valuable discussions. CL thanks the American Chemical Society Petroleum Research Fund for partial support of this research.

REFERENCES

[1] YAMAGUCHI S., OKIMOTO Y., TANIGUCHI H. and TOKURA Y., *Phys. Rev. B*, **53** (1996) 2926.
[2] ENGLISH S. R., WU J. and LEIGHTON C., *Phys. Rev. B*, **65** (2003) 220407(R).
[3] KOROTIN M. A. *et al.*, *Phys. Rev. B*, **54** (1996) 5309.
[4] ZOBEL C. *et al.*, *Phys. Rev. B*, **66** (2002) 020402.
[5] ASAI K. *et al.*, *Phys. Soc. Jpn.*, **67** (1998) 290.
[6] YAMAGUCHI S., OKIMOTO Y. and TOKURA Y., *Phys. Rev. B*, **55** (1997) R8666.
[7] ASAI K., GEHRING P., CHOW H. and SHIRANE G., *Phys. Rev. B*, **40** (1989) 10892.
[8] KOBAYASHI Y. *et al.*, *Phys. Rev. B*, **62** (2000) 410.
[9] ASAI K. *et al.*, *Phys. Rev. B*, **50** (1994) 3025.
[10] SENARIS-RODRIGUEZ M. A. and GOODENOUGH J. B., *J. Solid State Chem.*, **118** (1995) 323.
[11] NAGAEV E. L. and PODELSHCHIKOV A. I., *J. Phys. Condens. Matter*, **8** (1996) 5611.
[12] KHUNS P. L. *et al.*, *Phys. Rev. Lett.*, **91** (2003) 127202.
[13] WU J. and LEIGHTON C., *Phys. Rev. B*, **67** (2003) 174408.
[14] BURLEY J. C., MITCHELL J. F. and SHORT S., *Phys. Rev. B*, **69** (2004) 054401.
[15] MORENZONI E. *et al.*, *Physica B*, **289** (2000) 653.
[16] SEGALL M. D. *et al.*, *J. Phys. Condens. Matter*, **14** (2002) 2717.
[17] JESTÄAT TH. *et al.*, *J. Phys. Condens. Matter*, **10** (1998) L259.
[18] KOJIMA K. *et al.*, *Hyperfine Interact.*, **104** (1997) 37.
[19] CAMPBELL S. J. *et al.*, *J. Phys. Chem. B*, **107** (2003) 14289.
[20] BLUNDELL S. J. *et al.*, *J. Phys. Chem. Solids*, **65** (2004) 25.
[21] STØLEN S. *et al.*, *Phys. Rev. B*, **55** (1997) 103.
[22] UEMURA Y. J. *et al.*, *Phys. Rev. B*, **31** (1985) 546.
[23] MORENZONI E. *et al.*, *Nuclear Instrum. Methods B*, **192** (2002) 254.