

# A $\mu$ SR study of the ruthenium perovskites $\text{ACu}_3\text{Ru}_4\text{O}_{12}$ with $\text{A} = \text{Ca}, \text{Pr}, \text{Nd}$

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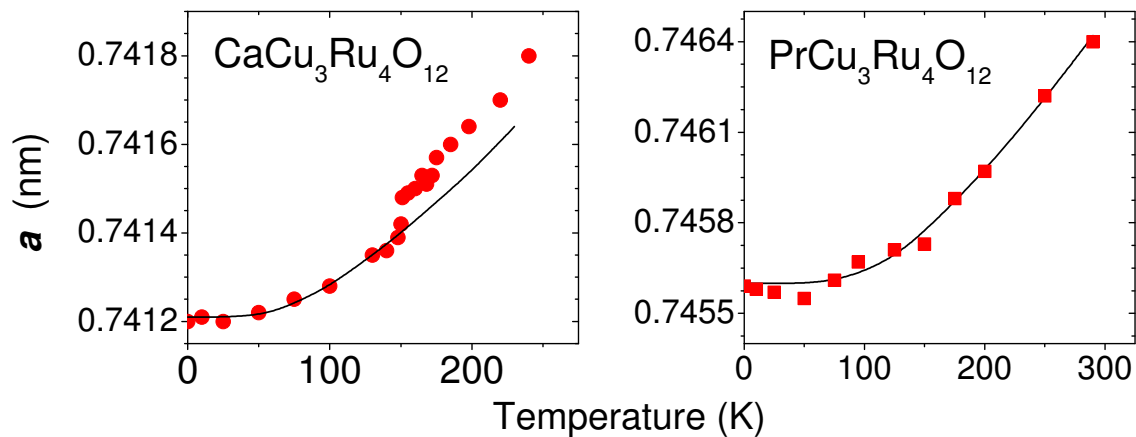
**Abstract.** The metallic ruthenium perovskites  $\text{ACu}_3\text{Ru}_4\text{O}_{12}$  with  $\text{A} = \text{Ca}, \text{Pr}, \text{Nd}$  were investigated by zero field (ZF) and weak transverse field (TF) muon spin rotation/relaxation ( $\mu$ SR) spectroscopy. The ZF spectra for  $\text{CaCu}_3\text{Ru}_4\text{O}_{12}$  show pure static Gaussian Kubo-Toyabe relaxation arising from the interaction between the muon spin and the nuclear moments of the Cu ions. This confirms that no atomic magnetic moment exists. A sudden increase of the lattice parameter  $a$  when heating above  $\sim 150$  K had previously been detected by neutron diffraction. The root mean square field at the muon site  $B_{rms}$  was found to be 0.15 mT independent of temperature, in particular around 150 K. Also, no change of spectral parameters is seen in the weak TF data in that temperature range. Those findings imply that the structural change around 150 K takes place without noticeably shifting atomic positions. The spectra for  $\text{PrCu}_3\text{Ru}_4\text{O}_{12}$  and  $\text{NdCu}_3\text{Ru}_4\text{O}_{12}$  are dominated by the interaction with the dynamic rare earth moments. The analysis requires the use of the electron-nuclear double relaxation formalism. The electronic part shows simple exponential relaxation typical for a paramagnet. It features, with reducing the temperature a steep increase of paramagnetic relaxation rate as is characteristic for an approach to a magnetic spin freezing transition from above. That result suggests that the magnetic ground states of  $\text{PrCu}_3\text{Ru}_4\text{O}_{12}$  and  $\text{NdCu}_3\text{Ru}_4\text{O}_{12}$  are spin frozen states, although bulk magnetic data give no direct evidence in that direction.

## 1. Introduction

The ruthenates  $\text{ACu}_3\text{Ru}_4\text{O}_{12}$  with  $\text{A} = \text{Ca}, \text{Pr}, \text{Nd}$  are metallic compounds having a modified perovskite structure [1]. This modification is described by a tilting of the  $\text{RuO}_6$  octahedra along the  $\langle 111 \rangle$  axis mainly arising from the bonding between the new C-site and oxygen [2] accompanied by the lowering of the Ru–O–Ru bond angle and the appearance of an almost square-planar coordinated C-site, while leaving the basic cubic structure intact. From this structural variation several unusual physical properties emerge and show a high sensitivity in case of chemical substitution at any ionic position.

The compound  $\text{CaCu}_3\text{Ru}_4\text{O}_{12}$  exhibits heavy fermion [3] and non-Fermi liquid properties [4] and shows characteristics of a classical intermediate valence (IV) system having low-energy charge fluctuations [5]. Neutron powder diffraction revealed a sudden increase of lattice constant  $a$  (i.e., an increase of unit cell volume) around 150 K with the basic crystal structure remaining





**Figure 1.** Temperature dependence of the lattice constant  $a$  from powder neutron diffraction measurements for  $\text{CaCu}_3\text{Ru}_4\text{O}_{12}$  (left) and for  $\text{PrCu}_3\text{Ru}_4\text{O}_{12}$  (right). The solid lines are anharmonic fits to the thermal expansion. After [5, 6].

conserved [5]. That feature is not seen in the rare earth ruthenates [6]. Fig. 1 depicts the situation in  $\text{CaCu}_3\text{Ru}_4\text{O}_{12}$  and  $\text{PrCu}_3\text{Ru}_4\text{O}_{12}$ . Since the volume increase is only seen in  $\text{CaCu}_3\text{Ru}_4\text{O}_{12}$ , that feature must be connected to its IV properties and be of electronic nature. For example, a transition from localized  $4d$  electrons above  $\sim 150$  K to itinerant  $4d$  band states below  $\sim 150$  K is proposed [5].

The rare earth homologues  $\text{PrCu}_3\text{Ru}_4\text{O}_{12}$  and  $\text{NdCu}_3\text{Ru}_4\text{O}_{12}$  also show heavy-fermion-like properties [7]. However, their magnetic behavior is largely determined by the localized  $4f$  moments of the rare earth constituents [6]. In order to suppress the influence of the  $d$ -electrons of Cu and Ru, the susceptibility of the analogous ( $4f$  states free)  $\text{LaCu}_3\text{Ru}_4\text{O}_{12}$  was subtracted. The pure  $4f$  inverse susceptibility  $\chi_{\text{Pr,Nd}}^{-1}$  shows proper Curie–Weiss (CW) behavior with moments close to the free ion values of  $\text{Pr}^{3+}$  and  $\text{Nd}^{3+}$  down to approximately 200 K. At lower temperatures the data on  $1/\chi$  deviate from the linear temperature dependence. This is attributed to crystalline electric field (CEF) interactions. At very low temperatures ( $T < 10$  K) the slope of the inverse susceptibility increases strongly. This is ascribed to a decreasing Curie constant implying, especially for  $\text{Pr}^{3+}$ , a ground state with a small magnetic moment. No indication for spin freezing is apparent. The extensive study of the rare earth ruthenates [6] includes electrical resistivity, heat capacity, NMR and NQR data, as well as inelastic neutron scattering work on the Pr compound. In all cases the results can consistently be explained within a CEF states model.

## 2. Experimental

The polycrystalline samples were synthesized by solid-state reactions as described in [8]. The crystal structures of the samples were verified by x-ray and neutron powder diffraction. For the  $\mu\text{SR}$  measurements the powders were put into an envelope made of thin aluminized Mylar tape and then mounted with similar tape on aluminum forks of the cryostat stick. The Dolly surface beam facility was used with the vertical Oxford variable temperature cryostat (VARIOX). Zero field (ZF) and transverse field (TF) measurements were carried out between 2 K and 200 K. The sample was large compared to the beam spot and also the VETO was enabled, so no background signal was to be expected. This was verified by TF measurements. Transverse fields were restricted to 5 mT to avoid beam bending and with it a change of spectral baseline (alpha-parameter). Alpha was found to be quite constant and only weakly temperature dependent.

The asymmetry spectra were least squares fitted using the WKM program (Technical University Braunschweig).

### 3. Results

#### 3.1. $\text{CaCu}_3\text{Ru}_4\text{O}_{12}$

In weak TF (5 mT) a single Gaussian damped oscillatory pattern:

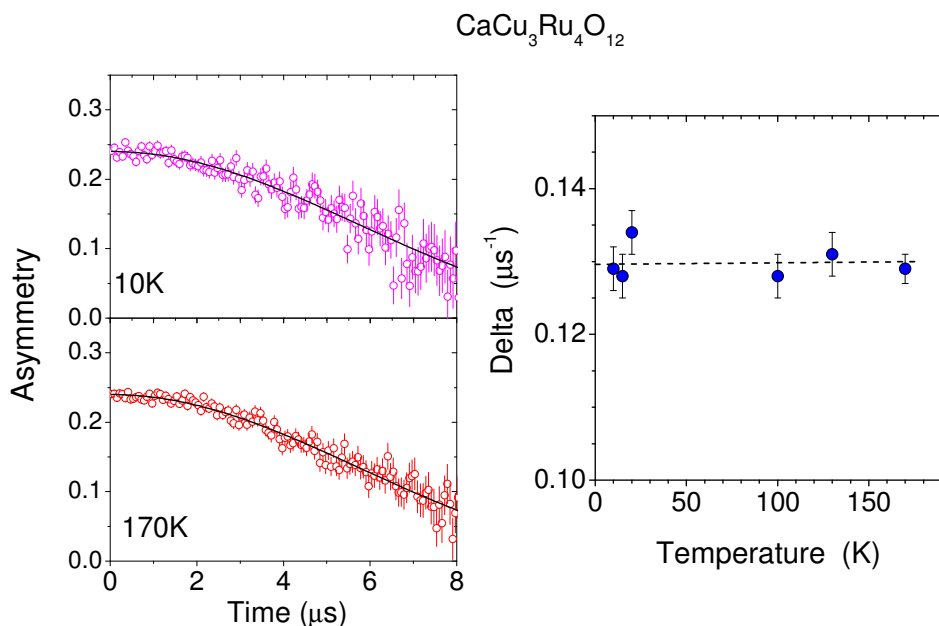
$$A_{TF}(t) = A_0 \exp(-\sigma^2 t^2) \cos(2\pi\nu_\mu t + \phi) \quad (1)$$

with full and temperature independent initial asymmetry ( $A_0 = 0.237 \pm 0.001$ ) is seen. The pure Gaussian relaxation means that the local field at the muon is static on the  $\mu\text{SR}$  timescale. The precession frequency  $\nu_\mu$  corresponds within the limits of error to the applied transverse field. This means that the muon stops at only one interstitial lattice site. Also independent of temperature is the relaxation rate  $\sigma = 0.085 \pm 0.003 \mu\text{s}^{-1}$ , revealing that the muon rests stationary at its single stopping site.

The ZF spectra are fully consistent with the TF data. Two typical examples of ZF spectra are depicted in Fig. 2-left. The time dependence of the asymmetry ( $A(t)$ ) clearly shows Gaussian decay. An initial Gaussian relaxation in a ZF pattern is the signature of static Gaussian Kubo-Toyabe (sGKT) relaxation [9]:

$$A_{sgkt}(t) = A_0[(2/3)(1 - \Delta^2 t^2) \exp(-\Delta^2 t^2/2) + (1/3)] \quad (2)$$

The sole parameter of physical relevance is the static relaxation rate  $\Delta$  which is related to the the width of the distribution of the field at the muon site. The mean field of the gaussian distribution in Eq.(2) is  $\langle B \rangle = 0$ . The distribution of the of magnitude of the field  $|B|$



**Figure 2.** Left: ZF spectra of  $\text{CaCu}_3\text{Ru}_4\text{O}_{12}$  at 10 K and 170 K. The solid lines are fits to a static Gaussian Kubo-Toyabe (sGKT) function. Right: Temperature dependences of the static width  $\Delta$ . The dashed line is a linear fit to the data points.

is Maxwellian with  $|B|^2 = \Delta^2/\gamma_\mu^2$ . One commonly uses the root mean square field  $B_{rms} = \Delta/\gamma_\mu$  to describe the distribution of the local field.

The sGKT function in total is not a simple Gaussian decay of asymmetry. After its initial Gaussian decay,  $A(t)$  reaches a minimum around  $t \approx 1.7/\Delta$ . It then recovers to the time independent value  $A_0/3$  for  $t \geq 3.5/\Delta$ . In the present case these features are outside the time window of the  $\mu$ SR spectrometer due to the small value of  $\Delta = 0.13 \mu\text{s}^{-1}$  (see below). Hence Fig. 2 is able to display only the very initial part of the sGKT function. This leads to a problem in fitting procedure. Using as fit function Eq.(2) with the parameters  $A_0$  and  $\Delta$  unrestricted, the system is unable to find the baseline. One needs to fix the initial asymmetry to the value obtained from the TF spectra ( $A_0 = 0.237$ , see above). This produces consistent results, in particular with respect to  $\Delta$ . The results are shown in Fig. 2-right.

One finds  $\Delta$  to be independent of temperature with a mean value of  $\Delta = 0.130 \pm 0.002$ , corresponding to  $B_{rms} \approx 0.15$  mT. This extremely low value points to nuclear dipole moments as the origin of the local field. Of the constituents of  $\text{CaCu}_3\text{Ru}_4\text{O}_{12}$ , oxygen is nearly 100%  $^{16}\text{O}$  which has no magnetic dipole moment. In Ca the only isotope having a magnetic moment ( $-1.3\mu_N$ ) is  $^{43}\text{Ca}$ , which, however, has a very low abundance (0.13%). Ru has two isotopes of interest ( $^{99}\text{Ru}$  and  $^{101}\text{Ru}$ ) with moderate abundances (13% and 17%) but with very low moment magnitudes ( $-0.6$  and  $-0.7\mu_N$ ). Cu consists to 100% of the two isotopes  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$ , both having sizable nuclear moments ( $2.2$  and  $2.4\mu_N$ ). Thus, the dominant source of the sGKT relaxation is the coupling between the muon spin and the Cu nuclear moments. Nuclear dipole moments are of course not really static, but their fluctuation rate is rather slow (often in the ms regime) and thus they appear static on the  $\mu$ SR time scale.

The pure sGKT spectra confirm that no ion with a magnetic moment is present in  $\text{CaCu}_3\text{Ru}_4\text{O}_{12}$ . From the constancy of  $B_{rms}(T)$ , in particular in the range of the transition region around 150 K, two additional conclusions can be drawn. Firstly, it confirms the conclusions of [5] that lattice symmetry is maintained and that the source of the transition is most likely a change in electron structure. Secondly, such a change in electron structure does not lead to the creation of even a very small atomic magnetic moment.

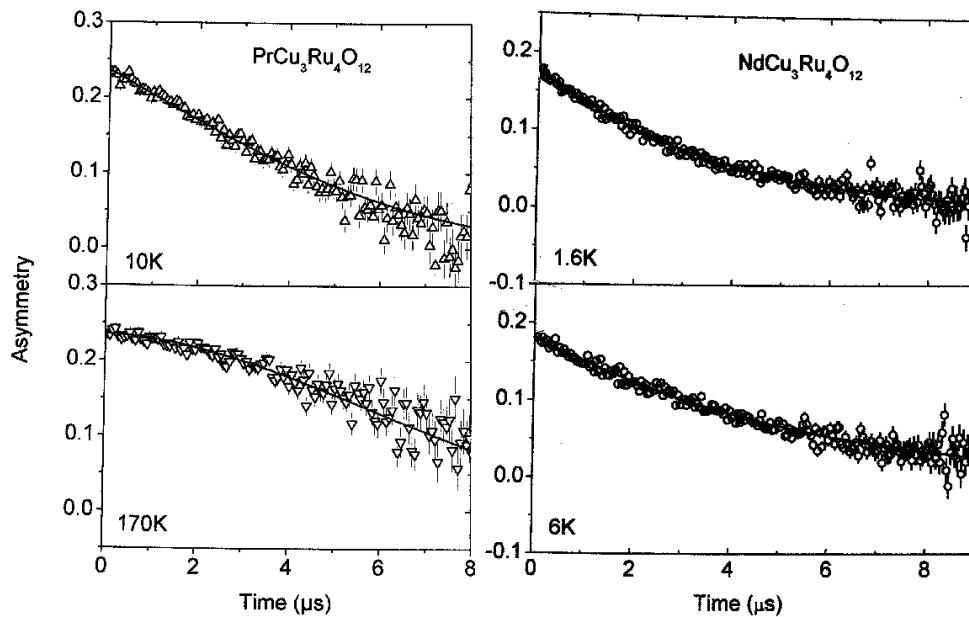
### 3.2. $\text{PrCu}_3\text{Ru}_4\text{O}_{12}$ and $\text{NdCu}_3\text{Ru}_4\text{O}_{12}$

The central feature determining the  $\mu$ SR spectra of the rare earth ruthenates is the coupling of the the localized  $4f$  moments to the muon spin. As long as no strong spin-spin correlations between the  $4f$  moments exist (e.g., in the absence of short-range or long-range magnetic order) the moments will fluctuate rapidly (free paramagnetic moments) leading to a simple exponential decay of asymmetry with rate  $\lambda$ . This rate is inversely proportional to the fluctuation rate  $1/\tau_{4f}$  of the rare earth moments. It may become quite small in the regime of fast fluctuation, meaning that the sGKT relaxation of the Cu nuclear is no longer negligible with respect to the exponential relaxation by the electronic  $4f$  moments. In a proper fit of the spectra of  $\text{PrCu}_3\text{Ru}_4\text{O}_{12}$  and  $\text{NdCu}_3\text{Ru}_4\text{O}_{12}$ , both relaxation channels have to be taken into account. In case the two interactions are independent of each other and occur on significantly different time scales, the total relaxation function can be well approximated by the product of the electronic and nuclear relaxation functions (electron-nuclear double relaxation):

$$A_{dr}(t) = A_0 \{ \exp(-\lambda t) \times [(2/3)(1 - \Delta^2 t^2) \exp(-\Delta^2 t^2/2) + (1/3)] \} \quad (3)$$

The conditions for applying Eq.(3) are well fulfilled here. The electronic moments fluctuate rapidly and rest on different ions ( $\text{Pr}^{3+}$  or  $\text{Nd}^{3+}$ ) than the static nuclear moments of Cu.

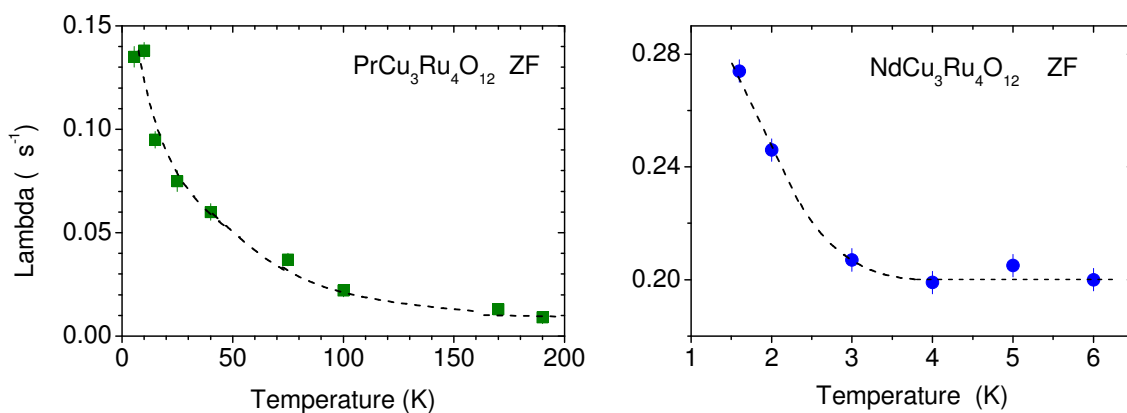
Typical ZF spectra of the two rare earth ruthenates least squares fitted with Eq.(3) are shown in Fig. 3. For reasons discussed above, we had to fix either the initial asymmetry ( $A_0 = 0.24$  for  $\text{PrCu}_3\text{Ru}_4\text{O}_{12}$ ) or the baseline parameter alpha ( $\alpha = 0.4$  for  $\text{NdCu}_3\text{Ru}_4\text{O}_{12}$ ), taking these values from the TF spectra. The nuclear static relaxation rate  $\Delta$  is  $0.13 \mu\text{s}^{-1}$  as in the case of



**Figure 3.** Typical ZF spectra of  $\text{PrCu}_3\text{Ru}_4\text{O}_{12}$  (left) and  $\text{NdCu}_3\text{Ru}_4\text{O}_{12}$  (right). The solid lines are fits to the electron-nuclear double relaxation discussed in text. The  $\text{NdCu}_3\text{Ru}_4\text{O}_{12}$  sample was slightly smaller, hence the initial asymmetry is somewhat lower.

$\text{CaCu}_3\text{Ru}_4\text{O}_{12}$ . The important result is the temperature dependence of the electronic relaxation rate  $\lambda$  as displayed in Fig. 4

Looking first at the situation in  $\text{PrCu}_3\text{Ru}_4\text{O}_{12}$ , one observes the typical behavior of  $\lambda(T)$  for a free paramagnetic ion. With rising temperature the fluctuation rate of the  $\text{Pr}^{3+}$  moments increases leading to a continuous reduction in magnitude of  $\lambda$ . The smoothness of the curve  $\lambda(T)$  indicates that no change of magnitude in the  $\text{Pr}^{3+}$  moments (e.g., by CEF effects) occurs in the temperature range covered. The steep rise of  $\lambda(T)$  seen at low temperatures is characteristic for critical slowing down of paramagnetic moments on approach to a spin freezing transition. The data of Fig. 4-left then point to a transition into a quasi static spin state (either long-range or



**Figure 4.** Temperature dependences of the electronic relaxation rates for  $\text{PrCu}_3\text{Ru}_4\text{O}_{12}$  (left) and  $\text{NdCu}_3\text{Ru}_4\text{O}_{12}$  (right). The dotted lines are guides to the eye only. Note the difference in temperature range.

short-range correlated) at low temperatures.

The situation in  $\text{NdCu}_3\text{Ru}_4\text{O}_{12}$  is alike as far as the steep increase of  $\lambda(T)$  at low temperatures is concerned. Again the immediate approach to a spin freezing transition is indicated. Unusual, and at present not understood, is the leveling-off of  $\lambda(T)$  at a fairly high value of  $\lambda$  only  $\sim 2$  K above the onset of critical slowing down.

In general, the relaxation rate  $\lambda$  in  $\text{NdCu}_3\text{Ru}_4\text{O}_{12}$  is about a factor of two larger in comparison to  $\text{PrCu}_3\text{Ru}_4\text{O}_{12}$ , although the free ion magnetic moments are nearly the same. The likely reason is the different CEF behavior of the two rare earth ions.  $\text{Nd}^{3+}$  is a Kramers ion, while  $\text{Pr}^{3+}$  is not. In the former case one expects the CEF ground state to be the maximum J doublet ( $\pm 9/2$ ), well isolated from excited states formed by lower J doublets. Spin fluctuation between well separated CEF states will be comparatively slow. In the non Kramers ion  $\text{Pr}^{3+}$  is the situation more complex. Its exact CEF ground state is not known, but expected to be an admixture of different J states, with the various possible CEF states not largely separated. While this may explain the difference in the magnitude of  $\lambda$ , the more normal behavior of  $\lambda(T)$  in CEF sensitive  $\text{PrCu}_3\text{Ru}_4\text{O}_{12}$  remains curious.

In summary, the nature of the magnetic ground states in the two rare earth ruthenates remains enigmatic.  $\mu\text{SR}$  points toward a spin frozen state, while magnetization data give no direct evidence for spin freezing. On the other hand, a dynamic state of correlated spins for  $T \rightarrow 0$  is not easily compatible with the present  $\mu\text{SR}$  data. Since the discussion of the susceptibility curve [6] is based on the influence of CEF interactions, one has to keep in mind, when comparing it to the  $\mu\text{SR}$  data, that the presence of the charged muon may lead to disturbances of the local symmetry around the magnetic ion. This in turn can induce a change in the CEF level scheme by the stopped muon. Such an effect is most likely to occur in  $\text{Pr}^{3+}$  compounds with a non-magnetic or weakly magnetic ground state. The situation of a "muon induced effect" has been observed previously in some cases, for example in  $\text{PrNi}_5$  [10]. However, in  $\text{Nd}^{3+}$  materials the CEF levels (usually Kramers doublets) are more sturdy and unlikely to respond significantly to the symmetry disturbance by the presence of the muon. Clearly, more extensive measurements are needed for both methods in order to clarify the complex magnetic situation in the low temperature range.

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