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Correlation between magnetic and electronic properties of the perovskite $HoBaCo_2O_5$

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Abstract

Muon spin rotation/relaxation experiments on the $HoBaCo_2O_5$ perovskite are presented. At low temperatures, two spontaneous frequencies are observed, which can be related to the weighted sum and the difference of the magnetic moments of Co^{2+} and Co^{3+} in the charge ordered state of $HoBaCo_2O_5$. A temperature-dependent depolarization of the muon spin polarization changes its behaviour at the charge order transition. These results are discussed in the context of the charge order transition and the transport properties of $HoBaCo_2O_5$.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Perovskite oxides (ABO_3; A = trivalent lanthanides or divalent alkali metals, B = transition metal ions) show a variety of interesting electronic, magnetic and structural properties. In particular, materials with B = Mn have been studied in great detail due to their colossal magnetoresistive effect (CMR). For the B = Co analogues, smaller CMR values have been found for $La_{1-x}Sr_xCoO_3$ [1], $La_{0.5}Ba_{0.5}CoO_3$ [2] and the layered cobaltites $RBaCo_2O_{5+\delta}$ (R = Eu, Gd, $\delta \sim 0.4$) [3]. The electronic and magnetic properties of the layered $RBaCo_2O_{5+\delta}$ compounds are controlled by their oxygen concentration, which defines the population of different Co electronic states; Co^{2+}:Co^{3+} = $(\frac{1}{2} - \delta)$:$(\frac{1}{2} + \delta)$ for $0.5 \leqslant \delta$ and Co^{4+}:Co^{3+} = $(\delta - \frac{1}{2})$:$(\frac{3}{2} - \delta)$ for $\delta \geqslant 0.5$. For the low oxygen content materials ($\delta = 0$), these chemical considerations imply an equal mixture of Co^{2+} and Co^{3+}.

At high temperatures, the $RBaCo_2O_5$ (R = Ho [4, 5], Dy [5], Tb [5], Y [6]) materials are semiconducting paramagnets and crystallize in the tetragonal symmetry $P4/mmm$ with unit cell dimensions $a = b = a_p$ and $c \sim 2a_p$ (here a_p is the perovskite lattice parameter). Just above ambient temperature (e.g. $T_N \sim 340$ K for Ho), the Co magnetic moments order in the so-called antiferromagnetic G-type structure, for which each Co moment is AF coupled to its six nearest neighbours. This is despite the fact that for one neighbour, the coupling is expected to be very weak, since there is no direct superexchange path through the oxygen-deficient Ho layer. This magnetic transition is associated with a structural distortion, leading to the new orthorhombic symmetry $Pmmm$ ($(b-a)/(b+a) \sim 5 \times 10^{-4}$) [4–6]. At $T_{CO} \sim 210$ K, a second structural transition occurs, leading to a doubling of the b axis and a change of the symmetry from $Pmmm$ to $Pmmb$. From an electronic point of view, the most important result of this transition is the splitting of the unique Co site into two crystallographically distinct ones. Hence, the $Pmmm \rightarrow Pmmb$ transition has been interpreted in terms of a charge order (CO) phase transition. At T_{CO}, the charge carriers, which can hop between Co ions above T_{CO}, are frozen out at every second Co ion, changing the situation from a dynamical mixture of 50% Co^{2+}:Co^{3+} ($T > T_{CO}$) to static charge order ($T < T_{CO}$). In addition, it has been suggested that the change in the strength of the magnetic moments at T_{CO} is related to a spin state transition of the Co ions [6]. This view has been challenged, however, by the observation of the continuous temperature dependence of the Co^{2+} magnetic moment through T_{CO} [5]. The change of the Co^{3+} magnetic moments at T_{CO} can be explained by the modification of the electronic states due to charge order alone—not requiring an additional spin state transition.

An interesting feature of the cobaltites is the occurrence of antiferromagnetic order at higher temperatures than for long range charge order ($T_{CO} < T_N$). In the intermediate temperature range, $T_{CO} < T < T_N$, the electrical resistivity exhibits a changeover from simple activation to a variable range hopping (VRH) [5]. It can be anticipated that this is associated with a slowing down of the charge-carrier hopping between the Co ions, indicating the occurrence of short range charge correlations or correlated polaronic states. Since the localization of the charge carriers leads to a difference of approximately $\sim 1\ \mu_B$ between the magnetic moments of the non-equivalent Co sites, the dynamics of the magnetic moments should be related to the charge-carrier hopping. Therefore, a study of the dynamics of the magnetic moments will give insight into the correlation between the magnetic and charge ordering phenomena in the $RBaCo_2O_5$ compounds.

Here, we present temperature-dependent muon spin rotation/relaxation (μSR) experiments on $HoBaCo_2O_5$. The observed temperature dependence of the muon spin rotation frequencies and associated dampings is discussed in connection with the magnetic structure obtained from neutron scattering and with the occurrence of the turnover of the resistivity in the range $T_{CO} < T < T_N$.

2. Experiments

The polycrystalline R = Ho sample used in the present study was previously investigated by neutron scattering studies in [4, 5]. The muon spin relaxation/rotation (μSR) measurements were performed at the μSR facility of the Paul Scherrer Institute (Villigen, Switzerland). The facilities used were the πM3 beamline with the GPS spectrometer and the πE3 beamline with the Dolly spectrometer, both equipped with a ^{4}He gas flow cryostat reaching temperatures between 2 and 300 K. Experiments were performed in zero applied magnetic field.

3. Results

For μSR experiments, polarized muons are injected into the sample and come to rest at interstitial sites in the crystal lattice. If an internal magnetic field is present, e.g. due to

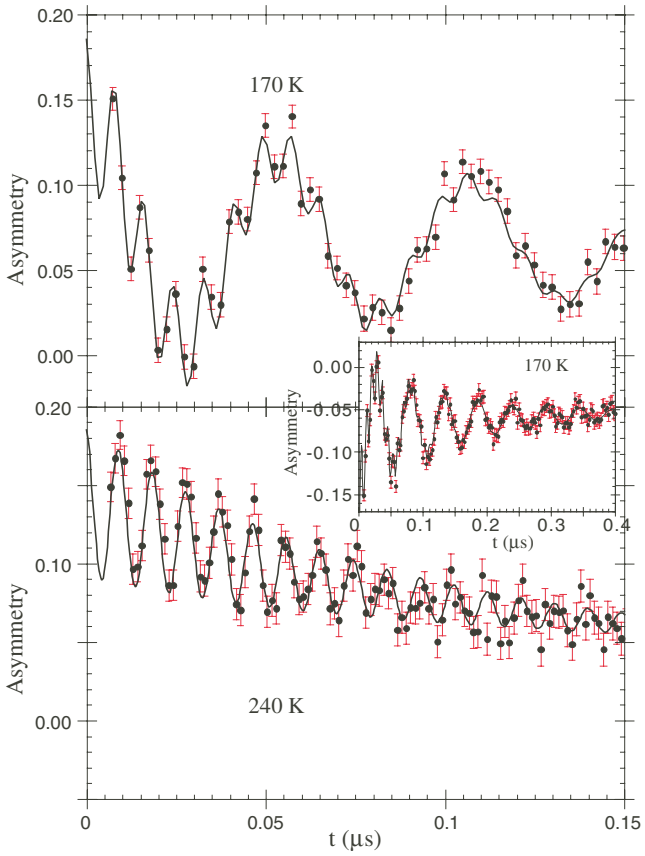

Figure 1. The zero-field muon spin rotation signal measured for $HoBaCo_2O_5$ at two different temperatures. The solid curve represents fits to equations (1) and (2). The inset shows the data taken at 170 K in a more extended time window.

magnetic order, the muon spin precesses at the Larmor frequency. After an average time $\tau_\mu = 2.2\ \mu$s, the muon decays, producing a positron which is emitted preferentially along the instantaneous direction of the muon spin. Hence, the detection in a given direction of a large number of decay positrons yields the values of the internal fields at the muon sites. In addition, the dynamics of the electronic magnetic moments leads to time variation of the internal magnetic fields causing depolarization of the muons. Muon depolarization can also be caused by a magnetic field distribution. Therefore, μSR provides a technique which allows us to obtain information on the microscopic magnetic behaviour of the materials investigated.

The time-dependent positron detection rate $N(t)$ is given by the function

$$N(t) = B + N(0)\exp(-t/\tau_\mu)[1 + A_{\rm tot}G_z(t)], \tag{1}$$

where B is a time-independent background, $N(0)$ is a normalization constant and the exponential accounts for the muon decay. The product $A_{\rm tot}G_z(t)$ is often called the μSR signal, where $A_{\rm tot}$ is the initial muon asymmetry parameter, and the envelope of $G_z(t)$ is known as the depolarization function.

Figure 1 shows two typical μSR signals recorded at $T = 170\ {\rm K} < T_{\rm CO}$ and $T_{\rm CO} < T = 240\ {\rm K} < T_{\rm N}$. The observed modulation of the signal suggests static magnetic fields at the muon stopping sites. A fast Fourier transform (FFT) for the spectrum recorded at $T = 170$ K

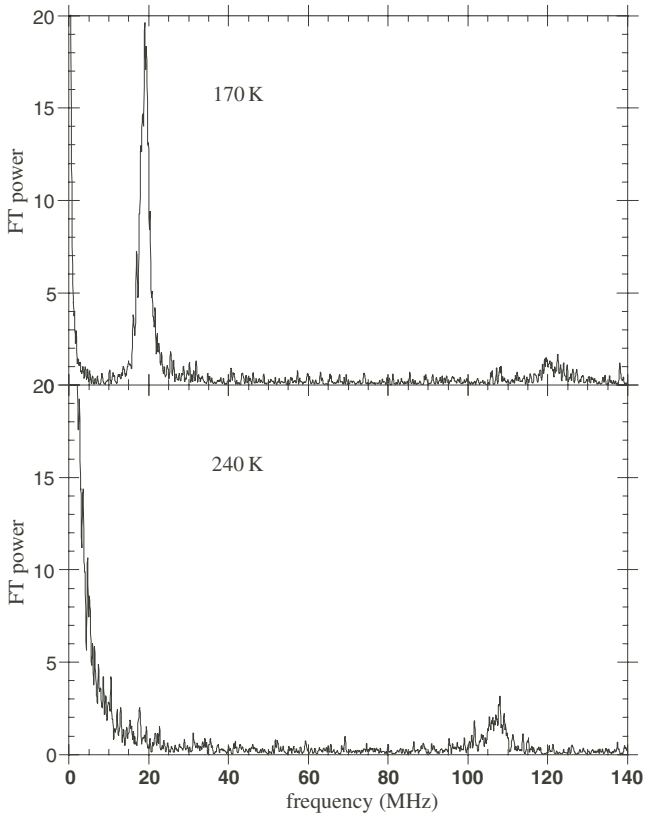

Figure 2. Fast Fourier transforms of μSR spectra taken at different temperatures for $HoBaCo_2O_5$.

reveals two peaks (figure 2), reflecting two muon spin precession frequencies and therefore two magnetically inequivalent muon stopping sites. For $T = 240$ K, a single peak is observed, indicating only one muon stopping site with a local magnetic field significantly different from zero. The data can therefore be described with $G_z(t)$ of the form

$$A_{\rm tot}G_z(t) = A_1\exp[-(\lambda_0 t)] + A_{\nu_1}\exp[-(\lambda_1 t)]\cos(2\pi\nu_1 t + \phi) + A_{\nu_2}\exp[-(\lambda_2 t)]\cos(2\pi\nu_2 t + \phi). \quad (2)$$

Here the phase ϕ is essentially given by the position of the positron detectors relative to the initial muon polarization and is slightly influenced by the uncertainty of the muon stopping time t_0. The first term in equation (2) arises from the non-zero projection of the muon spin polarization along the direction of the internal magnetic fields and is expected, for a randomly oriented polycrystalline material, to be 1/3 of the total asymmetry $A_{\rm tot}$ from the muons stopped in the sample ($A_{\rm tot} = A_1 + A_{\nu_1} + A_{\nu_2}$). The results of the best fit of equation (2) to the μSR spectra are shown in figures 3 and 4. In addition, all asymmetries A_1, A_{ν_1} and A_{ν_2} are found to be constant for $T > 120$ K with $A_1 \simeq A_{\rm tot}/3$. At lower temperatures however, all the asymmetries strongly decrease and the signal becomes unobservable for $T < 30$ K. A possible explanation for the reduction of the signal may be a redistribution of the muon stopping sites below 100 K to one or more sites with zero local magnetic field. Such a redistribution of stopping sites has been reported in the orthoferrites $RFeO_3$ (e.g. R = Y) [7]. The observed temperature dependences of the frequencies ν_1 and ν_2 (figure 3) differ strongly from one

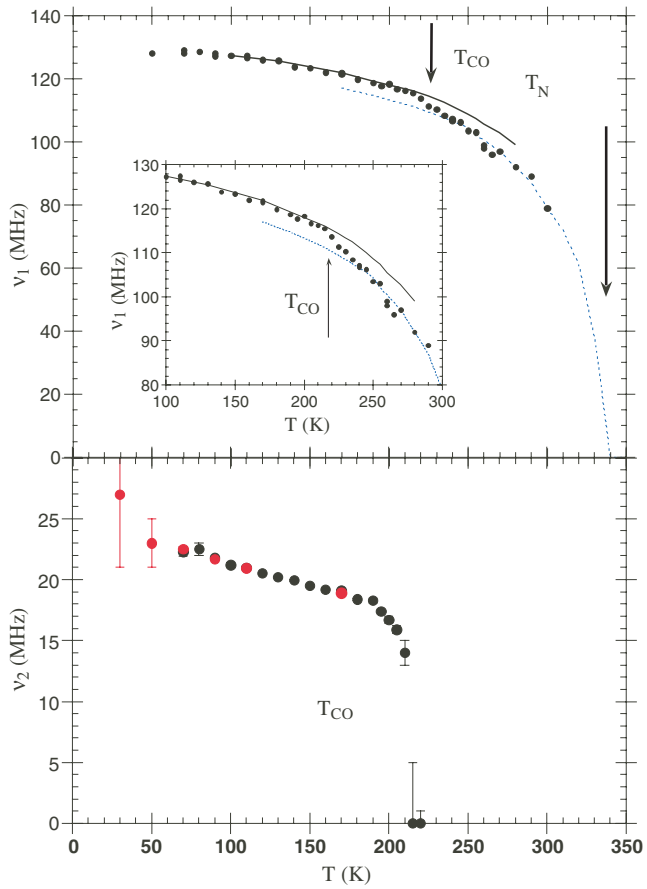

Figure 3. The temperature dependence of the spontaneous frequencies in $HoBaCo_2O_5$. The curves correspond to the extrapolation of frequencies above and below T_{CO}.

another. The frequency ν_1 decreases slightly and continuously with increasing temperature with only a small anomaly at $T = T_{CO}$, whereas ν_2 behaves similarly for $T < T_{CO}$ but drops sharply to zero in the vicinity of T_{CO}. A pronounced difference in the temperature dependences is also observed for the depolarization rates λ_1 and λ_2 (see figure 4). Below T_{CO}, λ_2 increases slightly approaching T_{CO}, where a clear maximum is observed. Above 220 K, λ_2 again increases. On the other hand, λ_1 is constant up to 250 K and shows no detectable anomaly at T_{CO}. Above 250 K, λ_1 starts to increase strongly. λ_0 is small with a very weak temperature dependence.

For a detailed interpretation of the observed behaviour of the muon frequencies and the associated depolarization rates, information on the muon stopping sites is required. The stopping sites can be determined by comparison with results obtained on other perovskite-based materials, such as $RFeO_3$ [7, 8], and with dipolar calculations of the local magnetic fields at the stopping sites. The local fields are given by $B_\mu = \nu 2\pi/\gamma_\mu$, where γ_μ is the gyromagnetic ratio of the muon. It has been shown for these oxide materials that the local fields are dominated by the dipolar fields of the magnetic ordered ions and that the contribution from the contact hyperfine fields can be neglected [7]. As input for the dipole calculations, the crystallographic and magnetic structures and the values of the magnetic moments at different

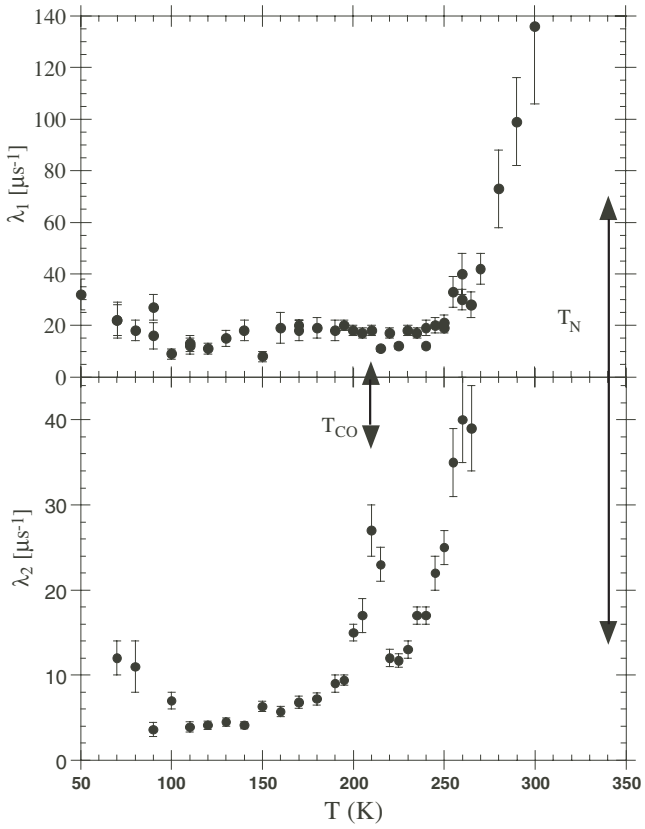

Figure 4. The temperature dependence of the muon spin depolarization rates in $HoBaCo_2O_5$.

temperatures obtained from the neutron diffraction experiments are used (see figure 5 for the crystal and magnetic structure).

Note that the magnetic structure reported from neutron diffraction for $T_{CO} < T < T_N$ indicates that the direction of the oriented magnetic moments lies along one of the principal directions in the basal plane. However, no distinction could be made between magnetic moments lying parallel to the *a* or *b* axes, since the corresponding orthorhombic distortion of the crystal structure is too small [5]. However, with neutron diffraction we could unambiguously determine that the moment is parallel to the *a* axis below T_{CO} and hence a flip upon cooling through T_{CO} from $\mu_{Co} \parallel b$ to $\mu_{Co} \parallel a$ is unlikely. Therefore, the only difference between the magnetic structures below and above T_{CO} lies in the periodic arrangement below T_{CO} of the different Co ions (Co^{2+} and Co^{3+}) possessing different magnetic moments.

An additional constraint for the muon stopping site is that the muon should lie approximately 1 Å from an oxygen ion forming a H-type bond as is typical for oxides [7] and the high-T_c superconductors [9]. Moreover, the fact that the asymmetries remain constant when crossing T_{CO} indicates that the locations where the muons are stopped remain unchanged above and below T_{CO}. In other words, the observed changes of the internal magnetic field are primarily due to changes of the magnetic structure and not to crystallographic changes. This consideration leads us to the two most probable sites of (0.213, 0.322, 0.19) and (0, 0.25, 0.06) labelled as site I (ν_1) and site II (ν_2), respectively (see figure 5). The calculated local fields at

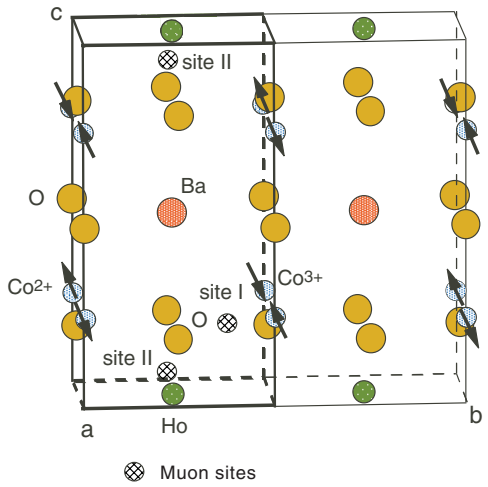

Figure 5. Crystal and magnetic structure and calculated muon stopping sites for $HoBaCo_2O_5$.

these sites are 8630 Oe (116 MHz) and 9360 Oe (126 MHz) (site I), and 0 Oe (0 MHz) and 1660 Oe (22.4 MHz) (site II) for $T = 300$ and 100 K, respectively.

4. Discussion

The present μSR data cannot distinguish between the two magnetic moments associated with Co^{2+} and Co^{3+}, nor can they determine the moment direction above T_{CO}, where the neutron results are also unable to give a definite answer. μSR or neutron diffraction studies using single crystals of $HoBaCo_2O_5$ could resolve these issues. Since the structural distortion is small, the frequency observed at site II is primarily related to the difference between the magnetic moments $\mu(Co^{2+}) - \mu(Co^{3+}) = \Delta\mu$, as is supported by our dipole sum calculations. On the other hand, the frequency observed at site I is mainly proportional to the weighted sum of the two magnetic moments $\mu(Co^{2+}) + \mu(Co^{3+})$, with a larger contribution of $\mu(Co^{2+})$. Therefore, to first order, the temperature dependence of ν_2 can be taken to be proportional to the magnetic order parameter of the additional magnetic moment $\Delta\mu$. The temperature dependence of $\Delta\mu$ shows a jump at T_{CO}, suggesting a first-order transition associated with the charge order. That the transition is first order is supported by the hysteresis in calorimetric measurements [5].

It is interesting to note that ν_2 increases from $T = 190$ to 80 K by a factor 1.25, which is significantly larger than the factor 1.1 for ν_1. This demonstrates that $\Delta\mu$ increases much faster with T than does the sum of the magnetic moments, indicating that the additional magnetic moment introduced by the charge order transition has a different temperature dependence to the total magnetic moments. The occurrence of an additional magnetic moment can also be seen in the temperature dependence of ν_1. Approximating this dependence above (full curve in figure 3) and below T_{CO} (broken curve in figure 3) leads to a difference of approximately 5% between the extrapolated and measured values at T_{CO}. This is in good agreement with our dipolar calculations, which lead to a 5% increase when calculating ν_1 using the neutron data.

Let us turn to the discussion of the depolarization rates λ_1 and λ_2. The charge order transition, and with it the associated increase in the magnetic moment of one of the Co ions, is of first order. Therefore only weak fluctuations are expected around T_{CO}, as reflected in

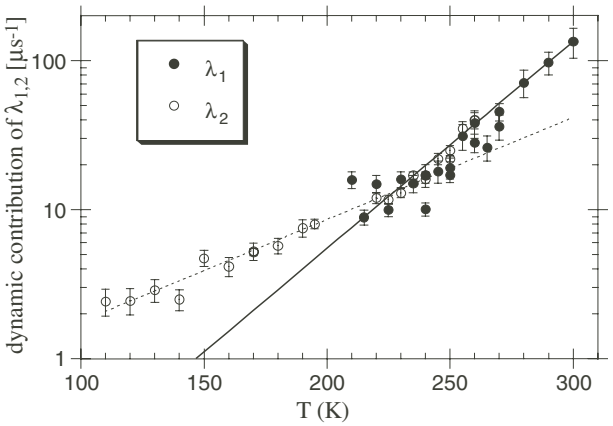

Figure 6. The dynamical contribution to the muon spin depolarization rate on a logarithmic scale. The lines correspond to fits to exponential functions for the data above and below T_{CO}.

the μSR depolarization rates. λ_1 remains constant at T_{CO}, and λ_2 shows only a significant enhancement within the vicinity of T_{CO}. The muon depolarization is a sum of the static distribution of magnetic fields at the stopping site and a dynamical contribution. The static contribution has a temperature dependence proportional to the local magnetic field (frequency ν) and hence cannot be invoked to explain the temperature-dependent anomalies. The increase of λ_1 and λ_2 for $T > T_{CO}$ is very strong and also cannot be explained simply by an increase due to the critical dynamics when approaching T_N at 340 K. Such a strong enhancement of the depolarization rate usually occurs only in the vicinity of the magnetic transition, as exemplified by the similar manganites [10, 14, 15].

As has been stated, the depolarization rate λ_0 is found to be essentially temperature independent and therefore does not reflect the anomalies observed in the other depolarization rates. Such a behaviour is indeed expected if the main source of fluctuations is the hopping of charge carriers. When a charge carrier hops from Co to Co, it changes the corresponding electronic state of the Co on the hopping timescale, and consequently also the magnetic moment. Such hopping will lead solely to a variation of the value of the magnetic moment at a given Co site but not of its direction. Consequently the field distribution at the muon sites would be strongly anisotropic and mainly *longitudinal*. As a result, and as is observed, the depolarization rate λ_0, which is sensitive to the *transverse* fluctuations, is not expected to sense the magnetic moment fluctuations between the Co^{2+} and Co^{3+} configurations. This is in contrast with the observation of the additional frequency ν_2 below T_{CO}. The vanishing of ν_2 for increasing temperatures can only occur when the hopping time of the electrons is fast compared to the μSR relaxation time, and the muon detects a zero average local field. In the regime where the hopping time is faster than the μSR relaxation time, an increase of the charge hopping time either has no effect or does lead to a decrease of the μSR relaxation (motional narrowing).

In figure 6, the dynamic contribution to the depolarization rates λ_1 and λ_2 is shown on a logarithmic plot. Both sets of data can be viewed as showing a universal depolarization rate λ. This depolarization can be described by two different exponential functions, corresponding to the depolarization below and above T_{CO}, with proportionality constants in the exponent of 0.016 ± 0.004 and 0.032 ± 0.004 K^{-1}, respectively. The depolarization rate around 100 K is of the order of 1 MHz, which, taking into account a coupling constant of about 20 MHz (see

figure 3), corresponds to a fluctuation time of the order of 10^{-8} s and is nicely compatible with the static charge order observed by neutrons. It is interesting to compare these results with those for the light lanthanides of the $RNiO_3$ family, in which charge order has been recently observed [11, 12] with $T_{CO} = T_N = T_{MI}$ [13] (T_{MI} = metal–insulator transition temperature). $RNiO_3$ is a relatively good metal for $T > T_{CO}$, whereas $RBaCo_2O_5$ exhibits only a gradual change in slope in the resistivity (semiconducting) [5]. Therefore, it could be assumed that the timescale of the fluctuations in this metallic phase of $RNiO_3$ is too fast to allow magnetic order above T_{CO}.

5. Conclusions

The muon spin rotation/relaxation measurements strongly support the occurrence of charge order at $T \sim 210$ K, in agreement with neutron and x-ray scattering experiments. The muon depolarization rate can be associated with the dynamics of the additional magnetic moment of the Co^{3+} compared to Co^{2+} and may reflect the charge dynamics. This dynamics can be described by two exponential functions with different exponents for $T < T_{CO}$ and $T_{CO} < T$. This observation of the charge dynamics, indirectly through the magnetic dynamics of the additional magnetic moments, is a new way to gain information on the timescale of the carrier hopping in these complex oxides, which can hardly be obtained otherwise.

Acknowledgments

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