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# Spin-chain magnetism in Eu-doped $Ca_3Co_2O_6$ and $Ca_3CoRhO_6$ investigated by Mössbauer spectroscopy

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We report the results of $^{151}$Eu Mössbauer effect and magnetization measurements in the Eu-doped $Ca_3Co_2O_6$ and $Ca_3CoRhO_6$, which are of great current interest in the fields of spin-chain magnetism and geometrical frustration. We find that there is a pronounced increase in the linewidth of the Mössbauer spectra below a certain temperature ($T^*$) that is well above the one at which three-dimensional magnetic ordering features set in. This unusual broadening of the spectra indicates the existence of a characteristic temperature in these "exotic" magnetic systems, which is attributable to the onset of *incipient* one-dimensional magnetic order. This is inferred from an intriguing correlation of $T^*$ with the paramagnetic Curie temperature (a measure of intrachain coupling strength in these cases).

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The investigation of the magnetic behavior of one-dimensional (1D) spin-chain systems has been an active direction of research for the past several decades in condensed matter physics. It was theoretically predicted long ago that a low dimensional (1D and 2D) chain with a nonzero exchange interaction cannot magnetically order at finite temperatures.[1] While no exception for this rule could be found in bulk forms of the materials in literature, a broad peak often appears in the plot of temperature ($T$) dependence of magnetic susceptibility ($\chi$) as a signature of short range intrachain fluctuations.[2] It is, however, remarkable that a few years ago, magnetic ordering in a 1D Co metal array was realized at low temperatures as detected by x-ray magnetic circular dichroism.[3] It is, therefore, of great interest to readdress this fundamental issue in magnetism by searching for bulk materials in which strong signatures that are due to intrachain magnetic ordering are seen.

In this Brief Report, we focus our attention on two spin-chain compounds, $Ca_3Co_2O_6$ and $Ca_3CoRhO_6$, which belongs to the $K_4CdCl_6$-type rhombohedral structure and which have attracted a lot of attention (including theoretical) in recent years due to a variety of novel features[4–11] exhibited by these compounds: a recent most fascinating finding being the onset of ferroelectricity at the magnetic transition.[6] In the former, NMR experiments by Sampathkumaran *et al.*[4] conclusively established that the Co at the (distorted) trigonal prismatic site is trivalent with a high-spin $d^6$ coordination and the one at the (distorted) octahedral coordination is in a low-spin $d^6$ nonmagnetic configuration. However, in the latter compound, trigonal prismatically coordinated Co is in a divalent high-spin ($d^7$) configuration with Rh at the octahedral site in a low-spin $d^5$ magnetic configuration.[7] The ferromagnetic (Ising) spin chains (made up of Co and Co-Rh, respectively), which are isolated by Ca ions and run along the $c$ axis, are arranged in a triangular fashion in the basal plane. See, for instance, Fig. 1 of Ref. 6 for a pictorial view of such crystallographic features. As a result of antiferromagnetic interchain interactions, the systems are topologically frustrated, which leads to a "not-so-common" 3D magnetic structure, which is called "partially disordered antiferromagnetic (PDA) structure," below about $T_N=24$ and 90 K, respectively ($T_N$ will be called $T_1$ hereafter). There is another complex magnetic transition below about (called $T_2$) 10 and 30 K, respectively. Thus, there are remarkable qualitative similarities in magnetic properties despite differences in the magnetism of the octahedral and trigonal prismatic sites in these two compounds. These materials attracted attention due to their application potential due to their large thermopower.[8] It is notable that recent magnetization studies on the epitaxially grown thin films[9] and nanorods[10] of the former reveal additional magnetic transitions at somewhat higher temperatures (40–60 K). It becomes, therefore, important to carefully address this issue of additional transition for bulk materials for further theoretical advancement of knowledge for these "exotic" compounds.

With these motivations, we have investigated the $^{151}$Eu Mössbauer spectral behavior as a function of temperature in the Eu-doped samples $Ca_{3-x}Eu_xCo_2O_6$ and $Ca_{3-x}Eu_xCoRhO_6$ ($x<0.5$). In order to make sure that doping does not cause any major perturbation of the magnetic properties, the focus is on the compositions with least amount of Eu; that is, $x=0.1$. However, we present relevant data for one series, namely, Rh-based series for additional compositions to support a logical conclusion. The main point of observation is that, below a certain temperature that is well above the long-range magnetic ordering temperature, there is a sudden onset of broadening of the spectra. This observation in the bulk form raises a question whether there exists a characteristic temperature ($T^*$), which apparently points to the *incipient* intrachain magnetic ordering as judged by the existence of its correlation with paramagnetic Curie temperature ($\theta_p$).

Polycrystalline samples of $Ca_{2.9}Eu_{0.1}Co_2O_6$ and $Ca_{3-x}Eu_xCoRhO_6$ ($x=0.1$, 0.3 and 0.5) were prepared by a solid state method as described in our earlier publications[4,5] starting from stoichiometric amounts of high purity (>99.99%) $CaCO_3$, $Co_3O_4$, $Eu_2O_3$, and Rh powder. The specimens obtained after a few heat treatments were found to be single phase by x-ray diffraction (Cu $K_\alpha$) within the detection limit (<1%) and the diffraction lines (in other words, the lattice constants) are found to smoothly shift with increasing Eu composition, exactly in the same way as noted for corresponding $Y$-substituted compositions.[11] In addition,

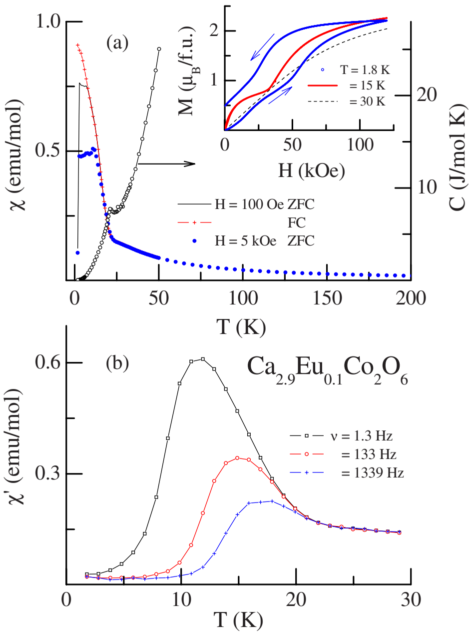

FIG. 1. (Color online) (a) Dc magnetic susceptibility ($\chi$) as a function of temperature measured in a magnetic field of 5 kOe and of 100 Oe and (b) frequency ($\nu$) dependence of real part *ac* $\chi$ for $Ca_{2.9}Eu_{0.1}Co_2O_6$. The isothermal magnetization data are shown in the inset of (a). The heat-capacity data are also shown in (a).

the samples were confirmed to be homogeneous by scanning electron microscopy. In order to magnetically characterize the samples, we have performed dc as well as ac magnetization ($M$) measurements (2–300 K) by employing commercial magnetometers. $^{151}$Eu Mössbauer effect measurements were performed by employing a $^{151}SmF_3$ source (21.6 keV transition) at selected temperatures.

We first present the results on $Ca_{2.9}Eu_{0.1}Co_2O_6$. Since the features in dc and ac magnetization are found to be essentially the same as that of the parent compound reported in several places in literature,[4] we will not elaborate on these findings [see Fig. 1(a)]. In brief, the magnetic susceptibility ($\chi$), for instance, measured with a magnetic field ($H$) of 5 kOe, exhibits a gradual increase with a decrease in temperature down to 22 K, below which there is a sudden increase, marking the onset of a previously known PDA order for $x=0.0$ at 24 K. The onset of 3D ordering is further supported by the presence of a peak in the heat-capacity data, as shown in Fig. 1(a). There is a bifurcation of the curves near 10 K for the zero-field-cooled (ZFC) and field-cooled (FC) conditions of the specimens, as demonstrated for $H=100$ Oe in Fig. 1(a). The isothermal $M$ data [inset of Fig. 1(a)] measured at 15 K (that is, between $T_1$ and $T_2$) is nonhysteretic and show a step at about one-third of saturation magnetization typical of a PDA structure. This step vanishes above $T_1$, as shown by the data at 30 K. At 1.8 K, the $M$-$H$ curve is hysteretic as expected.[4] AC $\chi$ exhibits [see Fig. 1(b) for the real part] an unusually large frequency dependence in the vicinity of the well-known magnetic transitions as in the parent compound. These results endorse that any knowledge obtained on this Eu-based composition is representative of the parent compound.

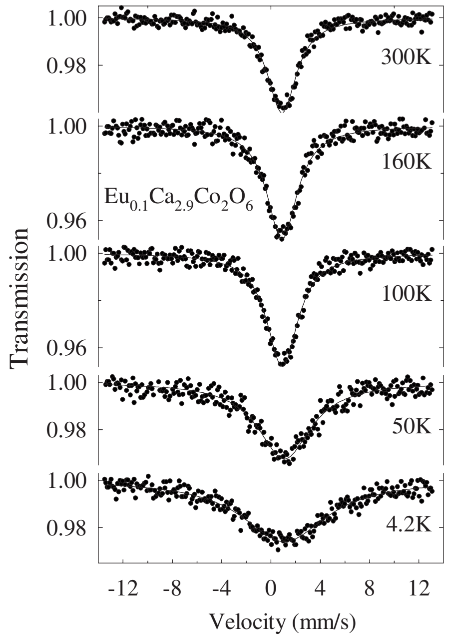

FIG. 2. $^{151}$Eu Mössbauer spectra for $Ca_{2.9}Eu_{0.1}Co_2O_6$.

The Mössbauer spectra at few representative temperatures (300, 160, 100, 50, and 4.2 K) are shown in Fig. 2. The continuous lines through the data points are obtained by least-squares fitting to a Lorentzian. The isomer shift is found to be about 1.0 mm/s, falling in a range for trivalent Eu ions, and it undergoes a usual weak thermal redshift with temperature. The linewidth ($W$) at half maximum at 300 K is $2.9\pm0.1$ mm/s and any possible quadrupolar contribution is accounted for within $W$. The most remarkable finding is that, while $W$ essentially remains constant above about 100 K, there is a sudden increase as the temperature is further lowered with a pronounced effect below about 75 K (see Fig. 3). It is very surprising that this sets in a temperature range that

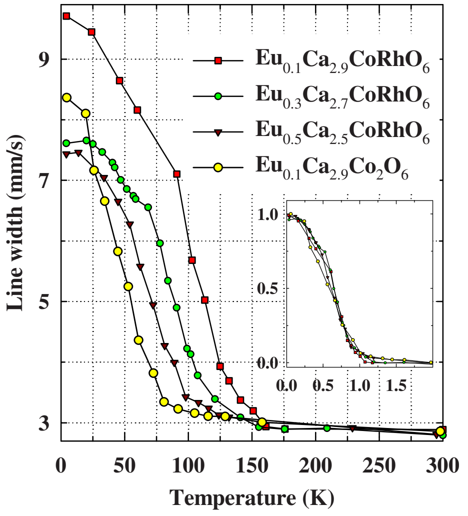

FIG. 3. (Color online) The linewidth at half maximum ($W$) ($\pm0.1$ mm/s) of the Mössbauer spectra. The universal curve of the normalized data, which is shown in the inset, is obtained by plotting $(W-W_{300K})/(W_{4.2K}-W_{300K})$ versus $T/T^*$.

is about thrice of (hitherto-known) magnetic-order onset temperature of $T_1$. However, interestingly, the further increase in $W$ below $T_1$ is sluggish as though the onset of partial antiferromagnetic ordering (2 out of 3) of spin-chains dampens the effect. For the aim of this Brief Report, we focus our further discussions on the $W$ behavior above $T_1$.

Generally speaking, $W$ is expected to attain the paramagnetic value even in quasi-1D systems[12] as soon as the three-dimensional magnetic ordering disappears. We propose that the observed broadening arises from a strong intrachain exchange coupling, as the temperature around which the broadening prominently appears is nearly the same as that of $\theta_p$ of about 80 K inferred from the $\chi$ studies extended to temperatures well above 300 K (Maignan *et al.*[4]). (From the positive sign of $\theta_p$, it is widely known that $\theta_p$ corresponds to intrachain ferromagnetic correlations in this family.) With this in mind, we conclude that magnetic ordering within the spin chains tends to set in around 80 K. It is intriguing to note that it is static enough to be sensed[13] within the Mössbauer time scale of about $10^{-8}$ s. As a result, there is a transferred hyperfine field ($H_{\mathrm{eff}}$) to the Ca site from the neighboring magnetically ordered Co ions. The broadening at 4.2 K corresponds to about 60 kOe. The corresponding value at 50 K is about 35 kOe, which is huge for this temperature range. Incidentally, the values of $H_{\mathrm{eff}}$ at the Co site has been shown to be negligible or comparatively very small as demonstrated by doped $^{57}$Fe Mössbauer effect measurements[14] or $^{59}$Co NMR measurements (Sampathkumaran *et al.*[4]), respectively. This finding is sufficient to prove that doped Eu does not go to the chain sites but to the Ca site. Incidentally, within the conventional relaxation mechanism (dynamic picture), it is rather difficult to understand the onset of abrupt broadening in a narrow temperature range and one would have expected a rather gradual (exponential) temperature dependence of $W$, as demonstrated for doped $^{57}$Fe in Ref. 14. As a manifestation of the incipient intrachain ordering, the nonlinear thermal excitation of moving domain walls (solitons or kinks) discussed in Ref. 15 for Ising spin-chain systems could result in the observed broadening, as demonstrated[16] for a similar line broadening well above 3D-magnetic ordering temperature in the $^{57}$Fe Mössbauer spectra of $\mathrm{FeCl_2(pyridine)_2}$. A change in the activation energy for the domain-wall propagation can result in a corresponding change in the slope of the plot in Fig. 3 near $T_1$. In any case, the Mössbauer data provide distinct evidence for the fact that one can define a $T^*$ related to the incipient intrachain magnetic ordering. Although, correspondingly, there is no well-defined anomaly in the $\chi(T)$ curve, one should take note of the observation that inverse $\chi(T)$ has been known[4] to show a deviation from the high temperature linearity around this temperature, possibly as a manifestation of incipient spin-chain ordering. It is also worth noting that there is a change in the functional form of temperature dependence of electrical resistivity around 80 K,[17] the origin of which also could lie in this.

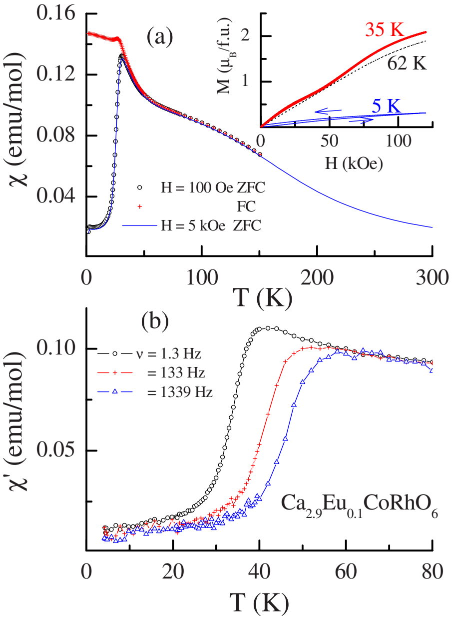

FIG. 4. (Color online) The magnetization data (as in Fig. 1) for $\mathrm{Ca_{2.9}Eu_{0.1}CoRhO_6}$. In (a), the curves for $H=100$ Oe and 5 kOe overlap.

We now turn to the results on $\mathrm{Ca_{3-x}Eu_xCoRhO_6}$ to endorse the above conclusions. As previously mentioned, the magnetic behavior of $\mathrm{Ca_3Co_2O_6}$ and $\mathrm{Ca_3CoRhO_6}$ look similar (Hardy *et al.*[5]) if one looks at the $\chi(T)$ normalized to respective $T_1$. However, it was reported[5] that there is a distinct broad peak in $\chi(T)$ around 100–125 K in the latter, which has been attributed to intrachain short-range correlations by traditional belief. This peak is more prominently seen for $x=0.1$ with the downward shift of $T_1$ to 50 K range (from 90 K for $x=0.0$), as indicated by a sudden upturn in $\chi$. This shift in $T_1$ is apparent from the fact that isothermal $M$ [see inset of Fig. 4(a)] shows a weak step only around 50 kOe at 35 K but not at 62 K.[4] Another magnetic transition in the vicinity of $(T_2=)30$ K is also visible [see Fig. 4(a)] in the dc $\chi(T)$ plot and the weakly hysteretic $M(H)$ behavior at 5 K is the same as that known for the parent compound. The huge frequency dependence of ac $\chi$,[5,11] as in the parent compound, in the vicinity of long-range magnetic ordering are retained for this composition as well [see Fig. 4(b)]. Therefore, qualitatively speaking, marginally doped Eu sample carries the physics of the parent compound. Therefore, we look at the Mössbauer spectra at selected temperatures and typical behavior of the spectra is shown in Fig. 5 (for 300, 160, 125, 100, and 4.2 K) for this composition. Focusing on the main point $W$, which is plotted in Fig. 3, shows a pronounced increase below $(T^*=)125$ K, which is far above $T_1$. Typical values of $H_{\mathrm{eff}}$ estimated from $W$ at 100 and 125 K are about 37 and 17 kOe, respectively. In the absence of high temperature ($>300$ K) $\chi$ data, it is rather difficult to get a precise estimate of $\theta_p$ to bring out a correlation with $W$. Nevertheless, an inference based on the $\chi$ data in the range 250–300 K could be made. The sign of $\theta_p$ thus obtained is positive, representing intrachain coupling and the value obtained (from the range 250–300 K) is about 125 K. This value is marginally smaller than that (140 K, Ref. 11) for the parent compound and comparable to $T^*$. This correlation is further established by the following observation based on the Mössbauer data on other compositions ($x=0.3$ and 0.5; the spectra are not shown here): The curve $W(T)$ shifts to lower temperatures with increasing concentration of Eu (see Fig. 3), as though $T^*$ decreases and there is a corresponding decrease in

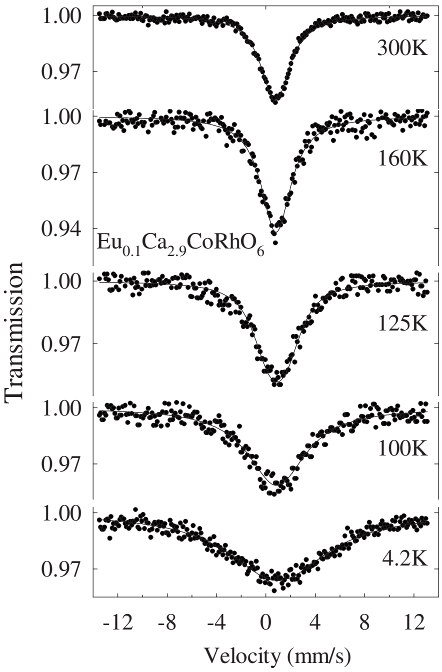

FIG. 5. $^{151}$Eu Mössbauer spectra for $Ca_{2.9}Eu_{0.1}CoRhO_6$.

$\theta_p$ (90 and 60 K) (nearly the same trend as in $Y$ substituted series, as presented in Ref. 11). A *key* support to the above interpretation is provided by the normalized plot, which is shown in the inset of Fig. 3; that is, the plot of the reduced linewidth $(W-W_{300\ \mathrm{K}})/(W_{4.2\ \mathrm{K}}-W_{300\ \mathrm{K}})$ versus the normalized temperature $T/T^*$ for all of the samples studied is an universal curve. The values of $T^*$, thus, are 80 K for $Ca_{2.9}Eu_{0.1}Co_2O_6$ and 150, 130, and 110 K for $x=0.1$, 0.3, and 0.5 of $Ca_{3-x}Eu_xCoRhO_6$, respectively. These values follow the trends in $\theta_p$.

Finally, Loewenhaupt *et al.*[5] reported the observation of a quasielastic line in the neutron diffraction data of $Ca_3CoRhO_6$ in the entire temperature range (not only above $T_1$ but also below $T_1$), which arises from intrachain interactions. In light of the present results, we have carefully reexamined the data presented in Fig. 5 of Ref. 5. An important point that has emerged is that the integrated intensity of the magnetic Bragg peak starts actually building at around 125 K, which is well above $T_1$ (of course, with a sharper increase below $T_1$ as expected), in the form of a "knee" at the expense of the diffuse peak. The diffuse Gaussian line also narrows below about 150 K. Thus, there is already a signal for spin-chain magnetism at a temperature well above $T_1$ in the neutron diffraction as well, which supports present conclusions.

To conclude, we provide microscopic experimental evidence for the existence of incipient magnetic order of spin chains through (doped) $^{151}$Eu Mössbauer spectroscopic studies in the spin-chain systems $Ca_3Co_2O_6$ and $Ca_3CoRhO_6$. The conclusion is based on an intriguing relationship between spectral broadening and the paramagnetic Curie temperature representing intrachain coupling. In addition, the present results bring out the need to recognize a characteristic temperature in future theoretical formulation of these exotic systems.

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