Crossover of the dimensionality of 3*d* spin fluctuations in LaCoPO

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dc magnetization and ^{31}P spin-lattice relaxation rate in the polycrystalline sample of LaCoPO suggest a spin-fluctuation dominated ferromagnetically ordered state. Moreover, NMR data clearly indicate a crossover from two-dimensional to three-dimensional spin fluctuations across T_C. In contrast to isotropic hyperfine field, H_{hf} at the ^{31}P site in LaFePO, H_{hf} is anisotropic in LaCoPO. The data of spin-lattice relaxation rate also exhibit anisotropic spin fluctuation. The anisotropy vanishes near T_C.

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I. INTRODUCTION

Newly discovered correlated electron systems LnT_M*Pn*O [Ln=4*f* rare-earth element, T_M=transition-metal element with more than half-filled 3*d* shell, and *Pn*=pnictogen element] show interesting electronic and magnetic properties such as high transition temperature superconductivity, itinerant ferromagnetism, giant magnetoresistance, spin-density wave (SDW), and structural instability.[1] In particular, LnFeAsO exhibit SDW and structural instability.[2–4] Moreover, they remain metallic to low temperature and only shows superconductivity (T_C in the range 26–55 K), when the SDW is suppressed toward zero temperature either through doping[5] or pressure.[6] In contrast, analogous phosphorous-based LaFePO and LaNiPO are nonmagnetic metals and exhibit superconductivity (T_C in the range 2–6 K) due to strongly correlated electrons in the undoped form at ambient pressure, with the magnetic ordering being suppressed due to the reduction in magnetic moments.[7–11] It is be noted that ^{31}P NMR results in ($La_{0.87}Ca_{0.13}$)FePO (Ref. 12) suggests the presence of short-range ferromagnetic correlations with no long-range magnetic ordering down to 2 K. However, in case of LaCoPO, the magnetic moment does not vanish completely due to odd number of electrons in 3*d* orbitals. It has been shown that its ground state is itinerant ferromagnet with $T_C \approx 43$ K, when measured in an external field of 0.1 T, with no superconducting transition down to 2 K.[13]

Recently, we presented ^{75}As NMR study in partially oriented parent and F-doped CeFeAsO system focusing the importance of 4*f* electron induced correlation effect over the obvious presence of the same due to 3*d* electrons.[14] In the present Brief Report, we report the results of dc magnetization and ^{31}P NMR in LaCoPO. ^{31}P being a spin 1/2 nucleus, the resonance line shape would be affected only by the magnetic interaction and hence offer the opportunity to obtain unambiguous information about the low-temperature electronic state. We have also performed ^{31}P NMR study in LaFePO for comparison. The present results in LaCoPO suggest a strong-field dependence on the onset (temperature) of ferromagnetic ordering suggesting the dominance of spin fluctuations even in the magnetically ordered state. Nuclear spin-lattice relaxation (T_1) data also confirms this with an indication of a crossover of the dimensionality of the ferromagnetic spin fluctuations near 130 K.

II. RESULTS AND DISCUSSION

Polycrystalline samples of LaCoPO and LaFePO were synthesized by solid-state reaction[7,13] and were characterized using powder x-ray diffraction at room temperature. The magnetic moment was measured with a superconducting quantum interference device magnetometer (MPMSXL 7 T, Quantum Design). The NMR measurements were carried out at 7.04 T with a conventional phase-coherent spectrometer (Thamway PROT 4103). The powder sample of LaCoPO was magnetically aligned using epoxy (Epotek-301).

The magnetic moment, *M* vs *T* curve (Fig. 1) for *H* =0.1 T shows sharp enhancement below 50 K, due to the ferromagnetic ordering, as reported earlier.[13] As the NMR measurements were done in a field of 7 T, the bulk magnetization was measured in this field and at other intermediate fields in order to compare the bulk and the local magnetic properties derived from the NMR results. It is observed that the enhancement of *M* due to the magnetic ordering starts at a higher temperature depending on the field strength compared to that observed in a field of 0.1 T. Such a strong-field dependence of T_C is also reported recently in layered compound $La_{1.2}Sr_{1.8}Mn_2O_7$.[15] One possible reason for this could be the existence of spin fluctuations in the ordered state. Application of a field of 7 T would reduce the effect of fluctuation and favor the ordering of the spins at much higher temperature. This is also supported by the observation of negative magnetoresistance in LaCoPO.[13]

Figure 2(a) shows a typical ^{31}P NMR spectrum in polycrystalline LaCoPO which is anisotropic in nature. This cor-

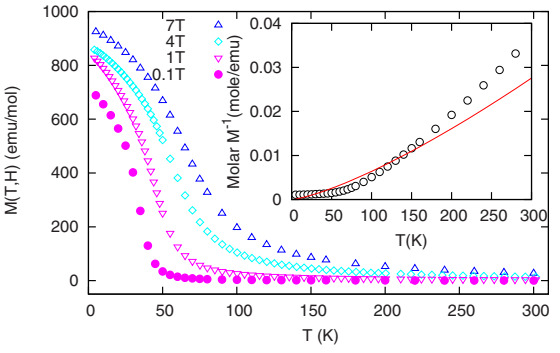

FIG. 1. (Color online) *M* vs *T* curve at 7 and 0.1 T. Inset: $1/M$ vs *T* curve; the solid line corresponds $T^{4/3}$.

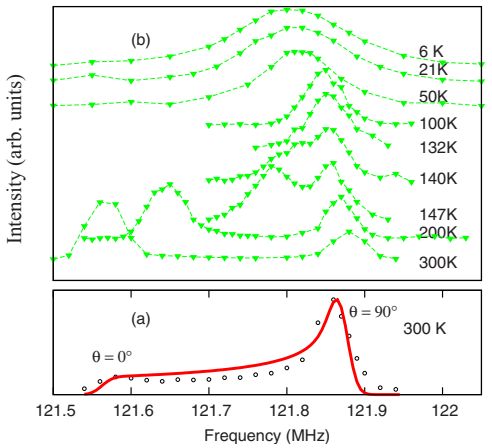

FIG. 2. (Color online) (a) Powder pattern of LaCoPO (open circle) along with the calculated spectrum (continuous line). (b) ^{31}P NMR spectra in partially aligned LaCoPO sample taken at 7.04 T, dotted line is for guide to eye.

responds to the powder pattern for a spin 1/2 nucleus with axially symmetric local magnetic field, as expected for tetragonal symmetry. The step in the low-frequency side corresponds to $H\|c$ (θ=0°) and the peak in high frequency corresponds to $H\perp c$ ($\theta=\pi/2$). The shift of the step with respect to the reference position (ν_R), corresponds to $K_\parallel$ and that of the maximum corresponds to $K_\perp$. In Fig. 2(b) we have presented spectra of partially oriented sample, where ~60% of the grains are oriented in the direction of $H\|c$. As a result we have obtained two well resolved peaks in a same spectrum. Taking advantage of the partial alignment, $K_\parallel$ and $K_\perp$ can be determined accurately. This allows us to measure $K_{\rm iso}$ and $K_{\rm ax}$ from the relations $K_{\rm iso}=2K_\perp/3+K_\parallel/3$ and $K_{\rm ax}=1/3(K_\parallel-K_\perp)$. As the temperature is lowered the peak at $H\|c$ shifts gradually toward the high-frequency side. Whereas, the peak at $H\perp c$ is shifted little toward the low frequency. Near 130 K, two peaks merge and start to broaden along with a small shift toward lower frequency. This temperature corresponds to the onset of the ferromagnetic transition in LaCoPO in a field of 7 T (Fig. 1). Merging of the two peaks suggests the vanishing of the anisotropy of the local magnetic field H_{local} near 130 K. A weak temperature dependence of the line position below 130 K along with a line broadening is expected for a magnetically ordered state. However, this broadening is not as high as it is in RFeAsO systems, where there is a huge enhancement of ^{75}As NMR linewidth in the ordered state due to the SDW transition. Whereas, in LaCoPO, the spectrum can be detected even at 4 K, well below T_C, suggesting a homogeneous ordered magnetic field along with an itinerant character of the Co 3d electrons responsible for the ordering. Figure 3(a) shows the variation in $K_\parallel$ and $K_\perp$ as a function of temperature.

The shift is mainly governed by the two contributions: (1) temperature independent K_0 due to conduction electrons and (2) temperature dependent $K(T)$ due to localized character of the d electrons. So, $K_{\rm total}=K_0+K(T)$, where

$$K(T)=H_{\rm hf}^{\rm d}\chi(T)/N_A\mu_B, \qquad (1)$$

where $H_{\rm hf}^{\rm d}$ is the hyperfine field per μ_B. As long as $H_{\rm hf}^{\rm d}$ remains unchanged, $K(T)$ is proportional to $\chi(T)$. Figures 3(b) and 3(c) show the variation in $K_{\rm iso}$ and $K_{\rm ax}$ with χ. Both the parameters show a linear variation in the range 130–300 K, with $H_{\rm hf}^{\rm iso}=2.79$ kOe/μ_B and $H_{\rm hf}^{\rm ax}=-4.24$ kOe/μ_B The value of $H_{\rm hf}^{\rm iso}$ is found to be much smaller than that reported in case of Ca-doped LaFePO ($H_{\rm hf}=12.5$ kOe/μ_B).[12] A significant deviation of the $K_{\rm iso}$ vs χ plot linearity, below 130 K, indicates a modification of the electronic wave function contributing to the hyperfine coupling, responsible for the temperature-dependent shift. There are two possibilities; one is the partial delocalization of the d electrons due to mixing with the s band near this temperature range and the other is the crystal-field effect.

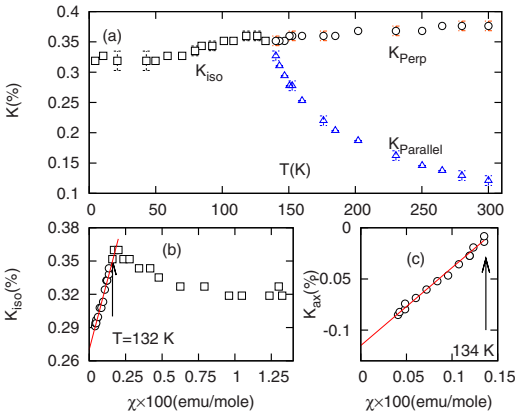

FIG. 3. (Color online) (a) Temperature dependence of ^{31}P NMR shift. [(b) and (c)] Represent variation in $K_{\rm iso}$ and $K_{\rm ax}$ with χ, respectively. The lines correspond linear fit.

To compare the effect of complete replacement of Co by Fe, ^{31}P NMR study in isostructural LaFePO was also performed. In this case a symmetric resonance line (inset of Fig. 4) was observed in the range 4–300 K with slow and gradual increase in linewidth and shift (Fig. 4), and both of these parameters become almost T independent below 50 K, as was reported earlier in Ca-doped LaFePO.[12] This T independent behavior of K below 50 K in LaFePO (which does not show ordering) is very similar to that in LaCoPO in the ordered state.

To verify the suggestion[13] that LaCoPO is an itinerant ferromagnet and the magnetic property should be governed by the spin fluctuations, we have measured T_1 at the peaks

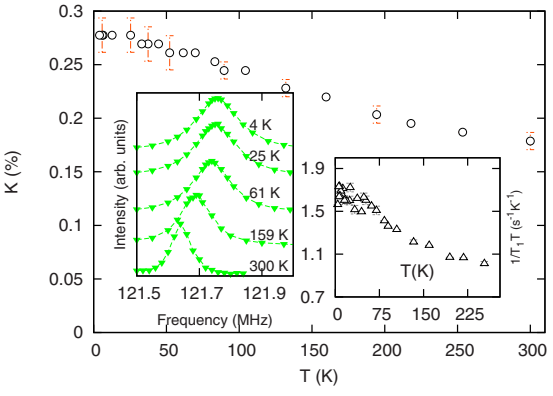

FIG. 4. (Color online) Variation in ^{31}P shift with T in LaFePO. Inset: ^{31}P NMR spectra and T vs $1/T_1T$ in LaFePO.

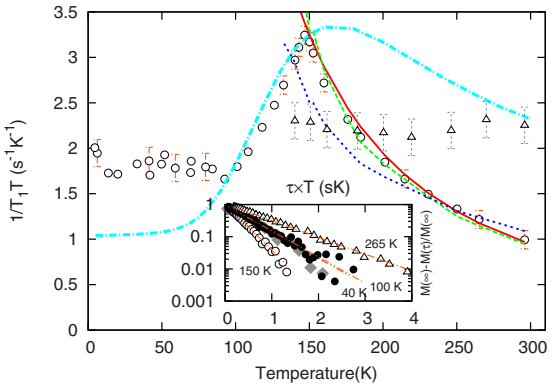

FIG. 5. (Color online) T dependence of $1/T_1T$ in LaCoPO; ○: $(1/T_1T)_{H\|c}$ and △: $(1/T_1T)_{H\perp c}$. The dashed and dotted curves correspond to $\chi^{3/2}$ and χ^1, respectively, as defined in Eq. (3) and continuous curve correspond to Eq. (4). The dot-dashed curve represents Eq. (5). Inset: recovery curves vs $\tau\times T$ at different temperatures in LaCoPO, fitted with a single exponential.

corresponding to $H\|c$ and $H\perp c$. The recovery of nuclear magnetization in each case follows a single exponential as expected for a spin-1/2 nucleus. This confirms the absence of any impurity contribution in ^{31}P NMR. Inset of Fig. 5 shows the recovery curve for the peak at $H\|c$ as a function of the product of the delay time (τ) and T. It clearly shows that T_1T decreases in the range 150–300 K and then increases till 100 K and stays constant down to 4 K, signifying a metallic character.

$(1/T_1T)_{H\|c}$ (Fig. 5) shows a faster increment in the range 150–300 K compared to that in LaFePO, indicating the effect of slowing down of the 3d spin fluctuations due to the development of short-range correlations above the magnetic transition temperature. The peak near 150 K suggests the development of long-range correlations below this temperature. This gradually reduces the contribution of 3d spin fluctuations to the ^{31}P nuclear relaxation process, below 150 K. Finally an almost T independent behavior below 100 K signifies the dominant role of the Korringa contribution due to s electrons in the relaxation process and a less significant role of 3d spin fluctuations, as expected in a magnetically ordered state. Thus the present NMR result confirm microscopically the occurrence of a long-range magnetic order in LaCoPO at a higher temperature in a field of 7 T, compared to that reported from magnetic-susceptibility data at H=0.1 T. For the peak at $H\perp c$, $(1/T_1T)_{H\perp c}$, shows a temperature-independent Korringa behavior, similar to that of $K_\perp$. Thus in LaCoPO, both the Knight shift and $1/T_1$ are anisotropic in the range 132–300 K.

$(1/T_1)_\alpha$ (α=a,b,c) is proportional to the fluctuations of the local magnetic field δh^2 perpendicular to the α axis. Thus, $(1/T_1)_{H\|c}\propto[\delta h_a^2+\delta h_b^2]$ and $(1/T_1)_{H\perp c}\propto[\delta h_a^2+\delta h_c^2>]$. The P site being axially symmetric, $\delta h_a^2=\delta h_b^2$. Since the contribution to $(1/T_1T)_{H\|c}$ comes from the fluctuations of the hyperfine field $\perp$ to c axis, the T dependence of $(1/T_1T)_{H\|c}$ indicates a slowing down of the Co 3d spin fluctuations in the a-b plane. On the other hand, $(1/T_1T)_{H\perp c}$ probes the fluctuations of the local field in c direction. So its T independent behavior suggests that the Co 3d spin fluctuations in LaCoPO is confined within the a-b plane. Thus $(1/T_1T)_{H\perp c}$ is governed only by the scattering due to conduction electrons.

Nature of spin fluctuation

In order to understand the nature of the magnetic correlations we have analyzed the $(1/T_1)_{H\|c}$ data using the theoretical models for the electron-spin-fluctuation (SF) contribution. In general $(1/T_1T)_{SF}$ is given by[16]

$$(1/T_1T)_{SF}\propto(\gamma_n A_{hf})^2\sum_q \chi''(q,\omega_n)/\omega_n, \tag{2}$$

where $\chi''(q,\omega_n)$ is the imaginary part of the transverse dynamical electron-spin susceptibility, γ_n and ω_n are the nuclear gyromagnetic ratio and Larmor frequency, respectively. When two-dimensional (2D) [three-dimensional (3D)] spin fluctuations are dominant,[12,17,18]

$$1/T_1T\propto\chi(q=0)^{3/2(1)}. \tag{3}$$

In the present case, K is proportional to χ in the range 150–300 K [Fig. 3(a)], so in calculation of $1/T_1T$ using Eq. (3), we have used K since the Knight shift probes the intrinsic spin susceptibility of the sample. It is seen from Fig. 5 that the experimental data agree satisfactorily with the calculated (continuous) curve of 2D spin fluctuation but theoretical (dotted) curve of 3D spin fluctuation cannot be fitted to the experimental data, suggesting the predominance of ferromagnetic 2D spin fluctuations in the paramagnetic phase. According to the extension of self-consistent renormalization (SCR) theory for 2D itinerant ferromagnetic metal near magnetic instability[18]

$$1/T_1T\propto T^{-3/2}(-\ln T)^{-3/2}. \tag{4}$$

The calculated (dashed) curve also matches well with the experimental results (Fig. 5). This finding also corroborates with the above conclusion.

On the other hand, according to (SCR) theory of spin fluctuations, for weak itinerant ferromagnet (WIF), the ferromagnetic (q=0) 3D spin-fluctuation contribution to $1/T_1T$ in presence of magnetic field, both in the paramagnetic and the ferromagnetic region is given by[19–21]

$$1/(T_1T)_{SF}=k\chi/(1+\chi^3H^2P)+\beta, \tag{5}$$

where P is a constant related to the area of the fermi surface of the magnetic electrons and k is related to the energy width of the dynamical spin-fluctuation spectrum. β is temperature independent and contains the sum of the contributions due to orbital moments of p and d electrons, Fermi contact contribution of s conduction electrons and that due to the spin dipolar interaction with p and d electrons. Figure 5 shows that the experimental curve deviates from Eq. (5) (dot-dashed curve) above 150 K and agrees in the range 80–150 K. So this relation is not satisfied in both the paramagnetic and the ordered state as it should.[21] It is seen that even in the ordered state, below 80 K the calculated curve lies below the experimental curve while the nature of both the curves remain same. A possible reason for this could be the presence of a small amount of nonmagnetic impurity, which would

reduce the magnitude of the measured bulk magnetic moment used for calculating $1/T_1T$ using Eq. (5). Since the nuclear relaxation time probes the intrinsic magnetic property of a system, the $1/T_1T$ data are expected to be more accurate compared to those calculated using bulk magnetization data, particularly at low temperatures. Furthermore, the anisotropic nature of the relaxation time reduces to zero, i.e., $(1/T_1T)_{H\|c}=(1/T_1T)_{H\perp c}$, near the temperature where the Knight-shift anisotropy also vanishes. This suggests that below T_C the spin fluctuation is 3D in nature. Since the spin fluctuation is 2D in nature above 150 K, the magnitude of T_1 should be greater than that in the case where 3D spin fluctuation dominates. Possibly this is the reason for the smaller value of T_1 obtained for the calculated value of $1/T_1T$ using Eq. (5) above 150 K.

Moreover, the SCR theory of WIF with 3D spin fluctuations[19,22] predicts that $1/\chi$ or $1/M$ should vary as $T^{4/3}$. However it can be seen from the inset of Fig. 1 that above 150 K $1/\chi$ deviates from this relation which indicates that there is a change in the nature of the spin fluctuation near T_C. Thus from magnetization and the relaxation data, we conclude that their is a crossover from 2D to 3D ferromagnetic spin fluctuations across 150 K. Below 100 K, the relaxation process is mainly governed by the Korringa process. The $1/T_1T$ vs T curve for LaFePO is shown in the inset of Fig. 4. The behavior is very similar to that reported in Ca-doped LaFePO. The slow but gradual increase in $1/T_1$ with T in the range 50–300 K could be a signature of the weaker short-range correlations among the $3d$ spins of Fe in LaFePO compared to that in LaCoPO.

Contribution of the anisotropy of K and $1/T_1T$ arises from both the dipolar and hyperfine fields. The former is proportional to the bulk susceptibility (χ). As in case of LaCoPO, χ increases in the range 135–300, so a decrease in the ^{31}P line-shape anisotropy in this range, clearly suggests a decrease in the anisotropy of the hyperfine field, with a negligible contribution from the dipolar field anisotropy.

III. CONCLUSION

The study of dc magnetization in LaCoPO in the range 4–300 K in presence of different magnetic fields, suggest the dominance of $3d$ spin fluctuations in the ferromagnetically ordered state. This is further confirmed by the ^{31}P nuclear T_1 measurements. The T dependence of $1/T_1T$ in LaCoPO suggests the dominance of 2D ferromagnetic spin fluctuations in the paramagnetic phase with a crossover to the 3D ferromagnetic spin-fluctuation regime near the ordering temperature. Moreover, both the static and the dynamic part of the hyperfine fields are anisotropic in the paramagnetic phase and each of them becomes isotropic in the ordered phase, where the bulk susceptibility (at 7 T) shows a sharp enhancement, due to the ferromagnetic ordering. In contrast, ^{31}P H_{hf} is isotropic in LaFePO in the range 4–300 K. Electronic-structure calculation[7,13] for both compounds show similar Fermi surface composed of hybridized P $3p_z$, Fe/Co $3d_{z^2}$, and $3(d_{xz},d_{yz})$ orbitals. The only probable difference in LaCoPO because of the presence of odd $3d$ electrons ($3d^7$) is the participation of the upper Fe $3d_{x^2-y^2}$ orbital along with the $3d_{z^2}$ states in the Fermi level inducing the magnetic moments in LaCoPO. More insight of the spin fluctuation might be revealed by studying NMR with a single crystal at different magnetic field.

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