Enhanced spin fluctuations in the As-based filled skutterudite $LaFe_4As_{12}$: A ^{139}La NMR and ^{75}As NQR study

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We have grown single crystals of the itinerant-electron weak ferromagnet $LaFe_4As_{12}$ (T_C=3.8 K) and refined its crystal structure parameters. We report experimental results of magnetic susceptibility and nuclear magnetic resonance at the La site and nuclear quadrupole resonance at the As site in the paramagnetic state for this compound. The temperature dependences of the static magnetic susceptibility, the ^{139}La Knight shift, and the reciprocal of the product of the spin-lattice relaxation time and temperature ($1/T_1T$) of both ^{139}La and ^{75}As nuclei can be consistently understood in terms of self-consistent renormalization theory of spin fluctuations for weak itinerant-electron ferromagnets.

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I. INTRODUCTION

The filled skutterudite compounds with the chemical formula MT_4X_{12} (M=alkali metal, alkaline earth, lanthanide or actinide; T=Fe, Ru or Os; X=P, As, or Sb) display a wide variety of strongly correlated electron phenomena.[1,2] While the majority of studies have addressed the filled skutterudite phosphides and antimonides, the filled skutterudite arsenides have received considerably less attention; although not for a lack of interesting physical phenomena, as shown by previous examination of polycrystalline materials.[3–8] The limited research in this direction may be due to preparation difficulties related to the elevated vapor pressure of arsenic. The introduction of a Cd:As flux for growing crystals of Pr and Ce filled skutterudite arsenides[9] has accelerated studies of this group of compounds. The intriguing physical properties[10] that are observed in these materials are mainly due to a subtle interplay between crystalline field effects and hybridization of localized 4f- and itinerant-electron states. Crystal structure, nuclear magnetic resonance (NMR), and thermoelectric power data obtained on single crystalline $LaOs_4As_{12}$ and $PrOs_4As_{12}$ were recently described in Ref. 11 where it was shown that their temperature dependences of thermoelectric power above ca. 80 K are very similar whereas magnetic susceptibility and ^{139}La NMR Knight shift in $LaOs_4As_{12}$ are much smaller than those in $LaOs_4Sb_{12}$. In contrast, itinerant-electron weak ferromagnetism (IEWFM) below T_c=5.2 K and high spin-fluctuation (SF) rates at higher temperatures were recently observed for $LaFe_4As_{12}$ polycrystalline specimens which were prepared by means of a high-pressure synthesis technique.[12] In this study, it was suggested that the IEWFM in $LaFe_4As_{12}$ occurs due to the Fe 3d electrons in $[Fe_4As_{12}]$ anions as in the case of $[Fe_4Sb_{12}]$ anions in alkali-metal iron antimonides $NaFe_4Sb_{12}$ and KFe_4Sb_{12}.[13,14] It is natural to compare the rather unexpected ferromagnetism in $LaFe_4As_{12}$ with physical properties of other $LaFe_4X_{12}$ compounds (X=P,Sb). $LaFe_4P_{12}$ is a simple and ordinary paramagnet, while $LaFe_4Sb_{12}$ is reported to be enhanced Pauli paramagnet. However an overall understanding of $LaFe_4Sb_{12}$ is yet missing due to controversy about the type of spin fluctuations. Ferromagnetic (FM) fluctuations have been concluded in both $LaFe_4As_{12}$ exhibiting IEWFM (Ref. 12) and $LaFe_4Sb_{12}$ which does not reveal magnetic order (Ref. 15). It was deduced from the temperature $T^{5/3}$ dependence of electrical resistivity. Antiferromagnetic (AFM) fluctuations in $LaFe_4Sb_{12}$ were suggested in Ref. 14.

NMR/nuclear quadrupole resonance (NQR) is a powerful tool in the study of magnetic properties of solids, since valuable information is obtained from the temperature dependence of Knight shift K and nuclear spin-lattice relaxation time T_1. We note that the $^{121,123}Sb$ NQR data in $LaFe_4Sb_{12}$ were explained by the presence of ferromagnetic fluctuations.[16,17] In a separate study, it was suggested that the compound remains in the localized electron state down to 1.4 K.[18] On the other hand, the results of the ^{139}La NMR studies on the filler atom in both $LaFe_4P_{12}$ (Ref. 19) and $LaFe_4Sb_{12}$ (Ref. 20) have been analyzed in terms of antiferromagnetic fluctuations.

In order to better understand the magnetism in $LaFe_4As_{12}$, we have crystallized the $LaFe_4As_{12}$ compound from a Cd:As flux and studied its properties by means of x-ray diffraction, NMR, NQR, and dc-magnetic susceptibility measurements.

In this paper, we report results for the magnetic properties of $LaFe_4As_{12}$ in the paramagnetic state via the microscopic probes of ^{139}La-NMR and ^{75}As-NQR. The ^{139}La and ^{75}As nuclei have natural abundances of 99.91% and 100%, respectively, and reasonable NMR/NQR signal sensitivities.

II. EXPERIMENTAL DETAILS

A. Synthesis (sample preparation)

Single crystals of $LaFe_4As_{12}$ were grown from elements with purities >99.9 by mineralization in a molten Cd:As flux at high temperatures and pressures as described previously for Pr and Ce filled skutterudite arsenides.[9] The elemental components of the $LaFe_4As_{12}$ skutterudite and the flux were taken in the atomic ratio La:Fe:Cd:As=1:4:12:48 ($LaFe_4As_{12}$+12$CdAs_3$), loaded into a quartz ampoule, and

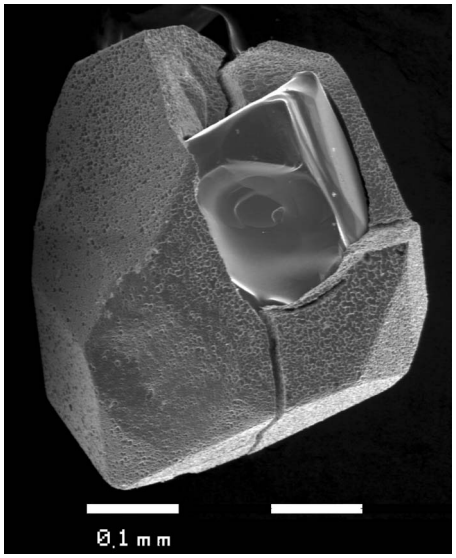

FIG. 1. Small $FeAs_2$ crystal overgrown by $LaFe_4As_{12}$ one.

sealed in a vacuum environment. The inside wall of the ampoule was covered with a layer of pyrolitic carbon. The ampoule was heated up from 350 to 820 °C at a rate of 20 °C/h in a home built high-pressure cell filled with 19 atm of Ar pressure, roughly equal to an estimated vapor pressure of the $CdAs_3$ flux in the ampoule at 820 °C. The main function of the Ar was to compensate for the inner ampoule pressure at high temperatures and thus avoid the possibility of ampoule explosion. The ampoule was then cooled down and heated repeatedly between 820 and 780 °C for three weeks with a rate 3 °C/h. Afterward, the ampoule was cooled to ambient temperature at a rate of 20 °C/h. The solidified flux with $LaFe_4As_{12}$ crystals was subsequently placed in a 20 cm long quartz ampoule and sealed under high vacuum. Then ampoule was then placed in a two zone furnace where the flux sublimated from a zone with a temperature of 600 °C to one with a temperature of 400 °C. Following sublimation, $LaFe_4As_{12}$ crystals with isometric, prismlike forms and dimensions ~1 mm were collected and cleaned in acid to remove possible $LaAs_2$ impurities from the skutterudite crystal surfaces prior to the measurements. The acid was unable to remove the $FeAs_2$ crystals which had a different morphology than the skutterudite crystals—parallelepipelike shape. The $FeAs_2$ crystals were also identified by their high and negative thermoelectric power ($S=-170$ μV/K) values which were measured using a home made thermoelectric probe. These results are consistent with the expected semiconducting and diamagnetic properties of $FeAs_2$.[12,21] In contrast, the value $S=+40$ μV/K at room temperature determined for $LaFe_4As_{12}$ indicates semimetallic behavior. Previous growth experiments of $PrFe_4As_{12}$ single crystals using the flux method described above[9] revealed that by extending the growth time, crystals as large as ~3 mm that are free of $FeAs_2$ can be obtained. Based on this experience, we performed similar growth experiments for $LaFe_4As_{12}$ which lasted for two months. These experiments produced crystals as large as ~2 mm. However, these specimens were not free of $FeAs_2$ impurities. As shown in Fig. 1, the $FeAs_2$ crystals (the smaller ones) overgrow the skutterudite crystals. The sharp edges of the former shows that, unlike in the case of $PrFe_4As_{12}$, the skutterudite phase does not consume the $FeAs_2$ crystals. On the other hand, one can also see several hollows on the surface of the skutterudite crystal, but none on the $FeAs_2$ crystal. This result occurs because of the following procedure. After the crystals were obtained by initial flux removal and acid rinsing, as for our typical procedure,[9] the crystals were then gradually heated under a vacuum of 10^{-4} mm Hg. At about 680 °C the crystals started to liberate As. The hollows that are revealed by etching the $LaFe_4As_{12}$ crystal in acid show that the liberated As comes only from the skutterudite. Therefore, it is apparent that the skutterudite phase is less stable than the $FeAs_2$ phase. It is also worth noting that less severe conditions, like those used in our initial procedure for flux removal, make the $LaAs_2$ impurity easily soluble, leaving the $LaFe_4As_{12}$ crystals nonsoluble.

We can sort the skutterudite specimens, by means of sifting, into batches with crystals of sizes smaller and larger than 0.25 mm. Powder diffraction measurements on the first batch revealed very few impurity peaks. Some of the largest crystals from the second batch were broken because of the $FeAs_2$ inclusions inside. As the inclusions were revealed, we could select the broken crystals with the highest amount of the impurity and thereby obtain specimens with enriched amounts of the $FeAs_2$ phase that had grown inside the skutterudite phase. Such samples showed several $FeAs_2$ impurity peaks in the powder x-ray diffraction data. The magnetization of these types of samples was smaller than that of the first batch, thus proving that the $FeAs_2$ impurity, even when grown inside the skutterudite phase, cannot be responsible for the ferromagnetic properties of the examined samples. As we have not detected any other impurities, we ascribe the observed ferromagnetism to the $LaFe_4As_{12}$ phase. The magnetization measurements reported below were performed on a selected sample of $LaFe_4As_{12}$ that was free of the $FeAs_2$ phase, as shown by powder x-ray diffraction.

B. Crystal structure investigation

The crystal structure of the $LaFe_4As_{12}$ specimens was examined by x-ray diffraction on a crystal with dimensions of $0.21\times0.18\times0.17$ mm^3 using a four circle x-ray diffractometer. The measurements were made at room temperature using a two-dimensional charge-coupled device detector. A total of 6625 reflections (502 unique, $R_{\text{int}}=0.0872$) were recorded and the structure was resolved by the full matrix least-squares method applying the SHELX-97 program with a final discrepancy factor $R1=0.0276$ [for $I>2\sigma(I)$, $wR2=0.0596$].[22,23]

C. Magnetic properties

The dc magnetization (M) and magnetic susceptibility ($\chi=M/H$) data were measured using a superconducting quantum interference device magnetometer (Quantum Design, Inc.). The measurements were made between 1.8 and 300 K in magnetic fields up to 5.5 T. The measurements were performed on a collection of a large number of randomly oriented single-crystal granules.

TABLE I. Atomic coordinates, displacement parameters and occupancy factors for $LaFe_4As_{12}$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	$U_{eq}(Å^2 \times 10^3)$	Occupancy factor
Fe	0.25	0.25	0.25	6(1)	1.00(2)
As	0	0.3456(1)	0.1546(1)	6(1)	1.01(2)
La	0	0	0	10(1)	1.00(2)

D. NMR/NQR measurements

For the NMR experiments, powdered material was obtained by crushing single crystals. The ^{139}La NMR measurements were performed for $T=20-294$ K using a Bruker Avance DSX 300 spectrometer operating at a field of 7.05 T and temperature controller ITC-503 (Oxford Instruments Co. Ltd.). The spectra were obtained by the Fourier transforms of the free-induction decay (FID) or spin-echo (SE) signals produced by a sequence of two pulses using quadrature detection and extended phase cycling procedures. The ^{139}La Knight shifts are given with reference to Ξ^{139}La $=0.14125641$, (IUPAC δ scale).[24] Here Ξ is defined as the ratio of the isotope specific frequency to that of ^{1}H in tetramethylsilane (TMS) in the same field. More positive values of Knight shifts correspond to higher frequency, low-field, paramagnetic deshielded values. Determinations of the nuclear spin-lattice relaxation time T_1 were made using conventional inversion recovery (IR) or saturation recovery (SR) pulse sequences. In every case the recovery of the signal amplitude after perturbation of the nuclear spins by radio-frequency RF pulses was found to follow a single exponential. The spin-lattice relaxation time T_1 was determined by fitting the data to the three-parameter magnetization recovery function $M(t)=M(\infty)$ $[1\text{-}C\exp(-t/T_1)]$ where $M(t)$ and $M(\infty)$ represent, respectively, the signal intensity at time t after inversion (saturation) and at thermal equilibrium. The quantities T_1, $M(\infty)$ and C were treated as adjustable parameters.

The ^{75}As ($I=3/2$) NQR measurements were made in the temperature range 20–294 K under zero external magnetic field. The NQR frequencies $\nu_{NQR}(T)$ were determined from the spectra obtained by the Fourier transform of the SE signals. The T_1 was measured using an SR pulse sequence. The recovery of the SE signal was fitted to $M(t)=M(\infty)$ $[1\text{-}C\exp(-3t/T_1)]$ appropriate to NQR with nuclear spin $I=3/2$.

III. RESULTS AND DISCUSSION

A. Crystal structure

Single crystal structural refinement shows that the unit cell of $LaFe_4As_{12}$ has the $LaFe_4P_{12}$-type structure ($Im-3$ space group) with 2 f.u. per unit cell, the chemical bond lengths La-As=3.1523(3) Å and Fe-As=2.366 11(15) Å and the unit-cell parameter $a=8.3273(2)$ Å. These results can be compared with earlier data where $a=8.3252(3)$ Å (Ref. 3) and 8.325(1) Å.[12] Other crystal structure parameters are summarized in Table I. The displacement parameter U_{eq} represents the average displacement of an atom vibrating around its lattice position and is equal to the mean-square displacement of a given type of atom along the Cartesian axes. The displacement parameters determined for the $LaFe_4As_{12}$ constituent atoms are typical for many lanthanide filled skutterudite arsenides.[9] The displacement factor for the lanthanide ion varies from 9×10^{-3} Å^2 for $PrFe_4As_{12}$ to 1.6×10^{-2} Å^2 for $PrOs_4As_{12}$. Thus, this factor is two to four times bigger than that of the remaining constituent atoms. The lanthanum ion is located inside an icosahedral cage formed by the 12 As atom nearest neighbors, and the large displacement parameter indicates that La atoms undergo large amplitude vibrations. On the other hand, the Fe atoms occupy octahedra formed by the 6 As atom nearest neighbors, where they do not undergo such large vibrations. In the limit of experimental accuracy, the occupancy factors for each lattice site in our sample ($LaFe_4As_{12}$) are equal to 1. This result indicates that we have grown stoichiometric crystals.

B. Magnetic properties

The temperature dependence of the magnetization, M, recorded at low magnetic field strength $H=500$ Oe [Fig. 2(a)] and low T "in-field" magnetization $M(T,H)$ isotherms [Fig.

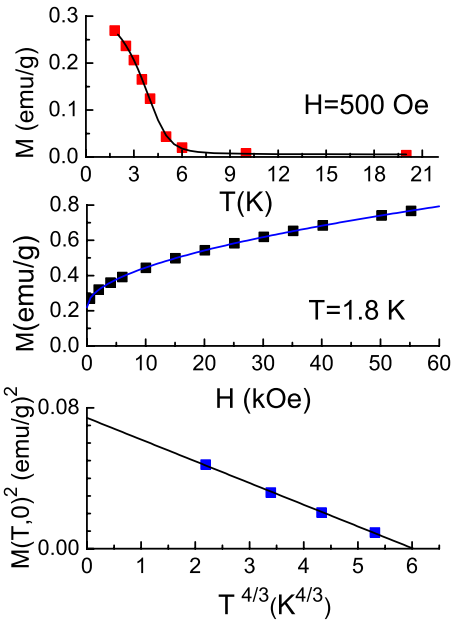

FIG. 2. (Color online) (a) Temperature dependence of magnetization measured at low magnetic field strength, (b) magnetization isotherm in ordered state at $T=1.8$ K, and (c) dependence of the squared spontaneous magnetization $M(T,0)$ versus $T^{4/3}$.

2(b)] are indicative of ferromagnetic order in our sample of $LaFe_4As_{12}$.

It has been shown[25,26] that the spontaneous magnetization at finite temperature, $M(T,0)$, can be extracted from the $M(T,H)$ curve from the expression

$$M(T,H) = M(T,0) + \lambda H^{1/2} + \chi H \tag{1}$$

where the $H^{1/2}$ term accounts for the suppression of spin waves by the field H, and the high field susceptibility, χ, is related to the exchange enhanced Pauli-spin susceptibility.

For temperatures close to T_C but away from criticality ($T \lesssim T_C$), thermally excited spin fluctuations, according to the conventional SF theory[27,28] give rise to a temperature dependence of the spontaneous magnetization of the form,

$$M(T,0) = M(0,0)[1 - (T/T_C)^{4/3}]^{1/2}. \tag{2}$$

The linear dependence $M^2(T,0) - T^{4/3}$ [Fig. 2(c)] is well described by Eq. (2).

The bulk nature of the IEWFM in $LaFe_4As_{12}$ has been showed by Tatsuoka *et al.*[12] in their magnetization, specific heat, electrical resistivity, and Hall-coefficient measurements. Presented on Fig. 2 magnetic characteristics of our sample confirm this feature, as well.

By making use of Eqs. (1) and (2), we have obtained for our sample, $T_C = 3.8$ K and $M(0,0) = 0.06\mu_B$/f.u. Both of these values are considerably lower than those reported in Ref. 12 ($T_C = 5.2$ K, $M(0,0) = 0.12\mu_B$/f.u.) thus suggesting higher La-filling factor in our sample. It is worth mentioning here that for nonmagnetic Yb^{2+} filler in $Yb_xFe_4Sb_{12}$ Ikeno and co-workers[29] have reported a monotonic decrease in both the Curie temperature and spontaneous magnetization with increasing x. Also in the case of $Pr_xFe_4Sb_{12}$, where magnetism is attributed to both Pr^{3+} and $[Fe_4Sb_{12}]$ ions,[30] a drastic change in magnetic ground state was observed, from ferromagnetic to nonmagnetic by increasing x from ~ 0.8 to ~ 1.[31] On the other hand, ferromagnetic ordering is observed in alkali-metal iron antimonides $NaFe_4Sb_{12}$ and KFe_4Sb_{12} which do not exhibit defects on the cation site.[13,14] Above T_C and in the paramagnetic state, the magnetization isotherms (M versus H) of $LaFe_4As_{12}$ are still slightly curvilinear at temperatures below about 10 K. They are nonlinear in intermediate magnetic fields and became linear in strong fields. Consequently, the M/H ratios are field dependent and likely do not represent the intrinsic susceptibility of $LaFe_4As_{12}$. Curvature in the M versus H isotherms up to $\simeq 6T_C$ often indicates the presence of short-range magnetic order in a sample. It is likely that the effect is due to a small concentration of unidentified paramagnetic impurities. If the impurity magnetization is attributed to isolated paramagnetic impurities, then it can be assumed to saturate in sufficiently strong magnetic fields. We do not make an attempt to analyze these effects in details. The problem was to correctly determine the intrinsic susceptibility of $LaFe_4As_{12}$ as this is the only contribution in which we are interested in the present work. In strong fields ($H > 2$ T), the M vs H plots are linear and an intrinsic magnetic susceptibility of $LaFe_4As_{12}$ is defined as $\chi_{\text{int}} \equiv \partial M/\partial H$. Our $LaFe_4As_{12}$ crystals do not show a presence ferromagnetic (e.g., metallic iron) impurities.

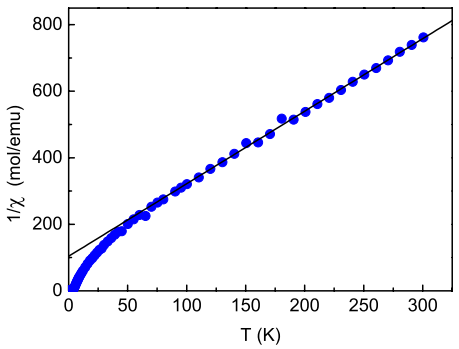

FIG. 3. (Color online) Temperature dependence of reciprocal magnetic susceptibility. The solid line represents the least-square linear fit of the data taken above $T = 100$ K.

The T dependence of the inverse magnetic susceptibility χ^{-1} is shown in Fig. 3. The reciprocal susceptibility of $LaFe_4As_{12}$ has a nonlinear temperature dependence and positive curvature just above T_C which is a common feature for itinerant-electron ferromagnets.[28] At higher temperatures, $\chi(T)^{-1}$ gradually bends downward from and finally obeys the Curie-Weiss (CW) law, $\chi(T)^{-1} = (T - \Theta_P)/C_P$, with a negative Curie-Weiss temperature $\Theta_P = -48$ K at temperatures above 100 K. Using $C_P = N_A\mu_{eff}^2/3k_B$, where N_A is the Avogadro number and k_B is Boltzmann constant, one obtains the effective paramagnetic moment $\mu_{eff} = 1.92\mu_B$/f.u. ($0.96\mu_B$/Fe when the behavior of the magnetic susceptibility is attributed mainly to the Fe $3d$ electrons). Our estimations of μ_{eff} and Θ_P are in fairly good agreement with those reported in Ref. 12.

The observed total susceptibility $\chi(T)$ per mole of $LaFe_4As_{12}$ can generally be expressed as follows:

$$\chi(T) = \chi_d(T) + \chi_0, \tag{3}$$

with

$$\chi_d(T) = \chi_{\text{La } 5d}(T) + 4\chi_{\text{Fe } 3d}(T), \tag{4}$$

$$\chi_0 = \chi_{\text{La-orb}} + \chi_{\text{La-dia}} + 4(\chi_{\text{Fe-orb}} + \chi_{\text{Fe-dia}}) + 12\chi_{\text{As}}, \tag{5}$$

where χ_{dia}, χ_{orb}, and χ_d are the diamagnetic, $5d(3d)$-orbital and $5d(3d)$-spin contributions, at La(Fe) sites, respectively. Finally, χ_{As} represents the susceptibility of As atoms.

However, the CW dependence of $\chi(T)$ at high temperatures strongly suggests that $\chi_0 \simeq 0$ due to the mutual compensation of positive and negative terms entering Eq. (5), and the spin-dependent contribution $\chi_d(T)$ determines the total magnetic susceptibility of $LaFe_4As_{12}$. The meaning of the sizable negative Θ_P at high temperatures is unclear and may indicate that antiferromagnetic fluctuations coexist with ferromagnetic fluctuations. In order to clarify this point, ^{75}As-NQR and ^{139}La-NMR experiments were undertaken.

C. ^{75}As NQR and ^{139}La NMR spectra

Since ^{75}As has a nuclear spin $I = 3/2$, a single NQR line appears at the resonance frequency, $\nu_{\text{NQR}} = \nu_Q\ (1 + \eta^2/3)^{1/2}$ where ν_Q represents the coupling of the nuclear quadrupole moment with an electric field gradient (EFG), and η represent the asymmetry parameter of the EFG.

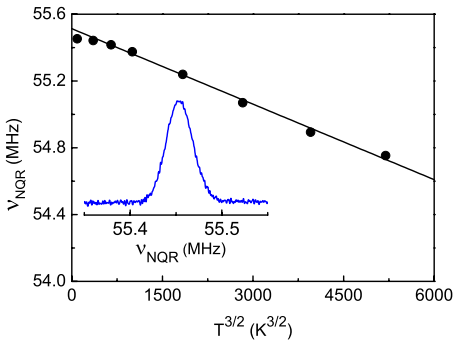

FIG. 4. (Color online) Temperature dependence of nuclear quadrupole resonance frequency ν_{NQR}. Inset: ^{75}As-NQR spectrum recorded at $T=20$ K.

The ^{75}As-NQR spectra in $LaFe_4As_{12}$ were observed around $\nu_{NQR}=55.4$ MHz at low T, as shown in Fig. 4. Similar magnitudes of ^{75}As ν_{NQR} equal to 56.5 and 56.7 MHz were found in $LaRu_4As_{12}$ and $PrRu_4As_{12}$, respectively.[32] The ^{75}As-NQR spectra in $LaFe_4As_{12}$ have a Gaussian-type shape (see inset of Fig. 4) with full width at half maximum (FWHM) of about 33 kHz over the entire investigated temperature range (20–294 K), indicating the high quality of the samples and a La-filling factor close to unity. We note that linewidths of 70–80 kHz in the T range of 0.3–300 K were reported for ^{75}As-NQR spectra in $LaRu_4As_{12}$ and $PrRu_4As_{12}$.[32] The single NQR line for $I=3/2$ precludes simultaneous determination of ν_Q and η. In the ^{121}Sb($I=5/2$) and ^{123}Sb($I=7/2$) NQR of $LaFe_4Sb_{12}$ and $YbFe_4Sb_{12}$ the value of $\eta\approx 0.37$ was previously extracted[16–18] and nearly the same magnitude of η is expected for the ^{75}As-NQR in $LaFe_4As_{12}$. The value of ν_{NQR} decreases monotonically with increasing temperature (see Fig. 4) and traces ν_Q if η is taken to be temperature independent, as was observed for ^{121,123}Sb NQR in $La_{0.88}Fe_4Sb_{12}$.[17] The temperature dependence of ν_{NQR} in $LaFe_4As_{12}$ is much stronger than that seen for $LaRu_4As_{12}$ and $PrRu_4As_{12}$ where it has been attributed to the thermal lattice expansion.[32] The effect of spin fluctuations on the electric field gradient in itinerant-electron magnet has been studied theoretically by Takahashi and Moriya[33]and verified experimentally by ^{55}Mn NMR in MnSi.[34]

Coupling between the quadrupole charge density and spin-density functions and the predicted relationship between $\nu_Q(T)$ and $\chi(T)$ is, however, not observed in the present case. On the other hand, the temperature dependence of ν_{NQR} in $LaFe_4As_{12}$ can be described quite well by the expression

$$\nu_{NQR}(T) = \nu_{NQR}(0)[1 - \alpha T^{3/2}] \quad (6)$$

for temperatures higher than about 50 K. Similar T dependences have been known for some time for simple metals such as Ga, In, Sb, and Cd and their alloys[35] as well as for intermetallic compounds of cerium[36] and uranium.[37] However, no satisfactory theoretical explanation of the $T^{3/2}$ temperature dependence of ν_Q has been presented in the literature. For a detailed review, see Ref. 38. The evaluated parameter $\alpha=2.807\times10^{-6}$ $K^{-3/2}$ in $LaFe_4As_{12}$ is about 1 order of magnitude smaller than for the nontransition metals mentioned above.

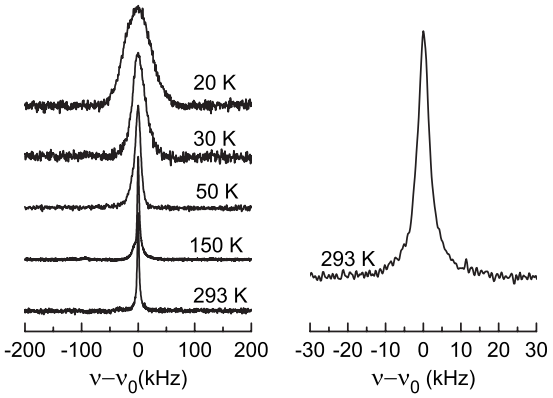

FIG. 5. Evolution of the ^{139}La NMR spectra with temperature. Spectrum at $T=293$ K shown in extended scale exhibits single Lorentzian shape.

The quadrupolar effects in ^{139}La NMR, in spite of the ^{139}La nuclear spin $I=7/2$, are weak because of the crystal site symmetry and large amplitude of the lanthanum atom vibrations. These factors make it possible to measure both the ^{139}La Knight shifts and spin-lattice relaxation rates $(1/T_1)$.

The single-line ^{139}La NMR spectra of the $LaFe_4As_{12}$ sample used in the present study have considerably smaller widths than those previously reported for $LaFe_4X_{12}$ compounds (X=P,Sb) with either incomplete or complete La-filling.[16–20] At high temperatures, the ^{139}La NMR lines in $LaFe_4As_{12}$ have a Lorentzian-type shape (Fig. 5) with a FWHM of about 3.2 kHz at 294 K, again confirming the high quality of the sample and a La-filling factor close to unity. Linewidths of about 20 kHz have been reported for ^{139}La NMR spectra of $LaFe_4P_{12}$,[19] and about 60 kHz at 100K for ^{139}La NMR spectrum of $LaFe_4Sb_{12}$, as estimated from Fig. 3 of Ref. 18. Complex line shapes ascribed to two nonequivalent positions of the La atom in the structure, and markedly larger widths have been reported for incomplete La-filled samples of $La_{\approx 0.9}Fe_4Sb_{12}$.[16,20]

The ^{139}La NMR Knight shifts, ^{139}K, in $LaFe_4As_{12}$ are large and negative. The temperature dependence of these shifts is shown in Fig. 6. At low temperatures where $\chi(T)$ exhibits a deviation from the CW law, ^{139}K(T) also deviates from the CW law. The temperature dependence of the ^{139}La

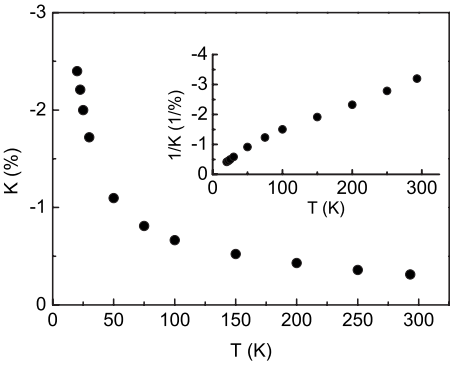

FIG. 6. Temperature dependence of the ^{139}La Knight shift (main panel) and its reciprocal (inset).

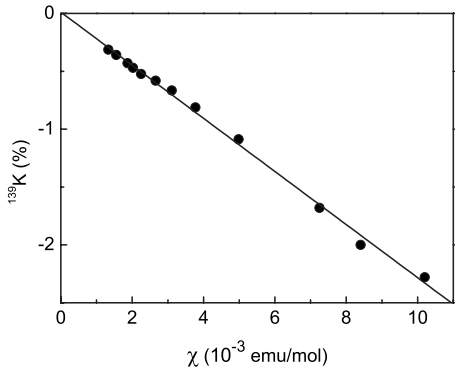

FIG. 7. ^{139}K(T) versus $\chi(T)$ plot. A linear least-square fit to the data is shown as solid line.

Knight shift in the paramagnetic state of $LaFe_4As_{12}$ reflects the behavior of the magnetic susceptibility which is attributed mainly to the Fe 3d electrons.

Neglecting any diamagnetic contribution to the Knight shift of La, ^{139}K(T) is expressed as

$$^{139}\mathrm{K}(T) = \mathrm{K}_{\mathrm{orb}} + \mathrm{K}_{\mathrm{spin}}(T) \tag{7}$$

where the contributions $\mathrm{K}_{\mathrm{orb}}$ and $\mathrm{K}_{\mathrm{spin}}(T)$ are attributed mainly to the La 5d-orbital current and 5d spins, respectively.

In Fig. 7, ^{139}K was plotted against χ with temperature as an implicit parameter. The ^{139}K(T) versus $\chi(T)$ plot is linear over the entire temperature range investigated (20–294 K). This result suggests that the hyperfine coupling constant A_{hf} can be treated as being temperature independent over this temperature range, and the deviation from the CW law below 100 K of both $\chi(T)$ and ^{139}K(T) is an intrinsic property of $LaFe_4As_{12}$.

Moreover, we infer that the 5d-spin susceptibility $\chi_{\mathrm{La}\,5d}(T)$ is proportional to the 3d-spin susceptibility $\chi_{\mathrm{Fe}\,3d}(T)$, with the reduction factor ξ associated with the decrease in the spin polarization at La site: $\chi_{\mathrm{La}\,5d}(T) = \xi \cdot \chi_{\mathrm{Fe}\,3d}(T)$. The zero intercept in the K vs χ plot indicates that the orbital contributions to both the local magnetic susceptibility at the La site and the ^{139}La-Knight shift are negligibly small. In that case,

$$^{139}\mathrm{K}(T) = {}^{139}A_{\mathrm{hf}}(d\text{-spin})\chi_d(T)/(N_A\mu_B) \tag{8}$$

where $^{139}A_{\mathrm{hf}}(d\text{-spin})$ is the hyperfine field per Bohr magneton μ_B. From the slope of the ^{139}K(T) vs $\chi_d(T)$ plot, we obtain $^{139}A_{\mathrm{hf}}(d\text{-spin}) = -12.8$ kOe/μ_B. The observed negative value has two possible origins:

(a) transferred hyperfine field arising from a conduction-electron-mediated exchange coupling between the Fe 3d electrons and the ^{139}La nucleus (preferably);

(b) the hyperfine field arising from the inner La ($1s-5s$) core polarization caused by the La 5d spins.

Our value of $^{139}A_{\mathrm{hf}}(d\text{-spin})$ is close to that for $LaFe_4Sb_{12}$, where the results of ^{139}La NMR Knight shifts and the measurements of ^{121}Sb NQR spin-lattice relaxation times were explained in terms of ferromagnetic fluctuations[16,17] in accordance with the self-consistent renormalization (SCR) theory of spin fluctuations.[28,39] Enhanced ferromagnetic fluctuations in $LaFe_4As_{12}$ are also evident through the enhanced magnetic susceptibility and large Knight shift of the ^{139}La nuclei above the Curie temperature. The NMR data and their interpretation for $LaFe_4Sb_{12}$ are, however, controversial. In Ref. 18, from the combined ^{139}La NMR Knight shift and ^{121}Sb NQR relaxation data, it was suggested that the compound remains in the localized electron state down to 1.4 K. On the other hand, the results of the ^{139}La NMR Knight shift and relaxation studies have been analyzed in terms of antiferromagnetic fluctuations,[20] mainly because of the observed $T^{1/2}$ dependence of $1/T_1$.

D. ^{139}La and ^{75}As spin-lattice relaxation rates

In order to further our understanding of the microscopic magnetic properties of $LaFe_4As_{12}$, we measured the temperature dependence of T_1 for the ^{139}La nuclei at $B_0 = 7.05$ T and ^{75}As at zero magnetic field. The SCR theory of spin fluctuations for itinerant-electron magnets developed by Moriya *et al.*[28] offers an explanation for the temperature dependence of the nuclear spin-lattice relaxation rate of nearly and weakly ferro- and antiferromagnetic metals. In general, the $(1/T_1)_{\mathrm{SF}}$ is given by

$$(1/T_1)_{\mathrm{SF}} \propto (\gamma_{\mathrm{n}} A_{\mathrm{hf}})^2 T \Sigma_q \chi''(\mathbf{q}, \omega_{\mathrm{n}})/\omega_{\mathrm{n}}, \tag{9}$$

where $\chi''(\mathbf{q}, \omega_{\mathrm{n}})$ is the imaginary part of the transverse dynamical electron-spin susceptibility, and γ_{n} and ω_{n} are the nuclear gyromagnetic ratio and NMR frequency, respectively.

The theory of spin fluctuations for weak itinerant ferromagnets predicts a temperature dependent spin-lattice relaxation rate at $T \gg T_C$ (where uniform spin susceptibility obeys the CW law) by the following relation:[28,39]

$$(1/T_1)_{\mathrm{SF}} \propto T/(T - T_C). \tag{10}$$

For weakly antiferromagnetic metals, when the staggered susceptibility $\chi(\mathbf{Q})$ above T_N shows CW behavior, theory predicts

$$(1/T_1)_{\mathrm{SF}} \propto T/(T - T_N)^{1/2}. \tag{11}$$

Figure 8(a) shows the temperature dependences of ^{139}La and ^{75}As spin-lattice relaxation rates $1/T_1$ for $LaFe_4As_{12}$ in the temperature range 20–294 K (well above the Curie temperature). It is evident that the $1/T_1$ data do not follow a $T^{1/2}$ dependence. Instead, the $1/T_1$ data are linear in T and, in each case, there exists a large T-independent term over the entire investigated range. The best fits of the $1/T_1$ vs T curve are obtained with $1/T_1 = A + BT$ or, equivalently, $1/T_1T = A/T + B$. Figure 8(b) presents the T dependencies of $(1/\gamma_{\mathrm{n}}^2 T_1 T)$. The data fall on two similar slightly shifted curves. This demonstrates that the relaxation processes for both types of nuclei are magnetic in origin over the measured T range. The experimentally found A/T terms resemble the Curie-Weiss term in Eq. (10) due to small value of $T_C \approx 4$ K. The term B (Korringa type) arises from the other relaxation mechanisms, mostly from the orbital contribution. It describes the Korringa relaxation process with $B = 1/(T_1T)_{\mathrm{orb}} \propto N^2(E_F)$, where $N(E_F)$ represents the d-band electron density of states (DOS) at the Fermi level.

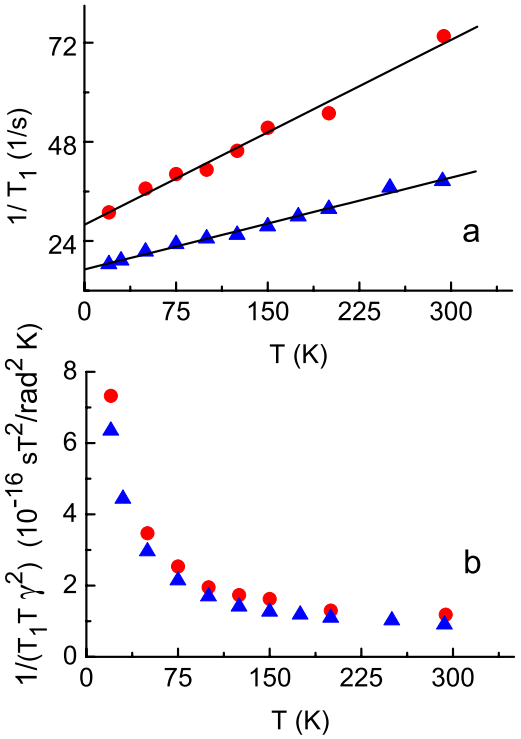

FIG. 8. (Color online) Temperature dependences of the nuclear spin-lattice relaxation rates, (a) $1/T_1$ and (b) $1/(T_1T\gamma_n^2)$. The solid lines are the least-square fits to $1/T_1=A+BT$ as described in the text. Circular and triangular symbols represent the data for ^{75}As and ^{139}La nuclei, respectively.

Consequently, Eq. (10), when corrected for the B term, matches the experimental data quite well [see Fig. 8(b)]. However, the agreement seems to be incidental since the CW law for the magnetic susceptibility of $LaFe_4As_{12}$ is fulfilled only above $T\approx 20T_C$ and, moreover, with a large and negative Curie-Weiss temperature $|\Theta_P|\approx 12T_C$. Negative Θ_P is frequently, but erroneously, used as the decisive argument supporting presence of antiferromagnetic fluctuations. ^{75}As NQR experiment performed in zero external field shows that antiferromagnetic fluctuations are absent in $LaFe_4As_{12}$. According to more detailed SCR theory for weak itinerant ferromagnets, the temperature-dependent ferromagnetic ($\mathbf{q}=0$) spin-fluctuation contribution to $1/(T_1T)$ in the presence of a magnetic field is given by the following relation:[40]

$$1/(T_1T)_{\mathrm{SF}}=[bM(T,H)/H]/\{1+aM^3(T,H)/H\} \qquad (12)$$

as confirmed in several experimental analyses.[40–43]

Quite frequently, $aM^3(T,H)/H\ll 1$, and in the paramagnetic region far above T_C where the magnetization $M(T,H)$ linearly increases with increasing applied field H, the ferromagnetic scaling holds near $\mathbf{q}=\mathbf{0}$ between dynamical and static uniform spin susceptibility

$$\chi''(\mathbf{q},\omega_{\mathrm{n}})/\omega_{\mathrm{n}}\propto\chi(T), \qquad (13)$$

Consequently, a linear relation between $1/T_1T$ and $\chi_d(T)$ is expected

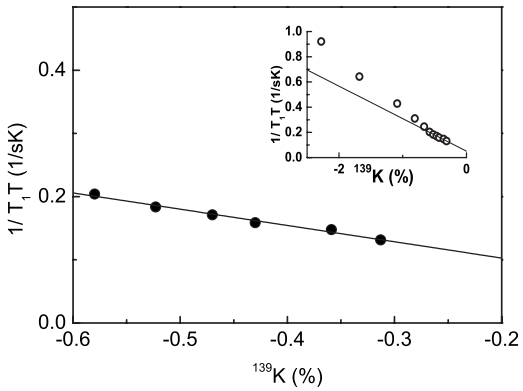

FIG. 9. $1/T_1T$ versus ^{139}K plot where the straight line is a best linear fit of the data to Eq. (15) for temperature range 125–293 K (main frame). Deviation from this relation is observed at lower temperatures (inset).

$$1/T_1T=b\chi_d(T)+(1/T_1T)_{\mathrm{orb}}. \qquad (14)$$

In the present case of $LaFe_4As_{12}$, where $^{139}\mathrm{K}(T)\propto\chi_d(T)$, the relation (14) can also be written as

$$1/T_1T=b'\,^{139}\mathrm{K}(T)+(1/T_1T)_{\mathrm{orb}}. \qquad (15)$$

In Fig. 9, the values of $1/(T_1T)$ are plotted against ^{139}K with the temperature as an implicit parameter between 125 and 294 K. Both T_1 and ^{139}K were measured at the same magnetic field strength $H=7.05$ T. Above 100 K, $1/(T_1T)$ satisfies the relations (14) or (15) and provides evidence for the development of ferromagnetic fluctuations. At lower temperatures $1/(T_1T)$ deviates from these relations (see inset of Fig. 9).

For the sake of completeness, we mention that temperature independence of $1/(T_1T)$ at high-T and peak of $1/(T_1T)$ at low-T describe the contribution to the relaxation rate resulting from Raman process of anharmonic phonons.[44] However, in subsequent paper[45] the authors of Ref. 44 have realized that theoretical calculations are somewhat model dependent, and modified previous result to the form:$1/T_1T\propto 1/\sqrt{T}$ at high T.

Recently, on the basis of the ^{139}La NMR and ^{121,123}Sb NQR data, it has been deduced that the anharmonicity occurs in $LaOs_4Sb_{12}$ due to the rattling motion of the La atoms.[46] Broad peak of ^{139}La $1/(T_1T)$ observed at about 50 K has been ascribed to the local fluctuations of the electric field gradient (EFG) at La site caused by this motion The relaxation rate of ^{139}La nuclei due to this effect is slow, and is not expected to be observed in $LaFe_4As_{12}$ (even if present) because relaxation rate due to ferromagnetic fluctuations is high enough to hide it.

In summary, we have grown single crystals of the itinerant-electron weak ferromagnet $LaFe_4As_{12}$, refined its crystal structure parameters, and measured its magnetic susceptibility, ^{139}La NMR Knight shift, and ^{139}La and ^{75}As spin-lattice relaxation rates ($1/T_1$). Neither ^{139}La nor ^{75}As ($1/T_1$) follow a $T^{1/2}$ dependence characteristic of antiferro-

magnetic spin fluctuations, contrary to results reported previously for $LaFe_4P_{12}$ and $LaFe_4Sb_{12}$. The temperature dependences of the static magnetic susceptibility, ^{139}La NMR Knight shift, and $1/T_1T$ for both ^{139}La and ^{75}As nuclei in $LaFe_4As_{12}$ are consistently understood in terms of SCR theory of spin fluctuations for week itinerant ferromagnets.

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