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High field nuclear magnetic resonance in transition metal substituted BaFe_2As_2

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We report high field ^{75}As nuclear magnetic resonance (NMR) measurements on Co and Cu substituted BaFe_2As_2 single crystals displaying same structural/magnetic transition $T_0 \simeq 128$ K. From our anisotropy studies in the paramagnetic state, we strikingly found virtually identical quadrupolar splitting and consequently the quadrupole frequency $\nu_Q \simeq 2.57(1)$ MHz for both compounds, despite the claim that each Cu delivers 2 extra $3d$ electrons in BaFe_2As_2 compared to Co substitution. These results allow us to conclude that a subtle change in the crystallographic structure, particularly in the Fe–As tetrahedra, must be the most probable tuning parameter to determine T_0 in this class of superconductors rather than electronic doping. Furthermore, our NMR data around T_0 suggest coexistence of tetragonal/paramagnetic and orthorhombic/antiferromagnetic phases between the structural and the spin density wave magnetic phase transitions, similarly to what was reported for K-doped BaFe_2As_2 [Urbano *et al.*, Phys. Rev. Lett. **105**, 107001 (2010)].
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I. INTRODUCTION

The Fe-based superconductors attracted great interest of the scientific community in the last few years because of their rich phase diagrams and unusual superconducting pairing mechanism.² In particular, the nature of the spin density wave (SDW) magnetic order which is usually preceded by a tetragonal-to-orthorhombic structural transition raised many debates among researchers due to its dubious and inconclusive first or second order character.² Superconductivity commonly emerges near the SDW order and, for some particular chemical substitution and/or pressure range, it is found to coexist microscopically with this magnetic phase. Furthermore, it seems to be a consensus that magneto-elastic effects must play an important role on the high temperature transitions and so in the superconductivity of Fe-arsenides.^{2–4} Such magneto-elastic effects may be even more crucial to explain the suppression of T_0 by either applying pressure or Fe isovalent substitution, when no effective electronic doping actually occurs. Moreover, there is increasing evidence that some chemical substitutions do not introduce delocalized electronic carriers into the system,^{5,6} but rather promote subtle changes in the local crystal electric field (CEF) configuration.^{7,8} It has been shown that such change in the CEF is indeed an important parameter and must be taken into account when determining the physical properties of this family of materials.^{4,8} Nonetheless, this issue remains controversial despite the enormous theoretical and experimental effort.²

In this work, we carried out high field ^{75}As nuclear magnetic resonance (NMR) measurements on transition metal

substituted $\text{BaFe}_{2-x}\text{M}_x\text{As}_2$ single crystals ($M = \text{Co}, \text{Cu}$) in order to further explore the scenario depicted above. NMR is a very suitable technique to probe local effects because it is site specific and sensitive to both electronic charge distribution and magnetic spin. Therefore, we intentionally chose specific concentrations of Co and Cu in our BaFe_2As_2 crystals so that they present the same structural/magnetic transition temperature T_0 . Our NMR results suggests a coexistence of tetragonal/paramagnetic and orthorhombic/antiferromagnetic phases around this critical temperature. More remarkably, our data demonstrate that subtle changes in the Fe $3d$ crystal electric field configuration must be occurring when one replaces Fe by other transition metals as Co^{2+} ($3d^7$) and Cu^{2+} ($3d^9$) in BaFe_2As_2 (Ba122).

II. METHODS

Single crystals of $\text{BaFe}_{2-x}\text{M}_x\text{As}_2$ ($M = \text{Co}, \text{Cu}$) were grown by In-flux growth method as described elsewhere.⁹ The crystals are typically $2.0 \times 2.0 \times 0.05$ mm³ thin platelets with the c -axis perpendicular to the sample basal plane. We performed energy dispersive spectroscopy (EDS) experimentes in order to determine the actual M concentration of the substituted M atoms. Electrical resistivity was measured using a conventional four probe technique with a Quantum Design PPMS-14T. NMR experiments were carried out at the National High Magnetic Field Laboratory (NHMFL) in Tallahassee, FL, using a NMR probe equipped with a goniometer for fine alignment of the crystallographic axes with respect to the external applied magnetic field. The field-swept ^{75}As NMR spectra ($I = 3/2$; $\gamma/2\pi = 7.2919$ MHz/T) were obtained by summing the Fourier transform of the spin-echo signal stepwise.

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III. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 shows the normalized electrical resistivity ρ_{ab} as function of temperature for both $\text{BaFe}_{1.99}\text{Cu}_{0.01}\text{As}_2$ (Cu122) and $\text{BaFe}_{1.99}\text{Co}_{0.01}\text{As}_2$ (Co122) at zero applied magnetic field. Both samples display $T_0 \simeq 128$ K, as shown by the pronounced peak in the curves. The difference between the curves below T_0 is presumably due to the presence of Cu^{2+} local moments¹⁰ that may contribute to the electronic scattering at low temperature. Such local moments are believed to be absent in Co substituted Ba122.

Figures 2(a) and 2(b) present the angular dependence of the ^{75}As spectrum at 150 K for both Co and Cu-doped Ba122 single crystals, respectively. The solid lines represent the NMR frequencies ν given by

$$\begin{aligned} \nu_{m \leftrightarrow m-1} = & \mu_0^{75}\gamma(1 - K^i)H_{\text{eff}} \\ & + \frac{\nu_{zz}}{2}(m - 1/2)(3 \cos^2\theta - 1 + \eta \sin^2\theta \cos 2\phi) \\ & + 2^{\text{nd}} \text{ order corrections.} \end{aligned} \quad (1)$$

The first term in Eq. (1) is the effective field H_{eff} and K^i is the knight shift along the i -axis. The second term is the 1st order quadrupolar shift for the three allowed transitions ($\Delta m = \pm 1$). The asymmetry parameter of the electric field gradient (EFG) is defined as $\eta = (\nu_{xx} - \nu_{yy})/\nu_{zz}$.

The ^{75}As NMR spectra ($I = 3/2$) show a sharp single central transition ($k + 1/2 \leftrightarrow -1/2$) with slightly broader satellite peaks from the ($\pm 1/2 \leftrightarrow \pm 3/2$) transitions. We should emphasize that the linewidths of the central peak, $\Delta\nu_{\text{Co}} \simeq 9(1)$ kHz and $\Delta\nu_{\text{Cu}} \simeq 15(1)$ kHz, are found to be very narrow considering substituted samples. This is an indicative that the employed In-flux growth technique is suitable for yielding high-quality chemically substituted BaFe_2As_2 .

In the paramagnetic (PM) state at 150 K, $\nu_{zz} = \nu_Q$ and $\eta = 0$ due to the high symmetry of the tetragonal phase

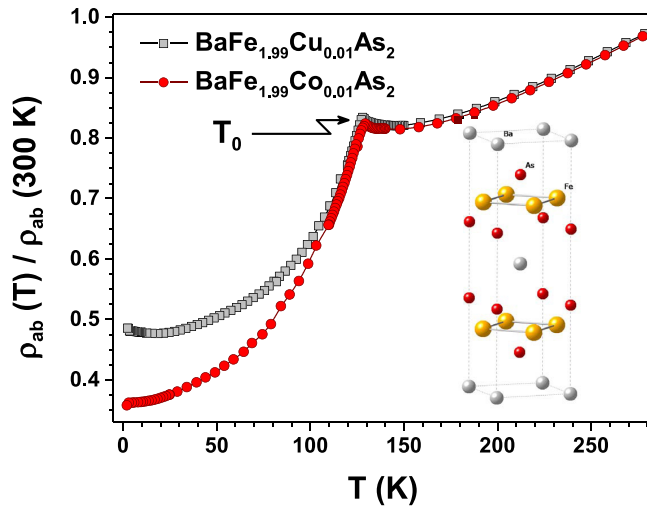


FIG. 1. Normalized in-plane resistivity as a function of temperature for both Co and Cu-doped BaFe_2As_2 single crystals. The peaks define $T_0 \simeq 128$ K. Lines are guide to the eyes. The tetragonal crystallographic structure of BaFe_2As_2 in the PM phase is also presented.

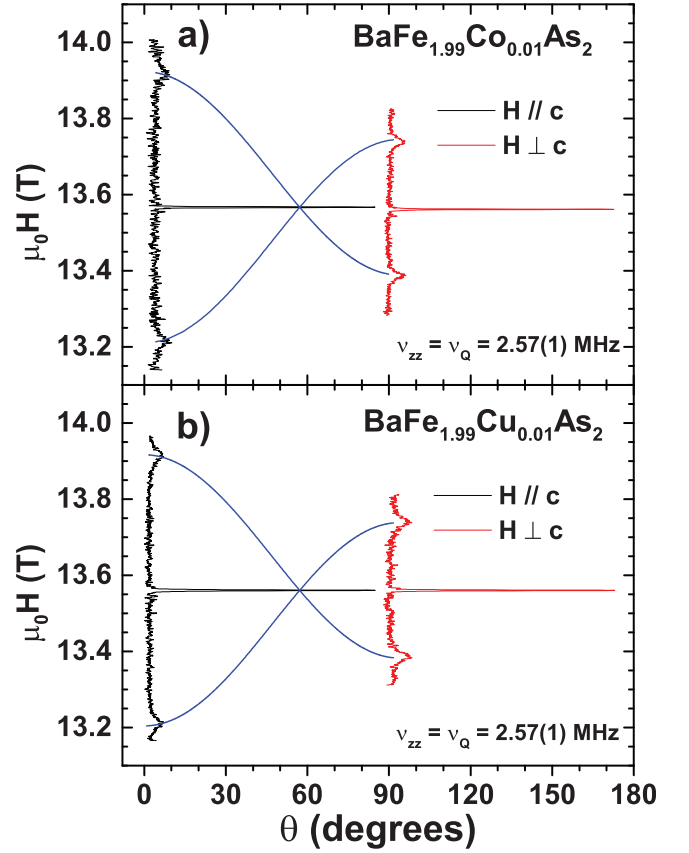


FIG. 2. High field ^{75}As NMR spectra at 150 K with $H \simeq 13.5630$ T ($\nu = 99.3070$ MHz) for (a) Co and (b) Cu-doped BaFe_2As_2 . The spectra present three main peaks arising from $m = 3/2$, $1/2$, and $-1/2$ transitions ($I = 3/2$). Solid blue lines are fits to the angular dependence of the satellite lines with Eq. (1) described in the text.

($\nu_{xx} = \nu_{yy} = \nu_{zz}/2$). Thus, from the fits (solid lines) shown in Fig. 2 we extracted the quadrupole frequency $\nu_Q \simeq 2.57(1)$ MHz for both samples. This ν_Q is slightly larger ($\sim 5\%$) than $\nu_Q \simeq 2.44(1)$ MHz observed for our pure compound also grown by In-flux method and confirms previous claiming that ν_Q increases with substitution.¹ This means that either Co or Cu substitution in Ba122 create virtually the same quadrupole splitting despite the apparent electronic doping difference in these samples. In fact, Cu substitution in $\text{Ba}(\text{Fe}_{1-x}\text{M}_x)_2\text{As}_2$ was claimed to introduce $3x$ extra electrons per Fe compared to a single x extra electron in Co substitution.¹¹ The quadrupole splitting is proportional to the EFG at the As site, V_{zz} , through the relation $\nu_Q = eQV_{zz}/2\sqrt{1 + \eta^2/3}$, where η is the asymmetry parameter of the EFG ($\eta = 0$ in the PM phase).^{1,12} V_{zz} arises from the hybridization between the As-4p and the Fe-3d orbitals and, thus, ν_Q must be directly proportional to the Fe-As distance/angle. Therefore, chemical substitution will modify the EFG in BaFe_2As_2 , i.e., will change its structural environment and, as a conclusion, ν_Q may be considered a very sensitive control parameter in this class of superconductors rather than electronic doping.

Figure 3 shows the central transition of the high field ^{75}As -NMR spectra of Cu and Co-doped BaFe_2As_2 with $H \perp c$ at temperatures around T_0 . The sharp central transition for temperatures above T_0 represents the ^{75}As -NMR signal in

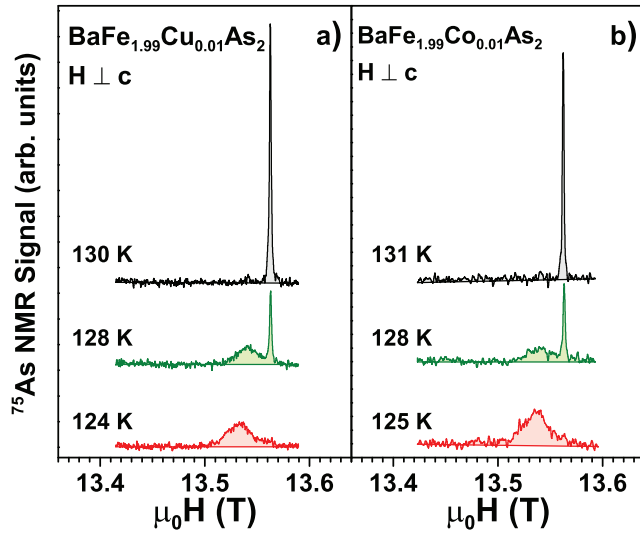


FIG. 3. Central transition ($+1/2 \leftrightarrow -1/2$) of the ^{75}As NMR spectrum for temperatures around T_0 and applied magnetic field $H \perp c$ for Cu and Co-doped BaFe_2As_2 . Phase coexistence is evident as revealed by the 2 distinct peaks in the same spectrum.

the tetragonal phase in the PM state. This peak displays an inexpressive shift as a function of temperature. Right below T_0 , the spectra reveals a sudden appearance of a broad line at slightly lower magnetic fields coexisting with the narrow line within a 5 K temperature range. The broad peak then grows and shifts rapidly, while the sharp peak is suppressed with further decreasing temperature. We define this temperature as the onset of the structural tetragonal-orthorhombic transition (namely, T_S) coexisting with the emergence of the broad central transition of the orthorhombic/magnetic phase. The sharp line completely disappears at a temperature that we define as T_{SDW} and only the broad peak related to the SDW long range ordered phase remains below this temperature. This behavior is similar for both Cu and Co doping and, although premature, one can affirm that it is exactly the same as previously observed for K-doped Ba122 .¹

IV. CONCLUSIONS

In summary, we have performed high field ^{75}As NMR experiments on high quality $\text{BaFe}_{2-x}(\text{Co}, \text{Cu})_x\text{As}_2$ single crystals with the same structural/magnetic T_0 transition temperature in order to shed new light on the issue regarding the role of chemical substitution in iron arsenide materials.

We obtained the same quadrupole frequency $\nu_Q \simeq 2.57(1)$ MHz for both Co122 and Cu122 samples. The lower T_0 and larger ν_Q values if compared to those found for the undoped Ba122 certify the incorporation of the dopants into the Fe sites in the lattice. Our high field NMR results also suggest coexistence of tetragonal/PM and orthorhombic/SDW phases within a ~ 5 K range of temperature below the

structural transition $T_S \simeq 130(1)$ K for both Cu and Co samples.

Therefore, the NMR results presented here demonstrate that the replacement of Fe by other transition metals, such as Co and Cu in BaFe_2As_2 , creates small distortions in the lattice modifying the distance between Fe and As atoms and so the hybridization between the Fe 3d and As 4p orbitals. This local effect seems to be way more relevant for the structural and magnetic transitions than the effective electronic doping introduced by the chemical substitution and would be very consistent with the tuning of distinct ground states in the phase diagrams for this family of materials as well as the emergence of superconductivity at the edge of the magnetic ordered phase by either applying pressure or Fe isovalent substitution. Our results might be relevant to improve our understanding of the interplay between the structural and magnetic degrees of freedom in these iron-arsenide materials.

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- ¹R. R. Urbano, E. L. Green, W. G. Moulton, A. P. Reyes, P. L. Kuhns, E. M. Bittar, C. Adriano, T. M. Garitezi, L. Bufaiçal, and P. G. Pagliuso, *Phys. Rev. Lett.* **105**, 107001 (2010).
- ²J. Paglione and R. L. Greene, *Nature Phys.* **6**, 645 (2010).
- ³V. Barzykin and L. P. Gor'kov, *Phys. Rev. B* **79**, 134510 (2009).
- ⁴E. Granado, L. Mendonça Ferreira, F. Garcia, G. d. M. Azevedo, G. Fabbri, E. M. Bittar, C. Adriano, T. M. Garitezi, P. F. S. Rosa, L. F. Bufaiçal, M. A. Avila, H. Terashita, and P. G. Pagliuso, *Phys. Rev. B* **83**, 184508 (2011).
- ⁵E. M. Bittar, C. Adriano, T. M. Garitezi, P. F. S. Rosa, L. Mendonça Ferreira, F. Garcia, G. d. M. Azevedo, P. G. Pagliuso, and E. Granado, *Phys. Rev. Lett.* **107**, 267402 (2011).
- ⁶S. Ideta, T. Yoshida, I. Nishi, A. Fujimori, Y. Kotani, K. Ono, Y. Nakashima, S. Yamaichi, T. Sasagawa, M. Nakajima, K. Kihou, Y. Tomioka, C. H. Lee, A. Iyo, H. Eisaki, T. Ito, S. Uchida, and R. Arita, *Phys. Rev. Lett.* **110**, 107007 (2013).
- ⁷Z. P. Yin, K. Haule, and G. Kotliar, *Nature Mater.* **10**, 932 (2011).
- ⁸P. F. S. Rosa, C. Adriano, W. Iwamoto, T. M. Garitezi, T. Grant, Z. Fisk, and P. G. Pagliuso, *Phys. Rev. B* **86**, 165131 (2012).
- ⁹T. M. Garitezi, C. Adriano, P. F. S. Rosa, E. M. Bittar, L. Bufaiçal, R. L. de Almeida, E. Granado, T. Grant, Z. Fisk, M. A. Avila, R. A. Ribeiro, P. L. Kuhns, A. P. Reyes, R. R. Urbano, and P. G. Pagliuso, *Brazilian J. Phys.* **43**, 223 (2013).
- ¹⁰P. F. S. Rosa, C. Adriano, T. M. Garitezi, T. Grant, Z. Fisk, R. R. Urbano, and R. R. Fernandes e P. G. Pagliuso, "Unconventional superconductivity in substituted BaFe_2As_2 revealed by pair-breaking studies," *Nature Scientific Reports* (submitted).
- ¹¹N. Ni, A. Thaler, J. Q. Yan, A. Kracher, E. Colombier, S. L. Bud'ko, P. C. Canfield, and S. T. Hannahs, *Phys. Rev. B* **82**, 024519 (2010).
- ¹²R. R. Urbano, E. L. Green, W. G. Moulton, A. P. Reyes, P. L. Kuhns, E. M. Bittar, C. Adriano, and P. G. Pagliuso, *J. Phys.: Conf. Ser.* **273**, 012107 (2011).