First order magnetic transition in single crystal CaFe$_2$As$_2$ detected by $^{75}$As NMR

S.-H. Baek,$^{1}$ N. J. Curro,$^{2}$ T. Klimczuk,$^{1,3}$ E. D. Bauer,$^{1}$ F. Ronning,$^{1}$ and J. D. Thompson$^{1}$

$^1$Los Alamos National Laboratory, Los Alamos, NM 87545, USA
$^2$Department of Physics, University of California, Davis, CA 95616, USA
$^3$Faculty of Applied Physics and Mathematics, Gdansk University of Technology, Narutowicza 11/12, 80-952 Gdansk, Poland

(Dated: November 18, 2008)

We report $^{75}$As Nuclear Magnetic Resonance data in a single crystal of CaFe$_2$As$_2$. The Knight shift, electric field gradient, and spin-lattice relaxation rate are strongly temperature dependent in the paramagnetic state, and change discontinuously at the structural transition temperature, $T_s = T_N = 167$ K. Immediately below, the NMR spectra reveal an internal field at the As site associated with the presence of a commensurate magnetic order. These results indicate that the magnetic and structural transitions in CaFe$_2$As$_2$ are first order and strongly coupled, and that the electron density in the FeAs plane is highly sensitive to the out-of-plane structure.

The discovery of superconductivity in LaFeAsO$_{1-x}$F$_x$ with $T_c = 26$ K [1] has attracted interest due to structural and magnetic similarities with high-$T_c$ cuprates. To date, much effort has been devoted to the search for new iron-based compounds exhibiting an even higher $T_c$. By replacing La with other rare earths, such as Sm [2, 3, 4], Ce [5], and Nd [6], $T_c$ has been raised to 55 K for Sm and to 54 K in the oxygen deficient RFeAsO$_{1-\delta}$ systems ($R=$ Nd [7], Gd [8]). In both cases, the magnetic and structural transitions in the undoped parent material are suppressed before entering the superconducting phase. Further studies have shown that the ternary FeAs compounds AFe$_2$As$_2$ ($A=$Ba, Sr, Eu, and Ca) share similar magnetic and structural properties as the RFeAsO parent compound [9-13], and exhibit superconductivity by doping A with K or Na [10, 14-16, 17] or by applying pressure [18, 19, 20] to suppress the magnetic and structural anomalies. These similarities suggest that the physics of both families of materials is dominated by FeAs layers and that ‘intercalated’ layers serve primarily as tunable charge reservoirs.

Because single crystals of the ternary compounds grow more easily and have a simpler structure than the quaternary compounds, they appear to be an ideal system to investigate the Fe-based superconductors. They form in the well-known ThCr$_2$Si$_2$-type crystal structure and undergo a spin-density wave transition which accompanies a structural transition from tetragonal I4/mmm to orthorhombic Fmmm. Neutron-diffraction studies find an ordered Fe moment of about $1 \mu_B$ that develops along the orthorhombic a axis with antiferromagnetic (AFM) wave vector $Q = (0, 0, 0)$ [21-22]. Superficially, we might expect, then, that the relationship among structure, static magnetic order, and spin dynamics would depend only weakly on the isovalent A atom. Establishing this expectation would provide a common framework for theoretical models of the parent compounds. As we will show, though, there are significant differences among the AFe$_2$As$_2$ materials.

In this Letter, we present $^{75}$As nuclear magnetic resonance (NMR) data in a single crystal of CaFe$_2$As$_2$. In addition to providing unambiguous evidence for a first order spin-density wave (SDW) instability that occurs simultaneously with a first order structural transition, these studies show that, in contrast to most bulk measurements, the low energy static and dynamic NMR properties (Knight shift, electric field gradient (EGF), and $T_1^{-1}$) differ significantly from the isostructural BaFe$_2$As$_2$ material.

Single crystals of CaFe$_2$As$_2$ (Ca122) were grown in Sn flux, using a slightly different recipe than described in Ref. [13]. The starting elements were placed in an alumina crucible and sealed under vacuum in a quartz ampoule. The ampoule was placed in a furnace and heated to $600 \degree C$ at $100 \degree C/hr$, and held at that temperature for 4 hours. This sequence was repeated at $900 \degree C$ and at a maximum temperature of $1075 \degree C$, with hold times of 4 hr, each. The sample was then cooled slowly ($7 \degree C/hr$) to $650 \degree C$, at which point the excess Sn flux was removed with the aid of a centrifuge. The resulting crystals, which form in the tetragonal ThCr$_2$Si$_2$ structure that can be viewed as layers of Ca capped by Fe-As tetrahedra along the c-axis, exhibit a first order transition at $167 \degree K$, which is slightly lower than $171 \degree K$ in Ref. [13]. This may indicate that the transition temperature is affected weakly by subtle changes in the growth condition or by the exact amount of substitutional Sn that is incorporated into the crystal from the Sn flux out of which crystals grow. However, Ca122 seems to tolerate little Sn doping, unlike BaFe$_2$As$_2$ in which the transition temperature is suppressed to $85 \degree K$ from $140 \degree K$ in Sn-free samples [10]. Regardless of the slightly lower transition temperature, the magnetic susceptibility $\chi(T)$ shows similar temperature and field dependences, and the resistivity data confirm the same anomaly at $167 \degree K$ and its thermal hysteresis as previously reported [13], indicating comparable quality of these single crystals.

Fig. 1(a) shows NMR spectra of $^{75}$As ($I = 3/2$) at $170 \degree K$ and at a fixed resonance frequency of $45 \mathrm{MHz}$, for both $H \parallel c$ (blue lines) and $H \perp c$ (red lines). The spectra are fit well by a nuclear Hamiltonian: $H = \gamma h (1 + K_\alpha) I_x H_0 + h \nu_c / 6 (I_0^2 - 1) + \eta (I_0^2 - I_0^4)$, where...
As NMR spectra in the paramagnetic state at a fixed frequency of 45 MHz. (a) Full spectra with satellites associated with both $H \perp c$ (red lines) and $H \parallel c$ (blue lines) obtained at 170 K. (b) Central transition spectra for both field orientations as a function of temperature. For $H \perp c$ (red), the strong temperature dependence of $\nu_Q$ dominates the line position. The inset shows $K$ vs. $T$ for $H \parallel c$ (blue) and $H \perp c$ (red), as well as $\nu_Q = \nu_c$ (yellow).

$K_\alpha$ is the magnetic shift in the $\alpha$ direction, $a, b, c$ are the unit cell axes, $\nu_c$ is the EFG in the $c$ direction, $\eta$ is the anisotropy factor, and the NQR frequency is given by $\nu_Q = \nu_c \sqrt{1 + \eta^2/3}$. We find that $\nu_c = 13.93$ MHz and $\eta = 0$ with the principal axis of the EFG tensor along the $c$-direction in the paramagnetic state at $T = 170$ K. This value is nearly 500% larger than $\nu_Q$ measured in BaFe$_2$As$_2$ [24, 27]. By measuring the temperature dependence of the satellite transition ($I = \pm \frac{3}{2} \leftrightarrow \pm \frac{1}{2}$) for $H \parallel c$ (not shown), we extract the temperature dependence of $\nu_c(T)$, shown in the inset of Fig. 1(b). The EFG increases by 16% between room temperature and $T_N$. This behavior contrasts sharply with that observed in BaFe$_2$As$_2$, where $\nu_c(T)$ decreases by the same amount over the same temperature range as shown in the inset of Fig. 3. The EFG at the As site is given by the sum of a lattice term ($\nu_l^\text{lattice} \propto 1/V_{\text{cell}}$) and an on-site term $\nu_l^\text{on-site}$. The changes in $\nu_c$ we observe far exceed the change of the unit cell volume $V_{\text{cell}}$ between both compounds and the lattice contraction over this range of temperature [13, 28], therefore the dominant contribution to the EFG must be on-site charge distribution in the As 4p orbitals. In contrast with the cuprates, our results indicate that the charge distribution in the FeAs planes changes dramatically from one material to the other, and probably reflects the sensitivity of the ground state to pressure. In fact, pressure-induced superconductivity is found at the relatively modest pressure of 0.4–0.8 GPa in CaFe$_2$As$_2$ compared to 2.8–3.5 GPa in SrFe$_2$As$_2$ and 2.5–5.5 GPa in BaFe$_2$As$_2$ [18, 19, 20]. These results may reflect different amounts of charge donation from the ionic layer.

The temperature dependences of the central transition in the paramagnetic (PM) state are shown in Fig. 1(b). The Knight shift ($K$) reveals a strong anisotropy of the spin susceptibility, as shown in the inset of Fig. 1(b). Like BaFe$_2$As$_2$, $K_{ab} > K_c$ suggests that the spin susceptibility is greater in the plane, which is also the case for LaO$_{0.9}$F$_{0.1}$FeAs [29]. In contrast, however, we find that $K_{ab}$ exhibits a shallow upturn just above $T_N$. The origin of this behavior is not understood. We have not attempted to extract the hyperfine coupling in CaFe$_2$As$_2$ since the susceptibility shows a strong paramagnetic impurity contribution.

At 167 K, we observe an abrupt change of the spectrum, as shown in Fig. 2. Both the central and satellite resonances are split by an internal field $H_{\text{int}}$ as a result of the hyperfine coupling between the As nuclei.

FIG. 2: Temperature dependences of $^{75}$As NMR spectra below the transition for $H \parallel c$. The spectra (blue lines) in the paramagnetic state split to six lines by the internal field $H_{\text{int}}$ in the ordered state. The red solid and dotted lines represent the split central lines and the satellites associated with each central line, respectively. One of satellites at highest fields was not measured due to the limited maximum field (9 T) in our magnet. Horizontal line (gray) denotes $T_N = T_S = 167$ K.

$K_\alpha$ is the magnetic shift in the $\alpha$ direction, $a, b, c$ are the unit cell axes, $\nu_c$ is the EFG in the $c$ direction, $\eta$ is the anisotropy factor, and the NQR frequency is given by $\nu_Q = \nu_c \sqrt{1 + \eta^2/3}$. We find that $\nu_c = 13.93$ MHz and $\eta = 0$ with the principal axis of the EFG tensor along the $c$-direction in the paramagnetic state at $T = 170$ K. This value is nearly 500 % larger than $\nu_Q$ measured in BaFe$_2$As$_2$ [24, 27]. By measuring the temperature dependence of the satellite transition ($I = \pm \frac{3}{2} \leftrightarrow \pm \frac{1}{2}$) for $H \parallel c$ (not shown), we extract the temperature dependence of $\nu_c(T)$, shown in the inset of Fig. 1(b). The EFG increases by 16% between room temperature and $T_N$. This behavior contrasts sharply with that observed in BaFe$_2$As$_2$, where $\nu_c(T)$ decreases by the same amount over the same temperature range as shown in the inset of Fig. 3. The EFG at the As site is given by the sum of a lattice term ($\nu_l^\text{lattice} \propto 1/V_{\text{cell}}$) and an on-site term $\nu_l^\text{on-site}$. The changes in $\nu_c$ we observe far exceed the change of the unit cell volume $V_{\text{cell}}$ between both compounds and the lattice contraction over this range of temperature [13, 28], therefore the dominant contribution to the EFG must be on-site charge distribution in the As 4p orbitals. In contrast with the cuprates, our results indicate that the charge distribution in the FeAs planes changes dramatically from one material to the other, and probably reflects the sensitivity of the ground state to pressure. In fact, pressure-induced superconductivity is found at the relatively modest pressure of 0.4–0.8 GPa in CaFe$_2$As$_2$ compared to 2.8–3.5 GPa in SrFe$_2$As$_2$ and 2.5–5.5 GPa in BaFe$_2$As$_2$ [18, 19, 20]. These results may reflect different amounts of charge donation from the ionic layer.

The temperature dependences of the central transition in the paramagnetic (PM) state are shown in Fig. 1(b). The Knight shift ($K$) reveals a strong anisotropy of the spin susceptibility, as shown in the inset of Fig. 1(b). Like BaFe$_2$As$_2$, $K_{ab} > K_c$ suggests that the spin susceptibility is greater in the plane, which is also the case for LaO$_{0.9}$F$_{0.1}$FeAs [29]. In contrast, however, we find that $K_{ab}$ exhibits a shallow upturn just above $T_N$. The origin of this behavior is not understood. We have not attempted to extract the hyperfine coupling in CaFe$_2$As$_2$ since the susceptibility shows a strong paramagnetic impurity contribution.

At 167 K, we observe an abrupt change of the spectrum, as shown in Fig. 2. Both the central and satellite resonances are split by an internal field $H_{\text{int}}$ as a result of the hyperfine coupling between the As nuclei.
and the ordered Fe moments. Since the central line is split into two resonances rather than simply shifted to lower field, we conclude that $H_{\text{int}}$ is either parallel or antiparallel to $H$, the applied field. In this case, the resonance fields are given by $H_{\text{central}} = \nu_0/\gamma \pm H_{\text{int}}$ and $H_{\text{sat}} = (\nu_0 - \nu_c)/\gamma \pm H_{\text{int}}$. The temperature dependences of $\nu_c(T)$ and $H_{\text{int}}(T)$ are shown in Fig. 3. We find that $H_{\text{int}} = 2.6 \pm 0.1$ T, which is a factor of two larger than the value of 1.3 T observed in BaFe$_2$As$_2$ [27]. Furthermore, we see only one value of $|H_{\text{int}}|$, indicating a commensurate magnetic structure. If the magnetic structure were incommensurate with the lattice, then the internal field would be distributed and the spectrum would not exhibit the sharp resonances seen in Fig. 2. Recent neutron scattering results are consistent with our data [28].

We also observe a discontinuous decrease in $\nu_c(T)$ at $T_N$, which is very similar to the case in BaFe$_2$As$_2$ (inset, Fig. 3), although the value of $\nu_c$ and its temperature dependence in the PM state is clearly different. The reason for the difference in $\nu_c$ between these two isostructural compounds is unclear, but may reflect the extreme sensitivity of the electronic structure to the out-of-plane atoms. Clearly, both the magnetic order parameter, given by $H_{\text{int}}(T)$, and a measure of the structural distortion, given by $\Delta \nu_c(T) = |\nu_c(T) - \nu_c(T_N)|$, are discontinuous at $T_N$, indicating the first-order nature of the transition in CaFe$_2$As$_2$. Upon warming the sample from the ordered state, the paramagnetic signal is recovered at 168 K, revealing a thermal hysteresis of 1 K in excellent agreement with results from neutron diffraction [25]. We attribute the upturn in $(T_1 T)^{-1}$ at temperatures well above $T_N$ to dispersive (paramagnon) excitations that recent neutron scattering experiments find at temperatures well above $T_N$ (~ 200 K) [32]. At $T_N$ we observe a discontinuous jump in $(T_1 T)^{-1}$ in both field directions, providing further evidence for the first-order character of the magnetic transition. Below $T_N$, $T_1^{-1}$ decreases exponentially with decreasing temperature. Upon further cooling, $(T_1 T)^{-1}$ approaches a constant value, suggesting a partially gapped density of states at the Fermi level that is expected for a SDW ground state. Qualitatively, all three compounds, CaFe$_2$As$_2$, BaFe$_2$As$_2$, and LaOFeAs exhibit similar spin lattice relaxation behavior, yet the absolute values of $(T_1 T)^{-1}$ differ dramatically. This difference is surprising since the As probes the spin fluctuations in similar FeAs planes in all three cases. There are two possible explana-

![FIG. 3: Temperature dependences of the order parameters obtained from NMR spectra in the ordered state for $H \parallel c$. $H_{\text{sat}}$ is proportional to the sublattice magnetization, and is a measure of the magnetic order parameter, while $\Delta \nu_c \equiv |\nu_c(T) - \nu_c(T_N)|$ is a measure of the structural distortion. The inset shows the temperature dependences of $\nu_c(T)$ for both CaFe$_2$As$_2$ and BaFe$_2$As$_2$ (the latter is reproduced from Ref. [27]).](image)
data reveal a discontinuity at $T_\text{LaOF eAs}$ (reproduced from [30]) as a function of $T$. The data reveal a discontinuity at $T_N$ and the formation of a gap at the Fermi level due to the SDW instability, and supports the first-order character of the magnetic transition. Clearly, the spin dynamics in the paramagnetic state is a strong function of the particular material.

FIG. 4: $(T_1T)^{-1}$ for CaFe$_2$As$_2$, BaFe$_2$As$_2$ (Ref. 28) and LaOFeAs (reproduced from [30]) as a function of $T$. The data reveal a discontinuity at $T_N$ and the formation of a gap at the Fermi level due to the SDW instability, and supports the first-order character of the magnetic transition. Clearly, the spin dynamics in the paramagnetic state is a strong function of the particular material.

tions for this difference: either (i) the hyperfine coupling between the Fe and the As changes between compounds, or (ii) the spectral density of spin fluctuations changes. However, the hyperfine coupling extracted from plots of $K$ versus $\chi$ are roughly identical in LaO$_{1-x}$F$_x$FeAs and BaFe$_2$As$_2$. Therefore, we conclude that the spectral density of spin fluctuations differs significantly between these compounds. One might argue that the single plane LaO$_{1-x}$F$_x$FeAs should exhibit different physics than the double plane AF$_2$As$_2$ compounds, but apparently the spin fluctuations even differ for different $A$ atoms. This result points to the extreme sensitivity of the low energy excitations in these materials to the particular structure of the out of plane atoms and the external pressure.

In conclusion, we have found that the magnetic and structural transitions occur simultaneously at 167 K in single crystal CaFe$_2$As$_2$. The antiferromagnetic transition is clearly first order and commensurate. Also, the discontinuous formation of the gap associated with a spin-density wave instability at 167 K was directly demonstrated by $T_1^{-1}$ measurements. Comparison with isostructural BaFe$_2$As$_2$ and another parent compound LaOFeAs, demonstrates the extreme sensitivity of both the static ($\nu_0$) and the dynamic ($(T_1T)^{-1}$) properties to the out-of-plane structure. Understanding this sensitivity and its ultimate connection to superconductivity may shed light on the optimal microscopic conditions for the highest $T_c$.

We thank Stuart Brown, Tuson Park, and Hanoh Lee for useful and delightful discussions. Work at Los Alamos National Laboratory was performed under the auspices of the US Department of Energy, Office of Science.