First-order magnetic transition in single-crystalline $CaFe_2As_2$ detected by ^{75}As nuclear magnetic resonance

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We report ^{75}As nuclear magnetic resonance (NMR) data in a single crystal of $CaFe_2As_2$. 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 structural and magnetic transitions in $CaFe_2As_2$ are first order and strongly coupled, and that the electron density in the FeAs plane is highly sensitive to the out-of-plane structure.

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The discovery of superconductivity in $LaFeAsO_{1-x}F_x$ with $T_c=26$ K (Ref. 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,[2–4] 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 (Ref. 7) and Gd (Ref. 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_2As_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 (Refs. 9 and 14–17) or by applying pressure[18–20] to suppress the magnetic and the 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 $ThCr_2Si_2$-type crystal structure and undergo a spin-density wave (SDW) 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 (1,0,1).[21–25] 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_2As_2 materials.

In this report, we present ^{75}As nuclear magnetic resonance (NMR) data in a single crystal of $CaFe_2As_2$. In addition to providing unambiguous evidence for a first-order 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 (EFG), and T_1^{-1}] differ significantly from the isostructural $BaFe_2As_2$ material.

Single crystals of $CaFe_2As_2$ (Ca122) were grown in Sn flux using a slightly different recipe than described in Ref. 12. The starting elements were placed in an alumina crucible and sealed under vacuum in a quartz ampule. The ampule was placed in a furnace and heated to 600 °C at 100 °C/h and held at that temperature for 4 h. This sequence was repeated at 900 °C and at a maximum temperature of 1075 °C, with hold times of 4 h, each. The sample was then cooled slowly (7 °C/h) to 650 °C, at which point the excess Sn flux was removed with the aid of a centrifuge. The resulting crystals, which form in the tetragonal $ThCr_2Si_2$ 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 K, which is slightly lower than 171 K in Ref. 12. 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 $BaFe_2As_2$, in which the transition temperature is suppressed to 85 K from 140 K in Sn-free samples.[9] 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 K and its thermal hysteresis as previously reported,[12] indicating comparable quality of these single crystals.

Figure 1(a) shows NMR spectra of ^{75}As ($I=3/2$) at 170 K and at a fixed resonance frequency of 45 MHz for both $H \parallel c$ (blue/dark gray lines) and $H \perp c$ (red/light gray lines). The spectra are fit well by a nuclear Hamiltonian $\mathcal{H}=\gamma\hbar(1+K_\alpha)\hat{I}_\alpha H_0+h\nu_c/6[(3\hat{I}_c^2-1)+\eta(\hat{I}_a^2-\hat{I}_b^2)]$, where K_α is the magnetic shift in the α direction, a,b,c are the unit-cell axes, ν_c is the EFG in the c direction, η is the anisotropy factor, and the nuclear quadrupole resonance (NQR) frequency is given

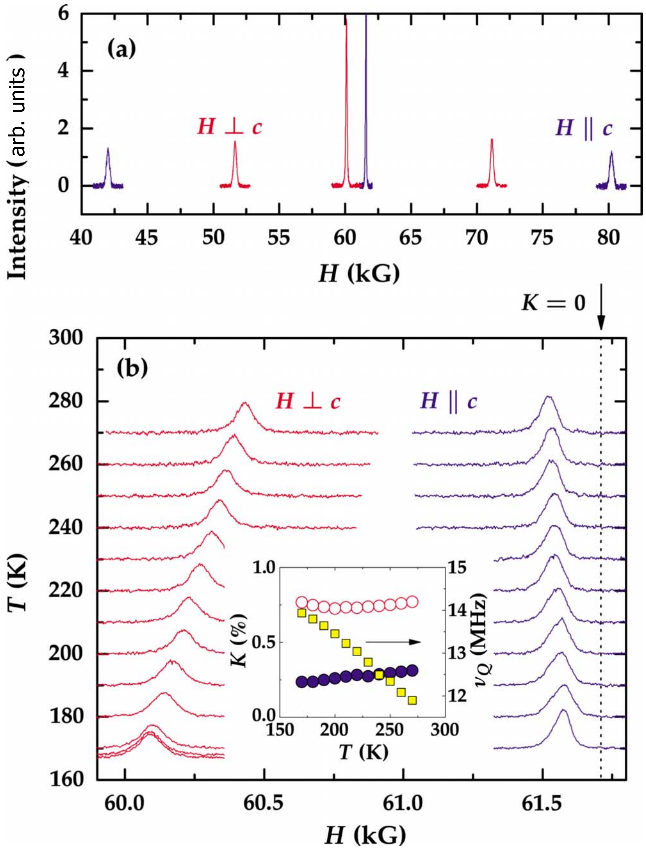

FIG. 1. (Color online) ^{75}As NMR spectra in the paramagnetic state at a fixed frequency of 45 MHz. (a) Full spectra with satellites associated with both $H\perp c$ (red/light gray lines) and $H\parallel c$ (blue/dark gray lines) obtained at 170 K. (b) Central transition spectra for both field orientations as a function of temperature. For $H\perp c$ (red/light gray hollow circles), the strong temperature dependence of ν_Q dominates the line position. The inset shows K vs T for $H\parallel c$ (blue/dark gray filled circles) and $H\perp c$ (red/light gray hollow circles), as well as $\nu_Q=\nu_c$ (yellow/gray squares).

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 (PM) state at $T=170$ K. This value is nearly 500% larger than the ν_Q measured in $BaFe_2As_2$.[26,27] By measuring the temperature dependence of the satellite transition ($I=+\frac{3}{2}\leftrightarrow+\frac{1}{2}$) for $H\parallel c$ (not shown), we extract the temperature dependence of $\nu_c(T)$, as 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 $BaFe_2As_2$, 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 ($\nu_c^{\mathrm{lattice}}\propto 1/V_{\mathrm{cell}}$) and an on-site term $\nu_c^{\mathrm{on\text{-}site}}$. The changes in ν_c that we observe far exceed the change in the unit-cell volume V_{cell} between both compounds and the lattice contraction over this range of temperature;[12,28] therefore the dominant contribution to the EFG must be the on-site charge distribution in the As $4p$ orbitals. In contrast to 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

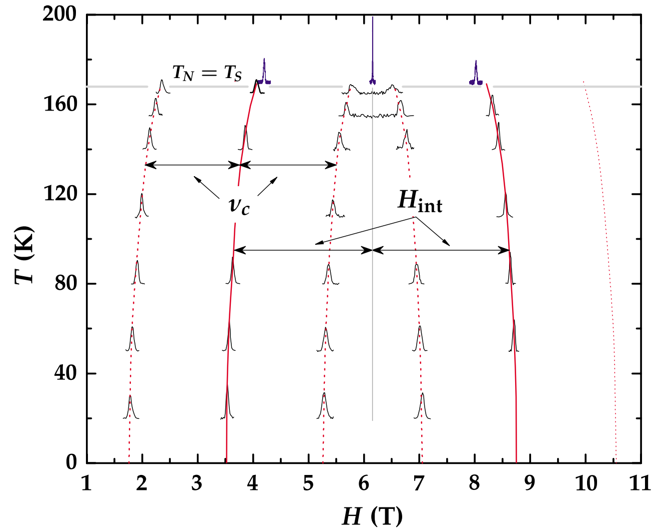

FIG. 2. (Color online) Temperature dependences of ^{75}As NMR spectra below the transition for $H\parallel c$. The spectra (blue/dark gray lines) in the paramagnetic state split to six lines by the internal field H_{int} in the ordered state. The red/gray solid and dotted lines represent the split central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

state to pressure. In fact, pressure-induced superconductivity is found at the relatively modest pressure of 0.4–0.8 GPa in $CaFe_2As_2$ compared to 2.8–3.5 GPa in $SrFe_2As_2$ and 2.5–5.5 GPa in $BaFe_2As_2$.[18–20] These results may reflect different amounts of charge donation from the ionic layer.

The temperature dependences of the central transition in the 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 $BaFe_2As_2$, $K_{ab}>K_c$ suggests that the spin susceptibility is greater in the plane, which is also the case for $LaFeAsO_{0.9}F_{0.1}$.[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 $CaFe_2As_2$ since the susceptibility shows a strong paramagnetic impurity contribution.

At 167 K, we observe an abrupt change in the spectrum, as shown in Fig. 2. Both the central and satellite resonances are split by an internal field H_{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 $\mathbf{H}_{\mathrm{int}}$ is either parallel or antiparallel to $\mathbf{H}$, which is the applied field. In this case, the resonance fields are given by $H_{\mathrm{central}}=\nu_0/\gamma\pm H_{\mathrm{int}}$ and $H_{\mathrm{sat}}=(\nu_0-\nu_c)/\gamma\pm H_{\mathrm{int}}$. The temperature dependences of $\nu_c(T)$ and $H_{\mathrm{int}}(T)$ are shown in Fig. 3. We find that $H_{\mathrm{int}}=2.6\pm0.1$ T, which is a factor of 2 larger than the value of 1.3 T observed in $BaFe_2As_2$.[26] Furthermore, we see only one value of $|H_{\mathrm{int}}|$, 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.[25]

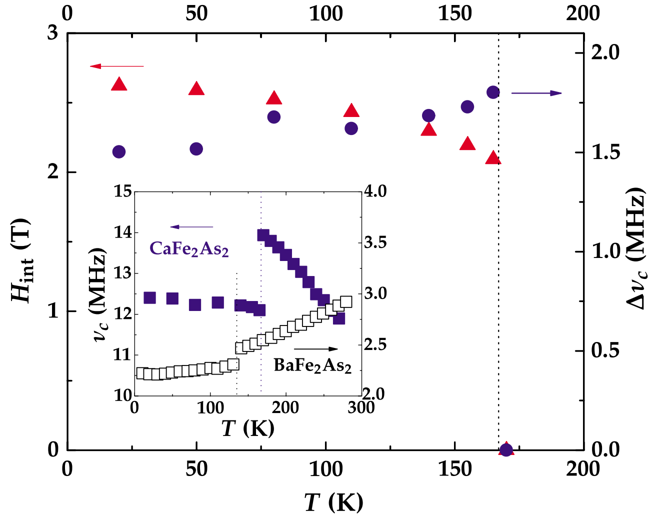

FIG. 3. (Color online) Temperature dependences of the order parameters obtained from NMR spectra in the ordered state for $H \parallel c$. H_{int} is proportional to the sublattice magnetization and is a measure of the magnetic order parameter, while $\Delta\nu_c \equiv |\nu_c(T) - \nu_c(T_N)|$ is a measure of the structural distortion. The inset shows the temperature dependences of $\nu_c(T)$ for both $CaFe_2As_2$ and $BaFe_2As_2$ (the latter is reproduced from Ref. 26).

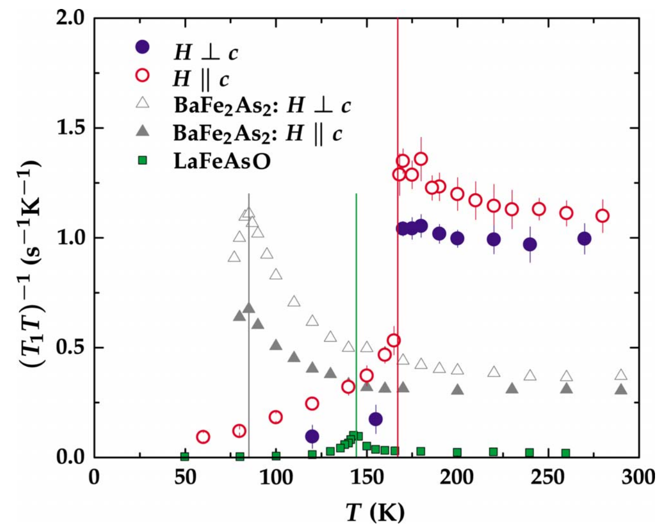

FIG. 4. (Color online) $(T_1T)^{-1}$ for $CaFe_2As_2$, $BaFe_2As_2$ (Ref. 27), and LaFeAsO (reproduced from Ref. 30) as a function of T. The data reveal a discontinuity at T_N and the formation of a gap at the Fermi level due to the SDW instability and supports the first-order character of the magnetic transition. Clearly, the spin dynamics in the paramagnetic state is a strong function of the particular material.

We also observe a discontinuous decrease in $\nu_c(T)$ at T_N, which is very similar to the case in $BaFe_2As_2$ (inset of Fig. 3), although the value of ν_c and its temperature dependence in the PM state is clearly different. The reason for the difference in ν_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 $H_{\mathrm{int}}(T)$, 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 $CaFe_2As_2$. 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 emphasize that there is no temperature range in which we observe either the magnetic or structural order parameter to be finite and the other one to be zero, indicating that both are intimately related. The temperature dependence of H_{int} observed in Fig. 3 is remarkably close to the temperature dependence of the ordered moment that develops below a first-order magnetic transition in isostructural $SrFe_2As_2$.[24]

The relationship among H_{int}, the ordered moments $\mathbf{S}_0$, and the magnetic structure is not straightforward. *A priori*, one might expect the hyperfine field to vanish at the As site due to its symmetric position between the four nearest-neighbor Fe sites. However, this is the case only if the transferred hyperfine coupling to the As atom is isotropic. Kitagawa *et al.*[26] reported a model for the hyperfine coupling in terms of anisotropic coupling tensors $\mathbf{B}$ between the four nearest-neighbor Fe moments and the As nucleus. In this case, $H_{\mathrm{int}} = 4B_{ac}S_0^x$ for the $\mathbf{Q} = (101)$ stripe magnetic structure.[25] Since the neutron-scattering data reveal $S_0 = 0.8\mu_B$ oriented along the 100 direction, we estimate $B_{ac} \sim 0.81$ T/μ_B. In this case, the transferred hyperfine coupling must be anisotropic in order to induce a hyperfine field. A second possibility is that the ordered moments are canted by the applied field and acquire a small component along the c direction, for which the isotropic component of the transferred hyperfine coupling does not vanish. If we use the isotropic values reported for $BaFe_2As_2$ (2.64 T/μ_B) (Ref. 26) and an ordered moment of $0.8\mu_B$, then we find that the moments must be tilted by $\sim 22.5°$ out from the ab plane.

The nuclear spin-lattice relaxation rate (T_1^{-1}) was determined by fitting the recovery of the nuclear magnetization using a Hahn-echo sequence after a saturating pulse. $(T_1T)^{-1}$ is shown in Fig. 4. At high temperatures $T \gg T_N$, $(T_1T)^{-1}$ approaches a constant value, as observed in $BaFe_2As_2$ (Ref. 27) and RFeAsO$_{1-x}$F$_x$ (R=La, Pr).[30,31] This Korringa-type behavior is expected in metallic systems and may reflect the coupling of the nuclei to the conduction electrons. With decreasing temperature, $(T_1T)^{-1}$ increases as T_N is approached. We attribute the upturn in $(T_1T)^{-1}$ to dispersive (paramagnon) excitations that recent neutron-scattering experiments find at temperatures well above T_N ($\sim$200 K).[32] At T_N we observe a discontinuous jump in $(T_1T)^{-1}$ 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, $(T_1T)^{-1}$ 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 ($CaFe_2As_2$, $BaFe_2As_2$, and LaFeAsO) exhibit similar spin-lattice relaxation behavior, yet the absolute values of $(T_1T)^{-1}$ 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 explanations 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 χ are roughly identical in $LaFeAsO_{1-x}F_x$ and $BaFe_2As_2$.[26,29] Therefore, we conclude that the spectral density of spin fluctuations differs significantly between these compounds. One might argue that the single plane $LaO_{1-x}F_xFeAs$ should exhibit different physics than the double plane AFe_2As_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 $CaFe_2As_2$. 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 $BaFe_2As_2$ and another parent compound LaFeAsO demonstrates the extreme sensitivity of both the static (ν_Q) 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.

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