^{23}Na and ^{75}As NMR study of antiferromagnetism and spin fluctuations in NaFeAs single crystals

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We report the ^{23}Na and ^{75}As nuclear magnetic resonance (NMR) studies on NaFeAs single crystals. The structure transition temperature T_S (55 K) and the spin density wave (SDW) transition temperature T_{SDW} (40.5 K) are determined by the NMR line splits. The spin-lattice relaxation rates indicate that the spin fluctuations are strongly enhanced just below T_S and drive a second order SDW transition. A fluctuating feature of the SDW ordering is also seen below the T_{SDW}. We further performed high-pressure NMR studies on NaFeAs, and found that the T_{SDW} increases by $\sim$7 K and the magnetic moment increases by $\sim$30% under 2.5 GPa pressure.

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The discovery of superconductivity in iron pnictides[1] has attracted intense research interest, and so far high-temperature superconductivity is achieved in many iron-based compounds upon doping. In particular, three classes with similar structures, including the 1111 structure RFeAsO$_{1-x}$F$_x$ (R = La, Nd, Sm, etc.),[2–4] the 122 structure Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$/Ba$_{1-x}$K$_x$Fe$_2$As$_2$ (Ref. 5), and the 111 structure LiFeAs/NaFeAs (Refs. 6–8) have been extensively studied. In their parent compounds, long-range antiferromagnetism (AFM), or the spin-density-wave (SDW), have been reported with a stripe-like magnetic structure.[9] There are renewed concerns on the nature of the magnetism regarding as to whether the SDW follows a local moment or a Fermi surface nesting picture. For the 111 class, the magnetism appears to be very weak. In LiFeAs, superconductivity is observed instead of the SDW ordering,[6] although the SDW fluctuations are seen above T_C (Ref. 10). In NaFeAs, the SDW order is observed with a low transition temperature.[11] Its magnetic moment is reported to be 0.09 μ_B/Fe by neutron scattering,[12] in contrast to the larger values of about 0.4 μ_B/Fe in the 1111 and about 1 μ_B/Fe in the 122 parent compounds.[5,9,13] From local density approximation (LDA) calculations, however, the band structures of all three classes are similar.[14–16]

One important fact is that the SDW order only develops at or below the structure transition, namely the high-temperature tetragonal (HTT) to the low-temperature orthorhombic (LTO) transition. It is conjectured that the structure transition is important for the SDW ordering and may also be important for superconductivity. For instance, it has been argued that both the structure phase transition and the SDW ordering are driven by a ferro-orbital ordering caused by the d_{xz} and d_{yz} orbitals.[17,18] The structure transition T_S and the SDW transition T_{SDW} are well separated in NaFeAs and the 1111 class, while in the 122 class the two transitions occur simultaneously. These distinctive properties open a window for studying the relation between the structure and magnetism.

In this Brief Report, we present our ^{23}Na and ^{75}As nuclear magnetic resonance (NMR) studies on nominally undoped NaFeAs single crystals, mainly focusing on the interplay of the structure and the magnetism. First, we determined the sharp SDW transition temperature ($T_{\text{SDW}} \approx 40.5$ K) and the structure transition temperature ($T_S \approx 55$ K) directly from the NMR, and a commensurate magnetic moment of $0.32 \pm 0.02 \ \mu_B$/Fe

far below T_{SDW}. Second, we study the correlation between the magnetism and the structure. Spin fluctuations, indicated by the spin-lattice relaxation rate change behaviors across the structure transition. We also found that both the SDW transition temperature and the magnetic moment are enhanced significantly under pressure.

The NaFeAs single crystals were synthesized by flux-growth method with NaAs as the flux and the detailed growth procedure was reported elsewhere.[19] For NMR, we chose crystals with typical dimensions of $3 \times 2 \times 0.1$ mm^3. The crystals were characterized by the magnetization measurements. We performed ^{23}Na and ^{75}As (both with $S = 3/2$) NMR studies, with the magnetic field either along the ab plane or the c axis. It is known that the chemical nonstoichiometry in the 111 class affects the magnetism significantly.[10] In this Brief Report, we primarily report the results of single crystals with a very small superconducting volume ratio (less than 2%), which turns out to have a very narrow NMR linewidth both above and below the T_{SDW}, indicating good chemical stoichiometry. The spin-lattice relaxation rate (SLRR) is deduced from the spin recovery after an inversion pulse. For the high-pressure study, we used a 2.5 GPa pressure cell. Silicon oil is used as the pressure medium and a piece of lead inside the NMR coil is used as a low-temperature manometer.

The SDW transition is seen clearly by the ^{23}Na spectra with field applied along the c axis, as shown in Fig. 1(a). The nuclear quadrupole splitting is $^{23}\nu_q \approx 0.525$ MHz, as evidenced by one center transition and two satellite lines at 45 K. As the sample is cooled below 40.5 K, each line splits into two species with equal frequency shift (denoted by the arrows with the same color), which shows the SDW ordering. The relative frequency split of the central transition $2\Delta f$ serves as an order parameter of the SDW transition. As shown in the inset of Fig. 1(a), the transition width is very narrow and Δf almost saturates at 5 K below the T_{SDW}. The ^{75}As spectra also have a line splitting below the SDW transition with $H \parallel c$, as shown in Fig. 2(a). The increase of the ^{75}As frequency shift Δf below the SDW transition is also shown in Fig. 2(a).

With $H \parallel ab$, the line splitting is absent for both ^{23}Na and ^{75}As (data not shown). The splitting of the NMR spectrum indicates two internal static hyperfine fields $H_{in} = \pm \Delta H$ along the c axis. The observation of the c-axis internal field on ^{75}As suggests a stripe AFM due to an off-diagonal hyperfine
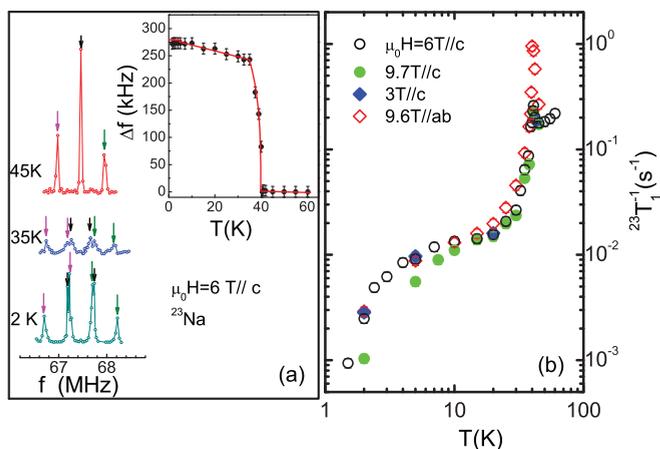
FIG. 1. (Color online) (a) The ^{23}Na NMR spectra (one center transition and two satellites with $^{23}\nu_q \approx 0.525$ MHz) at above and below the T_{SDW} (40.5 K), with the magnetic field applied along the c axis. Inset: The frequency shift of the ^{23}Na center transition below the SDW transition. (b) The spin-lattice relaxation rate of ^{23}Na with different field orientations and field amplitudes.

coupling between the ^{75}As nuclei and the Fe moments.[20] The sharp NMR spectrum far below the T_{SDW} suggests a commensurate order, which is consistent with the neutron data.[12] It is reasonable to have the same direction of the internal field for ^{23}Na and ^{75}As since two nuclei are on the inversion symmetry position to each other.

The HTT to the LTO structure transition can be inferred from ^{75}As satellites. In Fig. 2(b), one ^{75}As satellite (the high frequency one) is shown at different temperatures, with the magnetic field applied primarily along the a axis. When the sample is cooled down, the spectrum splits into two species at about 55 K, a signature of the structure transition. The spectrum splitting is caused by sample twinning, and domains
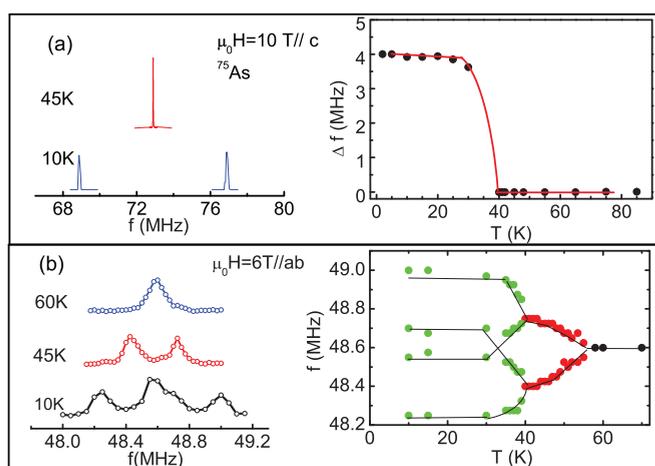

FIG. 2. (Color online) (a) The ^{23}As center transition with the magnetic field along the c axis (satellites not shown). Inset: The frequency shift of the center transition. (b) The ^{75}As NMR satellite spectrum ($^{75}\nu_q \approx 9.5$ MHz) at different temperaures. Inset: The temperature dependence of one ^{75}As NMR satellite frequency with the field applied primarily along one a axis but 3° off to the c axis.

with field along the a and b axes give different resonance frequencies. When the temperature goes down, the spectrum further splits at the SDW transition because the applied field is slightly off the ab plane.

We also analyze the SDW moment from spectrum splitting $2\Delta f$ of ^{75}As and ^{23}Na. In Figs. 1(a) and 2(a), the values of Δf for ^{75}As and ^{23}Na are shown at different temperatures. The frequency shift Δf is about 4.0 MHz at $T = 2$ K, corresponding to a hyperfine field $H_{in} \approx 0.55$ T for ^{75}As. For iron pnictides, the magnetic moment m is known to follow $m = H_{in}/4^{75}A_{hf}^{ac}$, where $^{75}A_{hf}^{ac}$ is the off-diagonal hyperfine coupling constant which is not directly measurable.[20] Here we employ $^{75}A_{hf}^{ac} \approx 0.43 T/\mu_B$ from BaFe$_2$As$_2$ (Ref. 20), and estimate the magnetic moment as $0.32 \pm 0.02 \mu_B$/Fe, which is close to the 1111 class. Comparing with the frequency shift of ^{23}Na, it gives $^{23}A_{hf}^{ac} \approx 0.027 T/\mu_B$.

Now we study the spin fluctuations from the spin lattice relaxation rate $1/T_1^{ab}$ ($H \parallel ab$) and $1/T_1^c$ ($H \parallel c$). The temperature dependences of $1/^{75}T_1^{ab}T$ and $1/^{75}T_1^c T$ are shown, respectively, in Fig. 3. From room temperature to 100 K, the $1/^{75}T_1 T$ decreases, which is also seen in other iron pnictides.[21] Below 100 K, the $1/T_1 T$ increases as the temperature drops with an upturn like behavior, and the $1/^{75}T_1 T$ is anisotropic with $^c T_1 /^{ab}T_1 \approx 1.5$. The upturn and the anisotropy of the SLRR are indications of strong SDW spin fluctuations.[20] The SDW transition temperature is shown at 40.5 K by the divergence of the $1/^{75}T_1 T$. Below T_{SDW}, the $1/^{75}T_1 T$ drops quickly because of the suppression of the spin fluctuations. Notably $1/^{75}T_1 T$ saturates with a constant value 0.015 s^{-1}K^{-1} at low temperatures, similar to that of BaFe$_2$As$_2$ (Ref. 20).

A correlation between the structure transition and SDW ordering can be seen from the SLRR data across the the structure transition. The spin fluctuations are significantly enhanced just below the structure transition, which is shown by the rapid increase of the $1/^{75}T_1 T$ below 55 K (Fig. 3). Such behavior is better shown by the temperature dependence of $^{75}T_1 T$ [Fig. 3 (inset)]. The antiferromagnetic spin fluctuations are usually shown by a Curie-Weiss-like behavior with $1/T_1 T = A/(T + \Theta)$. Fitting $^{75}T_1^{ab} T$ (or $^{75}T_1^c T$) with
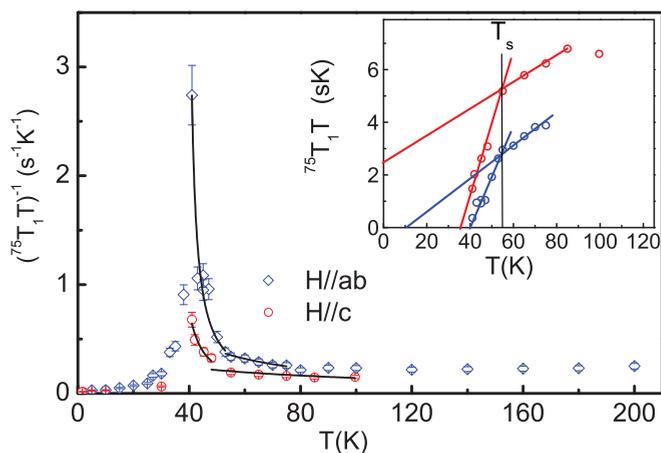

FIG. 3. (Color online) The temperature dependence of the $1/^{75}T_1 T$ of a NaFeAs single crystal, with $\mu_0 H = 10 T$. Inset: The temperature dependence of $^{75}T_1 T$, and the straight lines are fittings to $^{75}T_1 T \sim (T + \Theta)$ for temperatures above and below the T_S.

$T_1 T = (T + \Theta)/A$, two different lines are needed for above and below the structure transition. For $H \parallel ab$, the fitting gives $\Theta_{ab} \approx -10 \pm 5$ K (above T_S) and $\Theta_{ab} \approx -40 \pm 1$ K (below T_S).

The above values of Θ_{ab} have two implications. First, above T_S, Θ_{ab} is negative, which suggests that the spin fluctuation could lead to the magnetic ordering at a finite temperature even without the structure transition. This supports the J_1-J_2-J_c model that the structure transition is, in fact, caused by the spin fluctuations.[22,23] Second, the value $\Theta_{ab} \approx -T_{\text{SDW}}$ below T_S clearly indicates that the SDW is a second order transition. Since the large value of $-\Theta$ suggests stronger spin fluctuations,[21,24] the enhancement of the $-\Theta_{ab}$ below the structure transition and the second order SDW transition suggest that there is an interplay of the structure transition and the magnetism. In the LTO phase, the crystal a and the b axes are inequivalent, which gives an anisotropic coupling of J_{1a} and J_{1b} and may help the formation of the SDW ordering. A recent angle-resolved photoemission spectroscopy (ARPES) study on NaFeAs which revealed a band shift below T_s (Ref. 25), which may suggest that the band structure is also involved in the magnetic ordering.

Furthermore, since the structure phase transition and the magnetic phase transition are separated, the interlayer coupling J_c in NaFeAs is probably weaker than the 122 compounds from the picture of magnetically driven structure phase transition. From the measured values, we have $(T_S - T_{\text{SDW}})/T_{\text{SDW}} = 0.358$. According to Ref. 22, we can deduce that the interlayer coupling in NaFeAs is also weaker than the 1111 class. The weak interlayer coupling lifts the degeneracy of the structure phase transition and the SDW ordering. In this picture, the SDW transition is naturally a second order type.

We further study the structure effect to the magnetism under high pressure up to 2.56 GPa, and find that spin fluctuations, the T_{SDW}, and the moment size are greatly enhanced by pressure. The increase of the spin fluctuations under pressure is seen by the increase of $1/^{75}T_1^c T$ [Fig. 4(c)]. In Fig. 4(a), the normalized spectral weight of ^{75}As in the paramagnetic phase is shown at different temperatures. The sudden drop of the spectral weight upon cooling indicates the onset of the SDW ordering (defined as T_{SDW}). As shown in Fig. 4(a) (inset), the T_{SDW} increases with pressure, from 40.5 K at the ambient pressure to 47 K at 2.56 GPa. The magnetic moment also seems to increase. In Fig. 4(b), the spectrum of ^{23}Na is shown at different pressures ($T = 2$ K). The spectrum splitting clearly increases with pressure. The magnetic moment increases from $0.32\mu_B$ at $P = 0$ to $0.41\mu_B$ at $P = 2.56$ GPa. Our estimation is much larger than the neutron scattering data.[12] We note our estimation employs the hyperfine coupling constant obtained from $BaFe_2As_2$, which can be off if the hyperfine coupling constant is very different. The difference could also be partly caused by chemical stoichiometry[6,19] since NMR is a local probe and the neutron scattering measures the averaged magnetic moment.

The high-pressure data may suggest that the interlayer coupling J_c plays a crucial role in determining the phase transitions and the magnetic moment. If we assume the lattice spacing along the c axis changes more significantly with pressure than the a or the b axis, the pressure is probably more effective in strengthening the interlayer coupling J_c to
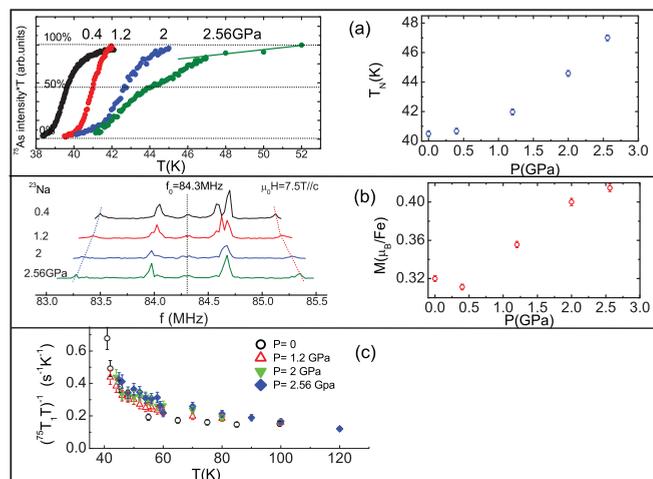

FIG. 4. (Color online) (a) The temperature dependence of the ^{75}As paramagnetic spectral weight at different pressures. The sharp drop of the signal indicates the onset of the SDW ordering. Inset: The onset T_{SDW} determined from the sudden drop of the spectral weight at different pressures. (b) The ^{23}Na NMR spectrum of NaFeAs under different pressures ($T = 2$ K). Inset: The SDW moment of NaFeAs estimated from the line splitting of ^{23}Na at different pressures. (c) The ^{75}As spin-lattice relaxation rate at different pressures.

enhance the SDW ordering.[26] Under pressure, the interlayer coupling J_c, mainly from d_{xz} and d_{yz} orbits increases because the lattice constant becomes smaller. Unfortunately, our NMR satellite is broadened at higher pressures, and we cannot determine the structure transition. Further study is necessary to disclose the relation between the T_{SDW} and T_S under pressure. Nevertheless, the increased SDW moment (by 30% at 2.56 GPa) and the T_{SDW} (by 18% at 2.56 GPa) draw the NaFeAs high-pressure phase closer to the 1111 class, which again supports that the c-axis coupling is weaker in NaFeAs.

We also observe a fluctuating feature of the SDW ordering below the T_{SDW}, which is not well understood. First, the spectrum splitting Δf of ^{23}Na [see Fig. 1(a) inset] shows two steps. The Δf increases quickly below T_{SDW}, and then increases slowly below 35 K, followed by a full saturation at $T = 10$ K. Second, the ^{23}Na linewidth broadens significantly between 40 and 30 K [see Fig. 1(a)], and narrows again at low temperatures. For ^{75}As, the spectrum is not measurable between 40 and 30 K, which indicates that the broadening is more significant. These temperature behaviors suggest the the SDW ordering still fluctuates in an intermediate temperature range below the T_{SDW}, unlikely due to a disorder effect.

Thermally activated domain walls may be an explanation of the above observation. In iron pnictides, the spin frustration is strong and several types of domain walls may be thermally activated in the stripe phase, such as the antiphase type and/or the c-axis misalignment boundaries.[27,28] Under such circumstances, the NMR spectrum narrows and the magnetic moment saturates simultaneously with decreasing temperature. Another possible explanation is that the fluctuating features are caused by an incommensurate modulation on the SDW, which becomes commensurate again at low temperatures.

In summary, our data reveal the interplay between the lattice structure and the magnetic ordering in the undoped NaFeAs.

First, our negative value of Θ_{ab} above the structure transition, from the fitting $1/T_1T = A/(T + \Theta)$, is consistent with the proposal of the magnetically driven structure phase transition. Second, the increase of $-\Theta_{ab}$ and the second order SDW transition below the structure transition suggest that the lattice/band structure, in return, strengthens the magnetic ordering. Third, the SDW ordering of NaFeAs is greatly enhanced upon pressure. We also observe the fluctuating features of the SDW ordering in an intermediate temperature below T_{SDW}, which may be caused by thermal fluctuations of domain walls, and/or high-temperature incommensurability. These magnetic properties should be important inputs for constructing the microscopic model of magnetism in iron pnictides.

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