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Antiferromagnetic order in Ca$_{10}$(Pt$_3$As$_8$)(Fe$_2$As$_2$)$_5$ observed by $^{75}$As NMR

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Abstract

$^{75}$As nuclear magnetic resonance (NMR) measurements carried out on underdoped, non-superconducting Ca$_{10}$(Pt$_3$As$_8$)(Fe$_2$As$_2$)$_5$ reveal physical properties that are similar but not identical to 122 superconductor parent compounds such as BaFe$_2$As$_2$. Results from the single crystal study indicate a phase transition to an antiferromagnetic (AF) state on cooling through $T$ $\sim$ 100 K, albeit nonuniformly. Specifically, the NMR lineshape reflects the presence of staggered hyperfine fields on the As sites associated with a striped AF order. The variation of the internal hyperfine field with temperature suggests that the phase transition to the AF state is discontinuous, and therefore likely coincident with the structural transition inferred from transport experiments.

(Some figures may appear in colour only in the online journal)
A break in slope in the resistivity–temperature curve at $T_s \sim 100$ K in the undoped or lightly-doped 10-3-8 material indicates a structural transition [17], which was also verified by polarized-light optical images [21]. A superconducting ground state is found at higher carrier concentrations, $x > 0.025$–0.030, where $x$ is the fraction of the Fe sites occupied by Pt, and the onset appears coincident with complete suppression of the structural transition. Nevertheless, no accompanying anomaly in the magnetic susceptibility has yet been reported [16, 17], casting doubt on the presence of a magnetic ground state. Consequently, it was suggested that the weak interlayer exchange suppresses the long-range magnetic order [17], even if AF spin fluctuations remain significant for producing superconductivity. Nuclear magnetic resonance (NMR) measurements serve as a local probe of the magnetic state, and, thus, provide an ideal tool for the investigation of the 10-3-8 system, and specifically to determine whether the ground state is antiferromagnetic.

Here we report $^{75}$As NMR experiments on a Ca$_{10}$ (Pt$_3$As$_9$)(Fe$_2$As$_2$)$_5$ single crystal for a wide range of temperature ($T = 1.65$–115 K) and applied magnetic field ($B_0 = 5$–11 T) values. Most of the results are qualitatively and quantitatively similar to that obtained from the 122 compounds, whereas some differences are observed in the temperature dependence of the spin lattice relaxation rate ($1/T_1$).

The Ca$_{10}$ (Pt$_3$As$_9$)(Fe$_2$As$_2$)$_5$ single crystal reported on here was prepared and characterized using methods described previously [16]. In this case, nominal Pt substitution at the Fe sites leads to a doping level of $x = 0.004 \pm 0.002$ as determined by wavelength dispersive spectroscopy (WDS) electron probe microanalysis [21]. The dimensions of the crystal studied are $\sim 3\, \text{mm} \times 1\, \text{mm} \times 0.3\, \text{mm}$. The resistance curve shown in the inset of figure 2(a) depicts measurements on a crystal from the same batch; transport properties of several additional crystals were examined, and in each case a change in slope in the range 95–105 K was observed, suggestive of a phase transition at a temperature $T_s$ that showed variation of approximately $\pm 5$ K from one crystal to another.

The coil containing the sample was mounted on a piezorotator, which allowed for an alignment precision of less than 1°. The temperature was regulated in a gas-flow $^4$He cryostat with variations limited to $\delta T/T < 1\%$. Field-swept NMR spectra were constructed by recording standard Hahn spin echo transients from the $^{75}$As nuclear spins ($I = 3/2$). Our expectation was for two very different As environments, since in addition to the FeAs layers, there are distant sites in the Pt–As skutterudite layer (see inset of figure 1(a)). However, only one environment was detected under our experimental conditions. Given the similarity of the results to those obtained for other FeAs-based compounds, we associate our observations with the $^{75}$As nuclear spins nearby the Fe ions. It is possible that the contribution from the skutterudite sites is suppressed due to the weak hyperfine coupling to the Fe spins, which then results in saturation of the associated transitions for very long relaxation times $T_1$. By itself, the weak coupling is not sufficient, since ordinarily the two spin populations will undergo mutual spin-flip transitions as a result of the nuclear dipolar interaction. However, significant hyperfine fields at the

![Figure 1. $^{75}$As field-swept spectrum for $B_0(\parallel, \perp)c^*$ and rf carrier frequency $\nu = 55.55\, \text{MHz}$: (a) in the paramagnetic phase at $T = 110$ K. The crystal structure showing the Ca–skutterudite–Ca spacer appears in the inset. (b) In the magnetic phase at $T = 1.65$ K. The inset shows the angular evolution of the spectrum’s magnetically split central transition (blue symbols), and the expected variation for the AF order discussed in the text (red lines).](image)
sites in the FeAs layers shift the relative transition frequencies, and could render this mechanism ineffective.

Spectra recorded at $T = 110$ and $1.65$ K are shown in figure 1. The spin of the $^{75}$As nucleus is $I = 3/2$, and thus its electric quadrupole moment is nonzero and couples to the lattice’s electric field gradient (EFG). Hence, the resonance frequencies are given by the eigenvalues of the Hamiltonian

$$\mathcal{H} = -\gamma \mathbf{H} \cdot \mathbf{B}_{\text{eff}} + \frac{h\nu_Q}{6} \left[ 3I_z^2 - I(I + 1) + \frac{1}{2} \eta (I_+^2 + I_-^2) \right].$$

Here, $\gamma = 7.292$ MHz $T^{-1}$ is the $^{75}$As nuclear gyromagnetic ratio, $\nu_Q$ is the quadrupole frequency, $\eta$ the asymmetry parameter, and $\mathbf{B}_{\text{eff}} = \mathbf{B}_0 + \delta \mathbf{B}$, where $\delta \mathbf{B}$ is the total internal field. For large magnetic fields ($\gamma h B_0 \gg h \nu_Q$) aligned with the principle axis $z$ of the EFG, satellite transitions ($I_z = (\pm 1/2 \leftrightarrow 3/2)$) are separated from the central transition ($1/2 \leftrightarrow -1/2$) by $\nu_Q$. Here, $\zeta$ is expected to be close to $c^\ast$.

For $T = 100$ K, in the paramagnetic phase, the linewidth (FWHM) of the central transition is $\delta \nu \sim 200$ kHz (400 kHz) for $\mathbf{B}_0 \parallel (\perp) c^\ast$, and the satellite transitions are separated from the central by the quadrupole frequency $\nu_Q = 9.0(2)$ MHz (the NMR parameters are summarized in table 1, along with those of other FeAs parent compounds). Not surprisingly, the linewidths are very broad compared to what is observed for crystals of 1111 or 122 compounds, since due to the low symmetry there are 5 magnetically inequivalent sites just in the FeAs layers, as well as evidence for disorder that will be discussed further below.

At low temperature (figure 1(b)), the spectrum for $\mathbf{B}_0 \parallel c^\ast$, covering the field range $5T \rightarrow 11$ T, is split into two sets of three maxima. This results from the hyperfine coupling of the $^{75}$As nuclei to the ordered Fe atomic moments, signaling the presence of long-range AF order. The spectral features are identified and labeled according to nuclear transition, as is the splitting $2B_{\text{int}} \approx 3$ T arising from the alternating hyperfine field. The observed peaks are relatively broad, indicating substantial real space variations of the internal field. For $\mathbf{B}_0 \perp c^\ast$, the spectrum remains non-split, even though broadened compared to the paramagnetic phase.

The internal field $B_{\text{int}}$ corresponds to one half of the peak separation of the corresponding nuclear transitions for $\mathbf{B}_0 \parallel c^\ast$. Upon rotation, the spectrum evolves as summarized in the inset of figure 1(b) for the central transition, and any remaining magnetic splitting is unresolved for $\theta = 90^\circ$. Just as for the 1111 [26] and 122 [27, 28] compounds, our observations are consistent with striped-phase antiferromagnetism, but with substantially more disorder. That is, the AF order is described by the wave vector $Q = (1, 0, n)$, with $n = 0, 1$.

Having established that the underdoped material has an AF ground state, we now consider the identification of the ordering temperature and whether it is distinct from the structural transition at $T_\theta \sim 100$ K. This distinction is difficult to make under the circumstances of broadened spectra, and what we determined to be a spatially inhomogeneous emergence of the AF order within the crystal employed. The onset of spectral broadening due to static magnetism is evident in figure 2(a), which illustrates the loss of the echo signal intensity originating from the paramagnetic phase. The onset occurs for $T \sim 100$ K, below which the change is monotonic and continuous. We take the magnetic ordering temperature to coincide with this onset, yielding $T_N = 100$ K. Note also that the spectral linewidth associated with the intensity shown in figure 2(a) remains unchanged even while the intensity is falling so significantly.

The sixth, lowest field maximum is not shown due to its overlap with $^{63,65}$Cu contributions arising from the NMR coil.
BaFe-smoother falloff of the internal field is seen in Co-doped (hashed symbols), the measurements were done with paramagnetic volume fraction. On approaching the transition, structural transition: $T_s \approx T_N$; in contrast, a significantly smoother falloff of the internal field is observed in Co-doped BaFeAs$_2$, for which $T_N < T_s$ [15]. Below we refer to $T_s$, $T_N$ generally as the transition onset temperature, $T \approx 100$ K. Although the order parameter for the structural transition forming below $T_s$ has not been identified, the link with AF striped order is suggestive of a low-temperature triclinic phase (since the high-symmetry phase is already triclinic), but with $a \neq b$.

The variation of the spin lattice relaxation with temperature, shown in figure 3, was evaluated by approaching the transition from both higher and lower temperatures. The high-temperature data includes results from the central transition ($-1/2 \leftrightarrow 1/2$) at $T = 0$, 90°. From the spectroscopic data, we concluded that the paramagnetic phase continues to exist but in spatially segregated regions for $T < T_N$. Here, the data for $T > 80$ K (solid symbols) are associated with the paramagnetic volume fraction. On approaching the transition from lower temperatures from within the magnetic phase (hashed symbols), the measurements were done with $\theta = 90^\circ$, over a temperature range from 1.7 to 75 K. For both cases, the values of $T_1^{-1}$ were defined by comparing the magnetization recovery $M(t)$ according to the expectation for magnetic relaxation of the $I = 3/2$ central transition,

$$\delta M(t) \sim [0.9e^{-6T_1} + 0.1e^{-1/(T_1)}].$$

The data were well-described by the expression (2) for $10 \leq T \leq 50$ K. For $T < 10$ K, the reported values were obtained from the same procedure, even though the magnetization recovery was consistent with a distribution of relaxation times. Specifically, a stretched exponential analysis ($\delta M(t) \sim e^{-(t/T_1)^\beta}$) results in $\beta = 0.5$–0.6. On warming past $T = 50$ K from the magnetic phase, the data are not well-described using the functional form in equation (2). This discrepancy in the detailed behavior may again be associated with chemical inhomogeneity in the material.

To address the question of whether the transition is continuous or discontinuous, or spatially inhomogeneous, we compare the temperature dependence of the internal field $B_{int}$ to that obtained from the chemically and structurally less complex, clean material BaFeAs$_2$ in figure 2(b), each normalized to $T_N$. Based on this comparison, the two materials behave analogously, and we therefore conclude that the transition to the low-temperature magnetic state is discontinuous for the ideal 10-3-8 phase, and therefore also that it is very close to and possibly coincident with the structural transition: $T_s \approx T_N$; it is very close to and possibly coincident with the structural transition: $T_s \approx T_N$; in contrast, a significantly smoother falloff of the internal field is seen in Co-doped BaFeAs$_2$, for which $T_N < T_s$ [15]. Below we refer to $T_s$, $T_N$ generally as the transition onset temperature, $T \approx 100$ K. Although the order parameter for the structural transition forming below $T_s$ has not been identified, the link with AF striped order is suggestive of a low-temperature triclinic phase (since the high-symmetry phase is already triclinic), but with $a \neq b$.

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The increase of the relaxation rate upon cooling in the paramagnetic phase is characteristic of AF spin fluctuations and is stronger than for the 122 compounds [22, 23]. Note that the data collected in the paramagnetic phase is associated with a significantly decreasing volume fraction for $T < 100$ K, the temperature of onset for the spatially inhomogeneous AF order. Once far into the magnetic phase, the relaxation rate first drops by an order of magnitude, but reaches a constant value below 50 K. This aspect appears different than the other materials, which exhibit relaxation rates decreasing much more steeply upon cooling. A possible explanation is in fluctuating domains or other dynamical effects, such as those associated with motion of discommensurations. In any case, if the origin is with slow collective dynamics, then the rate will be found dependent on the Larmor frequency.

To conclude, we have performed NMR spectroscopy on a single crystal of non-superconducting Ca$_{10}$(Pt$_3$As$_8$) (Fe$_2$As$_2$)$_2$. The ground state is antiferromagnetic, with wave vector $Q = (1, 0, n)$ ($n = 0, 1$), and forming inhomogeneously below the onset temperature $T_N = 100$ K. The results are similar in character and amplitude to what is observed in other FeAs compounds that are known to develop striped antiferromagnetism. Variation of the magnetic order parameter with increasing temperature is relatively weak,
and reminiscent of what is seen for a first order phase transition. Moreover, since $T_N$ coincides approximately to where anomalies in transport have been associated with a structural transition, we suggest that $T_N \approx T_s$. Our NMR measurements in the vicinity of $T_N$ are not straightforward to interpret due to the inhomogeneous onset and broadened spectra. A large and temperature-independent relaxation rate of the magnetic phase, extending from $T > 10$ K is not present in less complex iron arsenides, and possibly originates from the disorder in this system.

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