NMR Investigation of Superconductivity and Antiferromagnetism in $CaFe_2As_2$ under Pressure

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We report ^{75}As NMR measurements in $CaFe_2As_2$, made under applied pressures up to 0.83 GPa produced by a standard clamp pressure cell. Our data reveal phase segregation of paramagnetic and antiferromagnetic (AFM) phases over a range of pressures, with the AFM phase more than 90% dominant at low temperatures. *In situ* rf susceptibility measurements indicate the presence of superconductivity. ^{75}As spin-lattice relaxation experiments indicate that the ^{75}As nuclei sample the superconductivity while in the magnetically ordered environment.

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Like the cuprates, the newly discovered FeAs pnictide family of superconductors is notable for the emergence of a superconducting state with unusually high transition temperatures from a suppressed magnetic ground state. As such, it is important to establish the pairing interaction for each of the two systems, and further to identify what physical properties might be shared or different. For other systems in which superconducting ground states are stable only near to magnetically ordered ones, it is frequently suggested that magnetic excitations in the (almost ordered) high symmetry phase are necessary for the pairing, and more generally, the two order parameters may compete. Signatures for the role of magnetic fluctuations could also manifest in the order parameter symmetry. Consequently, the focus of many experimental studies is to examine trends in properties in the vicinity that the magnetic ordering temperature $T_N \rightarrow 0$, which is accomplished through doping by chemical substitution or through the application of high pressure.

The measurements reported here address the question of whether superconductivity exists in the antiferromagnetic (AFM) phase of the series of AFe_2As_2 ($A =$ Ca, Ba, Sr, Eu) compounds commonly referred to as 122, and are currently the subject of widespread activity, in part because high quality single crystals are available. The onset of magnetic order at a wave vector $\mathbf{Q} = (1, 0, 1)$ [1] in the undoped compounds occurs discontinuously upon cooling, and coincides with a structural distortion lowering the lattice symmetry from tetragonal ($\mathcal{T}$) to orthorhombic ($\mathcal{O}$). $CaFe_2As_2$ is notable because superconductivity was observed beyond relatively modest pressures, $\sim O(0.5$ GPa) [2,3]. However, identification of the superconducting phase was complicated by the results of subsequent neutron scattering measurements [4], which provided evidence for a transition to a so-called collapsed tetragonal ($c\mathcal{T}$) phase for $P \gtrsim 0.4$ GPa. It was first presumed that superconductivity occurs in the $c\mathcal{T}$ phase [5,6]. Later, it was shown that when He gas is used for the pressure medium, a line of first-order transitions separates the $\mathcal{O}$ and $c\mathcal{T}$ phases, but no superconductivity was found in either one under such conditions [7]. Evidently, the observation of superconductivity can only be attributed to some (so far) unspecified nonhydrostatic conditions: in the neutron scattering experiments [8], as well as in μ^+SR work [6], there was evidence for measurable volume fractions of segregated $\mathcal{O}$ and $c\mathcal{T}$ phases persisting over a wide range of applied pressures, 0.2–1.0 GPa. Also, the sharp phase transition to the $\mathcal{O}$ phase seen at ambient pressure broadened significantly when experiments were conducted in standard clamp pressure cells [9,10]. The determination of the superconducting phase remains an open question, and we note that phase segregation is not the only possibility; rather, coexistence is possible under some conditions in models where the SC state is competing for the Fermi surface with the spin-density wave [11].

In the following, we present our results of ^{75}As NMR measurements carried out in a clamp cell. *In situ* rf susceptibility measurements indicate the presence of superconductivity with significant shielding fractions. NMR spectra recorded at low temperatures indicate the majority volume fraction is in the AFM $\mathcal{O}$ phase. Some details of the observations are inconsistent with the proposal for coexistence. In particular, no significant moment reduction in the $\mathcal{O}$ phase is observed relative to the ambient pressure case, and the wave vector is commensurate and unchanged over the entire range of pressures studied. Further, while superconductivity is clearly detectable in the spin-lattice relaxation data for nuclei situated in the $\mathcal{O}$ phase, its origin is likely in vortex dynamics rather than hyperfine fields. We conclude that the detectable nuclei are at least close to a superconducting volume within distances of order of the penetration depth.

Single crystals of $CaFe_2As_2$ were prepared as described in Ref. [12]. ^{75}As ($I = 3/2$) nuclear magnetic resonance

(NMR) measurements were performed in a standard BeCu clamp-type pressure cell, using a silicone fluid for the medium. The pressures reported were determined by measuring the ^{63}Cu NQR frequency in Cu_2O powder sample at helium temperature [13]; the pressure set at $T = 300$ K is approximately 0.15–0.20 GPa or higher for all cases. For all measurements described here, the external field is applied along the c axis of the sample.

Figure 1(a) shows the temperature evolution of the central transition ^{75}As spectrum at $P = 0.34$ GPa at the fixed frequency $\nu = 42$ MHz. The spectral intensities I are multiplied by temperature for the purpose of relative comparison. For $T < 135$ K, the contribution to IT from the paramagnetic (PM) $\mathcal{T}$ phase starts to decrease but becomes negligibly small only at much lower temperatures. This behavior contrasts with the complete disappearance of the paramagnetic PM component below T_N at ambient pressure [14]. Coincident with the loss of PM signal, we observe the appearance and increase of signal intensity characteristic of the antiferromagnetically ordered (AFM) $\mathcal{O}$ phase. The temperature evolution of $I(P = 0.34\ \mathrm{GPa}, T)T$ across the spectrum, normalized at $T = 140$ K, is shown in the inset of Fig. 1(a). The trend in the spectra is clearly accounted for by a decreasing volume fraction of the $\mathcal{T}$ phase, accompanied by an associated increase in the $\mathcal{O}$ phase. Similar results were obtained for $P = 0.5$ GPa. At the same time, the internal field at the ^{75}As nuclei in the $\mathcal{O}$ phase is nearly independent of pressure, as shown in Fig. 1(b). As this quantity is the product of the hyperfine coupling constant and thermally averaged Fe spin moment, the observation indicates that the magnetic moment of $\mathcal{O}$-phase Fe is robust against applied pressure.

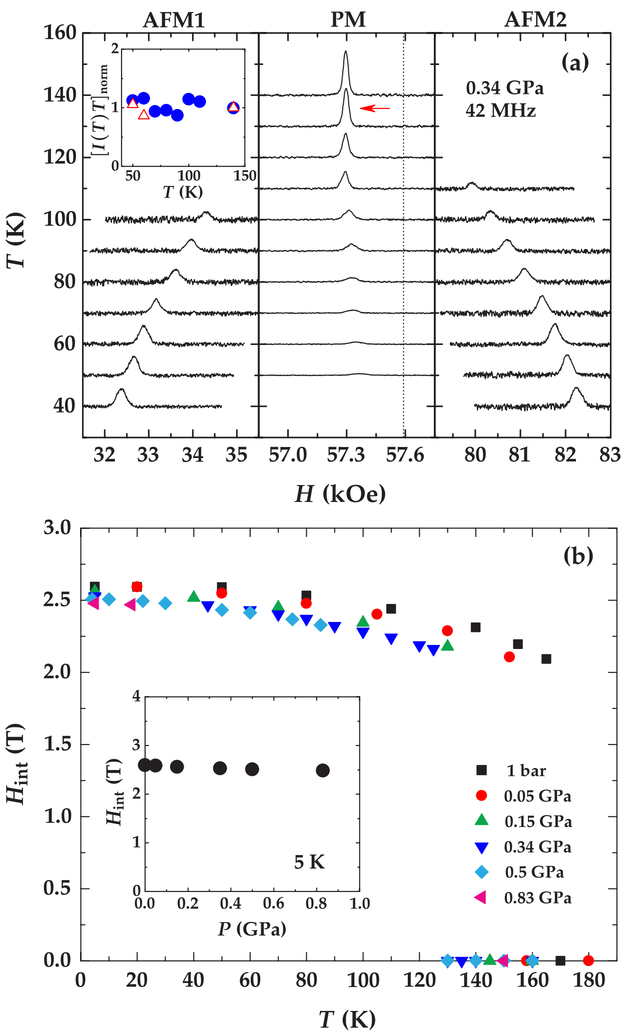

FIG. 1 (color online). (a) Field-swept ^{75}As spectra vs T at $P = 0.34$ GPa. In all cases, the carrier frequency $\nu = 42$ MHz. The intensity characteristic of the paramagnetic (PM) line appears in the center panel. Spectral intensity appearing in the side panels are shifted by hyperfine fields produced by the AFM ordering, and scaled ×3 for clarity. The phase change, from PM → AFM, occurs over a wide range of temperatures. The inset shows that the total nuclear magnetization from the three contributions, follows a Curie Law to within experimental uncertainty. Triangles are from data at $P = 0.5$ GPa. (b) Internal field H_{int} obtained from the magnetic field separation between AFM and PM absorption locations. The inset shows the pressure dependence of H_{int} at $T = 5$ K.

In Fig. 2(a) is a summary of the effect of P and T on the PM fraction. The range of temperatures over which two phases are observed broadens with increasing P [15]. For $P > 0.3$ GPa, we take note that the decrease in the PM volume fraction is relatively fast initially below T_N, then slows below 100 K. Accompanying the slower dropoff is a considerable broadening of the PM signal. T^* is defined as the temperature below which the PM fraction falls below 10% of the full intensity. Measurements of the PM component are reported only for the case that the measurement bandwidth exceeds the linewidth.

The rapid decrease of PM volume just below T_N is due to a nonuniform, progressive transformation to the $\mathcal{O}$ phase. The broadening of the PM line in Fig. 1(a) and the long tail in Fig. 2(a) seen below 100 K is tentatively ascribed to the presence of the remaining small volume fraction of $c\mathcal{T}$ phase. This means that, at $P = 0.83$ GPa, the volume of $c\mathcal{T}$ phase is largest at intermediate temperature and extrapolates to a negligible fraction for low $T \to 0$. Thus, the magnetic $\mathcal{O}$ phase is still dominant up to 0.83 GPa at low T, even though independent transport measurements showed the clear signature of the $\mathcal{T} - c\mathcal{T}$ transition at 150 K at this pressure [10]. The slow decrease of PM fraction and the associated line broadening for $T < 100$ K is consistent with recent neutron scattering results (see Fig. 4 in Ref. [8]).

The $P - T$ phase diagram obtained by monitoring the PM intensity is shown in Fig. 2(b). Included also are the structural transition temperature T_S and the SC transition temperature T_c, inferred independently from resistivity data [10]. As marked in the figure, >90% volume fraction is accounted for in the magnetic $\mathcal{O}$ phase at the super-

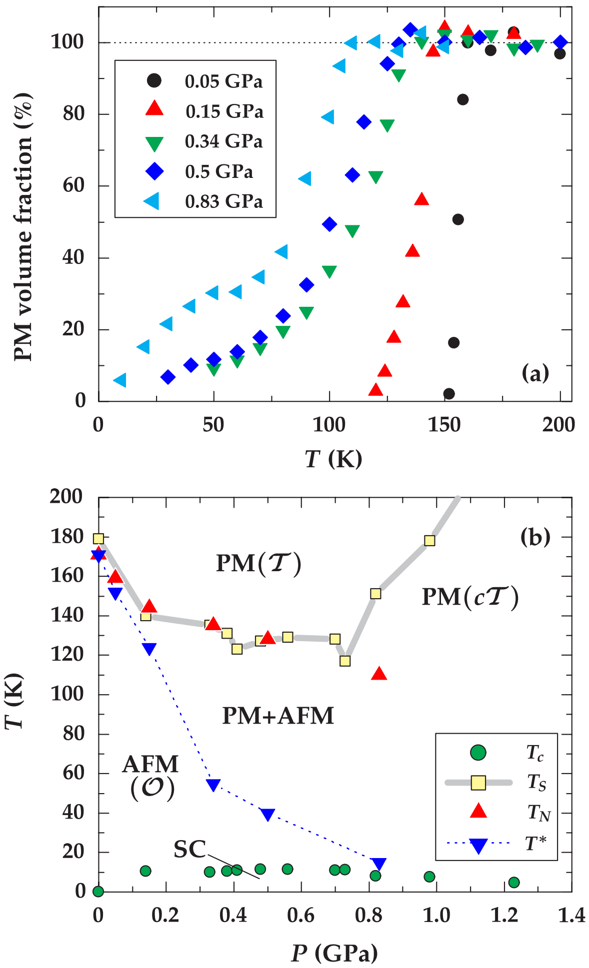

FIG. 2 (color online). (a) PM volume fraction versus temperature as a function of pressure, obtained by monitoring the temperature variation of the PM intensity multiplied by T. (b) Phase diagram obtained from (a). T^* represents the temperature at which PM intensity is 10% of the full intensity. Also shown is a line of superconducting transitions at T_c, obtained from transport experiments made under similar clamp-cell conditions [10].

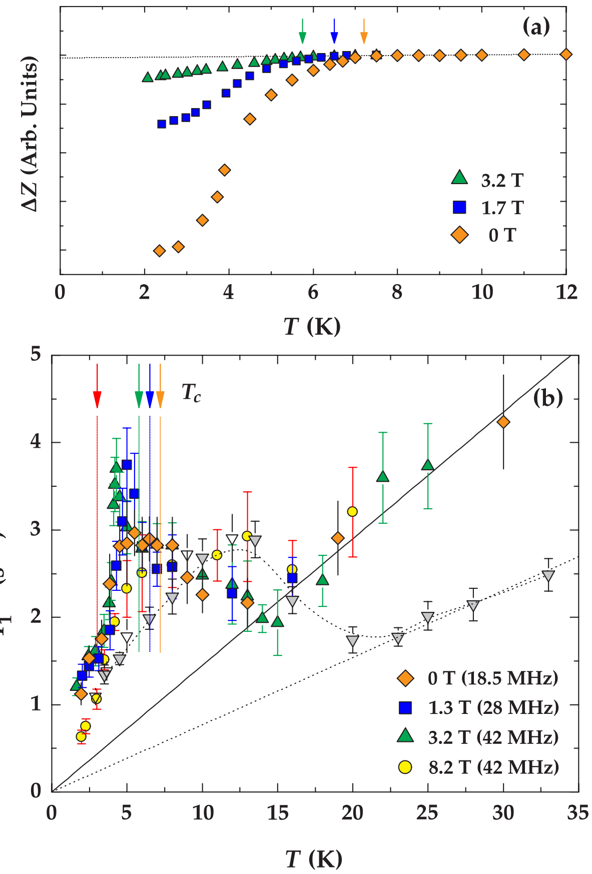

FIG. 3 (color online). (a) Loss of impedance ΔZ due to superconductivity measured in NMR tank circuit at 0.5 GPa. Down arrows denote T_c for each field. (b) ^{75}As T_1^{-1} versus T at $P =$ 0.5 GPa. Down triangles are data taken at ambient pressure at 45 MHz (closed: 3.6 T, open: 8.8 T).

conducting transition temperature at all pressures investigated. It would seem that the possibility that the SC is occurring in the minority PM volume in filamentary-grain boundary form is unlikely since the response of the NMR tank circuit, and the spin-lattice relaxation rate of the ^{75}As spins situated in the magnetic phase, both show clear signatures for the presence of superconductivity. Below we describe the results of these measurements.

The rf response of the NMR tank circuit confirming the presence of superconductivity is shown in Fig. 3(a). The zero-field SC onset at $T_c = 7.2$ K is in agreement with the transport measurements, as is the effect of an applied field ($dT_c/dH = 0.5$ K/T) [3]. The spin-lattice relaxation, recorded for the two AFM lines [Fig. 1(a)], exhibits features correlated with T_c. T_1^{-1} ($P = 0.5$ GPa) at the low-field line (AFM1, $B = 1.3$ and 3.2 T), shown in Fig. 3(b), is described by $(T_1T)^{-1} =$ constant at high temperature, but is enhanced relative to this form for $T < 15$ K. Also visible is a sharp peak superimposed on the broad feature and confined to a narrow temperature range just below T_c. In an attempt to associate directly the observation with superconductivity, the same measurement was carried out at $B = 8.2$ T on the AFM2 line while maintaining $\nu =$ 42 MHz, and in zero field at 18.5 MHz. The larger applied field completely eliminates all evidence for the sharp peak, although the broad enhancement remains. Similarly, the sharp maximum is absent from the zero-field experiments. Also shown in Fig. 3(b) are results from ambient pressure experiments for which there is no superconductivity; a similar broad enhancement of T_1^{-1} is still visible.

The variation of the relaxation rate at low temperatures, and sampling different fields and pressures, indicates that the sharp maximum in T_1^{-1} is linked to the superconducting transition, but likely results from vortex dynamics since it is absent at both high field and zero field. The broad enhancement of T_1^{-1} is present under all conditions, whether the sample is superconducting or not: evidently the broad peak is not a sufficient predictor for superconductivity. We do not comment further, except to note that the origin of the broad relaxation enhancement appears to be magnetic, possibly reflecting glassy dynamics of antiferromagnetic domains [16], and it is reminiscent of observations made in other FeAs superconductors [17,18]. A key question is whether the hyperfine fields in the $\mathcal{O}$ phase are influenced by the onset of the SC state. This onset could be manifested in terms of a spectral shift, a change in the amplitude or wave vector of the magnetic ordering, or in the hyperfine contribution to the relaxation rate. Presumably, the contributions to the relaxation rate are tuned by the magnetic field. In fact, no changes attributed to the onset of superconductivity *and* originating specifically with the hyperfine fields are observed. Therefore, we conclude that the $\mathcal{O}$ phase is not superconducting in isolation, even though here it is the (overwhelming) majority phase, and the observed shielding fraction is significant. On the other hand, the Korringa relaxation (above $\sim$15 K) at 0.5 GPa is twice that at atmospheric pressure, implying a factor of $\sqrt{2}$ larger density of states $N(0) \propto m_{\rm eff} n^{1/3}$, where n is the carrier density and $m_{\rm eff}$ is their effective mass. Whereas, the broad enhancement of T_1^{-1} below $\sim$15 K is not a sufficient condition for superconductivity, the pressure-induced increase of $N(0)$ *in the orthorhombic phase* may be a necessary requirement.

Finally, we comment on the observation of majority $\mathcal{O}$ phase at the pressures investigated in this study. Similar volume fractions are evident in neutron scattering studies [8], and these were attributed to nonhydrostatic conditions. To determine more specifically what aspects stabilize the $\mathcal{O}$ phase over the $c\mathcal{T}$ phase will require producing the relevant stress(es) under controlled conditions. For example, the structural order parameter $\delta = (a - b)/(a + b)$ will couple to an in-plane stress difference $\sigma_{xx} - \sigma_{yy}$. Consequently, the $\mathcal{O}$ phase is stabilized by this coupling, and particularly so when the transition is weakly first order. Variable stresses can lead to a broadening of the structural transition, and possibly to the predominance of the $\mathcal{O}$ phase at low temperatures and intermediate pressures. Similar reasoning could lead to small amounts of $\mathcal{T}$ phase at low temperatures, even though it is not a ground state under hydrostatic conditions. Thus, we cannot distinguish between two possibilities for superconductivity: it could occur in a small fraction of $\mathcal{T}$ and/or $c\mathcal{T}$ phase(s), or in the majority $\mathcal{O}$ phase. With respect to the latter possibility, we note that in Ref. [10], the detection of superconductivity in the clamped cells is attributed to doping into the $\mathcal{O}$ phase from a minority $c\mathcal{T}$ phase, and the increase of $(T_1T)^{-1}$ by approximately a factor of 2 with the application of pressure could be associated with such a change in carrier concentration.

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