75\textsuperscript{As} NMR study of antiferromagnetic fluctuations in Ba(Fe$_{1-x}$Ru$_x$)$_2$As$_2$

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Abstract

The evolution of 75\textsuperscript{As} NMR parameters with composition and temperature was probed in the Ba(Fe$_{1-x}$Ru$_x$)$_2$As$_2$ system where Fe is replaced by isovalent Ru. While the Ru end member was found to be a conventional Fermi liquid, the composition ($x = 0.5$) corresponding to the highest $T_c$ (20 K) in this system shows an upturn in the 75\textsuperscript{As} $^{1/T}$ below about 80 K, evidencing the presence of antiferromagnetic (AFM) fluctuations. These results are similar to those obtained in another system with isovalent substitution, BaFe$_2$(As$_{1-x}$P$_x$)$_2$ (Nakai et al 2010 Phys. Rev. Lett. 105 107003) and point to a possible role of AFM fluctuations in driving superconductivity.

(Some figures may appear in colour only in the online journal)

1. Introduction

The recent discovery of superconductivity in an iron based material [1], LaFeAs(O$_{1-x}$F$_x$), with a superconducting transition temperature $T_c = 26$ K and, soon after, the increase of $T_c$ to 43 K with applied pressure [2] has reigned the interest in superconductors. The main motivating factors for this interest are (i) the presence of Fe, which is normally not considered conducive to superconductivity and (ii) the superficial similarity to the high $T_c$ cuprates, in terms of the existence of FeAs layers.

The parent compound BaFe$_2$As$_2$ is a semimetal which crystallizes in a ThCr$_2$Si$_2$-type structure (I4/mmm) and exhibits a spin-density-wave (SDW) transition [3] at $\sim$140 K. Superconductivity is induced following electron/hole doping [4, 5], by applying pressure externally [6], by replacing As with isovalent P [7], or by replacing Fe with isovalent Ru [8].

Heterovalent substitutions manifestly give rise to a change in the carrier concentration in addition to other effects. Therefore, it appears interesting to investigate isovalent substitutions which might help to narrow down the relevance of various factors to superconductivity. Perhaps with this motivation, Ru substitution at the Fe site was attempted [8–10]. In the reported works relevant to single crystals, the authors were able to substitute Ru in place of Fe, however, only up to limits of $x = 0.37$ (in [9]) and $x = 0.5$ (in [10]). Very recently, Eom et al [11] prepared single crystals up to $x = 0.7$. On the other hand, in the work on polycrystalline Ba(Fe$_{1-x}$Ru$_x$)$_2$As$_2$ by Sharma et al [8], complete substitution was achieved. For Sr(Fe$_{1-x}$Ru$_x$)$_2$As$_2$ as well, Schnelle et al [12] achieved full substitution of Fe with Ru in polycrystalline samples. Ru substitution suppresses the long-range antiferromagnetic transition and superconductivity appears. The role played by antiferromagnetic spin fluctuations has been suggested to be important, towards a pairing mechanism.

From magnetic susceptibility measurements, Nath et al [13] have estimated the density of states at the Fermi level $D(\varepsilon_F)$ of BaRu$_2$As$_2$ to be 2.1 states eV$^{-1}$/formula unit. Thaler et al have done a detailed study on single-crystalline Ba(Fe$_{1-x}$Ru$_x$)$_2$As$_2$ samples where they have shown the similarity of its phase diagram with that of BaFe$_2$As$_2$ with pressure [9]. Brouet et al [14] have studied a Ba(Fe$_{0.8}$Ru$_{0.2}$)$_2$As$_2$ single crystal using electrical transport and photoemission spectroscopy and concluded that the electron and hole concentrations were equal to each other but double those in BaFe$_2$As$_2$. The increase in carrier concentration has been attributed to a large change in the band

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structure as compared to undoped BaFe$_2$As$_2$. From thermal conductivity measurements on Ba(Fe$_{0.64}$Ru$_{0.36}$)$_2$As$_2$ single crystal and comparing their data with other doping samples, Qiu et al [15] have shown that nodal superconductivity induced by isovalent doping (P at the As site and Ru at the Fe site) has the same origin. From electrical transport measurements, Eom et al [11] suggest that whereas there is a deviation from Fermi-liquid behaviour for compositions around the maximum $T_c$, overdoped compositions tend towards a Fermi-liquid behaviour. However, due to the difficulty in preparing single crystals of BaRu$_2$As$_2$, no comparison exists between the superconducting compositions and the Ru end member.

Nuclear magnetic resonance (NMR) has been instrumental in the case of cuprates in detecting antiferromagnetic fluctuations, the pseudo-gap, and other features. In the FeAs compounds as well, NMR has been extensively used to obtain a deeper understanding of various physics issues [16]. In fact, in the isovalent substituted system BaFe$_2$(As$_{1−x}$P)$_x$$_2$, $^{31}$P NMR was found to show the prominence of antiferromagnetic fluctuations above $T_c$ in the superconducting compositions [17]. However, up to now, no local probe investigations have been reported which might help us to understand the variation of properties in the Ba(Fe$_{1−x}$Ru$_x$)$_2$As$_2$ system. In this paper, we report $^{75}$As NMR measurements on Ba(Fe$_{1−x}$Ru$_x$)$_2$As$_2$ ($x = 0, 0.25, 0.5, 1$) samples. From our measurements, we show that the Ru end member behaves like a conventional Fermi liquid. In contrast, for the $x = 0.5$ sample ($T_c^{\text{nom}}$ = 20 K), $^{75}$As $\gamma T_1$ is constant at high $T$ but increases with decrease in $T$ below 80 K, suggesting the emergence of antiferromagnetic fluctuations. Also, no evidence of heavy Fermi-liquid behaviour in Ba(Fe$_{1−x}$Ru$_x$)$_2$As$_2$ is found from our NMR measurements.

2. Experimental details

Polycrystalline samples of Ba(Fe$_{1−x}$Ru$_x$)$_2$As$_2$ ($x = 0, 0.25, 0.5, 1$) were prepared at IGCAR as detailed in [8]. Basic characterization of the samples was done by means of x-ray diffraction, magnetization, and resistivity measurements. For NMR measurements, we tried to align the powder samples by mixing with Stycast 1266 epoxy and then curing overnight in an external magnetic field $H = 93,954$ kOe. $^{75}$As NMR measurements were carried out at IIT Bombay using a Tecmag pulse spectrometer in a magnetic field of 93,954 kOe using a room temperature bore Varian superconducting magnet. Variable temperature measurements were performed using an Oxford continuous flow cryostat, using liquid nitrogen in the temperature range 80–300 K and using liquid helium in the temperature range 4–80 K. The $^{75}$As has nuclear spin $I = \frac{3}{2}$ (100% natural abundance) and gyromagnetic ratio $\gamma T_2 = 7.2919$ MHz T$^{-1}$. Spectra were obtained by Fourier transforming the spin echo resulting from a $\frac{T}{2}$–$\tau$–$\frac{T}{2}$ pulse sequence. The spin–lattice relaxation time ($T_1$) was obtained by fitting the time dependence of the spin-echo intensity $m(t)$ with the formula

$$1 − m(t)/m(\infty) = A \exp(-t/T_1) + B \exp(-6t/T_1)$$  \hspace{1cm} (1)

following a $\frac{T}{2}$–$t$–$(\frac{T}{2}$–$\frac{T}{2})$ sequence where the $\frac{T}{2}$ pulse duration is $\sim 4$ $\mu$s. 

3. Results and discussion

X-ray powder diffraction revealed the presence of a small amount (several per cent) of FeAs as well as unreacted Fe and Ru present in the samples. The average Ru content is expected to be less than the nominal amount, as was already found by others [9, 10]. Another point to note is that the x-ray diffraction peaks for our $x = 0.5$ sample are broad compared to those of the end members. This is probably due to a distribution of Ru content for this sample. Similar broadened peaks were also found for Sr(Fe$_{1−x}$Ru$_x$)$_2$As$_2$ [18]. The inability of Thaler et al [9] and Rullier-Albenque et al [10] to obtain homogeneous single crystals of Ba(Fe$_{1−x}$Ru$_x$)$_2$As$_2$ with $x > 0.21$ is perhaps related to the difficulty in obtaining a sharply defined composition. In any case, whereas a small amount of extrinsic impurity or a distribution of Ru content does affect bulk properties like the magnetization and resistivity, using a local probe such as NMR we will be able to probe the intrinsic properties.

The resistivity and magnetic susceptibility (not shown here) evidence the occurrence of superconductivity in the BaFeRuAs$_2$ ($x = 0.5$) sample with a transition onset at $\sim 20$ K, similar to the findings of [8]. Following this basic characterization, we investigate the normal state properties using $^{75}$As NMR as a local probe. Before describing our measurements, we will first state some basic facts pertaining to the NMR of $^{75}$As nuclei. In the Ba(Fe$_{1−x}$Ru$_x$)$_2$As$_2$ system, $^{75}$As ($I = \frac{3}{2}$) is not at a site of cubic symmetry. This gives rise to a non-zero electric field gradient (EFG) at the $^{75}$As site and coupled with its electric quadrupole moment, there arise changes in the NMR lineshape as well as the spin–lattice relaxation behaviour. When the quadrupole term in the Hamiltonian is weak compared to the Zeeman term it is enough to consider the effects up to first order in perturbation theory. In this case, the central line ($\frac{1}{2} ← \frac{1}{2}$ transition) is unaffected while satellite lines appear corresponding to the $\frac{1}{2} ← \frac{3}{2}$ and $\frac{3}{2} ← \frac{1}{2}$ transitions. The positions of the satellite lines depend on the angle $\theta$ between the magnetic field direction and the direction made by the maximum of the EFG $V_{zz}$. When quadrupole effects are considered to second order (and for axial symmetry), the central line position (in the absence of anisotropy) also depends on $\theta$ and is given by the following equation:

$$v^{(2)}(\pm \frac{1}{2}) = v_0 + \frac{v_Q}{32v_0} \left[ I(I + 1) - \frac{3}{4} \right] (1 - \cos^2 \theta) (9 \cos^2 \theta - 1)$$  \hspace{1cm} (2)

where $v_Q$ is the quadrupole frequency and $v_0$ the Larmor frequency. For a randomly aligned polycrystalline sample the central lineshape is the powder average, resulting in two peaks corresponding to $\theta \approx 41.8^\circ$ and $\theta = 90^\circ$. It is known [19] that $v_Q$ for BaFe$_2$As$_2$ is about 3 MHz. The central line pattern for our randomly aligned BaFe$_2$As$_2$ sample can be generated (see the inset of figure 1) taking $v_Q = 3.028$ MHz. In going
from BaFe$_2$As$_2$ to BaRu$_2$As$_2$, these numbers are expected to change only nominally.

We have attempted to align the samples with the $ab$-plane in the applied field direction. As seen from the contrast between figure 1 inset (randomly aligned) and the curve for $x = 0$ (aligned sample) in the main part of figure 1, this is well achieved for BaFe$_2$As$_2$. However, it appears that the Ru substituted samples did not align in the field. This arises perhaps due to the absence of single crystallites in the powders. Nevertheless, our objectives from the spectra measurements are twofold: (i) to determine the Knight shift as a function of temperature and (ii) to irradiate the central line and then determine the spin–lattice relaxation rate. From measurements are twofold: (i) to determine the Knight shift as a function of temperature and (ii) to irradiate the central line for the central line for BaFe$_2$As$_2$ (blue dots), and the simulated spectrum (red line) for the central line for $v_0 = 3.028$ MHz and $\eta = 0$ (see the text).

Figure 1. $^{75}$As NMR spectra measured at room temperature in a fixed field of 93.954 kOe for all four Ba(Fe$_{1-x}$Ru$_x$)$_2$As$_2$ samples. The $^{75}$As reference frequency is marked by a dashed vertical line. Inset: the $^{75}$As NMR spectrum for a randomly oriented powder sample of BaFe$_2$As$_2$ (blue dots), and the simulated spectrum (red line) for the central line for $v_0 = 3.028$ MHz and $\eta = 0$ (see the text).

Figure 2. Shifts for various compositions are shown as a function of temperature $T$. For the metallic one ($x = 1$) the shift $K$ is nearly independent of $T$. For $x = 0.5$ the superconducting transition is manifested by a steplike change in $K$.

The measured spectra could be simulated assuming $K_x = K_y \approx K_z = K$, $v_0 = 3.028$ MHz and $\eta = 0$ (i.e., $V_{xx} = V_{yy}$). The isotropic shift is therefore determined using equation (2) ($K = \frac{v_0 - v_{ref}}{v_{ref}}$), $K$ gives useful information about the intrinsic susceptibility (having both spin and orbital contributions) of the sample. We have $K = K_{spin} + K_{chem}$, where $K_{spin} = \frac{A_{hf}x_{spin}}{N_A \mu_B}$ is the spin part of the Knight shift and $K_{chem}$ is the temperature independent chemical shift. The hyperfine coupling is $A_{hf}$ while $N_A$ and $\mu_B$ are the Avogadro number and the Bohr magneton, respectively. The temperature variation of the shift is shown in figure 2. As regards the value of the chemical shift, there is some disagreement in the literature. Ning et al [20] estimated the chemical shift from their measurement at 4.2 K. On the other hand, Kitagawa et al [21] obtained the chemical shift by plotting $K$ against $\chi$ and then extrapolating to zero susceptibility. Kitagawa et al commented that the value of $K_{chem} \sim 0.2\%$ (also found by Ning et al) seemed rather large and perhaps the extrapolation was not reliable. In view of this as well as the possibility that $K_{chem}$ might be composition dependent, we have not corrected our shift data for the chemical shift.

For $x = 1$, the shift is almost independent of temperature like for a conventional Fermi liquid. For the other three samples (including the superconducting composition) the shift value is higher than that for $x = 1$. Further, it increases linearly with temperature above 160 K. Below 160 K the shift is independent of the temperature for $x = 0.25$ and 0.5 samples. The drop in the shift at $\sim 20$ K for $x = 0.5$ is due to the superconducting transition. The SDW transition is seen at $140$ K and $70$ K for $x = 0$ and 0.25, respectively. The nearly unchanged shift in going from $x = 0$ to 0.5 indicates that the density of states at the Fermi level $D(\varepsilon_F)$ remains unchanged with substitution up to $x = 0.5$. On the other hand, the non-superconducting, metallic end member has a significantly smaller shift (and therefore $D(\varepsilon_F)$). If $K_{chem}$ is taken to be about 0.2% (as in [20]) the reduction in $K_{spin}$ is by a factor of 2 in going from $x = 0.5$ to 1. A similar trend is seen in BaFe$_2$(As$_{1-x}$P$_x$)$_2$ for the larger values of $x$ beyond the superconducting dome [17].

To study the low energy spin dynamics, $T_1$ is measured as a function of temperature for all the samples by the saturation recovery method. A representative data set for BaRu$_2$As$_2$ at 50 K and its fit with equation (1) are shown in the inset of figure 3.

For the $x = 1$ sample, the data could be fitted with $A:B = 1 : 9$ over the full temperature range as well as for other compositions for temperatures higher than about 60 K. At lower temperatures the ratio of the coefficients is about 4:6. The ratio of the coefficients is expected to be different from 1:9 if the relaxation is not magnetic. In the present case, it is possible that the lattice becomes soft prior to the superconducting transition and then quadrupolar
relaxation also contributes. However, there could be other possibilities. The variation of the relaxation rate divided by temperature as a function of temperature is shown in figure 3. Note that conventional, wide-band metallic systems will have a $T$ independent $K_{\text{spin}}$. Therefore, Korrington behaviour ($T$ independent $K_{\text{spin}}^2 T_1 T$) in a conventional metal implies constancy of $\frac{1}{T_1 T}$ with varying $T$. For the non-superconducting $x = 1$ composition, $\frac{1}{T_1 T}$ is seen to be independent of $T$ down to 4 K. Its shift is also found to be only weakly dependent on $T$. Of course, one needs to know $K_{\text{chem}}$ in order to make a quantitative comment about the variation with $T$ of $K_{\text{spin}}$ and consequently of $K_{\text{spin}}^2 T_1 T$. Since the present problem involves transferred hyperfine interactions, the relaxation rate may also be affected by the form factor (dependence on $q$ of the hyperfine couplings) which could lead to a deviation from the free-electron value of $K_{\text{spin}}^2 T_1 T$ as well as its expected independence of $T$. Our observed value of $K_{\text{spin}}^2 T_1 T$ for $x = 1$ is within an order of magnitude of the free-electron value and is also nearly independent of $T$ which, keeping the above limitations in mind, seems to suggest the validity of the Fermi-liquid picture for BaRu$_2$As$_2$. It is worth mentioning that Eom et al [11] also found Fermi-liquid behaviour for higher doping ($x \sim 0.7$) samples. In contrast, for the superconducting sample ($x = 0.5$), $T_1 T$ is independent of $T$ down to about 80 K, below which it shows an upturn before dropping at the superconducting transition at $T \sim 20$ K. The upturn in $T_1 T$ as a function of temperature has also been seen (in the context of iron pnictides) in BaFe$_2$As$_2$ in $^{31}$P NMR studies [17] and is believed to signify the existence of antiferromagnetic fluctuations. For $x = 0$ and 0.25, $\frac{1}{T_1 T}$ shows an anomaly at the SDW transition which is also seen in shift measurements. Compiling the published data on BaFe$_{1-x}$Ru$_x$)$_2$As$_2$ (single crystals and powders), we summarize its magnetic phase diagram in figure 4. Data for Sr(Fe$_{1-x}$Ru$_x$)$_2$As$_2$ are also shown for reference. The heavily overdoped region exhibits Fermi-liquid behaviour and near the top of the superconducting dome, there is a prominence of AFM fluctuations along with non-Fermi-liquid behaviour, according to the NMR data. The AFM/SDW part shows anomalies in the shift at the ordering temperature, as expected.

4. Conclusions

We have reported $^{75}$As NMR measurements for Ba(Fe$_{1-x}$Ru$_x$)$_2$As$_2$ ($x = 0, 0.25, 0.5, 1$) samples for the first time. The fully ruthenated sample ($x = 1$) is a conventional Fermi liquid as evidenced from shift and $T_1$ measurements. On moving towards the superconducting composition ($x = 0.5$), the density of states at the Fermi level increases. Further, for the $x = 0.5$ sample, $\frac{1}{T_1 T}$ shows an upturn with decreasing temperature indicative of the emergence of antiferromagnetic fluctuations. Our results suggest the importance of AFM fluctuations in the superconducting mechanism in the FeAs based systems. Similar results have been reported for isovalent P substitution at the As site [17].

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