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Mössbauer spectroscopy study of magnetic fluctuations in superconducting $RbGd_2Fe_4As_4O_2$

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ABSTRACT

^{57}Fe Mössbauer spectra were measured at different temperatures between 5.9 K and 300 K on the recently discovered self-doped superconducting $RbGd_2Fe_4As_4O_2$ with T_c as high as 35 K. Singlet pattern was observed down to the lowest temperature measured in this work, indicating the absence of static magnetic order on the Fe site. The intermediate isomer shift in comparison with that of the samples $RbFe_2As_2$ and GdFeAsO confirms the self doping induced local electronic structure change. Surprisingly, we observe two magnetic fluctuation induced spectral broadenings below ~15 K and ~100 K which are believed to be originated from the transferred magnetic fluctuations of the Gd^{3+} moments and that of the magnetic fluctuations of the Fe atoms, respectively.

1. Introduction

The discovery of superconductivity (SC) at 26 K in $LaFeAsO_{1-x}F_x$ [1] has led to many following discoveries of new superconductors containing the same basic FeX (X = As, Se) units that are responsible for the high temperature SC [2–6]. Among many other topics, tremendous results have been made regarding the phenomenon of SC and its interplay with magnetism [7–10]. One of the most promising scenarios for the observed SC is the spin fluctuation mediated pairing mechanism which is the common thread linking a broad class of superconductors including not only the Fe and Cu based materials but also the heavy fermion superconductors [10]. However, the debates on this issue have never stopped and further investigation on other new families of superconductors is highly encouraged.

As for the Fe based superconductors, SC can either be induced by chemical doping or external pressure [6] and SC in both situations were found to be closely related to their magnetic properties [8–10]. Interestingly, a third route towards SC, namely the self doping effect, was realized in $Sr_2VFeAsO_3$ [11], $Ba_2Ti_2Fe_2As_4O$ and $RbGd_2Fe_4As_4O_2$ [2,5,12]. Rich magnetism has been found and studied with SC for $Sr_2VFeAsO_3$ and it is found that magnetism and SC coexist in the freshly prepared $Sr_2VFeAsO_3$ [13]. However, the magnetism disappeared after long term storage of the sample indicating that it is meta-stable in nature which might be induced by defects or residual stress [13]. For the $Ba_2Ti_2Fe_2As_4O$ superconductor, neutron scattering measurements have been performed and no noticeable magnetism has been found. Additionally, nonmagnetic first principle calculations reproduced well the measured phonon spectra indicating again the nonmagnetic character of the superconducting $Ba_2Ti_2Fe_2As_4O$ [14].

On the other hand, Gd^{3+} moments were suggested to order at low temperatures within the superconducting ground state in $RbGd_2Fe_4As_4O_2$[5]. Despite the fact that the Gd^{3+} moments order in separate layers than the superconducting FeAs layer, a local probe study to see if there is any transferred magnetic fluctuations from the Gd^{3+} moments at the Fe site is very interesting. In addition, investigation of the local electronic structure around the Fe nucleus should be helpful to have a better understanding of the self doping induced SC.

Fruitful results regarding the local electronic structure and magnetic properties of the Fe based superconductors have already been obtained by Mössbauer spectroscopy in the past [15–22]. Therefore, in this work, we performed detailed ^{57}Fe Mössbauer spectroscopy measurements on the sample $RbGd_2Fe_4As_4O_2$ in the temperature range of 5.9–300 K. Our results reveal an intermediate electronic structure between that of the Fe in $RbFe_2As_2$ and GdFeAsO, suggesting that the self hole-doping effect really extends

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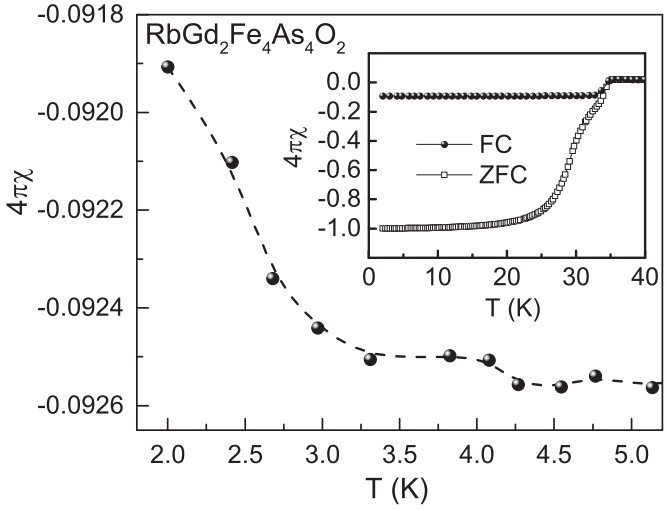

Fig. 1. Temperature dependence of the $4\pi\chi$ data of $RbGd_2Fe_4As_4O_2$ measured in the FC mode with 10 Oe magnetic field, revealing the ordering temperature of the Gd^{3+} moments, T_N ~3 K. Inset shows both the FC and ZFC data, showing the superconducting transition temperature, T_C ~35 K.

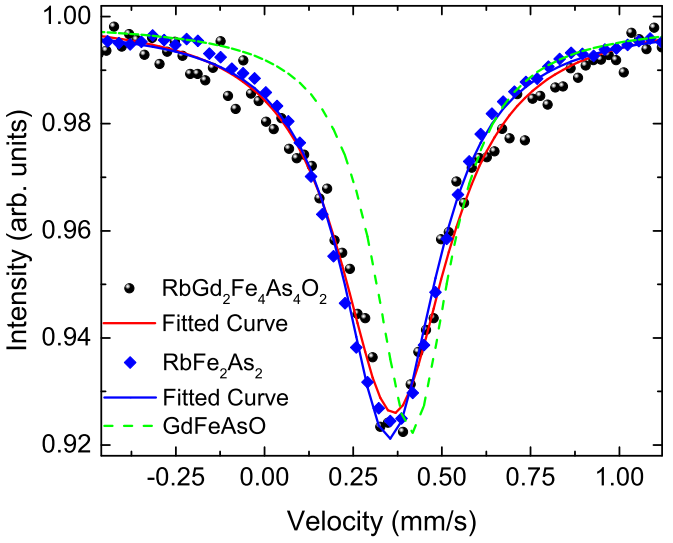

Fig. 2. The 300 K ^{57}Fe Mössbauer spectra of $RbGd_2Fe_4As_4O_2$ (black dots) and $RbFe_2As_2$ (blue diamond) together with singlet fits. The green dashed line is calculated curve of GdFeAsO using hyperfine parameters taken from Ref. [26]. Note that these spectra were shifted and normalized together for better view. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

to the Fe site. More interestingly, we found evidence of magnetic fluctuations at the Fe site not only due to that transferred from the Gd^{3+} moments but also due to the Fe moments itself. These results provide us a new system to further study the interplay of magnetism with SC.

2. Experiments

Polycrystalline material of $RbGd_2Fe_4As_4O_2$ was synthesized by a solid-state reaction method. Detailed preparation procedure and its physical properties have been reported earlier [5]. Two-phase Rietveld analysis of the X-ray diffraction pattern showed that the mass fraction of the main phase $RbGd_2Fe_4As_4O_2$ amounts to 94% and the only detectable impurity phase is unreacted Gd_2O_3 [5]. As shown later, this impurity phase is transparent to our ^{57}Fe Mössbauer measurements since it does not contain Fe element and thus has no influence on the data analyses. $RbFe_2As_2$ single crystal was grown with self flux method and measured at room temperature for comparison purpose. Detailed information with further physical characterization will be reported separately.

Transmission Mössbauer spectra (MS) at temperatures between 5.9 K and 300 K were recorded using a conventional spectrometer working in constant acceleration mode with a γ-ray source of 25 mCi ^{57}Co(Rh) vibrating at room temperature. The drive velocity was calibrated using sodium nitroprusside (SNP) powder and the isomer shifts (IS) quoted in this work are relative to that of the α-Fe foil at room temperature. The full linewidth (LW) at half maximum of the SNP spectrum was 0.244(2) mm/s and this value can be regarded as the resolution of the spectrometer. The absorber was prepared with a surface density of ~10 mg/cm^2 of natural iron. All the MS were analyzed with MossWinn 4.0 [23] program.

3. Results and discussion

In Fig. 1, we present the temperature dependence of the susceptibility data of $RbGd_2Fe_4As_4O_2$ below about 5 K measured in the field cooling (FC) mode with 10 Oe magnetic field. Inset of Fig. 1 is a plot of the susceptibility data measured in both zero field cooling (ZFC) and FC modes, showing the superconducting transition temperature, T_C ~35 K [5]. The increase of the FC data with decreasing temperature below T_{mag} ~3 K signals the onset of magnetic ordering of the Gd^{3+} moments. The upturn is not likely due to the small amount of Gd_2O_3 impurity phases since cubic Gd_2O_3 exhibits an antiferromagnetic transition at 1.6 K and monoclinic Gd_2O_3 has an antiferromagnetic transition at 3.4 K [24]. This conclusion is consistent with the low temperature upturn of the specific heat data [5] which suggests a bulk effect of this transition. As for the nature of this magnetic transition, it is most likely to be canted antiferromagnetism. This is consistent with the negative Curie–Weiss temperature obtained from the high temperature magnetic susceptibility data (not shown). Note that for a similar compound $RbDy_2Fe_4As_4O_2$ with Dy^{3+} magnetic moments becomes antiferromagnetically ordered below about 10 K [25]. Of course, future neutron diffraction measurements are needed to clarify this point.

One interesting feature of the compound $RbGd_2Fe_4As_4O_2$ is self doping induced superconductivity with a transition temperature as high as 35 K [5]. As shown by the structural characterization, actual self doping was suggested by the charge redistribution which was reflected from the structural reconstruction, namely the 'GdFeAsO' building block becomes slender while the '$RbFe_2As_2$' block goes the opposite when compared with the two separate compounds GdFeAsO and $RbFe_2As_2$ [5]. In order to see if this self doping effect really happens locally, namely at the Fe site, we compare the 300 K MS of the $RbGd_2Fe_4As_4O_2$ superconductor with that of the $RbFe_2As_2$ and GdFeAsO in Fig. 2. The MS of the GdFeAsO shown in Fig. 2 was calculated using hyperfine parameters taken from reference [26]. One can see that the center or IS of the MS shifts to positive direction from sample $RbFe_2As_2$ to $RbGd_2Fe_4As_4O_2$ and GdFeAsO, reflecting a decrease of the *s*-electron density at the Fe nucleus. To be quantitative, the fitted IS value for sample $RbGd_2Fe_4As_4O_2$ is IS = 0.364(6) mm/s which is much closer to the value of IS = 0.352(2) mm/s for sample $RbFe_2As_2$ when compared to the value of IS = 0.415(4) mm/s for sample GdFeAsO [26]. This is different with the case for the intermediate value of IS = 0.372(2) mm/s for the intergrown sample $CaKFe_4As_4$ in comparison with that of samples KFe_2As_2 IS = 0.311(1) mm/s and $CaFe_2As_2$ IS = 0.430(2) mm/s [27]. This could be due to different chemical environments of