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Local probe studies of Fe hyperfine field in $CaFe_2As_2$ by time differential perturbed angular distribution (TDPAD) spectroscopy and *ab initio* methods

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ABSTRACT

Applying the γ-ray perturbed angular distribution technique we have measured the magnetic hyperfine field and spin relaxation time of recoil implanted ^{54}Fe in single and polycrystalline $CaFe_2As_2$ over the temperature range 20–360 K, encompassing both tetragonal and orthorhombic structural phases of the material. The magnetic response of Fe in the high temperature tetragonal phase ($T \geqslant 180$ K), show Curie–Weiss type local susceptibility and Korringa like spin relaxation, reflecting the presence of localized moment on Fe. In the orthorhombic phase, the spin rotation spectra of ^{54}Fe show two magnetic hyperfine field components, both exhibiting quasi two dimensional magnetic ordering. The experimentally measured hyperfine field and Fe moment show good agreement with results obtained from *ab initio* calculations performed within the frame work of local spin density approximation (LSDA).

1. Introduction

The discovery of superconductivity in ternary ferro-pnictides with chemical formula XFe_2As_2 (X = Ca, Sr, Ba, and Eu) have sparked enormous interest amongst researchers, experimental and theoretical alike, in the past few years [1]. In particular, the compound $CaFe_2As_2$ has attracted considerable attention. The compound crystallizing in $ThCr_2Si_2$ (I4/mmm) type tetragonal structure at room temperature shows a first order structural transformation, changing to an orthorhombic phase below the transition temperature $T_s(T_N) \approx 170$ K [2]. Concomitant with the structure change, the compound also exhibits first order antiferromagnetic (AFM) and/or spin density wave (SDW) magnetic phase transition [3]. Furthermore, it has been observed that application of pressure stabilizes the tetragonal structure, while quenching the magnetism of Fe and enabling the appearance of a superconducting ground state when non-hydrostatic component of the applied pressure is present [4]. Similarly, partial substitution of the Ca with alkali metals or the Fe with transition metals like Co and Ni has been found to suppress structural and magnetic phase transitions and induce superconductivity [5]. These results suggest that superconductivity in $CaFe_2As_2$ as well as other compounds in the family is intimately linked with structural and magnetic degrees of freedom. It is now widely believed that AFM spin fluctuations play an important role on the pairing mechanism for superconductivity in these materials [6,7]. In this regard, it is important to understand the magnetism of Fe, above and below the structural transition. While, magnetism of Fe in the low temperature orthorhombic phase has been studied in great detail using many different techniques, much less is known about its magnetic behavior in the tetragonal phase. Also, despite extensive investigations, there are many ambiguities regarding the magnetism of Fe in the orthorhombic phase. For example, low temperature neutron diffraction studies reveal that Fe atoms carry local moment of 0.8 μ_B/Fe, ordered in a commensurate antiferromagnetic (AFM) structure [8], which was further supported by nuclear magnetic resonance (NMR), muon spin relaxation (μSR) and ^{57}Fe Mössbauer (MS) studies [9–12]. On the other hand, MS measurements by other groups have reported the observation of multiple sub spectra with widely different values of the hyperfine field that was attributed to an incommensurate magnetic ordering [5,13]. It has been argued that the observed distribution in hyperfine field may be arising from stress/strains produced while powdering the sample for MS measurements [11]. As far the tetragonal phase is concerned, whether Fe atoms carry local moment or not is still an open question. Determination of local moment of Fe in tetragonal (paramagnetic) phase of $CaFe_2As_2$ from bulk magnetic susceptibility fails because experimental data in this case do not show Curie–Weiss temperature dependence. Recent inelastic neutron scattering studies have detected the presence of short range spin correlation from which

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the paramagnetic moment of Fe was estimated to be 0.7 μ_B [14]. Compared to the experimental results, the magnetic moment estimated from theoretical calculations based on density functional approach have been found to be much higher [15–17]. In view of the intriguing and multifaceted magnetic behavior of $CaFe_2As_2$, it is desirable to carry out further microscopic investigations in single and polycrystalline samples of this compound, preferably using a different experimental technique.

The method of γ-ray time differential perturbed angular distribution (TDPAD), involving in-beam measurement of hyperfine interaction of isomeric nuclear states produced via fusion evaporation reaction, is an effective tool for local investigation of static and dynamic magnetic interactions in solids [18–20]. We have applied this technique to study the magnetism of Fe in $CaFe_2As_2$ above and below the phase transition by measuring the hyperfine interaction and spin relaxation rate of ^{54}Fe in which the $I^{\pi} = 10^{+}$ state with half-life $T_{1/2}$ = 360 ns, gyro-magnetic ratio g_N = 0.728(1) and nuclear quadrupole moment Q = 0.29(4) [21] is ideally suited for the microscopic detection of magnetic interaction with sensitivity much higher than the most commonly used ^{57}Fe probe in Mössbauer studies. The local susceptibility and spin relaxation data of ^{54}Fe, measured in the paramagnetic tetragonal phase show Curie–Weiss type temperature dependence reflecting the existence of local moment on Fe. Below the magnetic transition (orthorhombic phase) we find multiple magnetic hyperfine fields components and probable reasons have been discussed.

2. Experimental details

Single crystalline $CaFe_2As_2$ was prepared by the commonly used Sn flux method and was characterized by X-ray diffraction studies. The macroscopic magnetic properties of the samples were ascertained from magnetization measurements using a SQUID magnetometer. Fig. 1 shows the data for the single crystal as well as polycrystal samples measured in a field of 1 T, the single crystal showing the magnetic transition at 166 K whereas the other at 170 K. TDPAD measurements were performed in single as well as polycrystalline samples. A sample of size 10 mm × 10 mm × 0.5 mm cut from a large single crystal with its *c*-axis oriented perpendicular to the large plane was used for our measurements. The polycrystalline sample was prepared by grinding a few pieces of small single crystals and pressing the powder to a pellet of 10 mm diameter and 0.5 mm thick. The ^{54}Fe nuclei were produced via the nuclear fusion evaporation ^{45}Sc(^{12}C, p2n)^{54}Fe by bombarding a thin foil (0.9 mg/cm^2) of natural Sc with 40 MeV pulsed ^{12}C beam provided by the 14UD Pelletron accelerator at TIFR, Mumbai. The ^{54}Fe probe, recoiling out of the Sc target were implanted inside the $CaFe_2As_2$ host at a depth of ≈1 μm. The concentration of ^{54}Fe in the host is typically <1 ppm. The ^{54}Fe nuclei produced via the heavy-ion reaction have spins aligned perpendicular to the beam direction and therefore yield anisotropic distribution of the decaying γ-radiation. In the presence of extra nuclear field e.g. internal or external magnetic field, due to hyperfine interaction the nuclear spins precesses with Larmor frequency ω_L which in turn causes time dependent modulation of the γ-ray intensity. By detecting the γ-rays from the isomeric state one observes the usual life time decay superimposed with the modulation due to spin precession. The PAD time spectra were recorded using high purity Germanium (HpGe) and/or La(Ce)Br_3 scintillation detectors placed at angles $\theta = \pm 45^{\circ}$ and $\pm 135^{\circ}$ with respect to the beam direction. The time resolutions τ_r for the Germanium/La(Ce)Br_3 detectors were ≈5 ns and 850 ps respectively. Measurements were carried out in the temperature range 10–350 K under external magnetic field of 1–2 Tesla, applied perpendicular to the plane of the detectors. From the normalized coincidence counts, $N(\theta,t)$, of each detector the ratio function defined as

$$R(t) = \frac{N(+\theta,t) - N(-\theta,t)}{N(+\theta,t) + N(-\theta,t)} \quad (1)$$

were generated. The spectra obtained for the detector pairs at $\pm 135^{\circ}$ and $\mp 45^{\circ}$ were summed and fitted to perturbation function for magnetic hyperfine interaction in the presence of transverse applied field, given by the expression

$$R(t) = (-3/4)A_2 e^{-\lambda t} \sin(2\omega_L t - \phi) f(\omega\tau_r) \quad (2)$$

Here, A_2 is the amplitude of the oscillatory perturbation function, ω_L is the Larmor precession frequency, λ is the damping due to nuclear spin relaxation caused by dynamic fluctuation of Fe moment and/or inhomogeneity of local surrounding of the probe atom, and ϕ is the phase factor arising from finite bending of the incoming beam due to applied field. The factor $f(\omega\tau_r) = (\omega^2\tau_r^2/2))$ accounts for attenuation of R(t) due to finite time resolution of the detectors. It must be mentioned here that for the high spin state in ^{54}Fe probe, the electric quadrupole interaction frequency $\omega_E \propto Q/I^2$ is much weaker compared to ω_L and thus does not have serious influence on the analysis of our spectra. Further details on TDPAD experiments can be found elsewhere [18–20].

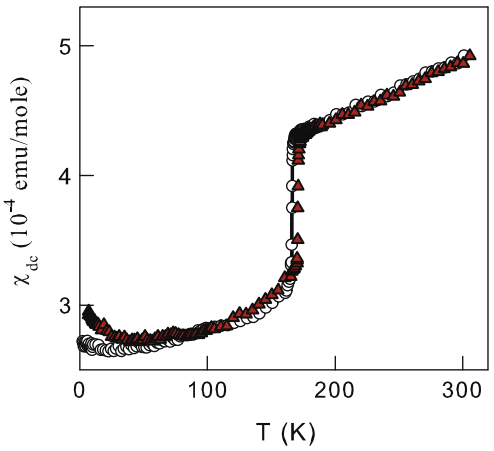

Fig. 1. DC magnetic susceptibility of single (○) and polycrystalline (△) $CaFe_2As_2$ measured as a function of temperature in applied field of 1 T using SQUID magnetometer. For the single crystal sample the magnetic field was applied along (100) direction.

3. Results and discussion

Figs. 2 and 3 show typical spin rotation spectra $R(t)$ of ^{54}Fe in single and poly crystalline $CaFe_2As_2$ at different temperatures along with corresponding Fourier transforms. The $R(t)$ spectra measured at all temperatures show well defined oscillations with high anisotropy indicating that the implanted ^{54}Fe atoms occupy unique lattice site. Considering the atomic size and the chemical properties of the elements present in the compound, the ^{54}Fe recoils are most likely to occupy the Fe site in $CaFe_2As_2$. Furthermore, the implanted ^{54}Fe is unlikely to occupy an interstitial site as the space available is too small to accommodate an additional atom. Spin rotation spectra measured above 180 K could be fitted by single component of magnetic interaction (Eq. 2) with ω_L changing with temperature. The spectra also show temperature dependent damping due to relaxation of nuclear spin caused by Fe spin fluctuation and/or inhomogeneity in the local environment of the probe atom. Below 180 K, the $R(t)$ spectra show visible beat pattern, indicating superposition of frequencies. Fourier analysis of the time spectra recorded in this temperature range show two well resolved frequency components with relative intensity ≈70:30.