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^{57}Fe Mössbauer Spectroscopy Studies of $CaFe_4As_3$

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We report the ^{57}Fe Mössbauer spectroscopy and dc magnetization studies of orthorhombic $CaFe_4As_3$, which undergoes two magnetic transitions with the formation of spin density wave at T_{N1} = 88 K (incommensurate) and T_{N2} = 26 K (commensurate). The magnetic Mössbauer spectroscopy spectra below T_{N1} are composed of four sub-spectra attributed to the four in-equivalent Fe crystallographic sites: three Fe ions are in the divalent state (Fe^{2+}) and one as Fe^{1+}. However, the magnetic lines are much broader than that below T_{N2}, indicating an incommensurate magnetic state. In the paramagnetic state, the Mössbauer spectroscopy spectra are composed of three doublets, one of them is related to Fe^{1+}. Evidence for spin fluctuations above T_{N1} is observed.

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Introduction

Recently, much attention has been focused on the research of Fe-based materials, because they reveal superconductivity with transition temperature comparable to cuprates. The building block of these materials is either Fe-As or Fe-Se layer formed by edge-shared $FeAs_4$ or $FeSe_4$ tetrahedra. Prior to chemical doping or application of pressure in so-called parent compounds, these Fe-As or Fe-Se layers exhibit long-range three-dimensional antiferromagnetic (AFM) spin-density-wave (SDW) order at $T_N \sim 140 - 150$ K or $520 - 550$ K with Fe^{2+} moment of 0.87(3) μ_B/Fe or 3.31 μ_B/Fe, respectively [1-2]. In $BaFe_2As_2$ the Fe moments are aligned within the *ab* plane [1], whereas neutron powder diffraction (NPD) shows that they are along the *c* axis in KFe_2Se_2 [2]. The major difference between the two systems, noticeable from several types of measurements, is that the temperature-composition phase diagrams show a generic behavior as a function of the substituent concentration (x) in the Fe-As based materials. This implies a systematic *suppression* of the magnetic transition by increasing x or pressure. Then, above a critical concentration (which depends on the substituent), superconductivity is observed [3-4]. On the other hand, the non-stoichiometric $A_zFe_{2-y}Se_2$ also becomes superconducting around $30 - 33$ K, but the AFM state persists even at low temperatures [5-6]. This means, in $A_zFe_{2-y}Se_2$, there is a *coexistence* of magnetism and superconductivity, since both states are confined to the same

Fe-Se crystallographic layer [5]. This makes the extensive search for new Fe-As based compounds inseparable from the search of new high - T_c superconducting materials.

The new compound $CaFe_4As_3$ is a good reference, as it has the same building block as Fe-As based superconducting compounds, i.e., edge – shared $FeAs_4$ tetrahedron. $CaFe_4As_3$ crystallizes in the orthorhombic structure (space group *Pnma)* with a = 11.873 Å, b = 3.740 Å and c = 1.574 Å [7], as reported in Ref. [8] and illustrated in Figure 1. NPD studies show that there are four independent Fe sites in the crystallographic unit cell, all of multiplicity four and in the (x, 1/4, z) positions as reported in Ref. [8]. Electrical resistivity, magnetic susceptibility and specific heat studies reveal the existence of two transitions [9-11]. Below T_{N1} ~ 88 K an incommensurate SDW along the b axis is observed, which undergoes below T_{N2} ~ 26 K to a commensurate SDW state in the *ac* plane [8].

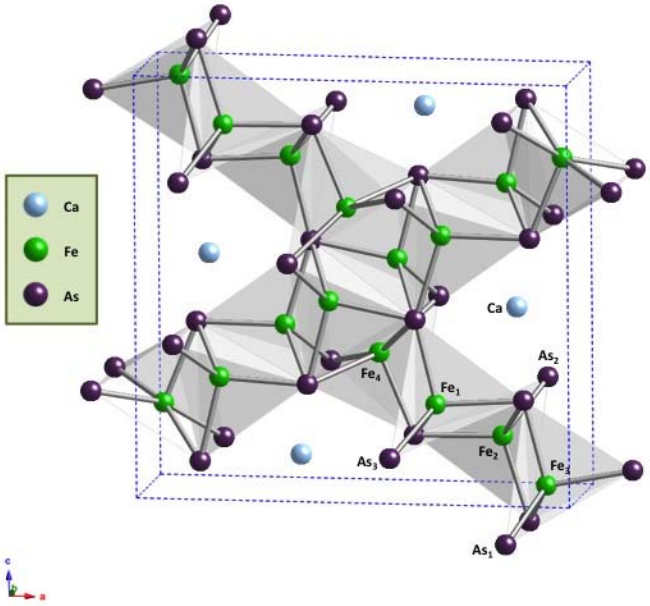

Figure 1: Crystallographic structure of $CaFe_4As_3$ with indication of four Fe sites.

Mössbauer spectroscopy (MS) of ^{57}Fe isotope seems particularly useful for studying $CaFe_4As_3$ system, as Fe makes the basic constituent of this compound. Formal charges of the various Fe ions can be assigned by assuming a complete electron transfer from the Ca and Fe cations to the As anions. In order to naturalize the unit cell charge, the formal Fe valences are three Fe^{2+} and one Fe^{1+} for Ca^{2+} and As^{3-}. Indeed, the room temperature (RT) MS study exhibits approximately two paramagnetic quadrupole subspectra with isomer-shifts (IS) of 0.32 (1) and 0.54(1) mm/sec and an intensity ratio of 3:1, thus confirming the

presence of the two Fe states [6]. Moreover, the substitution of Cr for Fe measured by NPD and MS show selectively Cr occupation in the Fe_4 site, which is attributed to the Fe^{1+} site [12].

Our focus in this report is the comprehensive ^{57}Fe MS studies of $CaFe_4As_3$ in both commensurate and incommensurate magnetic states as well as in the paramagnetic (PM) region. In the PM region, the MS spectra are actually composed of three subspectra (intensities 2:1:1) and that are attributed to three Fe^{2+} and one Fe^{1+} as identified by their isomer shifts (IS). Below T_{N1}, the MS are composed of four sub-spectra associated with the four in-equivalent Fe sites. In the commensurate region, the lines of all sub-spectra are much sharper than that in the incommensurate region.

Experimental details

Single crystals of $CaFe_4As_3$ were grown out of Sn flux. The detailed procedure is described in [9]. These crystals were ground into powder for measurements reported here. Zero-field-cooled (ZFC) temperature dependence of the magnetization measured under various applied fields was performed in a commercial MPMS5 Quantum Design SQUID magnetometer. Prior to recording ZFC curve, the SQUID magnetometer was adjusted to be in *"real"* H = 0 state. The ^{57}Fe Mössbauer studies of powder $CaFe_4As_3$ at temperatures 5 to 297 K, were performed using a conventional constant acceleration drive in transmission mode, in conjunction with a 50 mCi ^{57}Co:Rh source. The absorber was cooled to low temperatures in a Janis model SHI-850-5 closed cycle refrigerator. The spectra were analyzed in terms of least square fit procedures to theoretical expected spectra. The velocity-calibration was done by the spectrum of an α-iron foil. The reported IS are relative to this foil.

Experimental Results

Figure 2 shows the temperature dependence of magnetization (M) measured in the zero-field-cooled (ZFC) mode at 15 Oe for $CaFe_4As_3$ powder. The complicated temperature dependence of M is similar to that reported in Ref. [7]. The pronounced peak at T_{N2} = 26 K, the bent at T_{N1} = 88 K and a broad plateau at 88-112 K are readily observed. The isothermal field dependence of the magnetization M(H) measured at 5 and 140 K are presented in the inset. Both M(H) curves are not linear at low H. The linear part at 5 K reflects the AFM nature of the sample and the slope obtained is ~ 0.0135 emu/mole Oe. In the paramagnetic

range, the slope is ~0.0101 emu/mole Oe. The extrapolated values to H = 0 are 0.23 and 0.13 emu/g for T = 5 and 140 K, respectively. This means that a small fraction of a ferromagnetic extra phase is present, probably 0.06-0.1% of Fe, not detectable by x-ray diffraction and/or by MS. Above ~ 350 K, the compound follows the Curie-Weiss law [9].

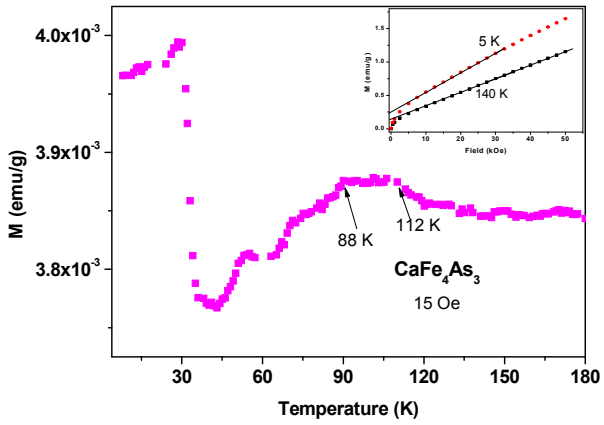

Figure 2: Temperature dependence of magnetization of $CaFe_4As_3$ powder measured at 15 Oe in ZFC mode. The isothermal magnetization at 5 and 140 K are shown in the inset.

^{57}Fe MS studies of $CaFe_4As_3$ at a wide range of temperatures have been performed. Figure 3 shows the MS of $CaFe_4As_3$ below (left panel) and above (right panel) T_{N1}. The hyperfine parameters deduced are summarized in Tables I – II. Due to the higher resolution in our spectra in comparison to those reported in Refs. [7, 12], we are confident that in the paramagnetic range (at 125 K and at room temperature), the spectra display *three* pure quadrupole spectra with a common line width of 0.263 mm/s and intensity ratio 2:1:1 (see Fig. 3). It seems that two of the Fe^{2+} sites are indistinguishable and have almost the same hyperfine parameters. The first two subspectra have similar IS (0.32 mm/s and 0.33 mm/s at 297 K) corresponding to Fe^{2+}, but possess different quadrupole interactions EQ (=¼e^2qQ) (see Table I). The hyperfine parameters of the third subspectrum are much larger: IS = 0.535 mm/s, and EQ = 0.248 mm/s, which may correspond to Fe^{1+} [6]. The larger IS values at 125 K, relative to that obtained at 297 K, is due to the thermal shift as expected.

T (K)		$2Fe^{2+}$	Fe^{2+}	Fe^{1+}
125	I.S. (mm/s)	0.45(1)	0.45(1)	0.67(1)
	EQ (mm/s)	0.10(1)	0.20(1)	0.26(1)

297	I.S. (mm/s)	0.32(1)	0.33(1)	0.53(1)
	EQ (mm/s)	0.10(1)	0.17(1)	0.25(1)

Table I: Isomer shift (IS) and quadrupole splitting (EQ) of $CaFe_4As_3$ in the paramagnetic state.

As can be seen in Fig. 3, the spectra display four equally intense subspectra (fixed intensity ratios) below T_{N1}, revealing additional magnetic splitting with distributions in hyperfine fields (H_{eff}) which is typical to spin density wave Mössbauer spectra. All subspectra were fitted with a fixed common line width of 0.284 mm/s. While the resolution of the separate absorption lines is reasonable at 5 K (below T_{N2}, the commensurate SDW region), the spectra become much worse at $T_{N2} < T < T_{N1}$ (the incommensurate SDW region), even though they display little change in total width. The observed four H_{eff} values

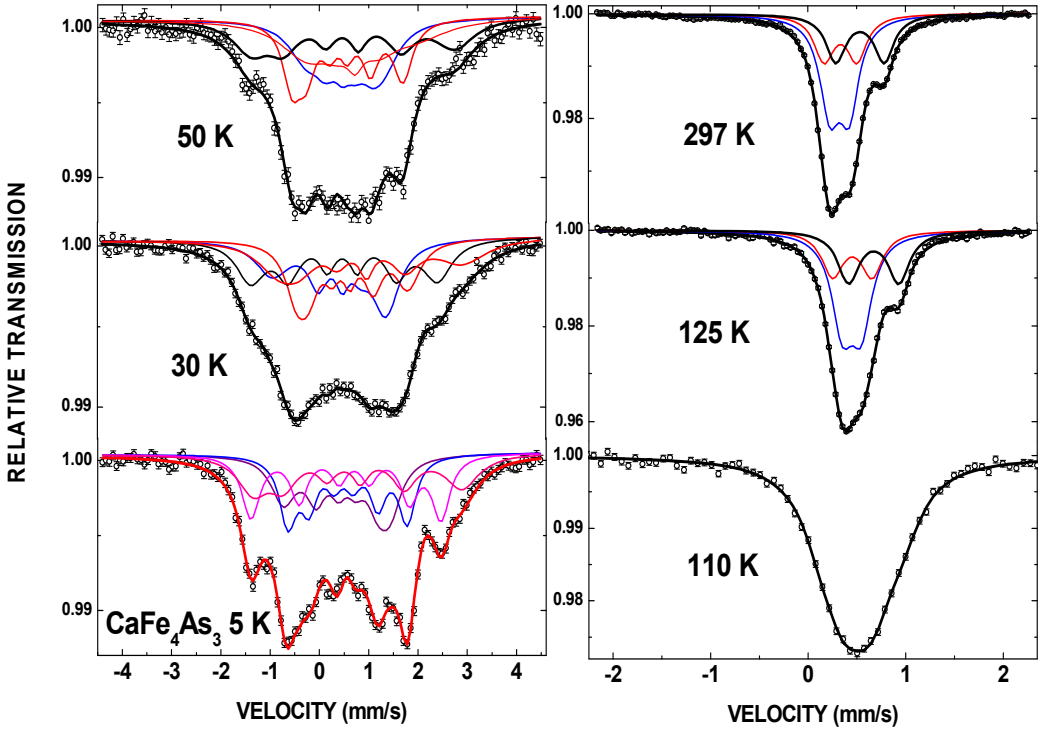

Figure 3: Mössbauer spectra of $CaFe_4As_3$ below (left) and above (right) T_{N1} = 88 K. Notice the different scales.

in Table II, are due to four in-equivalent Fe sites. At 5 K, the largest IS = 0.805 mm/s (in comparison with the others with IS less than 0.547 mm/s) is attributed to Fe_4 (Fe^{1+}),

following the assignment done in Refs. [8,12]. The higher IS values at 5 K relative to that obtained at room temperature, is due (as expected) to the second-order Doppler Effect. From the H_{eff} values obtained at 5 K one may deduce the saturated magnetic moment (M_S) acting on the Fe ions at low temperatures. In general, H_{eff} is proportional to the magnetic moment M_S. Therefore, the H_{eff} values obtained are attributed to M_S of the four sites deduced from NPD [8]. The constant of proportionality, $\beta = H_{eff}/M_s$, is ~ 6 T/μ_B in the present case. This value is much smaller than that obtained for Fe or Fe_2O_3 (~11-15 T/μ_B) and is consistent with the conclusion made in Ref. [13]. According to Ref. [13], β depends on various parameters, thus the scaling of H_{eff} and M_s is not unique. The spectrum obtained at 50 K is quite similar to that of 30 K (see Fig. 3). As it is in the incommensurate SDW state, the hyperfine values deduced at 50 K are not conclusive and therefore are not included in Table II. It is worth mentioning that magnetic spin fluctuations exist above T_{N1} = 88 K. Fig. 3 shows a broad spectrum at 110 K, compared to the spectra at 125 K and room temperature. This is consistent with the broad maximum observed in magnetization (see Fig. 2).

T (K)		Fe_1	Fe_2	Fe_3	Fe_4 (Fe^{1+})
5	IS (mm/s)±0.01	0.50	0.55	0.37	0.81
	EQ_{eff} (mm/s) ±0.01	0.03	0.08	-0.24	0.13
	H_{eff} (T) ±0.2	11.6	7.2	7.5	11.5
	M_S (μ_B) at 1.5 K	2.14	1.55	1.83	1.94
30	IS (mm/s)±0.01	0.48	0.55	0.43	0.84
	EQ_{eff} (mm/s) ±0.01	0.01	0.11	-0.20	0.18
	H_{eff} (T) ±0.2	11.7	7.0	7.2	11.6
	M_S (μ_B) at 30 K	1.40	1.61	1.67	1.84

Table II: Isomer shift (IS), effective quadrupole interactions (EQ_{eff}=EQ*½$(3\cos^2(\Theta)-1)$ (where Θ is the angle between the hyperfine field and the axis of the local electric field gradient responsible for the quadrupole interaction), magnetic hyperfine field (H_{eff}) of $CaFe_4As_3$ in the magnetic states, and the magnetic moment amplitudes M_S obtained from NPD studies [8].

As far as the MS studies are concerned, we may compare the magnetic properties of $CaFe_4As_3$ to the two related SDW $BaFe_2As_2$ and KFe_2Se_2 compounds, in which the Fe ions reside in one crystallographic site only. The various shapes of the SDW state for the $BaFe_2As_2$ system are discussed in details in Ref. [14]. $BaFe_2As_2$ is magnetically ordered at T_N = 136(1) K, with Fe^{2+} moments of 0.87(3) μ_B/Fe aligned within the basal plane [1]. Below T_N, all our MS spectra of $BaFe_2As_2$ were analyzed in terms of a superposition of

commensurate and incommensurate SDW subspectra with an average H_{eff} (5.53 ± 0.6 T at 5 K) [15]. Thus β = 6.3 T/μ_B was obtained, and is very similar to that of $CaFe_4As_3$. On the other hand, KFe_2Se_2 is AFM ordered up to ~ 520 K, with Fe^{2+} moments of 3.31 μ_B/Fe, which forms a collinear AFM structure along the *c* axis [2]. Our MS studies show clearly that H_{eff} = 28.1 T at 93 K. In contrast to Ref. [2], the best fit to the experimental data is obtained only when the Fe moments are tilted by $\theta \sim 44°$ from the *c* axis [16]. For KFe_2Se_2, the ratio β = 8.5 T/μ_B. Again, this proves that the scaling of H_{eff} and M_S is not unique as proposed in Ref. [13].

Another point of interest is the high IS obtained (0.81 mm/s at 5K) for one sub-spectrum of $CaFe_4As_3$, which is attributed to Fe^{1+} (Fe_4 site). Such a state is seldom observed. As stated above, one Fe ion must be in a lower formal valence while the rest three Fe ions are in the divalent state in order to preserve neutrality of $CaFe_4As_3$. High spin Fe^{1+} is not found in stable compounds, but its existence has been shown as a substitutional impurity in good insulator ionic lattices, as transients after radio-active decay as observed for ^{57}Co decay in TiO_2 [17], MgO or CaO or when $^{57}CoCl_2$ is doped into KCl [18-19]. The fact that the stable Fe^{1+} state is observed in a compact *metallic* system is unique and deserves more studies. Further experimental and theoretical work is needed to establish its entire physical and chemical properties.

In summary, the four in-equivalent Fe ions in $CaFe_4As_3$ undergo two magnetic transitions: (1) an incommensurate spin density wave order of the Fe ions below T_{N1} = 88 K and (2) a commensurate AFM structure below T_{N2} ~ 26 K. Our ^{57}Fe Mössbauer spectroscopy indicates that there is the relative large IS and EQ hyperfine parameters of one sub-spectrum in the paramagnetic range. This is attributed to the presence of a *stable* Fe^{1+}, a seldom-observed state.

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