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The magnetic structure of EuFe_2As_2 determined by RXS

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Magnetic resonant X ray scattering experiments have been performed on a single crystal of EuFe_2As_2 at the Eu L_3 absorption edge. This has permitted us to determine for the first time the orientation of Eu magnetic moments in the antiferromagnetic ordered phase below $T_N=19$ K as parallel to the a -axis. In addition, non-resonant magnetic X ray measurements indicate that Fe magnetic moments align along the same direction in the spin density wave phase ($T < T_S \sim 190$ K). Temperature dependences indicate that the interaction between both magnetic subcells is weak. However, a weak anisotropy is observed in Eu 5d orbitals distribution at $T \sim T_S$, which can be understood as a polarization effect induced by Fe magnetic ordering. The presence of other “forbidden” Bragg reflections at the Eu L_3 absorption edge in the orthorhombic phase suggests that the actual symmetry could be lower than $Fmmm$.

The very recent report of high T_C superconductivity in the $R\text{FeOAs}$ ($R=\text{La-Gd}$) family of materials [1-3] has been one of the most striking discoveries of the last years in condensed matter physics. This behavior has been since also observed on related compounds like hole doped $A\text{Fe}_2\text{As}_2$ ($A: \text{Ca, Sr, Ba, and Eu}$) [4,5]. The structure of the iron pnictides family is tetragonal at room temperature ($I4/mmm$), where A and Fe-As atom layers alternate along the c - axis. Despite their mutual interaction is not clear yet, doping on A sites has been observed to induce large effects on the electrical and magnetic properties of the latter and can induce high- T superconductivity [6]. In non-doped compounds, a structural transition takes place at $T_S \sim 150\text{-}200$ K where a and b axes become inequivalent. This transition is accompanied by a concomitant weak magnetic ordering of Fe atoms, described as an itinerant spin density wave (SDW). The existence of this phase and superconducting behavior are actually quite exclusive phenomena [3,7]. The questions that immediately arise are why this happens and what is the role played by the A cation. It is therefore assumed that here resides one of the key factors in determining the outstanding transport properties of these materials.

EuFe_2As_2 is a suitable compound to study the magnetic interaction between Eu and Fe atoms due to the huge magnetic moment of Eu^{2+} ions ($\sim 7 \mu_B$), which orders below $T_N \sim 20$ K in an antiferromagnetic (AFM) structure of A type, as derived from magnetic susceptibility and specific heat measurements [8]. The aforementioned structural transition occurs at 190 K lowering the symmetry from tetragonal to orthorhombic $Fmmm$, according to [9]. As already noted, this is accompanied by the ordering of Fe spins in a SDW propagating in the ab plane. Due to the strong absorption by Eu atoms, the determination of their precise moment orientation is difficult to be addressed by neutron diffraction and several possibilities have been proposed [10].

Resonant X ray Scattering (RXS) is able to distinguish between the different models thanks to its site selectivity and the higher resolution intrinsic of X-rays.

We have applied this technique on magnetic superstructure reflections associated to Eu and Fe ions ordering. Obtained results as a function of light polarization, temperature and rotation around the scattering vector (i.e. azimuthal-angle dependence) are here presented. The analysis clearly indicates that europium and iron magnetic moments are all oriented parallel to the crystal a - axis (Fig.1). The temperature dependence supports a picture where the interplay between both magnetic substructures seems to be limited, in agreement with previous results [11]. Finally, we also report on some “forbidden” Bragg reflections measured under resonant conditions at the $\text{Eu } L_3$ edge. Their presence suggests the existence of an anisotropy in the spatial distribution of $5d$ orbitals of Eu atoms in the Fe SDW ordered phase that would project

on the symmetry of the tensor of susceptibility, leading to the appearance of so-called ATS or Templeton scattering reflections [12,13]. Their possible origin is discussed later on.

Large single crystals of EuFe_2As_2 with typical dimensions $6 \times 4 \times 1\text{mm}$ were grown by the flux method, with starting composition $\text{Eu}:\text{Fe}:\text{As}:\text{Sn}$ in the ratio 1:2:2:19, where Sn was later removed by centrifugation. Crystals were thoroughly characterized by the x-ray Laue back reflection method, chemical composition analysis via EDAX, resistivity and magnetization measurements.

X ray scattering spectra were taken in the ID20 magnetic scattering beamline at the ESRF in Grenoble, France, by using both horizontal (π incident light) and vertical (σ incident light) scattering configurations [14]. Resonant measurements were performed in the vicinity of the Eu L_3 (6.97 keV) absorption edge while non-resonant data were recorded at 6.93 keV. The polarization of the scattered radiation was analyzed by means of a Cu (110) single crystal. All the spectra have been corrected for absorption.

Complementary neutron diffraction experiments have been carried out on a ~ 50 mg single crystal with neutron wavelength chosen at 4.74 \AA at polarized neutron instrument DNS at FRM II in Garching, Germany. The spin-flip scattering of both spin-density wave and Eu antiferromagnetic reflections were measured with a guide field perpendicular to the $(h, 0, l)$ and $(0, k, l)$ scattering planes. Thus, the observation of these reflections unambiguously confirms their magnetic nature.

In Figure 2, the top panels show the T dependence of some of the measured magnetic and non magnetic reflections with synchrotron X rays. For $T < T_N$ the propagation vector of the A-type AFM modulation is $(00l)$ while the one of Fe spins is $(h0l)$, with h, l odd in every case. Thus, we have collected magnetic X- ray scattering data on the (009) and (109) reflections near the transition temperatures T_N and T_S , which correspond to the Eu and Fe magnetic ordering, respectively. The (019) reflection is also shown though not associated to any magnetic ordering and its origin is later discussed.

These results can be compared with those obtained by neutron diffraction on the (003) and (103) reflections on a different EuFe_2As_2 crystal cut from the same boule as the one used in X ray measurements (Fig 2, bottom). The (004) is the unique Bragg reflection permitted by the crystal structure shown and it can be used as a reference for the T evolution of intensities. The (009) reflection is present only below ~ 19 K, while the (109) and (019) reflections appear at $T_S \sim 190$ K. Small differences between transition temperatures obtained by X- ray scattering and neutron measurements are due to X- ray beam heating effect on the sample [15].

It is important to carefully study the temperature dependence of the resonant and non-resonant intensity of the (109) reflection across T_N where Eu moments order antiferromagnetically. They both do not show any significant change. The non-resonant intensity is due to the magnetic signal coming from Fe atoms and it suggests that the magnetic ordering of Eu ions does not affect noticeably the Fe spin alignment. This result supports the picture of two well decoupled magnetic substructures (Eu and Fe) as already suggested by LSDA calculations [11]. Similar conclusions can be extracted from the neutron diffraction data.

In order to determine the orientation of Eu magnetic moments below $T_N=19$ K we have performed an azimuthal-angle dependence (rotation around the scattering vector) of a chosen magnetic reflection. Figure 3 shows the spectra of the (209) reflection in σ to π polarization channel (σ - π') at 10 K in the vicinity of the Eu L_3 edge. The (209) wavevector corresponds to that of the Eu AFM ordering. The spectrum is characterized by a strong resonance centered at 6.973 keV, i.e. about 2-3 eV beyond the Eu L_3 absorption edge (see fluorescence), with a tail extending to lower energies. The energy dependence is the result of the interference between the resonant (main feature) and non-resonant (weak) X-ray magnetic scattering [16], hardly detectable at energies above the Eu L_3 edge because of the signal to background ratio [15]. As expected for a resonant magnetic reflection, there is no component in the σ - σ' channel.

In the inset the resonant intensity in the σ - π' channel ($I_{\sigma-\pi'}$) as a function of the azimuthal angle is plotted with a simulation of the calculated evolution as a function of the Eu moments orientation, whether they are parallel to the a or b crystal axes, following the dipolar approximation from the theoretical expressions for resonant X-ray magnetic scattering [17]. Experimental results suggest that the Eu moments are collinear to the a axis. This is the same conclusion that can be extracted from the relation of $I_{\pi-\pi'}$ to $I_{\pi-s}$ for several magnetic reflections shown in Fig. 3(b).

We detected the (109) reflection at 6.93 keV (far from any absorption edge), related to the Fe magnetic ordering and did not find (019). Surprisingly, at resonance, $E \sim 6.975$ keV, we found non-zero intensity for both reflections. Figure 4 shows the normalized energy scans of the superlattice (109) and (019) reflections near the Eu L_3 absorption edge in the σ - π' channel at 30 K. The inset shows the off-resonance azimuthal dependence of (109), which agrees with the proposed orientation of Fe magnetic moments along the crystal a axis [10,18].

A main resonance characterizes both spectra, which is found at a similar energy. The actual shift is ~ 1 eV and their shape not superposable. We recall that non-resonant intensity is only

present in the (109) reflection. This is the signature of the Fe SDW magnetic ordering and confirms that our assignment of crystal axes is consistent. We ascribe the small differences at resonance to the interference between the resonant and non-resonant terms in the (109) reflection. Two different hypothesis can explain the resonant intensity in (109). First, Eu 5d states may be polarized by Fe SDW onset at 190 K thereby inducing a weak magnetic ordering with the same periodicity in Eu atoms. Some examples of similar phenomena on other magnetic materials can be found in literature [19]. Secondly, the resonance could be due to an anisotropy in the charge density distribution in Eu 5d orbitals, i.e. due to Templeton (or ATS) scattering. This argument would explain also the observation of the (019) reflection at resonance. The periodicity associated with (019) does not correspond to neither the Eu magnetic propagation vector nor the Fe one. Therefore, we conclude that (019) resonance has to be related to an anisotropic distribution of Eu 5d orbitals. This means that the atomic tensor of scattering of Eu atoms is also anisotropic. These findings could affect the sample crystallographic structure. Indeed, the reported *Fmmm* space group for $T < T_S$ is not compatible with the presence of ATS reflections. The appearance of ATS reflections is only allowed if some particular symmetry operations such as glide planes or screw axes are present in the space group [12,13,20,21]. In the *Fmmm* space group such symmetry elements are absent. However, it must be pointed out that the intensity of the (109) and (019) resonances is extremely weak to the point that it is comparable to the non- resonant magnetic signal from the Fe atoms (Fig.4) and 500 times smaller than the (209) (Fig.2). Therefore, deviations from the proposed structure must be extremely small and certainly below the resolution of powder diffraction experiments.

In summary, the magnetism of iron pnictides is strongly related to their very interesting conductive capabilities as it has been demonstrated by looking at its connection to the presence or the absence of the Fe SDW phase in doped compounds. In this sense, the very large magnetic moment of europium atoms in EuFe_2As_2 and its AFM ordering below 19 K makes it very suitable to test the correlations between both the Eu and (Fe,As) subcells. RXS has allowed to determine that Eu ions magnetic moments in the A-type AFM ordered phase (at $T < 19$ K) are aligned parallel to the crystal *a* axis. This is also the direction of alignment of Fe moments in the SDW phase at $T < T_S = 190$ K. We have also shown that the onset of the magnetic ordering of Eu ions does not induce any noticeable change in the Fe magnetic substructure by studying the temperature dependence, though the latter could induce a weak magnetic ordering in Eu atoms with Fe SDW propagation vector at $T < T_S$. Last, we note that the observation of the “forbidden” Bragg reflections at the Eu L_3 edge below T_S is originated

by the anisotropy of the scattering tensor. Such reflections, though weak, suggest that the crystal structure could differ from the proposed orthorhombic $Fmmm$ space. This is a key point because the character (first or second order) of the structural transition that takes place at T_S has been object of controversy in related compounds like $SrFe_2As_2$. In general, it is accepted the latter as the most likely possibility [6,9,11]. If this is true, the space group in the low temperature phase has to be a subgroup of $I4/mmm$ [22]. And amongst them, non-symmorphic to be able to accommodate the appearance of ATS signals.

We believe that the interplay between the different atoms electronic band structure and the low T structural issue could have a great importance and should be explored in a greater detail. It therefore remains as the main subject for a future deeper investigation.

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Figure captions

Figure 1. Magnetic structure of EuFe_2As_2 at $T < T_N$. The propagation vector defining the A-type AFM arrangement of Eu moments below T_N is (001) and that of Fe is (101) under T_S .

Figure 2. Temperature dependence of selected superlattice reflections collected by X-ray (top) and spin-flip scattering via polarized neutrons with a guide field perpendicular to the scattering plane (bottom). Top, left: (009) at the main resonance and (109) at 6.930 keV (filled symbols) and 6.976 keV (open symbols) around T_N ; top, right: (109) and (019) at 6.976 keV at $T \sim T_S$; bottom, left: (103) (squares) and (003) (circles) around T_N ; bottom, right: (004) (crosses) and (103) in a wide T range covering T_S and T_N .

Figure 3. (a) Energy dependence of the $\sigma\text{-}\pi'$ channel of (209) reflection (solid line) at 10 K. Fluorescence is shown for comparison (crosses). The inset shows the experimental azimuthal behaviour of the (209) reflection (circles) compared to the theoretical prediction in the case that Eu moments are aligned along crystal a (red solid line) or b (blue dashed) axes. (b) Experimental relation of $I_{\pi\pi'}/I_{\pi\sigma'}$ intensities of diverse reflections (filled circles) compared to the theoretical dependency expected for Eu moments aligned along a (empty circles) or b (triangles).

Figure 4. Energy dependence of (109) (solid line) and (019) (dotted line) superlattice reflections in the $\sigma\text{-}\pi'$ polarization channel at 30 K. The measured azimuthal evolution of (109) in this channel at 6.93 keV is shown (triangles) in the inset together with the calculated evolution (solid line) for Fe moments oriented parallel to the a crystal axis.

Figure 1

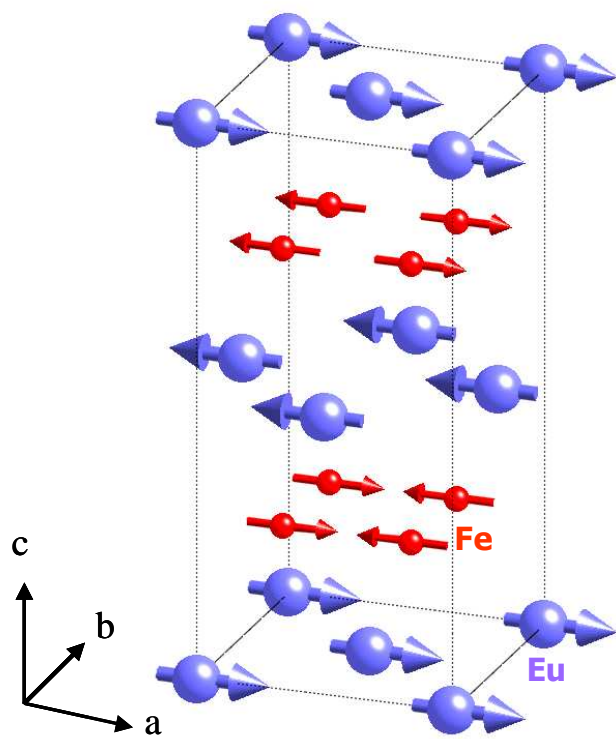


Figure 2

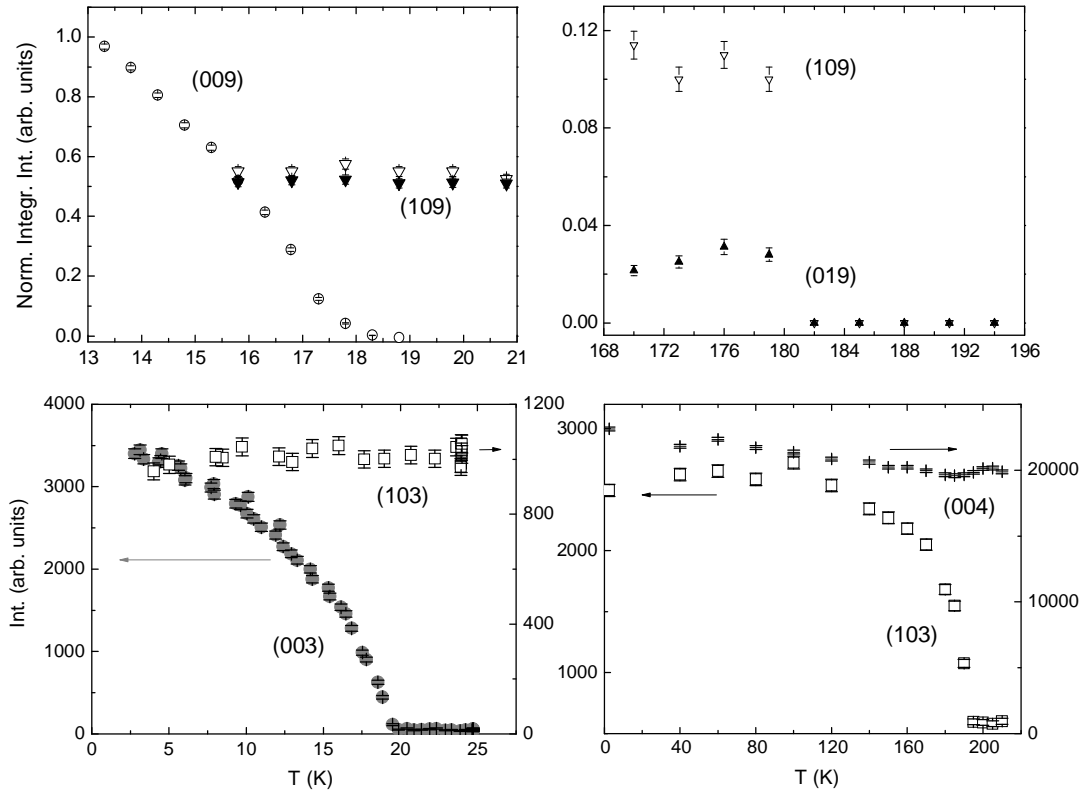


Figure 3

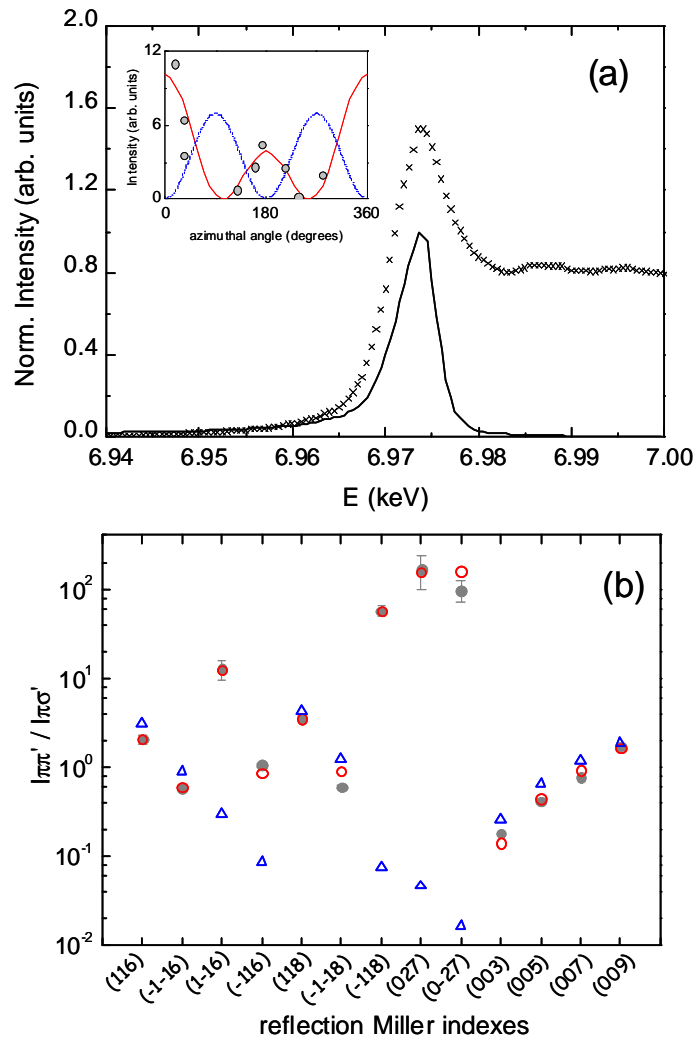


Figure 4

