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Mössbauer study of $Eu_{0.57}Ca_{0.43}Fe_2As_2$ and $Eu_{0.73}Ca_{0.27}(Fe_{0.87}Co_{0.13})_2As_2$: A comparison to '122' iron-based superconductors parent compounds $EuFe_2As_2$ and $CaFe_2As_2$

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ABSTRACT

^{57}Fe and ^{151}Eu Mössbauer spectra were obtained versus temperature for $Eu_{0.57}Ca_{0.43}Fe_2As_2$ compound with 3d and 4f magnetic order and $Eu_{0.73}Ca_{0.27}(Fe_{0.87}Co_{0.13})_2As_2$ re-entrant superconductor, where the finite resistivity reappears while approaching the ground state. They were compared with previously obtained spectra for parent compounds $EuFe_2As_2$ and $CaFe_2As_2$. It was found that substitution beyond the Fe-As layers does not lead to the rotation (canting) of the Eu^{2+} magnetic moments and does not generate Eu^{3+} states. On the other hand, re-entrant superconductor exhibits rotation (canting) of the Eu^{2+} moments on the c-axis of the unit cell leading to the transferred hyperfine magnetic field on iron nuclei. Divalent europium orders magnetically within the bulk of the re-entrant superconducting phase. The re-entrant superconductor remains in the inhomogeneous state close to the ground state with about 27% of the volume being free of 3d magnetism, while the remainder exhibits weak spin density wave. Those two regions slightly differ by the electric field gradient and electron density on iron nuclei.

1. Introduction

Iron-based superconductors of the '122' family are still very interesting compounds as they are a significant playground for competition between itinerant 3d magnetic order of the spin density wave (SDW) type (usually longitudinal and incommensurate) and superconductivity [1]. They could be prepared as relatively large single crystals of high purity and order free of other phases. Parent compounds of pnictides AFe_2As_2 (A = Ca, Sr, Ba, Eu) develop SDW accompanied by a slight lattice distortion from tetragonal to orthorhombic symmetry [2,3]. For the A elements being rare earths with non-zero localized 4f magnetic moments one observes antiferromagnetic order of these moments at much lower temperatures [4]. Superconductivity could be achieved by suppression of the SDW order (and lattice distortion as well) by either external pressure [5,6] or suitable doping on any site. One can apply electron doping, hole doping or *iso*-electronic substitution [7–9]. For the *iso*-electronic substitution to be successful one has to replace arsenic by e.g. phosphorus, i.e., one has to perturb significantly Fe-As layers with strong perturbation of the iron environment, as iron atoms are tetrahedrally coordinated by pnictogen [10]. It is interesting to note, that 4f antiferromagnetic order occurs within superconducting material as well, and doping leading to superconductivity usually causes some 4f magnetic moment reorientation (canting) with a generation of the 4f ferromagnetic component [11–14].

Mössbauer spectroscopy is very useful while looking at the peculiar magnetism of parent compounds [15–17] and iron-based superconductors [18–20]. The present contribution reports Mössbauer results obtained by means of ^{57}Fe and ^{151}Eu spectroscopy on the $Eu_{0.57}Ca_{0.43}Fe_2As_2$ compound being *iso*-electronic with compounds $EuFe_2As_2$ and $CaFe_2As_2$ [21]. Replacement of Eu by Ca does not perturb significantly Fe-As layer, and hence the $Eu_{0.57}Ca_{0.43}Fe_2As_2$ behaves like a parent compound with SDW magnetism and subsequent ordering of divalent Eu magnetic moments. On the other hand, the doubly substituted compound $Eu_{0.73}Ca_{0.27}(Fe_{0.87}Co_{0.13})_2As_2$ was found as re-entrant superconductor in similarity to the superconductor $Eu(Fe_{1-x}Co_x)_2As_2$, where superconductivity persists to the ground state [11]. Re-entrant

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behavior is observed here as a sharp transition to the superconducting state at about 12 K followed by the recovery to the normal state at about 2 K lower temperature. Doubly substituted compound is in the inhomogeneous state with a part of the volume developing weak SDW at low temperature. Recently a new '1144' family of iron-based stoichiometric superconductors has been discovered, e.g. $CaKFe_4As_4$ [22], based on the cell of the '122' family with layers separating Fe-As sheets being alternating and shifted Ca and K layers. These compounds do not exhibit 3d magnetism and crystallize in the orthorhombic symmetry [23].

2. Experimental

Single crystals of compounds were grown by Sn-flux method. The elements in respective molar ratios were loaded into alumina crucible and sealed in a silica tube under vacuum. The tube was heated slowly to 1050 °C and kept at this temperature for several hours, to dissolve all components. Then, it was cooled slowly at a rate of 2 °C/h to 650 °C. The liquid tin was decanted from the crucible at this stage. Residue of Sn was removed by etching in diluted hydrochloric acid.

The chemical composition of the grown single crystals was determined using EDS spectroscopy. The crystal structure and phase purity of the samples was characterized by powder X-ray diffraction using X'Pert Pro powder diffractometer equipped with a linear PIXcel detector and CuKα radiation. Electrical resistivity was measured using standard four-probe technique in a Quantum Design PPMS platform. Magnetic susceptibility measurements show that magnetic ordering of divalent europium in $Eu_{0.57}Ca_{0.43}Fe_2As_2$ occurs at about 12 K in comparison with 19 K for $EuFe_2As_2$. Divalent europium orders at about 11 K for $Eu_{0.73}Ca_{0.27}(Fe_{0.87}Co_{0.13})_2As_2$ as shown by the magnetic susceptibility results. On the other hand, 3d itinerant magnetic order starts at somewhat higher temperature than for both parent compounds $EuFe_2As_2$ (192.1 K) and $CaFe_2As_2$ (175.3 K), respectively [21], as shown by resistivity measurements.

Mössbauer transmission measurements for 14.41-keV transition in ^{57}Fe were performed using the RENON MsAa-3 spectrometer operated in the round-corner triangular mode and equipped with the LND Kr-filled proportional detector and He-Ne laser based interferometer used to calibrate a velocity scale. A single line commercial $^{57}Co(Rh)$ source kept at room temperature was applied. The Mössbauer absorber for $Eu_{0.57}Ca_{0.43}Fe_2As_2$ was prepared using 40 mg of the material in the powder form and the absorber thickness amounted to 20 mg/cm^2 of investigated material. The absorber of the $Eu_{0.73}Ca_{0.27}(Fe_{0.87}Co_{0.13})_2As_2$ was prepared using 42 mg of the material in the powder form and the absorber thickness amounted to 21 mg/cm^2 of investigated material. The cryostat SVT-400 by Janis Research Inc. was used to maintain temperature of absorbers. ^{151}Eu spectra for 21.6-keV resonant transition were collected applying $^{151}SmF_3$ source kept at room temperature and a scintillation detector. The WisseL spectrometer operated in the sinusoidal mode was used to collect spectra of the $Eu_{0.57}Ca_{0.43}Fe_2As_2$ and it was calibrated by means of the α-Fe absorber spectrum collected applying $^{57}Co(Rh)$ source – both kept at room temperature. Temperature of the absorber was set and controlled by means of the closed cycle SHI-850-5 Janis Research Inc. He-refrigerator. Spectra of the $Eu_{0.73}Ca_{0.27}(Fe_{0.87}Co_{0.13})_2As_2$ compound were collected using He cryostat to cool the absorber and by means of the RENON MsAa-4 spectrometer calibrated with the He-Ne laser based interferometer. Absorbers were prepared as a mosaic of crystals to avoid oxidation. Data for ^{57}Fe and ^{151}Eu Mössbauer hyperfine parameters were processed by means of the Mosgraf-2009 software within the transmission integral approximation [24]. Spectral shifts are reported versus room temperature α-Fe or versus room temperature $^{151}SmF_3$ source, respectively.

3. Results and discussion

Fig. 1 shows relative resistivity plotted versus temperature for three compounds of the composition $Eu_{1-x}Ca_xFe_2As_2$ and re-entrant superconductor $Eu_{0.73}Ca_{0.27}(Fe_{0.87}Co_{0.13})_2As_2$. Magnetic ordering of the 3d electrons is clearly seen for $Eu_{1-x}Ca_xFe_2As_2$ compounds with the highest ordering temperature being for the compound with intermediate composition. On the other hand, for the compound $Eu_{0.73}Ca_{0.27}(Fe_{0.87}Co_{0.13})_2As_2$ one can clearly see sharp transition from the metallic to the superconducting state at 12 K followed by re-entrant behavior below 10 K. A broad hump at lower temperatures seems typical for the gradual ordering of some magnetic moments.

Fig. 2 shows ^{57}Fe Mössbauer transmission spectra for the compound $Eu_{0.57}Ca_{0.43}Fe_2As_2$ measured at various temperatures (central panel). Corresponding spectra for parent compounds $EuFe_2As_2$ (left panel) and $CaFe_2As_2$ (right panel) are shown as well. The symbol S stands for the total central shift versus room temperature α-Fe, while the symbol Δ denotes electric quadrupole splitting (effective for the magnetically split spectra). The symbol $\sqrt{\langle B^2 \rangle}$ stands for the mean squared amplitude of the (incommensurate) spin density wave (SDW).

Fig. 3 shows shape of SDW denoted as $B(qx)$ versus phase shift qx and corresponding normalized distribution of the hyperfine magnetic field (absolute value) $W(B)$ versus hyperfine magnetic field B at 180 K and close to saturation for above compounds with well defined SDW. The symbol B_{max} stands for the maximum

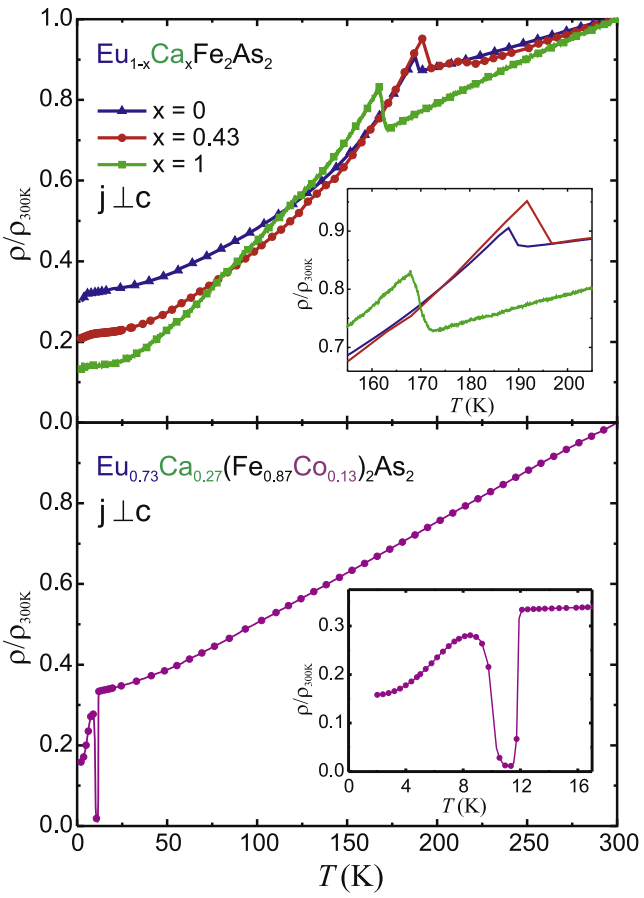

Fig. 1. Resistivity ρ normalized to resistivity at 300 K (ρ_{300K}) for compounds with well developed 3d magnetic order $Eu_{1-x}Ca_xFe_2As_2$ (x = 0, 0.43, 1) and re-entrant superconductor $Eu_{0.73}Ca_{0.27}(Fe_{0.87}Co_{0.13})_2As_2$ plotted versus temperature T. The current **j** was applied perpendicular to the c-axis.