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High-temperature superconductivity in $Eu_{0.5}K_{0.5}Fe_2As_2$

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$EuFe_2As_2$ shows a spin-density wave (SDW) type transition at 190 K and antiferromagnetic (AF) order below 20 K. Here, we have studied the effect of K substitution on the SDW transition at high temperature and AF Eu order at low temperature. 50% K substitution suppresses the SDW transition and in turn gives rise to high-temperature superconductivity below $T_c=32$ K, as observed in the electrical resistivity, AC susceptibility, as well as magnetization. A well defined anomaly in the specific heat provides additional evidence for bulk superconductivity. Below 10 K, short-range magnetic order of the Eu moments is suggested by a broad feature in the specific-heat data. Electronic structure calculations reveal very close similarity with the nonmagnetic superconductor $Sr_{0.5}K_{0.5}Fe_2As_2$, but yield localized $4f$ magnetic moments for the remaining Eu atoms.

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I. INTRODUCTION

Intense research for the past few months has lead to the discovery of several new superconductors with T_c as high as 52 K in the iron arsenide compounds.[1–8] Most intriguing among these superconductors is the fact that superconductivity occurs close to the magnetic-nonmagnetic borderline, probably indicating an unconventional (nonphononic) pairing mechanism. While the discussion about the mechanism and the conventional versus unconventional nature continues, we try to explore more materials with the aim to assist in sorting out this debate through more available experimental data on related compounds. Recently, we have shown that $EuFe_2As_2$ shows a spin-density wave (SDW) type transition at 190 K (Ref. 9) similar to that of $SrFe_2As_2$.[10] One may thus expect that appropriate substitution or application of pressure suppresses the SDW, leading to superconductivity at the magnetic-nonmagnetic borderline. Taking clue from the results of K-substituted $SrFe_2As_2$ (Ref. 2) we may expect that 50% K substituted $EuFe_2As_2$ shows superconductivity. We have prepared 50% K substituted $EuFe_2As_2$ and measured its low-temperature electrical resistivity, magnetic susceptibility, and specific heat. We indeed find compelling experimental evidence for bulk superconductivity in K-substituted $EuFe_2As_2$. Details of the experimental procedures and results are discussed below.

II. METHODS

A. Experiment

Polycrystalline samples of $Eu_{0.5}K_{0.5}Fe_2As_2$ were synthesized by solid-state reaction method. Stoichiometric amounts of the starting elements Eu (99.99%), K (99.9%), Fe (99.9%), and As (99.999%) were taken in an Al_2O_3 crucible which was then sealed in a Ta crucible under argon atmosphere. The sealed Ta crucibles were slowly heated to 900 °C and sintered for 24 h. After first heat treatment, the samples were thoroughly grounded and pressed into pellets and subjected to a second heat treatment. The sample preparation and handling was carried out inside a glove box ($O < 1$ ppm, $H_2O < 1$ ppm). Electrical resistivity and specific heat were measured using a physical properties measurement system (PPMS, Quantum Design, USA). The ac susceptibility was measured using homemade system while for the dc magnetic susceptibility a Quantum Design magnetic property measurement system (MPMS) was used.

B. Theory

In order to understand the influence of the K substitution in $EuFe_2As_2$, we have performed density-functional band-structure calculations using a full potential code FPLO (Ref. 17) within the local (spin) density approximation [L(S)DA]. Additionally, we have included the strong Coulomb repulsion in the Eu $4f$ orbitals on a mean-field level using the LSDA+U approximation applying the atomic-limit double-counting scheme.[18] We applied the Perdew-Wang[19] flavor of the exchange-correlation potential, self-consistency was reached on a well converged k mesh. The structural parameters and the value of $U=8$ eV for the Eu $4f$ states were kept identical to our previous work[9] on the unsubstituted system throughout all calculations.

III. RESULTS AND DISCUSSION

A. Experiment

The single-phase nature of the sample is confirmed using powder x-ray diffraction. Impurity phases amount to less than 5%. The sample crystallizes in the $ThCr_2Si_2$ type tetragonal structure with lattice parameters $a=3.8671(3)$ Å and $c=13.091(3)$ Å. The lattice-parameter values, as expected, are in between those of $EuFe_2As_2$ and KFe_2As_2. Energy dispersive x-ray analysis reveals that the composition of the sample is close to the expected 0.5:0.5:2:2 stoichiometry.

Figure 1 shows the temperature dependence of the electrical resistivity for $EuFe_2As_2$ and $Eu_{0.5}K_{0.5}Fe_2As_2$ samples. Unsubstituted $EuFe_2As_2$ exhibits a clear drop near 190 K due to SDW instability[9,11,12] and structural phase transition from tetragonal to orthorhombic symmetry.[13] In the K-substituted sample $Eu_{0.5}K_{0.5}Fe_2As_2$, the high-temperature anomaly due

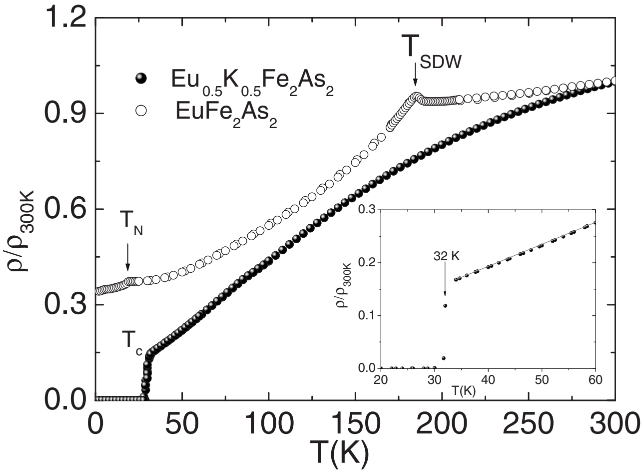

FIG. 1. Temperature dependence of the electrical resistivity of polycrystalline $EuFe_2As_2$ and $Eu_{0.5}K_{0.5}Fe_2As_2$. The arrows indicate anomalies at $T_{SDW}=190$ K and $T_c=30$ K. The lower inset shows the electrical resistivity data in temperature range between 20 and 60 K and the line indicates the linear decrease between 60 and 32 K.

to the SDW formation is completely suppressed. By contrast, a superconducting transition is observed at $T_c \approx 32$ K. The lower inset of Fig. 1 shows the low-temperature part of the resistivity. Note, that a linear temperature dependence is found above the superconducting transition.

Further confirmation of the superconducting transition at 32 K comes from ac magnetic susceptibility (Fig. 2) which shows a clear diamagnetic signal. dc magnetic susceptibility measured under zero-field-cooled (ZFC) and field-cooled (FC) conditions also confirm superconductivity. The ZFC diamagnetic signal below the superconducting transition is of the size expected for perfect diamagnetism of Pb. FC measurements also exhibit diamagnetism, the diamagnetic signal being 10% of the ZFC signal. The hysteresis between the ZFC and FC susceptibilities in the superconducting state is characteristic for type-II superconductors. We also observe a signature for short-range magnetic ordering of the Eu moments in the magnetic susceptibility below about 10 K.

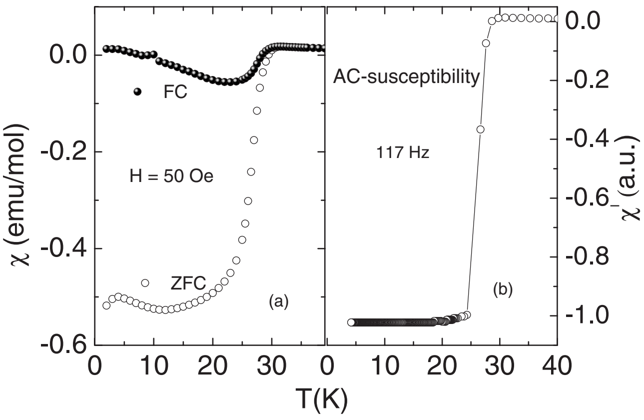

FIG. 2. Temperature dependence of $Eu_{0.5}K_{0.5}Fe_2As_2$. (a) dc magnetic susceptibility for zero-field-cooled and field-cooled experiments in an applied field of 50 Oe and (b) the real part of the ac susceptibility measured (background subtracted) with oscillating frequency of 117 Hz.

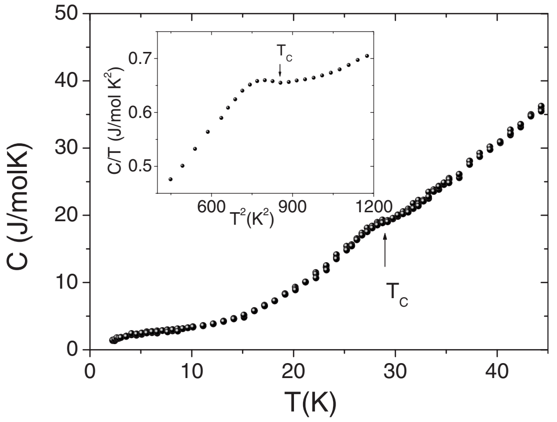

FIG. 3. Temperature dependence of the specific heat of $Eu_{0.5}K_{0.5}Fe_2As_2$ in the temperature range $4\ \mathrm{K} \leq T \leq 40$ K. The inset displays C/T vs T^2.

Since even 10%–20% superconducting volume fraction could provide zero resistivity as well as a diamagnetic signal similar to that of a pure superconductor, low-temperature specific-heat measurements were carried out to establish the bulk nature of superconductivity, as well as to probe the magnetism of the Eu^{2+} ions. The main part of Fig. 3 shows the temperature dependence of the specific heat plotted as C vs T in the temperature range 2–40 K. We observe a small but well defined anomaly associated with the superconducting transition providing clear evidence for the bulk nature of superconductivity. The observed anomaly is similar to the feature seen at the superconducting transition in $SrFe_{2-x}Co_xAs_2$.[14] It is even more pronounced in C/T vs T^2 shown in the inset. From this plot, one can estimate a step $\Delta C/T_c \approx 50\ \mathrm{mJ/mol\ K^2}$ in the specific heat at T_c. Unfortunately because of the presence of the magnetic contribution from Eu moments, it is difficult to correctly estimate the true normal-state γ value. Since γ of $SrFe_2As_2$ is reported as $10\ \mathrm{mJ/mol\ K^2}$ we assume the true gamma value of $EuFe_2As_2$ will be of the same order of magnitude, considering the fact that Eu is divalent in the absence of charge fluctuations and/or Kondo effect. Compared to this γ value, the size of $\Delta C/T_c$ we found in $Eu_{0.5}K_{0.5}Fe_2As_2$ is quite large, suggesting a strong-coupling scenario. Even though the mechanism for the superconductivity is not yet settled, the well defined specific-heat anomaly of this magnitude provides confidence about the bulk nature of superconductivity in $Eu_{0.5}K_{0.5}Fe_2As_2$. Such anomaly was absent in $LaO_{1-x}F_xFeAs$ compounds[15,16] and only a weak anomaly was observed in superconducting $SmO_{1-x}F_xFeAs$.[5] At low temperatures only a very broad bump suggesting a suppressed and broadened kind of magnetic order of Eu moments, very likely only a short range one, was observed below 10 K in contrast to a very pronounced lambda-type anomaly at 20 K in $EuFe_2As_2$.[9]

B. Theory

To study the changes in the electronic structure of $EuFe_2As_2$ due to a 50% substitution of K on the Eu site, we

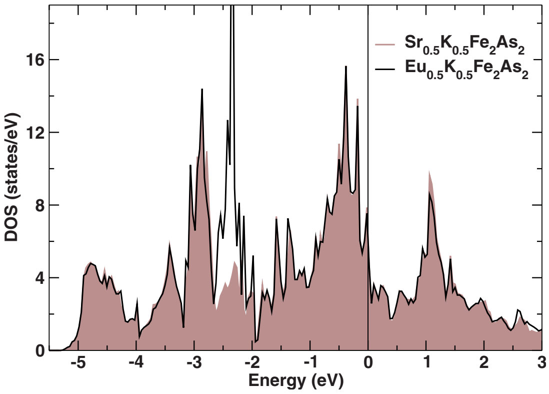

FIG. 4. (Color online) Comparison of the total DOS for $Eu_{0.5}K_{0.5}Fe_2As_2$ (LSDA+U, with nonmagnetic Fe sites) and $Sr_{0.5}K_{0.5}Fe_2As_2$ (LDA). The spin-up and spin-down DOS with nonmagnetic Fe sites for the $Eu_{0.5}K_{0.5}Fe_2As_2$ have been added together to make the comparison with the Sr analog easier. The large peak at −2.4 eV belongs to the spin-up Eu 4*f* states. The unfilled spin-down Eu 4*f* states are pushed to around 9.5 eV above the Fermi level.

constructed supercells of the unsubstituted system and replaced half of the Eu ions with K ions. To account for the strong Coulomb repulsion within the Eu 4*f* orbitals a typical U value [according to x-ray absorption spectroscopy and photoemission experiments] of $U=8$ eV has been chosen for the LSDA+U calculations. A variation of U within the physically reasonable range of 6…10 eV does not change our conclusions since this variation has negligible influence on the states at the Fermi level that is relevant for the superconductivity.

The calculated total density of states (DOS) of $Eu_{0.5}K_{0.5}Fe_2As_2$ is shown in Fig. 4 in comparison to that of $Sr_{0.5}K_{0.5}Fe_2As_2$. Except for the localized Eu 4*f* states at around −2.4 eV, the DOS of both these systems are quite similar.[20] As in the unsubstituted $EuFe_2As_2$, the Eu ions are in a stable 2+ state with a half filled 4*f* shell, and the position of the localized 4*f* level remains basically unchanged.[9]

Our previous work[9] on the unsubstituted system indicates that the Eu and Fe sublattices are quite decoupled and the ordering of the Fe sublattice at 190 K does not influence the ordering of the Eu moments at 20 K. Thus, the ordering of the Eu spin moments is mainly due to Eu-Eu interaction. In our $Eu_{0.5}K_{0.5}Fe_2As_2$ supercell, every other Eu site is replaced by a nonmagnetic K^{1+} ion. Although the influence of disorder cannot be accessed this way, we try to get a rough estimate for the reduction of the effective coupling comparing calculated total energies for different Eu spin arrangements (aligned and antialigned Eu spins). The difference in energy from these calculations is then mapped to a Heisenberg model to obtain the value of the effective exchange constant (J_{eff}). The value of the J_{eff} for the unsubstituted and the 50% K substituted $EuFe_2As_2$ systems are 2 and 0.3 K, respectively. Thus, replacing every other magnetic Eu^{2+} ion with a nonmagnetic K^{1+} ion reduces the effective Eu-Eu exchange strongly. However, even without this strong reduction of the effective exchange, the random filling of the square lattice with only 50% magnetic Eu ions should be sufficient to suppress long-range magnetic order by itself.

IV. CONCLUSION

To summarize, we have been successful in synthesizing a single phase sample of $Eu_{0.5}K_{0.5}Fe_2As_2$. Our comprehensive investigation of the electrical resistivity, ac and dc magnetic susceptibilities, and specific heat shows the suppression of the SDW transition and evidence for bulk type-II superconductivity below $T_c=32$ K. Substitution of 50% of Eu by K, however, has substantially broadened the Eu order which is then very likely only a short range one and shifted it to below 10 K. Further experiments are planned to probe the magnetism of Eu ions as well as to investigate the interplay of Eu magnetism with superconductivity.

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