

Electrical resistivity and specific heat of single-crystalline EuFe_2As_2 : A magnetic homologue of SrFe_2As_2

H. S. Jeevan,^{1,*} Z. Hossain,² Deepa Kasinathan,³ H. Rosner,³ C. Geibel,³ and P. Gegenwart¹

¹*I. Physikalisches Institut, Georg-August-Universität Göttingen, D-37077 Göttingen, Germany*

²*Department of Physics, Indian Institute of Technology, Kanpur 208016, India*

³*Max Planck Institute for Chemical Physics of Solids, D-01187 Dresden, Germany*

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We have grown single crystals of EuFe_2As_2 , and investigated its electrical transport and thermodynamic properties. Electrical resistivity and specific-heat measurements clearly establish the intrinsic nature of magnetic phase transitions at 20 and 195 K. While the high-temperature phase transition is associated with the itinerant moment of Fe, the low-temperature phase transition is due to magnetic order of localized Eu moments. Band-structure calculations point out a very close similarity of the electronic structure with SrFe_2As_2 . Magnetically, the Eu and Fe_2As_2 sublattices are nearly decoupled.

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I. INTRODUCTION

Investigations of the FeAs based compounds are presently on the rise within the condensed-matter community due to relatively high superconducting transition temperatures of electron or hole doped $R\text{FeAsO}$ ($R=\text{La}, \text{Sm}$) and hole doped $A\text{Fe}_2\text{As}_2$ compounds ($A=\text{Sr}, \text{Ba}$).¹⁻⁷ The FeAs layers common to both series of compounds seem to be responsible for superconductivity. Since superconductivity in this class of compounds coincides with the disappearance of a spin-density wave (SDW)-type magnetic transition, spin fluctuations of Fe moments are suggested to play a crucial role in establishing the superconducting ground state in these superconductors.⁸ The importance of spin fluctuations for unconventional superconductivity has already been realized while discussing the properties of heavy fermion superconductors such as CeCu_2Si_2 and CeMIn_5 ($M=\text{Co}, \text{Rh}, \text{Ir}$) as well as high T_c cuprates.⁹ Even though we already have numerous superconductors encompassing the whole range of temperature up to 160 K, the discovery of FeAs based superconductors was greeted with great attention primarily due to its apparent nonphononic origin and noncopper based origin. This is the first time that magnetic fluctuations of the “truly magnetic” element iron may produce superconductivity at such a high temperatures.

In $R\text{FeAsO}$ compounds, the superconducting transition temperature increases as one substitutes La by smaller rare-earth atoms: T_c rises from 28 K in $\text{LaFeAs}(\text{O}, \text{F})$ to 52 K in $\text{SmFeAs}(\text{O}, \text{F})$.^{1,3} Very recently, superconductivity has also been reported in $R\text{Fe}_2\text{As}_2$ compounds for $(\text{K}, \text{Ba})\text{Fe}_2\text{As}_2$ and $(\text{K}, \text{Sr})\text{Fe}_2\text{As}_2$ with superconducting transition temperatures as high as 38 K. As in the case of $R\text{FeAsO}$, the parent compound $R\text{Fe}_2\text{As}_2$ also exhibits a spin-density-type phase transition in the temperature range between 160 and 200 K for Ba and Sr compounds, which is suppressed by substituting K for the cationic site. The suppression of the SDW transition is accompanied by the appearance of superconductivity.^{4,6} Just like in BaFe_2As_2 and SrFe_2As_2 , the presence of a magnetic transition at 190 K in EuFe_2As_2 (Ref. 10) was reported more than a decade ago using Mößbauer spectroscopy. From the small value of the hyperfine field, the Fe magnetism was

suggested to be of itinerant character. Magnetic susceptibility as well as Mößbauer spectroscopy further revealed the magnetic order of localized Eu moments at 20 K. However, there are no reports of electrical transport or thermodynamic properties on this system yet. Because of the topical interest, we have therefore decided to prepare high-quality single-crystalline samples, and to investigate the phase transitions in this compound using electrical resistivity and specific-heat measurements.

II. METHODS

A. Experiment

Single crystals were obtained using a Bridgman method. Starting elements (Eu 99.99%, Fe 99.99%, and As 99.99999%) with a mole ratio of 1:2:2 were taken in an Al_2O_3 crucible, which was then sealed in a Ta crucible under argon atmosphere. The sample handling was done in a glove box under very pure environment (oxygen < 1 ppm and H_2O < 1 ppm). The sealed crucible was heated under argon atmosphere at a rate of 30 °C/h to 600 °C. The sample was kept at 600 °C for 12 h and then heated to 900 °C where again the sample was kept for 1 h. After this the sample was taken to 1300 °C, kept there for 3 h, and then slowly cooled. We obtained several platelike single crystals using this process. The quality of the single crystals was checked using the Laue method and powder x-ray diffraction as well as scanning electron microscopy equipped with energy dispersive x-ray analysis. Electrical resistivity and specific heat were measured using physical properties measurement system (PPMS) (Quantum Design, USA). Magnetic properties were measured using superconducting quantum interference device (SQUID) magnetometer procured from Quantum Design, USA.

B. Theory

We have performed density-functional band-structure calculations using two full potential codes: WIEN2K (Ref. 11) and FPLO,¹² using the local (spin) density approximation [L(S)DA] including spin-orbit coupling. Additionally, we

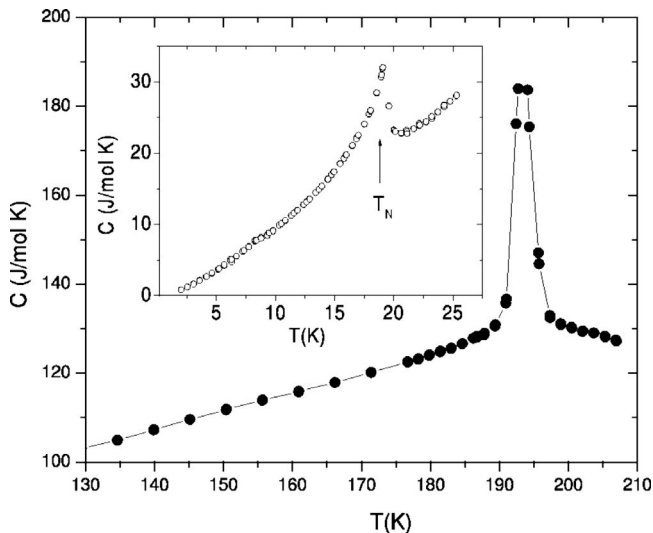


FIG. 1. Temperature dependence of the specific heat of EuFe_2As_2 in the temperature range between 130 and 210 K. The inset shows the low-temperature part from 2 to 25 K. The small bump around 8 K is due to small amounts of EuAs binary phase.

have included the strong Coulomb repulsion in the $\text{Eu } 4f$ orbitals on a mean-field level using the $\text{LSDA}+U$ approximation, applying the atomic-limit double-counting scheme.¹³ We used the Perdew-Wang¹⁴ flavor of the exchange-correlation potential and the energies were converged on a dense k mesh with 24^3 points. We used the current experimental lattice parameters. The As position ($z=0.362$) was taken according to Ref. 10. There exists no spectroscopy data for EuFe_2As_2 , therefore we have used a U of 8 eV, the standard value for an Eu^{2+} ion. The results were checked for consistency with varying U values. We did not apply U to the itinerant Fe $3d$ states.

III. RESULTS AND DISCUSSION

A. Experiment

Powder x-ray diffraction of the crushed single crystals confirms the single-phase nature of the single crystals that form in the ThCr_2Si_2 -type tetragonal structure with lattice parameters $a=3.907(4)$ Å and $c=12.114(3)$ Å, in good agreement with the values reported in the literature.¹⁰ Laue patterns reveal that platelike single crystals are oriented with their c axis perpendicular to the plates. The energy dispersive analysis with x-ray (EDAX) composition analysis shows that the crystals have uniform compositions with the expected ratio of the elements. There is a tiny percentage of EuAs binary phase in the sample.

Since the magnetic transitions of EuFe_2As_2 have already been reported using magnetic susceptibility and Mössbauer spectroscopy, we focus our investigation on electrical resistivity and specific-heat measurements. Figure 1 shows the specific-heat data taken in the temperature range between 2 and 210 K. The low-temperature part of the specific heat shows a lambda-type anomaly with a peak at $T_N=19$ K, associated with the magnetic transition of Eu moments. The

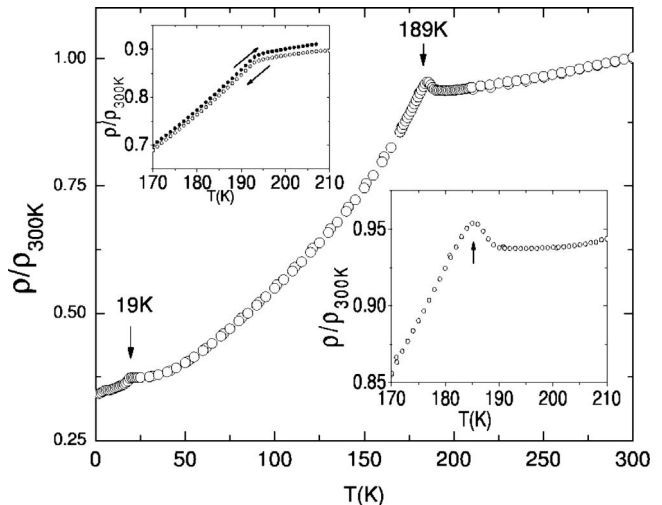


FIG. 2. Temperature dependence of the electrical resistivity of EuFe_2As_2 measured on a platelike single-crystalline sample down to 2 K. The arrow indicates anomalies at 19 and 189 K. The lower inset shows the electrical resistivity data in temperature range between 160 and 210 K. The upper inset shows corresponding data taken on a polycrystalline sample.

magnetic entropy associated with this transition is close to $R \ln 8$, as expected for $J=S=7/2$ Eu^{2+} ions. Even in the presence of a large lattice specific-heat background, a clear signature of the high-temperature transition is observed in the form of a very pronounced jump of the specific heat at $T_{\text{SDW}}=195$ K. This peak reaches a maximum value of more than 50 J/mol K (on top of the phonon contribution) in spite of the small value of the magnetic moment evidenced by the weak hyperfine field.¹⁰ The sharp peak would be compatible with a first-order phase transition, similar as found in SrFe_2As_2 .⁵

Further insight on the phase transitions is obtained from electrical resistivity of the single crystals for the current flowing within the ab plane (Fig. 2). The electrical resistivity decreases marginally with decreasing temperature down to 200 K. At ≈ 190 K, $\rho(T)$ shows a slight upturn leading to a peak before decreasing rapidly with further reduction in temperature. We attribute this increase in the resistivity to the opening of a gap at the Fermi surface due to the formation of the SDW. Similar resistivity signatures have previously been observed at the SDW transitions in, e.g., Cr metal,¹⁵ URu_2Si_2 ,^{16,17} and CeCu_2Si_2 .¹⁸ The fact that the resistivity upturn has not been observed in polycrystalline samples implies an anisotropic temperature dependence of the resistivity at T_{SDW} . Upon lowering the temperature from ≈ 180 to 20 K, the resistivity continues to decrease. At 20 K a further kink is found, which results from the ordering of localized Eu moments. The resistivity ratio $\rho(2 \text{ K})/\rho(300 \text{ K})=3$ is fairly small but of similar magnitude as found for many 122 compounds crystallizing in the ThCr_2Si_2 -type tetragonal structure.

Since EuFe_2As_2 has similar properties compared to BaFe_2As_2 and SrFe_2As_2 , one would like to suppress the Fe magnetism of this compound in order to induce superconductivity. As a first approach we tried to dope divalent Eu

with monovalent K similar to $(K, M)\text{Fe}_2\text{As}_2$ ($M=\text{Ba}, \text{Sr}$). Our starting composition was $\text{K}_{0.35}\text{Eu}_{0.65}\text{Fe}_2\text{As}_2$. However, our results suggest that a significant part of K evaporated out of the sample due to its high vapor pressure and due to our high-temperature crystal-growth method, resulting in a much lower K content in the sample. We found clear signatures of both magnetic phase transitions in the K-doped sample although the transition temperatures are reduced by a few degrees and the transitions are slightly broadened (not shown) compared to the parent compound. Obviously, we need to improve the doping process in order to suppress the SDW and induce superconductivity.

It is well known that the application of pressure is a suitable tool to change the valence state of Eu from a f^7 configuration to a f^6 state. This transition from Eu^{2+} to Eu^{3+} would provide an additional charge to the FeAs layer as an alternative way to chemical doping. Therefore, a study of the pressure dependence of the Eu valence is very promising.

B. Theory

To gain deeper insight into the electronic structure of EuFe_2As_2 and to locate the system within the AFe_2As_2 family, we carried out full potential electronic structure calculations within the L(S)DA and $\text{LSDA}+U$. Usually, for intermetallic Eu compounds, LSDA calculations result in a Eu^{3+} state with the Eu $4f$ electrons at the Fermi level ε_F . This well-known flaw is in contrast to experimental observations caused by the underestimation of the strong Coulomb repulsion U for the localized Eu $4f$ electrons within the L(S)DA. Adding the Coulomb correlation U on a mean-field level using $\text{LSDA}+U$, the $4f$ states split by about U into an occupied and an unoccupied complex. Surprisingly, already the LSDA for EuFe_2As_2 yields a Eu^{2+} state with the occupied Eu $4f$ complex at about -0.5 eV and the unoccupied about 4 eV above ε_F . This result suggests a rather stable divalent Eu state and is confirmed by our $\text{LSDA}+U$ where the seven occupied Eu $4f$ bands are shifted further down in energy (see Fig. 3).

Apart from the localized Eu $4f$, the resulting electronic density of states (DOS) is almost identical with the DOS of the isovalent SrFe_2As_2 (see Fig. 3), especially for the Fe $3d$ states close to ε_F . Within the physically realistic range, this result is independent of the choice of U . The strong similarity between both systems holds even for details of the band structure and the related Fermi surfaces (not shown). To study whether the small differences in the electronic structure arise from the change of structural parameters or from the change of the cation, we calculated the DOS for the crystallographic data of the Eu compound where Eu was replaced by Sr. Comparing the resulting DOS with that of SrFe_2As_2 , we can assign these differences almost exclusively to the change in crystal geometry rather than to the substitution of the magnetic Eu^{2+} ion by Sr.

In SrFe_2As_2 , only the Fe atoms are magnetic while in EuFe_2As_2 , there are two magnetic sublattices. This raises the question whether the ordering of the Eu moments around 20 K in EuFe_2As_2 is aided by the interaction with the Fe spins or just due to Eu-Eu interaction. In order to estimate the

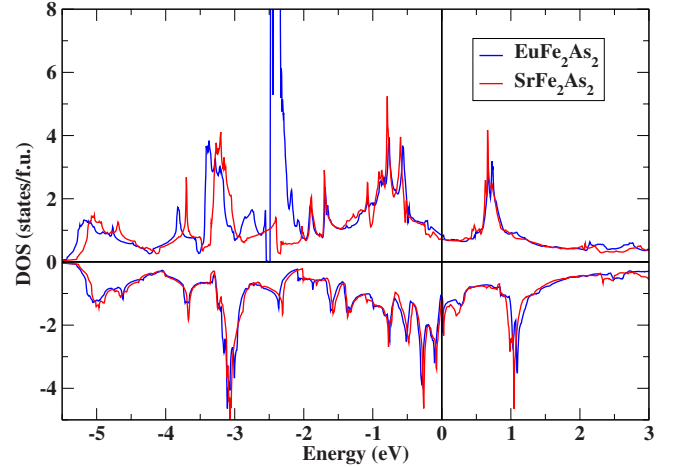


FIG. 3. (Color online) Comparison of the total DOS for EuFe_2As_2 ($\text{LSDA}+U$, with ferromagnetic interaction between the Eu and Fe spins) and SrFe_2As_2 (LSDA). The experimental lattice was used for both the compounds. The large peak for the spin-up states at -2.2 eV arises from the fully filled Eu $4f$ states. The unfilled Eu $4f$ states are at 9.5 eV above the Fermi level.

strength of the Eu and Fe sublattice interactions, we performed fixed spin moment calculations within the $\text{LSDA}+U$ formalism for ferromagnetic Eu and Fe sublattices. It is energetically favorable by 2.5 meV/f.u. to have the Eu and Fe moments parallel to each other rather than antiparallel. Since the Eu $4f$ states are quite localized, we can map the energy difference from our fixed spin moment calculations onto a simple Heisenberg model to get an estimate for an effective nearest-neighbor exchange (J_{eff}) between the Eu and Fe sublattice. We obtain a value of about 1 K for J_{eff} , which is rather small compared to the experimental ordering temperature for the Eu moments (≈ 20 K). This implies that the Eu and Fe sublattices are quite decoupled in this system.

Furthermore, the inclusion of spin-orbit coupling allows an estimate of the spin anisotropy for the compound. Comparing the total energies for Fe $3d$ spins laying the basal plane (along 100) and Fe spins pointing along the c axis (along 001), we find an easy-plane anisotropy of about 0.15 meV per Fe site. Our result is consistent with the magnetic structure proposed by recent neutron-scattering measurements on the magnetic homologue BaFe_2As_2 .¹⁹ For the $S = 7/2$ Eu^{2+} ion, we obtain a negligible (easy axis) anisotropy at the border of numerical accuracy, in agreement with the expectations for a spherical half-filled $4f$ shell.

To investigate the possibility of a pressure induced valency change of the Eu from $2+$ to $3+$, we performed a series of calculations for reduced unit-cell volumes of EuFe_2As_2 . We maintained a constant c/a ratio and a constant As z parameter. For up to a 35% reduction in the experimental volume, we did not observe evidence for a change in the valency of the Eu ion. This result suggests that only for very high pressures of the order of 50 GPa or above might a valence change of Eu be expected.

IV. CONCLUSION

We have grown single crystals of EuFe_2As_2 using a Bridgman technique in a closed Ta crucible. Measurements

of the electrical resistivity and the specific heat clearly establish the magnetic ordering of localized Eu moments at $T_N = 20$ K and itinerant Fe moments at $T_{SDW} = 190$ K. Band-structure calculations reveal a close similarity of the electronic structure of EuFe_2As_2 and SrFe_2As_2 . The Eu and Fe_2As_2 sublattices are nearly decoupled with Fe spins preferably oriented within the a - b plane. Our preliminary attempt to dope K in place of Eu did not produce a superconducting ground state. Further doping experiments are highly desirable to study possible superconductivity in this com-

pound and its interplay with the Eu magnetic moments.

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*Jeevan.Hirale@phys.uni-goettingen.de

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