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Angaben zur Veröffentlichung / Publication details:

Miclea, C. F., M. Nicklas, H. S. Jeevan, D. Kasinathan, Z. Hossain, H. Rosner, Philipp Gegenwart, C. Geibel, and F. Steglich. 2009. "Evidence for a reentrant superconducting state in EuFe2As2 under pressure." *Physical Review B* 79 (21): 212509. https://doi.org/10.1103/physrevb.79.212509.

Evidence for a reentrant superconducting state in $EuFe_2As_2$ under pressure

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(Received 6 March 2009; revised manuscript received 26 May 2009; published 15 June 2009)

We studied the temperature-pressure phase diagram of $EuFe_2As_2$ by electrical resistivity measurements. The spin-density-wave transition at T_0 associated with the FeAs-layers is continuously suppressed with increasing pressure, while the antiferromagnetic ordering temperature of the Eu^{2+} moments seems to be nearly pressure independent up to 2.6 GPa. Above 2 GPa a sharp drop of the resistivity, $\rho(T)$, indicates the onset of superconductivity at $T_c \approx 29.5$ K. Surprisingly, on further reducing the temperature, $\rho(T)$ is increasing again and exhibiting a maximum caused by the ordering of the Eu^{2+} moments, a behavior which is reminiscent of *reentrant* superconductivity as it is observed in the ternary Chevrel phases or in the rare-earth nickel borocarbides.

DOI: 10.1103/PhysRevB.79.212509 PACS number(s): 74.62.Fj, 74.10.+v, 74.25.Dw, 74.70.Dd

The recent discovery of high-temperature superconductivity (SC) in the *R*FeAsO compounds (*R*=La, Ce, Pr, Nd, Sm, Gd)[1–6] with superconducting transition temperature values above to 50 K (Refs. 3 and 4) has attracted strong interest in the scientific community. The *R*FeAsO compounds forming in the ZrCuSiAs-type tetragonal structure are closely related to AFe_2As_2 (*A*=Ca, Sr, Ba)[7–9] forming in the $ThCr_2Si_2$-type tetragonal structure. Both share a similar arrangement of Fe_2As_2 layers assumed to be the key for the SC occurrence in this class of compounds. Materials from both families show at $T_0 \approx 150-210$ K a structural transition from a tetragonal to an orthorhombic phase which is closely related to the formation of a spin-density-wave (SDW) type magnetic instability.[7,8,10–12]

In contrast to the AFe_2As_2 (*A*=Ca, Sr, Ba) compounds where only the iron possesses a magnetic moment, in $EuFe_2As_2$ an additional large, local magnetic moment of $7.5\mu_B$ is carried by Eu^{2+}.[13] Like the (*A*=Ca, Sr, Ba) members of the AFe_2As_2 family, $EuFe_2As_2$ exhibits a SDW transition around $T_0=190$ K related to the Fe_2As_2 layers but in addition, the magnetic moments of the localized Eu^{2+} order at $T_N=20$ K [10,13,14] in a so-called A-type antiferromagnetic (AF) structure.[15] $SrFe_2As_2$ has similar structural properties to $EuFe_2As_2$, its unit-cell volume being only 3% larger, and a comparable value of $T_0=210$ K.[8,16] Furthermore, aside from the Eu-4*f* part, the electronic density of states (DOS) of $EuFe_2As_2$ is almost identical to that of $SrFe_2As_2$.[10] Therefore, $SrFe_2As_2$ can be considered a nonmagnetic homolog of $EuFe_2As_2$. Provided that the two different kinds of magnetic ordering phenomena are reasonably well decoupled, the results of previous doping and pressure studies on $SrFe_2As_2$ (Refs. 17–19) would suggest the appearance of a superconducting phase on doping and/or at sufficiently high pressure in $EuFe_2As_2$, too. In fact, a recent investigation[20] confirmed the first prediction: $K_{0.5}Eu_{0.5}Fe_2As_2$ is superconducting below $T_c=30$ K. Further on, as a result of the replacement of half of the Eu by K, no clear signature of the ordering of the Eu^{2+} is present anymore.

Our electrical resistivity measurements under hydrostatic pressure on single crystalline $EuFe_2As_2$ indicate that the SDW transition is continuously suppressed upon applying pressure, while the magnetic ordering of the Eu^{2+} moments seems to be very robust against pressure. Above 2 GPa, a sharp drop of the resistivity indicates the emergence of a superconducting phase below $T_c \approx 29.5$ K this value being close to the one reported for $K_{0.5}Eu_{0.5}Fe_2As_2$.[20] Remarkably, we found an indication of *reentrant* SC as observed for example in the ternary Chevrel phases, e.g., $HoMo_6S_8$ (Ref. 21) or in the rare-earth nickel borocarbides, e.g., $HoNi_2B_2C$.[22]

Single crystals of $EuFe_2As_2$ were synthesized using the Bridgman method.[10] Powder x-ray diffraction confirmed the proper $ThCr_2Si_2$-type tetragonal structure and the single phase nature of the sample. Measurements of the electrical resistance were carried out using a standard four-probe technique with current flowing in the (*a*, *b*)-plane and magnetic field applied parallel to the current. The investigations were done from room temperature down to 1.8 K and in magnetic fields up to 7 T using a physical property measurement system (PPMS, Quantum Design). Pressures up to 2.6 GPa have been generated using a double-layer piston-cylinder-type pressure cell with an inner cylinder made from MP35N. Silicone oil was used as pressure transmitting medium. The temperature dependence of the superconducting transition temperature of a Pb sample mounted along the whole sample space, served as a pressure gauge. The narrow and pressure independent SC transition width of Pb confirmed the quasi-hydrostatic pressure conditions inside the pressure cell. Density functional band-structure calculations within the local (spin) density approximation [L(S)DA] have been performed using a full potential code FPLO.[24] The strong Coulomb repulsion in the Eu 4*f* orbitals have been included in a mean-field level using the atomic limit, double-counting scheme[25] in the LSDA+*U* approximation. A value of $U=8$ eV was used for the Eu 4*f* orbitals, but the resultant conclusions did not change within a range from 6 to 10 eV. The total energies were calculated on a dense mesh of *k* points using the Perdew-Wang[26] exchange-correlation potential.

Figure 1 shows the electrical resistivity, $\rho(T)$, of $EuFe_2As_2$ for different applied pressures. The absolute value of the room-temperature resistivity at ambient pressure,

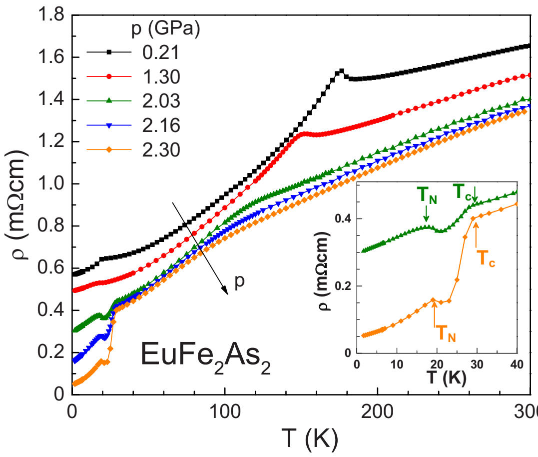

FIG. 1. (Color online) Electrical resistivity vs temperature for different applied pressures for single crystalline $EuFe_2As_2$. Inset: $\rho(T)$ at low temperature for $p=2.03$ GPa and $p=2.3$ GPa. The superconducting and the antiferromagnetic are marked by arrows.

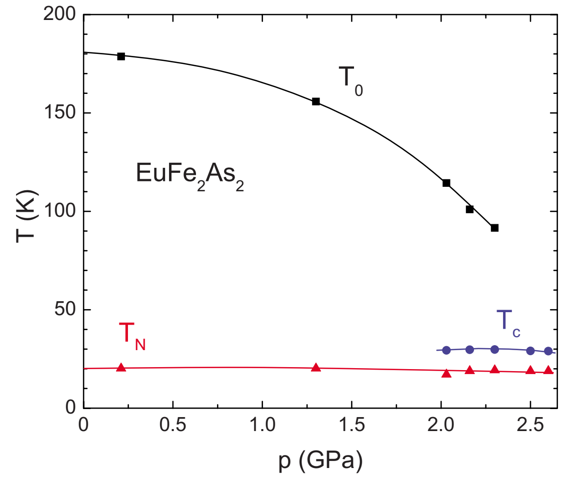

FIG. 2. (Color online) Pressure-temperature phase diagram of $EuFe_2As_2$ obtained from $\rho(T)$ data. The lines are guides to the eyes.

$\rho_{300\ \mathrm{K}} \approx 1.6$ mΩ cm, is typical for the $A\mathrm{Fe}_2\mathrm{As}_2$ materials. In the whole investigated pressure range the resistivity decreases continuously on decreasing temperature, with the exception of a clear anomaly indicating a SDW type of magnetic transition at T_0 at low pressures. With increasing pressure this anomaly broadens. At $p=2.3$ GPa only a change in slope in $\rho(T)$ is remaining; however, T_0 can be still determined from the local minimum in the second derivative of the resistivity, $\partial^2\rho/\partial T^2$. At higher pressures this anomaly cannot be any longer detected unambiguously. At low temperature a second anomaly appears around $T_N \approx 20$ K, indicating the magnetic ordering of the Eu^{2+} moments. $T_N(p)$ seems to be nearly pressure independent. At $p=2.03$ GPa for the first time a sharp drop of the resistivity appears around $T_c=29.5$ K. With increasing pressure this drop becomes even sharper and more pronounced, while its position stays almost constant. We ascribe this feature to the onset of SC. The complete formation of the superconducting state is interrupted by the ordering of the Eu^{2+} sublattice at $T_N < T_c$. The ordering of the Eu^{2+} ions causes an initial increase in $\rho(T)$ followed by a maximum on lowering the temperature. Our finding is reminiscent of *reentrant* SC in magnetic superconductors as has been previously observed for example in $HoMo_6S_8$ (Ref. 21) and in $HoNi_2B_2C$).[22] In the pressure range $p \geq 2.03$ GPa we take T_N as the temperature where the resistivity reaches its maximum below T_c. In the rare-earth nickel borocarbides this has been shown to be the proper procedure to determine T_N from resistivity, in this region of the phase diagram. To exemplify, in the inset of Fig. 1 the positions of T_c and T_N for two different pressures, 2.03 and 2.3 GPa, are marked by arrows. The resulting pressure-temperature phase diagram is presented in Fig. 2.

To get further insight in the relation of magnetic ordering of the Eu^{2+} moments and SC in $EuFe_2As_2$ under pressure we measured $\rho(T)$ at $p=2.16$ GPa in different external magnetic fields (cf. Fig. 3). As discussed before, the zero-field resistivity data show the typical behavior found in reentrant superconductors: after a drop at T_c, $\rho(T)$ is increasing again, showing a maximum at T_N, before further decreasing upon cooling. On increasing the magnetic field, the drop in resistivity shifts to lower temperatures. Already at a field of $B=0.5$ T, no maximum in $\rho(T)$ is visible anymore. Although a drop in resistivity is present in the whole investigated field range up to $B=7$ T, there is a qualitative difference between magnetic fields $B \leq 3$ T and $B > 3$ T. In the former case $\rho(T)$ is decreasing much stronger compared with the latter, dividing the data sets in two distinct groups. The small reduction in the resistivity in large magnetic fields is most likely still due to superconductivity since the AF phase seems to be suppressed at lower fields, $B < 2$ T.[15,23] To construct a T-B phase diagram we define T_x as the local minimum of the second derivative of $\rho(T)$, $\partial^2\rho/\partial T^2$, minimum which corresponds to the kink in $\rho(T)$. The phase diagram is depicted in the inset of Fig. 3. Upon reducing T, at low fields, the upper critical field B_{c2} is increasing linearly. Between 3 and 7 T, $B_x(T)$ shows a strong upturn. The resulting T-B phase diagram shows a clear enhancement of B_{c2} for fields above $B=3$ T and temperatures below $T \approx 20$ K. We find an initial slope of $|\partial B_{c2}/\partial T|_{T_c}=0.368$ T/K much smaller than the value found for $SrFe_2As_2$($|\partial B_{c2}/\partial T|_{T_c}=2.05$ T/K).[17] This would yield, for the dirty limit, an orbital critical field

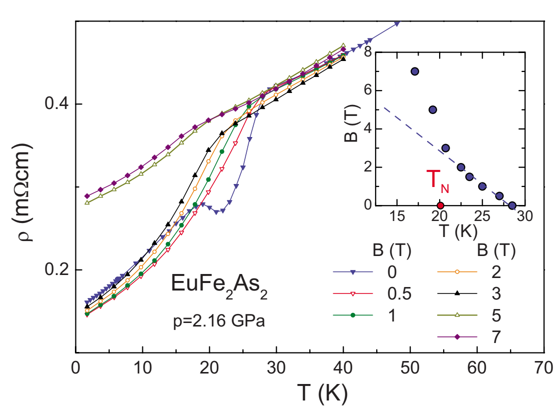

FIG. 3. (Color online) Electrical resistivity at $p=2.16$ GPa in different magnetic fields. Inset: temperature-magnetic field phase diagram. See text for details.

of only about $B_{c2}^{orb}(0)=0.69\ T_c|\partial B_{c2}/\partial T|_{T_c}\approx 7.5$ T. However, for $B\geq 3$ T we find $|\partial B_{c2}/\partial T|=1.1$ T/K.

Recently it has been shown that there is a volume collapse under pressure that precedes the onset of superconductivity in $CaFe_2As_2$.[27,28] Unfortunately, structural or spectroscopic data for $EuFe_2As_2$ under pressure are unavailable up to now. Thus the first problem we addressed with our band-structure calculations as a function of pressure for $EuFe_2As_2$ was the possibility of a similar volume collapse behavior and the ramifications to the SDW of Fe (suppressed or not) and the Eu valency (possible valence transition from Eu^{2+} to Eu^{3+}). During these calculations, the internal parameter for the As z position was held fixed at the experimentally determined position of the ambient pressure, while the c/a ratio was optimized at different reduced volumes. The calculations were done with the Fe spin moments aligned in a columnar magnetic structure pattern, as observed for the Sr homolog.[16] Our results do not indicate any tendency to a sudden collapse of the c axis within the experimentally applied pressure range. The SDW is fully suppressed for pressures larger than 5 GPa, while the Eu is stable in the 2+ state up to pressures larger than 10 GPa.

Another interesting question to answer is the strength of the AF interaction between the Eu^{2+} planes as a function of pressure. To evaluate this, we have calculated the energy difference between the ferromagnetic and antiferromagnetic (interplanes) arrangement of the Eu spins for various pressure values.[29] First results from the LSDA+U calculations show that pressure stabilizes the AF ordering of the Eu^{2+} planes along the c axis. The influence of spin-orbit coupling in this scenario is still under investigation. As a next step we have compared the change in the magnitude of the Fe moments as a function of pressure for both the Sr and Eu systems. The magnitude of the Fe moments, ordered in the columnar magnetic structure, decreases upon reducing the volume and finally is suppressed in a similar way for both systems.

Comparing the electronic structure under pressure of $EuFe_2As_2$ to that of the Sr homolog, a very close similarity remains between the two systems. T_c for the 50% K substituted $EuFe_2As_2$ is reduced by 6 K as compared to the 50% K substituted $SrFe_2As_2$. Also, in the current pressure study of the pure Eu system, a similar reduction (by 6 K) of T_c is observed compared to the Sr compound. But both the Sr and Eu homologs behave very similar at high temperatures (above the Eu magnetic ordering temperature). Therefore, one can conclude that the drop of the T_c together with the reduction of $|\partial B_{c2}/\partial T|_{T_c}$ are caused by the presence of paramagnetic Eu^{2+} ions at temperatures above the Néel ordering temperature.

To summarize, we have investigated the effect of hydrostatic pressure on the peculiar properties of $EuFe_2As_2$. The transition at T_0 corresponding to the lattice distortion and the formation of the SDW shifts with increasing pressure from 180 K at $p=0$ GPa down to 90 K at $p=2.3$ GPa. The corresponding anomaly in $\rho(T)$ has already become very weak at this pressure and cannot be observed any longer for $p\geq 2.5$ GPa, suggesting the critical point were this transition gets completely suppressed to be very close to $p=2.3$ GPa. Above 2 GPa, a sharp drop appears in $\rho(T)$ at $T_c=29.5$ K and becomes more pronounced upon further increasing pressure, indicating the onset of SC. The large and linear initial shift of T_c to lower temperatures with increasing field supports the superconducting nature of this transition. Thus the transition from the magnetic order of Fe moments to the superconducting state occurs in $EuFe_2As_2$ at a slightly smaller pressure than in $SrFe_2As_2$, which correlates with a slightly smaller initial unit-cell volume. Further on, assuming that the transition at T_0 is of first order (as suggested by most current investigations) and applying the Clausius-Clapeyron relation one finds a faster suppression of T_0 with increasing p, in accordance with a larger volume change at T_0 in $EuFe_2As_2$ ($\Delta V\approx -5\times 10^{-4}$ nm^3) compared to $SrFe_2As_2$ ($\Delta V\approx -3\times 10^{-4}$nm^3).[30] On the other hand, the latent heat at the transition, $\Delta H\approx 220$ J/mol,[10] is about the same as in $SrFe_2As_2$.[8] In the superconducting state, we observed a minimum in $\rho(T)$ below T_c, followed by a clear increase leading to a maximum at $T_N=20$ K. This points to reentrant SC due to the AF ordering of Eu. T_N does not seem to change significantly with pressure, as typically observed in Eu systems. While this reentrant behavior is suppressed at low fields $B\geq 0.5$ T, between $B=3$ T and $B=7$ T we observed a strong reduction in the drop in $\rho(T)$ below the transition as well as a strong decrease of the field dependence of the transition temperature.

Thus, our results suggest a very peculiar and interesting interaction between the superconducting state and the magnetism of the rare-earth ions in $EuFe_2As_2$ under pressure. Such reentrant SC has not been observed in the doped RFeAsO compounds and this makes $EuFe_2As_2$ unique among the layered FeAs systems. The occurrence of these phenomena seems to be related to the fact that at $B=0$, T_N is not much smaller than T_c.

We acknowledge the financial support of the DFG—MI 1171/1-1, DFG—Research Unit 960, DFG—Sonderforschungsbereich 463, and BRNS (Grant No. 2007/37/28).

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