Possible re-entrant superconductivity in EuFe$_2$As$_2$ under pressure

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We studied the temperature-pressure phase diagram of EuFe$_2$As$_2$ by measurements of the electrical resistivity. The antiferromagnetic 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 re-entrant superconductivity as it is observed in the ternary Chevrel phases or in the rare-earth nickel borocarbides.

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The recent discovery of high temperature superconductivity (SC) in the ReFeOAs compounds ($R=$La-Gd) with superconducting transition temperature approaching values up to 50 K attracted strong interest in the scientific community. The ReFeOAs compounds forming in the ZrCuSiAs-type tetragonal structure are closely related to $\mathrm{AF}_{2}\mathrm{As}_2$ ($\mathrm{A}=$Ca, Sr, Ba) forming in the ThCr$_2$Si$_2$-type tetragonal structure. Both share a similar arrangement of Fe$_2$As$_2$ layers assumed to be the key for the SC formation in this class of compounds. Materials from both families show at $T_0 \approx 150$ K – 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 in a so called A-type antiferromagnetic structure.

In contrast to the $\mathrm{AF}_{2}\mathrm{As}_2$ ($\mathrm{A}=$Ca, Sr, Ba) compounds where only the iron possesses a magnetic moment, in EuFe$_2$As$_2$ a large additional magnetic moment of $\mu_B$ is carried by Eu which is in the 2$^+$ state. Like the ($\mathrm{A}=$Ca, Sr, Ba) members of the $\mathrm{AF}_{2}\mathrm{As}_2$ family, EuFe$_2$As$_2$ exhibits a SDW transition around $T_0 = 190$ K related to the Fe$_2$As$_2$ layers, but additionally at $T_N = 20$ K the magnetic moments of the localized Eu$^{2+}$ moments order in a so called A-type antiferromagnetic structure. SrFe$_2$As$_2$ has similar structural properties, the unit-cell volume is only 3% larger, and a comparable value of $T_0 = 210$ K. Furthermore, aside from the Eu 4$f$ part, the electronic density of states (DOS) of EuFe$_2$As$_2$ is almost identical to the DOS of SrFe$_2$As$_2$. Therefore, SrFe$_2$As$_2$ can be considered as a non-magnetic homologue compound of EuFe$_2$As$_2$. Provided that the two different kinds of magnetic ordering phenomena are reasonably well decoupled the results of previous doping and pressure studies on SrFe$_2$As$_2$ would suggest the appearance of a superconducting phase on doping and/or at high pressure in EuFe$_2$As$_2$ too. Indeed, a very recent K doping investigation confirmed the first prediction: $\mathrm{K}_{0.5}\mathrm{Eu}_{0.5}\mathrm{Fe}_2\mathrm{As}_2$ is superconducting below $T_c = 30$ K. 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$_2$As$_2$ 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 which is close to the one reported for $T_c$ for $\mathrm{K}_{0.3}\mathrm{Eu}_{0.7}\mathrm{Fe}_2\mathrm{As}_2$ [19]. For the first time to our knowledge in FeAs based superconductors, we found an indication of re-entrant SC as observed in the ternary Chevrel phases, e.g. GdMo$_2$S$_6$ [20] or in the rare-earth nickel borocarbides, e.g. HoNi$_2$B$_2$C [21].

Single crystals of EuFe$_2$As$_2$ were synthesized using the Bridgman method. Powder X-ray diffraction confirmed the proper ThCr$_2$Si$_2$ 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 temperatures 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 superconducting transition temperature of lead served as a pressure gauge. The narrow transition width confirmed the quasi hydrostatic pressure conditions inside the pressure cell. The density functional band structure
calculations within the local (spin) density approximation (L(S)DA) have been performed using a full potential code FPLO [22]. The strong Coulomb repulsion in the Eu 4f orbitals have been included in a mean field level using the atomic limit double counting scheme [23] in the LSDA+U approximation. A $U$ value of 8 eV was used for the Eu 4f orbitals, but the resultant conclusions did not change for a range from 6 to 10 eV. The total energies were calculated on a dense mesh of $k$-points using the Perdew-Wang [24] exchange correlation potential.

Figure 1 shows the electrical resistivity, $\rho(T)$ of EuFe$_2$As$_2$ for different applied pressures. The absolute values of the room temperature resistivity $\rho(300K) \approx 1.6$ m$\Omega$cm at ambient pressure is typical for the AFe$_2$As$_2$ materials. In the whole investigated pressure range the resistivity decreases continuously on decreasing temperature, with the exception of a clear anomaly indicating SDW type of magnetic transition at $T_0$ at low pressures. With increasing pressure the peak broadens. At $p = 2.3$ GPa only a change of slope in $\rho(T)$ is remaining, however, $T_0$ can be still determined from the minimum in the second derivative of the resistivity, $d^2\rho(T)/dT^2$. At higher pressures this anomaly cannot be any longer unanimously detected. At low temperature a second anomaly appears around $T_N \approx 20$ K indicating the magnetic ordering of the Eu$^{2+}$ moment. $T_N(p)$ 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 does not change. We ascribe this feature in the resistivity 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$^{2+}$ causes an initial increase of $\rho(T)$ followed by a maximum on lowering the pressure. This behavior of $\rho(T)$ is reminiscent of re-entrant SC which has first been reported in GdMo$_6$S$_8$ [20] which belongs to the class of the ternary Chevrel phases. Furthermore, re-entrant SC has been found in the rare-earth nickel borocarbides (e.g. HoNi$_2$B$_2$C) [21]. In this pressure range ($p \geq 2.16$) 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. The resulting pressure-temperature phase diagram is presented in Fig. 2.

To get further insights in the relation of magnetic ordering of the Eu$^{2+}$ moments and SC in EuFe$_2$As$_2$ 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 re-entrant superconductors: after a first drop at $T_c$, $\rho(T)$ exhibits a maximum at $T_N$ before it further decreases upon lowering the temperature. On increasing 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 $B \geq 5$ T. In the first case $\rho(T)$ is decreasing much stronger compared with the latter, dividing the data sets in two distinct groups. The small reduction of the resistivity in large magnetic fields is similar in size to what is found at lower pressures, where no SC is present, below $T_N$ due to the reduced scattering of the conduction electrons on the ordered Eu$^{2+}$ moments. To construct a $T - B$ phase diagram we take the temperature $T_x$ of minima of the second derivative of $\rho$, $d^2\rho(T)/dT^2$, which is corresponding to the kink
in \( \rho(T) \). The phase diagram is depicted in the inset of Fig. 3. At low fields \( B_x(T) = B(T = T_x) \) is increasing linearly. Between 3 T and 5 T, \( B_x(T) \) shows a strong upturn. Having in mind the smaller drop of \( \rho(T) \) in large magnetic fields we suggest that the kink in resistivity at \( B = 5 \) T and 7 T should be attributed to the magnetic ordering of the Eu\(^{2+} \) moments. Therefore we include the data point obtained for \( T_N \) at zero magnetic field to propose a magnetic phase line. The resulting \( T - B \) phase diagram suggests the suppression of the SC phase once the \( H_{c2} \) line crosses the magnetic phase boundary. We find an initial slope of \( \partial B_{c2}(T) / \partial T \bigg|_{T_c} = -0.368 \) T/K much smaller compared to the value found in SrFe\(_2\)As\(_2\) \( \partial B_{c2}(T) / \partial T \bigg|_{T_c} = -2.05 \) T/K \( \) [10]. Accordingly, the estimated orbital critical field for superconductivity is only about \( B_{c2}(0) \approx 19.5 \) T.

A recent study of magnetization and magnetoresistance at atmospheric pressure reports a metamagnetic transition to a ferromagnetically polarized state in EuFe\(_2\)As\(_2\) already at about \( B_m = 1 \) T at \( T = 2 \) K for field applied in the \( ab \)-plane. Under pressure \( B_m \) seems to be much higher. Our resistivity measurements at \( p = 2.16 \) GPa point to the presence of AFM order in magnetic fields as high as 7 T. A possible explanation for the more robust AFM state could be the higher compressibility along \( c \)-axis compared with \( a \)-axis as has been found in SrFe\(_2\)As\(_2\) \( \) [23]. This should lead to a stronger magnetic coupling along the \( c \)-axis upon increasing pressure.

Recently it has been shown that there is a volume collapse under pressure that precedes the onset of superconductivity in CaFe\(_2\)As\(_2\) \( \) [26, 27]. Thus the first problem we addressed with our band structure calculations as a function of pressure for EuFe\(_2\)As\(_2\) 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\(^{3+} \)). The internal parameter for the As \( z \) position was held fixed at the experimental position of the ambient pressure during these calculations, while the \( c/a \) ratio was optimized at different reduced volumes. The calculations were done with the Fe spin-moments aligned in the columnar magnetic structure pattern, as observed for the Sr analogue \( \) [15]. Our results do not indicate any tendency to a sudden collapse of the \( c \)-axis under pressure. 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 antiferromagnetic interaction between the Eu\(^{2+} \) planes as a function of pressure. To evaluate this, we have calculated the energy difference between the ferromagnetic and anti-ferromagnetic (inter planes) arrangement of the Eu spins for various pressure values \( \) [28]. 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 volume and finally is suppressed in a similar trend for both systems.

Comparing the electronic structure of EuFe\(_2\)As\(_2\) to the Sr analogue, a very close similarity remains, under pressure, between these two systems. The \( T_c \) for the 50\% K-substituted EuFe\(_2\)As\(_2\) is reduced by 6 K as compared to the 50\% K-substituted SrFe\(_2\)As\(_2\). Also, in the current pressure study of the pure Eu system, a similar reduction (by 6 K) of the \( T_c \) is observed compared to the Sr analogue. But both the Sr and Eu analogues behave very similar at high temperatures (above the Eu magnetic ordering temperature). Therefore one can conclude that this decrease of the \( T_c \) together with the reduction of the \( \partial B_{c2} / \partial T \bigg|_{T_c} \) slope are caused by the presence of paramagnetic Eu\(^{2+} \) ions at temperatures larger than the Néel ordering temperature.

In summary, we have investigated the effect of hydrostatic pressure on the peculiar properties of EuFe\(_2\)As\(_2\). The transition at \( T_0 \) corresponding to the lattice distortion and the formation of the SDW shifts to lower temperatures with increasing pressure, 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 any longer observed 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 \( T_c \approx 29.5 \) K and becomes more pronounced with further increasing pressure, indicating

\[ \text{FIG. 3: (Color online) Electrical resistivity at } p = 2.16 \text{ GPa in different magnetic fields. Inset: temperature-magnetic field phase diagram. See text for details.} \]
the onset of superconductivity. The large and linear initial shift of $T_c$ to lower temperatures with increasing field supports the SC nature of this transition. Thus the transition from the magnetic order of Fe moments to the SC state occurs in EuFe$_2$As$_2$ at a slightly smaller pressure than in SrFe$_2$As$_2$, which correlates with a slightly smaller initial unit cell volume. Further on, assuming that the transition at $T_0$ is first order (as suggested by most current investigations) and thus the applicability of the Clausius-Clapeyron relation, the faster suppression of $T_0$ with increasing $p$ is in accordance with a larger volume change at $T_0$ in EuFe$_2$As$_2$ ($\Delta V \approx -5 \times 10^{-4} \text{nm}^3$) compared to SrFe$_2$As$_2$ ($\Delta V \approx -3 \times 10^{-4} \text{nm}^3$) [20], while the latent heat at the transition, $\Delta H \approx 220 \text{ J/mol}$ [10], is about the same as in SrFe$_2$As$_2$ [8]. In the SC state, we observed below $T_c$ a minimum in $\rho(T)$ followed by a clear increase leading to a maximum at around 20 K. This suggests re-entrant superconductivity due to the antiferromagnetic ordering of Eu. The Eu antiferromagnetic ordering temperature $T_N$ itself does not seem to change significantly with pressure, as typically observed in Eu systems. While this re-entrant behavior is suppressed at low fields $B \geq 0.5$ T, we observed between $B = 3$ T and $B = 5$ T a strong reduction of the drop in $\rho(T)$ below the transition as well as a strong reduction of the field dependence of the transition temperature. This suggests that once $T_c$ becomes smaller than $T_N$, superconductivity is completely suppressed and the left anomaly in $\rho(T)$ observed at $T_c$ is then related to $T_N$. Thus our results evidence a very peculiar and very interesting interaction between the superconducting state and the magnetism of the rare earth in EuFe$_2$As$_2$ under pressure. Such a re-entrant superconductivity as well as the suspected suppression of the SC state by the antiferromagnetic state at higher field have not been observed in the doped RFeAsO compounds and makes thus EuFe$_2$As$_2$ 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 $T_c$. That the magnetic order of Eu is able to suppress the superconductivity in the FeAs layers has likely strong implication for the symmetry of the SC order parameter.

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