Physica C 471 (2011) 476–479

Contents lists available at ScienceDirect

Physica C

journal homepage: www.elsevier.com/locate/physc

Dependence of magnetic ordering temperature of doped and undoped $EuFe_2As_2$ on hydrostatic pressure to 0.8 GPa

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ARTICLE INFO

Article history:
Received 19 March 2011
Accepted 18 April 2011
Available online 22 April 2011

Keywords:
Fe pnictide compound
Superconductivity
Magnetic order
High pressure
Eu compound

ABSTRACT

The ac susceptibility of single crystalline tetragonal $EuFe_2As_2$, $EuFe_2As_{1.4}P_{0.6}$, and $EuFe_{1.715}Co_{0.285}As_2$ has been measured over the temperature and hydrostatic (He-gas) pressure ranges 10–60 K and 0–0.8 GPa, respectively. For all three samples the magnetic ordering temperature (17–19 K) from the Eu sublattice increases linearly with pressure, presumably due to the enhanced exchange coupling between Eu-layers. No evidence for a superconducting transition was observed in the susceptibility for any sample over the measured temperature/pressure range.

1. Introduction

The high pressure variable has proven to be a valuable tool to further our understanding of superconducting materials. The lattice parameters of a single sample can be changed reversibly without introducing the disorder prevalent in doping experiments. However, in the recently discovered Fe-based pnictides the superconducting state appears to react very sensitively to the introduction of lattice strains such as those arising from the shear stresses introduced by nonhydrostatic pressure media [1]. As pointed out by Duncan et al. [2], high pressure studies on the compounds XFe_2As_2, where X = Ba, Sr, Ca, "have led to a bewildering array of confusing and apparently contradictory results". Single crystals of $CaFe_2As_2$, for example, are reported to become superconducting under a relatively low pressure $\leqslant$0.4 GPa if pressure media such as Fluorinert or silicone oil are used [3], whereas with much more hydrostatic He-gas pressure no sign of superconductivity could be detected to 0.7 GPa [4].

It is important to note that in such highly anisotropic materials such as these, pressure-dependent shear stress effects may occur in polycrystalline samples even under purely hydrostatic high-pressure conditions; the anisotropic compression of each crystallite in a polycrystalline sample results in shear stresses across each grain boundary to neighboring crystallites with different orientations. To establish the intrinsic dependence of the superconducting state on pressure for a given Fe-based material, it would thus appear to be essential to study only high quality single crystals and to apply pure hydrostatic pressure using He gas pressure medium. It is possible that these same considerations may apply in studies of the magnetic properties of Fe-based materials under pressure.

$EuFe_2As_2$ exhibits spin-density-wave order below $T_s \approx 185$ K involving the Fe-sublattice; under pressure T_s shifts rapidly to lower temperatures, disappearing completely above ~2.5 GPa [5]. The interactions between the strong local magnetic moments on each Eu site (Eu is divalent with a $4f^7$ orbital configuration) lead to type A antiferromagnetic order below 19 K, although the positive Curie–Weiss temperature points to predominantly ferromagnetic interactions [6]. Under pressure the magnetic ordering temperature reportedly remains constant to 2.6 GPa [7], increasing slowly at higher pressures before reaching a maximum near 55 K at ~9 GPa [5]. Only in a narrow region of pressure around 3 GPa has bulk superconductivity near 30 K been reported for $EuFe_2As_2$ [8]. The partial substitution of Co for Fe or of P for As in $EuFe_2As_2$ leads to a ferromagnetic ground state [9–11]; surprisingly, samples of polycrystalline $EuFe_2As_{1.4}P_{0.6}$ [10] and single-crystalline $EuFe_{1.78}Co_{0.22}As_2$ [11] have been reported to exhibit at ambient pressure ferromagnetism in coexistence with a superconducting transition near 26 K and 21 K, respectively, although only a very small fraction of full diamagnetic shielding was observed. In very recent work on well characterized single crystals of $EuFe_2As_{2-y}P_y$,

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doi:10.1016/j.physc.2011.04.011

Jeevan et al. [9] report that bulk superconductivity only exists in the narrow doping range $0.32 \leqslant y \leqslant 0.44$, and thus not for $y = 0.6$.

In this paper we measure the temperature-dependent ac susceptibility of $EuFe_2As_2$, $EuFe_2As_{1.4}P_{0.6}$, and $EuFe_{1.715}Co_{0.285}As_2$ under the application of hydrostatic He-gas pressures as high as 0.8 GPa; we find that the magnetic ordering temperatures increase linearly with pressure at the rates +0.35(3), +2.4(1), and +2.0(1) K/GPa, respectively. No evidence is found for a superconducting transition in the temperature range 10–60 K.

2. Experiment

High quality single crystals with nominal composition $EuFe_2As_2$ and $EuFe_2As_{1.4}P_{0.6}$ were prepared by solid reaction methods involving two steps. Firstly, polycrystalline $EuFe_2As_2$ and $EuFe_2As_{1.35}P_{0.65}$ were prepared in evacuated quartz tubes at 900 °C for 50 h and then the resulting materials were ground thoroughly, pressed into pellets, and loaded into Al_2O_3 crucibles. Secondly, the crucibles were sealed in evacuated quartz tubes and were heated to 1190 °C, held at this temperature for 24 h, and finally cooled to 1100 °C over 100 h. Many plate-like tetragonal-structure $EuFe_2As_2$ and $EuFe_2As_{1.4}P_{0.6}$ crystals were obtained. As seen in Fig. 1, X-ray diffraction from the (001) planes yields the lattice parameters $c = 1.207(7)$ nm and 1.188(7) nm, respectively. Comparison of these value of c with those obtained in the extensive studies by Jeevan et al. [9] on $EuFe_2As_{2-y}P_y$ crystals, where the doping level y for each crystal was determined by EDX, reveals that the actual level of P-doping for our crystal may be somewhat lower than the nominal value $y = 0.6$, but likely in the range $0.45 \leqslant y \leqslant 0.6$. As expected for this doping level no sign of a SDW transition was observed in $EuFe_2As_{1.4}P_{0.6}$ either in the ac susceptibility or electrical resistivity over the temperature range 4–300 K [12]. Single crystals of $EuFe_{1.175}Co_{0.285}As_2$ were grown by a self-flux method as described elsewhere [13].

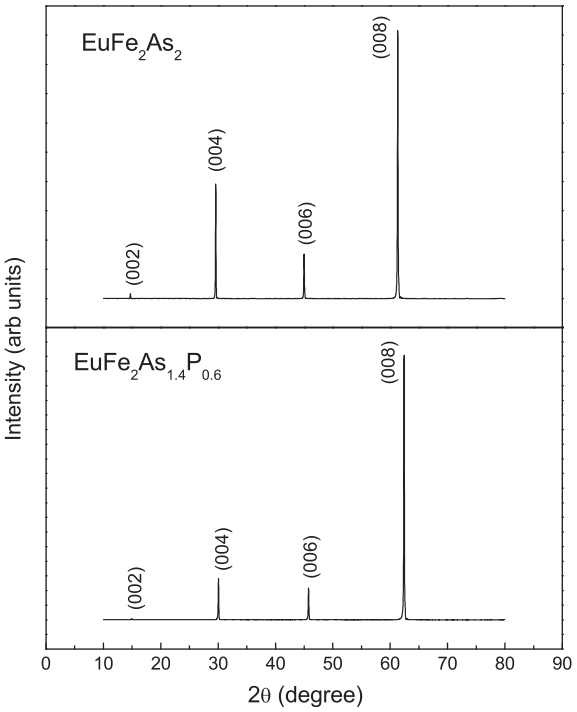

Fig. 1. X-ray diffraction pattern ($\lambda = 0.154$ nm) for (001)-plane oriented single crystals of tetragonal $EuFe_2As_2$ and $EuFe_2As_{1.4}P_{0.6}$; the data yield the c lattice parameters 1.207(7) nm and 1.188(7) nm, respectively. No impurity phases are visible.

To generate hydrostatic pressures as high as 0.8 GPa, a He-gas compressor system (Harwood Engineering) was used in combination with a CuBe pressure cell (Unipress). Pressures were changed near room temperature and held for 30–45 min before cooling down to 10 K to measure the temperature-dependent ac susceptibility $\chi(T)$ at 0.1 Oe rms and 1023 Hz applied magnetic field. These measurements were carried out under pressure to the same high accuracy as measurements at ambient pressure by surrounding the sample with a calibrated primary/secondary compensated coil system connected to a Stanford Research SR830 digital lock-in amplifier via a SR554 transformer preamplifier. A two-stage closed-cycle refrigerator (Balzers) was used to cool the pressure cell to low temperatures; measurements were carried out by slowly warming up through the transition at the rate ~100 mK/min.

All susceptibility measurements were repeated at least once to verify that the reproducibility of the ferromagnetic or antiferromagnetic transition temperature $T_{C,N}$ was within 20 mK. The temperature-dependent background signal from the empty coil system was measured and subtracted from the sample data. Unfortunately, due to the pressure- and temperature-dependent background signal, it was not possible to reliably extract the pressure dependence of the Curie constant or Curie-Weiss temperature from the paramagnetic ac susceptibility in the temperature region well above $T_{C,N}$. An approximate Curie-Weiss analysis is given below at ambient pressure over the limited temperature range 30–60 K.

All pressures were determined for the sample at a temperature near $T_{C,N}$ using a calibrated manganin gauge located at room temperature near the compressor system and connected via a 3 mm dia. CuBe capillary tube to the pressure cell at low temperature. Further details of the He-gas techniques used are given elsewhere [14].

3. Results and discussion

In Fig. 2 the real part of the ac susceptibility is plotted versus temperature to 60 K at ambient pressure for the doped and undoped $EuFe_2As_2$ crystals studied. Fitting the data for each in the temperature range 30–60 K results in the Curie-Weiss equations given in the figure and plotted as solid lines. The Curie constant

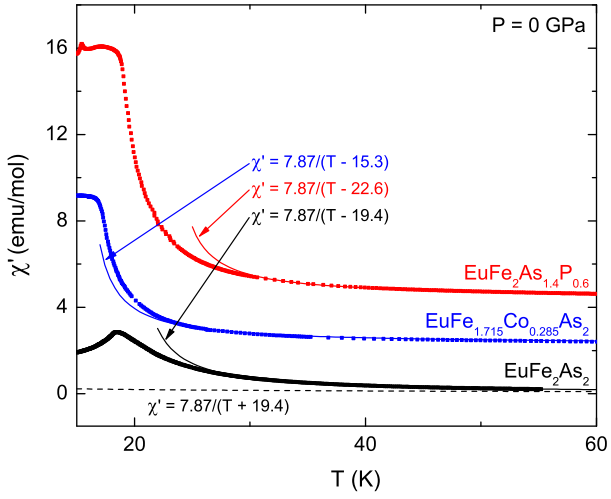

Fig. 2. Real part of the ac susceptibility versus temperature at ambient pressure for the three crystals studied. Ordinate scale applies to $EuFe_2As_2$. Data on doped crystals are shifted vertically for clarity. Equations are connected by arrows to respective data fits given by solid lines. Dashed line is plot of equation below it (see text).

is fixed at the value $C = 7.87$ emu/mole which corresponds to the full local magnetic moment corresponding to $J = S = 7/2$ for each Eu cation. The only fitting parameter used is the Curie-Weiss temperature which turns out to be positive in all three cases. These results are in reasonable agreement with those from previous studies [6,10,11]. It is interesting to note that the dashed line in the figure results if, in the Curie-Weiss equation for $EuFe_2As_2$, the sign of the Curie-Weiss temperature is changed from ferromagnetic to antiferromagnetic. That the data lies everywhere well above this dashed line emphasizes the dominant ferromagnetic nature of the interactions in this compound, in spite of the overall antiferromagnetic order. This strong ferromagnetic interaction is likely responsible for the fact that within each plane the Eu spins are aligned parallel to each other [6,15], pointing along the crystallographic a axis [16].

In Fig. 3a the temperature-dependent magnetic susceptibility of $EuFe_2As_2$ is plotted on an expanded scale for three different hydrostatic pressures. The Néel temperature T_N increases with pressure at the rate +0.35(3) K/GPa (see Fig. 4). The temperature-dependent ac susceptibilities of $EuFe_2As_{1.4}P_{0.6}$ and $EuFe_{1.715}Co_{0.285}As_2$ are shown in Fig. 3b and c; the anomaly near 15 K for both is not understood, but likely signals a minor spin rearrangement. In both cases the Curie temperature increases at the relatively rapid rates +2.4(1) and +2.0(1) K/GPa, respectively (see Fig. 4). It has been suggested [9] that the increase in the Curie temperature with P-doping in $EuFe_2As_{2-y}P_y$ for $y \geqslant 0.44$ arises from the rapid reduction in the c lattice parameter, and thus the separation of the Eu-layers, with increasing y. As the Eu-planes come closer together, the interplanar exchange coupling increases which leads to the observed enhancement of the Curie temperature T_C. This scenario is in qualitative agreement with the present results where the application of pressure to 8 GPa is known to rapidly decrease c in $EuFe_2As_{1.4}P_{0.6}$, with little or no change in a [12]. Whereas a 1% decrease in c through P-doping in $EuFe_2As_{2-y}P_y$ leads to an increase in T_C by ~18% [9], the present experiments together with Ref. [12] show that a 1% decrease in c by applying pressure enhances T_C by ~9%. The increase in T_C with P-doping thus appears to not be solely a chemical pressure effect.

We speculate that the relatively small pressure derivative $dT_N/dP = +0.35$ K/GPa found for $EuFe_2As_2$ may be the result of mixed ferro- and antiferromagnetic exchange interactions within and between the Eu layers and/or arise from exchange coupling between the SDW-ordered Fe-sublattice and the antiferromagnetically ordered Eu layers. More complete details of the pressure-dependent spin structures of these systems would be needed before one could attempt a more quantitative interpretation of the present data.

In contrast to a previous report of a superconducting transition near 26 K for $EuFe_2As_{1.4}P_{0.6}$ at ambient pressure [10], we observe no diamagnetic transition near 26 K (see inset in Fig. 3b [17]) within our instrumental resolution of better than 0.01 emu/mole which corresponds to ~0.2% of full diamagnetic shielding. In $EuFe_{1.715}Co_{0.285}As_2$ we also find no evidence for the superconducting transition near 21 K reported by Jiang et al. [11] for this same compound at the somewhat different doping level $EuFe_{1.78}Co_{0.22}As_2$. In fact, to an accuracy of 0.2% of full diamagnetic shielding, we do not observe any indication of a superconducting transition for any of the three samples over the temperature and pressure ranges 10–60 K and 0–0.8 GPa, respectively. As pointed out earlier, this absence of superconductivity in $EuFe_2As_{1.4}P_{0.6}$ is consistent with the findings of Jeevan et al. [9].

In Fig. 4 the magnetic ordering temperature is plotted versus hydrostatic pressure for the three crystals studied. One further (final) data point is shown for each crystal after the pressure was fully released to ambient. To check for possible temperature/pressure history effects such as we had observed for the superconducting transition temperature in polycrystalline $LaO_{1-x}F_xFeAs$ [18], a further experiment was carried out here for both doped $EuFe_2As_2$ crystals. For the Co-doped crystal, 0.3 GPa pressure was applied at room temperature but released at ~30 K, while for the P-doped crystal 0.85 GPa was applied at room temperature and released at ~78 K. For $EuFe_2As_2$ the pressure release (pts. 3 → 4 in Fig. 4) was

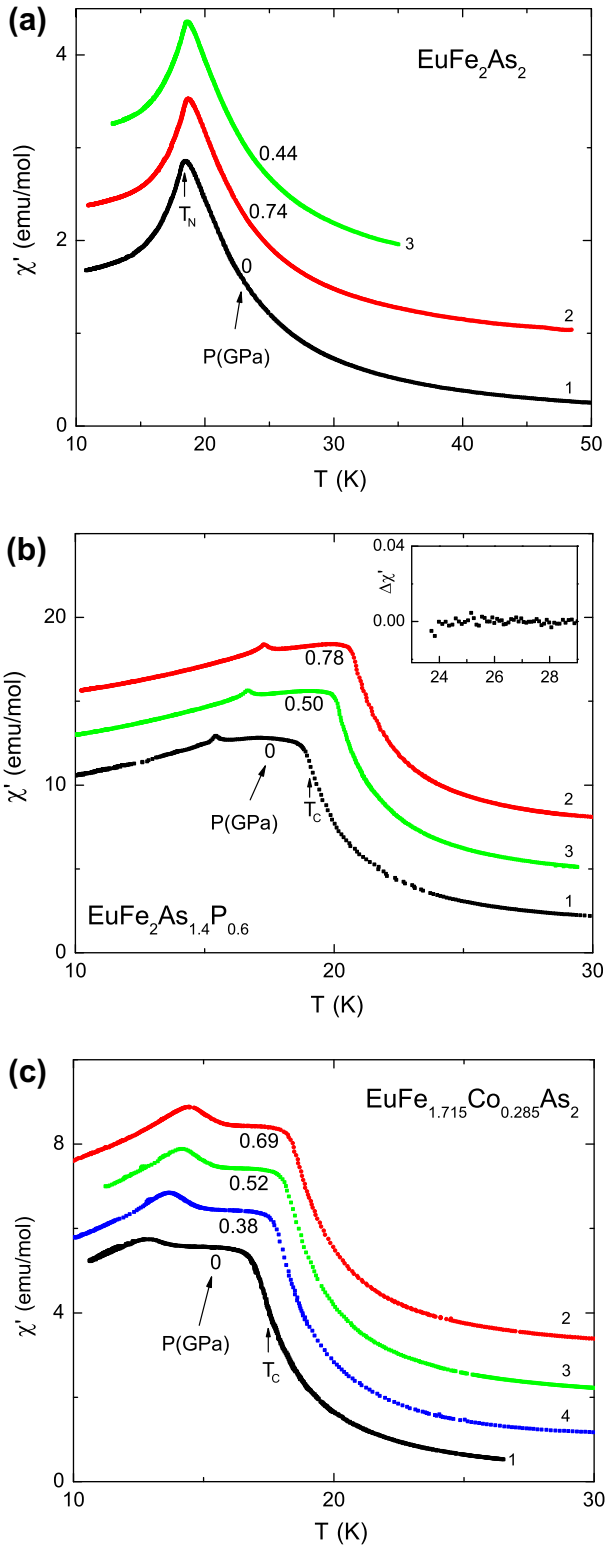

Fig. 3. Real part of the ac susceptibility versus temperature at different pressures for (a) $EuFe_2As_2$, (b) $EuFe_2As_{1.4}P_{0.6}$ (inset gives "nonmagnetic" susceptibility versus temperature near 26 K in same units as main figure), and (c) $EuFe_{1.715}Co_{0.285}As_2$. Ordinate scale applies to data at ambient pressure (0 GPa). Data at high pressures are shifted vertically for clarity. Short vertical arrows give location of Néel (T_N) or Curie (T_C) temperatures. Numbers give order of measurement.

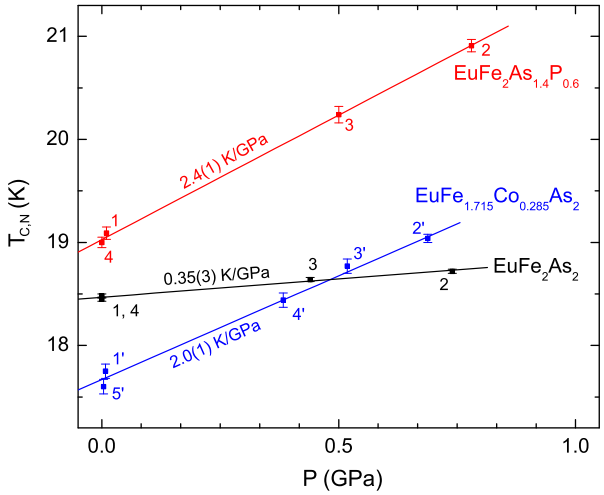

Fig. 4. Pressure dependence of the magnetic ordering temperature $T_{C,N}$ for the three samples studied. Value of pressure derivative $dT_{C,N}/dP$ is given for each. Numbers give order of measurement; primed numbers are used to distinguish data from the Co-doped crystal.

carried out at 150 K instead of room temperature. For all three samples the measured values of $T_{C,N}$ at ambient pressure were identical, within experimental accuracy, to the initial value at the beginning of the experiment. The absence of temperature/pressure history effects here is indicated by the fact that after the pressure release at low temperature the value of the magnetic ordering temperature reverts to its initial value at the beginning of the experiment.

In summary, in ac susceptibility measurements the magnetic ordering temperatures of three undoped and P- and Co-doped $EuFe_2As_2$ compounds are found to increase under hydrostatic (He-gas) pressure to 0.8 GPa, likely due to the rapid decrease in interplanar separation which promotes an enhanced ferromagnetic exchange interaction between Eu layers. At either ambient or high pressure no evidence is found for superconductivity in any compound studied for temperatures above 10 K.

Acknowledgments

The high-pressure studies at Washington University were supported by the National Science Foundation through Grant No. DMR-0703896 and by the Carnegie/DOE Alliance Center (CDAC) through NNSA/DOE Grant Number DE-FC52-08NA28554. One of Authors (LS) wishes to thank the National Science Foundation of China for its support of this research through Grant Nos. 10874230 and 11074294.

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