EuFe$_2$As$_2$ under High Pressure: an Antiferromagnetic Bulk Superconductor

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We report the ac magnetic susceptibility $\chi_{ac}$ and resistivity $\rho$ measurements of EuFe$_2$As$_2$ under high pressure $P$. By observing nearly 100% superconducting shielding and zero resistivity at $P = 28$ kbar, we establish that $P$-induced superconductivity occurs at $T_c \sim 30$ K in EuFe$_2$As$_2$. $\rho$ shows an anomalous nearly linear temperature dependence from room temperature down to $T_c$ at the same $P$. $\chi_{ac}$ indicates that an antiferromagnetic order of Eu$^{2+}$ moments with $T_N \sim 20$ K persists in the superconducting phase. The temperature dependence of the upper critical field is also determined.

KEYWORDS: iron pnictides, pressure-induced superconductivity, susceptibility, upper critical field

The discovery of superconductivity (SC) at a transition temperature $T_c = 26$ K in LaFeAsO$_{1-x}$F$_x$ by Kamihara et al.$^1$ has triggered extensive studies of SC in layered iron pnictides and related compounds. Rotter et al. found that BaFe$_2$As$_2$ with a simpler structure can be made superconducting by doping: $T_c = 38$ K in (Ba$_{1-x}$K$_x$)Fe$_2$As$_2$ with $x = 0.4$.$^2$ Perhaps more importantly, it is reported that 122 compounds of the form $A$Fe$_2$As$_2$ ($A =$ Ca, Sr, Ba, and Eu) can be tuned to SC by the application of high pressure $P$.$^3$–$^{10}$ $P$ tuning can provide opportunities to determine the nature of the iron-pnictide high-temperature SC without being adversely affected by disorder due to doping. However, most of these reports are based only on resistivity $\rho$ measurements and hence cannot establish the bulk nature of $P$-induced SC.$^{11}$ Even when magnetic measurements are reported, results are not conclusive: In ref. 5, magnetic measurements were performed on SrFe$_2$As$_2$ and BaFe$_2$As$_2$, but the observed volume fraction was expressed in arbitrary units. In ref. 9, the volume fraction of the $P$-induced superconducting phase of CaFe$_2$As$_2$ was estimated to be at least 50%, while in ref. 12 CaFe$_2$As$_2$ was reported not to exhibit SC under hydrostatic $P$ produced by the use of helium as a pressure-transmitting medium.

EuFe$_2$As$_2$ exhibits two phase transitions, at $T_o \sim 190$ K and $T_N \sim 19$ K, at ambient $P$.$^{13}$–$^{16}$
The transition at $T_0$ is a combined structural and magnetic transition, similar to those in the other 122 compounds: the crystal structure changes from tetragonal to orthorhombic and the Fe$^{2+}$ moments order antiferromagnetically. The transition at $T_N$ is due to the antiferromagnetic (AFM) ordering of the Eu$^{2+}$ moments. The AFM coupling of the Eu$^{2+}$ moments is rather weak: the field-induced paramagnetic state with a saturated moment of $\sim 7 \mu_B$/Eu is easily reached by the application of $\sim 1$ or 2 T in the $ab$-plane or along the $c$-axis, respectively.\textsuperscript{17} A temperature ($T$)-$P$ phase diagram has been determined from $\rho$ measurements:\textsuperscript{10} while $T_0$ decreases with $P$ and is not detected above $P = 23$ kbar, $T_N$ is nearly $P$-independent up to 26 kbar (the highest $P$ in ref. 10). The authors of ref. 10 state that $P$-induced SC at $T_c \sim 30$ K occurs above 20 kbar. However, their $\rho$ data (at $P = 21.6$ kbar) shows only a partial drop and approximately half of the normal-state $\rho$ appears to remain as $T \to 0$. Obviously, further experimental confirmation is necessary.

In this letter, we report measurements of the ac magnetic susceptibility $\chi_{ac}$ and $\rho$ of EuFe$_2$As$_2$ single crystals under high $P$. By observing a nearly 100% shielding volume fraction and a sharp resistive transition to the zero-resistivity state at $P = 28$ and 29 kbar, we establish that EuFe$_2$As$_2$ is a bulk superconductor at these values of $P$. We also show evidence that the AFM order of the Eu$^{2+}$ moments persists in the superconducting phase.

A single-crystal ingot of EuFe$_2$As$_2$ was grown by the Bridgman method from a stoichiometric mixture of its constituent elements. A $^3$He/$^4$He dilution refrigerator or a $^3$He refrigerator and a superconducting magnet were used for measurements. For the measurements of $\chi_{ac} (\chi' - i\chi'')$, a piece with an $ab$-plane area of 1.15 x 1.15 mm$^2$ and a $c$-axis thickness of 0.5 mm was cut. Note that the use of a thick sample enabled us to reliably estimate the volume fraction for the external field $B_{appl}$ in the $c$-direction. In the case of a thin sample, a large demagnetization factor for $B_{appl} \parallel c$ makes the estimation of the volume fraction very difficult. For measurements along the $c$-axis (in the $ab$-plane), the sample was placed in a clamped piston-cylinder pressure cell with the $c$-axis (the $ab$-plane) parallel to the cylinder axis. An ac modulation field ($f = 67.1$ Hz and $B_{ac} \sim 0.04$ mT) and external magnetic field $B_{appl}$ were applied along the cylinder axis. In order to estimate the size of the signal corresponding to 100% shielding, a piece of Pb with nearly the same dimensions as the sample was measured with the same pick-up coil for the two orientations (namely, the $c$-axis and $ab$-plane orientations). The accuracy of these estimations was estimated to be about $\pm 10\%$. For $\rho$ measurements, a thin sample with dimensions of $\sim 1$ x 0.2 x 0.03 mm$^3$ was exfoliated, where 0.03 mm is along the $c$-axis. After four gold wires were attached to a (001) surface with conducting silver paste, the sample was placed in a clamped piston-cylinder pressure cell with the longest axis, which is the electrical current direction, parallel to the cylinder axis. A standard four-contact method was used with a low-frequency ac current ($I = 0.1$ mA, $f = 17$ Hz), and the field $B_{appl}$ was applied parallel to the current. For both $\chi_{ac}$ and $\rho$ measurements, Daphne7474 (Idemitsu Kosan...
Fig. 1. (Color online) AC magnetic susceptibility $\chi' - i\chi''$ along the $c$-axis of EuFe$_2$As$_2$ for $P = 0$, 24, and 28 kbar (a) as a function of $T$ at a constant $B_{\text{appl}}$ and (b) as a function of $B_{\text{appl}}$ at a constant $T$. $B_{\text{appl}}$ was applied parallel to the $c$-axis. For $\chi''$ in (a), only data for $P = 28$ kbar are shown. The vertical lines with arrows at both ends indicate the estimated change in $\chi'$ corresponding to a 100% shielding volume fraction. In (a), $B_{\text{appl}} = 0, 0.25, 0.5, 1, 2, 4, 8, 12, 16$ T for $P = 28$ kbar. In (b), $T = 0.02, 10, 15, 20, 25$ K for $P = 28$ kbar. During the measurement of the $T = 0.02$ K curve at $P = 28$ kbar in (b), the field was kept at $B_{\text{appl}} = 17.8$ T for about 100 minutes for a technical reason, which caused a drop in $\chi'$ for unknown reasons.

Co., Ltd., Tokyo) was used as a pressure-transmitting medium.\textsuperscript{18} This oil does not solidify up to 37 kbar at room temperature (RT)\textsuperscript{19} and hence ensures hydrostatic-pressure generation in the present measurements (highest $P \sim$ 30 kbar). Furthermore, the pressure cells were cooled slowly ($\leq$ 1.5 K/min) from RT down to $\sim$ 20 K to prevent the possible development of nonhydrostaticity. Note that we always refer to the applied field $B_{\text{appl}}$, which may be different from the internal field by $\sim$ 1 T, because of the large saturation moment of Eu$^{2+}$.

Figure 1(a) shows $\chi_{ac}$ along the $c$-axis as a function of $T$ for various pressures and external
Fig. 2. (Color online) AC magnetic susceptibility $\chi' - i\chi''$ in the $ab$-plane of EuFe$_2$As$_2$ for $P = 29$ kbar as a function of (a) $T$ and (b) $B_{\text{appl}}$. $B_{\text{appl}}$ was applied in the $ab$-plane. The vertical lines with arrows at both ends indicate the estimated change in $\chi'$ corresponding to a 100% shielding volume fraction. In (a), $B_{\text{appl}} = 0, 0.25, 0.5, 1, 2, 4, 8, 12,$ and $16$ T. In (b), $T = 0.3, 5, 10, 15, 20,$ and $25$ K.

fields. At ambient $P$ ($P = 0$ kbar) and $B_{\text{appl}} = 0$ T, the real part $\chi'$ increases with decreasing $T$ and reaches a maximum at $T_N = 20$ K, below which the $T$ dependence is weak. This is essentially the same as the $T$ dependence of dc magnetic susceptibility.\textsuperscript{17} At $P = 24$ kbar and $B_{\text{appl}} = 0$ T, $\chi'$ exhibits a similar $T$ dependence with a maximum at 20 K, although it is enhanced over that at ambient $P$. This is consistent with the previous report that $T_N$ is almost $P$-independent.\textsuperscript{10} We observed no clear indication of SC at $P = 24$ kbar. A small field of $B_{\text{appl}} = 0.25$ T markedly changes the shape of the $\chi'$-$T$ curve, and when $B_{\text{appl}} = 0.5$ T no clear sign of $T_N$ is visible. At $P = 28$ kbar and $B_{\text{appl}} = 0$ T, $\chi'$ exhibits a large drop below $T_c = 31$ K, then increases with decreasing $T$ to reach a maximum at 20 K, and finally decreases again. The large drop in $\chi'$ indicates the occurrence of SC, and the size of the drop is consistent with 100% shielding, as indicated by the arrow in the figure. The maximum at 20 K indicates that the AFM ordering of the Eu$^{2+}$ moments still occurs in the superconducting phase. The feature associated with the magnetic transition is barely visible at $B_{\text{appl}} = 0.25$ T,
Fig. 3. (Color online) In-plane $\rho$ of EuFe$_2$As$_2$. (a) $T$ dependence from RT at $P = 25$ and 28 kbar. The inset shows $\rho$ at $P = 25$ kbar below $T = 40$ K. (b) $T$ dependence of $\rho$ at $P = 28$ kbar near the superconducting transition. $B_{\text{appl}}$ was applied parallel to the electrical current in the $ab$-plane: $B_{\text{appl}} = 0, 0.25, 0.5, 1, 2, 4, 8, 12, \text{and } 16$ T. (c) $B_{\text{appl}}$ dependence of $\rho$ at $P = 28$ kbar for $T = 10, 15, 20, \text{and } 25$ K. but is absent at $B_{\text{appl}} = 0.5$ T. With increasing $B_{\text{appl}}$, the superconducting transition shifts to lower $T$.

Figure 1(b) shows $\chi_{ac}$ along the $c$-axis as a function of $B_{\text{appl}}$ for various pressures and temperatures. At $P = 0$ kbar, $\chi'$ shows a large drop at approximately 1.5 T, indicating the entrance into the field-induced paramagnetic state, as is consistent with a previous magnetization study.\textsuperscript{17} At $P = 24$ kbar, $\chi'$ at $B_{\text{appl}} = 0$ is larger than that at $P = 0$ kbar, as is consistent with the $\chi'-T$ data explained above, and $\chi'$ shows a drop at approximately 0.5 T. The $\chi'$-$B_{\text{appl}}$ curves at $P = 28$ kbar show superconducting diamagnetism and its suppression with increasing $B_{\text{appl}}$. The curves at $T = 0.02, 10, 15, \text{and } 20$ K, namely, $T < T_N$, show a drop near 0.5 T, similar to the drop observed at $P = 24$ kbar.

We define $T_c$ (“$B_{c2}$”) as the temperature (applied magnetic field) where $\chi''$ deviates from the normal-state value. The reason why $\chi''$, not $\chi'$, is used is that $\chi'$ exhibits $T$ and field dependences in the normal state, which makes the unambiguous determination of the onset
Fig. 4. (Color online) Upper critical field \(B_{c2}\) of EuFe\(_2\)As\(_2\) under high \(P\). Note that the field values are based on the applied field \(B_{appl}\) and are not corrected for the magnetization.

of SC difficult in some cases [see the \(B_{appl} = 1\) T curve in Fig. 1(a) and the \(T = 25\) K curve in Fig. 1(b), for example]. The quotation marks attached to \(B_{c2}\) indicate that \(B_{c2}\) values are based on the applied field, not on the internal field. The superconducting phase diagram determined from the data in Fig. 1 is shown in Fig. 4.

Figure 2(a) shows \(\chi_{ac}\) in the \(ab\)-plane at \(P = 29\) kbar as a function of \(T\). With decreasing \(T\), the \(B_{appl} = 0\) T curve shows a large drop at \(T_c = 29\) K, then increases to reach a plateau between \(\sim 20\) and \(15\) K, and finally decreases. The magnitude of diamagnetism is nearly 100%. Although this is not typical of antiferromagnets, the plateau indicates a magnetic phase transition. Note that the \(T\) dependence of the magnetic susceptibility at ambient \(P\) shows a similar plateau when measured at \(B_{appl} = 0.5\) T.\(^{17}\) An indication of a magnetic phase transition is barely visible at \(B_{appl} = 0.25\) T, but is absent at 0.5 T. Figure 2(b) shows \(\chi_{ac}\) in the \(ab\)-plane at \(P = 29\) kbar as a function of \(B_{appl}\). The curves at \(T = 0.3, 5, 10, 15,\) and \(20\) K, namely \(T < T_N\), show a decrease with increasing field up to \(\sim 1\) T, similarly to the \(c\)-axis data. The superconducting phase diagram is shown in Fig. 4.

Figure 3(a) shows \(\rho\) at \(P = 25\) and \(28\) kbar as a function of \(T\). At \(P = 25\) kbar, a hump appears at approximately 100 K, indicating the existence of \(T_o\). \(\rho\) shows a sudden drop below 30 K and a hump at approximately 20 K, but does not reach zero (see the inset). This is similar to the data in ref. 10. At \(P = 28\) kbar, \(\rho\) decreases almost linearly with decreasing \(T\) from RT and exhibits a sharp drop to zero below 30 K. The midpoint \(T_c\) is 29 K. Figures 3(b) and 3(c) show resistive transition curves. The transition width increases as \(B_{appl}\) increases. To determine the superconducting phase diagram (Fig. 4), we define \(T_c\) ("\(B_{c2}\"\)) as the temperature (applied magnetic field) where \(\rho\) deviates from zero. This criterion gives a much better correspondence with magnetically determined values of \(T_c\) at large values of
$B_{\text{appl}}$, where the resistive transition widths are large, than the usual midpoint one, though it
gives a lower $T_c$ of 27 K at $B_{\text{appl}} = 0$ T.

Although ref. 10 suggested that $P$-induced SC coexists with the structural/magnetic tran-
sition at $T_o$, the present $\chi_{ac}$ and $\rho$ data indicate that bulk SC occurs only when $T_o$ is completely
suppressed. There is evidence from the $\mu$SR and NMR measurements of (Ba$_{1-x}$K$_x$)Fe$_2$As$_2$
that the apparent coexistence of the orthorhombic AFM phase and superconducting phase in
iron pnictide superconductors is not a true coexistence but can be explained by phase separa-
tion.$^{20,21}$ Also note that the critical pressure at which the structural/magnetic transition
disappears differs between ref. 10 and the present work: in ref. 10, no transition was detected
above $P = 23$ kbar, while a transition was detected at $P = 25$ kbar in our study. A very recent
high-$P$ study of SrFe$_2$As$_2$ showed that the critical pressure is very sensitive to the homogeneity
of the applied pressure and that it is higher when the pressure is more hydrostatic.$^{22}$ This
may explain the difference in the critical pressure between ref. 10 and the present work. As
shown in Fig. 3(a), the appearance of bulk SC is associated with the anomalous nearly $T$-
linear $\rho$. This and the fact that partial (or filamentary) and bulk SC occur below and above
the critical pressure of magnetism, respectively, bear resemblance to cases of $P$-induced SC in
some heavy-fermion compounds.$^{23,24}$ It is interesting to note that $T$-linear $\rho$ is also observed
in a wide $T$ range in optimally doped BaFe$_{1.8}$Co$_{0.2}$As$_2$.\textsuperscript{25}

The superconducting phase diagram (Fig. 4) indicates that “$B_{c2}$” is almost isotropic. The
initial slope -$d“B_{c2}”/dT$ at $T = T_c$ can be estimated to be 0.5(1), 0.6(2), and 0.19(4) T/K from
the $c$-axis $\chi_{ac}$, $ab$-plane $\chi_{ac}$, and $ab$-plane $\rho$ data for $B_{\text{appl}} \lesssim 0.5$ T, respectively. Although the
slope depends on the type of determination method for “$B_{c2}$”, the estimated slopes are much
smaller than those in the $P$-induced SC of other 122 compounds.$^{3,4,7}$ It is interesting to note
that a very large slope of 3.87 T/K was reported for Eu$_0.7$Na$_{0.3}$Fe$_2$As$_2$.\textsuperscript{26} The “$B_{c2}$”-$T$ curves
show a strong concave curvature above about 1 T. This reminds us of the $T$ dependence of $B_{c2}$
observed in the ternary molybdenum sulphide Sn$_{0.2}$Eu$_{0.8}$Mo$_{6.35}$S$_8$,\textsuperscript{27} which can be explained
by the Jaccarino-Peter compensation effect arising from the exchange interaction between
local moments and conduction carriers.$^{28}$

In conclusion, when the structural/magnetic transition is suppressed by high $P$, EuFe$_2$As$_2$
shows an anomalous nearly $T$-linear dependence of $\rho$ and becomes a bulk superconductor at
$T_c \sim 30$ K. The AFM order of the Eu$^{2+}$ moments at $T_N \sim 20$ K persists in the superconducting
phase. The upper critical field exhibits a unique $T$ dependence, which indicates the effect of
the exchange interaction between the Eu$^{2+}$ moments and conduction carriers.
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