Specific heat of the iron-based high-$T_c$ superconductor SmO$_{1-x}$F$_x$FeAs

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(Dated: May 23, 2008)

The specific heat $C(T)$ of new iron-based high-$T_c$ superconductor SmO$_{1-x}$F$_x$FeAs ($0 \leq x \leq 0.2$) was systematically studied. For undoped $x = 0$ sample, a specific heat jump was observed at 130 K. This is attributed to the structural or spin-density-wave (SDW) transition, which also manifests on resistivity as a rapid drop. However, this jump disappears with slight F doping in $x = 0.05$ sample, although the resistivity drop still exists. The specific heat $C/T$ shows clear anomaly near $T_c$ for $x = 0.15$ and 0.20 superconducting samples. Such anomaly has been absent in LaO$_{1-x}$F$_x$FeAs. For the parent compound SmOFeAs, $C(T)$ shows a sharp peak at 4.6 K, and with electron doping in $x = 0.15$ sample, this peak shifts to 3.7 K. It is interpreted that such a sharp peak results from the antiferromagnetic ordering of Sm$^{3+}$ ions in this system, which mimics the electron-doped high-$T_c$ cuprate Sm$_{2-x}$Ce$_x$CuO$_4$-$\delta$.

PACS numbers: 74.25.Bt, 74.25.Ha

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The recent discovery of superconductivity at $T_c = 26$ K in iron-based LaO$_{1-x}$F$_x$FeAs ($x = 0.05 - 0.12$) has attracted great attention. Following this initial work, more compounds with $T_c$ as high as 55 K were synthesized by replacing La with other rare-earth elements such as Sm$^{2.3+}$, Ce$^{3+}$, Nd$^{3+}$, Pr$^{3+}$, and Gd$^{3+}$. Due to their high superconducting transition temperature, which is second only to the high-$T_c$ cuprate superconductors, enormous experimental and theoretical efforts have been put on these materials to clarify their phase diagram and superconducting mechanism.

These quaternary rare earth transition metal arsenide oxides LnOFeAs ($Ln = La$, Sm, Ce, Nd, Pr, and Gd) form tetragonal ZrCuSiAs-type structure. It is believed that the Fe-As layers are responsible for the superconductivity and Ln-O layers provide electron carriers through fluorine doping, or very recently by simply introducing oxygen vacancies. Neutron scattering experiments have demonstrated that the undoped parent compound LaOFeAs develops long-range SDW-type antiferromagnetic order below 150 K. With increasing electron doping by fluorine, the SDW order is suppressed and superconductivity emerges, suggesting competing orders in these systems and similar phase diagram to the one in high-$T_c$ cuprates. Theoretically, electron-phonon coupling is not sufficient to explain superconductivity in LaO$_{1-x}$F$_x$FeAs, while antiferromagnetic interaction and Hund’s rule ferromagnetic interaction have been considered as the possible pairing mechanism.

Among the family of LnO$_{1-x}$F$_x$FeAs, specific heat was only studied for LaO$_{1-x}$F$_x$FeAs compounds so far. Clear specific heat jump was observed at the temperature about 150 K for LaOFeAs, which is accompanied by anomalies on resistivity, Hall coefficient, and Seebeck coefficient. Since structural transition was also found at 150 K by neutron scattering, and X-ray diffraction, at present it is unclear whether these resistivity and specific heat anomalies around 150 K are due to the structural or SDW transition, or to both. For superconducting LaO$_{0.9}F_{0.1}$FeAs, a nonlinear magnetic field dependence of the electronic specific heat coefficient $\gamma(H)$ has been found in the low temperature limit, which is consistent with the prediction for a nodal superconductor and suggests an unconventional mechanism for this new superconductor. However, it is surprising that no visible specific heat anomaly was detected near $T_c$ on the raw data for superconducting LaO$_{1-x}$F$_x$FeAs samples despite the large Meissner fractions and only a broadened anomaly of $(C(0T)) / T$ was observed. This result may reflect the low superfluid density in LaO$_{1-x}$F$_x$FeAs. For comparison, precise specific heat measurements on other compounds of this family are highly desired.

Here, we systematically study the specific heat of SmO$_{1-x}$F$_x$FeAs for $0 \leq x \leq 0.2$, with the maximum $T_c$(onset) = 54 K at $x = 0.2$. A specific heat jump was observed at 130 K for undoped $x = 0$ sample, indicating the structural or SDW transition. However, this jump disappears in the $x = 0.05$ sample. The specific heat $C/T$ shows clear anomaly near $T_c$ for $x = 0.15$ and 0.20 superconducting samples, which has been absent in LaO$_{1-x}$F$_x$FeAs. Sharp peak of $C(T)$ appears at 4.6 K for the parent compound SmOFeAs, and it shifts to 3.7 K with doping electrons in $x = 0.15$ sample. This specific heat peak should come from the antiferromagnetic ordering of Sm$^{3+}$ ions in this system, as in the electron-doped high-$T_c$ cuprate Sm$_{2-x}$Ce$_x$CuO$_4$-$\delta$.

The polycrystalline samples with nominal composition SmO$_{1-x}$F$_x$FeAs ($x = 0$, 0.05, 0.15, and 0.20) are the same ones as studied in Ref. 4, synthesized by conventional solid state reaction. The $x = 0$ and 0.05 samples are in single phase. A trace of impurity phases SmOF and SmAs can be observed in $x = 0.15$ sample, and these
impurities are estimated to be less than 10% in $x = 0.20$ sample. Specific heat measurements were performed in a Quantum Design physical property measurement system (PPMS) via the relaxation method and the results are presented per mole of atom (J/mol K). Magnetic field $H = 8$ T was applied for the optimally doped SmO$_{0.80}$F$_{0.20}$FeAs sample in zero and $H = 8$ T magnetic fields. Below the zero resistivity $T_c = 50$ K, one can see a clear specific heat anomaly. Such anomaly has been absent in the LaO$_{1-x}$F$_x$FeAs superconducting samples with large Meissner fractions.\textsuperscript{22,23} The difference may reflect the higher superfluid density in SmOFeAs. Indeed, the static antiferromagnetic SDW order and structural transition disappear in the doped superconducting LaO$_{1-x}$F$_x$FeAs samples, shown by neutron scattering and X-ray diffraction experiments.\textsuperscript{22,23} At low temperature there is a sharp peak for both $x = 0$ (nonsuperconducting) and 0.15 (superconducting) samples, which will be discussed later.

FIG. 2: (Color online) (a) Specific heat of optimally doped SmO$_{0.80}$F$_{0.20}$FeAs sample in zero and $H = 8$ T magnetic fields, plotted as $C/T$ vs $T$ close to $T_c$. The arrow marks zero resistivity $T_c = 50$ K. (b) $(C(0T)-C(8T))/T$ vs $T$ for the $x = 0.15$ and 0.20 samples. One can see a clear specific heat peak near the zero resistivity $T_c$ for both samples.

Fig. 1 shows the specific heat $C(T)$ of SmO$_{1-x}$F$_x$FeAs samples with $x = 0$ and 0.15. There is a clear specific heat jump close to 130 K for $x = 0$ sample (enlarged in the inset). Similar jump has been observed in LaOFeAs at 150 K.\textsuperscript{22,23} The specific heat jump at 130 K of SmOFeAs sample is consistent with the resistivity drop.\textsuperscript{2} As in LaOFeAs, the specific heat and resistivity anomalies in SmOFeAs are also attributed to a structural or SDW transition. We note that the phase transition temperature $T_s$ in SmOFeAs is about 20 K lower than that in LaOFeAs. The inset of Fig. 1 shows the lack of specific heat jump in the slightly F-doped $x = 0.05$ sample, although there is still a resistivity drop (but less sharp) at about 110 K.\textsuperscript{4} This result suggests that electron doping suppresses the magnetic order and structural distortion in SmOFeAs. Indeed, the static antiferromagnetic SDW order and structural transition disappear in the doped superconducting LaO$_{1-x}$F$_x$FeAs samples, shown by neutron scattering and X-ray diffraction experiments.\textsuperscript{22,23} At low temperature there is a sharp peak for both $x = 0$ (nonsuperconducting) and 0.15 (superconducting) samples, which will be discussed later.

Fig. 2a plots $C/T$ vs $T$ for the optimally doped SmO$_{0.80}$F$_{0.20}$FeAs sample in zero and $H = 8$ T magnetic fields. Below the zero resistivity $T_c = 50$ K, one can see a clear specific heat anomaly. Such anomaly has been absent in the LaO$_{1-x}$F$_x$FeAs superconducting samples with large Meissner fractions.\textsuperscript{22,23} The difference may reflect the higher superfluid density in SmO$_{1-x}$F$_x$FeAs. This is reasonable, since the maximum $T_c$ of SmO$_{1-x}$F$_x$FeAs is twice that of LaO$_{1-x}$F$_x$FeAs.

Although 8 T is far away from the upper critical field $H_{c2}$ which is higher than 60 T,\textsuperscript{23} we nevertheless plot $(C(0T)-C(8T))/T$ vs $T$ for the $x = 0.15$ and 0.20 samples in Fig. 2b. The obtained specific heat peak near the zero resistivity $T_c$ is sharper than that in LaO$_{0.9}F_{0.1-x}$FeAs.
The sharp peak comes from the antiferromagnetic ordering of Sm$^ {3+}$ ions in this system. Below we focus on the low temperature specific heat behavior of SmO$_ {1-x}$F$_x$FeAs at $T < 20$ K. In Fig. 3a, $C(T)$ of the $x = 0$ sample shows a very sharp peak at 4.6 K. With electron doping in the $x = 0.15$ superconducting sample, the peak shifts to 3.7 K and its height decreases. This low-temperature peak has not been seen in previous specific heat studies of LaO$_ {1-x}$F$_x$FeAs. Since the only difference between these two materials is the Ln$^ {3+}$ ions, i.e. non-magnetic La$^ {3+}$ and magnetic Sm$^ {3+}$ ions, this peak may relate to the magnetic ordering of Sm$^ {3+}$ ions. In fact, exactly the same specific heat behavior at low temperature has been observed in electron-doped high-$T_c$ cuprate Sm$_2$-$x$Ce$_x$CuO$_{4-\delta}$.

Antiferromagnetic ordering of the Sm$^ {3+}$ ions was found in Sm$_2$CuO$_4$ at $T_N = 5.9$ K, accompanied by a sharp specific heat peak. By substituting electron donor element Ce$^ {4+}$ for Sm$^ {3+}$ ions, the ordering temperature $T_N$ is lowered to 4.7 K in Sm$_ {1.85}$Ce$_ {0.15}$CuO$_ {4-\delta}$ with $T_c = 16.5$ K. Therefore the sharp specific heat peak below 5 K in SmO$_ {1-x}$F$_x$FeAs manifests the antiferromagnetic ordering of Sm$^ {3+}$ ions. Below $T_N$, the superconductivity co-exists with antiferromagnetism, as in Sm$_2$-$x$Ce$_x$CuO$_ {4-\delta}$.

Due to this antiferromagnetic specific heat peak, it is not easy to extrapolate the electronic specific heat coefficient $\gamma$ in the low temperature limit. In Fig. 3b, $C/T$ vs $T^2$ is plotted for the $x = 0.15$ sample in $H = 0$ and 8 T. The data between 14 and 20 K can be linearly fitted by $C/T = \gamma + \beta T^2$, which give $\gamma = 81.0$ and 83.7 mJ/mole K$^2$ for $H = 0$ and 8 T, respectively. This value of $\gamma$ is much higher than that obtained in LaO$_ {0.89}$F$_ {0.11}$FeAs ($T_c \approx 28$ K), $\gamma = 1.0$ mJ/mole K$^2$. For Sm$_ {1.85}$Ce$_ {0.15}$CuO$_ {4-\delta}$ with $T_c = 16.5$ K, the fitting also gave exceptionally large $\gamma = 103.2$ mJ/mole K$^2$.

It was speculated that the effects of magnetic correlation exist well above $T_N$, thereby making accurate determination of $\gamma$ difficult. In addition, since the fitting in Fig. 3b was done at relatively high temperature and over a small range from 14 to 20 K, the slope $\beta$ may not represent the phonon specific heat in the low-temperature limit, where it is proportional to $T^3$. Therefore the resulting $\gamma$ may be not reliable. In Fig. 3b, $\gamma$ only increases very slightly in $H = 8$ T and we are unable to examine its field dependence for SmO$_ {0.85}$F$_ {0.15}$FeAs sample. For superconducting LaO$_ {1-x}$F$_x$FeAs, there is no such antiferromagnetic specific heat peak and the data were fitted at low temperature, thus the extrapolated $\gamma \sim 1.0$ mJ/mole K$^2$ is more reliable and shows a steep increase with increasing magnetic field.

Fig. 4 plots the magnetic specific heat of SmOFeAs, $C_m = C - \gamma T - \beta T^3$, with $\gamma = 119.4$ mJ/mole K$^2$ and $\beta = 0.56$ mJ/mole K$^3$ obtained from the same fitting process as in Fig. 3b. The magnetic entropy $S$ associated with the magnetic transition is also calculated from the $C_m(T)$ and shown in the inset of Fig. 4. With increasing temperature, the entropy rapidly increases and then

FIG. 3: (Color online) (a) Low temperature specific heat of SmO$_ {1-x}$F$_x$FeAs samples with $x = 0$ and 0.15 in zero field. The sharp peak comes from the antiferromagnetic ordering of Sm$^ {3+}$ ions in this system. (b) $C/T$ vs $T^2$ for the $x = 0.15$ sample in $H = 0$ and 8 T. The lines are linear fits between 14 and 20 K.

FIG. 4: (Color online) Magnetic specific heat of SmOFeAs, $C_m = C - \gamma T - \beta T^3$. Inset: entropy associated with the magnetic transition.
saturates to the value of $\ln2$ within experimental error, indicating that the Sm$^{3+}$ ground state in the crystal field is a doublet for SmOFeAs.

In summary, we have systematically studied the specific heat of new iron-based high-$T_c$ superconductor SmO$_{1-x}$Fe$_x$As. First, a specific heat jump was observed at 130 K for the undoped $x = 0$ sample, corresponding to the structural or SDW transition. However, this jump disappears in the slightly F-doped $x = 0.05$ sample, indicating the suppression of the SDW order and structural distortion by electron doping in this system. Second, a clear specific heat anomaly can be seen near $T_c$ for superconducting SmO$_{1-x}$Fe$_x$As samples, while it has been absent in LaO$_{1-x}$Fe$_x$As. This result suggests higher superfluid density in SmO$_{1-x}$Fe$_x$As. Finally, sharp specific heat peak shows up at 4.6 K for $x = 0$ sample, and it shifts to 3.7 K upon electron doping in $x = 0.15$ sample. By comparing with the electron-doped high-$T_c$ cuprate Sm$_{2-x}$Ce$_x$CuO$_{4-\delta}$, this sharp peak is attributed to the antiferromagnetic ordering of Sm$^{3+}$ ions in SmO$_{1-x}$Fe$_x$As system.

We thank D. L. Feng and Y. Chen for useful discussions. This work is supported by the Natural Science Foundation of China, the Ministry of Science and Technology of China (973 project No: 2006CB601001), and National Basic Research Program of China (2006CB922005).

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