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Anomalous thermoelectric power in $SrFeO_{3-\delta}$ from charge ordering and phase separation

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We report the results from thermoelectric power (TEP), magnetization, and resistivity measurements on a series of oxygen-deficient $SrFeO_{3-\delta}$ samples. We find a large anomalous decrease in the TEP below ~70 K when $SrFeO_{3-\delta}$ is close to the tetragonal $Sr_8Fe_8O_{23}$ $(3-\delta=2.875)$ phase. This drop decreases and disappears when $SrFeO_{3-\delta}$ approaches the orthorhombic $Sr_4Fe_4O_{11}$ $(3-\delta=2.75)$ phase. Similar to other researchers, we find evidence for the onset of antiferromagnetic order at a similar temperature as well as a jump in the resistivity. We argue that the large drop in the TEP is a consequence of Verwey-like charge ordering in the $Sr_8Fe_8O_{23}$ phase. The decrease in the TEP drop as $SrFeO_{3-\delta}$ approaches the $Sr_4Fe_4O_{11}$ phase is consistent with $SrFeO_{3-\delta}$ being a mixture of the $Sr_8Fe_8O_{23}$ and $Sr_4Fe_4O_{11}$ phases.

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The transition metal oxides have been the object of extensive study for many years especially since the discovery of the cuprate superconductors and colossal magnetoresistance in the manganites. Recently, an increase in the resistivity has been reported below 70 K in $SrFeO_{3-\delta}$ accompanied by a large magnetoresistance.[1–4] It has been noted that the increase in the resistivity is reminiscent of the Verwey transition, long known in Fe_3O_4,[5,6] arising from a charge-ordered state of the Fe ions in one of the two inequivalent Fe sites, although it has recently been argued that Jahn-Teller distortions and multiorbital electronic correlations must also be considered.[7]

The Verwey transition in Fe_3O_4 is also accompanied by a large change in the thermoelectric power[8,9] (TEP) that is much larger than that seen near the metal-insulator transition temperature in the manganites.[10] It is therefore of interest to see if a Verwey-like increase in the resistivity in $SrFeO_{3-\delta}$ is also accompanied by a large change in the thermopower and ascertain the δ values where this occurs. It should be noted that there are very few studies where jumps in the TEP have been observed and modeled.[10] For this reason we have performed TEP, resistivity, and magnetization measurements on $SrFeO_{3-\delta}$ for a range of δ values between $SrFeO_3$ and $Sr_4Fe_4O_{11}$ and report our results in this paper.

$SrFeO_{3-\delta}$ is known to display a rich phase diagram for $3-\delta$ ranging from 3 to 2.75. There is evidence from Mössbauer measurements that a homogenous phase with random oxygen vacancies does not exist,[2,11] and that instead there is a mixture of cubic $SrFeO_3$, tetragonal $Sr_8Fe_8O_{23}$ $(3-\delta=2.875)$ and orthorhombic $Sr_4Fe_4O_{11}$ $(3-\delta=2.75)$ phases. The end member, cubic $SrFeO_3$, contains well-ordered FeO_6 octahedra and an Fe valence of +4. It displays helical antiferromagnetic order at ~140 K,[12] and a high conductivity.[13] The $Sr_4Fe_4O_{11}$ phase displays antiferromagnetism below 240 K and a semiconductor-like resistivity.[14] It contains FeO_5 units that form dimers and distorted FeO_6 octahedra, where the Fe valences are believed to be +4 and +3, respectively. The intermediate $Sr_8Fe_8O_{23}$ phase orders antiferromagnetically near 70 K and displays an order-of-magnitude resistivity increase below this temperature.[1] It contains Fe1 ions that are fivefold coordinated by oxygen and form dimers.[15] They are adjacent to Fe2 sites with distorted FeO_6 octahedra that are adjacent to Fe3 sites with FeO_6 octahedra. It has been argued that the Fe1 and Fe3 ions have a +4 valence and the Fe2 sites have a +3.5 valence and that the increased resistivity near 70 K arises from charge ordering of the Fe2 ions to Fe^{3+} and Fe^{4+}.[1,2] This charge-ordering mechanism is then similar to the original description of the Verwey transition in Fe_3O_4.

The TEP provides a valuable complement to conductivity measurements.[16–18] It is particularly powerful for ceramic material, for in composites the contribution from different phases is weighted by their thermal resistance, which shows a much weaker contrast between different materials than the many-orders-of-magnitude variations in their electrical resistance. As a consequence the sharp percolation effects familiar from resistance measurements of composite systems are not found in the TEP and it is relatively insensitive to the presence of electrically resistive grain boundaries. In the presence of extended-state conduction it relates to the energy dependence of the conductivity at the Fermi energy, and its temperature dependence can reveal interactions with phonons. The description is more complex in the presence of very strong correlations.

A series of polycrystalline $SrFeO_{3-\delta}$ samples (typically pellets of 10 mm diameter and 2 mm thickness) were synthesized by solid-state reaction from stoichiometric mixtures of $Sr(NO_3)_2$ and Fe_2O_3. These were prefired several times in air at 1200 °C for 12 h in order to obtain homogeneous compounds and were annealed in oxygen at a pressure of 6000 kPa for 24 h at 700 °C. The samples were then slow cooled to room temperature. It will be demonstrated below that the resulting sample had an oxygen deficit δ of 0.05. Samples were then annealed in 7.5% and 0.2% O_2 for 16 h at various temperatures (from 450 to 600 °C) in order to obtain a range of δ values and the mass was measured after each step in order to obtain an estimate of the oxygen change $\Delta\delta$. A large number of samples were prepared and five were selected across the range, $SrFeO_{2.95}$, $SrFeO_{2.865}$, $SrFeO_{2.81}$, $SrFeO_{2.79}$, and $SrFeO_{2.78}$.

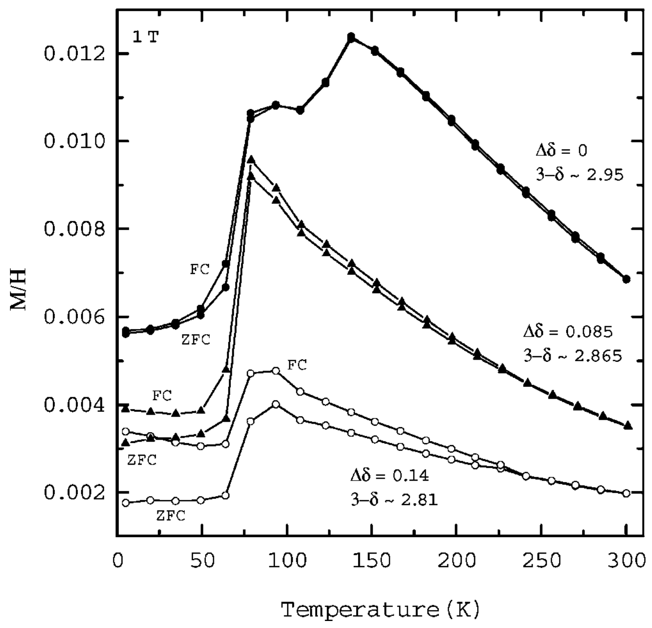

FIG. 1. Zero-field-cooled (ZFC) and field-cooled (FC) magnetization at 1 T for $\Delta\delta=0$ ($SrFeO_{2.95}$), $\Delta\delta=0.085$ ($SrFeO_{2.865}$), and $\Delta\delta=0.14$ ($SrFeO_{2.81}$).

The TEP was measured over 12 h as a function of temperature using the standard temperature differential technique. The resistivity was measured using bar-shape samples and the four-terminal method. Magnetization measurements, field cooled (FC) and zero-field cooled (ZFC), were carried out at 1 T using a superconducting quantum interference device (SQUID) magnetometer.

X-ray diffraction measurements have been performed (not shown) on all the samples and show single-phase material within the limit of detectibility. The Bragg peaks shifted to lower angles and a splitting of some of the peaks [e.g., the (200) peak] was observed as δ increased. This has been reported by other investigators and indicates a change in the unit cell.[4]

The ZFC and FC magnetization data are plotted in Fig. 1 at 1 T for three of the samples. Turning first to the as-prepared ($\Delta\delta=0$) sample, the peak observed at ~140 K is associated with helical antiferromagnetic order from $SrFeO_3$.[12] There is also a shoulder at ~70 K that arises from antiferromagnetic order in the tetragonal $Sr_8Fe_8O_{23}$ phase and by comparing these features with reports in the literature[1,2,19] we conclude that this sample contains a mixture of cubic and tetragonal phases and that the stoichiometry is close to $SrFeO_{2.95}$.

The 140 K peak is entirely absent in the $SrFeO_{2.865}$ sample, replaced by a strong and sharp peak at ~70 K, confirming that it is predominantly the $Sr_8Fe_8O_{23}$ phase. There is in addition an irreversibility starting at ~240 K, seen also in the $SrFeO_{2.81}$ sample where the peak at 70 K is not as pronounced. These results establish the presence of the orthorhombic $Sr_4Fe_4O_{11}$ phase,[4,14] which shows a Néel temperature of ~240 K and the irreversibility arises from spin frustration.[7]

The resistivity data are plotted in Fig. 2 for the (a) $SrFeO_{2.95}$, (b) $SrFeO_{2.865}$, and (c) $SrFeO_{2.81}$ samples. All the samples show a large increase in the resistivity at ~70 K of up to an order of magnitude, associated with charge-ordering in the tetragonal phase present in all of the samples.[1–3,20]

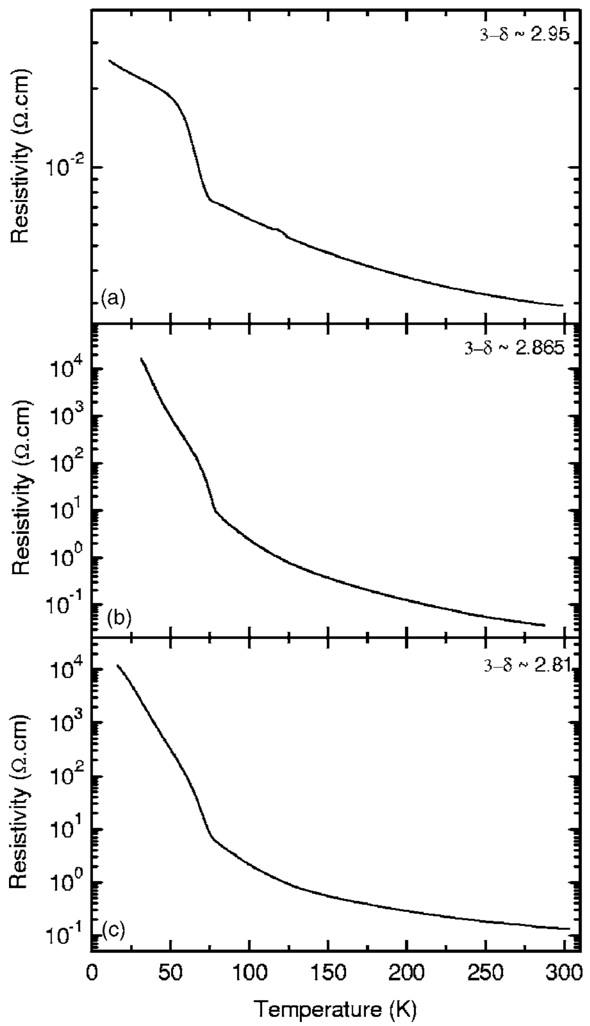

FIG. 2. Temperature dependence of the resistivity for (a) $SrFeO_{2.95}$, (b) $SrFeO_{2.865}$, and (c) $SrFeO_{2.81}$.

It is important to note that our polycrystalline samples possess intergrain and intragrain contributions to the resistivity. The feature at 70 K originates from the intragrain contribution while the general trend, the increase in the resistivity when the temperature decreases, is due to the intergrain contribution. Thus, the $SrFeO_{2.95}$ sample does not show the metallic-like resistivity observed in single crystals above ~70 K.[2] The resistivity increases with increasing oxygen deficiency as reported by other studies,[2,4] arising from mixed-phase conduction involving an increasing fraction of semiconducting $Sr_4Fe_4O_{11}$.

As described above, the TEP is relatively insensitive to the insulating surfaces covering conducting grains. TEP data for all of the samples are shown in Fig. 3. An abrupt drop in the TEP can be observed for the $SrFeO_{2.865}$ sample [Fig. 3(b)] at ~70 K where the drop in the TEP is $\Delta S \sim 118\ \mu V/K$. The decrease is clearly associated with the $Sr_8Fe_8O_{23}$ phase, which is dominant in that sample. An abrupt fall in the TEP is observed for higher oxygen defi-

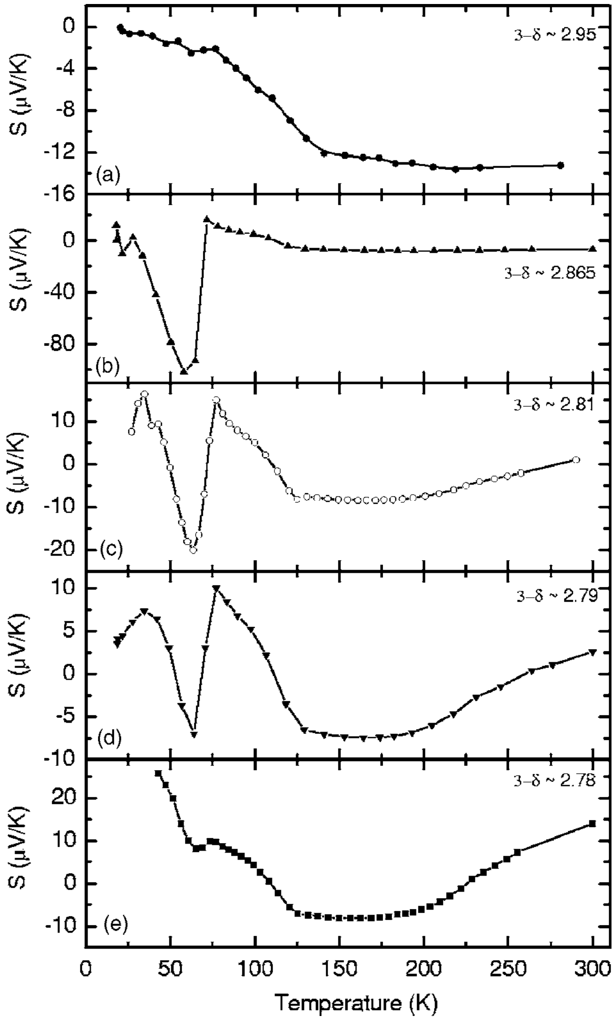

FIG. 3. TEP versus temperature for $SrFeO_{3-\delta}$ samples with (a) $SrFeO_{2.95}$, (b) $SrFeO_{2.865}$, (c) $SrFeO_{2.81}$, (d) $SrFeO_{2.79}$, and (e) $SrFeO_{2.78}$.

ciencies, as expected for a mixed-phase sample, with a magnitude that decreases with δ and nearly disappears for $3-\delta=2.78$. Thus, the magnitude of the effect decreases as the $Sr_8Fe_8O_{23}$ fraction decreases, although it disappears sooner than the limit $3-\delta=2.75$ where $Sr_4Fe_8O_{11}$ is expected to be the only remaining phase. The drop occurs at the magnetic ordering temperature and the resistivity change found in the $SrFeO_{2.865}$ sample; the effect clearly is related to charge ordering in the $Sr_8Fe_8O_{23}$ fraction of the sample. The large drop in the TEP below ~70 K signals a change in the nature of the charge carriers that must be expected to follow from charge ordering.

A large decrease in the TEP has been observed when the charge ordering is associated with a Verwey-like transition. For example, a drop of more than 70 μV/K was reported from TEP measurements on Fe_3O_4 near the Verwey transition temperature where charge ordering is not accompanied by a metal-insulator transition and the resistivity increases by approximately two orders of magnitude.[8,9] This can be compared with $La_{0.67}Ca_{0.33}MnO_3$ where a drop of ~6 μV/K was observed near the metal-insulator transition temperature.[10] Thus, the large drop in the TEP observed for the $Sr_8Fe_8O_{23}$ phase as well as the small increase in the resistivity (~ one order of magnitude) would appear to be reminiscent of a Verwey-like transition occurring at the magnetic ordering temperature in $Sr_8Fe_8O_{23}$.[1]

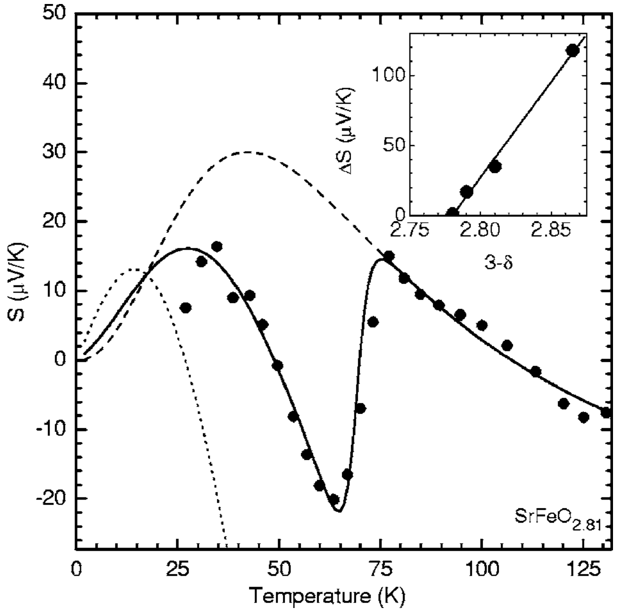

FIG. 4. TEP versus temperature for $SrFeO_{2.81}$. The solid curve is a simple two-phase fit to the data with 0.3 times the tetragonal TEP [Eq. (3)] and 0.7 times the orthorhombic TEP [Eq. (2), dashed curve]. The dotted curve shows the low-temperature contribution of the tetragonal phase. Inset: Plot of the drop in the TEP, ΔS, against $3-\delta$.

It should be noted that a rapid decrease in the TEP has also been reported in $Sm_{0.2}Ca_{0.8}MnO_3$.[21] However, the situation is more complicated and it may be somehow related to orbital ordering and short-range charge ordering.[21] It is unlikely that a similar mechanism occurs in $Sr_8Fe_8O_{23}$.

We show below that the composition dependence of the large drop in the TEP in our data can be described in terms of charge ordering of the $Sr_8Fe_8O_{23}$ phase within an inhomogeneous two-phase model similar to that used for $La_{0.67}Ca_{0.33}MnO_3$.[10] We base our model on the effective-medium approach, in which the transport coefficient of a composite is represented by a weighted average of those in the two components, their volume fractions and geometric arrangements. We can then expect that the TEP is represented by $S=yS_T+(1-y)S_O$, where S_T and S_O are the TEPs of the tetragonal and orthorhombic phases, respectively.[10,22] The fraction y depends upon the electrical resistivities and thermal conductivities of the two phases, their volume fractions, and geometric arrangement. In the expected absence of prominent percolation effects, the weights of the two terms are dominated by the volume fraction.

We model the TEP from the tetragonal phase by using the results from the sample with $3-\delta=2.865$ [Fig. 3(b)], which is close to the $3-\delta=2.875$ expected for that phase. The step at the charge-ordering temperature T_{CO} (69 K) requires different fits above and below that temperature. We have fitted the low-temperature data to

$$S_T = 149\tanh(T/26) - 4.2T, \quad T < T_{CO} = 69\text{ K}, \tag{1}$$

where S_T is in units of μV/K. A similar function has been used to fit the TEP from some other transition metal oxides.[17,18] The first term provides a positive drag-like TEP that vanishes at $T=0$. The second term is linear in temperature characteristic of the diffusion TEP. However, it is too large for a simple metal interpretation, but typical of the diffusion TEP found in the presence of charge hopping.[23]

It can be clearly seen in Fig. 3 that the TEP from all of the tetragonal-orthorhombic composites track closely at temperatures above T_{CO}. Careful comparisons show negligible differences in the temperature range from 70 to 130 K, indicating that in this temperature range the two phases show the same TEP. Thus, by subtracting the fraction of Eq. (1) that removes the small step we recover the orthorhombic-phase TEP,

$$S_O = (4443/T - 41.37)[\tanh(T/39.1)]^{3.256}, \quad 0 < T < 130\text{ K}, \tag{2}$$

and that serves also as S_T above T_{CO}. The transition between the low- and high-temperature expressions for S_T can be represented by a broadened Heaviside function, $H_B=0.5\{1-\tanh[(T-69)/3]\}$ and $1-H_B$. Therefore by combining Eqs. (1) and (2) and the Heaviside function, we can rewrite S_T from 0 to 130 K,

$$\begin{aligned} S_T = {} & [149\tanh(T/26) - 4.2T](0.5\{1 - \tanh[(T-69)/3]\}) \\ & + [(4443/T - 41.37)[\tanh(T/39.1)]^{3.256}] \\ & \times (0.5\{1 + \tanh[(T-69)/3]\}). \end{aligned} \tag{3}$$

It can be seen in Fig. 4 (solid curve) that this simple model provides a reasonable fit to the $3-\delta=2.81$ TEP data with $y=0.3$.

We show in the inset to Fig. 4 that there is an approximately linear decrease in the amplitude of the TEP drop near 70 K with increasing oxygen deficiency. It is important to note that the contribution from the tetragonal phase disappears before $3-\delta=2.75$. As discussed above this is unlikely to be related to percolative behavior and almost certainly signals the absence of the tetragonal phase for $3-\delta<2.78$.

There are additional features in the TEP data for temperatures above ~130 K that are not easy to relate to the electronic transport. Clearly the TEP is complicated and the interpretation is made more difficult by the mixture of phases. As a general trend we find that the TEP at 300 K increases systematically with decreasing oxygen content that corresponds to an average electron doping. A similar trend has been observed in other transition metal perovskites that include the high-temperature superconductors[16] and Sr_2FeMoO_6.[17]

In conclusion, we observe a large drop in the TEP in $SrFeO_{3-\delta}$ for $3-\delta=2.865$ to 2.78 at the temperature where the $Sr_8Fe_8O_{23}$ phase magnetically orders and displays charge ordering. We attribute the drop in the TEP to Verwey-like charge ordering from the $Sr_8Fe_8O_{23}$ fraction where $SrFeO_{3-\delta}$ is an inhomogeneous mixture of $SrFeO_3$, $Sr_8Fe_8O_{23}$, and $Sr_4Fe_4O_{11}$.

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