Thermoelectric Properties of LaFePO_{1-x} F_x and LaFeAsO_{1-x} F_x —Possibility of the Hidden Mass Enhancement of LaFeAsO $_{1-x}F_x$ —

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We investigated thermoelectric properties for polycrystalline oxypnictide LaFePO_{1-x} F_x and LaFeAsO_{1-x} F_x . The temperature (T) and F-doping dependences of resistivity (ρ) and Seebeck coefficient (S) are quite different between these compounds. In contrast to a monotonic T dependence and an absence of large F-doping dependences of ρ and S for LaFePO_{1-x} F_x , the S for LaFeAsO_{1-x} F_x for $0 < x \le 0.14$ take relatively large maximum absolute values of -60 to $-150 \,\mu\text{V/K}$ around 90–180 K, while the T dependence of ρ dramatically changes and the ρ monotonically decreases with the F-doping, leading to a large power factor of about $37 \,\mu W/K^2$ cm at 53 K and a dimensinless thermoelectric figure of merit (ZT) of about 0.08 at 110 K for LaFeAsO_{0.89}F_{0.11}. The non-monotonic behavior of S with the relatively large absolute value and the reported T dependence of Hall coefficient for LaFeAsO_{1-x} F_x seem to evidence an instability of an orbital order accompanying a stripe-type AF order even in the over F-doping region for LaFeAsO $_{1-x}F_x$ and indicate a possibility of a hidden mass enhancement of LaFeAsO_{1-x} F_x .

KEYWORDS: Oxypnictide, Thermoelectric Property, Orbital Order, Antiferromagnetic Order

1. Introduction

The discovery of superconductivity in oxypnictide LaFeAsO_{1-x} F_x with the critical temperature (T_c) of about 26 K¹ has caused great attentions of researchers on the related iron-pnictides and has led to the further discoveries of various new iron-pnictide superconductors with the isostructures.²⁾ The end compounds of the first iron-pnictide superconductors, LaFePO³) and LaFeAsO¹, have the socalled 1111 structure, where the conducting FePn (Pn = Por As) layeres formed by the edge-sharing $Fe Pn_4$ tetrahedrons and the insulating LaO layers are alternatively stacking. In LaFePO and LaFeAsO, the filling of electron can be controlled by substitutions of F for O^{1} or by the oxygen vacancy.⁴⁾ Such conducting iron-pnictides having natural super-lattice structures are expected to show a good thermoelectric property, as well as a higher T_c superconducting state. Actually, after the discovery of the superconductivity, some groups reported the relatively large thermoelectric propeties for some 1111 iron-pnictides.^{5,6)}

According to the theoretical works,⁷⁾ the electronic structures near the Fermi energy in the end compounds, LaFePO and LaFeAsO, are quite similar and are consisted of five sheets mainly originating in five-fold degenerated Fe 3dorbitals. However, their realized ground states are quite different; the former compound shows a transition from a paramagnetic metallic state to a superconducting state and the latter compound becomes a stripe-type antiferromagnetic (AF) metallic state at the ground state. According to the results of the angle-resolved photoemission spectroscopy (ARPES),⁸⁾ the electronic structure for LaFePO observed by the ARPES well agrees with the LDA calculated band dispersion with a shift of the calculated bands up to $\sim 0.11 \text{ meV}$ and a renormalization by a factor of 2.2, which indicate the itinerant ground state rather than the localized (Mott) ground state. On the other hand, the recent optical study⁹⁾ reported electronic correlations in the metallic LaFePO with the kinetic energy of the electrons reduced to half of that predicted by the band theory and proposed that the transport even in the most metallic superconducting oxypnictide, LaFePO, lies between the itinerant and local magnetic moment extreme. However, such a quantitative agreement has not been observed in LaFeAsO by the ARPES measurements. The most remarkable discrepancy with the band calculations lies in the cross-shaped Fermi surface near the M-point, which is quite different from the small electron pocket observed in LaFePO. These results indicate that the magnetic ordering, spin-orbit interaction, and orthorhombicity should be taken into account in order to explain the electronic structure for LaFeAsO.

In this paper, we investigate the F-doping dependences of thermoelectric properties for LaFePO and LaFeAsO and discuss an origin of a relatively good thermoelectric property of LaFeAsO $_{1-x}F_x$ by comparing the two systems. We propose that the better thermoelectric property for LaFeAsO_{1-x} F_x than that for LaFePO_{1-x} F_x originates in an instability of a $3d_{v_7}$ orbital order accompanying an instability of the stripe-type AF order and in a hidden mass enhancement of LaFeAsO_{1-x} F_x .

2. Experimental Procedure

Polycrystalline samples of $LaFePO_{1-x}F_x$ and LaFeAs- $O_{1-x}F_x$ were synthesized by using a two-step solid state reaction.¹⁰⁾ First, LaP and LaAs were prepared by reacting La elements and P or As chips in the evacuated silica tubes at 700 °C for 10 h and 850 °C for 15 h, respectively. The mixtures of LaAs, LaP, dehydrated Fe₂O₃, Fe and FeF₂ were pressed into pellets, and they were annealed in the evacuated

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Fig. 1. (Color online) Temperature (*T*) dependences of resistivities (ρ) of (a) LaFePO_{1-x}F_x and (b) LaFeAsO_{1-x}F_x. The results of LaFePO_{1-x}F_x for x = 0, 0.03, and 0.05 are from ref. 10.

silica tubes at $1100 \,^{\circ}$ C for 40 h. All procedures were performed in a highly pure Ar filled grove box. The resistivity was measured by a standard four probe method and the Seebeck coefficient and thermal conductivity were simultaneously measured by a steady state method.

3. Results

3.1 Resistivity, Seebeck coefficient, and power factor for polycrystalline $LaFePO_{1-x}F_x$ and $LaFeAsO_{1-x}F_x$

Figures 1(a) and 1(b) show the T dependences of resistivity (ρ) of our polycrystalline samples of LaFePO_{1-x}F_x and LaFeAsO_{1-x} F_x . In LaFePO_{1-x} F_x , the end compound of LaFePO already shows the low ρ of about $1.5 \,\mathrm{m\Omega \, cm}$ at room temperature and shows the superconducting transition at about 5.8 K.¹⁰ The low-T ρ for LaFePO_{1-x}F_x shows the T^2 dependence above T_c , as previously reported. In this compound, the electron doping by the substitution of F for O does not significantly affect the absolute value of ρ and the T dependences, as shown in Fig. 1(a). Such an absence of the large change of ρ with the F-doping is reported to originate in the absence of the F-doping dependence of structure in this compound.¹⁰⁾ The observed T_c^{10} is 5.8, 7.8, 8.0, 7.8, and 6.2 K, the observed residual resistivity ρ_0 are about $0.0676, 0.0771, 0.0788, 0.117, \text{ and } 0.203 \text{ m}\Omega \text{ cm}, \text{ and the } T^2$ coefficients A of $\rho (= \rho_0 + AT^2)$ are about 2.31, 2.78, 2.43, 3.31, and $3.14 \times 10^{-8} \,\Omega \,\mathrm{cm/K^2}$, for x = 0, 0.03, 0.05, 0.08, and 0.1, respectively.

In contrast to the results of LaFePO_{1-x}F_x, the ρ for LaFeAsO_{1-x}F_x is much affected by the F-doping. As shown in the Fig. 1(b), the ρ dramatically decreases and the *T*-dependence significantly changes with the increase in *x*. For x = 0 and 0.02, our samples show no superconducting transition till about 4 K, while for $x \ge 0.05$ the superconducting transitions occur at 14.5, 22.8, 25.2, 22.9, and 12.9 K for x = 0.05, 0.08, 0.1, 0.11, and 0.14, respectively. With the increase of *x* above 0.11, the ρ becomes as small as those of LaFePO_{1-x}F_x and becomes to be well fitted to the relation that $\rho = \rho_0 + AT^2$. The residual resistivity ρ_0 are 0.0501 and 0.0481 m Ω cm and the observed T^2 coefficients

are 1.75 and $1.66 \times 10^{-8} \Omega \text{ cm/K}^2$ for x = 0.11 and 0.14, respectively. Comparing with the previous results,^{11,12)} the ρ for LaFeAsO_{1-x}F_x does not seem to systematically change. This is not only because the ρ for a polycrystalline anisotropic compound largely depends on the sample but also because our polycrystalline samples are not so dense and include some impurities (especially for the low F-doped compounds).

The A/γ_n^2 values deduced by using the reported electronic specific heat coefficients (γ_n) of the normal state^{10,13)} are 0.226, 0.385, and $0.353 \times 10^{-3} \,\mu\Omega \,\text{cm}/\text{K}^2/(\text{mJ}/\text{K}^2 \,\text{mol})^2$ for LaFePO_{1-x} F_x for x = 0, 0.03 and 0.05, and are 0.673 and $1.15 \times 10^{-3} \,\mu\Omega \,\text{cm}/\text{K}^2/(\text{mJ}/\text{K}^2 \,\text{mol})^2$ for LaFeAs- $O_{1-x}F_x$ for x = 0.11 and 0.14. These values are much higher than the value of a correlated metal obeyed by the Kadowaki-Woods law. It is noted that these values of polycrystalline samples must be overestimated. However, since the values of ρ for our LaFeAsO_{0.89}F_{0.11} and LaFeAsO_{0.86}F_{0.14} are only a few times larger than those for the high-density samples prepared by a high-pressure synthesis technique,¹²⁾ the deviation from the Kadowaki-Woods law is thought to be essential for these oxypnictides. Such a behavior seems to be similar to that of $Sr_{1-x}La_x$ - $\operatorname{TiO}_{3-\delta}^{(14)}$, whose ρ at the low temperature is also well proportional to T^2 but the A/γ_n^2 values are 927, 11.2, and $1.34 \times 10^{-3} \,\mu\Omega \,\text{cm}/\text{K}^2/(\text{mJ}/\text{K}^2 \,\text{mol})^2$ for the carrier concetration n = 0.0052, 0.022, and 0.061 1/Ti, although the magnetic states are different. These results may indicate that another correlation, such as an electron-phonon coupling or a phonon-mediated electron-electron interaction, is dominant at the low temperature in these compounds.

Figures 2(a) and 2(b) show the *T* dependences of the Seebeck coefficient (*S*) for LaFePO_{1-x}F_x and LaFeAs-O_{1-x}F_x. As shown in Figs. 2(a) and 2(b), the sign of *S* are negative except for the *S* at the low *T* for LaFeAsO, indicating the *n*-type characteristics of these compounds. As well as the *T* dependences of ρ , the *T* dependences of *S* are quite different between two compounds. The observed *T* dependence of *S* for LaFePO is consistent with the previous



Fig. 2. (Color online) T dependences of Seebeck coefficients (S) of (a) LaFePO_{1-x} F_x and (b) LaFeAsO_{1-x} F_x .

result;¹⁵⁾ the absolute value decreases with the decrease of *T* from room temperature to about 90 K and shows the broad peak structure around 40 K. The 3% F-doping slightly changes the *T* dependence; the *S* becomes to monotonically decrease with the decreases of *T* down to T_c , although it also shows the broad peak structure around 40 K. However, as well as in the case of ρ , the further F-doping little changes the *T* dependence of *S*. The observed broad peak structure around 40 K may be due to the phonon drag effect, as observed in $Sr_{1-x}La_xTiO_{3-\delta}$.¹⁴⁾ Another possible origin will be discussed, later.

On the other hand, the LaFeAsO_{1-x}F_x compounds show quite different *T* and F-doping dependences of *S* from those of LaFePO_{1-x}F_x. Our result of *S* for LaFeAsO is also consistent with the results reported by some groups.^{2,6)} As shown in the Fig. 2(b), the sign of *S* for LaFeAsO is negative at room temperature. The absolute value slightly increases with the decrease of *T* near a structural transition temperature (T_s), and around T_s it starts to largely decrease. With the further decrease in *T*, the sign of *S* changes from negative to positive just below an AF transition temperature (T_N). These behaviors perhaps originate in the multi-band nature of the electronic state of LaFeAsO. In contrast to the case of LaFePO_{1-x}F_x, the 2% F-doping dramatically changes the *T* dependence;²⁾ the sign of *S* becomes to be always negative above T_c and the *S* takes a maximum absolute value ($S \sim -150 \,\mu\text{V/K}$) around T_s and T_N . Even if both T_s and T_N disappear with the further F-doping, the maximum absolute values of *S* remain large, -60 to $-150 \,\mu\text{V/K}$ around 90–180 K, in spite of the dramatic decrease of ρ , leading to a large power factor at the low temperature.

Figures 3(a) and 3(b) show the *T* dependences of power factor ($PF \equiv S^2/\rho$) for LaFePO_{1-x}F_x and LaFeAsO_{1-x}F_x. Reflecting the differences of the *T* and F-doping dependences of ρ and *S*, the *T* and F-doping dependences of the *PF* are quite different between two compounds. For the Fdoped LaFePO, the *PF* values at room temperature are about $0.8 \,\mu\text{W/K}^2$ cm and are slightly enhanced above *T*_c. On the other hand, the *PF* values for the F-doped LaFeAsO take broad peak structures around 50–110 K, as shown in Fig. 3(b). In this study, the observed maximum *PF* is about $37 \,\mu\text{W/K}^2$ cm at 53 K for LaFeAsO_{0.89}F_{0.11}, which is comparable to the reported value⁶⁾ for LaFeAsO_{0.86}.

3.2 Thermal conductivity and dimensionless thermoelectric figure of merit for polycrystalline $LaFePO_{1-x}F_x$ and $LaFeAsO_{1-x}F_x$

Thermal conductivities (κ) for LaFePO_{1-x}F_x and LaFeAsO_{1-x}F_x are shown in Figs. 4(a) and 4(b) where the



Fig. 3. (Color online) T dependences of power factors (*PF*) of (a) LaFePO_{1-x} F_x and (b) LaFeAsO_{1-x} F_x .

dotted lines show the electronic contributions (κ_{el}) to κ deduced by the Wiedemann-Franz law and the solid lines show $\kappa - \kappa_{el}$. Since our polycrystalline samples are not so dense, the κ is perhaps largely affected by the grain boundary especially for the low F-doped LaFeAsO_{1-x}F_x. Therefore, the observed κ values are smaller than the previous results for the high-density samples.^{6,12,16}

As shown in Fig. 4(a), the κ for LaFePO_{1-x}F_x are 2-3 W/Km at room temperature and do not show a dramatic change down to about 50 K. On the other hand, the κ for LaFeAsO shows an abrupt increase at T_s (not at T_N), as shown in Fig. 4(b), which is consistent with the previous results.^{6,16)} The F-doping blurs the change around T_s and a distinct anomaly has not been observed for $x \ge 0.05$. For x = 0.05, 0.08, and 0.1, the κ dose not show a distinct T dependence, while, for x = 0.11 and 0.14, it clearly increases with the decrease of T down to about 50 K. Such differences are perhaps due to the κ_{el} . Actually, for $x \ge 0.05$, the T dependences of $\kappa - \kappa_{el}$ do not largely change with the F-doping, as shown in Fig. 4(b). As previously reported,¹⁷⁾ for all superconducting compounds in LaFeAsO_{1-x} F_x , there is no distinct decrease of κ below T_c , although the simultaneously measured S becomes zero at T_c as shown in Fig. 2(b).

Figures 5(a) and 5(b) summarize the *T* dependences of dimensionless thermoelectric figure of merits ($ZT \equiv S^2/\rho\kappa = PF/\kappa$) for LaFePO_{1-x}F_x and LaFeAsO_{1-x}F_x. As shown in Fig. 5(a), the *ZT* values for LaFePO_{1-x}F_x at room temperature are less than 0.009 and monotonically decrease with the decrease in *T* down to 100 K. On the other hand, the *ZT* values for the F-doped LaFeAsO are 0.02–0.08 around 100–150 K, because of the enhancement of *S* around 100–150 K in spite of the relatively low ρ , as shown in Figs. 2(a) and 2(b). The observed maximum *ZT* is 0.08 at 110 K for LaFeAsO_{0.89}F_{0.11}, which is the largest value among the *ZT* values⁶⁾ ever reported for iron-pnictides.

4. Discussion

4.1 Origin of the T dependences of Seebeck coefficients

The differences between the *ZT* values of LaFePO_{1-x}F_x and LaFeAsO_{1-x}F_x mainly come from the differences of the electronic transport properties such as ρ and *S* as discussed in §3.1. Such differences of the transport properties apparently come from the existence of the AF and structural transitions for LaFeAsO_{1-x}F_x.^{2,18)} The LaFePO_{1-x}F_x compounds are in a paramagnetic (PM) state and the structure belongs to a tetragonal lattice with a space group of *P4/nmm* below room temperature.¹⁵⁾ The lattice parameters little change with the F-doping. Such an absence of the large crystallographic change is proposed to cause the small change of *T*_c and the physical properties for LaFePO_{1-x}F_x.¹⁰⁾ which is consistent with the absence of the large F-doping dependence of *S* in this study.

In contrast to LaFePO_{1-x} F_x , the low F-doped LaFeAsO compounds show the transition from the PM state to the stripe-type AF state and the structural transition from a tetragonal lattice with a space group of P4/nmm to an orthorhombic lattice with a space group of Cmma,¹⁸⁾ as shown in Fig. 6(a). According to the previous reports,¹⁸⁾ the AF transition temperature T_N is just below a structural temperature T_s , and slightly decreases from about 140 K to about 120 K with an increase of x. The AF transition



Fig. 4. (Color online) *T* dependences of thermal conductivities (κ) of (a) LaFePO_{1-x}F_x and (b) LaFeAsO_{1-x}F_x. The dotted lines show the electronic contributions (κ_{el}) to κ deduced by the Wiedemann-Franz law and the solid lines show $\kappa - \kappa_{el}$.



Fig. 5. (Color online) T dependences of dimensionless figure of merits (ZT) of (a) LaFePO_{1-x} F_x and (b) LaFeAsO_{1-x} F_x .



Fig. 6. (Color online) (a) The F-doping dependences of the structural (T_s , open circles), AF (T_N , open squares), and superconducting (T_c , closed circles) transition temperatures with that of the maximum *S* (S_{max} , closed squares). The presented T_s , T_N , and the structures in the phase diagram are from ref. 18. The closed downward triangle expresses the temperature (T_{Smax}) where the *S* take maximum values. The solid and dotted lines are guide to eyes. The insets show the expected intermediate spin state (spin = 1) of Fe²⁺ ions in the FeAs₄ tetrahedrons. (b) The F-doping dependences of the electronic specific heat coefficient of the normal state (γ_n) for LaFePO_{1-x}F_x and LaFeAsO_{1-x}F_x. The closed diamonds, the closed downward triangles, and the closed upward triangles show γ_n for LaFePO_{1-x}F_x reported in refs. 10, 15, and 20, espectively. The close circles show γ_n for LaFeAsO_{1-x}F_x reported in ref. 13. The chain and dotted lines are guide to eyes.

disappears above x = 0.03, while the structural transition persists till x = 0.05.¹⁸⁾ For $x \ge 0.05$, the LaFeAsO_{1-x}F_x compounds are also in the PM metallic state above T_c with a P4/nmm tetragonal lattice, but the orthorhombic structural distortion is reported to be left¹⁸⁾ in this regime. Figure 6(a) superposes our results of the maximum $S(S_{max})$ on the phase diagram. For $x \le 0.03$, the S take maximum at T_{Smax} near T_s and T_N , while it keeps taking a relatively large maximum values around 90–180 K after the disappearance of the structural and AF transitions with the increase of x above 0.05. Comparing the results of LaFePO_{1-x}F_x, these results strongly suggest that the correlation of AF order and the residual orthorhombic structural distortion much affect the S as well as the ρ .¹⁰

In order to understand the origin of the differences of the *S* between the two compounds and the observed large *S* for the F-doped LaFeAsO, in the first approximation we make a rough analysis of the results by using a conventional 3D parabolic band model with a single carrier^{14,19} (see Appendix). In this model, the *S* is proportional to $m^*n^{-2/3}T$, where the m^* is an effective mass and *n* is a carrier density. When the m^* and *n* are constant, the relation expresses the well-known *T*-linear dependence of *S* for a metal. If the densities of electrons doped into these compounds were



Fig. 7. (Color online) The *T* dependences of $(|S|/T)^{3/2}$ for (a) LaFeP-O_{1-x}F_x and (b) LaFeAsO_{1-x}F_x. The insets show the *T* dependences of *S*/*T* for these compounds.

determined by the formal valences and the observed large S values for LaFeAsO_{1-x} F_x originated in m^* , the electronic specific heat coefficients (γ_n) for LaFeAsO_{1-x}F_x would be larger than those for LaFePO_{1-x} F_x corresponding to the S values, because $\gamma_n \propto m^* n^{1/3}$ in the framework. However, as shown in Fig. 6(b), the $\gamma_n^{(13)}$ for LaFeAsO_{1-x}F_x is smaller than that 10,15,20 for LaFePO_{1-x}F_x, and it monotonically decreases with the F-doping although the maximum $S(S_{max})$ shows the critical-like behavior around $x \sim 0.1$. Therefore, if the framework is held, the n must not be determined by the formal valence. Then, we plot the T dependences of $(|S|/T)^{3/2}$ and S/T in Fig. 7 and their insets. It is quite interesting that the T dependences of $(|S|/T)^{3/2}$ for both LaFePO_{1-x} F_x and LaFeAsO_{1-x} F_x are qualitatively similar to those of the Hall coefficients $(R_{\rm H})$.^{10,21,22)} These results strongly suggest that the overall T dependences of the S for the F-doped LaFePO and LaFeAsO are mainly governed by the T dependences of the n.

4.2 Possibilities of the instability of orbital order and the hidden mass enhancement of $LaFeAsO_{1-x}F_x$

In order to understand the origin of the *T* dependences of the *S* for these compounds, it is necessary to understand the origin of the *T* dependences of the $R_{\rm H}$. According to the

results in ref. 21, the $R_{\rm H}$ for LaFeAsO increases and shows an abrupt increase around T_s with the decrease of T, indicating that the structural transition from the tetragonal structure to the orthorhombic one dramatically suppresses the *n* although the ρ drops below T_s .^{1,2)} To explain the experimental results, the mobility of carrier (μ_c) must dramatically increase, i.e., something to disturb the electronic transport is dramatically suppressed by the structural transition. It is natural to think that the origin of this increase of $\mu_{\rm c}$ is due to the suppression of fluctuations of the Fe 3d orbital by the orbital order associated with the structural transition proposed by some theoretical predictions²³⁻²⁵⁾ on the base of an intermediate spin state of Fe²⁺ ion as shown in the inset of Fig. 6(a). The electrons participating in the orbital order are localized, so the n dramatically decreases, while the μ_c of the itinerant carriers that do not participate in the orbital order dramatically increases because of the suppression of the orbital fluctuation.

The electron doping by the substitution of F for O suppresses the orbital order as evidenced by the disappearance of the structural transition and that of the associated AF transition [Fig. 6(a)]. However, the instability of the orbital order may persist in the over F-doped region especially near the phase boundary, as partially supported by the residual orthorhombic structural distortion in the tetragonal phase.¹⁸⁾ This instability may cause the T dependences of the $R_{\rm H}$ for the over F-doped LaFeAsO; the development of the correlation of the orbital order gradually reduces the *n* of the itinerant electrons with the decrease of T, leading to the reported increase of $R_{\rm H}^{13,22}$ with the decrease of T. It is noted that the slight enhancement of the $R_{\rm H}$ and S observed at the low temperatures in $LaFePO_{1-x}F_x$ may be also due to the instability of this orbital order rather than phonon drag effect. Such a residual instability of the orbital order in the metallic state may cause the deviation from the Kadowaki-Woods law.

Lastly, we make a rough estimation of the m^* for LaFePO_{1-x} F_x and LaFeAsO_{1-x} F_x by using the 3D parabolic metallic band model with a single carrier (electron) on the assumption that the suppression of the n due to the instability of the orbital order actually occurs. In this simple model, $S/T \propto m^* n^{-2/3}$ and $\gamma_n \propto m^* n^{1/3}$, so $[(|S|/T)^{3/2} \gamma_n^3]^{2/9} \propto m^*$. By using the maximum $(|S|/T)^{3/2}$ values at about 25 K for LaFePO_{1-x} F_x in Fig. 7(a) and the reported values of $\gamma_n^{(10)}$ for LaFePO_{1-x} F_x , we deduce the m^* for LaFePO_{1-x} F_x . As for LaFeAsO_{1-x} F_x , we calculate the m^* by using the maximum $(|S|/T)^{3/2}$ values at about 30 K in Fig. 7(b), the reported values of $\gamma_n^{(13)}$ for x = 0.05, 0.11, and 0.14, and the extrapolated values of γ_n for x = 0.08 and 0.1 in Fig. 6(b). Figure 8 summarizes the F-doping dependences of the deduced m^* normalized by that for LaFePO in the tetragonal phase. This rough analysis shows that the m^* around x = 0.05-0.1 of LaFeAsO_{1-x}F_x are larger than those of $LaFePO_{1-x}F_x$, $LaFeAsO_{0.89}F_{0.11}$, and $LaFeAsO_{0.86}F_{0.14}$. As observed around a Mott transition,^{26–29)} such a mass enhancement (in Fig. 8) with the absence of the enhancement of γ_n [in Fig. 6(b)] is perhaps due to the renormalized spin or orbital fluctuation of Fe ions around a critical region above x = 0.05, and should be related to the mechanism of the superconducting state $^{30-32)}$ as well as the relatively good low-T thermoelectric properties in these iron-pnictides.



Fig. 8. (Color online) The F-doping dependences of the effective mass (m^*) normalize by the m^* for LaFePO. The solid circles and the solid squares are the normalized m^* for LaFePO_{1-x}F_x and LaFeAsO_{1-x}F_x, respectively (see text).

5. Summary

In this study, we systematically investigate the thermoelectric properties for polycrystalline LaFePO_{1-x} F_x and LaFeAsO_{1-x} F_x and discuss an origin of a relatively good thermoelectric property of LaFeAsO_{1-x} F_x by comparing the properties of these compounds. The observed maximum power factor is about $37 \,\mu\text{W}/\text{K}^2$ cm at 53 K for LaFeAs-O_{0.89}F_{0.11} and the maximum dimensionless thermoelectric figure of merit (ZT) is about 0.08 at 110 K for LaFeAs-O_{0.89}F_{0.11} which is larger by an order than those for LaFeP- $O_{1-x}F_x$. This observed relatively large ZT at the low temperature for LaFeAsO $_{0.89}F_{0.11}$ is due to the low resistivity (ρ) and the large Seebeck coefficient (S). According to our rough analysis by using a 3D parabolic band model with a single carrier, the low ρ in the over F-doped region in LaFeAsO_{1-x} F_x is perhaps not only due to an increase of an electron density (n) by the F-doping, but also due to a suppression of an orbital fluctuation of Fe ions by the residual instability of the orbital order proposed in LaFeAsO by some theoretical works. Furthermore, the relatively large S for the over F-doped LaFeAsO may originate not only in the smaller *n* than that expected from the formal valence due to the residual instability of the orbital order, but also in the mass enhancement around the structural and magnetic phase boundary due to the renormalized spin or orbital fluctuations. Such a mass enhancement may be related to the mechanism of the superconducting state as well as the relatively good low-Tthermoelectronic properties in these iron-pnictides.

Appendix

According to the previous reports,⁸⁾ both LaFePO and LaFeAsO have multiple bands (three hole-like bands and two electron-like bands) and multiple Fermi surface sheets, so both hole and electron should contribute to the transport properties for LaFePO_{1-x} F_x and LaFeAsO_{1-x} F_x . In this paper, in order to capture the overall picture of the origin of the difference of the *S* between two series, we make a following discussion on the basis of experimental results and make a rough analysis in the text by using a 3D parabolic bnad model with a single carrier.

Both end compounds, LaFePO and LaFeAsO, are assumed to have three hole bands and two nearly degenerate electron bands. Their Seebeck coefficients, *S*, are expressed as follows:

$$S = \frac{S_{h1}\sigma_{h1} + S_{h2}\sigma_{h2} + S_{h3}\sigma_{h3} + S_{e1}\sigma_{e1} + S_{e2}\sigma_{e2}}{\sigma_{h1} + \sigma_{h2} + \sigma_{h3} + \sigma_{e1} + \sigma_{e2}}$$
$$\approx \frac{(S\sigma)_h + 2S_e\sigma_e}{\sigma}.$$
 (A·1)

where

$$(S\sigma)_{\rm h} = S_{\rm h1}\sigma_{\rm h1} + S_{\rm h2}\sigma_{\rm h2} + S_{\rm h3}\sigma_{\rm h3},$$
 (A·2)

$$\sigma = \sigma_{h1} + \sigma_{h2} + \sigma_{h3} + \sigma_{e1} + \sigma_{e2}, \qquad (A.3)$$

$$S_{e1} \approx S_{e2} \approx S_{e},$$
 (A·4)

$$\sigma_{e1} \approx \sigma_{e2} \approx \sigma_{e}.$$
 (A·5)

For LaFeAsO, the absolute value of S (-10 to $30 \mu V/K$) is much smaller than the maximum absolute value of S (about -150 $\mu V/K$) for LaFeAsO_{1-x}F_x and the sign changes with the decrease of T, which is perhaps due to the competition between the contributions of hole and electron. Then, we roughly assume that $S \approx 0$ for LaFeAsO, so $(S\sigma)_h +$ $2S_e\sigma_e \approx 0$. In the case of LaFeAsO_{1-x}F_x, we also assume that the changes of the transport properties come only from the increase of electron densities in the electron bands. Then, the σ for LaFeAsO_{1-x}F_x is expressed by $\sigma \approx \sigma_h + 2(\sigma_e +$ $\Delta \sigma_e)$, where $\sigma_h = \sigma_{h1} + \sigma_{h2} + \sigma_{h3}$ and $\Delta \sigma_e$ is the increase of the contribution of electron to the conductivity. The σ for LaFeAsO_{1-x}F_x much increases with the F doping as shown in Fig. 1(b), so $\sigma_h + 2\sigma_e \ll 2\Delta\sigma_e$. Then, the Seebeck coefficient for LaFeAsO_{1-x}F_x is approximately expressed as follows,

$$S + \Delta S \approx \frac{(S\sigma)_{\rm h} + 2(S_{\rm e} + \Delta S_{\rm e})(\sigma_{\rm e} + \Delta \sigma_{\rm e})}{\sigma + 2\Delta\sigma_{\rm e}} \\ \approx \frac{2\Delta S_{\rm e}\sigma_{\rm e} + 2(S_{\rm e} + \Delta S_{\rm e})\Delta\sigma_{\rm e}}{2\Delta\sigma_{\rm e}} \approx S_{\rm e} + \Delta S_{\rm e}$$
(A·6)

where ΔS and ΔS_e is the change of *S* and S_e with the F-doping, respectively. The total Seebeck coefficient for LaFeAsO_{1-x}F_x can be approximated by the contribution of the electron band.

In the case of LaFePO_{1-x} F_x , the same approximation cannot be done, because LaFePO is already a good metal without the F-doping and the conductivity little changes with the F-doping, as shown in Fig. 1(a). Then, we roughly assume that $S \approx S_e \approx S_h \approx 0$, comparing with the maximum absolute value of *S* (about -150 µV/K) for LaFeAsO_{1-x} F_x . Furthermore, the σ for LaFePO is assumed to be governed by the electron conductivity, $\sigma \approx 2\sigma_e$, which is partially supported by the facts that the R_H and *S* are negative and the mobility of electron is estimated to be much higher than that of hole by the ARPES. Then, the total Seebeck coefficient for LaFePO_{1-x} F_x becomes as follows:

$$S + \Delta S \approx \frac{(S\sigma)_{\rm h} + 2(S_{\rm e} + \Delta S_{\rm e})\sigma_{\rm e}}{2\sigma_{\rm e}} \approx \frac{2(S_{\rm e} + \Delta S_{\rm e})\sigma_{\rm e}}{2\sigma_{\rm e}}$$
$$\approx S_{\rm e} + \Delta S_{\rm e}. \tag{A.7}$$

It can also be approximated by the contribution of the electron band.

In the above discussions, the assumptions and approximations are rather rough and may partially be incorrect. However, the above conclusions are consistent with the facts that both S and $R_{\rm H}$ are negative and that the T dependences of $(|S|/T)^{3/2}$ quite resemble those of $R_{\rm H}$, as shown in Fig. 6. Paradoxically, the consistency seems to strongly suggest that the transport properties for these oxypnictides are governed by the contribution of the electron bands.

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