

## Suppression of the superconducting transition of $R\text{FeAsO}_{1-x}\text{F}_x$ ( $R=\text{Tb}$ , $\text{Dy}$ , and $\text{Ho}$ )

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A suppression of superconductivity in the late rare-earth  $R\text{FeAsO}_{1-x}\text{F}_x$  materials is reported. The maximum critical temperature ( $T_c$ ) decreases from 51 K for  $R=\text{Tb}$  to 36 K for  $\text{HoFeAsO}_{0.9}\text{F}_{0.1}$ , which has been synthesized under 10 GPa pressure. This suppression is driven by a decrease in the Fe-As-Fe angle below an optimum value of  $110.6^\circ$ , as the angle decreases linearly with unit-cell volume ( $V$ ) across the  $R\text{FeAsO}_{1-x}\text{F}_x$  series. A crossover in electronic structure around this optimum geometry is evidenced by a change in sign of the compositional  $dT_c/dV$ , from negative values for previously reported large  $R$  materials to positive for  $\text{HoFeAsO}_{0.9}\text{F}_{0.1}$ .

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Rare earth ( $R$ ) oxypnictides  $R\text{FeAsO}$  (Ref. 1) were recently discovered to superconduct when doped, with critical temperatures surpassed only by the high- $T_c$  cuprates. Several families of superconducting iron pnictides have subsequently been discovered.<sup>2</sup> These all have layered structures containing AsFeAs slabs with Fe tetrahedrally coordinated by As. The main types are the 1111 materials based on  $R\text{FeAsO}$  or  $M\text{FeAsF}$  ( $M=\text{Ca}, \text{Sr}, \text{Ba}$ ), the 122 phases  $M\text{Fe}_2\text{As}_2$ , and the 111  $A\text{FeAs}$  ( $A=\text{Li}, \text{Na}$ ) family. The related binaries  $\text{FeX}$  ( $X=\text{Se}, \text{Te}$ ) are also superconducting.

The electron-doped 1111 materials  $R\text{FeAsO}_{1-x}\text{F}_x$  and  $R\text{FeAsO}_{1-\delta}$  materials remain prominent as they have the highest  $T_c$ 's, up to 56 K, and allow lattice and doping effects to be investigated through variations in the  $R^{3+}$  cation size and the anion composition. A strong lattice effect is evident at the start of the rare-earth series, as  $T_c$  rises from 26 K for  $\text{LaFeAsO}_{1-x}\text{F}_x$  to 43 K under pressure,<sup>3,4</sup> and to a near-constant maximum 50–56 K in the  $R\text{FeAsO}_{1-x}\text{F}_x$  and  $R\text{FeAsO}_{1-\delta}$  series for  $R=\text{Pr}$  to  $\text{Gd}$ ,<sup>5–10</sup> but whether lattice effects ultimately enhance or suppress superconductivity for the late  $R$ 's has been unclear. The late rare-earth  $R\text{FeAsO}_{1-x}\text{F}_x$  materials and the oxygen-deficient  $R\text{FeAsO}_{1-\delta}$  superconductors require high-pressure synthesis, leading to significant challenges as single phase samples are difficult to prepare, and accurate analyses of cation stoichiometries and O and F contents are difficult. To investigate the effect of the lattice for later  $R$ , we have synthesized multiple samples of  $R\text{FeAsO}_{0.9}\text{F}_{0.1}$  ( $R=\text{Tb}$ ,  $\text{Dy}$ , and  $\text{Ho}$ ) under varying high-pressure conditions. Here we report superconductivity in  $\text{HoFeAsO}_{0.9}\text{F}_{0.1}$  for which the maximum  $T_c$  of 36 K is markedly lower than in the previous  $R$  analogs. This is part of a systematic suppression of superconductivity by the smaller, late  $R$  cations.  $\text{HoFeAsO}_{0.9}\text{F}_{0.1}$  also shows a reversal in the sign of the compositional  $dT_c/dV$  ( $V$ =unit-cell volume) compared to the early  $R$  materials, confirming that the decreasing  $R$  size has a significant effect on the bands contributing to the Fermi surface.

Polycrystalline ceramic  $R\text{FeAsO}_{1-x}\text{F}_x$  samples ( $R=\text{Tb}$ ,  $\text{Dy}$ , and  $\text{Ho}$ ) were synthesized by a high-pressure method and investigated by powder x-ray diffraction, magnetization, and

conductivity measurements.<sup>11</sup> Initial results for  $R\text{FeAsO}_{1-x}\text{F}_x$  ( $R=\text{Tb}$  and  $\text{Dy}$ ) were published elsewhere.<sup>12</sup> Both materials were found to be superconducting with maximum  $T_c$ 's of 46 and 45 K, respectively. Little difference in superconducting properties between samples with nominal compositions of  $x=0.1$  and  $0.2$  were observed, and the  $x=0.2$  materials were generally of lower phase purity, and so the  $x=0.1$  composition was used in subsequent syntheses. The best samples typically contain  $\sim 80\%$  by mass of the superconducting phase with residual nonsuperconducting  $R_2\text{O}_3$  and  $R\text{As}$  phases also present. The sample purity and superconducting properties are not sensitive to synthesis pressure over a range that moves to higher pressures as  $R$  decreases in size;  $R=\text{Tb}$  and  $\text{Dy}$  superconductors were respectively prepared at 7–10 and 8–12 GPa, heating at 1050–1100 °C. Repeated syntheses of  $\text{TbFeAsO}_{1-x}\text{F}_x$  gave several samples with higher  $T_c$ 's than the above value, the highest value is  $T_c(\text{max})=51$  K (Fig. 1). Further  $\text{DyFeAsO}_{1-x}\text{F}_x$  samples did not show higher transitions than before, so we conclude that  $T_c(\text{max})$  in this system is 45 K.

Tetragonal  $\text{HoFeAsO}_{0.9}\text{F}_{0.1}$  was obtained from reactions at 10 GPa pressure and the properties of six  $\text{HoFeAsO}_{0.9}\text{F}_{0.1}$  samples prepared under varying conditions are summarized

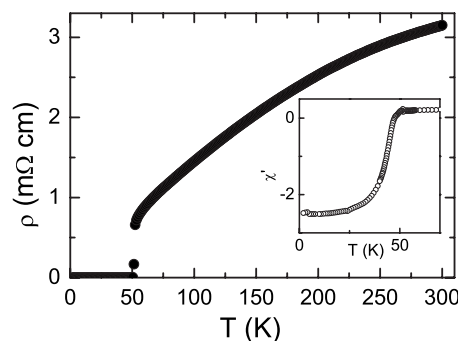


FIG. 1. Resistivity and (inset) susceptibility data for an optimum sample of  $\text{TbFeAsO}_{0.9}\text{F}_{0.1}$ , showing a sharp superconducting transition at  $T_c=51$  K. The sample was prepared at 7 GPa and 1050 °C.

TABLE I. Synthesis conditions (all samples were synthesized at 10 GPa), refined lattice parameters and volume,  $T_c$ 's, mass fractions, and superconducting volume fractions for  $\text{HoFeAsO}_{1-x}\text{F}_x$  samples.

Sample	$t_{\text{synth}}$ (hr)	$T_{\text{synth}}$ (°C)	$a$ (Å)	$c$ (Å)	Vol (Å <sup>3</sup> )	$T_c$ (K)	Mass frac. (%)	Diamag. frac. (%)
1	2	1150	3.8246(3)	8.254(1)	120.74(3)	29.3	75	70
2	2	1100	3.8272(2)	8.2649(8)	121.06(2)	33.0	74	85
3	1	1150	3.8258(5)	8.264(2)	120.96(4)	33.2	73	76
4	3	1100	3.8282(5)	8.261(2)	121.07(5)	33.7	84	74
5	2	1100	3.8282(2)	8.2654(7)	121.13(2)	35.2	81	57
6	2	1100	3.8297(7)	8.270(2)	121.30(7)	36.2	58	46

in Table I. Crystal structure refinements and phase analysis were carried out by fitting powder x-ray diffraction data (Fig. 2).<sup>13</sup> Magnetization measurements demonstrate that all six  $\text{HoFeAsO}_{1-x}\text{F}_x$  samples are bulk superconductors with  $T_c$ 's of 29–36 K (Fig. 3). Resistivities show smooth high-temperature evolutions without apparent spin-density wave anomalies. The transitions to the zero resistance state have widths of less than 4 K.

Although all of the samples in Table I have the same starting composition, small variations in synthesis pressure and temperature result in a dispersion in  $x$  around the nominal 0.1 value for the  $\text{HoFeAsO}_{1-x}\text{F}_x$  phase and corresponding variations in superconducting properties.  $T_c$  increases to a maximum value,  $T_c(\text{max})$ , at the upper solubility limit of  $x$  in  $R\text{FeAsO}_{1-x}\text{F}_x$  systems,<sup>7</sup> and this is consistent with the observation that the superconducting phases in samples 1, 3, and 4, which are heated at high temperatures or for longer times and so are likely to have a slightly lower F content, have lower  $T_c$ 's (average 32.1 K) than the other three samples, made under nominally identical “optimum” conditions, which have average  $T_c=34.8$  K. Sample 6 shows the highest  $T_c=36.2$  K and the lowest proportion of the  $\text{HoFeAsO}_{1-x}\text{F}_x$  phase and a correspondingly low diamagnetic volume fraction. This demonstrates that the sample is at the upper limit of the superconducting composition range and so gives a realistic  $T_c(\text{max})$  for the  $\text{HoFeAsO}_{1-x}\text{F}_x$  system.

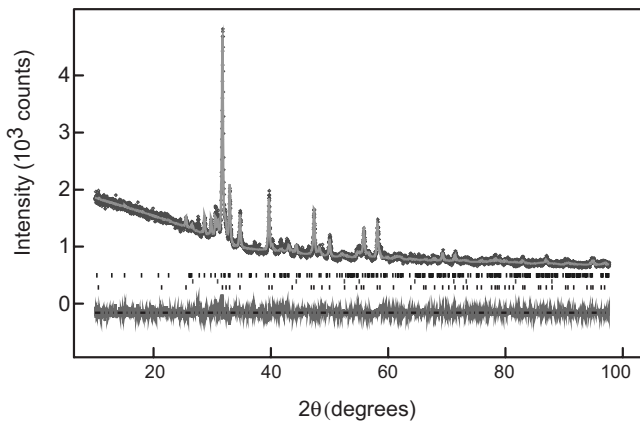


FIG. 2. Fitted x-ray diffraction profile for  $\text{HoFeAsO}_{0.9}\text{F}_{0.1}$  (sample 5) at room temperature. The Bragg markers (from top to bottom) are for the minority phases,  $\text{Ho}_2\text{O}_3$  and  $\text{HoAs}$ , and for  $\text{HoFeAsO}_{0.9}\text{F}_{0.1}$ .

Although the doping values  $x$  for the high-pressure  $R\text{FeAsO}_{1-x}\text{F}_x$  samples are not known precisely, comparing ensembles of samples with similar phase purities made under similar conditions reveals a clear suppression of superconductivity by lattice effects for heavier  $R$ . For example, all of our  $\text{TbFeAsO}_{1-x}\text{F}_x$  superconductors have higher  $T_c$ 's (five  $\text{TbFeAsO}_{1-x}\text{F}_x$  samples,  $T_c=45\text{--}51$  K) than all of the  $\text{HoFeAsO}_{1-x}\text{F}_x$  materials (in Table I). The  $T_c(\text{max})$  values of 51, 45, and 36 K for  $R\text{FeAsO}_{1-x}\text{F}_x$  with  $R=\text{Tb}$ ,  $\text{Dy}$ , and  $\text{Ho}$ , respectively, thus represent the trend correctly.

Figure 4 shows a plot of the maximum critical temperatures,  $T_c(\text{max})$ , against unit-cell volume for many reported  $R\text{FeAsO}_{1-x}\text{F}_x$  and  $R\text{FeAsO}_{1-\delta}$  systems and our above materials.  $T_c(\text{max})$  rises slowly as cell volume decreases for  $R=\text{La}$  to  $\text{Pr}$  and then shows a broad maximum, between  $R=\text{Pr}$  and  $\text{Tb}$  in the  $R\text{FeAsO}_{1-x}\text{F}_x$  materials, before falling rapidly as  $R$  changes from  $\text{Tb}$  to  $\text{Dy}$  to  $\text{Ho}$ . This trend is not seen in the reported  $R\text{FeAsO}_{1-x}$  superconductors, where  $T_c(\text{max})$  remains approximately constant,<sup>14,15</sup> apparently because they have larger cell volumes than their  $R\text{FeAsO}_{1-x}\text{F}_x$  analogs (see Fig. 4).

The size of the  $R^{3+}$  cation tunes the electronic properties through variations in the geometry of the  $\text{FeAs}$  slab. A trend between the  $\text{As-Fe-As}$  (or equivalent  $\text{Fe-As-Fe}$ ) angle and  $T_c$  has been reported for the early  $R$  materials.<sup>16</sup> The upper panel of Fig. 4 shows representative reported values for optimal  $R\text{FeAsO}_{1-x}\text{F}_x$  superconductors including our  $R=\text{Tb}$ ,  $\text{Dy}$ , and  $\text{Ho}$  materials. This demonstrates that the angle decreases monotonically with  $R$  size and so does not show a universal correlation with  $T_c(\text{max})$ . The  $T_c(\text{max})$  variation in the  $R\text{FeAsO}_{1-x}\text{F}_x$  series is described by a simple  $\cos(\phi - \phi_0)$  function, shown in Fig. 4, where the value of the  $\text{As-}$

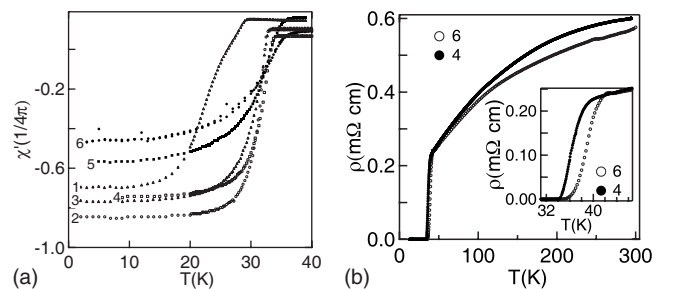


FIG. 3. Superconductivity measurements for  $\text{HoFeAs}_{0.9}\text{F}_{0.1}$ ; (a) ac magnetic volume susceptibility for the six samples; (b) resistivities for samples 4 and 6.

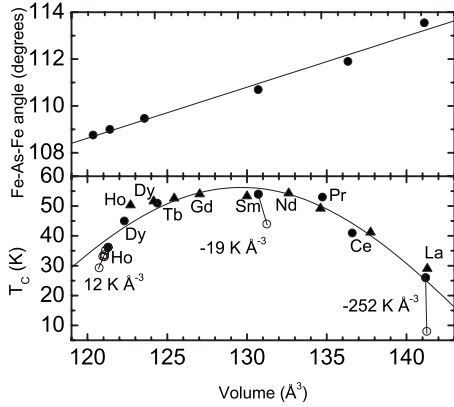


FIG. 4. Variation in Fe-As-Fe angle  $\phi$  (upper panel) and superconducting  $T_c$  (lower panel) with unit-cell volume for different  $R\text{FeAsO}_{1-x}\text{F}_x$  (circles) (Refs. 19, 22, 5, 7, and 12) and  $R\text{FeAsO}_{1-\delta}$  (triangles) (Refs. 14 and 15).  $T_c(\text{max})$  points are shown as filled symbols. The fit of equation  $T_c(\text{max})=T_c(\text{max})_0\cos A(\phi-\phi_0)$  with parameters  $T_c(\text{max})_0=56$  K,  $A=0.03$ , and  $\phi_0=110.6^\circ$  is also shown.  $dT_c/dV$  values are derived from the data for suboptimally doped materials (open symbols) in the  $R=\text{La}$  (Ref. 19),  $\text{Sm}$  (Ref. 7), and  $\text{Ho}$  (this Brief Report) systems.

Fe-As angle corresponding to the global maximum  $T_c$ ,  $\phi_{\text{max}}=110.6^\circ$ , is close to the ideal  $109.5^\circ$  value for a regular  $\text{FeAs}_4$  tetrahedron. All five of the Fe  $3d$  bands are partially occupied and contribute to the Fermi surface of the iron arsenide superconductors through hybridization with As  $4s$  and  $4p$  states.<sup>17</sup> Decreasing the tetrahedral angle through  $109.5^\circ$  marks the crossover from tetragonal compression to elongation of the  $\text{FeAs}_4$  tetrahedra. In a crystal-field model, this reverses the splittings of the  $t_2$  and  $e$   $d$ -orbital sets and so a significant crossover in the real electronic structure is likely to occur near  $109.5^\circ$ .

Evidence for the above crossover also comes from a discovered change in the sign of the compositional  $dT_c/dV$  near optimum doping in the  $R\text{FeAsO}_{1-x}\text{F}_x$  systems.<sup>18</sup> The unit-cell parameters and volume for the six  $\text{HoFeAsO}_{1-x}\text{F}_x$  samples in Table I show a positive correlation with  $T_c$  (Fig. 5), in contrast to early  $R=\text{La}$  (Ref. 19) and  $\text{Sm}$  (Ref. 7) analogs, where lattice parameters and volume decrease with increasing  $T_c$ . The  $T_c, V$  points for near-optimally doped  $R=\text{La}$ ,  $\text{Sm}$ , and  $\text{Ho}$   $R\text{FeAsO}_{1-x}\text{F}_x$  superconductors are shown in Fig. 4 together with the derived  $dT_c/dV$  values.  $dT_c/dV$  for a single  $R\text{FeAsO}_{1-x}\text{F}_x$  system follows the overall trend in  $dT_c(\text{max})/dV$  for different  $R$ 's, changing from a negative value at large  $R=\text{La}$  to a small positive slope at  $R=\text{Ho}$ .

The compositional  $dT_c/dV$  for a given  $R\text{FeAsO}_{1-x}\text{F}_x$  system reflects two competing effects of variations in the fluoride content  $x$  on the lattice volume.  $\text{F}^-$  is slightly smaller than  $\text{O}^{2-}$  so the anion substitution effect gives a negative

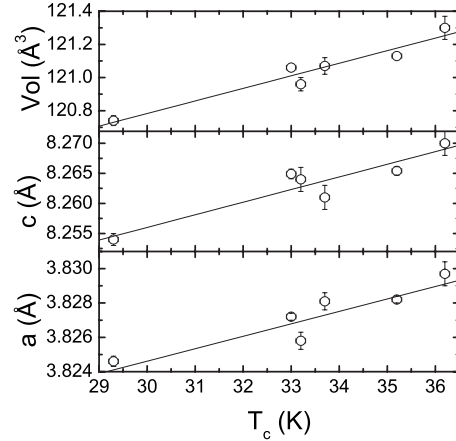


FIG. 5. Variations in  $T_c$  with the tetragonal unit-cell parameters and volume for the six  $\text{HoFeAsO}_{1-x}\text{F}_x$  samples in Table I.

contribution to the compositional  $dT_c/dV$ , independent of  $R$ . The concomitant effect of doping electrons into the Fe  $d$  bands tends to expand the lattice (and increase  $T_c$ ), but the magnitude of this positive  $dT_c/dV$  term depends on the nature of the bands at the Fermi surface. The observed shift from negative to positive  $dT_c/dV$  as  $R$  changes from  $\text{La}$  to  $\text{Ho}$  shows that the decreasing size of the  $R^{3+}$  cation leads to significant changes in the Fermi surface, with volume-expanding (antibonding) bands more prominent for smaller  $R$ . Calculations have confirmed that the electronic structure near the Fermi level is sensitive to such small changes in the As  $z$  coordinate (equivalent to changing the Fe-As-Fe angle).<sup>20</sup> Small changes in the contributions of the  $d$  bands are likely to be particularly important in a multigap scenario for superconductivity, as evidenced in gap measurements of  $\text{TbFeAsO}_{0.9}\text{F}_{0.1}$  and other iron arsenide materials.<sup>21</sup>

In summary, our analysis of multiple samples of  $R\text{FeAsO}_{1-x}\text{F}_x$  ( $R=\text{Tb}$ ,  $\text{Dy}$ , and  $\text{Ho}$ ) superconductors demonstrates that the maximum critical temperature falls from 51 K for  $R=\text{Tb}$  to 36 K for the previously unreported  $\text{Ho}$  analog. Hence, the effect on the lattice of substituting smaller late rare earths in the  $R\text{FeAsO}_{1-x}\text{F}_x$  lattice suppresses superconductivity. This lattice control appears to be through tuning of the interatomic angles in the  $\text{FeAs}$  layer, with the optimum angle being  $110.6^\circ$ , near the ideal tetrahedral value. The compositional  $dT_c/dV$  changes sign around the optimum angle evidencing significant changes in the Fermi surface. It appears difficult to increase the critical temperatures above 56 K in 1111 type iron arsenide materials through tuning lattice effects, although the possibility of higher  $T_c$ 's in other structure types remains open.

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- <sup>13</sup>HoFeAsO<sub>0.9</sub>F<sub>0.1</sub> has a tetragonal structure (space group *P4/nmm*; results from fit shown in Fig. 2; goodness of fit  $\chi^2 = 1.60$ , residuals;  $R_{wp} = 3.94\%$ ,  $R_p = 3.02\%$ ; cell parameters  $a = 3.8282(2)$  Å,  $c = 8.2654(7)$  Å; atom positions  $[x, y, z]$  and isotropic temperature ( $U$ ) factors; Ho  $[\frac{1}{4}, \frac{1}{4}, 0.1454(4)]$ ,  $0.044(2)$  Å<sup>2</sup>; As  $[\frac{1}{4}, \frac{1}{4}, 0.6659(5)]$ ,  $0.029(2)$  Å<sup>2</sup>; Fe  $(\frac{3}{4}, \frac{1}{4}, \frac{1}{2})$ ,  $0.014(2)$  Å<sup>2</sup>; O,F  $(\frac{3}{4}, \frac{1}{4}, 0)$ ,  $0.26(2)$  Å<sup>2</sup>). The secondary Ho<sub>2</sub>O<sub>3</sub> phase is in a high-pressure *B*-type rare-earth oxide modification, space group *C2/m*,  $a = 13.841(2)$  Å,  $b = 3.4984(5)$  Å,  $c = 8.608(1)$  Å,  $\beta = 100.08(1)^\circ$ .
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