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

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A suppression of superconductivity in the late rare-earth \( R \text{FeAsO}_{1-x}F_x \) materials is reported. The maximum critical temperature \( (T_c) \) decreases from 51 K for \( R=\text{Tb} \) to 36 K for \( \text{HoFeAsO}_{0.9}F_{0.1} \), which has been synthesized under 10 GPa pressure. This suppression is driven by a decrease in the \( \text{Fe-As-Fe} \) angle below an optimum value of 110.6°, as the angle decreases linearly with unit-cell volume \( (V) \) across the \( R \text{FeAsO}_{1-x}F_x \) 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 \( \text{HoFeAsO}_{0.9}F_{0.1} \).

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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. 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 \( M \text{FeAsF} \ (M=\text{Ca, Sr, Ba}) \), the 122 phases \( M \text{Fe}_2\text{As}_2 \), and the 111 \( \text{AFeAs} \ (\text{A} = \text{Li, Na}) \) family. The related binaries \( \text{FeX} \ (\text{X} = \text{Se, Te}) \) are also superconducting.

The electron-doped 1111 materials \( R \text{FeAsO}_{1-x}F_x \) 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 \( \text{LaFeAsO}_{1-x}F_x \) to 43 K under pressure,3,4 and to a near-constant maximum 50–56 K in the \( R \text{FeAsO}_{1-x}F_x \) and \( R \text{FeAsO}_{1-\delta} \) series for \( R=\text{Pr} \) to \( \text{Gd} \),5–10 but whether lattice effects ultimately enhance or suppress superconductivity for the late \( R \)’s has been unclear. The late rare-earth \( R \text{FeAsO}_{1-x}F_x \) 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 \( R \text{FeAsO}_{0.9}F_{0.1} \) \( (R=\text{Tb}, \text{Dy}, \text{and Ho}) \) under varying high-pressure conditions. Here we report superconductivity in \( \text{HoFeAsO}_{0.9}F_{0.1} \) 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. \( \text{HoFeAsO}_{0.9}F_{0.1} \) also shows a reversal in the sign of the compositional \( dT_c/dV \) \( (V=\text{unit-cell volume}) \) 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 \( R \text{FeAsO}_{1-x}F_x \) samples \( (R=\text{Tb}, \text{Dy}, \text{and Ho}) \) were synthesized by a high-pressure method and investigated by powder x-ray diffraction, magnetization, and conductivity measurements.11 Initial results for \( R \text{FeAsO}_{1-x}F_x \) \( (R=\text{Tb} \) and \( \text{Dy}) \) were published elsewhere.12 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 \( \approx 80\% \) by mass of the superconducting phase with residual nonsuperconducting \( \text{RO}_3 \) and \( \text{RA} \) 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 \( \text{TbFeAsO}_{1-x}F_x \) 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 \( \text{DyFeAsO}_{1-x}F_x \) samples did not show higher transitions than before, so we conclude that \( T_c(\text{max}) \) in this system is 45 K.

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

![Fig. 1. Resistivity and (inset) susceptibility data for an optimum sample of \( \text{TbFeAsO}_{0.9}F_{0.1} \), showing a sharp superconducting transition at \( T_c=51 \) K. The sample was prepared at 7 GPa and 1050 °C.](image-url)
in Table I. Crystal structure refinements and phase analysis were carried out by fitting powder x-ray diffraction data (Fig. 2). Magnetization measurements demonstrate that all six HoFeAsO$_{1-x}$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 HoFeAsO$_{1-x}$F$_x$ phase and corresponding variations in superconducting properties. $T_c$ increases to a maximum value, $T_c$\textsubscript{max}, at the upper solubility limit of $x$ in RFeAsO$_{1-x}$F$_x$ systems,\cite{7} 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 HoFeAsO$_{1-x}$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 $T_c$\textsubscript{max} for the HoFeAsO$_{1-x}$F$_x$ system.

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

![FIG. 3](image_url) Superconductivity measurements for HoFeA$_{0.9}$F$_{0.1}$: (a) ac magnetic volume susceptibility for the six samples; (b) resistivities for samples 4 and 6.
optimum doping in the $T_c$ The covered change in the sign of the compositional parameters $R$ shows. The fit of equation $T_c(\text{max})=T_c(\text{max})\cos(\phi-\phi_0)$ with parameters $T_c(\text{max})=56$ 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 $R=$La (Ref. 19), Sm (Ref. 7), and Ho (this Brief Report) systems.

Fe-As angle corresponding to the global maximum $T_c$, $\phi_{\text{max}}=110.5^\circ$, is close to the ideal $109.5^\circ$ value for a regular FeAs$_4$ tetrahedron. All five of the Fe 3$d$ bands are partially occupied and contribute to the Fermi surface of the iron arsenide superconductors through hybridization with As 4$s$ and 4$p$ states. Decreasing the tetrahedral angle through $109.5^\circ$ marks the crossover from tetragonal compression to elongation of the 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 RFeAs$_{1-x}$F$_x$ systems. The unit-cell parameters and volume for the six HoFeAs$_{1-x}$F$_x$ samples in Table I show a positive correlation with $dT_c/dV$ as $R$ changes from La to 36 K for the previously unreported Ho analog. Hence, the effect on the lattice of substituting smaller late rare earths in the $R$FeAs$_{1-x}$F$_x$ lattice suppresses superconductivity. This lattice control appears to be through tuning of the interatomic angles in the 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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11Samples were synthesized from stoichiometric amounts of RAs, FeO$_2$, FeF$_2$, and Fe, using a Walker multianvil module within a 100 ton press. The products were dense, black, sintered polycrystalline pellets. Powder x-ray diffraction data were collected on a Bruker AXS D8 diffractometer using Cu K$_\alpha_1$ radiation. Data were recorded at 10 $\leq 2\theta \leq 100^\circ$ with a step size of 0.007$^\circ$ for Rietveld analysis. ac magnetic susceptibility was measured from 3 to 50 K with a field of 0.5 Oe oscillating at 117 Hz using a Quantum Design SQUID magnetometer. Electrical resistivity was measured by a four-probe method between 1.7 and 300 K using a Quantum Design physical property measurement system and an APD cryocenics closed cycle refrigeration unit with an in-house built sample stage.
13HoFeAsO$_3$F$_{0.1}$ has a tetragonal structure (space group P4/mmm; 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 $a =3.828(2)$ Å, $c=8.2654(7)$ Å; atom positions [x,y,z] and isotropic temperature (U) factors; Ho [1/2,1/2,0.1454(4)], 0.044(2) $Å^2$; As [1/2,1/2,0.6659(5)], 0.029(2) $Å^2$; Fe (0,0,0), 0.014(2) $Å^2$; O.F (1/2,1/2,0) 0.26(2) $Å^2$). The secondary Ho$_2$O$_3$ 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, $c =8.6081(1)$ Å, $\beta=100.08$° ($^\circ$).
18The compositional $dT_c/dV$ quantifies the changes in $T_c$ and unit-cell volume $V$ due to variations in doping level $x$ at constant (atmospheric) pressure, and is complementary to the pressure-induced $dT_c/dV$ at constant $x$. Both derivatives are negative for LaFeAsO$_1-x$F$_x$, and we thus predict a positive pressure-induced $dT_c/dV$ (pressure suppression of superconductivity) for HoFeAsO$_1-x$F$_x$.