Recently, high-transition-temperature (high-$T_c$) superconductivity was discovered in the iron pnictide RFeAsO$_{1-x}$F$_x$ ($R$, rare-earth metal) family of materials. We use neutron scattering to study the structural and magnetic phase transitions in CeFeAsO$_{1-x}$F$_x$ as the system is tuned from a semimetal to a high-$T_c$ superconductor through fluorine (F) doping, $x$. In the undoped state, CeFeAsO develops a structural lattice distortion followed by a collinear antiferromagnetic order with decreasing temperature. With increasing fluorine doping, the structural phase transition decreases gradually and vanishes within the superconductivity dome near $x = 0.10$, whereas the antiferromagnetic order is suppressed before the appearance of superconductivity for $x > 0.06$, resulting in an electronic phase diagram remarkably similar to that of the high-$T_c$ copper oxides. Comparison of the structural evolution of CeFeAsO$_{1-x}$F$_x$ with other Fe-based superconductors suggests that the structural perfection of the Fe–As tetrahedron is important for the high-$T_c$ superconductivity in these Fe pnictides.

A detailed analysis of the low-temperature CeFeAsO$_{1-x}$F$_x$ structures reveals that F doping does not change the Fe–As distance but reduces the Ce–As distance and Fe–As–Fe angles (Fig. 4). These results suggest that the main effect of F doping is to transfer electrons from the Ce–O/F layers to the As–Fe–As block (Fig. 4a), thereby decreasing the distance between them with electron doping due to increased Coulomb attraction. Comparison of the structural evolution of CeFeAsO$_{1-x}$F$_x$ with other rare-earth Fe pnictides and (Ba$_{1-x}$K)$_x$Fe$_2$As$_2$ (refs 12,25) suggests that the Fe–As–Fe bond angle decreases systematically for materials...
with increasing $T_c$ (Fig. 5). The results suggest that the structural perfection of the Fe–As tetrahedron is crucial for the high-$T_c$ superconductivity in these Fe pnictides.

We use neutron diffraction to study the structural and magnetic phase transitions in polycrystalline non-superconducting CeFeAsO$_{1-x}$F$_x$ with $x = 0, 0.02, 0.04$ and 0.06 and superconducting CeFeAsO$_{1-x}$F$_x$ with $x = 0.08, 0.10$ and 0.16. $T_c$ values for $x = 0.08$ and 0.10 are shown in the insets of Fig. 3a and b respectively, and $T_c$ for $x = 0.16$ is $35$ K; all measurements were determined by susceptibility measurements using a commercial superconducting quantum interference device. Our samples are made using the method described in ref. 8. Our neutron experiments were carried out on the BT-1 high-resolution powder diffractometer and BT-7 thermal triple-axis spectrometer at the NIST Center for Neutron Research, Gaithersburg, Maryland. Some measurements were also carried out on the HB-3 thermal triple-axis spectrometer at the High Flux Isotope Reactor, Oak Ridge National Laboratory.

In previous work, it was found that LaFeAsO undergoes a structural distortion below 155 K, changing the symmetry from tetragonal (space group P4/nmm) to monoclinic (space group P112/m) (ref. 13) or orthorhombic (space group Cmma) (ref. 26), followed by a long-range commensurate AFM order with a collinear spin structure below $\sim 137$ K (ref. 13). For convenience in comparing the low-temperature nuclear and magnetic structures, we use the orthorhombic Cmma space group to describe the low-temperature structural data in this article. As CeFeAsO$_{1-x}$F$_x$ has rare-earth Ce, which carries a local magnetic moment and therefore is different from the non-magnetic La in LaFeAsO$_{1-x}$F$_x$ (ref. 13), we first need to determine whether this material has the same lattice distortion and magnetic structure as LaFeAsO$_{1-x}$F$_x$. Our high-resolution neutron powder diffraction measurements on BT-1 confirm that the lattice symmetry of CeFeAsO also exhibits the tetragonal to orthorhombic transition below $\sim 158$ K (Figs 1d and 2a), where the $(2,2,0)$ peak in the tetragonal phase is split into $(0,4,0)_0$ and $(4,0,0)_0$ peaks in the orthorhombic phase (Fig. 2a, inset).

To see if the Fe spins in CeFeAsO exhibit the same magnetic order as that of LaFeAsO (ref. 13), we carried out measurements on BT-7. The Ce moments order magnetically below $\sim 4$ K (ref. 8 and Fig. 2e), and thus we took data at 40 K to avoid any possible induced-moment influence of Ce on the intensities of the Fe magnetic peaks (Fig. 1c). Comparison of Fig. 1c with the same scan at 160 K (see Supplementary Information) and with Fig. 3c in ref. 13 for LaFeAsO immediately reveals that the Fe magnetic unit cell in CeFeAsO can be indexed as $\sqrt{2}a_N \times \sqrt{2}b_N \times c_N$, where $a_N$, $b_N$ and $c_N$ are nuclear lattice parameters of the unit cell (see Table 1). This indicates that CeFeAsO has the same collinear in-plane Fe AFM structure as that of LaFeAsO, but the $c$-axis nearest-neighbour spins are parallel in CeFeAsO rather than anti-parallel as in LaFeAsO. Hence, there is no need to double the unit cell along the $c$ axis (Fig. 1a), and an excellent fit to the data is achieved using the magnetic and nuclear unit cells in Fig. 1a,b, as shown by the solid red line in Fig. 1c. The ordered iron moment is $0.8(1)\mu_B$ at 40 K, where numbers in parentheses indicate uncertainty in the last decimal place and $\mu_B$ denotes the Bohr magneton. The magnitude of the Fe moment...
in CeFeAsO is about twice that of the Fe ordered moment in LaFeAsO (ref. 13). We also determined the Ce magnetic structure using data collected at 1.7 K (see Supplementary Information) and found a strong coupling between the Fe and Ce moments below 20 K (Fig. 2e–g). The Ce and Fe ordered moments at 1.7 K are 0.83(2) $\mu_B$/Ce and 0.94(3) $\mu_B$/Fe, respectively. Our determined

| Temperature (K) | Intensity (counts/3 min) |
|-----------------|---------------------------|
| 2 K             | 400                       |
| 40 K            | 800                       |
| 150 K           | 600                       |

**Figure 2** Structural and magnetic phase transition temperatures as a function of increasing F doping in CeFeAsO$_{1-x}$F$_x$. The data in a–d and e–g were collected on BT-1 and BT-7, respectively. The $Q$-scans for $x = 0.06$ (inset in h) were carried out on HB-3 using a similar set-up as BT-7. The BT-1 diffractometer has a Ge(3,1,1) monochromator and an incident beam wavelength of $\lambda = 2.0785$ Å. a–d, Temperature dependence of the (2,2,0)$_T$ ($T$ denotes tetragonal) neutron scattering nuclear reflection intensity (vertical axes) indicative of a structural phase transition$^{13}$ for various $x$. The insets show the neutron scattering (2,2,0)$_T$ reflection intensity (in arbitrary units) as a function of scattering angle above and below the transition temperatures$^{13}$. a–d. Temperature dependence of the order parameter at the magnetic Bragg peak position (1,0,2)$_M$ as a function of F doping. The intensity in vertical axes is obtained by subtracted the measured (1,0,2)$_M$ peak intensity from the background scattering at positions away from the Bragg peak. The large increase in intensity below 4 K is due to Ce ordering, as confirmed by the temperature dependence of the Ce-only magnetic Bragg peak (0,0,1)$_M$ (see Supplementary Information). The inset in h shows the doping dependence of the (1,0,2)$_M$ Bragg peak normalized to the nuclear Bragg peak intensity. The peak positions and widths are essentially doping independent, suggesting that the AFM order is commensurate at all doping levels. The error bars indicate one standard deviation.
Ce and Fe magnetic structures are shown in Fig. 1a,b. However, we caution the reader that future single-crystal work might be necessary to confirm the proposed Ce spin structure in Fig. 1a. The lack of the c-axis unit-cell doubling in the Fe magnetic structure of CeFeAsO is different from that of LaFeAsO, but identical to the Fe spin structure in PrFeAsO, which has an Fe ordered moment of 0.48(9) \( \mu_B/\text{Fe} \) (refs 27,28). On the other hand, Fe magnetic ordering in NdFeAsO has the same spin structure as LaFeAsO but with a moment of only 0.25(7) \( \mu_B/\text{Fe} \) (ref. 29). Assuming that the observed AFM order in different rare-earth oxypnictides indeed arises from a spin-density-wave (SDW) instability in a nested Fermi surface\(^{19–21,30}\), it is unclear how the different observed Fe AFM structures/moments for different rare-earth oxypnictides can be explained by their differences in band structures, as most of the calculations are carried out for LaFeAsO.

Having shown that the lattice distortion and Fe magnetic unit cells are similar between CeFeAsO and LaFeAsO, it is important to determine the evolution of the lattice and magnetic structures with increasing F doping as superconductivity is induced. If the collinear AFM order in CeFeAsO and LaFeAsO is a SDW instability arising from a nested Fermi surface\(^{19–21,30}\) similar to that of the pure metallic Cr (refs 31,32), electron doping will change the electron and hole pocket sizes, but may induce incommensurate SDW order\(^{31}\). For Cr (refs 31,32), where the SDW order has a long-wavelength incommensurate magnetic structure, electron/hole doping quickly locks the SDW to commensurate antiferromagnetism with an ordered moment that is doping independent\(^{31}\). Figure 2 summarizes the structural and magnetic phase transition data for CeFeAsO\(_{1-x}F_x\) with \( x = 0, 0.02, 0.04 \) and 0.06. Inspection of Fig. 2a–d and its insets immediately reveals that the onset lattice distortion temperature (seen as the initial drop in the (2,2,0)\(_T\) peak intensity) and the magnitude of the lattice distortion (the low-temperature splitting of the (0,4,0)\(_O\) and (4,0,0)\(_O\) peaks) both decrease gradually with increasing \( x \) (Fig. 1d).

To see if the tetragonal to orthorhombic structural phase transition in CeFeAsO\(_{1-x}F_x\) can survive superconductivity, which appears for samples with \( x > 0.06 \) (ref. 8), we carried out extra measurements on \( x = 0.08 \) and 0.10 samples at BT-1 and BT-7. Susceptibility measurement data in the insets of Fig. 3a,b show the onset of superconductivity at 27 K and 33 K for \( x = 0.08 \) and 0.10 samples, respectively. Although the (2,2,0)\(_T\) peak does not reveal a clear splitting at 1.5 K indicative of an antiferromagnetic distortion for the \( x = 0.08 \) sample, its width at low temperature is clearly broader than that at 175 K owing to the orthorhombic distortion (Fig. 3a). Detailed analysis of the BT-1 spectra confirms that the Cmma space group describes the low-temperature data better than the P4/mmm space group, thus indicating that superconductivity can survive in either the tetragonal or orthorhombic crystal structure.
(2,2,0)_T peak. Figure 3c shows the full-width at half-maximum (FWHM) of the peak as a function of temperature and it is clear that the tetragonal to orthorhombic phase transition occurs near 60 K. For comparison, we also carried out similar measurements for the x = 0.10 sample (Fig. 3b). Although analysis of the low-temperature BT-1 spectrum again suggests that the Cmma space group fits the data better than the P4/nmm space group, the diminishing differences between the tetragonal and orthorhombic crystal structures means we were unable to determine a structural phase transition temperature. Thermal triple-axis measurements on the x = 0.08 sample reveal no evidence of static long-range AFM Fe ordering (Fig. 3d), thus suggesting that static AFM order competes directly with superconductivity. To summarize the systematic work of Figs 2 and 3, we plot in Fig. 1d the structural and magnetic phase diagram of CeFeAsO_{1-x}F_x together with superconducting transition temperatures determined from susceptibility measurements on neutron samples and earlier work\(^6\). These results are remarkably similar to the phase diagram of copper oxides\(^3\)–\(^5\), and may have important theoretical implications\(^6\)–\(^18\).

Figure 4 summarizes the impact of F doping on the crystal structure of CeFeAsO_{1-x}F_x obtained from our detailed refinement analysis of the BT-1 data. The undoped CeFeAsO has an orthorhombic low-temperature structure with c > a > b (Fig. 4a). Doping fluorine gradually suppresses both the a- (the long Fe–Fe nearest-neighbour distance) and c-axis lattice constants while leaving the b axis (the short Fe–Fe nearest-neighbour distance) essentially unchanged (Fig. 4b). The system almost becomes tetragonal at x = 0.10 with a = b, and the c-axis lattice constant continues to decrease with increasing doping for x > 0.10. The reduction in the c-axis lattice constant is achieved through a large reduction of the Ce–As block distance, while the Ce–O/F and As–Fe–As block distances actually increase with increasing F doping (Fig. 4c,e). This suggests that the effect of F doping is to bring...
the Ce–O/F charge transfer layer closer to the superconducting As–Fe–As block, thereby facilitating electron charge transfer (Fig. 4a) as confirmed by recent X-ray absorption spectroscopy measurements. As the Fe–As distance (2.405 Å) is essentially doping independent (Fig. 4e), the strong hybridization between the Fe 3d and the As 4p orbitals is not affected by electron doping. On the other hand, if we assume that the Fe–Fe nearest-neighbour (J₁) and next-nearest-neighbour effective exchange couplings (J₂) are mediated through the electron Fe–As–Fe hopping and controlled by the Fe–As–Fe angles, Fig. 4d suggests that J₂ and one of the nearest-neighbour exchange constants (J₁) decrease with increasing doping while the other J₁ remains unchanged.

In a previous study on the phase diagram of oxygen-deficient RFeAsO₁₋ₓ (ref. 9), it was found that systematically replacing R from La to Ce, Pr, Nd and Sm in RFeAsO₁₋ₓ resulted in a gradual decrease in the a-axis lattice parameters and an increase in Tc. If Tc for different Fe-based superconductors is indeed correlated to their structural properties, a systematic trend between Tc and the Fe–As–Fe bond angles would be expected to be found, because the exchange couplings (J₁ and J₂) are directly related to the Fe–As–Fe bond angles (Fig. 5a). Figure 5b,c shows the Fe–As(P)–Fe angles and Fe–Fe/Fe–As(P) distances versus maximum Tc for different Fe-based rare-earth oxypnictides (ref. 10) and Ba₁₋ₓKₓFe₂As₂ (ref. 12) superconductors. Although the Fe–Fe/Fe–As(P) distances may not have a clear trend amongst different Fe-based superconductors (Fig. 5c), it is remarkable that the maximum Tc seems to be directly related to the Fe–As(P)–Fe angles for a variety of materials (Fig. 5b) and the highest Tc is obtained when the Fe–As(P)–Fe angle reaches the ideal value of 109.47° for the perfect FeAs tetrahedron with the least lattice distortion. This suggests that the most effective way to increase Tc in Fe-based superconductors is to decrease the deviation of the Fe–As(P)–Fe bond angle from the ideal FeAs tetrahedron, as the geometry of the FeAs tetrahedron might be correlated with the density of states near the Fermi energy.

In summary, we have mapped out the structural and magnetic phase transitions of CeFeAsO₁₋ₓFₓ and found that the Fe static AFM order essentially vanishes before the appearance of superconductivity. The phase diagram of CeFeAsO₁₋ₓFₓ is therefore remarkably similar to that of the electron-doped high-Tc copper oxides (ref. 3). In a recent μSR and Mössbauer spectroscopy study on the phase diagram of LaFeAsO₁₋ₓFₓ, Luetkens et al. argue that the antiferromagnetism to superconductivity transition is first order and the orthorhombic structure does not coexist with superconductivity. In contrast, X-ray scattering and μSR experiments on SmFeAsO₁₋ₓFₓ suggest coexistence of static antiferromagnetism and the orthorhombic structure with superconductivity in the underdoped regime. Although our neutron diffraction experiments confirm no static AFM order for LaFeAsO₁₋ₓFₓ at x = 0.05, consistent with the μSR study, we find clear evidence for the orthorhombic lattice distortion. These results suggest that the orthorhombic structure can survive superconductivity in LaFeAsO₁₋ₓFₓ, much like CeFeAsO₁₋ₓFₓ discussed here and SmFeAsO₁₋ₓFₓ (ref. 41). As superconductivity in the LaFeAsO₁₋ₓFₓ (refs 60, 40), CeFeAsO₁₋ₓFₓ,}}
In addition to suppressing the static antiferromagnetism and inducing superconductivity, F doping also reduces the long axis of the orthorhombic structure and decreases the Fe–As–Fe bond angle. Comparison of the structural parameters of various Fe-based superconductors reveals that the Fe–As–(F)–Fe bond angle decreases systematically for superconductors with increasing T_c values and reaches its maximum value for the ideal FeAs tetrahedral angle. This means that the structural distortion from the ideal FeAs tetrahedron is critical to the superconducting transition temperature and must be taken into account as we consider a mechanism for high-T_c superconductivity in these Fe-based materials.

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