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Suppression of orbital ordering by chemical pressure in $FeSe_{1-x}S_x$

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We report a high-resolution angle-resolved photoemission spectroscopy study of the evolution of the electronic structure of $FeSe_{1-x}S_x$ single crystals. Isovalent S substitution onto the Se site constitutes a chemical pressure which subtly modifies the electronic structure of FeSe at high temperatures and induces a suppression of the tetragonal-symmetry-breaking structural transition temperature from 87 to 58 K for $x = 0.15$. With increasing S substitution, we find smaller splitting between bands with d_{yz} and d_{xz} orbital character and weaker anisotropic distortions of the low-temperature Fermi surfaces. These effects evolve systematically as a function of both S substitution and temperature, providing strong evidence that an orbital ordering is the underlying order parameter of the structural transition in $FeSe_{1-x}S_x$. Finally, we detect the small inner hole pocket for $x = 0.12$, which is pushed below the Fermi level in the orbitally ordered low-temperature Fermi surface of FeSe.

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The nature and origin of the ordered phases found in proximity to high-temperature superconductivity relate directly to the mechanism of unconventional superconductivity [1]. In the iron-based superconductors, the parent nonsuperconducting phases typically exhibit a magnetic stripe ordering, which breaks fourfold symmetry. However, in certain regions of the phase diagram, the fourfold symmetry of the lattice is broken at a higher temperature T_s than the onset of magnetism. One explanation is that this so-called *nematic* phase nevertheless originates from magnetic interactions, which in some models may pick out a particular direction to break fourfold symmetry without long-range magnetic ordering [1]. Alternatively, it has been suggested that T_s corresponds to an orbital instability breaking the degeneracy of the Fe d_{xz} and d_{yz} orbitals, distinct from magnetic order [2–5]. FeSe provides a fascinating test case for these ideas, since it undergoes a structural transition at $T_s = 87$ K but does not magnetically order [6] and has been the subject of intense theoretical study [7–9]. Detailed studies of the electronic structure in the tetragonal-symmetry-broken phase [10–14] have found a prominent splitting of bands with d_{xz} and d_{yz} orbital character, which also manifests in strong distortions of the Fermi surface. However, this *orbital ordering* has been found to be sensitive to both physical pressure [15,16] and substrate-induced strain in multilayer thin film samples [13,17]. Chemical pressure, as in isovalently substituted $FeSe_{1-x}S_x$, provides another tuning parameter which can be used to study how the electronic structure evolves as orbital order is suppressed, helping to establish the nature of the order parameter associated with T_s, and determining to what extent the orbital fluctuations found in proximity to the ordered phase may play a role in the unconventional superconductivity.

In this Rapid Communication we report a high-resolution angle-resolved photoemission spectroscopy (ARPES) study of the electronic structure of S-substituted β-FeSe single crystals. In the high-temperature tetragonal phase, we find that the sizes of the Fermi surfaces and the Fermi velocities both increase with S substitution. The suppression of the structural transition T_s by S substitution correlates with a reduction of the electronic anisotropy and the splitting of bands with d_{xz} and d_{yz} orbital characters, which onset at T_s. This provides strong evidence that the instability towards orbital ordering drives the fourfold symmetry-breaking transition. Finally, we show that the inner hole pocket which is pushed below the Fermi level in the orbitally ordered low-temperature Fermi surface of FeSe [10] does cross the Fermi level in $FeSe_{1-x}S_x$ for $x = 0.12$.

Experimental details. Samples were grown by the $KCl/AlCl_3$ chemical vapor transport method [18,19]. ARPES measurements were performed at the I05 beamline at the Diamond Light Source, UK. Single crystal samples with sizes $\approx 1 \times 1$ mm were cleaved *in situ* below 15 K at a pressure lower than 2×10^{-10} mbar. Samples were carefully oriented with the scattering plane along M-Γ-M (Fe-Fe bond direction). Measurements were performed using linearly polarized synchrotron light at 20–80 eV, employing a Scienta R4000 hemispherical electron energy analyzer. Band structure calculations were performed in WIEN2K [20] using the generalized gradient approximation [21].

High-temperature ARPES data. Figure 1 shows a comparison of ARPES data of $FeSe_{1-x}S_x$ single crystals for $x = 0$ and $x = 0.15$ at temperatures above T_s. The quality of the ARPES spectra of the substituted crystals remains high, since the Fe $3d$ orbitals which dominate the low-energy electronic structure are not directly affected by the substitutional disorder outside of the Fe plane. The comparison between the ARPES spectra and the density functional theory (DFT) calculations in Fig. 1 reveals several important differences, as has been previously reported [10–13]. First, all observed pockets are substantially smaller than DFT predictions [10]. Secondly, the predicted γ hole band with d_{xy} character [Fig. 1(c)] is found to not cross the Fermi level but remains ~ 50 meV below it [Fig. 1(d)] with a particularly large band renormalization of ~ 8 compared to the other bands [10,22]. Thirdly, the outer electron band δ with d_{xy} character is not observed in experiments [Fig. 1(g)].

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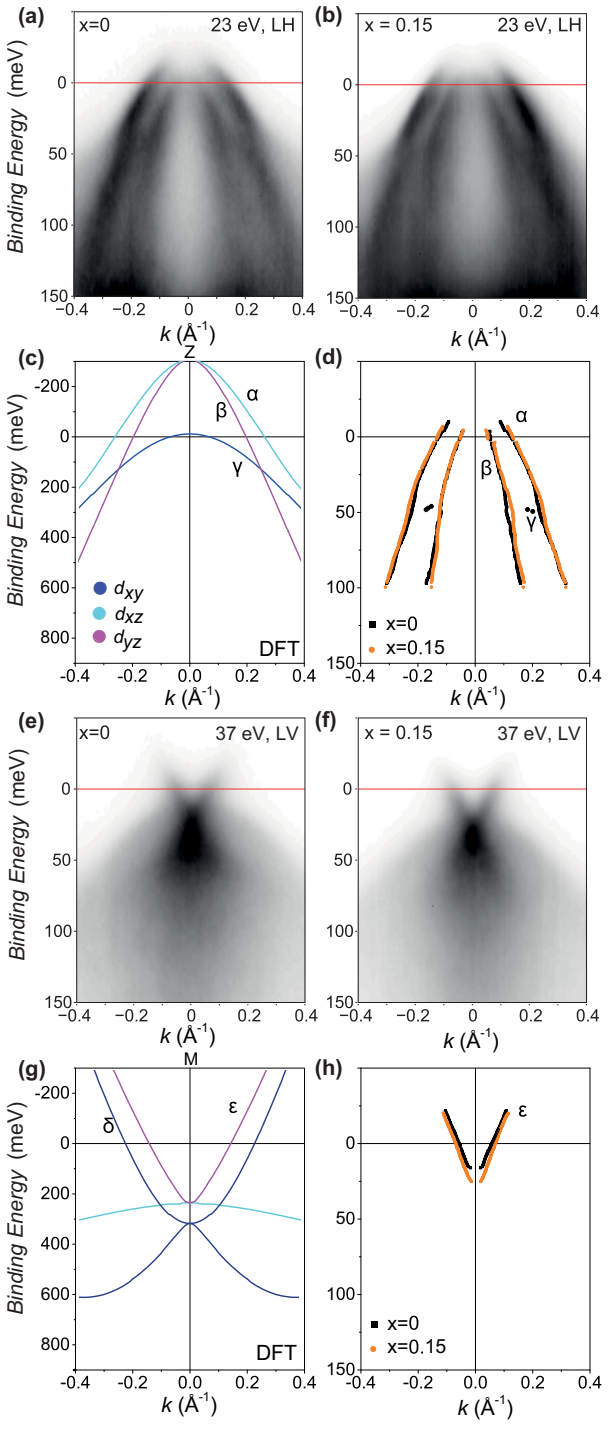

FIG. 1. (Color online) High-temperature electronic structure of $FeSe_{1-x}S_x$. ARPES data for (a) $x = 0$ and (b) $x = 0.15$ for the holelike bands at the Z point (measured using a photon energy of 23 eV). (c) Band dispersions from a DFT calculation at the Z point, compared to (d) the extracted peak positions (from fits to MDCs) for $x = 0$ and $x = 0.15$. (e)–(h) ARPES data, DFT calculation, and extracted band positions for the electron pockets at the M point (at 37 eV). The predicted outer electron band δ with d_{xy} orbital character is not observed. Bands are labeled $\alpha - \epsilon$, as in previous studies [10,22].

The effect of substituting smaller S ions onto the Se site results in a lattice contraction [23] and intuitively might result in a greater orbital overlap, increasing the bandwidth. In order to perform a quantitative comparison, we extract the band positions from constrained fits to the momentum distribution curves (MDCs), focusing on the high-symmetry cuts through the Z and M points, as shown in Figs. 1(d) and 1(h) for $x = 0$ and $x = 0.15$ and summarized in Table I in the Supplemental Material (SM) [24]. We find two systematic features as a function of S substitution: the Fermi surfaces generally increase in size, and additionally the Fermi velocities (dE/dk at E_F) increase, although both only by $\sim 10\%$. These two trends may explain the suppression of T_s, since an increase in the size of Fermi surfaces is likely to reduce the degree of particle-hole Fermi surface nesting (which would be perfect in the limit of pointlike Fermi surfaces), while the increase in Fermi velocities corresponds to a reduction in the density of states at the Fermi level, reducing the bare susceptibility and thereby suppressing the orbital instability.

Suppression of orbital ordering with S substitution. In Figs. 2(a)–2(h) we show how the electron pockets observed in a cut through the M point evolve with S substitution, above and below T_s. At high temperatures, only the ϵ band (with d_{xz}/d_{yz} orbital character and defined in Fig. 1) is observed [25]. A prominent feature of ARPES studies of FeSe in both bulk crystals [10,11] and multilayer thin films [13,17] is a splitting of intensity at the M point below T_s, which we denote Δ_M. This splitting, reaching $\Delta_M = 49(2)$ meV for bulk FeSe, corresponds to a splitting of the bands with d_{yz} and d_{xz} orbital characters at the M point in the Brillouin zone [10–13], which are degenerate in the high-temperature fourfold-symmetric phase. The value of Δ_M is much larger than what would be expected from DFT calculations simply taking into account the small orthorhombic distortion of the lattice [10], which was taken to be one indication that the structural transition at T_s is primarily an electronic instability, and more specifically due to orbital ordering. Therefore, the splitting Δ_M, extracted from the positions of peaks in the energy distribution curve (EDC) at the M point [Fig. 2(k)], is one experimental proxy order parameter for the orbital ordering which can be studied as a function of temperature and S substitution.

The orbital ordering, which can alternatively be described as the development of an orbital polarization $\Delta n = n_{xz} - n_{yz}$, also manifests as a distortion of the Fermi surface. As shown in the low-temperature Fermi surface map in Fig. 2(j), sections of the electron pockets with d_{yz} orbital character contract while d_{xz} sections expand, leaving an elongated and anisotropic Fermi surface, which is observed to form a cross shape due to the effect of sample twinning [10]. Experimentally, we can extract the Fermi wavevector k_F of the d_{yz} portion of the electron pocket from peak fits of the MDC at E_F [see Figs. 2(e)–2(h)] and follow the Fermi surface distortion as a function of temperature, as shown in Fig. 2(l). This provides another proxy order parameter for the orbital ordering, which we define as $\Delta k_F = k_F - k_{F0}$ [10], where k_{F0} is the Fermi wavevector k_F just above T_s in the tetragonal phase.

Figures 2(m) and 2(n) show how these two proxy order parameters for the orbital ordering, the band splitting Δ_M and Fermi surface distortion Δk_F, both evolve systematically as a function of temperature and S substitution. The onset of both

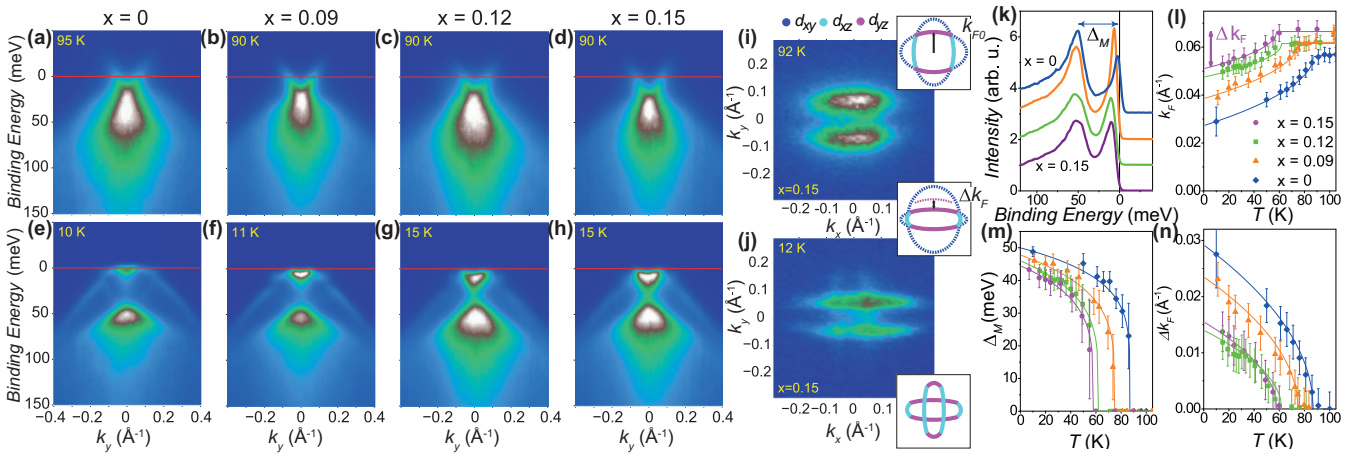

FIG. 2. (Color online) Suppression of orbital ordering with S substitution on the electron pockets. (a)–(h) ARPES data for a cut through the M point (Γ-M-Γ direction) at low and high temperatures for $FeSe_{1-x}S_x$ with $x = 0$–0.15 showing the prominent splitting of intensity below T_s. (i) High- and (j) low-temperature Fermi surface maps for $x = 0.15$. Cartoon insets show schematic Fermi surface above T_s (top), which is distorted below T_s (middle), and the experimental case of twinned crystals where the d_{xy} electron band is not observed (bottom). (k) Comparison of low-temperature EDCs at the M point showing the reduction of the splitting parameter, Δ_M, with S substitution. (l) Temperature dependencies of the Fermi k_F vector of the d_{yz} portion of the Fermi surface, indicating a distortion Δk_F which onsets at T_s. The temperature dependence of the extracted order parameters of the orbital ordering, (m) Δ_M and (n) Δk_F, as a function of S substitution, as discussed in the main text. Solid lines are guides to the eye.

parameters coincides with T_s (as determined separately from anomalies in resistivity measurements [26]) and both follow an order-parameter-like temperature dependence, as shown in Figs. 2(m) and 2(n). The fact that both order parameters decrease systematically with S substitution is strong evidence that the reduction of orbital ordering is directly related to the suppression of T_s in $FeSe_{1-x}S_x$ (see also Fig. 4).

The emergence of the inner hole band for $x = 0.12$ at low temperatures. We now consider the evolution of the hole pockets with S substitution at low temperatures, as shown in Fig. 3. Similar to the electron pockets, the degree of Fermi surface anisotropy on the hole pockets reduces with S substitution, as indicated by the reduced splitting of the two k_F values of the outer hole band, α, as shown in Figs. 3(a)–3(f) and Table I in the SM. In all samples at high temperature the inner β hole band forms a tiny three-dimensional (3D) pocket around Z [see Figs. 1(a) and 1(b)], where a splitting of $\sim$20 meV [10] between the α and β hole bands occurs due to spin-orbit coupling only [27]. At low temperature an extra splitting associated with the orbital ordering [27] pushes the β band below the Fermi surface [10,14] in FeSe, as can be seen by the lack of features in the Fermi level MDC for FeSe in Fig. 3(a). However, as the orbital ordering is reduced with S substitution, this inner pocket can exist at low temperatures once more, and is clearly observed at $x = 0.12$ [Fig. 3(c)]. The photon-energy dependence shown in Fig. 3(g) (which is equivalent to a k_z dispersion) shows that it forms a 3D pocket around Z, not extending throughout the Brillouin zone, and also seen in the detailed map of the Fermi surface around the Z point in Fig. 3(h). This pocket will also break fourfold symmetry, as indicated by the inset to Fig. 3(h). This new hole pocket could appear as an additional low frequency in quantum oscillation measurements [26] in addition to those corresponding to three different bands in previous reports [10,28,29].

Figure 4(a) shows a proposed phase diagram of $FeSe_{1-x}S_x$ based on the experimental values of the structural and superconducting transition temperatures extracted from our resistivity measurements (to be presented elsewhere [26]) and Refs. [23,30]. With S substitution there is a strong suppression of the structural transition, whereas the T_c of the superconducting state remains relatively constant for low x. As shown in Figs. 4(b) and 4(c), both the low-temperature Δ_M and $\Delta k_F/k_{F0}$ extracted from our ARPES data reduce with x, correlating with T_s in the phase diagram. A similar trend was also found in thin films [11,17], where Δ_M and T_s are found to increase for thinner samples which are more strained. Thus, the systematic change of the degree of orbital ordering with S substitution, as measured by our two experimental proxy order parameters, indicates that the true electronic order parameter associated with the structural transition in $FeSe_{1-x}S_x$ is the orbital polarization $\Delta n = n_{xz} - n_{yz}$. Therefore, the transition at T_s corresponds to an instability of the electronic structure of this iron-based superconductor in the charge/orbital channel, which is distinct from the stripe spin density wave phase observed in other systems such as $BaFe_2As_2$.

Studies of FeSe under applied physical pressure have found that the structural transition T_s is initially suppressed in a similar manner to the chemical pressure effect of S substitution [15,16], although the magnetic phase [15,31] and high-temperature superconductivity [32] found under higher physical pressures have not been reported to occur in $FeSe_{1-x}S_x$ [23,30] (at ambient pressure [33]). NMR studies found that spin fluctuations in FeSe increase in magnitude with physical pressure [34] while T_s is suppressed [15,16], suggesting that magnetic interactions are not crucial for the structural instability. On the other hand, our ARPES results show a direct correlation between the decrease in T_s and the suppression of orbital ordering under chemical pressure

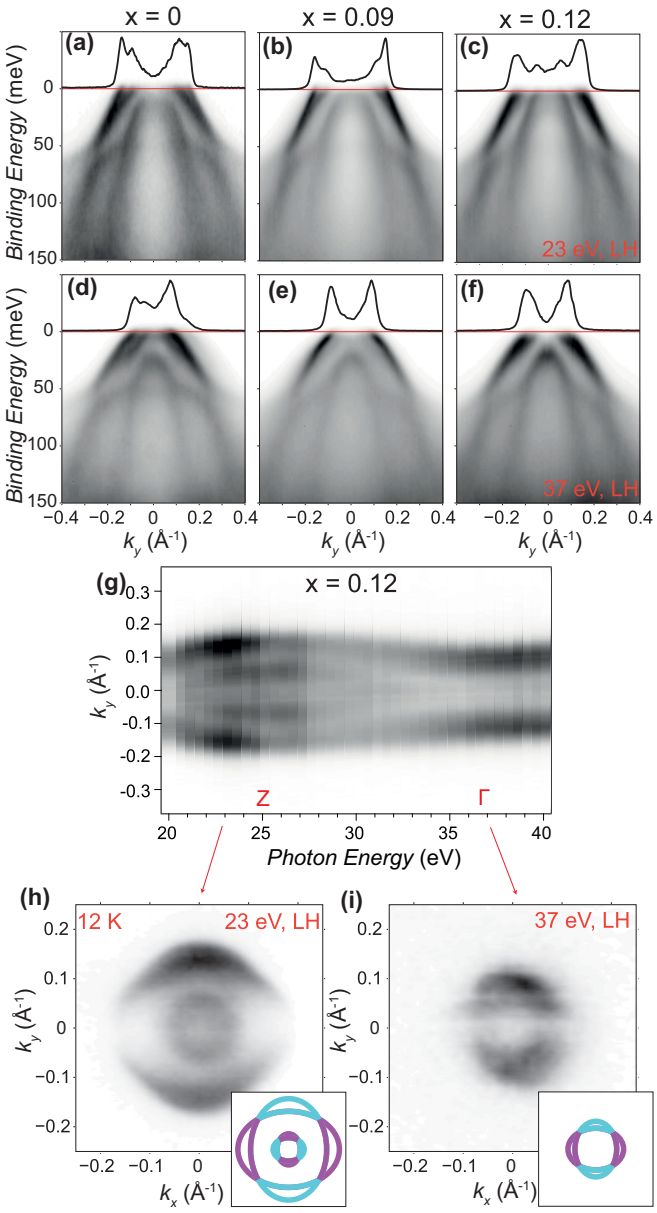

FIG. 3. (Color online) Emergence of the small inner hole band at low temperatures for $x = 0.12$. (a)–(c) ARPES data for a high-symmetry cut through the center of the Brillouin zone at 23 eV (near the Z point) at $T \approx 11$ K for $x = 0$–0.12. Solid black lines are the MDCs at the Fermi level, indicating the splitting of the outer hole band α and the emergence of the inner β band for $x = 0.12$. (d)–(f) As above, but for a cut at the Γ point (37 eV). (g) Photon energy dependence of the Fermi level MDC at $x = 0.12$, indicating that the inner hole band forms a 3D pocket around the Z point, as also shown by the Fermi surface maps at (h) the Z (23 eV) and (i) Γ point (37 eV). Cartoon insets show how the apparent splitting of bands arises from Fermi surface distortion and sample twinning.

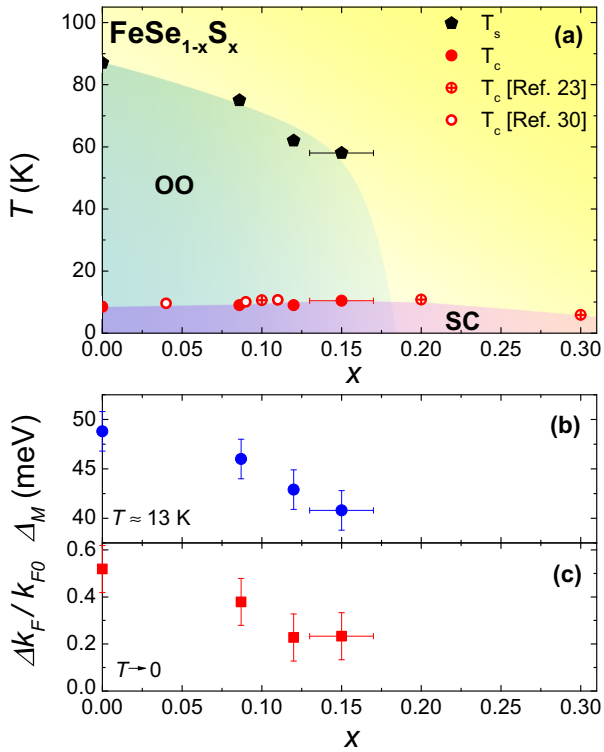

FIG. 4. (Color online) Proposed phase diagram of $FeSe_{1-x}S_x$. (a) T_s and T_c values extracted from our resistivity measurements [26], compared to literature values of T_c reported in Ref. [23] (resistivity midpoint) and Ref. [30] (heat capacity). OO and SC refer to orbital order and the superconducting phase, respectively. (b) and (c) Evolution of the band splitting, Δ_M, and Fermi surface deformation, $\Delta k_F / k_{F0}$, with S substitution at low temperature, demonstrating that the magnitude of the orbital ordering is directly correlated with the suppression of T_s.

(Fig. 4). However, the fact that the superconductivity in $FeSe_{1-x}S_x$ seems to be almost independent of the orbital ordering and there is no pronounced superconducting dome in the absence of any magnetic phase [Fig. 4(a)] counts against orbital fluctuations providing a major component of the unconventional pairing mechanism. The small size of all Fermi surfaces and the absence of the inner hole pocket, in particular, gives FeSe a very different electronic structure to other Fe-based superconductors. However, the emergence of the inner hole pocket in $FeSe_{1-x}S_x$ could have a significant impact on the susceptibility and pairing interactions, and it is also likely to emerge when orbital ordering is suppressed under physical pressure in FeSe. The exact nature of the orbital ordering is likely to be more complex than simply a uniform site-centred ferro-orbital ordering between d_{xz} and d_{yz} orbitals [7,14,27,35], and future studies using strain to detwin samples may shed light on the details of the orbital mechanism. An alternative viewpoint is that the Fermi surface deformations which are suppressed with S substitution could be interpreted as a manifestation of a d-wave Pomeranchuk instability, which is predicted to be weakened as the size of the Fermi surface increases [36].

In summary, our high-resolution ARPES study of $FeSe_{1-x}S_x$ single crystals has established that the chemical pressure increases the size of the Fermi surface pockets and Fermi velocities at high temperature. Most importantly, we have shown the decrease of T_s is associated with a suppression of orbital order with S substitution, by observing a reduced splitting of d_{xz} and d_{yz} orbitals and weaker Fermi surface anisotropy. These results demonstrate that this orbital ordering

is the true order parameter of the tetragonal-symmetry-breaking transition at T_s in FeSe. Finally, these subtle changes to the electronic structure lead to the appearance of the inner hole band in the low-temperature Fermi surface. $FeSe_{1-x}S_x$ is emerging as a key system to help resolve long-standing controversies related to the role of spin and orbital degrees of freedom in the iron-based superconductors.

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