SUPERCONDUCTIVITY

The FeSe riddle

Electron–phonon coupling has been considered as a possible mechanism behind the high superconducting critical temperature of FeSe monolayers. The doping dependence of the superconductivity casts serious doubt that it plays a decisive role.

I. I. Mazin

The observation of superconductivity in FeSe monolayers[1] grown on $SrTiO_3$ substrates specially prepared to have oxygen vacancies at the surface is probably the most exciting discovery in the last five years in the field of Fe-based superconductors. Spectroscopic probes have shown a superconducting gap persisting at temperatures as high as 65 K (ref. 2), and there is some evidence that the onset may be as high as 100 K (ref. 3). Different superconducting pairing mechanisms, including spin fluctuations and electron–phonon coupling, have been summoned to explain this high critical temperature, T_c. Writing in *Nature Materials*, Kosuke Nakayama and colleagues shed some light on this lively debate, by investigating the superconducting behaviour of FeSe mono- and multilayers grown on $SrTiO_3$ and its evolution with potassium doping[4]. The results demonstrate a common pairing mechanism in FeSe monolayers and other Fe-based superconductors.

The Fermi surfaces of pnictides and bulk FeSe are characterized by two or more hole bands in the centre, Γ, of the Brillouin zone and two electron bands in the corner, M, as shown in Fig. 1a. In these materials, antiferromagnetic spin fluctuations with the wavevectors close to **ΓM** span these two sets of the Fermi surfaces and can cause pairing. This superconducting state is called $s_{\pm}$, because it has the full rotational symmetry, and the superconducting order parameter flips its sign between both sets[5]. In fact, a sign change of the order parameter is a nearly universal requirement in the presence of strong spin fluctuations.

The topology of the Fermi surface in FeSe monolayers, however, is different: the hole pockets sink below the Fermi level. (See Fig. 1a and b for comparison.) This topology may still allow the formation of $s_{\pm}$ superconductivity, but only in the weak coupling regime, where the coupling constant $\lambda << 1$. However, in this regime T_c is proportional to e^{-1/λ^2}, and thus strongly suppressed[5]; on the contrary, T_c in FeSe monolayers reaches record values among Fe-based superconductors.

Although the electron–phonon interaction is very weak in pnictides, an enhancement through proximity with the substrate could provide an alternative explanation for the observed high T_c.

In fact, first-principles calculations[6] suggest that the electron–phonon coupling constant in the monolayer grown on pristine $SrTiO_3$ is larger than in the FeSe bulk; however, its value is still much smaller than that needed to explain T_c as high as 65 K. While impurity phonons are not taken into account in these calculations, they are unlikely to dramatically increase the total coupling constant. From an experimental point of view, a recent study[7] showed some shadow bands in FeSe monolayers, shifted with respect to the main bands, and this was explained by an enhanced coupling of a phonon mode with a particular electronic band. This, however, may have little effect on the total electron–phonon coupling constant. Rather, it seems likely that these shadow bands are impurity modes associated with interfacial defects[7], which is consistent with the fact that FeSe monolayers are not superconducting if grown on graphene or $SrTiO_3$ with a vacancy-free surface.

One of the fingerprints that distinguish phonon-induced superconductivity from magnetic pairing mechanisms is its dependence on doping and pressure. Phonon frequencies and electron-ion scattering usually depend monotonically on such factors over a broad range. On the contrary, a relatively narrow, dome-like superconducting area in the phase diagram is typical for electronic and magnetic mechanisms[8]. The complete phase diagram is, therefore, important to clarify the physical mechanism behind the high-T_c superconductivity, but it has been challenging to obtain that of the FeSe monolayers as a function of doping. In fact, doping in these layers is usually induced by oxygen vacancies in the $SrTiO_3$ surface, which lead to the formation of bridging Se atoms shared between FeSe and $SrTiO_3$; hence, the doping level in a monolayer cannot be changed without altering the interface with the substrate.

Nakayama and colleagues[4] overcome this problem by working with FeSe multilayers grown on $SrTiO_3$ and depositing individual potassium atoms on top of them. As expected, without any K doping, the superconducting temperature rapidly goes down with the number of

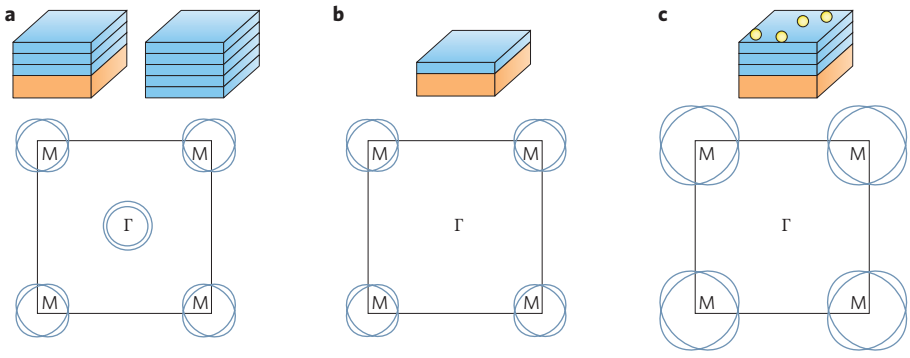

Figure 1 | Schematics of the topology of the Fermi surface of FeSe as a function of thickness and doping. **a**–**c**, Fermi surface topology in the bulk or in a three-monolayer film (**a**), in a one-monolayer film (**b**), and in a K-covered three-monolayer film (**c**)[4]. FeSe layers are represented in blue, the $SrTiO_3$ substrate in orange, and K atoms by yellow dots. The black square denotes the crystallographic Brillouin zone, two blue contours near Γ are hole Fermi surfaces, and those near M are the electron ones. Figure adapted from ref. 4, Nature Publishing Group.

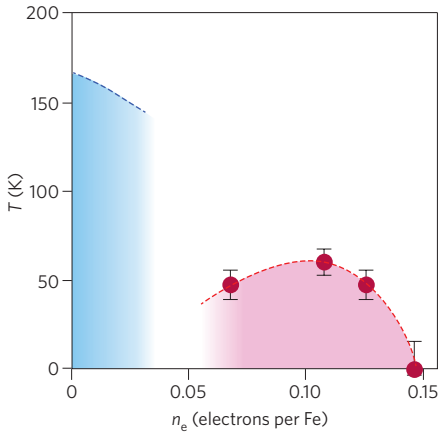

Figure 2 | Phase diagram of bulk FeSe as a function of doping, n_e. The dome-shaped red area represents the superconducting phase. The red dots are the critical temperatures for different doping levels experimentally measured by Nakayama and colleagues[4]. The red dashed line is a guide to the eye. Below a certain temperature (dashed blue line) the lightly doped material shows antiferromagnetic order (blue area). Figure adapted from ref. 4, Nature Publishing Group.

FeSe layers, consistent with the idea that superconductivity originates at the interface between FeSe and $SrTiO_3$. Moreover, by doping the top surface with K atoms, the authors were able to access a large range of doping concentrations, and to demonstrate that the superconducting phase has a narrow dome-like shape — just as in bulk Fe-based superconductors — with a maximum at about 0.1 electrons per Fe atom as shown in Fig. 2. Importantly, they showed that the Fermi-surface topology of their doped multilayers is analogous to that of the FeSe monolayer (Fig. 1c). These experimental results suggest that the phononic hypothesis is probably incorrect and point to an electronic — and probably magnetic — origin for the superconductivity of FeSe monolayers. In fact, they strongly suggest a pairing mechanism similar to that taking place in other Fe-based superconductors, based on some type of *s* state.

Although this experiment clarifies some fundamental aspects of the superconductivity in FeSe, it also raises new questions. Given the proximity to magnetism, s_{++} superconductivity (where the order parameters have the same sign in the hole and the electron bands) seems unlikely. Alternatively, a state where two concentric electron Fermi-surfaces feature different signs of the order parameter[5] could lead to a sign-changing superconductivity, but no microscopic mechanism generating such pairing symmetry has been offered so far, and a recent experimental paper[9] argued against such symmetry. Also, *d* wave superconductivity, typical of high-T_c cuprates, has been excluded[5].

The results reported by Nakayama and colleagues do not solve the conundrum of the high-T_c superconductivity in FeSe monolayers, but makes it even more mysterious. Combining them with other experimental facts, we observe that the 'usual' spin fluctuations responsible for superconductivity in pnictides should be much less efficient here, and electron–phonon coupling seems inconsistent with the phase diagram; yet, T_c is extraordinarily high. Moreover, the absence of localized in-gap states in tunnelling[9] suggests a constant-sign order parameter, which seems incompatible with proximity to magnetism. Indeed, FeSe constitutes a genuine riddle. ❐

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DISLOCATION NETWORKS

Shedding coherent light on defects

With Bragg coherent diffractive imaging it is now possible to image the evolution of the entire dislocation network within a microcrystal during growth and dissolution.

Felix Hofmann

Dislocations are atomic-scale lattice defects that play a central role in determining the properties of crystalline materials. For example, they govern the strength of structural alloys, influence crystal growth and can be detrimental to the performance of semiconductor devices. Fundamental understanding of their structure and behaviour is essential if we are to engineer dislocations to enhance material properties. Transmission electron microscopy has transformed the study of dislocations, allowing them to be imaged with near-atomic resolution. However, the need for thin, electron-transparent samples and high vacuum limits the feasibility of transmission electron microscopy for *in situ* studies. Writing in *Nature Materials*, Jesse Clark, Johannes Ihli and collaborators demonstrate the ability to non-destructively monitor the whole network of dislocations within a micrometre-sized calcite crystal using a relatively new X-ray diffraction technique called Bragg coherent diffractive imaging (BCDI)[1]. They follow the evolution of this network during repeated growth and dissolution of the crystal, shedding light on the fundamental physics governing the crystallization process, and the role played by dislocations.

Screw dislocations are line defects in which atoms are arranged in a helix around a central core (Fig. 1a). This structure plays an important role in crystal growth, as the resulting atomic step on the sample surface provides an energetically favourable location for the formation of the next atomic layer[2]. On the other hand, during crystal dissolution, atoms at dislocations are removed more quickly from the crystal, leading to the formation of pits. These etch pits provided the earliest means of observing individual dislocations and served to validate the first X-ray topography images of dislocations[3–5]. While topography is arguably the most well-established X-ray technique for viewing dislocations, it is confined to large samples containing few dislocations.