nature physics

LETTERS

PUBLISHED ONLINE: 12 MAY 2013 | DOI: 10.1038/NPHYS2617

Sudden reversal in the pressure dependence of T_c in the iron-based superconductor KFe_2As_2

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Proximity to an antiferromagnetic phase suggests that pairing in iron-based superconductors is mediated by spin fluctuations[1–4], but orbital fluctuations have also been invoked[5]. The former typically favour a pairing state of extended *s*-wave symmetry with a gap that changes sign between electron and hole Fermi surfaces[6–9] ($s_{\pm}$), whereas the latter yield a standard *s*-wave state without sign change[5] (s_{++}). Here we show that applying pressure to KFe_2As_2 induces a sudden change in the critical temperature T_c, from an initial decrease with pressure to an increase above a critical pressure P_c. The smooth evolution of the resistivity and Hall coefficient through P_c rules out a change in the Fermi surface. We infer that there must be a change of pairing symmetry at P_c. Below P_c, there is compelling evidence for a *d*-wave state[10–14]. Above P_c, the high sensitivity to disorder rules out an s_{++} state. Given the near degeneracy of *d*-wave and $s_{\pm}$ states found theoretically[15–19], we propose an $s_{\pm}$ state above P_c. A change from *d*-wave to *s*-wave would probably proceed through an intermediate $s + id$ state that breaks time-reversal symmetry[20–22].

KFe_2As_2 is a stoichiometric iron arsenide with a superconducting critical temperature $T_c = 4$ K. It is a member of the extensively studied 122 family of iron-based superconductors[23]. Single crystals can be grown with very high purity, making it by far the cleanest of the iron-based superconductors. Its high hole concentration is such that its Fermi surface does not contain the usual electron pocket at the X point (of the unfolded Brillouin zone); it consists mainly of three hole-like cylinders: two located at the zone centre (Γ) and one at the corner (M; Fig. 1a). There is no antiferromagnetic order, but there are antiferromagnetic spin fluctuations, detected by inelastic neutron scattering[24]. In iron-based superconductors, spin fluctuations generally favour the $s_{\pm}$ pairing state in which the gap changes sign between hole and electron pockets[1–4] (Fig. 1b). In the absence of the electron pocket at X, this mechanism becomes much less effective, and functional-renormalization-group calculations find that a *d*-wave state (Fig. 1c) is the most stable state in KFe_2As_2 (ref. 15). Other theoretical methods find that $s_{\pm}$ and *d*-wave states are very close in energy[17,18]. Experimentally, thermal conductivity studies in KFe_2As_2 make a compelling case for *d*-wave symmetry[10–13]: line nodes are found to be vertical and present on all Fermi surfaces, and the thermal conductivity is independent of impurity scattering, as expected of symmetry-imposed line nodes[25]. A *d*-wave state is also consistent with penetration depth data[14]. However, in a recent angle-resolved photoemission spectroscopy (ARPES) study of KFe_2As_2, vertical line nodes in the gap were observed on only one of the three Fermi surfaces[26]. To explain this, a particular kind of $s_{\pm}$ state was proposed[27] where the sign change is between the two Γ-centred hole pockets (Fig. 1d).

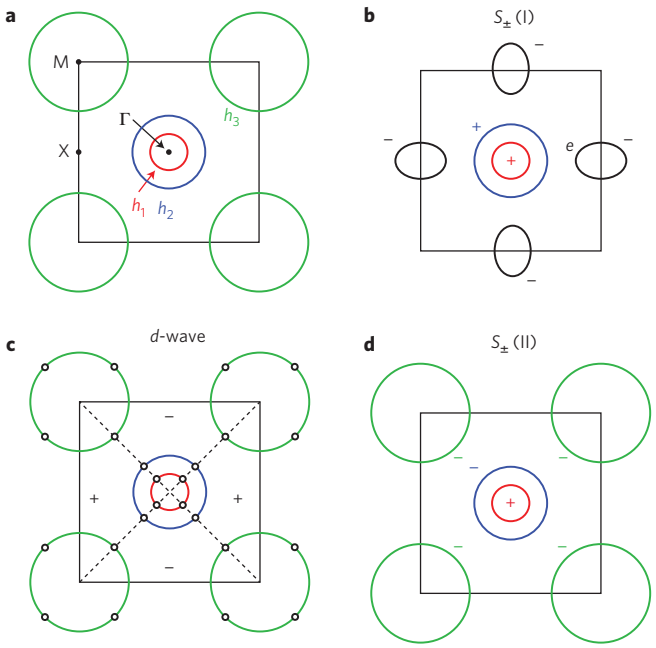

Figure 1 | Fermi surface of KFe_2As_2 and possible superconducting states. **a**, Schematic of the main Fermi surface sheets of KFe_2As_2, in the $k_z = 0$ plane, shown in the unfolded Brillouin zone (with one Fe per unit cell)[3]. It consists of two zone-centred hole pockets (h_1 and h_2) and one hole pocket at M (h_3). **b**, Sketch of the main Fermi surface sheets of $K_{1-x}Ba_xFe_2As_2$, at $x = 0.4$, with an electron pocket (*e*) at X (and no hole pocket at M)[3]. The standard $s_{\pm}$ pairing state (type I) involves full gaps on each pocket, with a sign change from + on the hole pockets (h_1, h_2) to − on the electron pocket (*e*). **c**, *d*-wave pairing state[16], where the gap changes sign as the azimuthal angle crosses the zone diagonals (dashed lines). This symmetry forces the gap to have nodes (zeros) on all Fermi surface sheets that cut those diagonals (small open circles). **d**, Illustration of an $s_{\pm}$ pairing state (type II) where the gap changes sign from + on the inner Γ-centred hole pocket (h_1) to − on the outer Γ-centred hole pocket (h_2) (see ref. 27).

To help clarify the situation, we have studied the effect of hydrostatic pressure on KFe_2As_2, by measuring the resistivity and

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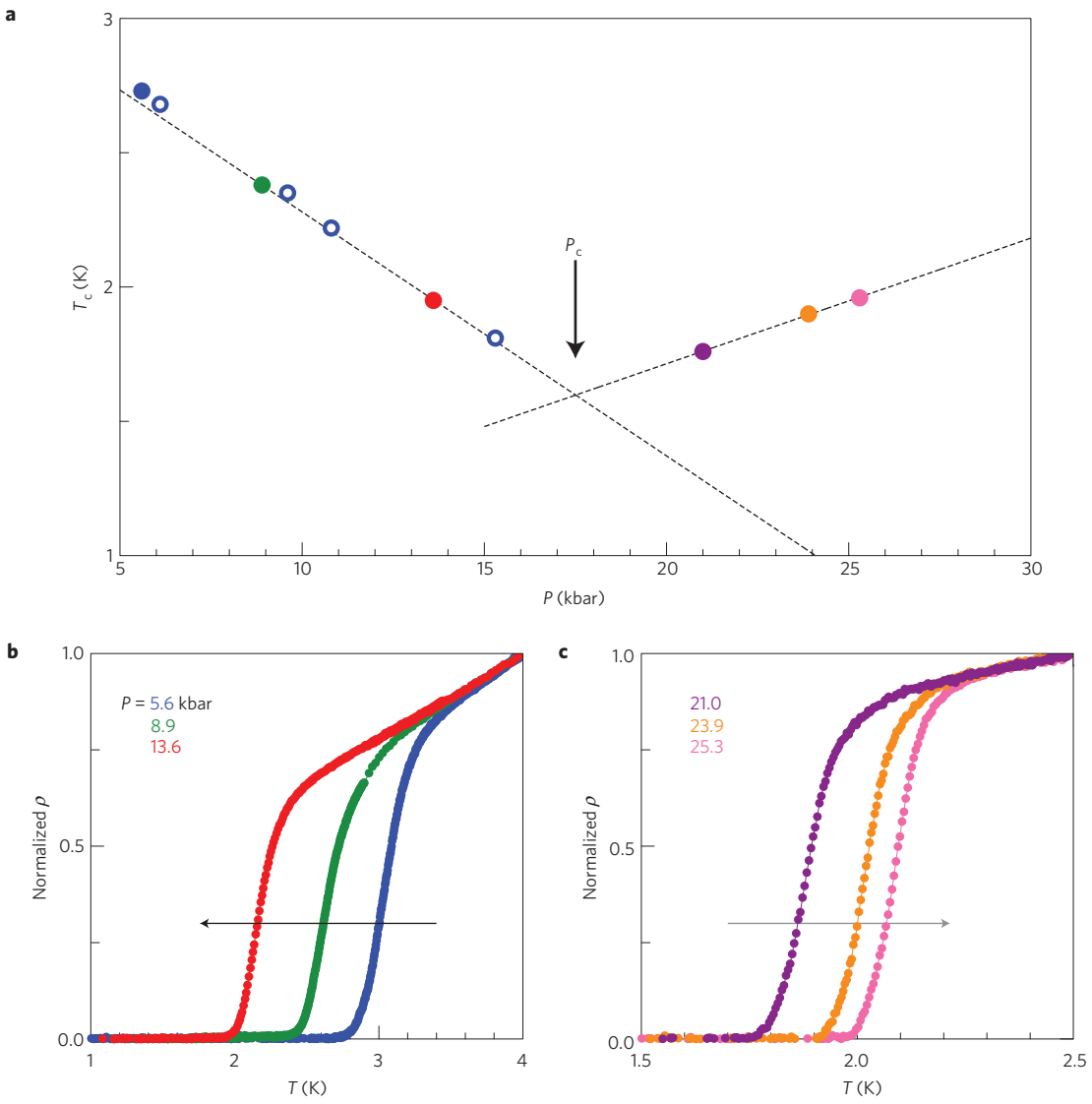

Figure 2 | Pressure dependence of T_c in KFe_2As_2. a, Pressure dependence in KFe_2As_2, with filled circles representing sample A (from colour-coded resistivity data in **b**,**c**) and open circles sample B. The critical pressure $P_c = 17.5$ kbar marks the transition from a decreasing to an increasing T_c. The dashed lines are linear fits to the data within 10 kbar on either side of P_c. **b**, Isobars of $\rho(T)$ in sample A, normalized to unity at $T = 4$ K, for three pressures below P_c, as indicated. **c**, The same as in **b**, for pressures above P_c, with ρ normalized at $T = 2.5$ K. T_c is the temperature below which $\rho(T) = 0$. The relative accuracy on T_c is better than ±2% (Supplementary Fig. S2); the relative uncertainty on the value of pressure is ±0.2 kbar. The grey arrows show how T_c moves with pressure.

Hall effect in two single crystals, labelled sample A and sample B (Supplementary Information). As seen in Fig. 2a, we find that T_c decreases initially with pressure, as found elsewhere[28], but once the pressure is increased above a critical value $P_c = 17.5$ kbar, it suddenly starts to rise. T_c varies linearly on either side of P_c, producing a V-shaped dependence of T_c on P. This sharp inversion in the effect of pressure on T_c is our central finding, reproduced in both samples (Supplementary Fig. S1). There are two possible mechanisms: a Lifshitz transition, whereby the Fermi surface undergoes a sudden change; or a phase transition with broken symmetry. In Fig. 3a, we see that the Hall coefficient R_H in the $T = 0$ limit remains completely unchanged by pressure, right through P_c (Fig. 3b). A Lifshitz transition, such as the appearance of an electron pocket, would produce a sudden change in $R_H(0)$. It can therefore be excluded as a possible cause for the rise of T_c beyond P_c.

We deduce that a phase transition occurs at P_c. Any density-wave or structural transition that breaks translational symmetry would reconstruct the Fermi surface, and cause associated anomalies in the transport properties. Such transitions are therefore ruled out by the absence of any anomaly in R_H (Fig. 3b) and in the electrical resistivity ρ (Fig. 3c) at P_c. Note that density-wave phases such as the antiferromagnetic phase in $Ba_{1-x}K_xFe_2As_2$ with $x < 0.4$ generally compete with superconductivity and so produce a dome-shaped curve of T_c versus P or x (refs 1,2,12), not a V-shaped curve as seen here (Fig. 2a). We conclude that what occurs at P_c is not a transition in the normal-state electronic properties, but a transition to a superconducting phase of a different symmetry.

For the phase above P_c, the effect of impurity scattering on T_c rules out the standard s_{++} state. At ambient pressure, 4% Co impurities in KFe_2As_2 suppress T_c to zero[13]—the critical value of the residual resistivity being $\rho_0^{crit} = 4.5\,\mu\Omega$ cm (refs 11,13). This is consistent with a d-wave state, whose T_c is expected to vanish when the scattering rate is of the order of T_c (ref. 11). We measured the resistivity of a sample of KFe_2As_2 with 3.4% Co impurities, in which $\rho_0 = 3.8\,\mu\Omega$ cm and $T_c = 1.7$ K at ambient pressure (Supplementary Fig. S3). Under pressure, the T_c of this Co-doped

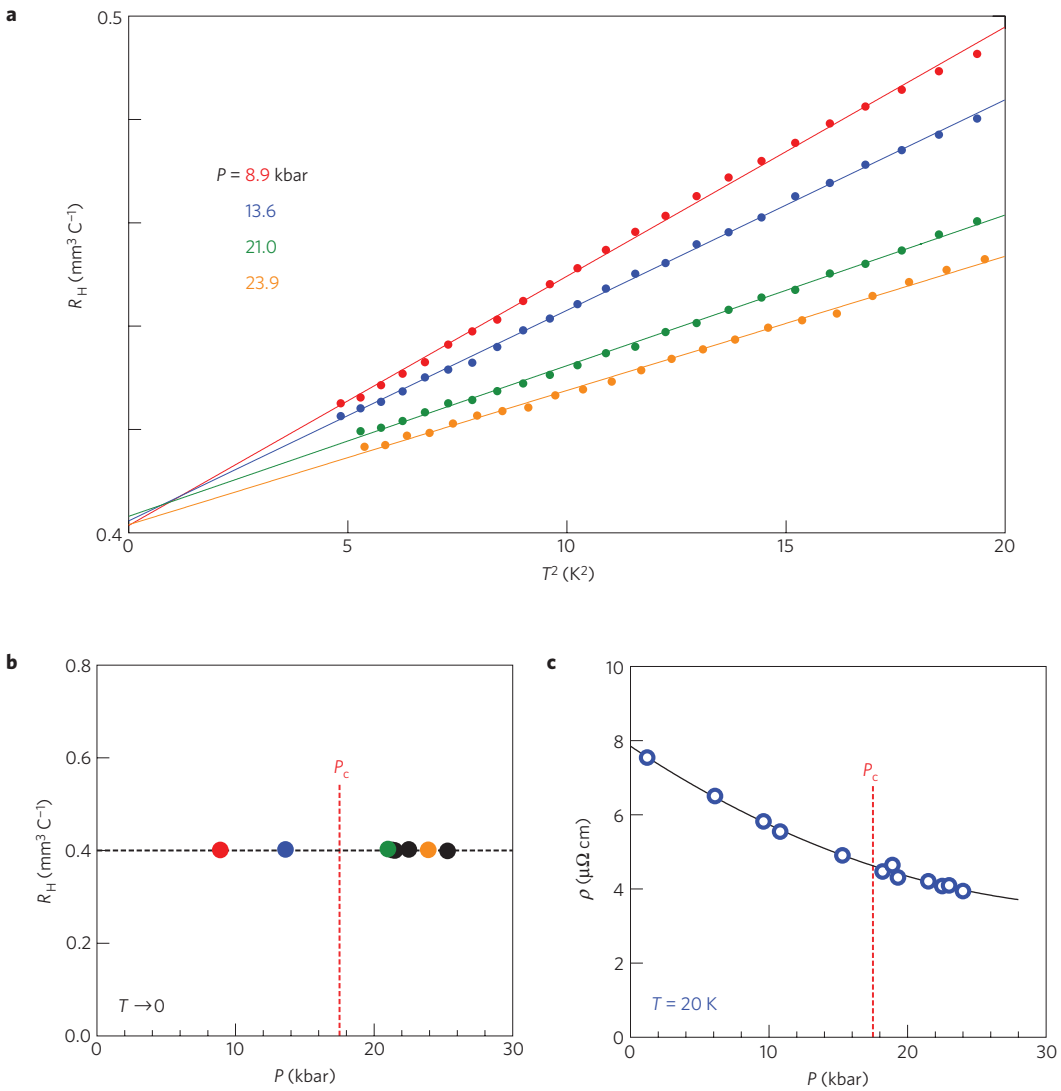

Figure 3 | Hall coefficient and resistivity of KFe_2As_2 under pressure. a, Hall coefficient R_H of KFe_2As_2 as a function of temperature, plotted as R_H versus T^2, measured in sample A for a magnetic field of 13 T along the *c* axis of the tetragonal lattice, at different values of the applied pressure *P*, as indicated (see also Supplementary Fig. S4). The lines are linear fits to the data, extrapolated to $T = 0$ to yield the residual values, $R_H(0)$. **b**, Pressure dependence of $R_H(0)$, seen to remain completely unchanged throughout the range investigated. **c**, Pressure dependence of ρ measured in sample A at $T = 20$ K, seen to decrease monotonically through P_c. The solid line is a smooth fit through all data points.

sample is suppressed to zero and does not re-emerge above P_c (Fig. 4). This shows that the superconducting state above P_c cannot be s_{++}, a state that is insensitive to non-magnetic impurities. Neither could this high-pressure state be the same $s_{\pm}$ state as in the usual $BaFe_2As_2$-based superconductors (with an electron pocket at X), because T_c in these materials is very robust against impurity scattering[29].

A plausible candidate for the phase above P_c is the $s_{\pm}$ state proposed in ref. 27 (for ambient pressure), with a sign change between the two hole pockets at Γ (Fig. 1d). Given the similarity of these two pockets, inter-band scattering is likely to be significant and T_c is therefore expected to be rather sensitive to disorder, as observed. The fact that, above P_c, T_c rises even though ρ continues to decrease (Fig. 3c) is consistent with calculations for this type of $s_{\pm}$ state, which require that the interaction between fermions be largest at small momentum transfer[27]. As mentioned above, this type of $s_{\pm}$ state is consistent with the ARPES study that finds a large, angle-dependent gap on the two Γ-centred hole pockets and a small nodeless gap on the M-centred hole pocket[26]. We suggest that the state measured by ARPES at ambient pressure is this $s_{\pm}$ state, stabilized at the cleaved (polar) surface of KFe_2As_2 even though the bulk is in a *d*-wave state.

In iron-based superconductors with a Fermi surface that contains hole and electron pockets (Fig. 1b), the natural proximity of $s_{\pm}$ and *d*-wave states was nicely revealed by calculations[19] where the strength of the (π, π) spin fluctuations (connecting two nearby electron pockets) was gradually increased for a fixed strength of $(\pi, 0)$ spin fluctuations (connecting hole and electron pockets). A V-shaped variation of T_c is obtained, as the superconducting phase goes from $s_{\pm}$ to *d*-wave. Impurity scattering suppresses T_c on both sides of the transition and opens up an intermediate region without superconductivity[19]. This is the phenomenology we observe in KFe_2As_2, where an analogous mechanism of competing interactions may be at play even if the Fermi surface does not contain an electron pocket.

Our proposal is that the V-shaped dependence of T_c on pressure in KFe_2As_2 reflects a change of pairing symmetry, most likely from a *d*-wave state below P_c to an $s_{\pm}$ state above P_c. To confirm this interpretation, measurements that probe the superconducting state below T_c will be needed, especially above P_c. Note that when *d*-wave

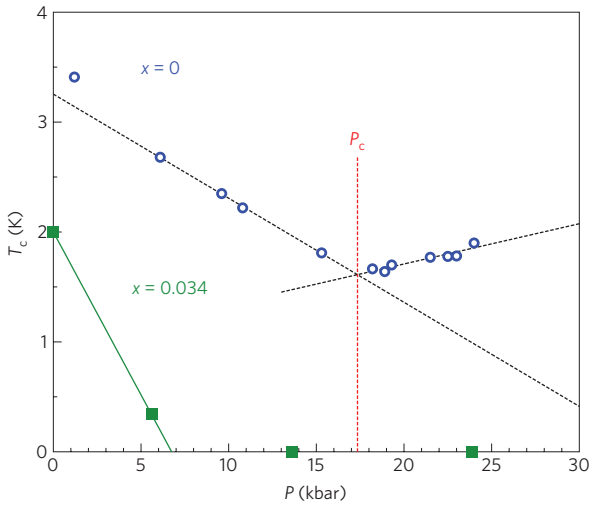

Figure 4 | Effect of impurity scattering on T_c in KFe_2As_2. Pressure dependence of T_c in KFe_2As_2 for a nominally pure sample (open circles, sample B) and a sample with 3.4% Co impurities (filled squares, $K(Fe_{1-x}Co_x)_2As_2$ with $x = 0.034$, from resistivity data in Supplementary Fig. S3). The dotted lines are linear fits to the pure data within 10 kbar on either side of P_c. The solid green line is a linear fit to the first two data points of the impure sample. Note how T_c is suppressed by the addition of impurities both below and above P_c, showing that the pairing states on both sides of the transition are highly sensitive to impurity scattering.

and *s*-wave phases come together, an intermediate $s + id$ phase that breaks time-reversal symmetry is likely to intervene[19–22,30]. One signature of such a phase is a spontaneous internal magnetic field that appears below T_c, which could in principle be detected with muons, in clean samples of KFe_2As_2 at pressures near P_c.

Received 17 December 2012; accepted 28 March 2013; published online 12 May 2013

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Acknowledgements

We thank A. V. Chubukov, R. Fernandes, A. J. Millis, R. Thomale and S-C. Zhang for fruitful discussions, and S. N. Faucher for his help with some of the measurements. Work at Sherbrooke was supported by a Canada Research Chair, the Canadian Institute for Advanced Research, the Canada Foundation for Innovation, NSERC and FQRNT. Work done in China was supported by the National Natural Science Foundation of China, the Strategic Priority Research Program (B) of the Chinese Academy of Sciences, and the National Basic Research Program of China.

Author contributions

F.F.T., A.J-F. and M-È.D. performed the transport measurements and analysed the data. J-P.R. and F.F.T. prepared the samples with contacts for the high-pressure experiments. S.R.d.C. and N.D-L. designed the pressure set-up and provided expertise on the pressure measurements. A.F.W., X-G.L. and X.H.C. grew the pure and Co-doped single crystals of KFe_2As_2. F.F.T., A.J.F., N.D-L. and L.T. wrote the manuscript. L.T. supervised the project.

Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to L.T.

Competing financial interests

The authors declare no competing financial interests.