Upper critical field reaches 90 tesla near the Mott transition in fulleride superconductors

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Controlled access to the border of the Mott insulating state by variation of control parameters offers exotic electronic states such as anomalous and possibly high-transition-temperature \(T_c\) superconductivity. The alkali-doped fullerides show a transition from a Mott insulator to a superconductor for the first time in three-dimensional materials, but the impact of dimensionality and electron correlation on superconducting properties has remained unclear. Here we show that, near the Mott insulating phase, the upper critical field \(H_{c2}\) of the fulleride superconductors reaches values as high as \(\sim 90\) T—the highest among cubic crystals. This is accompanied by a crossover from weak- to strong-coupling superconductivity and appears upon entering the metallic state with the dynamical Jahn–Teller effect as the Mott transition is approached. These results suggest that the cooperative interplay between molecular electronic structure and strong electron correlations plays a key role in realizing robust superconductivity with high-\(T_c\) and high-\(H_{c2}\).
The interplay between superconductivity and electron correlations is one of the central issues in condensed matter physics. Superconducting (SC) materials based on Mott insulators, such as two-dimensional (2D) cuprates and organic charge-transfer salts, are model platforms that have been extensively studied thus far. A dome-like dependence of the SC transition temperature \( T_c \) as a function of tuning parameters, such as carrier doping and pressure, has been discussed as a fingerprint of unconventional superconductivity. Recent physical and chemical pressure studies of \( \text{Cs}_3\text{C}_{60} \) have revealed that the family of cubic fullerides \( \text{A}_3\text{C}_{60} \) (A: alkali metal), where superconductivity emerges from the Mott insulating state driven by dynamical intramolecular Jahn–Teller (JT) distortions and strong Coulomb repulsion, is a new example of superconductors that show a dome-like SC phase diagram as a function of unit-cell volume \( V \) (refs 4–9). This suggests the importance of strong electron correlation to SC mechanisms and the need for further treatment beyond conventional framework of theory. Recent study has revealed a crossover in the normal state from the conventional Fermi liquid to a nontrivial metallic state where JT distortions persist (JT metal)\(^9\)\(^{12}\). There, localized electrons coexist with itinerant electrons microscopically and heterogeneously.

The dependence of the upper critical field \( H_{c2} \) on \( T_c \) is relevant to the understanding of the dome-like SC phase because \( H_{c2} \) is determined by the coherence length (the size of the Cooper pair) as well as the strength of the pairing potential. Therefore, \( H_{c2} \) is also important to understand the underlying mechanism of the superconductivity. However, for the fullerides, \( H_{c2} \) as a function of \( V \) has not as yet been determined due to the very large \( H_{c2} \) and the need for high pressure to access superconductivity in \( \text{Cs}_3\text{C}_{60} \).

Here we report measurements of \( H_{c2} \) using a pulsed magnetic field in \( \text{Rb}_x\text{Cs}_{3-x}\text{C}_{60} \), where superconductivity appears near the Mott transition even at ambient pressure\(^2\). In proximity to the Mott transition, \( H_{c2} \) is enhanced up to \( \sim 90 \) T, which is the highest among cubic superconductors. We uncovered that \( H_{c2} \) and the pairing strength increase concomitantly with increasing lattice volume near the Mott transition, suggesting that molecular characteristics as well as electron correlations play important roles for realizing superconductivity with high \( T_c \) and high \( H_{c2} \) in molecular materials.

### Results

**Temperature dependence of upper critical field.** \( H_{c2} \) of the fulleride superconductors (Fig. 1a) \( \text{Na}_2\text{CsC}_{60} \), \( \text{K}_3\text{C}_{60} \), and \( \text{Rb}_x\text{Cs}_{3-x}\text{C}_{60} \) (0 < \( x \) ≤ 3), has been measured by a radiofrequency technique in pulsed magnetic fields\(^13\) up to 62 T (see Methods). In \( \text{Rb}_x\text{Cs}_{3-x}\text{C}_{60} \) with \( x \) = 1, the dynamical JT distortions (Fig. 1b) persist down to low temperature and coexist with the metallic state, and superconductivity emerges from this JT metal state (\( V_{\text{max}} \) < \( V < V_c \), in Fig. 1c). Figure 2 shows temperature (\( T \)) variations of frequency shift \( \Delta f \) as a function of the magnetic field \( H \) for \( \text{Rb}_x\text{Cs}_{3-x}\text{C}_{60} \) (\( x = 2, 0.75 \), and 0.35) (see also Supplementary Fig. 1). The \( T \) dependence of \( H_{c2} \), \( H_{c2}(T) \), was determined as a point at which \( \Delta f \) intercepts the normal-state
background (arrows in Fig. 2). $H_{c2}(T)$ curves for $\text{A}_{2}\text{C}_{60}$ are plotted in Fig. 3a,b for $V_{\text{F}} \leq V_{\text{max}}$ and $V_{\text{max}} < V < V_{\text{cr}}$ in the proximity of the Mott transition, respectively. $H_{c2}(T)$ increases linearly with decreasing $T$ near $T_c$ and has a tendency to saturate at low temperatures. No obvious upturn of $H_{c2}(T)$ is found in any of the samples measured, implying that $H_{c2}(T)$ can be understood within a simple single-band picture despite the multiband nature of the triply degenerate $t_{1u}$ orbitals of $C_{60}^{--}$ anions, in contrast to MgB$_2$ and iron pnictides where multiband and multigap behaviour with upturn or quasilinear $T$ dependence down to $T_1$ is commonly observed.

**Volume dependence.** In spin-singlet superconductors, $H_{c2}$ is determined by two distinct effects, i.e., the orbital and the Pauli paramagnetic effect. The orbital limit and Pauli limit are given by $H_{c2}^{\text{orb}}(0) = 0.697T_c$, $dH_{c2}/dT|_{T=T_c} = \Phi_0/2\pi\xi_{\text{GL}}$ and $H_P = \Delta_0/\sqrt{2m_h}$, respectively ($\Phi_0$, $\xi_{\text{GL}}$, $\Delta_0$, and $m_h$ are the flux quantum, Ginzburg–Landau (GL) coherence length, superconducting gap and Bohr magneton, respectively)\textsuperscript{14,15}. In a weak-coupling BCS superconductor, the Pauli limit is $H_{c2}^{\text{PBCS}}[T] = 1.84T_c[K]$. A simple estimation from $H_{c2}^{\text{orb}}(0)$ gives $\xi_{\text{GL}} = 1.84 - 4.6$ nm (Supplementary Table 1), which is comparable to the lattice constant. It should be noted that the fullride superconductors are in the dirty limit, $\ell \ll \xi_0$ ($\ell$ and $\xi_0$ are the mean free path and Pippard coherence length, respectively), as demonstrated by transport and optical measurements\textsuperscript{16,17}. The orientational disorder of the $C_{60}^{--}$ anions can account for the short $\ell$, which is comparable to the intermolecular separation. The relation $\xi_{\text{GL}} = 0.697T_c$ in the dirty limit, where $\xi_0 = \hbar v_f/\pi\Delta_0$ and $m^* = \hbar^2/(k_B T_c)$ ($v_f$, $m^*$, $k_B$, and $N$ are the Fermi velocity, effective mass, Fermi momentum, and number of electrons per $C_{60}$, respectively) for the parabolic band approximation yield $H_{c2}^{\text{orb}}(0) = 0.22\Phi_0/\Delta_0(\xi_{\text{GL}}/\ell)^{1/2}$ (in the extreme cases $H_{c2}^{\text{orb}} \gg H_P$ or $H_{c2}^{\text{orb}} < H_P$, $H_{c2}(0)$ is determined solely by $H_{c2}^{\text{orb}}$ or $H_P$, respectively).

**Discussion**

$H_{c2}(0)$ values reaching $\sim 90$ T are remarkably high for 3D materials. Typical examples of 3D superconductors are cubic Nb$_3$Sn ($H_{c2}(0) = 30$ T, $T_c = 18$ K), which is well known as a material for a SC magnet\textsuperscript{18} and Ba$_1$K$_2$Bi$_4$O$_9$ ($H_{c2}(0) = 32$ T, $T_c = 28$ K)\textsuperscript{19}. MgB$_2$ exhibits strong anisotropy ($H_{c2}(0) = 49$ T and $34$ T parallel to the $ab$ plane and $c$ axis, respectively, $T_c = 39$ K)\textsuperscript{18} due to its anisotropic electronic structure. $H_{c2}(0)$ of the fullerides is even higher than that of recently discovered H$_3$S superconductors with likely a cubic structure ($H_{c2}(0) \approx 70$ T, $T_c = 203$ K)\textsuperscript{20} despite its much higher $T_c$. In 2D systems under in-plane applied fields, the orbital effect is quenched and higher $H_{c2}$ can be expected. Very large $H_{c2}$ compared with low $T_c$ has been demonstrated in iron-gated Mo$_2$S$_3$ ($H_{c2}(0) = 52$ T, $T_c = 9.7$ K)\textsuperscript{21,22} and monolayer NbSe$_2$ ($H_{c2}(0) = 32$ T, $T_c = 3.0$ K)\textsuperscript{23}. In the bulk materials, the in-plane $H_{c2}$ of the cuprates is exceptionally high at above 100 T. However, $H_{c2}$ is no longer a thermodynamic transition line, but a crossover line due to thermal fluctuations. Contrastingly, $H_{c2}$ in pnictides with $T_c \approx 30$ K is as large as that of fullerides\textsuperscript{24}. Therefore, our results highlight the uniquely high $H_{c2}$ measured in the fulleride superconductors that are cubic, and thus, 3D.
Figure 3 | Upper critical field in fullerene superconductors. Temperature dependence of the upper critical field for (a) $V \leq V_{\text{max}}$ and for (b) $V_{\text{max}} < V < V_{c}$. The solid lines represent fits using equation (1). (c) Normalized $H_{c2}(T)/H_{c2}(0)$ as a function of normalized temperature $T/T_{c}$. The solid and dashed lines represent calculated $H_{c2}(T)$ using the extended WHH formula (equation (1)) with $z = 1.5$ and $\lambda_{0} = 4.4$ and the conventional WHH formula in the dirty limit, respectively. (d) $H_{c2}(0)$, obtained from fits using equation (1), are plotted as a function of volume per $C_{3}^{2}$ anions. Error bars represent s.d. of the fit to $H_{c2}(T)$ curves. Conventional BCS values of the Pauli limiting field $H_{c2}^{\text{BCS}}$ are also shown. (e) Evolution of $2\Delta_{0}/k_{B}T_{c}$ and $H_{c2}(0)/T_{c}$ with approaching to the Mott transition. Error bars on $2\Delta_{0}/k_{B}T_{c}$ and $H_{c2}(0)/T_{c}$ are calculated from the s.d. in the values of $H_{c2}(0)$ estimated from the least-squares fits of equation (1) to $H_{c2}(T)$ data. $2\Delta_{0}/k_{B}T_{c}$, obtained from NMR measurements is taken from ref. 9. Inset shows $V$ dependence of $m^{*}/m_{0}N^{1/3}$ derived using $H_{c2}^{\text{BCS}}(0)$, $\Delta_{0}$, and $V$. Error bars are calculated from the s.d. in the values of $H_{c2}(0)$ estimated from the least-squares fits of equation (1) to $H_{c2}(T)$ data.

Estimated from $H_{c2}$. In Fig. 3e, the $V$ dependences of $2\Delta_{0}/k_{B}T_{c}$, which is related to the strength of the pairing interaction, and $m^{*}/m_{0}N^{1/3}$ ($m_{0}$ is the bare electron mass) are shown. At low $V$, $2\Delta_{0}/k_{B}T_{c}$ is comparable to the BCS weak-coupling limit value of 3.52. In contrast with the dome-shaped $T_{c}, 2\Delta_{0}/k_{B}T_{c}$ continuously increases with increasing $V$ and reaches values as large as 6, indicating a crossover from weak- to strong-coupling superconductivity on approaching the Mott transition. This is in good agreement with the previous nuclear magnetic resonance results for $\text{Rb}_{x}\text{Cs}_{3-}x\text{C}_{60}$ at ambient pressure$^{9}$ and for both fcc- and A15-$\text{Cs}_{3}\text{C}_{60}$ under pressure$^{25,26}$, implying universal behaviour in the fullerides. On the other hand, $m^{*}/m_{0}N^{1/3}$ is almost constant, indicating that both $H_{p}/T_{c}$ and $H_{c2}^{\text{BCS}}(0)/T_{c}$ are solely proportional to $2\Delta_{0}/k_{B}T_{c}$. These results lead to the conclusion that the enhancement of $H_{c2}(0)$ is dominated by the strong-coupling effect developing near the Mott transition.

We here recall $H_{c2}(0)$ of other families of high-$T_{c}$ or strongly correlated superconductors, i.e., cuprates, organic κ-(ET)$_{2}$X, and pnictides$^{24,27-31}$, having a dome-like SC phase and a proximate antiferromagnetic phase. In Fig. 4, $H_{c2}(0)/T_{c}$ is displayed as a
Error bars on control parameters in high-effective pressure measured from estimated from the least-squares fits of equation (1) to the SC dome. This is ascribed to the variation of and cuprates. In the pnictides, $H_{c2}(0)$ for the out-of-plane field ($H \perp c$) in cuprates since there are no reliable estimates of $H_{c2}(0)$ for $H \perp c$. A remarkable feature of the fullerenes is that $H_{c2}(0)/T_c$ appears to be strongly enhanced at $x \leq 1$, where the JT metal phase emerges (Fig. 1c), with retaining nearly optimal $T_c$ and $H_{c2}(0)$ values near the Mott transition. This is in marked contrast to the pnictides and cuprates. In the pnictides, $H_{c2}(0)/T_c$ is almost constant across the SC dome. This is ascribed to the variation of $\Delta_0$, which linearly scales with $T_c$ (ref. 32), implying constant coupling strength. Moreover, in pnictides, $T_c$ and $H_{c2}(0)$ are strongly reduced upon decreasing doping, associated with the appearance of the antiferromagnetic phase. Non-monotonic behaviour in cuprates appears with mass enhancement near $p = 0.08$ and 0.18, which originates from phase competition between superconductivity and Fermi-surface reconstruction or charge-density-wave order$^{27}$. This is distinct from the continuous evolution of $H_{c2}(0)$ in the fullerenes (Supplementary Fig. 2), suggesting the absence of any competing states. In $\kappa$-(ET)$_2$X, there is no competing phase near the Mott transition and the molecular degrees of freedom are not relevant to the superconductivity in contrast to the fullerenes. Moreover, the SC pairing is mostly mediated by purely electronic interaction, in contrast to the fullerenes, where there is considerable controversy because of comparable energy scales in the electron–phonon and electron-electron interactions$^{33,34}$. $\kappa$-(ET)$_2$X shows qualitatively similar behaviour with the strong-coupling effects near the antiferromagnetic phase$^{25}$. However, the enhancement of $H_{c2}(0)/T_c$ is much weaker than that in the fullerenes. Therefore, the steep enhancement of $H_{c2}(0)/T_c$ and $2\Delta_0/k_BT_c$ upon entering the JT metal phase cannot be explained solely by the electron correlation effect, highlighting the uniqueness of fullerenes among the high-$T_c$ or strongly correlated superconductors. We also emphasize that it is difficult to reconcile the strong-coupling effect with the electron–phonon coupling alone$^{25}$. Our results establish the importance of both molecular characteristics, absent in the atom-based superconductors, involving the dynamical JT effect and the resulting renormalization of the electronic structure and electron correlation effects for both the high-$T_c$ and the high-$H_{c2}$ in the fullerenes, as supported by the recent theoretical calculations$^{33}$. This provides a new perspective on realizing robust superconductivity with high $T_c$ and $H_{c2}$ in molecular materials.

Methods
Sample synthesis and characterization. Fullerene superconductors Na$_2$CoC$_{60}$, K$_2$C$_{60}$, and Rb$_x$Co$_{3-x}$C$_{60}$ ($0 < x < 53$) were synthesized by solid-vapor reaction method as described in ref. 9. The samples used here were identical to those in ref. 9. For Rb$_x$Co$_{3-x}$C$_{60}$ with $x = 0.5$, 1, and 2, our samples correspond to Rb$_x$Cs$_{3-x}$C$_{60}$ (Sample I), RbCo$_2$C$_{60}$ (Sample I), and Rb$_2$CoC$_{60}$ (Sample II) in ref. 9, respectively. The samples were characterized by synchrotron X-ray powder diffraction and magnetization measurements. The phase fraction of the fcc phase was larger than 70% and typical shielding fraction was $\sim 90\%$.

Measurements of $H_{c2}$. Contactless radiofrequency (r.f.) penetration depth measurements were performed using a proximity detector oscillator technique$^{13}$ and a pulsed magnetic field up to 62 T in Los Alamos NHMFL. The typical resonant frequency was $\sim 28$ MHz. The r.f. technique is highly sensitive to small changes (approximately 1–5 nm) in the r.f. penetration depth $\lambda$, and thus, it is an accurate method for determining $H_{c2}$ of superconductors. Powder samples were compressed into pellets and sealed in thin glass capillaries with a small amount of He gas. Coils that generate and detect microwave signals are directly wound around the capillary (inset of Fig. 2a). The relative change of $\lambda$ is proportional to the relative change of the resonating frequency $\nu$ through the inductance of the coil, that is, $\Delta\nu/\nu = \Delta\lambda/\lambda$ (ref. 13). Upper critical field $H_{c2}$ was determined from the field dependence of the frequency shift $\Delta\nu$ (Supplementary Fig. 1) as the point at which the slope of the r.f. signal in the superconducting state intercepts the slope of the normal state background.

Data availability. The data that support the findings of this study are available on request from the corresponding authors (Y.K. or Y.I.).

References
1. Imada, M., Fujimori, A. & Tokura, Y. Metal-insulator transitions. Rev. Mod. Phys. 70, 1039–1263 (1998).
2. Kanoda, K. Recent progress in NMR studies on organic conductors. Hyperfine Interact. 104, 235–249 (1997).
3. Uemura, Y. J. Commonalities in phase and mode. Nat. Mater. 5, 253–255 (2009).
4. Gain, A. Y. et al. Bulk superconductivity at 38 K in a molecular system. Nat. Mater. 7, 367–371 (2008).
5. Darling, G. R., Gainin, A. Y., Rosseinsky, M. J., Takabayashi, Y. & Prassides, K. Intermolecular overlap geometry gives two classes of fulleride superconductor: Electronic structure of 38 K Tc, Cs,C60. Phys. Rev. Lett. 101, 136404 (2008).
6. Takabayashi, Y. et al. The disorder-free non-BCS superconductor Ca$_2$CuO$_2$ emerges from an antiferromagnetic insulator state. Science 323, 1585–1590 (2009).

7. Ganin, A. Y. et al. Polymorphism control of superconductivity and magnetism in Ca$_2$CuO$_2$ close to the Mott transition. Nature 466, 221–225 (2010).

8. Klupp, G. et al. Dynamic Jahn-Teller effect in the parent insulating state of the molecular superconductor Cu$_2$C$_6$O$_4$. Nat. Commun. 3, 912 (2012).

9. Zadik, R. H. et al. Optimized unconventional superconductivity in a molecular Jahn-Teller metal. Sci. Adv. 1, e1500059 (2015).

10. Capone, M., Fabrizio, M., Catellani, C. & Tosatti, E. Colloquium: Modeling the unconventional superconducting properties of expanded A$_4$C$_6$O$_4$ fullerenes. Rev. Mod. Phys. 81, 943–958 (2009).

11. Akashi, R. & Arita, R. Nonempirical study of superconductivity in alkali-doped fullerides based on density functional theory for superconductors. Phys. Rev. B 88, 054510 (2013).

12. Balbassare, L. et al. The strength of electron electron correlation in Ca$_2$CuO$_2$. Sci. Rep. 5, 15240 (2015).

13. Altarawneh, M. M., Milke, C. H. & Brooks, J. S. Proximity detector circuits: An introduction. Rev. Sci. Instrum. 85, 525–531 (2014).

14. Werthamer, N. R., Helfand, E. & Hohenberg, P. C. Temperature and purity dependence of the superconducting critical field, $H_{c2}$. III. Electron spin and spin-orbit effects. Phys. Rev. 147, 295–302 (1966).

15. Clogston, A. M. Upper limit for the critical field in high superconductors. Phys. Rev. Lett. 9, 266–267 (1962).

16. Palstra, T. T. M., Haddon, R. C., Hebard, A. F. & Zaamen, J. Electronic transport properties of K$_2$Cu$_2$X films. Phys. Rev. Lett. 68, 1054–1057 (1992).

17. Iwasa, Y., Tanaka, K., Yasuda, T., Koda, T. & Koda, S. Metallic reflection spectra of K$_2$Cu$_2$O$_4$. Phys. Rev. Lett. 69, 2284–2287 (1992).

18. Gurevich, G. et al. Very high upper critical fields in MgB$_2$ produced by selective tuning of impurity scattering. Supercond. Sci. Technol. 17, 278–286 (2004).

19. Affronte, M. et al. Upper critical field of Ba$_2$K$_2$BO$_3$ single crystals. Phys. Rev. B 49, 3502–3510 (1994).

20. Drozdov, A. P., Erements, M. I., Troyan, I. A., Ksenofontov, V. & Shlykin, S. I. Conventional superconductivity at 203 kelvin at high pressures in the sulfur hydride system. Nature 525, 73–77 (2015).

21. Saito, Y. et al. Superconductivity protected by spin-valley locking in ion-gated MoS$_2$. Nat. Phys. 12, 144–149 (2016).

22. Lu, J. M. et al. Evidence for two-dimensional Ising superconductivity in gated MoS$_2$. Science 350, 1353–1357 (2015).

23. Xi, X. X. et al. Ising pairing in superconducting NbSe$_2$ atomic layers. Nat. Phys. 12, 139–143 (2016).

24. Wang, Z. S. et al. Electron doping dependence of the anisotropic superconductivity in BaF$_2$-NiAs$_2$. Phys. Rev. B 92, 174509 (2015).

25. Potočnik, A. et al. Size and symmetry of the superconducting gap in the f.c.c. Ca$_2$CuO$_2$ polymorph close to the metal-Mott insulator boundary. Sci. Rep. 4, 6425 (2014).

26. Wzietek, P. et al. NMR study of the superconducting gap variation near the Mott transition in Ca$_2$CuO$_2$. Phys. Rev. Lett. 112, 066401 (2014).

27. Grissomanche, G. et al. Direct measurement of the upper critical field in cuprate superconductors. Nat. Commun. 5, 3280 (2014).

28. Shimoo, Y. et al. Upper critical fields of pressurized organic superconductors $\kappa$-(BEDT-TTF)$_2$X in the magnetic fields parallel to the layer. Synth. Met. 133–134, 197–200 (2003).

29. Ohmichi, E., Ishiguro, T., Yamada, J., Anzai, H. & Osada, T. Upper critical field of $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$Br](NCS)$_2$ in magnetic fields parallel to the layer. Synth. Met. 133–134, 245–246 (2003).

30. Agosta, C. C. et al. Experimental and semiempirical method to determine the Pauli-limited field in quasi-two-dimensional superconductor as applied to $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$: Strong evidence of a FFLO state. Phys. Rev. B 85, 214514 (2012).