Bulk evidence of anisotropic s-wave pairing with no sign change in the kagome superconductor CsV₃Sb₅

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The recently discovered kagome superconductors AV₃Sb₅ (A = K, Rb, Cs) exhibit unusual charge-density-wave (CDW) orders with time-reversal and rotational symmetry breaking. One of the most crucial unresolved issues is identifying the symmetry of the superconductivity that develops inside the CDW phase. Theory predicts a variety of unconventional superconducting symmetries with sign-changing and chiral order parameters. Experimentally, however, superconducting phase information in AV₃Sb₅ is still lacking. Here we report the impurity effects in CsV₃Sb₅ using electron irradiation as a phase-sensitive probe of superconductivity. Our magnetic penetration depth measurements reveal that with increasing impurities, an anisotropic fully-gapped state changes to an isotropic full-gap state without passing through a nodal state. Furthermore, transport measurements under pressure show that the double superconducting dome in the pressure-temperature phase diagram survives against sufficient impurities. These results support that CsV₃Sb₅ is a non-chiral, anisotropic s-wave superconductor with no sign change both at ambient and under pressure.
temperature $T^*$ ~ 78 K driven by electron correlation\textsuperscript{14-17}. The CDW transition is accompanied by a 2$a_0$ × 2$a_0$ × 2$c_0$ or 2$a_0$ × 2$a_0$ × 4$c_0$ superlattice composed of modulated star-of-David and inverse star-of-David patterns (where $a_0$ and $c_0$ indicate the lattice constants above $T^*$), which breaks translational symmetry\textsuperscript{18-20}. More intriguingly, it has been reported that additional symmetries, such as time-reversal symmetry (TRS) and rotational symmetry (RS), can be broken below $T^*$\textsuperscript{18,21}. Since the superconducting transition takes place inside the unusual CDW phase, a fundamental question arises as to whether the superconducting pairing mechanism in $\text{AV}_3\text{Sb}_5$ is conventional or not\textsuperscript{22}. Theories on the kagome lattice near van Hove filling have proposed that unconventional superconductivity beyond the electron-phonon mechanism can be realized by electron correlation effects\textsuperscript{9,23-27}. Spin and charge fluctuations can lead to spin-triplet $p$- and $f$-wave\textsuperscript{28,29} and chiral $d$-wave superconductivity\textsuperscript{1}, whereas bond-order fluctuations can promote anisotropic $s$-wave\textsuperscript{30} and chiral $d$-wave superconductivity. In the support of the above, first-principle calculations have pointed out that the Bardeen-Cooper-Schrieffer (BCS) theory (electron-phonon mechanism) cannot explain the experimental $T_c$ values, suggesting an unconventional pairing mechanism in $\text{AV}_3\text{Sb}_5$\textsuperscript{26}. Experimentally, however, the superconducting gap symmetry of $\text{AV}_3\text{Sb}_5$ is highly controversial, and whether TRS is broken or not is still elusive. Thermal conductivity measurements in $\text{CsV}_3\text{Sb}_5$\textsuperscript{31} and $\mu$SR measurements in $\text{Rb}/K\text{V}_3\text{Sb}_5$\textsuperscript{32} have suggested a nodal gap structure. In contrast, magnetic penetration depth\textsuperscript{18} and scanning tunneling spectroscopy (STS)\textsuperscript{33} studies in $\text{CsV}_3\text{Sb}_5$ have suggested a nodeless gap structure. Nuclear magnetic/quadrupole resonance (NMR/NQR) measurements in $\text{CsV}_3\text{Sb}_5$\textsuperscript{34} have shown a finite Hebel-Slichter coherence peak in $1/T_1T$ and a decrease in Knight shift below $T_c$, which exclude spin-triplet superconductivity. Regarding the TRS in the superconducting state, Josephson STS measurements in $\text{CsV}_3\text{Sb}_5$\textsuperscript{35} have suggested a possible roton pair-density wave, corresponding to an unconventional superconducting state with TRS breaking. Contrastingly, $\mu$SR studies in $\text{CsV}_3\text{Sb}_5$\textsuperscript{32} have reported that TRS is not broken in the superconductivity state. In addition to the above results at ambient pressure, high-pressure studies\textsuperscript{36,37} have revealed that the CDW phase is suppressed by the application of pressure, accompanied by the emergence of a superconducting dome, indicating the close relationship between the CDW and superconductivity. Moreover, recent $\mu$SR experiments under pressure\textsuperscript{38,39} have suggested that TRS is broken in the superconducting state when the CDW phase is suppressed by applying pressure. Therefore, to clarify the pairing mechanism of the kagome superconductors, it is crucial to pin down the superconducting gap symmetry of $\text{AV}_3\text{Sb}_5$ both at ambient and high pressure, including whether TRS is broken or not. In general, the conventional phonon-mediated pairing mechanism leads to a superconducting gap opening all over the Fermi surface, while unconventional pairing mechanisms, such as spin fluctuations, can lead to an anisotropic gap with nodes where the superconducting gap becomes zero. Thus, experimental observations of the low-energy quasiparticle excitations determine whether the gap structure has nodes or not. In addition to clarifying the presence or absence of nodes in the gap, determining the sign of the gap function also provides a...
superconductivity), the Cooper pairs are destroyed by impurity properties\textsuperscript{43,44}. In multiband systems and here, is one of the phase-sensitive probes that are applicable to In contrast, the non-magnetic impurity effect, on which we focus multiband systems due to the complexity of the scattering processes. highly required to determine the pairing symmetry of superconductors with sign-changing order parameters, such as chiral

d wave. Therefore, phase-sensitive probes are

to determine the pairing symmetry of AV\textsubscript{3}Sb\textsubscript{5}.

There are several experimental probes that are sensitive to the sign of gap functions, such as Josephson junction\textsuperscript{40}, quasiparticle interference\textsuperscript{41}, and neutron scattering techniques\textsuperscript{41}. In general, however, the analysis of such interference effects is complicated in multiband systems due to the complexity of the scattering processes. In addition, most of them require good surface/interface conditions. In contrast, the non-magnetic impurity effect, on which we focus here, is one of the phase-sensitive probes that are applicable to multiband systems and reflect the bulk superconducting properties\textsuperscript{41,44}. In s-wave superconductors with no sign-changing order parameter, the Cooper pairs are not destroyed by non-magnetic impurity scattering, and both \( T_c \) and quasiparticle density of states (DOS) are little affected by disorder (the so-called Anderson’s theorem\textsuperscript{43}) (Fig. 2e). In contrast, in the case of nodeless superconductors with sign-changing order parameters, such as chiral \( d \)-wave and \( s \)-wave superconductors (note that considering the electronic structure of the present kagome system, one cannot expect sufficient interband interactions to induce the \( s \)-wave superconductivity), the Cooper pairs are destroyed by impurity scattering, which suppresses \( T_c \) rapidly and induces impurity states associated with the Andreev bound state (Fig. 2f). In this case, additional low-energy quasiparticle excitations appear near the zero energy, e.g., leading to a change in the temperature dependence of the magnetic penetration depth \( \lambda \) from exponential to \( T^2 \)\textsuperscript{43,46}.

Here, we show that superconductivity in Cs\textsubscript{3}V\textsubscript{3}Sb\textsubscript{5} is robust against impurities both at ambient and under high pressure. Our magnetic penetration depth measurements reveal that with increasing impurities, a highly anisotropic fully gapped superconducting state changes gradually to an isotropic full-gap state without showing impurity-induced Andreev bound states, which excludes any of sign-changing symmetries. Moreover, transport measurements under high pressure show that the superconducting dome in the pressure-temperature (\( P-T \)) phase diagram survives against sufficient impurities. These results suggest that the superconducting gap function in Cs\textsubscript{3}V\textsubscript{3}Sb\textsubscript{5} is non-chiral and non-sign-changing s-wave.

Results

Electron irradiation effects on the CDW and superconducting transition temperatures

In this study, we used electron irradiation to systematically introduce non-magnetic impurities into Cs\textsubscript{3}V\textsubscript{3}Sb\textsubscript{5} single crystals (see Methods and Supplementary Information Sec. I). In this method, high-energy electron beam irradiation creates vacancies in the crystal\textsuperscript{37}, acting as point defects without changing the electronic structure and lattice constants (see Supplementary Information Sec. II). Figure 1d, e
shows the temperature dependence of resistivity $\rho(T)$ at ambient pressure in samples with irradiated doses of 0 (pristine), 1.3, 3.3, and 8.6 C/cm$^2$. The residual resistivity ratio (RRR) of the pristine sample is ~84, indicating the high quality of our crystals. As the dose increases, the residual resistivity $\rho_0$ increases (also see Fig. 1h), and the RRR value decreases. The change in $\rho(T)$ with impurities is successive for the irradiation dose in the whole temperature range. Furthermore, our X-ray structural analysis and Hall coefficient measurements show the absence of any change in the lattice parameters and carrier density induced by electron irradiation. These results indicate that the non-parallel shift with impurities in $\rho(T)$ is most likely due to the multiband nature of the present kagome system (for more details, see Supplementary Information Sec. III). Along with this, both the CDW and superconducting transition temperatures $T_c$ and $T$ showed to a lower temperature (Fig. 1g). In general, non-magnetic impurity scattering can suppress long-range orders because the introduced defects shorten the coherence length. Indeed, the suppression of CDW order by impurities has been theoretically studied$^{34}$. The suppression of $T_c$ has also been confirmed by the Meissner effect measured by the normalized frequency shift of a tunnel diode oscillator (TDO) (Fig. 1f). Note that the superconducting transition becomes sharper with increasing dose, which may be related to the suppression of superconducting phase fluctuations$^{45}$ or the change in skin depth due to impurity scattering. The sharp superconducting transition width in the 8.6 C/cm$^2$ irradiated sample with sufficient disorder indicates that the defects are introduced quite uniformly inside the crystals.

Non-magnetic impurity effects on low-energy quasiparticle excitations in the superconducting state

Next, we turn to the impurity effect on low-energy quasiparticle excitations in the superconducting state. Magnetic penetration depth $\lambda$ is one of the most fundamental properties of superconductors sensitive to low-energy quasiparticle excitations$^{18,43}$. In this study, we measured the magnetic penetration depth of the pristine and irradiated CsV$_3$Sb$_5$ single crystals down to 50 mK by using the TDO in a dilution refrigerator (see Methods). Figure 2a–d shows the change in the magnetic penetration depth $\delta\lambda(T) = \lambda(T) - \lambda(0)$ (where $\lambda(0)$ is the absolute value of the penetration depth at 0 K) at low temperatures for the pristine and 1.3, 3.3, and 8.6 C/cm$^2$ irradiated samples. In the pristine sample, $\delta\lambda(T)$ shows a flat temperature dependence at low temperatures below 0.1$T_c$ (Fig. 2a), indicating a fully gapped superconducting state in CsV$_3$Sb$_5$. To examine the low-energy quasiparticle excitations in the pristine sample, we applied a power-law fit $\delta\lambda(T) \propto T^n$ to the experimental data. In general, in the case of nodal superconductors with line and point nodes, the exponent $n$ gives 1 and 2 in the clean limit, respectively. We obtained $n = 2.8$ from the fitting (Fig. 2a), indicating the absence of nodes in the gap (or conversely, the presence of a finite gap). Then, to quantitatively evaluate the gap value, we tried to fit the data with the fully gapped s-wave model $\delta\lambda(T) \propto T^{\nu + 1/2} \exp(-\Delta_0/k_B T)$, where $\nu = 3$ is the Boltzmann constant and $\Delta_0$ is the superconducting gap. We obtained an extremely small gap value $\Delta_0 = 0.47 k_B T_c$ (which is consistent with the previous study$^{34}$), suggesting the existence of gap minima $\Delta_{\text{min}}$ coming from the anisotropic gap nature of CsV$_3$Sb$_5$ as discussed later. One of our key findings is that the fully gapped behavior in $\delta\lambda(T)$ is robust against disorder (Fig. 2b–d). The flat temperature region at low temperatures expands to a higher temperature region with increasing dose. In the case of fully gapped superconductors with sign-changing order parameters, $\delta\lambda(T)$ is expected to change from an exponential to a $T^2$ dependence with increasing impurities because of the impurity-induced DOS (Fig. 2f)$^{24}$. In sharp contrast, our experimental observations show that $\Delta_0$ and $n$ obtained from the fitting rather increase with increasing dose (Fig. 2g, h), indicating no impurity-induced DOS in the superconducting gap. These results provide strong bulk evidence that the superconducting gap structure of CsV$_3$Sb$_5$ is nodeless without a sign-changing gap.

For a more detailed analysis of the superconducting gap structure, we derived the normalized superfluid density $\rho_s(T)/\rho_0 = \Delta(T)/\Delta_0$ (where $\Delta_0$ is assumed to be equal to $\lambda(0) = 387$ nm for the pristine sample, and $T$ and $\lambda$ are the mean free path and coherence length, respectively) for more details, see Supplementary Information Sec. IV). Figure 3a shows the obtained $\rho_s(T)$ curve as a function of $T/T_c$ for each sample. In all the samples, $\rho_s$ shows a flat temperature dependence at high temperatures, which extends to a higher temperature region with increasing dose. This is again inconsistent with a nodal gap structure.

Here, we consider a multigap model to analyze the overall temperature dependence of $\rho_s$. In CsV$_3$Sb$_5$, the Fermi surfaces are formed by two different orbitals: one is derived from the $d$-orbitals of V, forming a hexagonal Fermi surface around the K point and two triangular Fermi surfaces around the Γ point, while the other is from the $p$-orbitals of Sb, forming a circular Fermi surface around the Γ point (Fig. 1c). The Fermi surfaces derived from the V $d$-orbitals determine the physical properties of this material, and three equivalent $\mathbf{q}$ vectors$^{12,23,24}$ are considered to give rise to anisotropic pairing interactions$^{17}$. Indeed, recent STM measurements$^{49}$ have reported the emergence of an anisotropic superconducting gap as well as an isotropic gap below $T_c$. We therefore consider a multigap model with an anisotropic but nodeless superconducting gap with six-fold symmetry ($\Delta_1 \propto \mathbf{I} + \alpha \cos(6\phi)$) and an isotropic superconducting gap ($\Delta_2 \propto \text{const}$) on two cylindrical Fermi surfaces (Fig. 3b). Note that an isotropic two-gap model cannot produce reasonable results for irradiated samples (for more details, see Supplementary Information Sec. V). We fitted the experimental data with the anisotropic multigap model (Fig. 3a) and obtained the gap values $\Delta_1$ and $\Delta_2$ as a function of dose (Fig. 3c). As the dose increases, the difference between the maximum and minimum values of $\Delta_2$ decreases, and eventually, all the gaps become almost identical. This is due to the averaging effect between the two gaps introduced by impurity-induced intra/interband scattering, and a very similar behavior has been observed in the prototypical multigap superconductor MgB$_2$.$^{21}$ This evidences nodeless multigap superconductivity with a sign-preserving order parameter in CsV$_3$Sb$_5$, which excludes the possibility of spin-triplet $p$- and $f$-wave and chiral $d$-wave superconductivity.

Pair-breaking effect

To discuss the impurity effect on $T_c$ more quantitatively, we next introduce a pair-breaking parameter $g = \hbar/\xi_{\text{rmp}}T_c$, where $\xi_{\text{rmp}} = h/\sqrt{\rho_0 \nu T_c}$ is the impurity scattering time and $T_c$ is the superconducting transition temperature of the pristine sample$^{19,40}$. The suppression of $T_c$ is plotted as a function of $g$ and compared to other superconductors with and without sign-changing order parameters (Fig. 3d). $T_c$ of CsV$_3$Sb$_5$ is rapidly suppressed at a low irradiation dose but starts to saturate at moderate irradiation doses. The initial rapid suppression of $T_c$ is considered to be related to the reduction of the anisotropy of $\Delta_2$ (Fig. 3c), as discussed later. The $T_c$ suppression above 1.3 C/cm$^2$ irradiation dose is much slower than those in superconductors with sign-changing order parameters such as $d$-wave, rather similar to those in $s$-wave superconductors without sign-changing gaps. These results also support that multigap $s$-wave superconductivity with no sign change is realized in CsV$_3$Sb$_5$ at ambient pressure.

Impurity effects on the high-pressure superconducting phase

To further investigate the non-magnetic impurity effect on the superconducting phase of CsV$_3$Sb$_5$ under pressure, we constructed the
4.8 and 8.6 C/cm² irradiated samples (Fig. 4e) near the CDW endpoint. We conducted the same experiments for the GPa inside the CDW phase, while the second peak locates at MgB₂. Therefore, these results suggest that the superconducting gap parameter changes with the relatively large value of E₂ ≈ 2.3 approaches the dirty limit (see Supplementary Information Sec. V).

As already discussed in Fig. 3d, the irradiation dose of 8.6 C/cm² induces anisotropic d-wave superconducting gap structure at disorder, the introduction of electron irradiation changes the anisotropic superconducting gap structure to an isotropic one. Gap sizes obtained from the fitting analysis of the superfluid density as a function of dose. Red circles and blue diamonds represent the maximum and minimum values of the anisotropic gap, Δ₁, max and Δ₂, respectively. Green squares represent the gap values of the isotropic gap Δ₂. Dotted lines are guides for the eyes.

**Discussion**

Recent μSR measurements under pressure²⁷ have reported that the superconducting pairing symmetry near P₂ has a finite superconducting gap across the Fermi surface and breaks TRS. As a possible symmetry, chiral dₜ₋₋₋ₕ ± idₓᵧ, or pₓ ± ipᵧ, wave superconductivity has been discussed²⁷,²⁸. However, such unconventional superconductivity is expected to be sensitive to disorder, because the chiral states have sign-changing order parameters which would produce Andreev bound states by impurities. Our present results show that the superconducting state under high pressure is robust against disorder. These findings seem to be inconsistent with the chiral dₜ₋₋₋ₕ ± idₓᵧ and pₓ ± ipᵧ wave states. To fully understand the relationship between our disorder effects and the μSR results, further theoretical and experimental studies on the high-pressure phase in the kagome systems are highly desired. We note that the TRS breaking has been observed in the CDW phase, and thus the possible fluctuations of chiral CDW order in the high-pressure phase on the time scale of μSR measurements may be an important issue.

Another important aspect of our findings is that the CDW endpoint shifts to lower pressure with irradiation, followed by the second peak of the superconducting double dome (Fig. 4d, h, l), suggesting that the CDW is closely related to the superconductivity in the present system. Recent theoretical calculations in AV₃Sb₅ have proposed that bond-order fluctuations originating from the triple-q vectors corresponding to the (inverse) star of David pattern induce anisotropic pairing interactions, leading to anisotropic s-wave superconductivity. This theory can explain the relatively high Tc in AV₃Sb₅ that cannot be
reproduced by the BCS theory and the anisotropic superconducting gap structure in CsV3Sb5 obtained in the present study. Moreover, in such anisotropic s-wave superconductivity, the introduction of impurity scattering averages out the anisotropic gap, changing to the isotropic gap. In this case, $T_c$ drops rapidly at an initial introduction of impurities, but as the gap becomes isotropic, the reduction of $T_c$ saturates and becomes much slower than that expected in the Abrikosov-Gor'kov (AG) theory. These expectations are in good agreement with our observations of the $T_c$ suppression in CsV3Sb5. We note that a possible transition from a $p$-wave to an $s$-wave state caused by impurities may explain the initial rapid suppression of $T_c$. However, our present results exclude the possibility of a nodal superconducting state in the pristine sample, which is at odds with the $p$-wave state. The gradual change in the superconducting gap inferred from the temperature dependence of the superfluid density suggests that an impurity-induced transition from a full-gap chiral state to a non-chiral $s$-wave state is also unlikely. This is reinforced by the pSR measurements at ambient pressure, which report that chiral superconductivity in the pristine sample at ambient pressure can be ruled out. Thus, our present results support a new type of unconventional superconductivity due to bond-order fluctuations on the kagome lattice in CsV3Sb5, where the gap function is non-sign-changing $s$-wave. In the present kagome superconductors, the possibility of a loop-current phase with broken TRS and a nematic phase with broken RS has been pointed out above the superconducting phase. Therefore, elucidating the intertwining of these unusual normal and superconducting phases, which is commonly seen in high-$T_c$ cuprates and iron-based superconductors, will pave the way to understanding novel quantum phases of matter in condensed matter physics.

**Methods**

**Single crystal growth**

High-quality single crystals of CsV3Sb5 were synthesized using the self-flux method. All sample preparations are performed in an argon glovebox with oxygen and moisture < 0.5ppm. The flux precursor was formed through mechanochemical methods by mixing Cs metal (Alfa 99.98%), V powder (Sigma 99.9%), and Sb beads (Alfa 99.999%) to form a mixture which is ~50 at.% Cs0.4Sb0.6 (near eutectic composition) and 50 at.% VSb2. Note that prior to mixing, as-received vanadium powders were purified in-house to remove residual oxides. After milling for 60 min a pre-seasoned tungsten carbide vial, flux precursors are extracted and sealed into 10 mL alumina crucibles. The crucibles are
nested within stainless steel jackets and sealed under argon. Samples are heated to 1000 °C at 250 °C/h and soaked for 24 h before dropping to 900 °C at 100 °C/h. Crystals are formed during the final slow cool to 500 °C at 1 °C/h before terminating the growth. Once cooled, the crystals are recovered mechanically. Samples are hexagonal flakes with a brilliant metallic luster. The elemental composition of crystals was assessed using energy-dispersive X-ray spectroscopy (EDS) using an APREO-C scanning electron microscope.

Electron irradiation
Electron irradiation with the incident electron energy of 2.5 MeV was performed on SIRIUS Pelletron accelerator operated by the Laboratoire des Solides irradiés (LSI) at École Polytechnique. To prevent defect migration and agglomeration, the sample temperature was kept at ~20 K during irradiation which produces stable vacancy-interstitial Frenkel pairs. Subsequent warming to room temperature causes annealing of interstitials, which have a lower migration energy, leaving a uniform population of vacancy type defects. The electron irradiation of 1.3, 3.3, and 8.6 C/cm² was performed at the same beam time (run#1), while the irradiation of 4.8 C/cm² was conducted at another beam time (run#2).

Electrical resistivity measurements
The electrical resistivity was measured at ambient and high pressure by the 4-terminal method using a Physical Property Measurement System (PPMS) from Quantum Design with the lowest temperature of about 1.8 K. The resistivity under pressure was measured using a piston cylinder cell to generate pressure up to ~2.5 GPa and daphne 7373 as a pressure medium in PPMS. The pressure value in the sample was determined from the superconducting transition temperature Tc of Pb under pressure, using the relation P = (7.70 - Tc)/0.365. Note that when the 4.8 C/cm² irradiated sample was set in the piston cell, even before pressure was applied, the resistivity value changed, probably due to cracks, so we have corrected it to the value before pressure was applied.

Magnetic penetration depth measurements
The temperature variation of the in-plane magnetic penetration depth δλ(T) = λ(T) / λ(0) was measured by using a tunnel diode oscillator technique (TDO) with the resonant frequency of ~13.8 MHz in a dilution refrigerator down to ~50 mK. The sample was mounted on a sapphire rod with Aipiezoon Grease, then inserted into a copper coil in the LC circuit. The frequency shift δf in the TDO is related to the change of magnetic susceptibility δχ by the following equation, δf = -(f0Vc / (2Vr(1 - N)))δχ, where f0 is the resonant frequency without the sample, Vc and Vr are the sample and coil volume, respectively, and N is the demagnetization factor. δχ is related to δλ by the following equation, δλ = δλR / R, where R is a constant determined by the geometry of the sample from the calculation. Thus, δf is related to δλ by the following equation, δf = -(f0Vc / (2VR(1 - N)))δλ.

Data availability
All data supporting the findings of this study are available within the paper and its Supplementary Information. Source data are provided with this paper.

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Author contributions

K.H. and T.S. conceived the project. M.R., K.I., K. Ogawa, K. Okada, Y.M., K.H., and T.S. performed magnetic penetration depth measurements and analyzed the data. Y.T., K. Okada, K.M., and Y.U. carried out high-pressure measurements. M.R. and S.L. performed electrical transport and X-ray diffraction measurements. R.G. and M.K. conducted electron irradiation experiments. B.R.O. and S.D.W. carried out sample preparation. M.R., K.H., and T.S. prepared the manuscript with inputs from R.G., M.K., B.R.O., and S.D.W. All authors discussed the experimental results.

Competing interests

The authors declare no competing interests.

Additional information

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