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ABSTRACT

Doped SrTiO₃ is a superconductor whose pairing mechanism is still not fully understood. The response of a superconductor to impurities has long been used to obtain insights into the nature of the superconducting state. Here, the superconductivity of SrTiO₃ films that are doped or alloyed with different rare earth ions, which carry a magnetic moment, is investigated. It is shown that large concentrations (up to a few percent) of rare earth ions with unpaired *f*-electrons, such as Sm and Eu, do not reduce the superconducting critical temperature and critical fields. The finding is independent of whether the rare earth ion acts as a dopant or is an isovalent impurity. The interactions between the superconducting condensate and the magnetic dopants that could result in the observed insensitivity to magnetic impurities are discussed.

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Superconductivity in electron-doped SrTiO₃ was discovered almost 60 years ago.¹ Already early on it was recognized that certain aspects of its superconductivity, including a Fermi energy that is much lower than the Debye temperature, challenge standard BCS theory. At present, there exist several different proposals for the pairing mechanism in SrTiO₃ (see Ref. 2 for a recent review). Moreover, SrTiO₃ can also be a polar superconductor that undergoes a ferroelectric transition prior to becoming superconducting.^{3–5} In superconductors with broken inversion symmetry spin-orbit coupling becomes important, which can lead to unconventional superconductivity.^{6–9}

A test of the nature of a superconductor is its response to disorder.¹⁰ While conventional (*s*-wave) superconductors are protected against nonmagnetic disorder according to Anderson's theorem,¹¹ magnetic impurities strongly reduce the superconducting transition temperature due to the exchange coupling between the impurity spins and those of the conduction electrons.¹² Unconventional superconductors show a different response to disorder. For example, cuprate superconductors tend to be equally sensitive to nonmagnetic and magnetic impurities.¹³ This has been attributed to the importance of magnetism in the Cooper pairing mechanism¹⁴ or the anisotropy of the order parameter.¹⁰ A high degree of sensitivity to any kind of disorder is believed to be a hallmark signature of odd-parity superconductors.^{10,15} It has, however, also been suggested that spin-orbit coupling and/or multiband effects can make odd-parity and topological superconductors more robust against disorder.^{16–19} Interestingly, certain kinds of magnetic impurities are believed to offer a route to topological superconductivity.²⁰

The purpose of the present study is to investigate the effect of magnetic impurities on the superconductivity of SrTiO₃. Oxygen vacancies, Nb, and La are traditionally used as donor dopants in superconducting SrTiO₃.^{1,21,22} More recently, SrTiO₃ doped with Nd and Sm has been shown to also become superconducting.^{3,23,24} Unlike La, these dopants introduce localized *f*-states, which carry a magnetic moment. Surprisingly, however, the superconducting transition temperatures (*T*_c) and the superconducting dome are identical for magnetic and non-magnetic dopants.^{3,23,24} While there are indications that disorder from the dopant atoms is detrimental to superconductivity in SrTiO₃,⁵ the insensitivity to their magnetic moment does not easily fit within a conventional picture of isolated magnetic impurities that would strongly suppress the transition temperature of the superconductor.

The purpose of the present study is to separate the effect of the magnetic properties of the impurity ion from its properties as a dopant. To this end, we investigate SrTiO₃ films with a fixed Sm dopant concentration (we already know that Sm is not detrimental to superconductivity). We then co-alloy the films with different amounts of Eu. Like Sm, Eu has unpaired *f*-electrons (the electronic configurations are 4*f*⁵ for Sm³⁺ and 4*f*⁷ for Eu²⁺) and substitutes for Sr. In contrast to Sm, Eu is divalent (like Sr) and thus does not donate free carriers to the conduction band.

Coherently strained films of R:Sr_{1–x}Eu_xTiO₃, where the *n*-type dopant *R* is either La³⁺ or Sm³⁺, were grown on (001) (LaAlO₃)_{0.3}(Sr₂TaAlO₆)_{0.7} (LSAT) single crystals by molecular beam epitaxy (MBE), as described elsewhere.²⁵ Sm-doped films were

co-alloyed with Eu^{2+} with x ranging between 0 and 0.03. For fully strained films, the in-plane strain ($\sim 1\%$) is sufficient for the films to undergo a ferroelectric transition below 100 K at the carrier densities investigated here.⁴ Here, the film thicknesses were 170, 167, and 187 nm for samples with 0.5%, 2% and 3% Eu, which is near the critical thickness for strain relaxation.²⁶ Onset of a small degree of strain relaxation was detected in x-ray diffraction for some films (see the [supplementary material](#)). The Sm (or La) concentration determines the free carrier concentration, while the Eu concentration was estimated from the flux during film growth. Optimal doping (peak of the superconducting dome) corresponds to a carrier density $n_{3D} \cong 1 \times 10^{20} \text{ cm}^{-3}$ and results in $T_c \cong 600 \text{ mK}$, about twice that of unstrained SrTiO_3 . The Eu-alloyed films were slightly underdoped with n_{3D} ranging between 5 and $8 \times 10^{19} \text{ cm}^{-3}$ (0.3%–0.5%). The variation in carrier density corresponded to the difference in Sm doping. To confirm that the films were polar, second harmonic generation and cross-sectional high-angle annular dark-field (HAADF) imaging in scanning transmission electron microscopy (STEM) were performed (see the [supplementary material](#)).

Films were patterned into Hall bars using optical lithography, Ar ion milling, and a Ti/Au liftoff procedure to define Ohmic contacts. Electrical measurements between 300 and 2 K were performed in a Quantum Design Dynacool system. The carrier density was estimated from the low field Hall effect at 300 K. Measurements of the superconducting transition temperature were carried out in an Oxford Instruments Triton dilution refrigerator with a base temperature of 12 mK. T_c was defined as corresponding to the temperature at which the resistivity was 5% of the normal state resistivity. Upper critical fields (H_{c2}) were taken as 95% of the normal state resistivity for both in-plane and out-of-plane field configurations.

Figure 1(a) shows the sheet resistance (R_s) as a function of temperature (T) for samples with varying Eu concentrations. All samples are superconducting with T_c of 600, 550, and 500 mK for samples with 0.5%, 2%, and 3% Eu, respectively. The values for T_c are greater than those of unstrained films [300 mK (Ref. 3)] indicating that the partial strain relaxation seen in x-ray diffraction was not sufficient to reduce T_c to its unstrained value. As shown in Fig. 1(b), the minor variations in T_c can entirely be attributed to the differences in n_{3D} between the films. This finding will be further confirmed below, when we compare the change in T_c with the change expected from the superconducting dome. Thus, the addition of up to 3% Eu does not affect T_c .

Similarly, both in-plane and out-of-plane H_{c2} values are sensitive to small variations in carrier density, but are not affected by the addition of Eu (Fig. 2). The anisotropy of H_{c2} in parallel and perpendicular fields varies with n_{3D} , similar to films without Eu.²⁴

To further illustrate the insensitivity of the superconductivity to the presence of Eu, we compare in Fig. 3 the values of T_c and $\mu_0 H_{c2}$ as a function of n_{3D} for the Eu-alloyed films with a larger dataset of Sm- and La-doped SrTiO_3 films grown on LSAT. The Eu-alloyed films follow the trend observed for all samples, despite the additional localized f -states. The most important factor determining T_c is the carrier density, independent of the type of dopant used or the presence of Eu. A change of carrier density by about $3 \times 10^{19} \text{ cm}^{-3}$ leads to a 90 mK difference in T_c and a 0.5 T difference in H_{c2} . This is in line with samples without Eu, where, on average, for a similar change in carrier density, T_c and H_{c2} change by 110 mK and 0.6 T, respectively.

Table I summarizes the parameters of the samples studied. The estimated elastic scattering lengths (l_e) are 6, 9, and 15 nm for the films with 0.5%, 2%, and 3% Eu, respectively. Here, $l_e = \nu_F / \tau_e$, where τ_e is the scattering time, ν_F the Fermi velocity and $\tau_e = (\sigma m^*) / (ne^2)$, where σ is the conductivity at 2 K, m^* is the effective mass ($1.8 m_e$) and $\nu_F = \hbar \pi (3n_{3D})^{1/3} / m^* \cong 1.3 \times 10^7 \text{ cm/s}$. Here, l_e scales with the Sm dopant content (not with the Eu content) and l_e is greater than the average Eu–Eu distance ($l_{\text{Eu–Eu}}$), see Table I. The residual resistivity in the normal regime is thus not controlled by the neutral Eu impurities but controlled by other defects, especially the charged Sm dopants, as seen previously in La doped samples.²⁷ Moreover, l_e is smaller than the superconducting coherence length calculated from BCS theory, $\xi_0 = \sqrt{\phi_0 / 2\pi H_{c2}}$, which indicates that the films are in (or close to) the dirty limit ($l_e \ll \xi_0$). The dirty limit is consistent with the fact that ξ_0 scales with l_e and explains the strong dependence of H_{c2} on the dopant concentration in all samples, as seen in Fig. 3.

We conclude that the superconductivity of SrTiO_3 is insensitive not only to magnetic dopants, like Sm and Nd, but also to f -states introduced by a rare earth ion that does not act as a dopant. We note that this finding is remarkable—for most superconductors suppression of T_c is generally expected upon addition of a magnetic ion. The insensitivity to magnetic impurities necessarily invalidates the application of any of the models commonly used to describe superconductors containing isolated impurities, including those that take Kondo screening into account.^{28–31}

FIG. 1. (a) Sheet resistance (R_s) as a function of temperature for strained, Sm-doped SrTiO_3 films alloyed with 0.5% Eu (sample A), 2% Eu (sample B), and 3% Eu (sample C), respectively. (b) Comparison of n_{3D} and T_c for the three samples.

FIG. 2. Sheet resistance (R_s) for strained, Sm-doped SrTiO_3 films alloyed with 0.5% Eu (sample A), 2% Eu (sample B), and 3% Eu (sample C), respectively, as a function of (a) an in-plane (ip) magnetic field and (b) an out-of-plane (oop) magnetic field. Upper critical fields for samples A, B, and C for (c) in-plane and (d) out-of-plane fields in comparison with n_{3D} .

FIG. 3. Comparison of (a) T_c and (b) out-of-plane H_{c2} as a function of n_{3D} for La and Sm-doped SrTiO_3 with no Eu with the Eu-alloyed films in this study. The data from the La-doped samples is from Ref. 24 and the data from the Sm-doped samples (no Eu) is from Ref. 3. Some of the La-doped films were partially relaxed, which lowers T_c (see Ref. 24 for a discussion). All films were grown by the same MBE technique on LSAT substrates.

TABLE I. Summary of film parameters.

Sample	n_{3D} (cm^{-3})	T_c (mK)	$H_{c2 \text{ IP}}$ (T)	$H_{c2 \text{ oop}}$ (T)	$l_{\text{Eu-Eu}}$ (nm)	l_e (nm)	ζ_{IP} (nm)	ζ_{oop} (nm)
0.5% Eu	8×10^{19}	600	1.4	1	2.3	6	15	18
2% Eu	7×10^{19}	550	1	0.6	1.4	10	18	23
3% Eu	5×10^{19}	500	0.6	0.4	1.3	15	23	27

Kondo screening can make superconductors somewhat less sensitive to magnetic impurities, provided that the Kondo temperature, T_K , is much greater than T_c .^{29,31} The Kondo effect should be evident as a resistivity minimum near T_K , which has previously been observed in SrTiO₃.³² Here, only the sample with 0.5% Eu concentration shows a resistance upturn (see the [supplementary material](#)). The resistance upturn occurs at ~ 90 K which is much higher than expected T_K for rare earth magnetic impurities.³³ The resistance upturn is also seen in some samples with La dopants (no Eu), which carry no net spin, and we have previously associated it with the ferroelectric transition.^{3,4} Thus, there is no evidence that Kondo screening plays any role in the robustness of superconductivity in SrTiO₃ to magnetic impurities.

The most likely explanation is that magnetically doped SrTiO₃ cannot be described within a picture of isolated magnetic impurities. In particular, the role of interactions between the conducting electrons and the magnetic impurities should be considered. Ruderman–Kittel–Kasuya–Yosida (RKKY) interactions lead to magnetic order and can also suppress the Kondo effect,³⁴ which may explain why it is not observed in rare earth doped SrTiO₃. For impurity separations that are smaller than the coherence length, as is the case here, RKKY produces weak antiferromagnetic interactions and, as a result, superconductivity is influenced only weakly by the impurities.³⁵ Moreover, a recent theoretical study shows that overlapping Yu–Shiba–Rusinov (YSR) bound states associated with magnetic impurities can produce a strong antiferromagnetic interaction due to hybridization with the superconducting condensate,³⁵ an interaction that is distinct from RKKY.

Clearly, further investigations are needed to clarify (experimentally and theoretically) the interactions between the magnetic impurities and the superconducting condensate, taking into consideration also the role of spin–orbit coupling present in noncentrosymmetric films. The next step would be to examine additional characteristics of the superconducting state, going beyond critical fields and transition temperatures, that might reveal any differences between rare earth doped/alloyed SrTiO₃ and SrTiO₃ doped with the usual nonmagnetic dopants.

AUTHORS' CONTRIBUTIONS

S.S.-R. and L.G. contributed equally to this work.

See the [supplementary material](#) for the results from x-ray diffraction, second harmonic generation, and scanning transmission electron microscopy studies. Also shown is the temperature dependence of the resistance in the normal state.

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DATA AVAILABILITY

The data that support the findings of this study are available within the article and its [supplementary material](#).

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