Carrier-Controlled Ferromagnetism in SrTiO3

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Magnetotransport and superconducting properties are investigated for uniformly La-doped SrTiO3 films and GdTiO3/SrTiO3 heterostructures, respectively. GdTiO3/SrTiO3 interfaces exhibit a high-density 2D electron gas on the SrTiO3 side of the interface, while, for the SrTiO3 films, carriers are provided by the dopant atoms. Both types of samples exhibit ferromagnetism at low temperatures, as evidenced by a hysteresis in the magnetoresistance. For the uniformly doped SrTiO3 films, the Curie temperature is found to increase with doping and to coexist with superconductivity for carrier concentrations on the high-density side of the superconducting dome. The Curie temperature of the GdTiO3/SrTiO3 heterostructures scales with the thickness of the SrTiO3 quantum well. The results are used to construct a stability diagram for the ferromagnetic and superconducting phases of SrTiO3.

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Two-dimensional electron liquids at interfaces between two insulating oxides, such as LaAlO3/SrTiO3, have generated tremendous excitement because of unique properties, such as strong electron correlations, superconductivity, and ferromagnetism [1–4]. While superconductivity is a known bulk property of SrTiO3 [5], ferromagnetism is not a property of either material and has so far only been observed for LaAlO3/SrTiO3 interfaces [3,6–9]. Furthermore, recent studies indicate the coexistence of superconductivity and ferromagnetism at these interfaces [6–8]. These observations raise a number of scientific questions. Among these, the most important question is whether ferromagnetism, and its coexistence with a superconducting state, is an intrinsic, many-body property of a 2D electron liquid in SrTiO3 or caused by extrinsic contributions, such as disorder, defects, or impurities [10]. Pointing to impurities as the cause are observations of ferromagnetic regions that form nonuniform patches [8] and inconsistencies in the appearance of magnetism in samples grown under the same conditions [11]. In addition, a large fraction of the interfacial charge at LaAlO3/SrTiO3 interfaces appears to be localized, indicating the presence of traps [12], and mobile charge densities are an order of magnitude less than what is needed to compensate for the polarization discontinuity [13].

In this study, ferromagnetism in SrTiO3 and its coexistence with superconductivity are investigated in two different structures: extreme-electron-density electron liquids at GdTiO3/SrTiO3 interfaces and uniformly doped SrTiO3 films. The charge carriers, which reside in the SrTiO3 for both structures, have fundamentally different origins: for the uniformly doped SrTiO3 films, La-dopant atoms provide the carriers, while, for the GdTiO3/SrTiO3 interfaces, carriers are due to the interface. In particular, similar to LaAlO3/SrTiO3 interfaces, GdTiO3/SrTiO3 heterostructures exhibit a fixed polar charge, due to the dipole moment associated with the Gd3+O2-/Ti3+O2- bilayers along the (001) surface normal of GdTiO3. Unlike LaAlO3/SrTiO3, however, GdTiO3/SrTiO3 interfaces grown by molecular-beam epitaxy (MBE) exhibit mobile carrier densities that are remarkably well predicted by the electrostatic requirements of the compensation of the polar discontinuity at the interface [14]. Carrier densities are (3–4) × 10^14 cm^2, or approximately 1/2 electron per surface unit cell, at each GdTiO3/SrTiO3 interface for all heterostructures containing more than one unit cell of SrTiO3 [14]. The staggered band alignment causes the mobile charge to reside in the SrTiO3, which is the wider-band-gap material [14]. These interfaces allow for doping of narrow SrTiO3 quantum wells to extremely large and mobile carrier concentrations. For example, by sandwiching a few-unit-cell-thick SrTiO3 layer between two GdTiO3 layers, carrier concentrations in the SrTiO3 approach one electron per site, conditions under which electron correlation effects should appear [15,16].

In this paper, we show that both types of samples, uniformly doped SrTiO3 films and high-density 2D electron gases at GdTiO3/SrTiO3 interfaces, exhibit ferromagnetism. A ferromagnetic phase-stability region appears on the high-density side of the superconducting dome in the phase diagram, and, at an intermediate carrier concentration, both phases coexist.
We investigate three types of high-electron-concentration samples grown by MBE: GdTiO$_3$/SrTiO$_3$ heterostructures grown on (LaAlO$_3$)$_{0.3}$(Sr$_2$AlTaO$_6$)$_{0.7}$ (called LSAT) substrates, containing either a single electrically active interface (GdTiO$_3$/SrTiO$_3$/LSAT) or two active interfaces (GdTiO$_3$/SrTiO$_3$/GdTiO$_3$/LSAT), and two uniformly La-doped SrTiO$_3$ films of about 40-nm thickness (with nominal dopant densities of $1 \times 10^{20}$ cm$^{-3}$ and $9 \times 10^{20}$ cm$^{-3}$, respectively) grown on LSAT substrates. Details of the MBE growth procedures have been described in detail elsewhere [14,17,18]. Previous studies have demonstrated a close correspondence between La-dopant concentrations in the SrTiO$_3$ and mobile carrier densities, down to dopant concentrations of approximately $1 \times 10^{17}$ cm$^{-3}$ [19]. These results provide evidence for the absence of additional sources of carriers, such as oxygen vacancies, and of traps such as transition metal impurities or Sr vacancies (which would reduce the carrier concentrations relative to the La-dopant concentration), on the parts-per-million level. Furthermore, positron-annihilation studies of the La-doped films indicate Sr-vacancy concentrations of no more than approximately $1 \times 10^{16}$ cm$^{-3}$ in these films [20]. We note that the carrier densities in the uniformly doped samples investigated here are slightly less than the dopant concentration, because of the well-known surface depletion of SrTiO$_3$ [21]. For the SrTiO$_3$/GdTiO$_3$ heterostructures, the thickness of the SrTiO$_3$ layer was varied between 1 and 10 nm.

Ohmic contacts to the GdTiO$_3$ and SrTiO$_3$ layers were 300 nm Au/50 nm Ti and 300 nm Au/20 nm Ni/40 nm Al, respectively, with Au contact being the topmost layer in each case. Magnetoresistance measurements were carried out in Van der Pauw geometry using the Physical Properties Measurement System (PPMS from Quantum Design). The sweep rates were varied between 0.005 and 0.01 T/s and all results (such as hysteresis and Curie temperature) shown here were found to be independent of the sweep rate. For the Hall measurements, the magnetic field $B$ was varied between 0.1 T. The 2D carrier concentration $n$ was calculated as $n = 1/(e \cdot R_H)$, where $R_H$ is the measured 2D Hall coefficient. Low-temperature measurements of the uniformly doped samples were performed in a dilution refrigerator, capable of temperatures down to 12 mK and magnetic field up to 9 T. The low-temperature magnetoresistance was measured using a standard lock-in technique at a frequency of 13 Hz. Magnetization was measured using a SQUID magnetometer (the Magnetic Properties Measurement System from Quantum Design).

Figure 1(a) shows the longitudinal magnetoresistance, $R(B)$, where $B$ is the magnetic field, of a 1-nm SrTiO$_3$ quantum well sandwiched between two GdTiO$_3$ layers, measured in four-terminal geometry. The sheet carrier density of this sample, as extracted from the Hall resistance, is about $9 \times 10^{15}$ cm$^{-2}$ at room temperature and about $1 \times 10^{15}$ cm$^{-2}$ at 5 K, corresponding to a 3D carrier density of about $1 \times 10^{22}$ cm$^{-3}$ in the 1-nm quantum well. Negative magnetoresistance is apparent at low temperatures (below 10 K), as has been previously reported for La-doped SrTiO$_3$ [22]. Concurrent with the appearance of negative magnetoresistance, $R(B)$ becomes hysteretic, indicating ferromagnetism, when the magnetic field was in-plane and perpendicular to the current. We use the appearance of hysteresis to define the Curie temperature of the ferromagnetic transition, $T_{Cur}$. We note that, although extrinsic effects (the possibility of which is further discussed below) in ferromagnets may give rise to magnetoresistance hysteresis, the presence of a hysteresis nonetheless implies ferromagnetic ordering [23]. The shape of the hysteresis is very similar to that observed by Brinkman et al. for a LaAlO$_3$/SrTiO$_3$ interface [3]; however, here it occurs at almost an order-of-magnitude higher temperature than in Ref. [3].

![Figure 1](image-url)
Heterostructures with a single interface and 1-nm SrTiO$_3$, which contain half the carrier density or less (sheet carrier densities of $4 \times 10^{14}$ cm$^{-2}$ at room temperature and $1.9 \times 10^{14}$ cm$^{-2}$ at 5 K; the latter corresponding to a 3D concentration of $1 \times 10^{21}$ cm$^{-3}$), also show ferromagnetic hysteresis, albeit at a lower $T_C$ of about 3 K. 

Samples with thicker SrTiO$_3$ layers (2 nm) did not show any magnetoresistance hysteresis above 2 K. In addition to the hysteresis in $R(B)$, all samples that exhibit hysteresis show an increase in resistance as the temperature is lowered, indicating a departure in the nature of conduction from conventional metallic systems [24]. For data from a sample with a slightly thinner SrTiO$_3$ layer, see Ref. [24].

GdTiO$_3$ layers are ferrimagnetic [17,25], and it is therefore entirely conceivable that the magnetism of the carriers in the SrTiO$_3$ is induced by the proximity to the GdTiO$_3$ or spillover of carriers into the GdTiO$_3$. However, the following observations can also be made: (i) Ferromagnetism is absent in samples with SrTiO$_3$ layers that are thicker than 2 nm, despite similar sheet carrier densities and proximity to the GdTiO$_3$. (ii) The Curie temperature of GdTiO$_3$ is substantially higher (approximately 20 K; see Fig. 2) than $T_{Cm}$ of any of the 2D electron liquids investigated here. (iii) Ferromagnetism also appears in highly doped bulk SrTiO$_3$, when no GdTiO$_3$ layer is present, albeit at much lower temperatures, as we will discuss next.

Figure 3 shows $R(B)$ for 44-nm-thick SrTiO$_3$, uniformly doped with La to a density of $9 \times 10^{20}$ cm$^{-3}$, measured at $T = 12$ mK. Here, $B$ is applied perpendicular to the current and parallel to the growth direction [i.e., perpendicular to the (001) growth surface]. Magnetoresistance hysteresis is evident for this sample. The hysteresis shape is very similar to that of the 2D electron gases discussed above and to that at a LaAlO$_3$/SrTiO$_3$ interface [3]. The onset of the hysteresis occurs at $T_{Cm} = 700$ mK, substantially lower than that of the 2D electron liquid of the GdTiO$_3$/SrTiO$_3$ samples. The carrier concentration is above the maximum density for which SrTiO$_3$ becomes superconducting [26]; hence, only the ferromagnetic behavior is evident. La-doped SrTiO$_3$ samples with a reduced doping density of $1 \times 10^{20}$ cm$^{-3}$ (Fig. 4) lie in a regime where superconducting correlations are expected to be important [22,26]. In Fig. 4, evidence for both a superconducting zero-resistance state (defined by a transition temperature, $T_{Cs}$) and a ferromagnetic state is apparent. At 12 mK, sweeping
$B$ from negative to positive fields, two features indicative of the two states are measured: a sharp drop to $R(B) = 0$ below $B = -1.7$ T, followed by a departure from $R(B) = 0$ at $B = 0.2$ T [the red curve in Fig. 4(a)]. This departure from the zero-resistance state is hysteretic [Fig. 4(b)]. The temperature dependence of $R(B)$ [Fig. 4(a)] shows the evolution of the superconducting and ferromagnetic states and demonstrates that the two transition temperatures are different ($T_{Cs} = 315$ mK and $T_{Cm} = 500$ mK for this sample). At very low temperatures, the superconducting ground state dominates, and only a weak hysteresis is observed. As the temperature is increased, a slow transition to a ferromagnetic ground state is apparent. At 450 mK, only the hysteretic component of $R(B)$ remains. The magnetoresistance hysteresis of the La-doped SrTiO$_3$ samples shows that ferromagnetism occurs in SrTiO$_3$ even in the absence of any proximity to a ferrimagnetic layer and is thus a bulk property of SrTiO$_3$ at sufficiently high La-doping concentrations. A third sample with an even lower La-doping concentration ($3 \times 10^{19}$ cm$^{-3}$ grown on a SrTiO$_3$ substrate) shows superconductivity only below 100 mK and no ferromagnetism. Bulk doping of SrTiO$_3$ with La to higher carrier densities is possible [16,27], but, to obtain the carrier densities of the quantum wells (up to $1 \times 10^{23}$ cm$^{-3}$ in this study), the material would be more appropriately described as Sr-doped LaTiO$_3$, which is a well-known antiferromagnet [28,29]. LaTiO$_3$, up to Sr-doping concentration of approximately 10%, exhibits a weak, canted ferromagnetic moment [28]. Although even the highest La-doping concentration (of about 5%) in this study is far from this regime, it is possible that locally such weak ferromagnetic correlations exist.

Figure 5 summarizes the correlation between the 3D carrier concentration in SrTiO$_3$ and the ferromagnetic (this study) and superconducting (literature and this study) transition temperatures. Data from both bulk and 2D electron liquids are shown in the same graph. For the uniformly doped films, a ferromagnetic-phase stability region appears on the high-density side of the superconducting dome in the phase diagram, and, for a range of carrier concentrations, both phases coexist, as was evident in Fig. 4. The results from these samples provide evidence that the ferromagnetic phase of SrTiO$_3$ at sufficiently high La-dopant concentrations is likely not mediated by unintentional defects such as oxygen vacancies or Fe impurities. Impurity-related ferromagnetism typically persists to very high temperatures (see, e.g., Ref. [10]), which is different from what is observed here. The results from the uniformly doped films are consistent with recent reports of a field-induced Kondo effect in field-gated SrTiO$_3$ structures, which can be considered a precursor to the ferromagnetism at higher carrier densities [30]. When the data from the heterostructures and uniformly doped films are combined, as shown in Fig. 5, the ferromagnetism appears to depend strongly on carrier concentration, even though carriers are introduced via two fundamentally different mechanisms (interface and conventional doping). However, more studies are needed to determine the degree to which the proximity to one or two GdTiO$_3$ interfaces, respectively, acts to increase the ferromagnetic transition temperature in the heterostructures, and to clarify the role of the La dopants in the uniformly doped films.

Theoretical models of the ferromagnetism in doped SrTiO$_3$ should address the potential roles of band filling, Coulomb repulsion [31], and the coexistence with a superconducting state. Theory should consider the importance of the role of the degree of filling of different bands and subbands in the SrTiO$_3$ structure [6], which are derived from the three degenerate $t_{2g}$ $d$ orbitals of Ti [32], the role of strain and band degeneracy (note that all samples that exhibited ferromagnetism were grown on LSAT, causing compressive biaxial stress in the SrTiO$_3$ structure), as well as the shape of the observed hysteresis, in particular, the decrease in resistance as the magnetic field reaches the coercive field. Finally, the dependence of ferromagnetism on the quantum-well thickness in the SrTiO$_3$ heterostructures implies that electric-field gating may be used to modulate both ferromagnetism and superconductivity.

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FIG. 5. Superconducting and ferromagnetic transition temperatures of SrTiO$_3$ as a function of carrier concentration. Literature data for the superconducting transition temperatures are from Appel et al. [33]. The sheet carrier densities of the quantum wells ($n_{3D}$) were converted to 3D carrier concentrations ($n_{1D}$) according to $n_{3D} = n_{2D}/t$ cm$^{-3}$, where $t$ is the thickness of the quantum well and $n_{2D}$ is the carrier concentration determined from the Hall measurements at 5 K.
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