Charge Transport in a Polar Metal

Jialu Wang\textsuperscript{1}, Liangwei Yang\textsuperscript{1}, Carl Willem Rischau\textsuperscript{2}, Zhuokai Xu\textsuperscript{1}, Zhi Ren\textsuperscript{1}, Thomas Lorenz\textsuperscript{3}, Joachim Hemberger\textsuperscript{3}, Xiao Lin\textsuperscript{1}\textsuperscript{*} and Kamran Behnia\textsuperscript{3,4}

\textsuperscript{1} School of Science, Westlake Institute for Advanced Study, Westlake University, 18 Shilongshan Road, 310024 Hangzhou, China
\textsuperscript{2} Department of Quantum Matter Physics, University of Geneva, 1205 Geneva, Switzerland
\textsuperscript{3} II. Physikalisches Institut, Universität zu Köln, Zülpicher Str. 77, 50937 Köln, Germany
\textsuperscript{4} Laboratoire Physique et Etude de Matériaux (CNRS-UPMC), ESPCI Paris, PSL Research University, 75005 Paris, France

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The fate of electric dipoles inside a Fermi sea is an old issue, yet poorly-explored. \(\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3\) hosts a robust but dilute ferroelectricity in a narrow \((0.002 < x < 0.02)\) window of substitution. This insulator becomes metallic by removal of a tiny fraction of its oxygen atoms. Here, we present a detailed study of low-temperature charge transport in \(\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3-\delta\), documenting the evolution of resistivity with increasing carrier concentration \((n)\). Below a threshold carrier concentration, \(n^*(x)\), the polar structural phase transition has a clear signature in resistivity and Ca substitution significantly reduces the 2 K mobility at a given carrier density. For three different Ca concentrations, we find that the phase transition fades away when one mobile electron is introduced for about 7.9±0.6 dipoles. This threshold corresponds to the expected peak in anti-ferroelectric coupling mediated by a dipolar counterpart of Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction. Our results imply that the transition is driven by dipole-dipole interaction, even in presence of a dilute Fermi sea. At higher carrier concentrations, our data resolves slight upturns in low-temperature resistivity in both Ca-free and Ca-substituted samples, reminiscent of Kondo effect and most probably due to oxygen vacancies.

I. INTRODUCTION

The concept of a polar or 'ferroelectric' metal was first proposed by Anderson and Blount in 1960s \cite{Anderson1960}. They considered a continuous structural phase transition breaking the inversion symmetry and leading to the appearance of a polar axis in a metal. This appears counter-intuitive since one expects mobile electrons to strongly screen electric field. Recently, however, 'ferroelectric' metallicity was reported in \(\text{LiOsO}_3\) \cite{Ge2009}. It was found that this stoichiometric metal shows a structural phase transition to non-centrosymmetric rhombohedral phase \((R3c)\) below 140 K. The polar structural transition, which manifests itself as a kink in resistivity of this metal, is analogue to what occurs in its insulating ferroelectric cousins \(\text{LiNbO}_3\) and \(\text{LiTaO}_3\) \cite{Ge2009}.

Paraelectric solids close to a ferroelectric transition \cite{Ge2009} provide another platform for a meeting between metallicity and ferroelectricity. One example is \(\text{PbTe}\), a narrow-gap semiconductor close to a ferroelectric instability. The unavoidable presence of doping defects makes available \(\text{PbTe}\) samples dilute metals. Isovalent substitution of \(\text{Pb}\) by \(\text{Ge}\) leads to a structural phase transition from cubic to a non-centrosymmetric rhombohedral phase \cite{Ge2009}, which would have been ferroelectric in absence of mobile electrons. The ferroelectric-like transition was revealed by X-ray diffraction, inelastic neutron and Raman scattering \cite{Ge2009}. Charge transport in presence of local dipoles was studied several decades ago \cite{Li1990,Dresselhaus1990}.

\(\text{SrTiO}_3\) single crystals, in contrast to \(\text{PbTe}\), can be made stoichiometric enough to be insulating. Proximity to a ferroelectric quantum critical point \cite{Rischau2018,Fei2013} is manifested by a large electric permittivity of \(\text{SrTiO}_3\) \((\varepsilon_r > 20000)\) \cite{Kaminsky1977}. As a consequence, this insulator displays a number of intriguing properties \cite{Kaminsky1977}. A FE state emerges upon substitution of a tiny fraction of \(\text{Sr}\) ions with \(\text{Ca}\) \cite{Rischau2018}. Moreover, this quantum paraelectric can become a dilute metal (with a carrier concentration as small as \(\approx 10^{10} \text{ cm}^{-3}\)) upon oxygen reduction \cite{Rischau2018} \cite{Fei2013}. The dilute metal undergoes a superconducting transition below 0.3 K \cite{Rischau2018} \cite{Xin2019}.

Rischau et al. have recently found that a superconducting phase coexists with a FE-like instability in \(\text{n-doped Sr}_{1-x}\text{Ca}_x\text{TiO}_3-\delta\) and superconductivity and ferroelectricity \((\text{FE})\) may be intimately linked \cite{Rischau2019}. The FE transition of insulating \(\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3\) was found to survive in metallic \(\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3-\delta\). Being a metal, the latter does not show a bulk reversible electric polarization and cannot be a true ferroelectric. Nevertheless, it shows anomalies in various physical properties at the Curie temperature of the insulator. For example, Raman scattering found that the hardening of the FE soft mode in the dilute metal is indistinguishably similar to what is seen in the insulator \cite{Rischau2019}. The anomaly in resistivity was found to terminate at a threshold carrier density \((n^*)\), near which the superconducting transition temperature was enhanced \cite{Rischau2019} providing evidence for a link between superconducting pairing and ferroelectricity, a subject of present attention \cite{Kaminsky2019} \cite{Kaminsky2020}.

\(\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3-\delta\) is an attractive platform to study the interaction between electric dipoles and mobile electrons. Its metallicity and ferroelectricity are both di-
hute. Therefore, the distance between dipoles and mobile electrons can be separately tuned but kept much longer than the interatomic distance. In this paper, we present a study of low-temperature electrical resistivity in dozens of Sr$_{1-x}$Ca$_x$TiO$_{3-\delta}$ single-crystals with $x = 0$, 0.22%, 0.45%, 0.9%. We find that the magnitude of low-temperature mobility is significantly reduced below $n^*(x)$ and the mean-free-path gently peaks near $n^*(x)$, where the quadratic temperature dependence of resistivity is restored. Moreover, we find that $n^*$ is proportional to $x$, implying the threshold density occurs at a fixed ratio between the inter-carrier and the inter-dipole distance. We will argue that these features are all consistent with the hypothesis of a dipolar RKKY interaction, which was theoretically proposed a quarter-century ago [33]. At much higher carrier densities ($n > 5 \times 10^{19}$ cm$^{-3}$), we observe a slight upturn in low-temperature resistivity of Ca-free and Ca-substituted samples and attribute it to a Kondo effect associated with oxygen vacancies.

II. RESULTS

The upper panel (a-I) of Fig. 1 plots the low temperature dependence of resistivity for Sr$_{1-x}$Ca$_x$TiO$_{3-\delta}$ at low $n$ and $x = 0.22\%$, 0.45%, 0.9%. In Fig. 1a, 1e and 1i, resistivity shows an anomaly at lowest $n$ for all three groups of samples. Increasing n-doping, the anomaly shifts to lower temperatures, evolves into a minimum and finally disappears at a threshold doping ($n^*(x)$), seen in Fig. 1b-1d, 1f-1h and 1j-1l. Rischau et al. found that in selected samples at $x = 0.22\%$ and 0.9%, this anomaly occurs close to where the structural phase transition was detected by Raman spectroscopy, sound velocity and thermal expansion measurements [21]. Most recently, thermal expansion measurements documented the evolution of the structural phase transition in Sr$_{1-x}$Ca$_x$TiO$_{3-\delta}$ ($x = 0.9\%$), starting from the insulating phase and extending deep into the metallic phase [34]. The study found that below $n^*$, the transition temperature and the magnitude of the transition-induced anomaly continuously decreased with increasing carrier concentration. Above $n^*$, a small residual anomaly with a concentration-independent temperature scale was observed to survive. No sign change in the thermal expansion coefficient ($\alpha$) was observed at $n^*$. Thus, the corresponding Grüneisen ratio $\alpha/C_p$ ($C_p$ is the specific heat) does not change sign. This implies either the absence of a quantum critical point at $n^*$ or its insensitivity to uniaxial pressure [34].

Fig. 1m shows a 3D plot of the phase diagram of Sr$_{1-x}$Ca$_x$TiO$_{3-\delta}$ with two tunable parameters ($n$ and $x$). In the $n = 0$ plane, Sr$_{1-x}$Ca$_x$TiO$_3$ becomes ferroelectric when $x_c > 0.18\%$. Above this critical concentration of Ca substituents, $T_c$ scales with $x$ following $T_c \sim |x - x_c|^{1/2}$ [15]. The anomaly in resistivity of n-doped samples is shown with green, blue and red symbols for $x = 0.22\%$, 0.45%, 0.9% respectively.

The anomaly caused by the structural phase transition (strictly speaking, only a true FE state at $n = 0$) shifts to lower temperatures with increasing $n$. At a threshold doping ($n^*(0.22\%) \approx 5 \times 10^{18}$ cm$^{-3}$, $n^*(0.45\%) \approx 1 \times 10^{19}$ cm$^{-3}$ and $n^*(0.9\%) \approx 2 \times 10^{19}$ cm$^{-3}$), resistivity becomes metallic down to lowest temperatures (see panels, 1d, 1h, 1l).

The low-temperature resistivity of strontium titanate follows a simple quadratic temperature dependence: $\rho = \rho_0 + AT^2$ [35, 36]. Elastic scattering is represented by residual resistivity, $\rho_0$, intimately linked to the asymptotic low-temperature mobility set by disorder. Inelastic scattering among electrons sets the temperature-dependent $AT^2$ term. Both these terms are affected differently below and above $n^*(x)$.

The quadratic temperature dependence is drastically affected upon the introduction of Ca atoms. In Fig. 1, the anomaly is suppressed as the $n^*$ term decreases. This shows the Ca atoms strongly stabilize the metallic state, and that restoring RTA in Sr$_{1-x}$Ca$_x$TiO$_{3-\delta}$ is equivalent to increasing the carrier density below $n^*$.
2, the resistivity of Sr$_{1-x}$Ca$_x$TiO$_{3-\delta}$ with $x = 0.22\%$, 0.45\% and 0.9\%, is plotted vs. $T^2$ and compared with Ca-free samples of similar $n$. As seen in the upper panel, which shows typical data for $n < n^*(x)$, the resistivity shows a minimum followed by an upturn, in presence of the structural phase transition. In contrast, in SrTiO$_{3-\delta}$ with similar $n$, $T^2$ dependence of resistivity persists down to lowest temperatures [34, 36]. The lower panel of Fig. 2 shows the behavior at $n \approx n^*(x)$. One can see that the $T^2$ resistivity of Ca-doped samples is restored. Moreover, the slope is similar in Ca-substituted and Ca-free samples. In other words, the prefactor of quadratic resistivity, which strongly depends on carrier concentration but not on residual resistivity, is similar in Ca-substituted and Ca-free samples at the same carrier density. Let us note that this strict Fermi-liquid behavior at $n^*(x)$, indicates that is not a ‘quantum critical point’ where a non-Fermi-liquid behavior is commonly sought and often found. This is in agreement with the absence of a sign change in thermal expansion [34]. The other implication of this observation is that below $n^*(x)$, electrons suffer additional inelastic scattering in presence of aligned dipoles. The destruction of the structural phase transition at $n^*(x)$ suppresses this additional mechanism and restores the $T^2$ resistivity associated with electron-electron scattering [35]. This implies that in the FE-like state, additional scattering generates a drastically non-Fermi-liquid behavior.

The presence of FE-like order affects the elastic scattering of the carriers too. The Hall mobility ($\mu$) at 2K for Sr$_{1-x}$Ca$_x$TiO$_{3-\delta}$ with $x = 0, 0.22\%, 0.45\%, 0.9\%$ is presented in Fig. 3. The mobility $\mu$ is extracted from Hall resistivity $\rho_{xy}$ and longitudinal resistivity $\rho_{xx}$ using $\mu = \rho_{xy}/\rho_{xx}$. As seen in the figure, $\mu$ increases with the decreasing in the carrier density ($n$) following an approximate power law $\mu \sim n^{-\alpha}$ shown by the dashed lines. For SrTiO$_{3-\delta}$, the power law behaviour persists down to $n \sim 2 \times 10^{18} \text{cm}^{-3}$. Below this concentration, it begins to saturate and then drops at even lower carrier concentrations with the approach of the metal-insulator transition [16, 19].

In many doped semiconductors, the mobility decreases with increasing carrier concentration [37, 38]. This has been often discussed in the framework of ionized impurity scattering [39]. Several features distinguish the 2K mobility of metallic strontium titanate from ordinary doped semiconductors. First of all, the dependence of mobility with carrier concentration is very steep (i.e. $\alpha$ in $\mu \sim n^{-\alpha}$ is close to unity). Second, this mobility is strongly temperature dependent and passes from a room-temperature value of 5 cm$^2$V$^{-1}$s$^{-1}$ to 20000 cm$^2$V$^{-1}$s$^{-1}$ at liquid He temperature [40, 41]. This latter value implies that the low-temperature carrier mean-free-path becomes much longer than the interdopant distance ($l_{ee} = n^{-1/3}$) in contrast to the ionized-impurity-scattering scenario.

It has been argued [42] that these peculiar features of mobility in dilute metallic strontium titanate can be traced back to the long effective Bohr radius, $a_B^*$, of the parent insulator. The large electric permittivity [43] elongates the Bohr radius to 600 nm, which is to be compared to 1.5 nm in silicon. This in turn affects the Thomas-Fermi screening length of the metal, which depends on it:

$$r_{TF} = \sqrt{\frac{\pi a_B^*}{4k_F}}$$

The combination of a large $a_B^*$ and a small $k_F$ elongates the screening length and therefore short-distant irregularities in the dopant distribution are smoothed out. This simple approach yields this expression for mobility [42]:

$$\mu \propto a_B^{*1/2}n^{-5/6}$$

Fig. 3a confirms that this expression gives a surprisingly good account of the variation of 2 K mobility with $n$ in SrTiO$_{3-\delta}$ [42]. As seen in Fig. 3b-d, Ca substitution leads to a slight decrease in the exponent of the power law exponent ($\alpha$). More importantly, a clear deviation from the power-law behaviour occurs below $n^*(x)$ marked by vertical arrows. In other words, the carrier mobility is significantly reduced when the system orders. Fig. 3e shows the mean-free-path ($\ell$), which presents a mild maximum marked by three arrows at $n^*(x)$. Well above this threshold density of $n^*(x)$, the mean-free-path of the Ca-doped and Ca-free samples gradually merges. Thus, we conclude that the presence of the FE-like order inside the metal has drastic consequences for elastic scattering of electrons too.

Fig. 3f shows $n^*$ extracted from our data as a function of $n_{Ca}$. One can see that the two concentrations are
proportional to each other. In other words, the threshold inter-electron distance ($l^*_{ee}$) linearly scales with the average distance between Ca ions ($n_{Ca}^{-1/3}$), the slope of which indicates that the destruction of the FE-like order happens when there is one mobile electron per $7.9 \pm 0.6$ Ca ions.

III. DISCUSSION

Thus, we find that below a threshold concentration: i) an additional mechanism for inelastic scattering sets in; ii) the low-temperature mobility is significantly reduced. Moreover: iii) this threshold density for the destruction of the polar metal is proportional to Ca concentration and; iv) at this density carrier mean-free-path gently peaks. We are now going to argue that these observations support a picture in which off-center Ca sites generate electric dipoles interacting with each other inside a Fermi sea.

Let us begin with a fundamental question: what drives the FE transition in the insulating Sr$_{1-x}$Ca$_x$TiO$_3$ for $0.0018 < x < 0.02$? According to the scenario invoked by previous authors [15, 43], an off-site Ca atom generates an electric dipole, which couples to the soft transverse optical phonon of the host lattice. Theory [44] had predicted that cooperative phenomena between paraelectric defects in an easily polarizable crystal lead to polar clusters whose size is set by the polar correlation length of the host lattice ($r_c$). The latter depends on the velocity and the frequency of the soft mode of the host polarizable lattice ($r_c = v_s/\omega_0$) [45, 46]. With cooling $r_c$ increases, the interaction between clusters becomes stronger and at a sufficiently low temperature, cluster percolation leads to a ferroelectric order. A transverse Ising model, treating dipoles as pseudospins, has been successful in describing the Sr$_{1-x}$Ca$_x$TiO$_3$ phase diagram [47, 48].

In an ordinary ionic crystal, there is no mean-field basis for favoring ferroelectricity. This is because the electric field generated by a dipole does favor opposite alignments for a neighboring dipole along perpendicular orientations (Fig. 4a). In an easily polarizable crystal, on the other hand, the interaction becomes ferroelectric over a polarization length ($r_c$), thanks to the presence of soft transverse optic phonon modes. Since $r_c$ is significantly longer than the typical distance between dipolar impurities, sizable ferroelectric clusters [44, 46] (Fig. 4b) become energetically stable. This paves the way for the emergence of long-range order.

This approach provides a satisfactory explanation for
Sr coupling between dipoles destroys the ferroelectric order in SrTiO$_3$, according to our observations, anti-ferroelectric and anti-ferroelectric coupling between dipoles alters the order for $n<1$. In a highly-polarizable lattice, the interaction is ferroelectric one, impeding the emergence of long-range ferroelectricity. b) The central dipole (open arrow) can interact either ferroelectrically (in blue) or anti-ferroelectrically with dipoles (in red). a) In an ordinary ionic crystal, the interaction is ferroelectric along one orientation and anti-ferroelectric along the perpendicular one, impeding the emergence of long-range ferroelectricity. b) In a highly-polarizable lattice, the interaction is ferroelectric over a length scale, $r_c$, longer than the interdopant distance, $\ell_{dd}$. This allows the formation of large ferroelectric cluster composed of many dipoles. The typical size of these clusters is set by $r_c$. c) In the presence of a Fermi sea, ferroelectric and anti-ferroelectric coupling between dipoles alternate radially. According to our observations, anti-ferroelectric coupling between dipoles destroys the ferroelectric order in Sr$_{1-x}$Ca$_x$TiO$_3$ at a carrier density of $n^*(x)$, which corresponds to $2k_F\ell_{dd} = \pi$.

A second question arises by the existence of $n^*(x)$. Why does the order eventually fade away and what does this threshold density correspond to?

The first question brings to mind a remark by Landauer [51] according to which, neither electric field nor carrier concentration can be strictly homogeneous in a metal containing defects. This is particularly true in our case, where the Thomas-Fermi screening length is very long by a combination of long Bohr radius and small Fermi-wave vector. When the carrier density is as low as $10^{18}$ cm$^{-3}$, Eq.1 yields $r_{TF} \approx 80$ nm, much longer than the distance between the dipoles or the $r_c$ of the insulator. The Fermi sea is too dilute to impede dipolar interaction. The attenuation of mobility implies enhanced electric-field inhomogeneity brought by the alignment of dipoles, providing additional support for picturing persistent electric interaction in spite of a Fermi sea.

The second question leads us to an additional interaction mechanism offered to electric dipoles in presence of a Fermi sea (see Fig. 4c). This was proposed first by Glincuk and Kondakova in 1992 [33]. The opposite charges of an electric dipole are expected each to generate Friedel oscillations inside a Fermi sea, which is a distinct source of dipolar interaction. Indeed, it is established that localized magnetic spins inside a Fermi sea generate similar oscillations and interact through what is known as the Ruderman-Kittel-Kasuya-Yosida (RKKY) mechanism [34]. Glincuk and Kondakova proposed a dipolar analogue of RKKY interaction. This dipole-dipole interaction ($V_{dd,RT}$) depends on the magnitude of the electric dipole moment and has an alternating sign as a function of the inter-dipole distance ($\ell_{dd}$) and Fermi wave vector ($k_F$) [33]:

$$V_{dd,RT} \propto \frac{\cos(2k_F\ell_{dd})}{\ell_{dd}^3}$$

(3)

This expression for interaction between two dipoles is to be compared with what is expected in vacuum:

$$V_{dd,V} \propto \frac{1}{\ell_{dd}^4}$$

(4)

or in a highly-polarizable insulator with a polarization correlation radius of $r_c$: [45]:

$$V_{dd,C} \propto \frac{\exp(-\ell_{dd}/r_c)}{r_c\ell_{dd}^3}$$

(5)

According to Eq.3, the parallel alignment of nearest dipoles becomes energetically unfavorable when $\cos(2k_F\ell_{dd}) = -1$ or $2k_F\ell_{dd} = \pi$. Assuming an isotropic Fermi surface ($k_F = (3\pi^2n)^{1/3}$), one finds that this will happen when $\frac{\pi}{2} = \frac{2\pi}{7}$. In other words, the destructive interaction is expected to occur when the there is $\frac{2\pi}{7} \approx 7.6$ dipoles per mobile electron. This is very close to what we observe experimentally. We note the presence of a higher order term is not expected to change the outcome significantly.

Thus, invoking RKKY-like interaction between electric dipoles inside a polar metal provides a straightforward

FIG. 4. Dipole-dipole interaction in three contexts. The central dipole (open arrow) can interact either ferroelectrically (in blue) or anti-ferroelectrically with dipoles (in red). a) In an ordinary ionic crystal, the interaction is ferroelectric along one orientation and anti-ferroelectric along the perpendicular one, impeding the emergence of long-range ferroelectricity. b) In a highly-polarizable lattice, the interaction is ferroelectric over a length scale, $r_c$, longer than the interdopant distance, $\ell_{dd}$. This allows the formation of large ferroelectric cluster composed of many dipoles. The typical size of these clusters is set by $r_c$. c) In the presence of a Fermi sea, ferroelectric and anti-ferroelectric coupling between dipoles alternate radially. According to our observations, anti-ferroelectric coupling between dipoles destroys the ferroelectric order in Sr$_{1-x}$Ca$_x$TiO$_3$ at a carrier density of $n^*(x)$, which corresponds to $2k_F\ell_{dd} = \pi$.
explanation to the experimentally-observed magnitude of $n^*$ for three different Ca contents. The fact that $n^*(x)$ is proportional to $x$ becomes a simple consequence of the presence of $k_F l_{dd}$ in Eq.3. In this picture, while the dipolar interaction which generates the ferroelectric order in the insulator is governed by $V_{dd,C}$ in Eq.5, as argued previously [45], the one destroying it in the metal is expressed by $V_{dd,R}$ in Eq.3. Note that: the relative weight of the two interactions (ferroelectric coupling driven by strong polarization and aniferroelectric coupling mediated by the Fermi sea) remains an open issue.

One may be tempted by an alternative picture in which the FE-like transition is destroyed because the screening length shrinks with increasing carrier concentration. However, since this evolution is very slow ($r_{TF} \propto n^{-1/6}$), it would be very hard to explain the linear proportionality between $n^*$ and $x$.

What happens to the electric dipoles when the carrier density exceeds $n^*(x)$? According to the thermal expansion measurements [54], a smeared anomaly continues to survive. One may speculate that a non-percolative dipole glass [55] persists at higher densities. In our study of resistivity, we cannot see any significant difference between Ca-free and Ca-substituted strontium titanate when $n > n^*(x)$. On the other hand, we do see small upturns in resistivity, reminiscent of the Kondo effect, which constitutes yet another source of information.

Low-temperature resistivity of Sr$_{1-x}$Ca$_x$TiO$_{3-\delta}$ (with $x = 0.9\%$) above $n^*(x)$ is shown in Fig. 5a-5d. One can see that a less pronounced upturn re-appears above $n^*(x = 0.9\%)$. Similar data for Ca-free samples are shown in Fig. 5e-5f for comparison. No clear upturn can be seen in Fig. 5e and 5f with $n$ below $5.2 \times 10^{19}$ cm$^{-3}$. With further increase of carrier concentration, a small upturn appears. No clear difference between Cdoped and Ca-free samples can be detected. We note however, that these upturns in resistivity correspond to a relative change of several $10^{-3}$. This is orders of magnitudes smaller than what can be seen in Fig. 2 for $n < n^*$. Their small magnitude as well as their presence in Ca-free samples point to an origin which is not the one discussed above in the presence of the phase transition.

As seen in Fig. 5c and 5g, the temperature dependence of these upturns is roughly logarithmic. The logarithmic temperature dependence of resistivity is reminiscent of the Kondo effect, which arises when a localized spin couples to a Fermi sea [54]. It is now known that the Kondo effect can arise when any Two-Level-System (TLS) is embedded in a Fermi sea [54] and experiments [56-58] have documented a variety of non-magnetic counterparts of the original Kondo effect. Our upturns in resistivity, both by their magnitude and temperature dependence are reminiscent of what Matsushita et al. observed in Ti-doped PbTe and attributed to charge Kondo effect. The valence degeneracy of Ti dopants was identified as the driver of the Kondo effect [58].

The origin of the Kondo effect in our system is yet to be pinned down. Oxygen vacancies are the principal suspects. By distorting the TiO$_6$ octahedra, they can generate degeneracies in different degrees of freedom. Moreover, they are suspected to host $d^0$ magnetism [59]. One cannot forget, however, the unavoidable presence of magnetic impurities at the ppm level in SrTiO$_3$ [60, 61].

The absence of this upturn below $5 \times 10^{19}$ cm$^{-3}$ and its gradual appearance at higher densities begs explanation. The evolution of the T-square resistivity prefactor may provide one. In presence of a large temperature-dependent resistivity, a small sub-percent upturn may be undetectable. However, this hypothesis fails to explain the gradual fading of the effect at even higher carrier concentrations. Why the upturn is most prominent at lower $x$? A possible clue is provided by the well-established fact that in general, the Kondo physics of magnetic impurities above a threshold concentration is replaced by a spin-glass state. In the case of iron impurities in silver [62] this threshold is about a percent. The same may happen to the Kondo effect of oxygen vacancies. Note that this is yet another argument against extrinsic magnetic impurities as the source of the Kondo effect.

In summary, we found that the existence of the FE order in insulating Sr$_{1-x}$Ca$_x$TiO$_3$ deeply affects charge transport in dilute metallic Sr$_{1-x}$Ca$_x$TiO$_{3-\delta}$. Below a threshold of carrier concentration $n^*(x)$, inelastic and elastic scattering of carriers are both amplified. This threshold density scales with Ca content. Both these features can be explained by invoking the survival of electric dipole interaction inside the Fermi sea via the dipolar counterpart of RKKY interaction. At higher carrier con-
centrations, deep inside the metallic state, clear but tiny upturns of resistivity are detectable, which are reminiscent of the Kondo effect and most probably associated with oxygen vacancies.

IV. METHODS

SrTiO$_3$ and Sr$_{1-x}$Ca$_x$TiO$_3$ single-crystals with $x = 0.22\%$, 0.45\%, 0.9\% were commercially obtained. Mobile electrons were introduced by generating oxygen vacancies. In order to remove oxygen atoms, samples were sealed with high-purity Ti powder (99.99\%) in an evacuated quartz tube and annealed in an oven. Samples with various electron carrier concentrations (from 10$^{10}$ to 10$^{21}$ cm$^{-3}$) were obtained by varying the annealing temperature between 700 and 900 °C. Resistivity was measured through the four-terminal method down to 1.8K in Quantum Design PPMS. Hall effect is measured concomitantly under magnetic field to determine the carrier density ($n$).

V. DATA AVAILABILITY

All data supporting the findings of this study are available within the paper.

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