Metallicity of oxygen-deficient EuTiO$_3$

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We report on a study of charge transport in EuTiO$_{3-x}$ single crystals with carrier density tuned across several orders of magnitude. Comparing this system with other quasi-cubic perovskites, in particular strontium titanate, we draw a comprehensive picture of metal-insulator transition and dilute metallicity in this $ABO_3$ family. Because of a lower electric permittivity, the metal-insulator transition in EuTiO$_{3-x}$ occurs at higher carrier densities compared to SrTiO$_3$. At low temperature, a distinct $T^2$ resistivity is visible. Its prefactor $A$ smoothly decreases with increasing carrier concentration in a similar manner in three different perovskites. Our results draw a comprehensive picture of charge transport in doped quantum paraelectrics.

During the last decade, the metal-insulator transition (MIT) in weakly doped SrTiO$_3$ has attracted renewed interest. The pure compound is a highly insulating quantum paraelectric [1], which on the one hand becomes ferroelectric by a partial substitution of Sr by Ca (Sr$_{1-x}$Ca$_x$TiO$_3$, 0.002 $\leq x \leq 0.12$) [2, 3]. On the other hand it becomes metallic upon reduction (SrTiO$_3$)$_2$ [4] and even superconducting [5] at remarkably low carrier concentrations, which identified SrTiO$_3$ as the most dilute superconductor [6]. Furthermore, a ferroelectric-like transition inside the superconducting phase has been observed in compounds with both, Ca substitution and oxygen vacancies (Sr$_{1-x}$Ca$_x$TiO$_3$)$_2$ [7]. Apart from reduction, SrTiO$_3$ has been subjected to other variants of n-type doping by, e.g., substituting Ti$^{4+}$ with Nb$^{5+}$ (SrTi$_{1-x}$Nb$_x$O$_3$) [8, 9], or Sr$^{2+}$ with La$^{3+}$ (Sr$_{1-x}$La$_x$TiO$_3$) [10, 11]. In all three cases a $T^2$ behavior of the resistivity is found [12, 13]. For many systems, the prefactor $A$ of $\rho(T) = \rho_0 + AT^2$ is related to the electronic specific heat coefficient $\gamma$, since both depend on the Fermi energy $E_F$, as is expressed in the Kadowaki-Woods ratio $A/\gamma^2$ [14]. Furthermore, $E_F$ itself depends on the carrier density $n$ and one may expect a particular scaling behavior in $\rho(T)$ as shown for metallic SrTiO$_3$-δ [10, 11].

In order to investigate these phenomena in other systems, EuTiO$_3$ is a prime candidate, because both materials are similar in many aspects. Sr$^{2+}$ and Eu$^{2+}$ have almost the same ionic radius [15]. Both compounds have the ideal cubic perovskite structure (space group $Pm\overline{3}m$) at room temperature and undergo a structural phase transition to tetragonal ($I4/mcm$) upon cooling [20, 21], and both are quantum paraelectrics [11, 23, 53]. Nevertheless, there are also clear differences. SrTiO$_3$ crystals are transparent, whereas EuTiO$_3$ is black, what can be understood from band structure calculations yielding a band gap of 1 eV [24], whereas SrTiO$_3$ has a gap of 3.2 eV [25]. SrTiO$_3$ is non-magnetic in contrast to EuTiO$_3$ where Eu$^{2+}$ has a large, local magnetic moment of $\mu_{\text{BH}}$. These moments order antiferromagnetically below $T_N = 5.5$ K in a G-type configuration [26, 27].

The research on n-doped EuTiO$_3$ is sparse. To our knowledge only five publications exist: One report deals with poly- and single-crystalline EuTi$_{1-x}$Nb$_x$O$_3$ with $x \leq 0.3$ [28] and another two with single-crystalline Eu$_{1-x}$La$_x$TiO$_3$ ($x \leq 0.1$ [29, 30]). Studies of oxygen-deficient EuTiO$_3$ are restricted to ceramics [31] and thin films [32]. Here, we present a detailed study of single-crystalline EuTiO$_{3-\delta}$ tuned from semiconducting to metallic via reduction. We derive the electron mobility and discuss its temperature dependence in comparison to that of SrTiO$_3$. We find an $AT^2$ resistivity behavior of metallic EuTiO$_{3-\delta}$ where $A$ systematically decreases with increasing charge-carrier content, which is discussed in a larger context of charge transport in weakly doped perovskite oxides.

The EuTiO$_3$ crystals were grown by the floating-zone technique. We used polycrystalline powders of Eu$_2$O$_3$ (chemical purity 99.99 %), TiO (99.5 %), and TiO$_2$ (99.99 %) as starting materials. The powders were mixed for 1 h and the mixture was pressed to a cylindrical rod at 50 MPa. In order to avoid emergence of Eu$^{3+}$ via oxygen capture, we skipped preliminary powder reactions and put the pressed rod directly into the floating-zone system. Centimeter-sized single crystals were grown in argon atmosphere using a growth speed of 10 mm h$^{-1}$ and a relative rotation of the rods of 30 rpm. X-ray powder diffraction measurements verified phase purity and Laue images confirmed single crystallinity.

The as-grown crystal was cut into cuboid pieces with all faces being {100} planes. In order to induce electron doping, the samples were annealed in sealed fused-quartz tubes with low argon pressure ($\lesssim 10^{-5}$ mbar) and titanium metal powder (99.99 %) acting as oxygen catcher. The quartz tubes were heated for 10 h at tem-
peratures between 650 °C and 850 °C depending on the intended carrier concentration. In order to have an indicator for homogeneity, in each run two samples with different thicknesses (0.2 mm and 0.4 mm) were annealed simultaneously in the same quartz tube. Resistivity and Hall effect measurements were carried out by a standard four-probe and six-probe method, respectively, using a home-built dipstick setup for wet cryostats.

Figure 1 shows the resistivity $\rho(T)$ as a function of temperature for semiconducting pristine EuTiO$_3$ determined by DC measurements (black dashed line) and dielectric spectroscopy (green solid line) in comparison to metallic EuTiO$_{3-\delta}$ which were cut from the same single crystal and oxygen reduced. (b) Charge carrier concentrations $n$ of all samples deduced from Hall effect measurements at various temperatures. The inset in (a) shows Arrhenius plots of $n(T)$ and of the conductivity $\sigma(T)$ together with linear fits (dotted lines). Note the scale breaks in both main panels.

![Figure 1](image-url)

**FIG. 1.** (a) Resistivity $\rho(T)$ as a function of temperature for semiconducting pristine EuTiO$_3$ determined by DC measurements (black dashed line) and dielectric spectroscopy (green solid line) in comparison to metallic EuTiO$_{3-\delta}$ which were cut from the same single crystal and oxygen reduced. (b) Charge carrier concentrations $n$ of all samples deduced from Hall effect measurements at various temperatures. The inset in (a) shows Arrhenius plots of $n(T)$ and of the conductivity $\sigma(T)$ together with linear fits (dotted lines). Note the scale breaks in both main panels.

The absence of homogeneous samples between pristine and metallic EuTiO$_{3-\delta}$ hinders an exact determination of the MIT. The lowest carrier density of $10^{20}$ cm$^{-3}$ yields an upper boundary for the critical carrier density $n_c$ of the MIT and is about four orders of magnitude larger than the corresponding one ($\approx 10^{16}$ cm$^{-3}$) of SrTiO$_3$. This difference can be understood by comparing the permittivities $\varepsilon$ of EuTiO$_3$ and SrTiO$_3$. While SrTiO$_3$ has an extremely large $\varepsilon$ of roughly 20000 at low temperatures [1], that of EuTiO$_3$ is smaller by a factor of 50. We find $\varepsilon \approx 400$ [33] in agreement with previous single-crystal data [33], whereas smaller values are reported for ceramics [23, 34].

Of course, these values were obtained for pristine EuTiO$_3$. For doped samples, one defines an effective Bohr radius $a_B^* = a_B^* m^*/m^*$, which renormalizes $a_B \approx 0.5$ Å of the hydrogen atom by taking into account the permittivity $\varepsilon$ and the band mass $m^*$. The so-called Mott criterion [35] compares $a_B^*$ as a measure for the overlap of the electronic wave functions to the average distance between donor atoms $n^{-1/3}$. The huge low-temperature $\varepsilon$ of SrTiO$_3$ results in an effective Bohr radius of about
6700 Å, compared to \( a_B^* \approx 130 \) Å for EuTiO\(_3\). Here, we use \( m^* = 1.5m_e \) as determined for the lowest lying conduction band of SrTiO\(_3\)\(_{0.5}\) [30] for both SrTiO\(_3\) and EuTiO\(_3\). The much smaller value of \( a_B^* \) explains that \( n_c \) of EuTiO\(_3\) is about four orders of magnitude larger than that of SrTiO\(_3\). In passing, we also note that the influence of the above-mentioned inhomogeneities in the oxygen-defect concentrations is suppressed more rapidly with increasing \( a_B^* \). Figure 2 (a) shows the scaling behavior \( n_c/a_B^* = K \) as dashed lines for different values of \( K \). Experiments on doped semiconductors have detected a sharp MIT at a critical density of \( n_c \) and the available data follows a scaling relation with \( K = 0.25 \) [37, 38], which corresponds to the so-called Mott criterion [35]. In perovskite oxides, there is no experimental data resolving a sharp MIT at \( n_c \) and metallicity is observed in EuTiO\(_3\), SrTiO\(_3\) [4], and KTaO\(_3\) [39, 40] at carrier densities which are much larger than expected according to the Mott criterion. Nevertheless, these carrier densities scale with \( a_B^* \).

In Fig. 2 (b) we show the mobility \( \mu = 1/(ne\rho) \) of metallic EuTiO\(_3\)\(_{0.5}\) as a function of temperature in double-logarithmic scales. There is a plateau-like behavior below 40 K, where all \( \mu(T) \) curves are ordered by carrier density \( n \), i.e., \( \mu(n) \) systematically decreases with increasing \( n \). Note that there are additional kinks resulting from the magnetic order at \( T_N = 5.5 \) K, which are of course also present in \( \rho(T) \), but hardly visible in the representation of Fig. 1(a). In the high-temperature regime, the mobility curves decrease due to increasing electron-phonon scattering and seem to approach an \( n \)-independent power law as is observed in SrTiO\(_3\) [42].

In Fig. 2 (c), we compare the mobility data of EuTiO\(_3\)\(_{0.5}\) with \( 10^{20} \) cm\(^{-3} \) \( < n < 10^{21} \) cm\(^{-3} \) to that of four SrTiO\(_3\)\(_{0.5}\) samples with \( 10^{17} \) cm\(^{-3} \) \( < n \lesssim 10^{20} \) cm\(^{-3} \). Because SrTiO\(_3\)\(_{0.5}\) is already metallic for very low carrier densities, higher mobilities than in EuTiO\(_3\)\(_{0.5}\) are reached. In the low-temperature regime all curves are ordered by increasing \( n \), even across both compounds. On an absolute temperature scale, the mobility curves \( \mu(T,n) \) of SrTiO\(_3\)\(_{0.5}\) merge upon about 200 K and fall below those of EuTiO\(_3\). In order to accommodate the different structural transition temperatures \( T_s \), we normalize the temperature axis for both materials to their respective \( T_s \), which is 260 K for EuTiO\(_3\) [31] and 105 K for SrTiO\(_3\) [11, 111]. After this rescaling, the data sets of EuTiO\(_3\)\(_{0.5}\) and SrTiO\(_3\)\(_{0.5}\) appear to systematically extend each other towards higher and lower charge carrier concentrations, respectively. This suggests that the soft modes related to the antiferrodistortive structural phase transition may play a significant role for the charge carrier mobility. Recently, both the magnitude and temperature dependence of the mobility in SrTiO\(_3\)\(_{0.5}\) have attracted attention [43, 44]. Mischenko et al. [43] argue that a polaronic approach can lead to a scattering rate larger than the thermal energy of carriers in agreement with the data. Ab initio calculations by Zhou et al. [44] reproduce the experimentally observed \( T^{-3} \) temperature dependence of the mobility of SrTiO\(_3\)\(_{0.5}\) [42], but the calculated absolute value is an order of magnitude larger than the experimental data. Moreover, in these theoretical approaches the antiferrodistortive soft mode does not play a key role, whereas the apparent scaling between the two systems suggests its importance in setting the magnitude and the temperature dependence of the mobility.

Figure 3 shows the resistivity \( \rho \) as a function of \( T^2 \) together with fits of the form \( \rho(T) = \rho_0 + AT^2 \) (dashed lines). The fits deviate from the data for high temperatures and with increasing carrier density the temperature range of the \( T^2 \) behavior systematically increases, which is in agreement with the findings for SrTiO\(_3\)\(_{0.5}\).
In SrTiO$_{3-\delta}$ we have an additional deviation at low temperatures that is related to the magnetic transition at $T_N = 5.5$ K. Figure 3 (a) shows the prefactor $A$ from these fits as a function of $n$ in double-logarithmic scales. Here, we compare $A(n)$ for EuTiO$_{3-\delta}$ to that of SrTiO$_{3-\delta}$, Sr$_{1-x}$La$_x$TiO$_3$, and SrTi$_{1-x}$Nb$_x$O$_3$ [14–16], and we also include $A(n)$ of the non-titanate perovskite $K_{1-x}Ba_xTaO_3$ [45]. All titanate systems follow a general trend as is marked by dotted black lines, which are guides to the eye and indicate power laws $A \propto n^\alpha$ with $\alpha = -4/3, -2/3, -1$. Band structure calculations for n-doped SrTiO$_3$ [15] yield a model with three bands that are filled consecutively with increasing $n$. The critical carrier densities $n_{c1}$ ($n_{c2}$), at which the filling of the second (third) band sets in, are known from experiments [30] and illustrated by background-color boundaries. Below $n_{c1}$, where only the first band is filled, a power law $n^{-4/3}$ is seen as is expected for a single parabolic band with $E_F \propto n^{2/3}$ and a simple $A \propto E_F^{-2}$ relation. When the second band starts to be filled at $n_{c1}$, the exponent $\alpha$ of $A \propto n^\alpha$ suddenly increases and finally approaches $-1$, which does not change much above $n_{c2}$.

The increase of $\alpha$ is a natural consequence of a three-band system. If we consider the most simple case of three parabolic bands with band minima at energies $E_i$, effective masses $m_i$, and densities of states $g_i(E) \propto m_i^{-1/2} \sqrt{E-E_i}$, then each band contributes

$$n_i(E_F) = \frac{1}{3 \pi^2} \left( \frac{2 m_i}{\hbar^2} \right)^{3/2} \int_{E_i}^{E_F} \sqrt{E-E_i} \, dE$$

to the total electron density $n(E_F) = \sum_i n_i(E_F)$. We use the band masses $m_0 = m_2 = 1.5m_e$ and $m_1 = 3.5m_e$ from Shubnikov-de-Haas measurements of SrTiO$_{3-\delta}$ [30] and adjust $E_{1,2}$ to 2 meV and 10 meV, respectively, to match the experimental critical carrier densities [16]. From the inverse function $E_F(n)$ we calculate $A(n) \propto E_F^{-2}(n)$ which describes the data of the doped titanates over almost the entire range of $n$, as is shown by the thick line in Fig. 3 (a). This also holds for the exponent $\alpha$ of $A \propto n^\alpha$ obtained from the slope of $\log A$ vs. $\log n$ (Fig. 3(b)). In view of the simple model, which neglects deviations from the parabolic band shapes as well as their anisotropy, this good agreement with the experimental data is remarkable. The available $A(n)$ data of the non-titanate perovskite $K_{1-x}Ba_xTaO_3$ [45] fit into this picture as well, because this material has lower effective masses (0.55$m_e$ to 0.8$m_e$) [40]. Consequently, at a given carrier concentration $n$, the Fermi energy is larger and the prefactor $A$ is lower compared to the titanates. A more sophisticated theoretical treatment could provide a generalized uniform description of the $A(n)$ behavior for an even larger variety of metallic perovskite oxides with low carrier densities.

In summary, we present a detailed report of the metal-insulator transition in oxygen-deficient single-crystalline EuTiO$_3$, which shows many similarities with that in SrTiO$_3$. However, it sets in at a much higher carrier concentration (factor 10$^4$), which results from the smaller permittivity of EuTiO$_3$, implying a smaller effective Bohr radius $a_B^*$, i.e., a smaller overlap of the electronic wave functions. We show that metallicity in three perovskite
oxides scales with the effective Bohr radius $a_B^*$, but it emerges at a carrier density much larger than suggested by the Mott criterion. The low-temperature mobility of metallic EuTiO$_3$ and SrTiO$_3$ systematically increases with decreasing charge carrier concentration across both materials. This generic behavior even extends to the high-temperature decrease of the mobility if the temperature axes are rescaled by the respective structural transition temperatures. We find an $AT^2$ behavior in $\rho(T)$ of metallic EuTiO$_{3-\delta}$ where the prefactor $A(n)$ systematically decreases with increasing charge carrier density $n$ and even quantitatively agrees with $A(n)$ of doped SrTiO$_3$. This general behavior of $A(n)$ can be described within a three-band model.

Appendix A: Dielectric Spectroscopy

In order to determine the dielectric and transport properties towards higher resistivities, contact based impedance spectroscopy was applied to single crystals of nominally undoped EuTiO$_3$ from the same batch as described in the main part of the paper. These measurements were performed in a commercial $^4$He-flow cryomagnet (QUANTUM-DESIGN PPMS). The samples were prepared as small platelets in capacitor geometry with typical dimensions of thickness $d \approx 0.5$ mm and cross section $A \approx 4$ mm$^2$. The contacts were formed using silver paint. The determination of the sample and contact dimensions, respectively, together with the difficulty of precise consideration of stray fields leads to an uncertainty of the absolute values of up to 10%. In contrast to the DC measurements, no four-point but a two-point geometry was used. The reason is that for dynamical measurements frequency-dependent contact contributions do not cancel out by separating current and voltage channel but generate additional effects difficult to control. Therefore, the strategy is to identify the well-defined contact contributions and to discriminate them from intrinsic sample properties as described below.

The measurements were carried out employing high-frequency-compatible coaxial waveguides and a homemade coplanar microstrip sample holder. For frequencies $1 \text{ Hz} \leq \nu \leq 1 \text{ MHz}$ we used a high-impedance frequency response analyzer (NOVOCONTROL). For frequencies $100 \text{ kHz} \leq \nu \leq 100 \text{ MHz}$ we used a vector network analyzer (ZNB8, Rohde&Schwarz) and evaluated the complex impedance $Z^*(\nu)$ via the scattering coefficients $S_{12}$ and $S_{22}$. In both cases, applied voltages were kept below 1 V. Conductivity $\sigma'$ and permittivity $\varepsilon'$ of the sample were derived from the measured complex impedance via

$$\frac{1}{Z^*(\nu)} = \frac{A}{d} \sigma'(\nu) - i \frac{A}{d} 2\pi \nu \varepsilon_0 \varepsilon'(\nu).$$

All measurements were performed with the electric field along crystallographic $\{100\}$ axes of the room-temperature cubic phase.

The higher frequency confidence boundary of the measurement range is set by the limited phase resolution $\propto \nu \varepsilon'/\sigma'$. The lower confidence boundary for the determination of the intrinsic material properties is set by the influence of the contact electrodes and shall be discussed in the following. At the contact interfaces between sample and silver electrodes, Schottky-type depletion layers are formed. This leads to an additional capacitive contribution $C_C$ and a serial contact resistance $R_C$. Together, they form an $RC$ element in series with the intrinsic sample impedance which gives rise to Maxwell-Wagner-type relaxational effects [49]. However, for frequencies $2\pi \nu > 1/R_C C_C$ the contacts effectively are short-circuited [50, 51]. This allows us to reliably evaluate the intrinsic sample conductivity. As the contact resis-

![FIG. 5. (a) Temperature dependence of the permittivity $\varepsilon'$ measured for frequencies $1 \text{ Hz} \leq \nu \leq 100 \text{ MHz}$. The steep rise of $\varepsilon'(T)$ for higher temperatures and lower frequencies marks the onset of contact contributions to the capacitance of the sample. The dashed line is fitted via the Barrett formula [52]. The inset shows the anomaly in the permittivity at the antiferromagnetic transition $T_N \approx 5.5K$. (b) Corresponding conductivity data $\sigma'(T)$. The contact-dominated regime lies at lower conductivity values due to the additional contribution of the contact resistance. The crossover towards intrinsic conductivity takes place where the measurement frequency meets the relaxation rate $1/R_C C_C$ which shifts to lower values for lower temperatures. The inset displays the determined intrinsic conductivity in an Arrhenius-type presentation with linear fit (black solid line).](image-url)
tance $R_C$ depends strongly on the temperature, the corresponding crossover frequency from contact-dominated to intrinsic response is temperature-dependent as well. This crossover is clearly seen in Fig. 4 both, in the permittivity as well as in the conductivity. The low-$T$/high-$\nu$ limit of the frequency- and temperature-dependent data represents the intrinsic quasi-static permittivity $\varepsilon$ (Fig. 4(a)). The corresponding intrinsic conductivity is marked in green in Fig. 5(b) and is connected to the resistivity determined by four-point DC measurements via $\sigma = 1/\rho_{DC}$.

The physical properties of undoped EuTiO$_3$ are discussed in the main paper and shall be only briefly resumed at this point. EuTiO$_3$ is a quantum paraelectric in which despite the correlations of the electric dipole degrees of freedom a long-range order is prevented by quantum fluctuations. The fingerprint of such type of behavior is the Curie-like rise of the permittivity towards lower temperatures which does not lead to a divergence but saturates at an elevated value for $\varepsilon(T \to 0)$. This behavior of $\varepsilon(T)$ is displayed as high-$\nu$ limit in Fig. 5(a) and can be modeled employing the well known Barrett formula [52]

$$\varepsilon(T) = \frac{C}{(T_\Omega/2) \coth(T_\Omega/2T)} - T_0 + \varepsilon_{\infty}$$

in which $T_\Omega$ denotes the influence of quantum fluctuations and $T_0$ represents the paraelectric Curie-temperature at high temperatures. The fit of the high-frequency data up to 200 K reveals values of $T_\Omega \approx 160 \text{ K}$ and $T_0 \approx -190 \text{ K}$. The first value is comparable to the findings of [53] and four times higher compared to SrTiO$_3$ [54, 55] comprising much stronger influence of quantum fluctuations. The latter value differs in magnitude from [53] where a considerably smaller temperature range could be evaluated, but is also negative denoting rather antiferroelectric correlations in EuTiO$_3$. Below the antiferromagnetic transition at $T_N \approx 5.5 \text{ K}$ clear deviations from the Barret-type behavior evolve (inset of Fig. 5(a)), which denote the presence of significant magneto-electric coupling. In the same temperature range where $\varepsilon(T)$ shows a Barrett-type behavior the intrinsic conductivity reveals a purely thermally activated temperature dependence. The Arrhenius plot shown the inset of Fig. 5(b) displays a reciprocal $T$ dependence of the logarithmic conductivity over more than ten orders of magnitude! This behavior can be fitted assuming an effective energy barrier of $\approx 102 \text{ meV}$.

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