Electron-Phonon Interaction and Charge Carrier Mass Enhancement in SrTiO3

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Abstract

We report a comprehensive THz, infrared and optical study of Nb-doped SrTiO3 as well as dc conductivity and Hall effect measurements. Our THz spectra at 7 K show the presence of an unusually narrow (12 GHz) phonon mode near 50 cm⁻¹, indicating a significant electron-phonon coupling.

Reference


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Electron-Phonon Interaction and Charge Carrier Mass Enhancement in SrTiO$_3$


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We report a comprehensive THz, infrared and optical study of Nb-doped SrTiO$_3$ as well as dc conductivity and Hall effect measurements. Our THz spectra at 7 K show the presence of an unusually narrow ($<2$ meV) Drude peak. For all carrier concentrations the Drude spectral weight shows a factor of three mass enhancement relative to the effective mass in the local density approximation, whereas the spectral weight contained in the incoherent midinfrared response indicates that the mass enhancement is at least a factor two. We find no evidence of a particularly large electron-phonon coupling that would result in small polaron formation.

To address these issues, we have measured the optical reflectivity and transmission of double side polished, 5 × 5 mm$^2$ ([100] face) single crystals of SrTi$_1-x$Nb$_x$O$_3$ between 300 K and 7 K by time-domain THz spectroscopy (TPI spectra 1000, TeraView Ltd.), Fourier transform infrared spectroscopy, and photometric IR-UV spectroscopy, in the range from 0.3 meV to 7 eV. To obtain a detectable transmission, we have used for each composition several samples of different thicknesses (8–60 μm), adopted to the spectral range and value of the optical transmission. The Hall carrier concentrations were 0.105%, 0.196%, 0.875%, and 2.00% at 7 K, which were within 5% of those measured by the wavelength-dispersive x-ray spectroscopy, and within 12% of the Nb concentration specified by the supplier (0.1%, 0.2%, 1.0%, and 2.0%, respectively, Crystec, Berlin). Compared to earlier measurements [9–13], we expand the lower limit of the spectral range from 1.2 meV [11] to 0.3 meV. The real and imaginary part of $\epsilon = \epsilon' + (4\pi/\omega)i\sigma_1$ were obtained from inversion of the Fresnel equations of transmission and phase (below 12 meV for the samples with $x = 0.001$ and 0.002), from inversion of the Fresnel equations of reflection and transmission coefficients (above 0.1 eV), and from Kramers-Kronig analyses of the reflectivity spectra (2–80 meV) with Drude-Lorentz fits [14] to aforementioned reflectivity, transmission, and phase spectra up to 7 eV, and $\rho_{dc}$.

The gap of SrTiO$_3$ is revealed as the sharp onset of the optical conductivity at 3.3 eV in all samples (Fig. 1). The absorption peak at 2.4 eV, with intensity proportional to the charge carrier density, reveals optical excitation of the doped t$_{2g}$ states to the empty e$_g$ states. The only subgap contributions to the optical conductivity of undoped SrTiO$_3$ (Fig. 1) are the three infrared active phonons at 11.0, 21.8, and 67.6 meV (at room temperature). The lowest one exhibits a strong redshift upon cooling, and saturates at about 2.3 meV at 7 K. Upon doping this mode

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hardens for all temperatures, reaching 8.5 meV at 7 K at 2% doping. For the present discussion, the most important effect of substituting Nb is to dope electrons, which yields a clearly distinguishable Drude peak, which is broad at 300 K but gets extremely narrow (<2 meV) at low temperatures, as shown in Fig. 1. This unusually narrow Drude peak is the coherent part of the polaronic conduction in n-doped SrTiO₃ as will be argued below. For the 0.9% and 2% doped samples, the metallic conductivity is directly visible from the increase of the reflectivity below the soft optical phonon (see Ref. [15]). In addition, we observe a broad asymmetric midinfrared absorption, which increases with doping, confirming the result of Calvani et al. [9]. This band evolves into a double peak structure when the temperature is lowered to 7 K (Fig. 1). Using first principles local-density approximation (LDA) calculations [16], we have verified that interband transitions within the t₂g manifold are orders of magnitude too weak to account for the observed intensity. We will argue below that the observed line shape can be understood as a multi-phonon sideband of the free carrier (Drude) response. As mentioned before, the effective mass of the charge carriers m* can be obtained by analyzing the Drude spectral weight. In Fig. 2 we show the spectral weight W(ω), defined as

\[ W(\omega) = \int_0^{\omega_c} \sigma_1(\omega) d\omega. \]  

The electronic contribution 8W(∞) = ω_p^2 = 4πne^2/m, where e and m are the free electron charge and mass, and n is the electron density. The contribution of the infrared phonons manifests itself in W(ω) as steps, e.g., at 8.5 meV in the 2% doped sample (Fig. 2). Such a strong phonon close to the Drude peak requires experimental data that extend beyond the soft phonon frequency. (i) The ε₁(ω) and ε₂(ω) data below 3 meV measured by time-domain THz spectroscopy (for x = 0.001 and 0.002) and (ii) far-infrared reflectivity (above 2 meV for x = 0.001 and 0.002, and above 4 meV for x = 0.009 and 0.02) are crucial for the separation of the spectral weight in the Drude peak from the large contribution by the soft phonon mode. This is particularly important for the lower doped samples, where the Drude spectral weight is one order of magnitude smaller than the spectral weight of the soft optical mode. For the two lowest dopings we apply the partial sum rule [Eq. (1)] with cutoff frequencies \( \hbar \omega_c \) = 1.5 meV (0.1%) and 2.0 meV (0.2%), which are larger than the Drude relaxation rate but below the soft phonon (see Fig. 1) [19], yielding \( \hbar \omega_p = 116 \pm 18 \text{ meV} \) and \( 159 \pm 23 \text{ meV} \), \( \hbar \omega_p = 412 \pm 53 \text{ meV} \) and \( 527 \pm 61 \text{ meV} \) for the samples.

FIG. 1 (color online). The optical conductivity of SrTi_{1-x}Nb_xO_3 for x = 0.001, 0.002, 0.009, and 0.02 at 300 K (top) and 7 K (bottom), together with the dc conductivity (dots). For clarity the spectral windows corresponding to the extreme infrared, far-infrared, midinfrared, and visible ranges are displayed with different magnifications.

FIG. 2 (color online). The integrated optical spectral weight of SrTi_{1-x}Nb_xO_3 as a function of photon energy and relative to the charge carrier concentration, at 7 K. The Drude spectral weight is separately shown for x = 0.9% and x = 2% (dashed lines).
FIG. 3 (color online). Experimental plasma frequency at 7 K derived from the spectral weight of the Drude peak (squares) together with that from the band-structure calculations [16] (solid line) as a function of the free carrier concentration (from Hall effect). The circles display the total electronic spectral weight at 3 eV. The inset shows the corresponding effective carrier mass $m'/m = (W_{\text{mir}} + W_{\text{Drude}})/W_{\text{Drude}}$, with $x = 0.001, 0.002, 0.009,$ and 0.02, respectively, shown by the red squares in Fig. 3. Defining the mass renormalization of the charge carriers as the ratio of the total electronic spectral weight at 3 eV, $W_{\text{total}}$, and the Drude spectral weight, $W_{\text{Drude}}$, $m'/m = W_{\text{total}}/W_{\text{Drude}}$, we observe a twofold mass enhancement, i.e., $m'/m = 2.0 \pm 0.3$ for the low charge carrier densities considered in the present study (Fig. 3, inset). The calculated LDA band mass $m_h = 0.63m_e$, which implies $m'/m_h = 3.0 \pm 0.4$. For $0.001 \leq x \leq 0.02$, the band-structure value [16] of the Fermi energy, $E_F$, ranges from 0.02 to 0.1 eV, relative to the bottom of the lowest $t_{2g}$ band, which coincides with the energy of the relevant longitudinal optical phonon, $\hbar\omega_{\text{LO}} = 0.1$ eV [20,21]. This is a difficult parameter range to describe theoretically where none of the usual approximations, i.e., $\hbar\omega_{\text{LO}}/E_F < 1$ or $\hbar\omega_{\text{LO}}/E_F \gg 1$, are applicable. For the present discussion we consider the latter limit, appropriate for the lower doped samples. It takes as a starting point the model of a single polaron [22,23], characterized by the coupling constant $\alpha$. Within a variational approximation, Feynman [22] deduced the relation $m'(\alpha)$ valid in the range $0 < \alpha < 12$. Applying Feynman’s relation to the experimental $m'$ values, we obtain a doping independent value $3 < \alpha < 4$, in excellent agreement with the value $\alpha = 3.6$ from the Fröhlich model in a polar medium with multiple optical phonon branches [24].

The optical conductivity shows a broad absorption band between 0.1 and 1 eV (Fig. 1). The $f$-sum rule, $8W(\infty) = \omega_p^2$, is almost satisfied at 3 eV (Fig. 3), demonstrating that the intensity in this midinfrared band compensates to a large extent the deficit of Drude spectral weight. Such spectral weight redistribution between the “coherent” (Drude) and the “incoherent” (midinfrared) contributions of the optical conductivity suggests that the mass enhancement reflects coupling of electrons to bosonic degrees of freedom, most probably phonons. A spectral shape similar to the observed midinfrared band at 300 K (Fig 1) was calculated by Emin [25], who considered the photoionization spectrum out of the potential well formed by the lattice deformation of the polaron. Upon cooling, the maximum of this band remains between 200 and 350 meV, and at 7 K an additional peak emerges on the low-energy side with a maximum varying from 120 (0.1%) to 140 meV (2%). Devreese et al. [26,27] have numerically found a broad midinfrared band with (for intermediate couplings) a peak at lower energies. They explain it as a multiphonon band and the peak as a relaxed state of an electron optically excited within the polaronic potential well. The model predicts the maxima of the two bands to be at 0.065$\alpha^2\hbar\omega_{\text{LO}}$ and 0.14$\alpha^2\hbar\omega_{\text{LO}}$. With $\alpha = 4$ this corresponds to 110 meV and 230 meV, consistent with the experimentally observed positions (Fig. 1).

Figure 4 shows the temperature dependence of the spectral weight of both the Drude peak and the midinfrared band. Upon increasing temperature, our data show an increase of the midinfrared spectral weight, as earlier observed by Ref. [9], and a decrease of the same amount of Drude spectral weight, contrary to the expectation that thermal fluctuations undo the self-trapping and reduce the effective mass [28,29]. Kabanov and Ray explained this with a two-fluid model of delocalized carriers and localized polarons pinned to impurity sites [30]. However, in this model the Hall coefficient depends strongly on temperature and becomes completely suppressed at low temperatures, in contradiction to the almost constant Hall coefficient of our Nb-doped SrTiO$_3$ crystals [15]. While Ciuchi et al. [31] have demonstrated that the polaron radius decreases when the temperature is increased, the authors maintain that the polaron mass will decrease with increas-

FIG. 4 (color online). Experimental temperature dependence of the spectral weight of both the Drude peak (circles) and the midinfrared band (squares) for $x = 2.0\%$ and $x = 0.9\%$. 

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ing temperature. Theoretical work until now has concentrated on the properties of a single polaron, while the important (but quite difficult) problem of the polaron liquid remains to be solved. In this respect we conjecture that in its ground state the electron-phonon interacting system forms a homogeneous fluid, which is uniformly accelerated by an external electric field, without excitation of the vibrational degrees of freedom. Since the charge fluid is no longer uniform at finite $T$ due to thermal charge density excitations, its translation upon applying an electric field becomes increasingly hindered by coupling to the lattice vibrations when we increase the temperature, resulting in a reduced Drude spectral weight and an increase of the midinfrared spectral weight. The relevant temperature scale for this to occur is the Fermi temperature, less than 1000 K for the highest doped sample. The aforementioned process whereby a polaron will escape from its self-trapped potential will occur on the (higher) energy scale of the polaron binding energy, i.e., approximately 2000 K.

In conclusion, we observe an unusually narrow Drude peak in electron-doped SrTiO$_3$ at 7 K for charge carrier concentrations between 0.1% and 2% per unit cell, which is less than 1 meV for the lowest dopings. The suppression of the Drude spectral weight reveals a mass enhancement between two and three, which is caused by the electron-phonon coupling. The missing spectral weight is recovered in a series of midinfrared sidebands resulting from the electron-phonon coupling interaction, traditionally associated with the polaronic nature of the charge carriers. The effective mass yields an intermediate electron-phonon coupling strength, $3 < \alpha < 4$, thus suggesting that the charge transport in electron-doped SrTiO$_3$ is carried by large polarons. Increasing the temperature depletes further the Drude spectral weight, corresponding to an increase of the free carrier mass. This behavior, which is opposite to that of an isolated polaron, may signal that the low-temperature state of matter is a polaron liquid.

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[16] We employed the linear augmented plane wave method as implemented in the WIEN2k code (Karlheinz Schwarz, Techn. Universitat Wien, Austria, 2001) and the generalized gradient approximation for the exchange-correlation potential in the form proposed by J.P. Perdew, K. Burke, and M. Ernzerhof [Phys. Rev. Lett. 77, 3865 (1996)]. Calculations have been performed in the high-temperature perovskite structure ($a = 3.905 \AA$) as well as in the low-temperature tetragonal structure (group No. 140, $14/mcm$, $a = 5.529 \AA$, $c = 7.824 \AA$, $O_4 = 0.244^\circ$). Optimizing the $O$ position in the calculations yields $O_4 = 0.223$. Nb doping was simulated by changing the nuclear charge of Ti from 22 to 22 $+$ $x$, or that of Sr from 38 to 38 $+$ $x$. Fermi-surface integrals were evaluated using the $k$-point meshes up to $28 \times 28 \times 28$. Our first principles results show a substantially weaker effect of the tetragonality compared to the semiempirical calculations of Mattheiss [17] (less than 4 meV splitting of the otherwise degenerate states at $\Gamma$, compared to $\sim 20$ meV). This, in fact, resolves a long-standing controversy between the band structure of Ref. [17] and the de Haas–van Alphen measurements of Gregory et al. [18].