

Reflectance and Raman Spectra of Metallic Oxides, LaSrCoO and CaSrRuO : Resemblance to Superconducting Cuprates

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We have measured reflectance, ellipsometric, and Raman spectra on thin films of isotropic metallic oxides $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ and $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{RuO}_3$. The spectra strongly resemble those of cuprate superconductors. In particular, reflectance is a nearly linear function of frequency throughout the infrared, and the electronic Raman scattering continuum is nearly independent of energy. Neither of the compounds is superconducting down to 4.2 K, while their electronic excitations spectra are apparently like those of the cuprates. Hence, it seems unlikely that the corresponding "anomalous" dielectric response could be the sole root of high-temperature superconductivity.

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So far, high-temperature superconductivity (HTSC) remains quite a rare chemical phenomenon. It has been unequivocally observed only in layered cuprates [1], which may all be considered alike since HTSC is believed to originate in CuO_2 layers; indeed, the "passive" layers can be varied, but these may merely act as spacers and charge reservoirs [2]. Given their infrequent occurrence, one could suspect that HTSC compounds might possess some exceptional normal state characteristics, as well. Therefore, much effort has been devoted to identification of such properties, since clearly that could guide both the theory and the search for new HTSC materials.

Extensive spectroscopic studies of cuprate superconductors have indeed revealed the universal presence of some unusual features. First, throughout the infrared region—almost all the way up to the screened plasma frequency, which is typically found near 1 eV—the reflectance decreases with frequency in an almost linear manner. Second, electronic Raman scattering takes place in the same spectral range, and its intensity is nearly independent of frequency. These two features are illustrated in insets to Figs. 1 and 2, where we have compiled broad-range reflectance and Raman spectra [3–5], respectively, for a few cuprate superconductors (single crystals or optical-quality epitaxial thin films). Similar spectra have indeed been reported by several other groups; overall, there is a reasonable consensus, at least insofar as the raw experimental data are concerned.

However, interpretation of these spectroscopic features is still a matter of great controversy. For example, ever

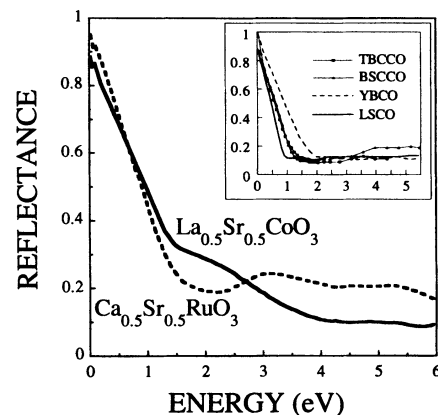


FIG. 1. Broad-range specular reflectance spectra of $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{RuO}_3$ (broken line) and $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ (solid line). Inset: Reflectance spectra [3] of $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$, $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$, $\text{YBa}_2\text{Cu}_3\text{O}_7$, and $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$.

since 1987 spectroscopists have been debating [5,6] whether the infrared absorption has only one electronic component (the free charge carrier response) or two (the Drude response plus a "midinfrared band"). Theorists, on their side, have proposed a vast number of HTSC theories, models, and scenarios (see, for example, Refs. [7–10]), and hence as many explanations for the optical spectra of cuprates.

There may be one aspect, though, in which many of these theories seem to converge, and which may therefore deserve attention: The *normal* state of high-temperature

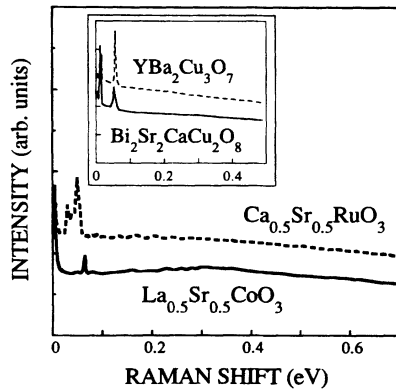


FIG. 2. Broad-range Raman scattering spectra of $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{RuO}_3$ (broken line) and $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ (solid line). Inset: Raman spectra [3,4] of $\text{YBa}_2\text{Cu}_3\text{O}_7$ and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$.

superconductors is frequently envisioned as being quite anomalous. This anomalous normal state (ANS) should have certain experimental fingerprints; the well-known list advanced by Varma *et al.* [7] includes the two spectroscopic features described above, the linear dependence of dc resistivity on temperature and of the tunneling conductance on voltage, etc. Note that all these “anomalies” should be interconnected, since presumably they originate from the same peculiar spectrum of excitations.

The importance of ANS derives mainly from its possible association with HTSC. For example, the above shapes of optical and Raman spectra have been asserted to constrain the dielectric response in such a way that $\text{Re}[\epsilon^{-1}(q, \omega)]$ must be negative over a sizable region of the (q, ω) space, which causes effective attraction, pairing, and superconductivity with high critical temperatures [7]. The assumption that HTSC arises from ANS has been made in conjunction with other pairing mechanisms, as well. The two should then be expected to correspond to one another; HTSC should appear only in ANS metals, and in every one of them.

Indeed, such an important conjecture should be tested experimentally. A difficulty here is that basically every theory defines ANS differently. In some sense, the key issue is to determine which definition is the right one, i.e., to identify the way in which the normal state of high- T_c materials is really anomalous. In this paper, we concentrate on the above two spectroscopic features—which play an important role in at least some of the models for HTSC—and try to clarify their relation to ANS.

With this motivation, we have studied a few compounds from the LaSrCoO and CaSrRuO families that have transport properties similar to those of the high- T_c superconductors. They are all metallic, with resistivity increasing approximately linearly with temperature, and reaching a few hundred $\mu\Omega$ cm at room temperature. However, neither of the new oxides showed any signs

of superconductivity down to the lowest temperatures investigated (4.2 K). We have succeeded in synthesizing optical-quality, large-area thin films of these compounds, and recording their reflectance, ellipsometric, and Raman spectra, as detailed below. This allows for a systematic comparison, based on a uniform methodology, to be made with cuprate superconductors.

Single-crystal epitaxial films of $\text{Ca}_x\text{Sr}_{1-x}\text{RuO}_3$ with $0 \leq x \leq 1$ were grown on deliberately miscut (100) SrTiO_3 substrates by single-target, off-axis sputtering [11]. Film thickness was about 500 nm, which is several times larger than the optical penetration depth, and hence the substrates did not affect the spectra. The stoichiometric composition of the films was verified by Rutherford backscattering spectroscopy. The film texture was found to be purely {110} normal to the substrate, with single in-plane orientation according to x-ray diffraction analysis using a four-circle diffractometer. Ion channeling study provided χ_{\min} [i.e., the ratio of the backscattered yield along (100) to that in a random direction] of about 2%, which is close to the value of Si single crystals. Atomic force microscopy revealed (root-mean-square) surface roughness less than 7 Å. Typical resistivity at room temperature was $\rho(T = 300 \text{ K}) \approx 340 \mu\Omega \text{ cm}$. Further details, including the results of magnetization measurements, can be found in Ref. [11].

Thin films of $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ were grown on (100) MgO substrates by pulsed laser deposition [12]. X-ray diffraction analysis showed a pseudocubic structure with a lattice constant of 3.82 Å. The films were oriented epitaxially with the (001) axis perpendicular to the substrate. Ion channeling study provided $\chi_{\min} \approx 8\%$ due to the large lattice mismatch with the substrate. The room-temperature resistivity was $\rho(T = 300 \text{ K}) \approx 150 \mu\Omega \text{ cm}$, and isotropic [12].

Reflectance spectra were recorded using a Bio-Rad FTS-40V Fourier-transform far-infrared spectrometer, a Bio-Rad FTS-40 Fourier-transform midinfrared spectrometer, a Spectra-Tech IR-PLAN microscope (coupled to the midinfrared spectrometer, but equipped with a dedicated liquid-nitrogen-cooled HgCdTe detector), and a near-infrared through near-ultraviolet Perkin-Elmer Lambda-9 double-beam, double-monochromator spectrophotometer. The diffuse reflectance spectra were recorded using a Perkin-Elmer 60 mm Integrating Sphere coupled to the Lambda-9 spectrophotometer. Ellipsometric measurements were performed on a model 445A15 Rudolph Instruments Automatic Spectro-Ellipsometer. All the films studied here showed high specular and small diffuse reflectance, and had very homogeneous, mirrorlike appearance.

Raman spectra were recorded in the backscattering geometry using the 514.5 or 488.0 nm radiation from an argon-ion laser, and they were analyzed by a triple scanning Spex spectrometer. The samples were kept in vacuum or in He gas to eliminate spectral

lines due to scattering in air. The radiation density was kept low to prevent heating and damage of the films.

In Fig. 1 we show the broad-range reflectance spectra, and in Fig. 2 the broad-range electronic Raman scattering spectra of $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{RuO}_3$ and $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$, taken at room temperature. The laser plasma lines and the detector noise were filtered out, and the corrections were made to account for the system's spectral response; no further data processing is needed for our present purpose. (Actually, we have also determined the complex dielectric functions, investigated the temperature dependence of the spectra, and studied other related compounds such as CaRuO_3 and SrRuO_3 ; however, these details will be presented elsewhere.)

Comparison of the spectra displayed in Figs. 1 and 2 shows that there is striking similarity between the HTSC materials, on one hand, and non-HTSC oxide metals $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{RuO}_3$ and $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$, on the other hand. In particular, the latter two compounds also show reflectance that is a nearly linear function of frequency throughout the infrared. They show an electronic Raman scattering continuum that is nearly independent of frequency, as well.

To be more precise, the broad spectral range covered in this study can naturally be divided into three regions: low (below 0.1 eV), intermediate, and high (above ca. 1.5 eV). Physically, these can be characterized as the phonon frequency range, the region of strong midinfrared and near-infrared electronic absorption and electronic Raman continuum, and the interband transition range, respectively. In the intermediate frequency range the spectra of the oxides under study are virtually indistinguishable from those of the cuprates. In this region, the spectral functions show little temperature dependence—more exactly, none within the experimental error—again just like in cuprates. The similarity extends into the low-frequency region; this is particularly clear for the electronic Raman continuum (see Fig. 2). Essentially, the only differences are that the phonon frequencies are not identical and that there is no superconducting gap in the compounds considered here [13].

So, $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{RuO}_3$ and $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ are rather akin, spectroscopically, to the cuprate superconductors. From the data available in the literature [14], we have found that a few other metallic cobaltates ($\text{Nd}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$, $\text{Bi}_2\text{Ba}_3\text{Co}_2\text{O}_9$, and $\text{Bi}_2\text{Sr}_3\text{Co}_2\text{O}_9$), titanates ($\text{Sr}_{0.9}\text{La}_{0.1}\text{TiO}_3$ and $\text{Ba}_{0.93}\text{La}_{0.07}\text{TiO}_3$), vanadates (V_2O_3), and even NbSe_3 also show similar reflectance spectra. Thus, the family of metals with ANS-like spectra may well be even larger.

Similarity of optical and Raman spectra indeed implies existence of similar electronic excitations. Apparently, non-HTSC metals exist with dielectric properties which are quite alike, over a broad spectral range, to those of the cuprates. Hence, it appears unlikely that pairing and HTSC

could arise solely as a consequence of such a dielectric response.

The present comparison may actually provide some clues about the nature of this dielectric response. Since several of the aforementioned oxides are not magnetic—not even when they are undoped and insulating—it appears unlikely that the anomalous scattering could exclusively be of magnetic origin. By similar reasoning, it seems that one could rule out theoretical scenarios which tie the anomalous spectral properties to the reduced dimensionality of the cuprates (e.g., to specific properties of a two-dimensional electron gas): apparently, some cubic crystals manifest quite similar behavior.

On the other hand, a distinct property shared by all the oxide metals discussed above is that of being a very polar compound, with cohesion energy that is of predominantly ionic origin. The *bare* electron-lattice interaction cannot but be strong in such materials. That could conceivably cause the anomalous scattering and dielectric properties which are indeed unusual for ordinary metals—but perhaps fairly frequent in metallic oxides [15].

Given that the electronic excitations in some titanates, vanadates, cobaltates, and ruthenates look quite similar to those in the superconducting cuprates and bismuthates, one may be tempted to reinforce the search for possible (high-temperature?) superconductivity in these other oxide metals. On the other hand, it is also possible that, apart from the peculiar dielectric response, some other properties are necessary for HTSC and unique to cuprates: HTSC is quite exceptional, after all. Further detailed comparative studies would be helpful in resolving this important issue.

In conclusion, we have synthesized high-quality, large-area thin films of $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{RuO}_3$ and $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$, and recorded their reflectance, ellipsometric, and Raman spectra. We found a substantial similarity between the HTSC materials, on one hand, and these two compounds, on the other hand. In particular, they all show reflectance that is a nearly linear function of frequency throughout the infrared, as well as an electronic Raman scattering continuum that is nearly independent of frequency. From these similarities, we conclude that all of these materials should have similar electronic excitations and similar anomalous dielectric response, which is thus unlikely to be the sole root of HTSC.

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