METHOD OF KRAMERS-KRONIG:
ANALYSIS OF OPTICAL FUNCTIONS OF HIGH-TEMPERATURE SUPERCONDUCTOR La$_2$CuO$_4$

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Abstract

The full complex of fundamental optical functions parallel and perpendicular to the c axis of single crystals LaCuO$_4$ is determined at 293 K (0.1 - 16 eV) and 80 K (1-5 eV) from Kramers-Kronig analysis of reflectivity data. Strong anisotropy of spectra obtained is observed.

Introduction

One of primary objectives of superconductivity research has been to raise the transition temperature $T_c$. It was established [1] that in the range 20-40 K $T_c$ occurs for system La$_{2-x}$M$_x$CuO$_{4-y}$ with M=Ba, Ca, Sr. A schematic representation of the phase diagram has been presented in [2].

At high temperature these materials are in the body-centered $I4/mmm$ $K_2NiF_4$ structure [3]. When the temperature is lowered below 500 K LaCuO$_4$ transforms to a single-face-centered orthorhombic $D_{2h}^{18}$ structure [4]. But its structure is only a slight distortion ($\approx$ 1% difference between a and b) of the $K_2NiF_4$ tetragonal structure. Existence of a lower-symmetry structure at low temperature is also possible [5].

The parameters of the lattice are determined in [4-5]. LaCuO$_4$ exhibits strong anisotropy behavior. In this material Cu-O$_2$ layers are present, which form the a-b planes. A series of electronic structure calculations have been carried out [6-9]. The results of these calculations are compared in [10] with the experimental data.

Optical measurements

The results of numerous optical experiments have been reported previously (see review [10]). Photoemission was investigated in [11]. Mid- infrared absorption (0.1-1.2 eV, 10 K) is described in [12]. The Raman spectra were obtained in [13-14]. The analysis of ellipsometric data was executed in [15] at room temperature from 0.7 to 4.9 eV.

The big number of articles are devoted to investigation of reflectivity spectra of LaCuO$_4$ crystals. However most of the earlier optical studies on high-$T_c$ cuprate La$_{2-x}$Sr$_x$CuO$_4$ materials have been carried out on ceramic polycrystallin samples, as in [16,19] and other papers (see references in [20]).

Sometimes the flat surface was obtained by polishing with Al$_2$O$_3$ powder which was sufficient for optical measurements in the wavelength range $\lambda \geq 300A^0$. The growing of large
qualitative monocrystals allows to carry out measurements in polarized light (E||c and E⊥c).

Optical reflectivity spectra of LaCuO₄ have been measured over a wide spectral range (0.1-40 eV [21], 0.004-35 eV [22]), as well as in visible region (0.3-6 eV [20]) however only at room temperature.

The difference between the two polarizations is significant except in the very high-energy region. The most intensive structures were observed in LaCuO₄ in region 6-9 eV. A very weak peak at approximately 2 eV was discovered in the E⊥c spectrum in [19,21]. Strong anisotropy is observed in [15]. For E||c the optical spectra are nearly featureless, while for E⊥c there is a sharp peak in Im(ε).

The reflectivity spectra of LaCuO₄ at liquid nitrogen temperature (∼60 incident) over an energy range 1 to 5 eV were obtained using DFS-12 monochromator and a Glan-Thomson polarizing prism, with high resolution (1nm/mm) and accuracy (about 0.03%) [24]. The light source was a 200 W xenon lamp and a 100 W galogen lamp. Samples were cooled by liquid nitrogen through a copper block.

The spectra R have been measured at 293 K and 80 K in detail. Reflectivity spectra of the sample similar in composite to LaCuO₄ have nonpolarized step at 1.7 eV, principal maximum at 2.08 eV (E⊥c), step at ∼2.98 eV and minimum at 3.6 eV (E⊥c) and also a broad step at 2.4 eV (E||c). Increasing of temperature from 293 to 80 K transforms the step at 2.4 eV into clear-cut maximum at 2.36 eV.

Calculations of optical functions

Kramers-Kronig relationships [25,26] were used in [15] with the aim of calculations of reflectivity R from experimental ε₁, ε₂. On the contrary in [21] Kramers-Kronig transformations allowed to calculate from known R the effective electron density and the imaginary part of the dielectric constant, which indicates that the damage on the sample surface suffered by polishing is not serious. The value of optical conductivity σ was calculated in this work. The comparison between results obtained experimentally and those calculated from band theory [8] was carried out.

Our problem was to obtain the set of majority of known optical functions for polarized light (E||c and E⊥c). Using Kramers-Kronig analysis, basing on our experimental results [24] and taking into account the data of article [22] the full complex, containing fourteen optical functions was calculated over an energy interval 0.1-16 eV at 293 K.

In this work we examine the following functions: reflection coefficient R, absorption coefficient μ, real (ε₁) and imaginary (ε₂) parts of permittivity, refractive index n, absorption index k, functions of bulk (−Im ε⁻¹) and surface (−Im (ε+1)⁻¹) plasmons, effective number of valence electron nₑ, effective permittivity εₑ and differential functions α, β. All these functions are represented in Figs 1-6.

The peculiarities of function R are described earlier in [24]. The spectra of μ are very similar to R. The maximal value of μ is observed at 6-9 eV. The functions n, ε₁ are correlate with the spectrum of R in interval 0.1-3 eV and fall off steeply at hν > 3 eV. The spectra of k, ε₂ have a marked difference from R at hν > 5 eV.

The functions of bulk and surface plasmons have noticeable structures at energies 7-9 eV and 11-13 eV respectively. The functions nₑ, εₑ are monotone and effective permittivity attained saturation at 16 eV. The differential function α descends monotonically and has very
weak particularities in all energy interval. Function \( \beta \) is antistructural to \( R \) and has more noticeable structures especially at \( h\nu > 12 \text{ eV} \).

![Optical functions](image)

Fig. 1-6. Optical functions \( R, \mu; \varepsilon_1, \varepsilon_2; n, k; -\text{Im}\varepsilon^{-1}, -\text{Im}(\varepsilon+1)^{-1}; n_{ef}, \varepsilon_{ef}; \alpha, \beta \) at temperature 293 K for polarization \( \mathbf{E}||\mathbf{e} \) (full line) and polarization \( \mathbf{E}\perp\mathbf{e} \) (dashed line).
Fig. 7-10 illustrate the results obtained at 80 K. We examined functions $R$, $n$, $\varepsilon_1$ and $k$, $\mu$, $\varepsilon_2$ in the range 1-5 eV. The functions $n$ and $\varepsilon_1$ are similar to those of $R$ only in case of $E \parallel c$. All functions have noticeable structures at energies $\approx 2$ eV, however maxima of $n$, $\varepsilon_1$ are shifted in the region of smaller energies.

In case of $E \parallel c$ we observe very weak structures at $h\nu \approx 2-2.5$ eV, the half of enumerated functions have not clear maxima. So, strong anisotropy is observed for optical spectra of superconductor LaCuO$_4$. The results obtained in this work may be useful in practical aims and for determination of the origin of optical transition in LaCuO$_4$ in the light of the theoretical predictions.

References