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Structural properties of \((\text{Nd}_{0.33}\text{Eu}_{0.2}\text{Gd}_{0.47})\text{Ba}_2\text{Cu}_3\text{O}_y\) studied by magnetic and infrared measurements

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Abstract. Reflectance of a single crystal of the \((\text{Nd}_{0.33}\text{Eu}_{0.2}\text{Gd}_{0.47})\text{Ba}_2\text{Cu}_3\text{O}_y\) superconductor was measured as a function of frequency from 35 to 8000 cm\(^{-1}\) and for temperatures from 10 to 300 K. The Kramers-Kronig analysis with appropriate extrapolations was used to calculate response functions. The AC conductivity displays phonons at frequencies typical for the whole family of REBa\(_2\)Cu\(_3\)O\(_y\) cuprates. The Drude term is rather low in comparison to optimally doped cuprates. The spectra were fitted to study temperature dependence of their parameters.

1. Introduction

Infrared spectroscopy (IRS) probes the excitations of individual and collective modes in cuprates in a non-destructive way. The far-infrared region is of special interest, because it may contribute to prove or disprove the existence of the superconducting gap and it is suitable for research of the excitations, which are probably most relevant for explanation of high-\(T_c\) superconductivity. Our material, \((\text{Nd}_{0.33}\text{Eu}_{0.2}\text{Gd}_{0.47})\text{Ba}_2\text{Cu}_3\text{O}_y\) (NEG-123), belongs to the RE-BCO (RE = rare earth) family, the first member of which, \(\text{YBa}_2\text{Cu}_3\text{O}_y\), was found by Wu et al. [1,2]. In ternary compounds of this kind the yttrium ion is replaced by three rare earth ions, usually so called light rare earths (LRE). They tend to sit on both the Ba and rare earth sites and, for higher concentration, form clusters of LRE/Ba solid solution. An excessive concentration of such clusters can lead to degradation of superconducting properties. In order to prevent that, these materials are mostly prepared in a reduced oxygen atmosphere [3,4]. The clusters have size comparable with vortex core diameter or coherence length \(\xi\), and represent therefore effective vortex pinning centres. These centres contribute to formation of magnetic field gradient, which, according to the Maxwell equations, is related to electrical current. The above mentioned substitution contributes to a stronger pinning, and thus to a stronger critical current than in YBCO.
In this paper we report electric, magnetic and optical properties of the single crystal with the aim to clarify the role of the LRE/Ba substitution on infrared response and other physical properties of this material. There are practically no papers dealing with this topic on ternary solutions. Our clarification is based on comparison with YBCO.

2. Experimental details
Powders of Nd$_2$O$_3$, Eu$_2$O$_3$, Gd$_2$O$_3$, and BaCO$_3$ were mixed in the nominal composition. The single crystal NEG-123 was grown from melt in air and then oxygenated at 683 K. The crystal was approximately rectangular with dimensions $a = 1.5$ mm, $b = 2.0$ mm, and $c = 0.5$ mm, where the labelling corresponds to the crystallographic axes of the sample. The temperature dependence of the DC conductivity, $\sigma_{\text{DC}}$, was measured by means of a standard four-probe method. The electrodes were prepared in line, in the $ab$ planes, by evaporation of gold and annealed at 873 K for 1 hour in 1 atm of oxygen with flowing rate 2 ml/s. The cooling rate after annealing was 2.5 K/min. Then four Al-Si leads were ultrasonically attached to the sample. Voltage leads were positioned between current leads. The electrical conductivity was calculated using Ohm’s law, where voltage was measured by the AC Transport Option of the commercial system PPMS 9 (Quantum Design) on cooling from 300 to 10 K, in magnetic fields between 0 and 2 T. The external magnetic field was parallel with $c$ axis of the sample. The amplitude of the electric current was about 10 mA and its frequency was about 10 Hz. The reason of the choice of the AC current was the higher sensitivity than with DC measurement due to digital signal filtering. Magnetic hysteresis loop (MHL) was measured at 77 K by means of a vibrating sample magnetometer (VSM) in the PPMS 9. The MHL was measured with $c$ axis parallel to the external magnetic field, with the field sweep of 0.72 T/min. The magnitude of the critical current density $J_c$ was estimated by means of the extended Bean model for a rectangular sample \cite{5}, $J_{c} = 6\Delta M[\alpha^2 c^3(3b-a)]$, where $\Delta M$ is the difference of the magnetic moments of the upper and lower branches of the MHL. The reflectance spectra in the $ab$ plane were measured in a cryostat between 35 and 8000 cm$^{-1}$ at temperatures varying from 10 to 300 K. In order to determine precisely the reflectance and compensate for the surface roughness, the irregular shape, and the small area of the sample, we used a method of overcoating. The sample was mounted on a cone, measured first intact and then coated \textit{in situ} with a reference metal (gold), the latter measurement being taken as reference. Reflectance of the samples was detected by a DTGS (deuterated triglycine sulphate) detector using a non-polarized radiation to get a reasonable signal level from the small crystal.

3. Results
The temperature dependence of the electrical resistivity $\rho$ is plotted for various magnetic fields in figure 1 (a). The resistivity was a linear function of temperature with a slope $4.4.10^6$ Ω.cm.K$^{-1}$ in the normal state; the electrical conductivity $\sigma = 1/\rho$ ranged from 605 $\Omega^{-1}.cm^{-1}$ at 300 K to 1297 $\Omega^{-1}.cm^{-1}$ at 100 K. With increasing magnetic field the critical temperature decreased. At the same time, the transition width increased from 2.4 K at 0 T to 6.3 K at 2 T. Figure 1 (b) shows the critical current density of the NEG-123 crystal, determined from magnetic hysteresis loops by means of the extended Bean model. The $J_c(B)$ curve ($B = \mu_0 H$, $\mu_0$ is the permeability of the vacuum) exhibited a primary peak at $B = 0$ T with $J_c = 21.0$ kA/cm$^2$ and a secondary peak at $B = 2.0$ T with $J_c = 20.0$ kA/cm$^2$.

Figure 2 summarizes the results obtained by infrared measurements. In panels (a) and (b), the frequency dependence of reflectance of the NEG-123 single crystal is shown for selected temperatures between 10 and 300 K in both the normal and superconducting state. The whole spectrum, displayed in panel (a) is ranging from 0 to 8000 cm$^{-1}$. Panel (b) shows details in the far-infrared region between 35 and 800 cm$^{-1}$. The knowledge of the frequency dependence of reflectance, $R$, allowed us to determine optical constants by means of the causality principle, expressed, in this case, by the Kramers-Kronig transformation. This transformation requires the whole spectrum of frequencies, ranging from zero to infinity. As we had data only from 35 to 8000 cm$^{-1}$, we had to extrapolate them to zero on the lower end and to infinity on the upper end. The transformation yielded phase difference between impacting and reflected EM radiation. From the magnitude and phase of complex reflectance,
any response function can be calculated. In our case, the results are represented by the real part of electrical conductivity, $\sigma_1$, and the real part of the relative permittivity, $\varepsilon_1$. In the normal state we used
Hagen-Rubens extrapolation \( R = 1 - A\sqrt{\omega} \) for frequencies from 0 to 35 cm\(^{-1}\), where 
\[ A = \frac{\sqrt{2/15\sigma_{dc}}} {\sigma_{dc}} \] and \( \sigma_{dc} \) is a real part of electrical conductivity at \( \omega = 0 \) cm\(^{-1}\). This extrapolation is correct under the assumption that the crystal behaves as a metal in the normal state in the given frequency range. The parameter \( A \) was obtained by fitting experimental data at low frequencies. The extrapolation for frequencies above 8000 cm\(^{-1}\) was done using data from YBCO from 8000 to 282000 cm\(^{-1}\) [6]. Between 282000 and 10\(^{6}\) cm\(^{-1}\) we used the \( R \sim \omega^3 \) dependence [7]. Assuming that electrons start to be free above 10\(^{6}\) cm\(^{-1}\), we used the free-electron limit extrapolation, \( R \sim \omega^4 \), above this limit [7].

Assuming validity of the two-fluid model with embedded Lorentz oscillators [8] in the superconducting state, at T = 10 K, we used the extrapolation \( R = 1 - B_1\omega^4 \) between 0 and 35 cm\(^{-1}\). The parameter \( B_1 \) was obtained by fitting the experimental data at low frequencies. The reflectance spectrum above 8000 cm\(^{-1}\) was extrapolated in the same way as in the normal state because of lack of experimental data for frequencies above 8000 cm\(^{-1}\).

The \( \sigma_1(\omega) \), and \( \varepsilon_1(\omega) \) dependences obtained from the Kramers-Kronig transformation are presented in figures 2 (c,d), respectively. Comparing figures 2 (b,c,d), one can see that \( R(\omega) \), \( \sigma_1(\omega) \), and \( \varepsilon_1(\omega) \) exhibit similar features, namely several peaks between 100 and 600 cm\(^{-1}\), attributed to phonons. All the quantities also exhibited a strong peak at about 1300 cm\(^{-1}\), not shown in these figures but visible in Fig. 2 (a). We attributed this feature to the middle-infrared absorption band. Free charge carriers contributed in the normal state to the peak in conductivity at \( \omega = 0 \). A clear increase and narrowing of the Drude peak with decreasing temperature can be seen in figure 2c. In the superconducting phase at 10 K, the peak disappeared from the spectrum due to opening of superconducting gap. A strong sharpening of the absorption features was observed, too.

We used Drude-Lorentz model for the simultaneous analyses of \( R(\omega) \), \( \sigma_1(\omega) \) and \( \varepsilon_1(\omega) \) functions in the normal and superconducting state of the sample in the following form:

\[
\varepsilon(\omega) = \frac{\omega_p^2}{\omega^2 + i\omega/\tau} + \sum_{j=1}^{N} \frac{\omega_j^2}{\omega_j^2 - \omega^2 - i\omega\gamma_j} + \varepsilon_{\infty}
\]

\[
R = \left| \frac{\sqrt{\varepsilon - 1}}{\sqrt{\varepsilon + 1}} \right|^2
\]

where \( \varepsilon(\omega) \) is the complex relative permittivity of the sample. The first term on the right side of equation (1) is Drude contribution of the free charge carriers. \( \omega_p \) is the plasma frequency; \( 1/\tau \) is the frequency independent damping. The sum represents infrared active phonons and middle-infrared band, which were considered in the form of Lorentz curves. \( \omega_j \) is the oscillator strength of \( j \)-th Lorentzian, \( \omega_j \) is its resonant frequency, and \( \gamma_j \) is its width. \( N \) is the total number of the considered Lorentzians. Finally, \( \varepsilon_{\infty} \) denotes the value of the dielectric function at infinity. We also used Fresnel relation for reflectance in case of normal incidence given in equation (2). In table 1 we summarize values of the parameters of the Drude term in the normal state of the sample. The quantity \( \sigma_0 \) is a value of \( \sigma_1 \).

| \( T \) (K) | \( \sigma_0 \) (\( \Omega^2 \cdot \text{cm}^{-1} \)) | \( 1/\tau \) (cm\(^{-1}\)) | \( \omega_p \) (cm\(^{-1}\)) | \( \lambda_{ab} \) (Å) |
|-------------|-----------------|--------------|-----------------|-------------|
| 300         | 2417            | 126          | 4272            | 25000       |
| 200         | 4437            | 81           | 4656            | 18500       |
| 100         | 6998            | 69           | 5386            | 14700       |
Figure 3. Ratio of the $\sigma_1$ ($T = 300$ K – solid curve, $T = 200$ K – dashed curve, and $T = 100$ K – short dashed curve) to the Drude contribution ($T = 300$ K – dotted curve, $T = 200$ K – dash dotted curve, and $T = 100$ K – dash dot dotted curve).

at zero frequency. Skin depth in $ab$ plane at $\omega = 35$ cm$^{-1}$ is $\lambda_{ab} = (2/\sigma_0 \mu_0 \omega)^{1/2}$ under assumption that conductivity of the single crystal is high and equal $\sigma_0$ below 35 cm$^{-1}$. Figure 3 shows evolution of the Drude term with temperature in the normal state of the sample. The experimental data were fitted by equation (1). The Lorentzians were subtracted from the function after the fit.

For the orthorhombic phase of YBa$_2$Cu$_3$O$_7$ single crystal [9] the group theory predicts an existence of 21 infrared-active phonons, distributed among three irreducible representations $7B_1u + 7B_2u + 7B_3u$ corresponding to three different polarizations. In our experiment we measured non-polarized reflectance, but we could identify only 4 phonons for all temperatures and for frequencies from 35 to 605 cm$^{-1}$.

4. Discussion

The electric resistivity of the crystal displayed in figure 1 shows behaviour typical for cuprates under the same experimental conditions. The corresponding magnitude of electrical conductivity obtained by four-probe method at 96 K was 1450 $\Omega^{-1}$.cm$^{-1}$, the value being rather low in comparison with high-quality untwinned YBCO single crystals [10], where the analogous value is about 14300 $\Omega^{-1}$.cm$^{-1}$, i.e. about 10 times larger. If we also compare the four-probe value with the value obtained from infrared measurement, we find that the four-probe one is about 4.0 to 5.4 times smaller than the infrared one. We attribute this discrepancy mainly to the irregularity in the sample shape. The contact resistance could also play a certain role.

The transition width $\Delta T_c$ was by about 4 K narrower than in YBCO for all fields except of 0 T, where our transition was only by 3 K narrower [10]. The field dependence of $\Delta T_c$ exhibits the usual scaling behaviour, $\Delta T_c \sim B^{2/3}$ [11]. We did not observe any vortex-glass-transition knee at the transition probably because of the lack of experimental data.

The relatively high primary peak on the $J_c(B)$ curve can be attributed to some large (relative to the coherence length, $\xi$) defects present in the sample, however we have no direct evidence for them at the moment. The secondary peak of the $J_c(B)$ curve is caused by point-like defects, namely by LRE/Ba solid solution clusters and oxygen vacancies [12]. The contribution of the LRE/Ba clusters was recently confirmed on similar samples ideally oxygenated under high oxygen pressures (100 and 160 bar) [13].

The infrared spectra in the normal state of the sample exhibited features similar to those observed in YBCO [9]. The Drude term at 300 K yielded a similar value of the DC electrical conductivity (i.e. value of $\sigma_1$ at 0 cm$^{-1}$) as reported in [10]. The temperature dependences of $\sigma_0$ and $1/\tau$ in the normal
state were in a reasonable agreement with the experimental data on YBCO [14], although our values agreed only in the order of magnitude and were lower. The values of skin depth were in the same order of magnitude as those in literature [15]. The difference may be explained by possible material disordering due to substitution of Y with Nd, Eu, and Gd. The observed phonon frequencies were slightly lower than those for YBCO, which may be explained by the higher mass of Nd, Eu, and Gd ions in comparison to Y. The conductivity spectra showed a sharp decrease in conductivity below 100 cm$^{-1}$ accompanied by sharpening of the phonon peak at 160 cm$^{-1}$ at superconducting phase transition. The strong effect is attributed to condensation of free electrons during superconducting transition, when the superconducting gap is opened. This results in vanishing of the Drude term from the conductivity spectra.

5. Conclusion

We succeeded to measure reflectance spectra on a relatively small and not ideally flat NEG-123 single crystal, together with electric and magnetic properties. The optical response functions from the reflectance measurements were calculated using the Kramers-Kronig transformation with low- and high-frequency extrapolations of the experimental reflectance. The reflectance spectra were successfully fitted within Drude-Lorentz model so that the temperature dependence of the model parameters could be obtained. The response functions obtained from the fit were consistent with those obtained from the Kramers-Kronig analysis. A significant drop of the Drude term was observed just at the critical temperature in the conductivity spectrum.

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