QUASI ONE-DIMENSIONAL HOPPING CONDUCTIVITY OF THE NON-STOICHIOMETRIC SPIN-LADDER $CaCu_2O_3$ SINGLE CRYSTALS

K.G. Lisunov[1*], E.K. Arushanov[1, 2], N. Wizent[2], A. Waske[2], J. Werner[2], N. Tristan[2], C. Sekar[2], G. Krabbes[2], G. Behr[2], and B. Büchner[2]

[1]*Institute of Applied Physics, Academy of Sciences of Moldova, 5, Academiei str., MD-2028, Chisinau, Republic of Moldova*

[2]*Leibniz Institute for Solid State and Materials Research, IFW Dresden, 20, Helmholtzstr., D-01069, Dresden, Germany*

[*]*Corresponding author, e-mail: kgl-is-here@rambler.ru, kgl40@hotmail.com*

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Abstract

Resistivity, ρ (T), of the spin-ladder compound $CaCu_2O_3$ is investigated between $T \sim 100 - 350$ K. Both nearest-neighbor hopping, ρ (T) ~ exp (E_a/kT), and variable-range hopping, ρ (T) ~ exp $[(T_0/T)^{3/4}]$, quasi one-dimensional conductivity mechanisms are observed above and below $T \sim 200$ K, respectively. The activation energy E_a and the VRH characteristic temperature T_0 exhibit high sensitivity to the cation (Ca, Cu) content, attributable to a corresponding variation of the concentration of intrinsic defects associated with Cu vacancies. On the other hand, no direct dependence of E_a and T_0 on the excess oxygen concentration is found.

1. Introduction

The spin-ladder systems have attracted much attention in recent years due to the predicted spin gap and the possible appearance of the "d-wave" superconductivity in the hole-doped even-leg systems [1]. The structure of $CaCu_2O_3$ belonging to the group of spin-ladder compounds resembles that of $SrCu_2O_3$, differing by a non-planarity of network formed by Cu and O atoms [2].

The resistivity, ρ(T), in the $CaCu_2O_3$ single crystals is governed by hopping mechanisms, including the quasi one-dimensional (1D) nearest-neighbor hopping (NNH) followed by the quasi-1D variable-range hopping (VRH) when T is decreased [3]. The latter has been interpreted with the model of Fogler, Teber, and Shklovskii (FTS) [4], treating $CaCu_2O_3$ as a three-dimensional (3D) array of disordered quasi-1D electron crystals, with importance of the Coulomb correlations [3].

Here we investigate the resistivity of as-grown $CaCu_2O_3$ single crystals and those annealed under high oxygen pressure to obtain information about hopping mechanisms and energy spectrum of charge carriers in both as-grown and annealed samples. Special attention is paid to the role of the cation (Ca, Cu) and oxygen non-stoichiometry, revealed by comparison with previous results [3].

2. Results and discussion

Single crystals of $CaCu_2O_3$ have been grown using the traveling solvent floating zone method with a CuO-rich solvent. The growth is carried out in a four-lamp optical FZ furnace at 5 bar oxygen pressure and a pulling rate of 1 mm/h with counter-rotation of seed and feed

rods. The growth direction of crystals is approximately parallel to the direction of the copper-oxide chain **b** [010]. Annealing was carried out in two steps at 550°C (96 h) and 400°C (48 h) at a high oxygen pressure of 200 bar. The composition of the as-grown (# 1ag) and the oxygen annealed (# 1an) samples studied, given by the relative concentrations of Ca (x), Cu (y), and O (z), was determined by the electron probe microanalysis, yielding x = 13.24, y = 35.82, z = 50.94 for # 1ag and x = 12.61, y 34.72, z = 52.67 for # 1an (in at %). An appreciable excess of Cu and a respective deficiency of Ca is a typical feature of this material [4].

The resistivity was measured in the geometry of **j** || **b**. As can be seen from Fig. 1, strongly activated ρ (T) dependence is observed in both samples.

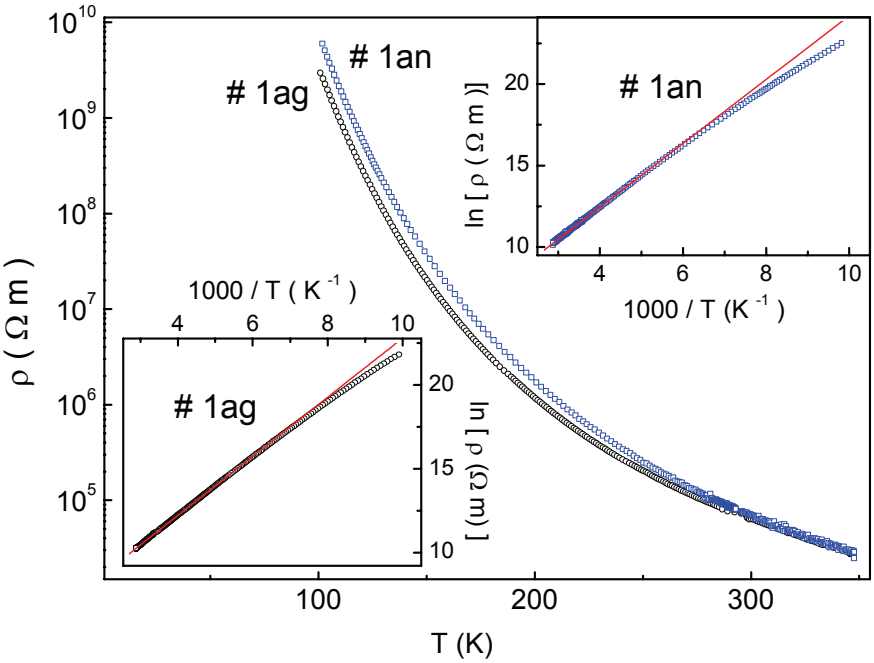

Fig. 1. The plots of ρ vs. T for # 1ag and # 1an. Insets: the plots of ln ρ vs. 1/T for # 1ag and # 1an.

The dependence of ρ on T suggests electron localization and hopping charge transfer. As follows from the insets to Fig. 1, the NNH conductivity with the law ρ (T) = ρ_{0n} exp [E_a / (kT)] is observed in both samples at high T, where E_a = 0.152 eV (# 1ag), 0.168 eV (# 1an) is the activation energy and ρ_{0n} = 176 Ω m (# 1ag), 101 Ω m (# 1an) is the prefactor. Comparing with the data obtained previously in another $CaCu_2O_3$ sample, # 2b (grown in oxygen atmosphere doped with 8% argon) [3], which is characterized by another non-stoichiometry of α = 0.146, β = 0.039, and γ = 0.005 of the explicit formula $Ca_{1-\alpha}Cu_{2+\beta}O_{3+\gamma}$ [and, consequently, x = 14.48, y = 34.57, and z = 50.95 at %, respectively, which can be evaluated from α, β and γ – see Eq. (2) below], namely with $E_a^{(2b)}$ = 0.38 eV [3], one can find the values of $E_a^{(2b)}$ / $E_a^{(1ag)}$ = 2.50 and $E_a^{(2b)}$ / $E_a^{(1ag)}$ = 2.26, where the upper index refers to the corresponding sample.

Deviation of the plots in the insets to Fig. 1 from linearity with decreasing T is connected to the VRH regime, where the resistivity is given by a general law, ρ (T) = ρ_{0v} exp [(T_0 / T)^p] [4]. Here ρ_{0v} is the prefactor, T_0 is the VRH characteristic temperature and the exponent p depends on the dimensionality of a system and on the VRH conductivity mechanism [3–5]. To determine p we analyze the local activation energy, $E_{loc} \equiv d\ ln\ \rho\ /\ d\ (kT)^{-1}$ [5]. From the last two equations one can find: ln [E_{loc} / (kT)] = ln p + p ln T_0 + p ln (1/T), and p can be obtained as the slope of the linear part of the plot of ln [E_{loc} / (kT)] vs. ln (1/T). In the top panels of Fig. 2, the value of p = 1 is observed at high T, corresponding to the NNH con-

ductivity (cf. insets to Fig. 1), whereas $p = 3/4$ at low T. From the linear fit of the plots in the bottom panels of Fig. 2 we find $\rho_{0v} = 8.57\ \Omega$ m, 7.58 Ω m for # 1ag and # 1an, respectively, and the VRH characteristic temperatures $T_0^{(1ag)} = 5.39\times10^3$ K for # 1ag and $T_0^{(1an)} = 5.74\times10^3$ K for # 1an. Comparing with $T_0^{(2b)} = 17.3\times10^3$ K obtained for # 2b [3], one can see that the ratios of $T_0^{(2b)}/T_0^{(1ag)} = 3.21$ and $T_0^{(2b)}/T_0^{(1an)} = 3.01$ are close to those of $E_a^{(2b)} / E_a^{(1ag)}$ and $E_a^{(2b)} / E_a^{(1ag)}$, respectively, following the same order of sequence (see above).

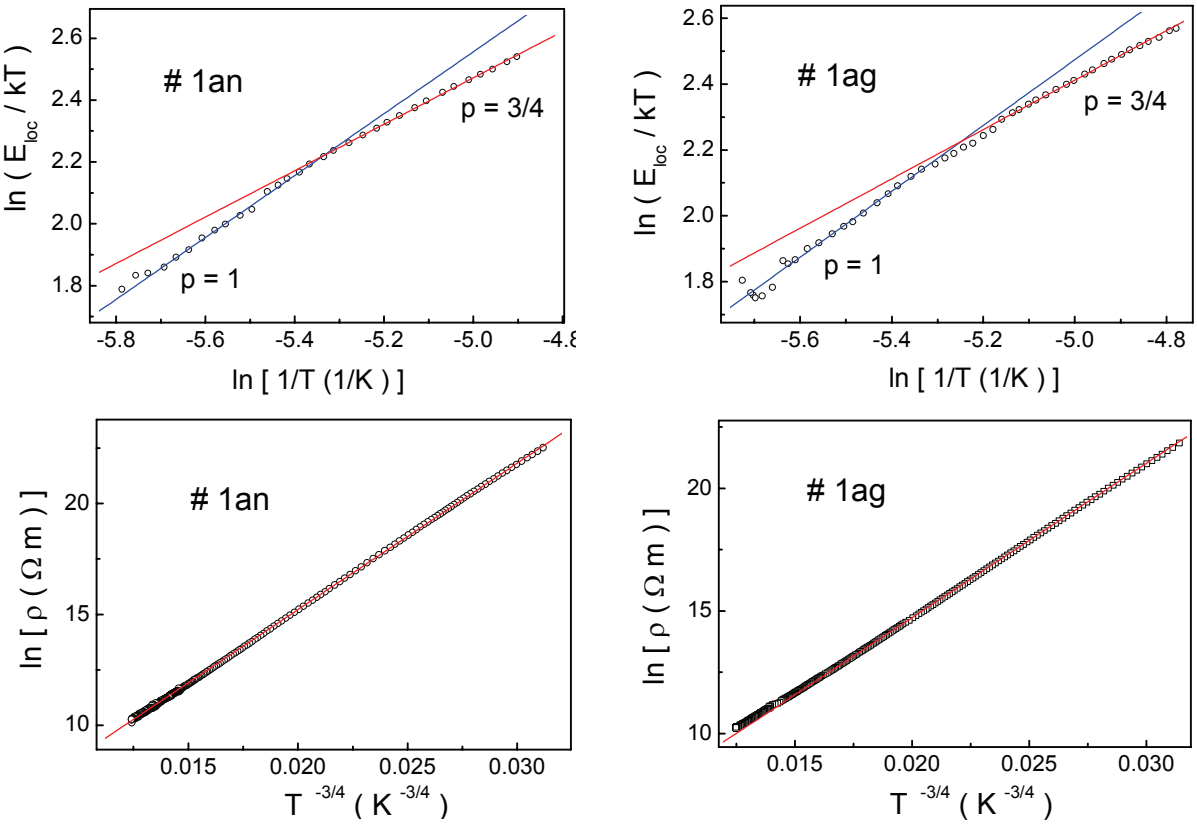

Fig. 2. The plots of ln (E_{loc}/kT) vs. ln ($1/T$) (top panels) and of ln ρ vs. $T^{-3/4}$ (bottom panels) for # 1ag and # 1an. The lines on the top panels are drawn for $p = 1$ and $p = 3/4$.

The law $\ln \rho \sim T^{-3/4}$ agrees with predictions of the FTS model [4], supporting our previous results [3] (see Introduction). Indeed, according to this model, $CaCu_2O_3$ can be treated as an array of quasi-1D chains, consisting of metallic Cu–O–Cu rods with the average length $l = (Na_\perp^2)^{-1}$, where $a_\perp$ is the interchain spacing, bounded with impurities with volume concentration N, which fill in the 3D space of the crystal. The quasi-1D hopping charge transfer is realized due to a strongly anisotropic electron transfer integral [6] by tunneling of the electrons between the rods. It has been shown that $p = (\mu + 1) / (\mu + d + 1)$, where d is the dimensionality, $\mu = 0$, 1, or 2 is the exponent in the law $g(\varepsilon) \sim |\varepsilon|^{\mu}$, and $g(\varepsilon)$ is density of states (DOS) of charge excitations along the chains [4]. For $d = 1$ and $\mu = 2$ we infer $p = 3/4$ coinciding with the values of p found above (top panels of Fig. 2). The law $g(\varepsilon) \sim \varepsilon^2$ means existence of a parabolic Coulomb gap near the Fermi energy, implying importance of the Coulomb correlations in formation of the electron energy spectrum of $CaCu_2O_3$.

According to the FTS model, E_A and T_0 are given with the expressions

$$E_A = C_1\, e^2 / (\kappa\, l) \quad \text{and} \quad T_0 = C_2 \frac{e^2}{\kappa l k}\left[\frac{a_\perp^2\sqrt{r_s}}{\xi_\perp^2}\ln\left(\frac{l}{a_\perp}\right)\right]^{1/3}, \qquad (1)$$

respectively, where C_1 and C_2 are constants, κ is the dielectric permittivity, $\xi_\perp = a_\perp / ln\,[e^2/(\kappa a t_\perp)]$ is the localization length for interchain hopping, a is the mean distance between the electrons along the chain, $t_\perp$ is the interchain hopping integral, $r_s = a / a_B$, and a_B is the Bohr radius.

Equations (1) permit us to discuss the sensitivity of E_a and T_0 to the non-stoichiometry of the samples. However, this requires utilization of the parameters α, β, and γ, known only for # 2b, which are connected to x, y, and z with equations

$$x = (1 - \alpha) / \sigma,\ y = (2 + \beta) / \sigma,\ z = (3 + \gamma) / \sigma, \qquad (2)$$

where $\sigma = 6 - \alpha + \beta + \gamma$. On the other hand, only two out of three Eqs. (2) are independent due to the constraint equation $x + y + z = 1$. An additional condition connecting α, β, and γ can be directly addressed to the nature of impurities (defects) in our compound.

It follows from the data of α, β, and γ for # 2b (see above) that $\alpha > \beta$, or $N_{Ca}^{(st)} - N_{Ca} > N_{Cu} - N_{Cu}^{(st)}$, where N_{Ca}, N_{Cu} are the (absolute) concentrations of Ca and Cu ions in a non-stoichiometric compound and $N_{Ca}^{(st)}$, $N_{Cu}^{(st)}$ are those in the stoichiometric $CaCu_2O_3$. This means presence of vacancies in the cation sublattice with the total concentration, N_v, given by the expression

$$N_v = (N_{Ca}^{(st)} - N_{Ca}) - (N_{Cu} - N_{Cu}^{(st)}). \qquad (3)$$

The excess Cu ions can occupy Ca sites in the lattice [7]. For the case of $\alpha > \beta$ a complete order means existence of only the Ca vacancies, V_{Ca} (that is, only excess Cu ions occupy the Ca sites), whereas any disorder of the cation sublattice leads to appearance of both V_{Ca} and the Cu vacancies, V_{Cu}, so that $N_v = N_v^{(Ca)} + N_v^{(Cu)}$. Generally, at $\alpha > \beta$ we can write

$$N_v^{(Cu)} = C_3\, N_v \text{ and } N_v^{(Ca)} = (1 - C_3)\, N_v, \qquad (4)$$

where the parameter C_3 lies between 0 (the complete order or $N_v^{(Ca)} = N_v$, $N_v^{(Cu)} = 0$) and 1/2 (the complete disorder with random distribution of vacancies over the cation sublattice, $N_v^{(Ca)} = N_v^{(Cu)} = N_v / 2$). Any case of $C_3 > 0$ means presence of the Cu vacancies, which become very probable candidates for impurities (defects) in $CaCu_2O_3$ governing the hopping charge transfer. In this case we can put $N = N_v^{(Cu)}$, then the first of Eqs. (1) and Eq. (2) yield $E_a = C_1\, C_3\, (e^2\, a_\perp^2 / \kappa)\, N_v$. If C_3 varies only weakly from sample to sample, we obtain the expression

$$N_v / E_a = C, \qquad (5)$$

where $C \equiv \kappa / (C_1 C_3\, e^2\, a_\perp^2)$ is a constant. Below we show that using the data of α, β, and γ for # 2b, the data of x, y and z and those of E_a for all samples, the values of α, β and γ in # 1ag and # 1an can be determined. Eventually, our conjecture of $N = N_v^{(Cu)}$ will be confirmed if the following conditions will be satisfied: (i) $\alpha > \beta$ *in all samples*, (ii) $(\alpha - \beta)|_{2b} > (\alpha - \beta)|_{1an} > (\alpha - \beta)|_{1ag}$ and (iii) sensitivity of E_a to the oxygen content γ is weak. The latter means that excess oxygen does not contribute to the formation of defects directly.

The solutions of Eqs. (2) can be presented in a form

$$\alpha\,(\gamma) = [(4 + \gamma)\, x + y - 1] / (x + y - 1) \text{ and } \beta\,(\gamma) = [2 - 2\, x - y\,(5 + \gamma)] / (x + y - 1), \qquad (6)$$

where γ is arbitrary. Using conventional relations $N_{Ca} = (1 - \alpha) N_{Ca}^{(st)}$ and $N_{Cu} = [(2 + \beta)/2]\, N_{Cu}^{(st)}$ we obtain the cation concentrations as functions of γ

$$N_{Ca}(\gamma) = \frac{(3+\gamma)x}{1-(x+y)}\, N_{Ca}^{(st)} \text{ and } N_{Cu}(\gamma) = \frac{(3+\gamma)y}{2[1-(x+y)]}\, N_{Cu}^{(st)}. \qquad (7)$$

Substituting Eqs. (7) into Eq. (3) we obtain the dependence of N_v (γ) and evaluate the constant C with Eq. (5), using the known data for # 2b. Then, the values of $\gamma = 0.071$ and 0.282 for # 1ag and # 1an, respectively, are obtained with Eqs. (5) and (7), whereas those of $\alpha = 0.202$, $\beta = 0.159$ for # 1ag and $\alpha = 0.214$, $\beta = 0.163$ for # 1an are evaluated with Eq. (6). Finally, the concentrations of the cations (in units of 10^{22} cm^{-3}), $N_{Ca} = 1.150$, 1.133, and 1.231; $N_{Cu} = 3.111$, 3.118, and 2.938 for # 1ag, # 1an, and # 2b, respectively, are obtained with Eqs. (7), while that of oxygen (in units of 10^{22} cm^{-3}), $N_O = 4.424$, 4.730 and 4.330 for # 1ag, # 1an and # 2b, respec-

tively, are calculated with expression $N_O = [(3 + \gamma)/3]\ N_O^{(st)}$, where N_O and $N_O^{(st)}$ are concentrations of oxygen in a non-stoichiometric and stoichiometric compounds, respectively.

As follows from the data above the condition (i) is satisfied, meaning the existence of cation vacancies in all samples investigated. The condition (ii) is satisfied as well, following precisely the corresponding relations between the values of E_a: $E_a^{(2b)} > E_a^{(1an)} > E_a^{(1ag)}$. Such behavior implies that along the direction of # 2b → # 1an → # 1ag the excess of Cu ions (β) increases more rapidly than the deficit of Ca ions (α): $\alpha - \beta = 0.107$, 0.051, and 0.043 for # 2b, # 1an and # 1ag, respectively, which annihilates cation vacancies by filling them in with excess Cu ions. Therefore, due to Eq. (4) the concentration of V_{Cu} is also diminished, leading to the corresponding diminution of $E_a \sim N_v^{(Cu)}$. No regular dependence of E_a on γ can be observed, too. Indeed, in the samples # 1ag and # 1an the cation content is similar (and variation of E_a is weak), whereas γ varies by 4 times. Therefore, the condition (iii) is satisfied. In addition, it is evident that the concentration of cations in the samples varies only by ~ 0.2 – 2%, which supports that the parameter C_3 is independent of the sample. Hence, the values obtained for α and β and their variation in the samples investigated are consistent and support the conjecture of $N = N_v$ meaning that Cu vacancies play the role of impurities (defects) in formation of the quasi-1D hopping charge transfer in $CaCu_2O_3$. The concentration of these defects can be obtained with Eqs. (3) and (4) in conditions of complete disorder, when $C_3 = 1/2$, yielding $N_v^{(Cu)} \sim 3\times10^{20}$ cm^{-3}, 4×10^{20} cm^{-3}, and 8×10^{20} cm^{-3} as reasonable estimations for # 1ag, # 1an, and # 2b, respectively, constituting ~ 1–3% of the Cu sites.

Finally, the second of Eqs. (1) can be presented in a form $k\ T_0 = C_2'\ E_a\ G$, where C_2' is a constant and the factor $G = \{r_s^{1/2} \ln (l / a_\perp) \ln [e^2 / (\kappa\ a\ t_\perp)]\}^{1/3}$ consists of the logarithmic terms and the term $r_s^{1/6}$, which vary only weakly from sample to sample. Therefore, the principle role in the variation of T_0 is played by the same mechanism as that of E_a discussed above, which explains the close values of the ratios of $E_a^{(2b)} / E_a^{(1ag)}$ and $T_0^{(2b)} / T_0^{(1ag)}$ as well as closeness of $E_a^{(2b)} / E_a^{(1an)}$ and $T_0^{(2b)} / T_0^{(1an)}$ which has been mentioned above, whereas the differences between them are attributable to the weakly varying factor G.

3. Conclusions

Investigations of the resistivity of the spin-ladder $CaCu_2O_3$ single crystals in this work give evidence for a quasi-1D NNH conductivity at high T followed by a quasi-1D VRH conductivity when T is decreased. The quasi-1D hopping conductivity in $CaCu_2O_3$ is governed by the FTS mechanism [4] proposed for a 3D array of the quasi-1D electron crystals with importance of the Coulomb interaction between the electrons, which supports our previous results [3]. The observed variation of the NNH activation energy E_a and the VRH characteristic temperature T_0 between the samples with various contents of Ca, Cu, and O is attributable to the cation non-stoichiometry and corresponding changes in the concentration of Cu vacancies, whereas no direct sensitivity to the excess oxygen non-stoichiometry is found.

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