Relationship between electrical resistance and thermal expansion coefficient in YBCO and Ti$_{67}$Al$_{33}$

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Abstract. Experimental study of thermal coefficients of both electrical resistance and volume expansion in nanostructured superconducting ceramics YBa$_2$Cu$_3$O$_{7-\delta}$ and intermetallic Ti$_{67}$Al$_{33}$ alloy was performed. In both compounds we found a correlation between the temperature dependences of these coefficients. Formation and relaxation of charge excitations in conductors with a nonmetallic type of interatomic bonds are discussed. We point that, to explain temperature dependence of the conductivity, one should take into account an anharmonicity of atomic vibrations.

1. Introduction
Complete understanding of nature of the conductivity phenomenon is still absent not only for oxide superconductors, but even for metal conductors with a mixed type of interatomic bonds. The theory of electrical resistance of such conductors is in crisis [1]. It cannot describe a conductivity mechanism in high-temperature superconductors and intermetallic, in which there are no free charge carriers, as in classical metals. There is no unambiguous interpretation of the negative value of the temperature coefficient of resistance (TCR) for conductors with high static disorder. There is also a contradiction between the direct and inverse dependences of the conductivity on relaxation times during restoration of the drift and diffusion charge equilibrium, represented by the Bloch and Maxwell expressions, respectively. Although both cases suggest relaxation times of the system to its new equilibrium state, after the establishment of the electric potential gradient. The oxygen index $\delta$ strongly impacts physical properties of the YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO) high temperature superconductor (HTSC) with a perovskite-like structure. Depending on it, the YBCO crystalline structure is transformed from tetragonal to orthorhombic. This transition is accompanied by a change in the type of conductivity: from semiconducting to metallic with emerging superconductivity below $T_c$. Transition to the superconducting state and increase in $T_c$ values correlate with the peculiarities of the lattice change, mainly, its parameters $c$ and $b$ [2]. Obviously, change in these parameters can occur not only as a result of a decrease in the $\delta$ value, but also in dependence on the temperature [3–5]. As a rule, no attention is paid to the features of the temperature dependence of the thermal expansion coefficient (TEC), although experiments [3–5] indicate its anomalous change in vicinity of the phase transition temperature $T_c$.

Intermetallics are metallic compounds whose structure is formed due to “mixed” interatomic bonds: covalent, ionic and metal. These alloys are characterized by high absolute values of the electrical resistivity $\rho$ saturated at high temperatures. Moreover, they can have negative TCR values [1,6]. Alloys with a hexagonal structure close to Ti$_3$Al represent the Hume-Roserie phases having
A nanostructured ceramic sample based on optimally oxygenated YBa2Cu3O7−δ with a density of 5.7 g/cm³ was synthesized by the method described in [13]. The structure, morphology and electrical resistance of this sample are described in details in [14]. The polycrystalline intermetallic compound Ti 67 at.% – Al 33 at. % was made of grade titanium (99.8%) and grade aluminum (99.995%) in a water-cooled copper crucible using argon-arc melting. The temperature dependences of the conductivity of materials is characterized by an abnormal decrease in $T_e$ with increasing temperature. For example, intermetallic Ti67Al33 is a subtraction alloy, in which part of the sites occupied by Ti are vacant. Vacancies activate of diffusion processes in such alloys. Thermal randomization leads to disorder of Al atoms in unit cells. Loose-packed crystalline structures, among other things, are characterized by an abnormal decrease in TEC with increasing temperature.

A reliable data on the temperature dependences of the conductivity of materials is only provided by experimental studies. Based on these data for metals and alloys presented in [8-10] we found relationship between the $\rho(T)$ and the product of the of TEC and temperature:

$$\rho(T) = \rho_0 + \rho^* \beta(T)T. \quad (1)$$

Here $\beta = 3\alpha$ is the volumetric thermal expansion coefficient for polycrystalline samples; $\rho_0$ is the electrical resistivity obtained by extrapolation to 0 K; $\rho^*$ is a characteristic resistivity which is constant in the entire temperature range and has the same value in both ordered and disordered phases of the conductor. The product $\rho^* \beta(T)T$ is the contribution to $\rho(T)$ due to the thermal excitation of various subsystems (electron, phonon, magnetic, etc.) of the atomic lattice. In Refs. [8-11] the relation (1), following from the virial theorem [12] for condensed matter, has been validated in the framework of the recognized positions of the conductivity theories. This relation indicates the decisive role of thermal deformation in the formation of electrical resistance of conductors. A correlation between TCR and TEC was previously established [8-11] in pure metals as well as in alloys with spin and atomic ordering. In this paper, we present results of experimental study of temperature dependences of TCR and TEC in YBCO and Ti67Al33 intermetallic compound.

2. Experimental details

2.1. Samples preparation

A nanostructured ceramic sample based on optimally oxygenated YBa2Cu3O7−δ with a density of 5.7 g/cm³ was synthesized by the method described in [13]. The structure, morphology and electrical resistance of this sample are described in details in [14]. The polycrystalline intermetallic compound Ti 67 at.% – Al 33 at. % was made of grade titanium (99.8%) and grade aluminum (99.995%) in a water-cooled copper crucible using argon-arc melting of a consumable electrode.

2.2. Experimental methods

The temperature dependences $\rho$ and $\alpha$ were obtained for the same sample YBa2Cu3O7−δ in order to ensure the objectivity of the analysis of relation between TCR and TEC. The resistivity was measured in a helium atmosphere inside the cryostat. The external cavity of the cryostat was vacuumized. The electrical resistance was measured by standard four-probe method using Keithley 2002 multimeter in automated data acquisition setup. Silver paste of the SP-40 plus grade was used to make electric contacts to the samples. The temperature was measured with a copper-constantan thermocouple (type T). The values of the electronic component of the TEC $\beta_e$ in the superconducting state (for ceramics $\beta_e = 3\alpha_e$) were calculated from the Grüneisen expression:

$$\beta_e = \gamma_e \frac{C_e \chi}{V}, \quad (2)$$

using the experimental heat capacity data $C_e$ obtained for the same sample [15]. The average value of the conversion coefficient ($\gamma_e \chi V \approx 4.04 \cdot 10^{-4} J^{-1} \mathrm{mol}^{-1}$) for ceramics YBCO, which practically does not change in the superconducting state, was found from experimental values of $C_e/T$ and $\alpha_c/T$ measured at temperatures of 80K, 90K and 100K in [5]. Such data set allows us to compare the features in the temperature dependences of $\rho$ and $\alpha_e$ obtained for the same sample. As for Ti67Al33 sample, $\rho(T)$ and $\alpha(T)$ were measured in the range from 300 to ~1000 K using the four-probe method and the quartz dilatometry in the same experiment.

3. Results and Discussion
Since different types of conductivity are manifested in YBCO and Ti67Al33 compounds, the question arises - drift or diffusion processes of restoration of charge equilibria are realized in these compounds. The theoretical calculation of $\rho(T)$ dependence, based on the concepts of charge drift in metals, is carried out according to the Drude – Bloch formula:

$$\rho_{D,B}(T) = \frac{mne^2\tau(T)}{\varepsilon_0}.$$  \hspace{1cm} (3)

For non-metals, Maxwell’s formula is usually recommended:

$$\rho_M(T) = \frac{\tau_M(T)}{\varepsilon_0},$$  \hspace{1cm} (4)

where $n$, $e$ and $m$ are the concentration, charge and mass of electrons; $\varepsilon_0$ is the electric constant. As can be seen, a contradiction of the concepts of relaxation times $\tau_{D,B}$ and $\tau_M$, which are inversely and directly proportional $\rho$ respectively. Although in both cases, this is the time of the system relaxation to its original state after violation of the charge uniformity under the electric potential gradient.

In [8], it was shown that the mean free path for drift conductivity, given by the scattering cross section for thermal excitations of the lattice, is equal to:

$$\tau_{D,B} = \tau^* / \beta(T)T,$$  \hspace{1cm} (5)

The time of “spreading” of charge excitation in the case diffusion conductivity is equal to:

$$\tau_M = \tau^* / \beta(T)T.$$  \hspace{1cm} (6)

In both cases, $\tau^*$ is a characteristic charge decay time, i.e. its theoretical limit, which is of the order of $10^{-16}$-$10^{-17}$ s. The experimental values of $\beta(T)T$ vary from 0 to 0.1 and change by six or more orders of magnitude. Taking into account (5) and (6), the temperature dependence of resistivity (3) and (4) can be reduced to the general expression (1) which equally well describes $\rho(T)$ dependences of both metals and alloys [9-11]. That is, the above contradiction is excluded if we take into account the effect of the anharmonicity of atomic vibrations in the corresponding concepts. This gives us hope to understand features on $\rho(T)$ dependences in conductors with low or even changing concentration of charge carriers. Since a change in the charge carriers concentration affects the $\rho(T)$ dependence, one can expect a correlation between $\alpha_0 = d\rho/dT$ and $\alpha = d\rho/dT$.

According to the virial theorem [12], in the superconducting state at atmospheric pressure with temperature increase up to $T_c$, the volume should also increase because of an increase in the total energy of the system spent on destruction of pairs of charge excitations. This is confirmed by results of the works [3-5]. Authors have found an anomaly in the behavior of TEC for YBCO upon transition to the superconducting state, similar to that in the electronic component of heat capacity.

Figure 1 shows the temperature dependences TCR and TEC for nanostructured ceramics with a density of 5.7 g/cm³, with a metallic type of conductivity, directly in vicinity of $T_c$. As seen, features on the temperature dependences of TCR and TEC in (Fig. 1a, b), caused by transition to the superconducting state of phases with different $T_c$ values, coincide in temperature. Our data on the anomaly of $\alpha_0/T$ vs $T$ behavior are in good agreement with the results obtained for microcrystalline ceramics YBa$_2$Cu$_3$O$_{7-\delta}$ in [5] (see inset in Fig. 1b). The highlighted region in the inset of Fig. 1b demonstrates the anomalous behavior of the TEC under superconducting transition when changing the type of conductivity. The similarity in the behavior of the temperature dependences of TCR and TEC indicates a close relationship between $\rho$ and deformation of the atomic lattice near $T_c$.

A close relationship between the temperature dependences of TCR and TEC is also observed in Ti67Al33 alloy demonstrating a non-monotonic temperature dependence of conductivity. As seen in Fig. 2, the role of thermal deformation of the lattice, determined by the anharmonicity of atomic vibrations, is significant not only in the formation of the relaxation time of charge excitations, but also in the activation of the process of their excitation. From room temperature to ~520°C, the metallic character of conductivity is replaced by a semiconducting one, which is observed up to ~770°C, and above this temperature it again changes to metallic. From 300 to ~770°C an increase in TEC leads to an increase of the concentration of charge excitations, similar to semiconductors, as a result of the weakening of covalent bonds. Above ~770°C, after reaching delocalization of local charge excitations, the TCR is proportional to TEC, as expression (1) predicts.
The relation $\alpha_e/T$, in Fig. 1 and 2, represents the electronic contribution to thermal expansion in experimental temperature dependence of volume expansion.

![Figure 1](image1.png)

**Figure 1.** Temperature dependences of the coefficients of electrical resistivity and electronic contribution to the thermal expansion of YBCO. In the inset: $\alpha_e/T$ from [4].

![Figure 2](image2.png)

**Figure 2.** Temperature dependences of TCR and TEC of intermetallic Ti$_{67}$Al$_{33}$

The critical behavior in the highlighted temperature range from $\sim$720°C to $\sim$830°C (there is a large data scattering in this region), apparently, is associated with the transition from strong to weak electron localization in this conductor. As seen in Fig. 2, the temperature dependences of TCR and TEC correlate that evidence of the decisive role of thermal deformation in the formation of electrical resistance, regardless of the type of conductivity. A change in the type of conductivity can be observed...
in Fig. 2, where at ~520°C, the TCR sign is inverted. A definite correlation of these parameters is observed for YBCO (Fig. 1) in the region of the superconducting transition.

This is consistent with the existing microscopic interpretation of the $\rho(T)$ dependence, since the finite conductivity according to the theory is largely determined by the deformation potential of the lattice of interacting atoms. The obtained results give hope for a microscopic interpretation of the dependence $\rho(T)$ for materials with a mixed type of bond and conductivity. In the next step towards the microscopic interpretation of the $\rho(T)$ dependences in HTSC materials and intermetallic one should study the role of anharmonicity in the formation of charge carriers.

4. Conclusions

A correlation between the temperature dependences of TCR and TEC is observed in YBCO and intermetallic compound. It indicates the decisive role of the change in the interatomic distances, caused by the anharmonicity of atom vibrations, not only in formation of the scattering potential for charge carriers, but also in the formation the carriers themselves, as a result of the weakening of covalent bonds and changes in ion polarization. Proportionality of $\rho(T)$ to the $\beta(T)T$ product, associated with a change in interatomic bonding forces due to thermal fluctuations and anharmonicity of atomic vibrations, as well as the connection of $\alpha_p$ with $\alpha$, give hope to developed an universal description for electrical conductivity in HTSC materials and intermetallic.

Acknowledgments

This work was supported by state assignment FZNZ–2020–0002 and in part the Russian FBR No. 18-08-00092a. The studies were performed on the equipment of the Center for Collective Use “Analytical Spectroscopy” (Research Laboratory of Nanotechnology and Nanomaterials).

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