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PERIODIC CHANGES IN THE STATE OF A 4f METAL COMPOUND UNDER PRESSURE

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The statement is proved that in the framework of experimentally achievable pressure the existing compounds containing rare-earths can be characterized as those belonging to one of the three states depending on distance RE-O: an electronic state, a vibronic state, in particular a state of electronic-vibronic equilibrium, and a semiconductor-metal state. The hypothesis is put forward that the mechanism of realization of superconducting state in PrBa₂Cu₃O_{6,6} can be considered as a change in the ratio of semiconductor and metallic conductivities in the substance.

Keywords: electronic-vibronic equilibrium, high-temperature superconductivity, PrBa₂Cu₃O_{6,6}, conductivity.

1. Introduction

In earlier work [1] the properties of 3d configuration of La_{0,5}Ca_{0,54}MnO_{3+x} were considered and explained within the framework of a hypothesis of electronic-vibronic dynamic equilibrium.

In the proposed work the same hypothesis is extended to 4f configuration by consideration of compounds with Pr. As noticed, the decrease of distance between rare-earth and oxygen renders very strong influence on properties of a substance, moving it from an electronic state through a vibronic to a semiconductor-metal state. Thus, the compound can get in a so-called electronic-vibronic state of dynamic equilibrium. When the RE–O bond length appears to be less than 2 Å, the substance begins to show semiconductor properties moving to metallic ones under pressure. For the compounds in a semiconducting-metal state, for example PrBa₂Cu₃O_{6,6}, we shall try to explain the occurrence of high-temperature superconductivity, considering only the change of a kind of conductivity in the substance.

2. Three possible states of the electron system of a rare-earth compound

The properties of this system can be described in terms of three possible states.

2.1. Electronic state

The choice of this term stems from the term vibronic state. The spectra of the same rare-earth ion entering into the composition of various substances (or the same substance under different thermodynamic conditions) can differ strongly. The first group of spectra contains the spectra of rare-earth ethyl sulphates. They consist of faint narrow lines (Fig. 1,*b*). Some of the energy levels are degenerate. What is the cause of these specific features? The narrow lines correspond to the assumption of a near-adiabatic approximation, namely, fast electrons and a slow nucleus. This assumption leads to the only electronic state and, hence, to narrow lines.

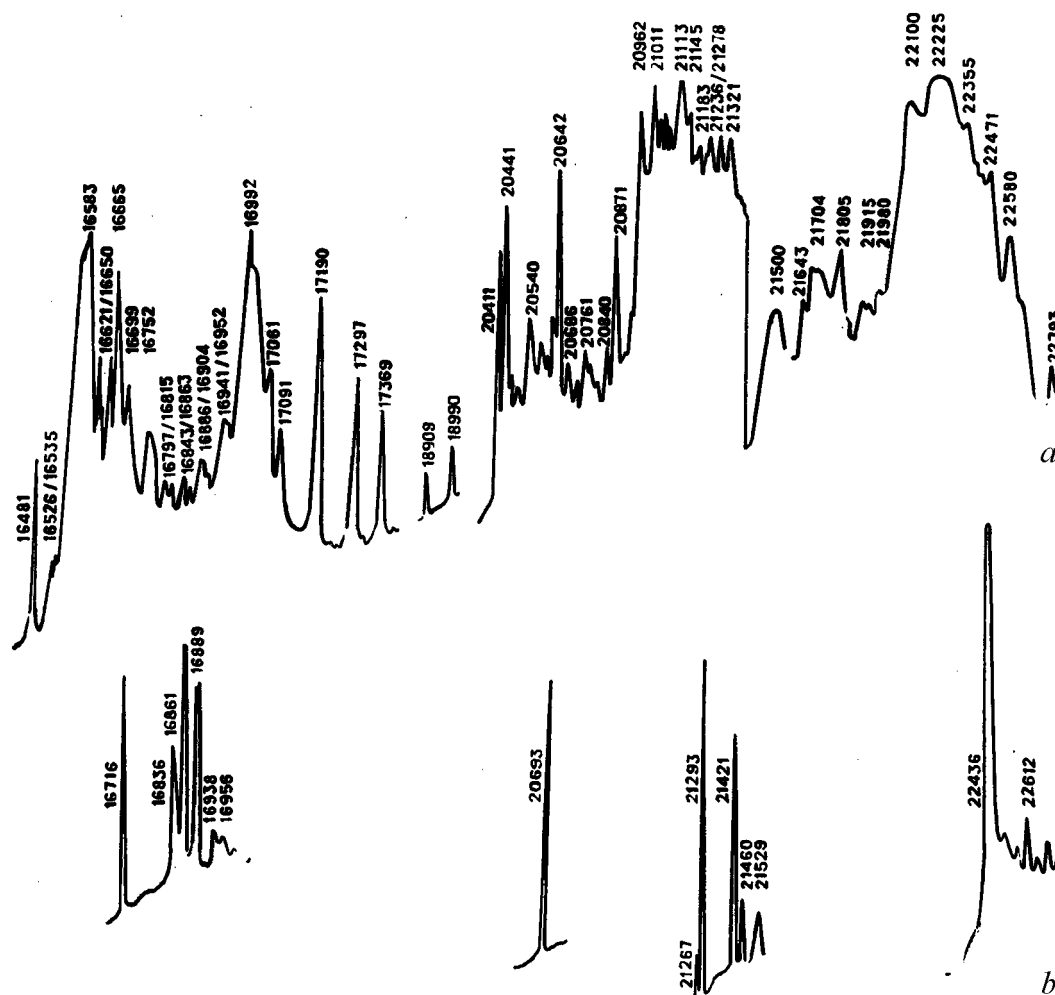


Fig. 1. Spectra of the vibronic state of cesium molybdate with praseodymium impurity (*a*) (room temperature, the Pr–O1 bond length is 2.38 Å and the Pr–O2 bond length is 2.54 Å) and of the electronic state of lanthanum ethyl sulphates with a praseodymium impurity (*b*) (the Pr–O1 bond length is 2.47 Å and the Pr–O2 bond length is 2.65 Å) recorded at atmospheric pressure for $T = 4.2$ K

The low intensities of these lines are explained by the fact that the $4f^n$ configuration is almost isolated [2]. Transitions between the levels of this configuration are forbidden as rigorously as these electrons are isolated from the environment. Finally, the degeneracy of the levels is also related to the isolation of this configuration. Jahn and Teller [3] noted that, when considering the Jahn-Teller effect, one should exclude the orbitally degenerate states where the electrons are not involved in the formation of a chemical bond in a molecule. Indeed, displacements of the nuclei in this case do not disturb these states. This is the case for inner electron shells in the paramagnetic ionic salts of rare-earth elements [3].

In the case of the electronic state, the spectrum (Fig. 1,*b*) can be easily interpreted (Table 1) [4–7] and the local magnetic moment can be readily calculated [7].

Table 1

Calculated spectrum of the $4f^2$ configuration in the electronic state

$LSJ \pm \mu$	$E, \text{ cm}^{-1}$
112 ± 1	22450.7
112 ± 2	22447.5
112 ± 0	22416.8
111 ± 0	21295.4
111 ± 1	21280.2
110 ± 0	20690.5
202 ± 1	16934.4
202 ± 2	16862.9
202 ± 0	16754.9

The energy of electrostatic interaction between two f electrons isolated from the environment can be described as

$$\langle LS | \frac{1}{r_{1,2}} | LS \rangle = \sum_k f_k(l, L) F^k, \quad k = 0, 2, 4, 6, \quad (1)$$

where the angular coefficient is

$$f_k(l, L) = (-1)^L \left[(2L+1) (-1)^{\frac{(2l+k)}{2}} \begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix} \right]^2 \begin{Bmatrix} l & l & L \\ l & l & k \end{Bmatrix}$$

and F^0, F^2, F^4 , and F^6 are radial Slater integrals.

In the case of spin-orbit interaction, the matrix element is equal to

$$\langle LSJ | H_{SO} | L'S'J \rangle = \chi(LS, L'S'J) \xi_{4f}, \quad (2)$$

where

$$\chi(LS, L'S'J) = (-1)^{L'+S+J} [l(l+1)(2l+1)]^{\frac{1}{2}} \langle LS || V^{11} || L'S' \rangle \begin{Bmatrix} L & S & J \\ S' & L' & 1 \end{Bmatrix}$$

and ξ_{4f} is a fitting parameter.

The interaction between $4f^2$ electrons and the crystal field is described by [5]

$$\begin{aligned} \langle SLJM | H_{cf} | S'L'J'M' \rangle &= \sum_k \sum_q B_k^q (-1)^{J-M} \begin{Bmatrix} J & k & L' \\ M & q & M' \end{Bmatrix} \times \\ &\times (-1)^{S'+L'+J+k} [(2J+1)(2J'+1)]^{\frac{1}{2}} \begin{Bmatrix} J & k & J' \\ L' & S & L \end{Bmatrix} \times \\ &\times (-1)^k [(-1)^L + (-1)^{L'}] [(2L+1)(2L'+1)]^{\frac{1}{2}} \begin{Bmatrix} L & k & L' \\ l & l & l \end{Bmatrix} (-1)^l (2l+1) \begin{Bmatrix} l & k & l \\ 0 & 0 & 0 \end{Bmatrix} \delta_{SS'}. \end{aligned}$$

As follows from the properties of the $3j$ and $6j$ symbols,

$$M + q + M' = 0,$$

$$k \geq 2J, k \geq 2L \text{ and } k \geq 2l.$$

The crystal-field parameters are

$$B_k^q = \left(\frac{2k+1}{4\pi} \right)^{\frac{1}{2}} \sum_i \frac{ee_i}{R^{k+1}} Y_k^q(\theta_i, \phi_i),$$

where subscripts k and q belong to the Legendry polynomials.

The magnetic moment of an isolated $4f^n$ configuration is calculated and compared with experimental data in [8]:

$$M = g \sqrt{J(J+1)},$$

where

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}.$$

2.2. Vibronic state

This term was proposed by the authors of the pioneering work [9]. This group of compounds contains rare-earth molybdates (Fig. 1,a). The spectra of these substances have strong broad lines, and all degeneracies are removed. The Kramer's doublets for odd n in a $4f^n$ configuration are exceptions. In this case, a rare-earth ion is assumed to be so close to the surrounding ions that the bonds between them are specified not by the long bond of outer electrons but rather by the short bond determined by the inner $4f^n$ configuration. A mixture of various electron configurations provides a high spectral intensity due to the absence of any forbiddenness. The participation of $4f^n$ electrons in crystal bonds provides the absence of any degenerate levels. The authors of [10,11] noted that any symmetrical position of nuclei (except for those located in one straight line) is unstable for a degenerate electronic state. As a result of this instability, nuclei shift so that the symmetry of their configuration breaks to an extent that the degeneracy of the term is completely removed. In particular, the normal electronic term of a symmetric (nonlinear) molecule is considered to be only a nondegenerate term [10,11]. In this case, small intervals in an electronic spectrum indicate slow

electronic motion with a velocity comparable to the nuclear motion velocity. So, the nuclear motion cannot be separated from the electronic motion [12].

As a result, every state of a set of nuclei continuously changing in certain limits corresponds to all changing electronic states and the spectrum has broad bands. In [13], we were the first to show that a high pressure can transform the electronic state of a rare-earth compound into its vibronic state (Fig. 2) [14]. These states stand rather far from each other, and the boundary between them is controlled by the bond length between a rare-earth ion and the surrounding ions (Table 2) [15].

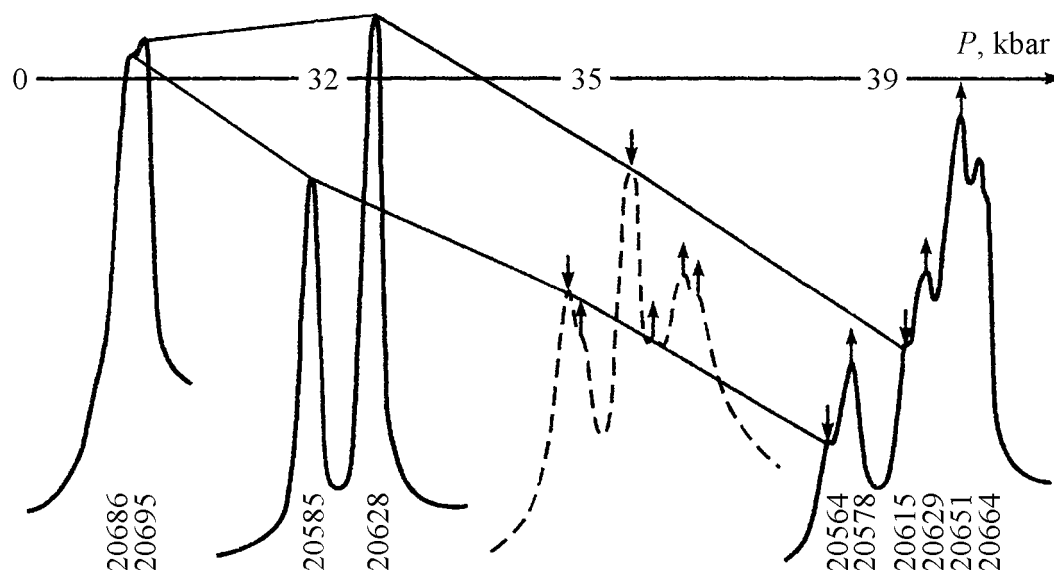


Fig. 2. Transformation of the spectrum of praseodymium ethyl sulphate at 78 K from the electronic type at atmospheric pressure into the vibronic type as the pressure increases to 39 kbar. With temperature gradual increase from 78 to 160 K at a pressure of 39 kbar, the vibronic state in this compound breaks and transforms into the electronic state [14]

Table 2

Critical distance (Å) for the transition from electronic-vibronic state for various rare-earth ions and ligands

RE	RE-O	RE-Cl	RE-F
Ce	2.40	2.81	2.33
Pr	2.38	2.79	2.31
Nd	2.36	2.77	2.29
Pm	2.34	2.75	2.27
Sm	2.33	2.74	2.26
Eu	2.32	2.73	2.25
Gd	2.31	2.72	2.24
Tb	2.30	2.71	2.23
Dy	2.29	2.70	2.22
Ho	2.28	2.69	2.21
Er	2.27	2.68	2.20
Tu	2.26	2.67	2.19
Yb	2.25	2.66	2.18

State of dynamic electronic-vibronic equilibrium. The hypothesis described above implies a jump-like transition from the electronic into the vibronic state. For praseodymium and oxygen, this occurs when the distance between them becomes smaller than 2.38 Å. However, the authors of [1,16,17] present experimental data that require a more complex concept. For example, the Pr–O distances in PrBa₂Cu₃O₇ determined by different methods are different. As determined by neutron diffraction, these distances are approximately 2.45 Å [18], whereas, as determined from the X-ray absorption fine structure (XAFS), some of these distances are still equal to 2.45 Å and the others are 2.27 Å [19]. The other structural relations determined by both methods remain the same. In other words, the differences concern only the position of the oxygen ion. It is important that the distance of 2.45 Å is larger and the distance of 2.27 Å is smaller than the critical distance.

When explaining these different praseodymium-oxygen distances in the YPrBa-CuO system, one has to take into account that the XAFS method can determine changes in a structure at a time resolution of 10⁻¹⁶ s, whereas a diffraction method can do so at a resolution of only 10⁻¹³ s. Therefore, the authors of [16,17] assumed that the praseodymium-oxygen distance changes from 2.27 to 2.63 Å and that the former method determines two limiting oxygen positions and the latter, the average position (2.45 Å). In other words, the lifetime of the short-lived state is shorter than 10⁻¹³ s (which is the time resolution of neutron diffraction) and is longer than 10⁻¹⁶ s (which is the time resolution of the XAFS method). Thus, there appears an intermediate stage, namely, the stage of dynamic electronic-vibronic equilibrium, where a substance alternately has the properties of the electronic and vibronic states. For example, a chemical bond is alternately long and short; the magnetic moment is alternately local or extended over the entire molecular complex; and the sample can alternately be either an insulator or a conductor. It is clear that this short-lived hard-to-detect state should substantially affect certain properties. For example, it was unclear for a long time why all (R)BaCuO compounds (R is a rare-earth element) having the same structure exhibit high-temperature superconductivity except for a praseodymium-containing compound. First, we would like to state that, for superconductivity to occur, the lifetime of this state must be longer than the lifetime of a Cooper pair. As shown in [16], the lifetime of an electronic-vibronic state in this case is shorter than the lifetime of a Cooper pair. Therefore, for superconductivity to be detected in such compounds, they must not form this short-lived electronic-vibronic state irrespective of the contribution (vibronic or electronic) determining this short time. These compounds should be transformed into the state of electronic-vibronic equilibrium with a sufficiently long lifetime, which will be possible if the distance between a rare-earth ion with a degenerate ground state and its neighbors decreases further. In this case, the lifetime of the vibronic state increases and the lifetime of the electronic state decreases.

As a result, the faint weak line spectrum should change into a strong broadband spectrum. As an example, we consider praseodymium ethyl sulphate. Its structure was studied comprehensively in [20] and is often used as a model for comparison.

Praseodymium is surrounded by nine neutral water molecules, which is one of the causes of a weak external influence on the state of the $4f$ configuration. Each three molecules lie in one plane and form equilateral triangles. In two small triangles the Pr–O distance is 2.47 Å and in the medium triangle and the large triangle the Pr–O distance is 2.65 Å. At 25 kbar, these distances decrease to 2.38 and 2.56 Å, respectively [14]. Fig. 2 shows the transformation of the narrow-band «electronic» spectrum of praseodymium ethyl sulphate 77 K into a broadband «vibronic» spectrum as the pressure increases from atmospheric to 39 kbar. These pressure-induced changes are removed upon heating to 160 K. At this temperature, an increase in the praseodymium-oxygen distance breaks the vibronic state and the spectrum recorded at a pressure of 39 kbar returns almost exactly to its shape recorded for 77 K at 32 kbar.

As noted, superconductivity in the PrBaCuO system is suppressed because of the formation of a short-lived electronic-vibronic state. This state appears upon a fluctuation-assisted transition from the electronic into the vibronic state, while the predominant long-lived state is the electronic state. In other words, the short lifetime of the electronic-vibronic state is specified by the lifetime of the vibronic contribution. Therefore, if this time increases (it should increase as the Pr-O distance decreases as compared to the critical distance), the lifetime of the electronic-vibronic state becomes longer than the lifetime of the Cooper pair at a certain time; as a result, a superconducting state appears. These considerations are supported by the experimental data from [21,22]. Let us analyze the lattice parameters c of the $\text{R}\text{Ba}_2\text{Cu}_3\text{O}_7$ (R is a rare-earth ion) superconducting compounds fabricated by a traditional method [18,23] (Fig. 3). The lattice parameters c of all compounds, except for a praseodymium-containing compound, are seen to lie in one curve, and the lattice parameter of the latter is well below them. This suggests

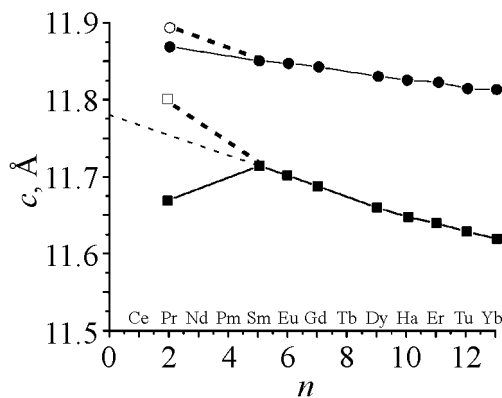


Fig. 3. Dependence of the lattice parameter c on the number of electrons n in f -shell for $\text{R}\text{Ba}_2\text{Cu}_3\text{O}_6$ (○, ●; R is a rare-earth ion) and $\text{R}\text{Ba}_2\text{Cu}_3\text{O}_7$ (□, ■). ●, ■ – the data for traditionally grown crystals [18]; ○, □ – the data for radiation-assisted growth of crystals with R = Pr [21,22]

that an increase in the lattice parameter c of the latter compound makes this compound superconducting. This result was achieved in [21,22], where this compound was synthesized by a new method: the parameter c increased, and the compound transformed into a superconducting state. The superconducting transition temperature T_c is 56 K, and the lattice parameter c is very large [23] and lies above its expected value in the general curve. It is reasonable to apply a high pressure to decrease this parameter, and the authors of [21,22] realized this idea. As the pressure grows to 93 kbar, T_c increases to 105 K. At a higher pressure, c is likely to become smaller than the optimum value and T_c begins to decrease.

Here, we do not consider any mechanism. Therefore, we return to the hypothesis of electronic-vibronic equilibrium, whose lifetime is shorter than the lifetime of the Cooper pair because of the short lifetime of the vibronic state. As the pressure increases, the life-time of the electronic state will decrease and the lifetime of the vibronic state will increase; so the lifetimes of both states will be longer than the Cooper-pair lifetime. Thus, the compound will transform into a superconducting state. As the pressure increases, the relation between the lifetimes continuously approaches an optimum relation. In this case, T_c will increase. However, there should be a time when this temperature begins to decrease due to a decrease in the electronic-state lifetime. As the pressure increases further, superconductivity should disappear.

2.3. Semiconductor-metal state

Received in 1998 experimental data on the temperature dependence of electrical resistivity [21,22] show that under pressure the properties of $\text{PrBa}_2\text{Cu}_3\text{O}_{6.6}$ vary from semiconductor to metallic.

Let's assume that the compound, in which the R–O bond length (R is a rare-earth ion) is less than 2 \AA , is in a specific semiconductor-metallic state. We introduce the concept of semiconducting and metal conductivities:

$$\begin{aligned} \sigma_1(T) &= \frac{1-n}{\rho_0 + \alpha T}, \\ \sigma_2(T) &= \frac{n}{(\rho_0 + \alpha T) \exp\left(\frac{\Delta E}{2kT}\right)}, \end{aligned} \quad (3)$$

here the parameter n is the portion of semiconductor conductivity in the material, ρ_0 is the residual resistivity, α is a temperature coefficient, and ΔE is the width of the energy gap. The parameter n can vary from 0 to 1. For $n = 0$, $\sigma_2(T) = 0$, and the material possesses only metallic conductivity; when $n = 1$, $\sigma_1(T) = 0$, and the material has only semiconductor conductivity. The metallic contribution is predominant at a high temperature, and the semiconducting contribution – at a low temperature.

From the analysis of the metallic and semiconductor properties of the compounds containing rare-earth ions, a fundamental trait of high-temperature superconductors is revealed: at a certain temperature T , the values of $\sigma_1(T)$ and $\sigma_2(T)$ are equal, i.e., their curves cross [23]. Semiconductor conductivity dominates at high temperatures, while metallic conductivity dominates at low ones. A special resonant interaction of these conductivities occurs in this case, with which the material's conductivity can be formally represented as the sum of these values.

In view of this, the experimental temperature dependence of the resistance, $\rho_{\text{exp}}(T)$, can be described by the expression:

$$\rho(T) = \frac{1}{\sigma_1(T) + \sigma_2(T)} = \frac{\rho_0 + \alpha T}{(1-n) + n \exp\left(\frac{-\Delta E}{2kT}\right)}. \quad (4)$$

The values of the adjustable coefficients ρ_0 , ρ , n , and $\Delta E/2k$ were calculated by trial and error with a software program, on the assumption that with a specific set of these coefficients, the value provided by equation (4) coincides, to an accuracy, with the experimental value of $\rho_{\text{exp}}(T)$ [21] at the corresponding temperature.

After analyzing the data obtained, we selected the coefficients with which equation (4) fairly accurately describes the experimental curve at $P = 0$ as far as T_c : $n = 0.942$, $\rho_0 = 0.0078 \text{ m}\Omega\cdot\text{cm}$, $\alpha = 0.00057 \text{ m}\Omega\cdot\text{cm}/\text{K}$, and $\Delta E/2k = 270 \text{ K}$ [23]. However, below T_c the theoretical curve drops smoothly to 0 without displaying a transition to a superconducting state (Fig. 4).

If graphs of $\sigma_1(T)$ and $\sigma_2(T)$ (Fig. 5,*a*), calculated using the already selected coefficients, are constructed according to (3), we find that they intersect at T which does not coincide with T_c in the experiment. However, if $\sigma_2(T)$ is multiplied and $\sigma_1(T)$ is divided by the same factor, so that n remains in the region of the change, then the point of their intersection shifts. Thus, at $P = 0$ with $0.364\sigma_1(T)$ and $2.75\sigma_2(T)$ we get an intersection of the curves at $T_c = 56 \text{ K}$ (Fig. 5,*b*), that corresponds to the experimental results. The amendments for $\sigma_1(T)$ and $\sigma_2(T)$ are calculated similarly, they correspond to experimental curve under pressure [21,22]. The calculation has shown that these amendments decrease with increase of pressure and at about 9 GPa become equal to unity (Table 3).

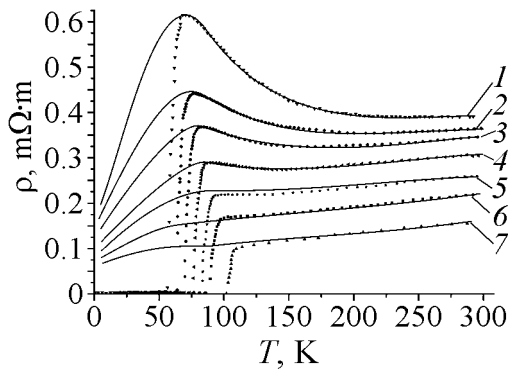


Fig. 4. Temperature dependences of the electrical resistivity of $\text{PrBa}_2\text{Cu}_3\text{O}_{6.6}$ at various pressures (1 – $P = 0$, 2 – 1.2, 3 – 2.0, 4 – 3.0, 5 – 4.0, 6 – 6.0, 7 – 9.3 GPa). Solid lines were calculated under the assumption of suppressed superconductivity [23], and points demonstrate the experimental results [21,22]

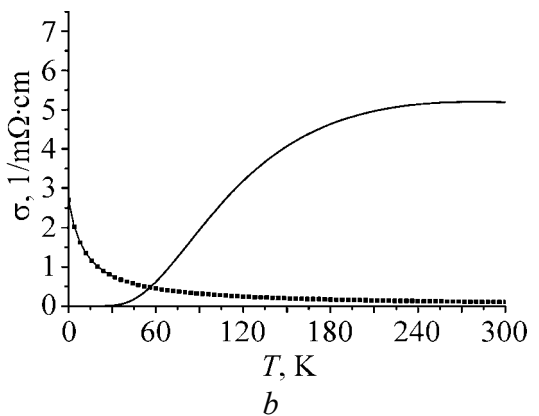
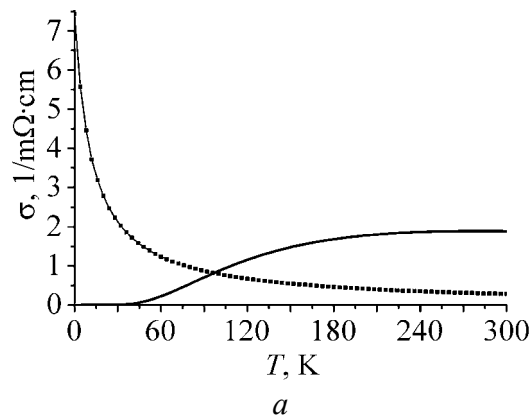


Fig. 5. Temperature dependences of metallic $\sigma_1(T)$ (—■—) and semiconductor $\sigma_2(T)$ (—) conductivities for $P = 0$ without correction (*a*) and with correction $0.364\sigma_1(T)$ for metallic and $2.75\sigma_2(T)$ for semiconductor conductivities (*b*)

Table 3

The amendments for $\sigma_1(T)$ and $\sigma_2(T)$, that shift the point of intersection of these conductivities, under pressure [21,22]

P , GPa	Amendment of $\sigma_1(T)$	Amendment of $\sigma_2(T)$
1.0	2.75	0.364
1.2	2.12	0.472
2.0	1.82	0.550
3.0	1.55	0.645
4.0	1.39	0.719
6.0	1.16	0.867
9.3	1.08	0.926

At the intersection, $\sigma_1(T)$ and $\sigma_2(T)$ are equal. This means that, at this point, the $\text{PrBa}_2\text{Cu}_3\text{O}_{6.6}$ crystal displays properties of both a semiconductor and a metal. The transition to a superconducting state occurs when the metallic conductivity $\sigma_1(T)$ suppresses the semiconductor conductivity $\sigma_2(T)$. Then, taking into account the conditions for transition to a superconducting state, equation (4) with the correction for the conductivities can be written as follows:

$$\rho(T) = \frac{1}{0.364\sigma_1 + 2.75\sigma_2} - \frac{1}{0.364\sigma_1 - 2.75\sigma_2}. \quad (5)$$

Fig. 6 shows a graph of $\rho(T)$ obtained using equation (5), which agrees with the experimental curve at $P = 0$ [21,22].

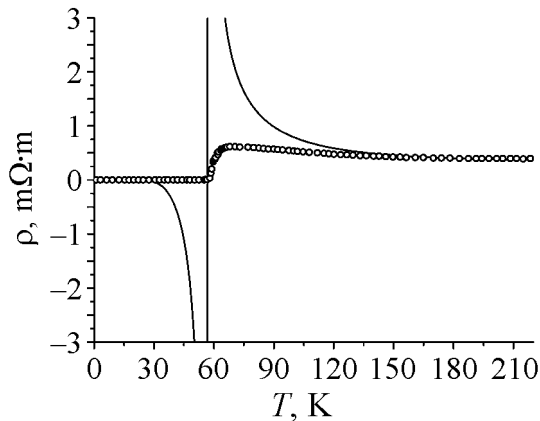


Fig. 6. Temperature dependence of electrical resistance with the transition to a superconducting state for $P = 0$: — — $\rho_{\text{theor}}(T)$ (Eq. (5)), -○- $\rho_{\text{exp}}(T)$

For $\rho(T)$ under pressure we have also a good agreement with the experiment [21,22].

3. Conclusion

We have shown that, as the pressure increases, a rare-earth compound transforms from the electronic into an electronic-vibronic state and undergoes substantial changes. For example, its spectrum changes from a faint narrow-line spectrum into a strong broadband spectrum. At the further decrease of the R–O bond length the substance is in a semiconductor-metallic state. Therefore, for $\text{PrBa}_2\text{Cu}_3\text{O}_{6.6}$ the

result of this study is a combination of values for the conductivities $0.364\sigma_1(T)$ and $2.75\sigma_2(T)$ (and only these conductivities), that describes the whole set of experimental values obtained, including the superconducting transition. Consequently, the material's transition to a superconducting state can be associated with a change in the ratio of conductivities in the crystal, which can be considered analogous to the occurrence of Cooper pairs in a low-temperature superconductor.

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ПЕРИОДИЧНІ ЗМІНЕННЯ В СТАНІ 4f-МЕТАЛІЧНОЇ СПОЛУКИ ПІД ТИСКОМ

Обґрунтовується твердження, що в рамках тиску, який можна експериментально досягти, існуючі з'єднання, що містять рідкісні землі, можуть бути охарактеризовані належністю до одного з трьох станів залежно від відстані RE–O: електронного, вібронного (зокрема, стан електрон-вібронної рівноваги) та напівпровідниково-металічного. Висувається гіпотеза, що механізм реалізації надпровідного стану в $\text{PrBa}_2\text{Cu}_3\text{O}_{6.6}$ можна розглядати як зміну співвідношення напівпровідникової та металічної провідностей у речовині.

Ключові слова: електрон-вібронна рівновага, високотемпературна надпровідність, $\text{PrBa}_2\text{Cu}_3\text{O}_{6.6}$, провідність

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ПЕРИОДИЧЕСКИЕ ИЗМЕНЕНИЯ В СОСТОЯНИИ 4f-МЕТАЛЛИЧЕСКОГО СОЕДИНЕНИЯ ПОД ДАВЛЕНИЕМ

Обосновывается утверждение, что в рамках экспериментально достижимого давления существующие соединения, содержащие редкие земли, могут быть охарактеризованы принадлежностью к одному из трех состояний в зависимости от расстояния RE–O: электронному, вибронному (в частности, состоянию электрон-вибронного равновесия) и полупроводниково-металлическому. Выдвигается гипотеза, что механизм реализации сверхпроводящего состояния в $\text{PrBa}_2\text{Cu}_3\text{O}_{6.6}$ можно рассматривать как изменение соотношения полупроводниковой и металлической проводимостей в веществе.

Ключевые слова: электрон-вибронное равновесие, высокотемпературная сверхпроводимость, $\text{PrBa}_2\text{Cu}_3\text{O}_{6.6}$, проводимость