

PACS: 74. 72. –h  
UDC: 538.945

## The crystal-chemical structure and "high-temperature" superconductivity (HTSC) of multi-component metal–oxide compounds

Yu.I. Boyko<sup>1</sup>, V.V. Bogdanov<sup>1</sup>, R.V. Vovk<sup>1</sup>

*1 V. Karazin Kharkov National University, 4 Svobody Sq., 61022 Kharkiv, Ukraine,*

ORCID: 0000-0003-2634-3549

DOI: 10.26565/2222-5617-2018-28-07

An analysis of the crystal structure of high-temperature superconductors of the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  type is provided and the reasons for the formation of specific chemical bonds between different ions leading to the formation of negative U-centers clusters in this compound is discussed. Experimental facts are also discussed, which indicate a close relationship between the crystal-chemical structure of metal-oxide compounds and their anomalous electric conductivity.

On the basis of the analysis, the conditions for the selection of elements for the synthesis of compounds characterized by a higher temperature of transition to the superconducting state are formulated.

**Keywords:** high-temperature superconductors, structure, negative U-centers.

В роботі проведено аналіз кристалічної структури високотемпературних надпровідників типу  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  і обговорені причини формування специфічних хімічних зв'язків між різними іонами, що призводять до утворення кластерів з негативних U-центрів в цієї сполуці. Обговорено також експериментальні факти, що свідчать про тісний взаємозв'язок кристалохімічної структури метал–оксидних сполук з їхньою аномальною електричною провідністю.

На підставі проведеного аналізу сформульовані умови вибору елементів для синтезу сполук, що характеризуються більш високою температурою переходу до надпровідного стану.

**Ключові слова:** високотемпературні надпровідники, структура, негативні U-центри.

*We dedicate our work to the memory of the outstanding scientist and teacher Yakov Yevseevich Geguzin in connection with the 100th anniversary of his birth. The authors remember with great warmth the years of close cooperation with Ya. E., note his great enthusiasm, benevolence, and also thank for the many tips that contributed to the emergence of new ideas and publications, including this article.*

### Introduction

The discovery in 1986–1987 of the "high-temperature" superconductivity (HTSC) of multi-component metal-oxide compounds (anomalous electrical conductivity in the range of temperatures exceeding the boiling point of liquid nitrogen 77 K) aroused great interest in the study of the properties of this class of materials [1, 2]. These materials include a number of compounds which can be described by the general chemical formula,  $\text{RBA}_2\text{Cu}_3\text{O}_{7-x}$ , where  $\text{R} = \text{Y}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Dy}, \text{Ho}, \text{Tm}, \text{Yb}, \text{Lu}$ . Among them the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  compound was most thoroughly and comprehensively studied. The temperature of transition to the superconducting state of this compound is  $T_c \approx 90 \text{ K}$ , which is an order of magnitude higher than the  $T_c$  of metallic superconductors. In addition to the above-mentioned compounds, the group of metal-oxide high-temperature superconductors also includes compounds  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10-x}$  and  $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10-x}$ , characterized by the maximum transition temperature observed up to the present time:  $T_c = 110$  и  $125 \text{ K}$  respectively.

The most important task of researches which are carried out after discovery of high-temperature superconductors, is searching for new compounds which have a superconductivity at even higher temperatures, up to room ones ( $\approx 300 \text{ K}$ ). However, to date, this problem has not been solved, and the main cause of failure of many attempts to obtain such a compound, is the lack of understanding of the mechanism of unique microscopic electric conduction of HTSC oxides. An attempt to explain this phenomenon using the BCS theory ("Phonon" pairing of electrons, which causes low-temperature superconductivity of simple metals and their alloys [3]), was unacceptable. This conclusion was made after publication of the so-called "isotope effect" study results [4]. In this study in the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  compound 75% of  $^{16}\text{O}$  oxygen ions were replaced by  $^{17}\text{O}$  ions of the "heavy" oxygen isotope. Such a substitution significantly affected the phonon spectrum of the crystal, however, it did not lead to a noticeable change in the transition temperature  $T_c$ . In this case, a detailed study of the nature of elementary charge carriers in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  showed that

superconductivity in this compound is realized by paired electrons, as in the case of "low-temperature" superconductivity of metals.

Thus, the physical nature of the mechanism that determines the pairing of electrons, as well as the reason for the stability of these pairs up to a temperature of  $\approx 100$  K, remain unconfirmed until now. A large number of different models were proposed to answer the above questions. In particular, the possible role of electronic excitations was discussed: plasmons, excitons, spin fluctuations etc. in the process of formation of coupled charge carriers [5, 6]. In addition, the possibility of electron pairing was also associated with formation of specific structures – the so-called "superlattices", characterized by a parameter that is much higher than the lattice parameters of the main substance [7, 8]. However, none of the above models was confirmed by an adequate experiment, which clearly demonstrates in its favor.

In this respect, the most reasonable and consistent with a large number of experimental evidence is a concept proposed by the authors [9, 10]. According to the idea developed in these papers, the pairing of electrons in high-temperature superconductors is due to the formation in them of special elements of the structure – clusters consisting of a set of "negative U-centers". Upon reaching a certain size and number of clusters a special energy spectrum of electrons is formed, allowing two-electron transitions from oxygen ions to neighboring pairs of copper ions, which ultimately determines the superconductivity of metal-oxide compounds.

In the work we propose, using the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  compound as an example, we analyze the crystal structure and discuss the reasons for the formation of specific chemical bonds between different ions, leading to the formation of negative U-centers clusters in this substance. Experimental facts are also discussed, which indicate a close relationship between the crystal-chemical structure of metal-oxide compounds and their anomalous electric conductivity.

The results of this work can be used in further studies to find ways of obtaining new compounds, having electrical superconductivity at temperatures much higher than the boiling point of liquid nitrogen, up to room temperature.

#### **Analysis of crystal-chemical structure of metal-oxide compounds on the example of compound**

##### **$\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$**

From the position of crystal-chemistry multi-component metallic oxide  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  belong to complex isodesmic substances with an ion-covalent bond type [11]. In this compound the oxygen ion O (anion)

forms chemical bonds with three different metal ions – Y, Ba, Cu (cations). A peculiarity of the structures of this type is the following: while the metal ions are necessarily only bound to oxygen, each oxygen ion is bound to three different cations.

To achieve a stable (thermodynamically equilibrium) structure of this compound, the electric charge of the anion must be locally neutralized. To fulfill this condition, it is necessary that the sum of the electrostatic valencies of the individual anion bonds with all cations should be equal to the value of its negative charge. In turn, the electrostatic valence of each cation is determined by its charge, reduced by a factor of  $n$ , where  $n$  is the coordination number (the number of ions surrounding the cation). In accordance with this, when forming an isodesmic structure, the number of ions around each cation should always exceed its individual valence. The presence of three different cations and of one anion in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  and the requirement of the stability of this compound cause the formation of a specific "perovskite-like" crystal structure defective in oxygen [11]. In this case, the actual value of the charges of all ions and their exact distribution in the forming crystal lattice is a secondary factor. The requirement of fulfilling the electrical neutrality condition of the compound leads to the situation that some of ions can change their valency, and some of them may be absent, breaking the stoichiometry of the compound, however, while maintaining the necessary correspondence between the electric charges.

The specified features of the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  crystal-chemical structure formation leads to the fact that its crystal lattice in the absence of a deficit in oxygen, i.e. with the value of the parameter  $x \approx 0$ , is characterized by a specific mutual arrangement of ions, which from the point of view of crystallography is described by an orthorhombic unit cell (Fig. 1a). A distinctive feature of this cell is that it is layered and contains two configurations of the oxygen surroundings by copper ions: tetrahedral pyramid in planes  $\text{CuO}_2$  and a rhombus in the form of chains  $\text{CuO}$  in the basal plane (ab) [12]. In this case, the Cu ions in the basal plane neighbor with the O ions only along the axis (b), and along the (a) axis in this plane there are no O ions at all, which in turn determines the orthorhombic symmetry of the forming elementary crystal cell. The Cu ions located along the (c) axis in the space between the planes of the Ba and Y ions are surrounded by five O ions, forming the planes  $\text{CuO}_2$ .

With decrease in the oxygen content, i. e. with increase in the parameter  $x > 0$ , oxygen vacancies arise mainly in the basal plane, since the  $\text{CuO}$  chains are characterized by the minimum energy of the chemical

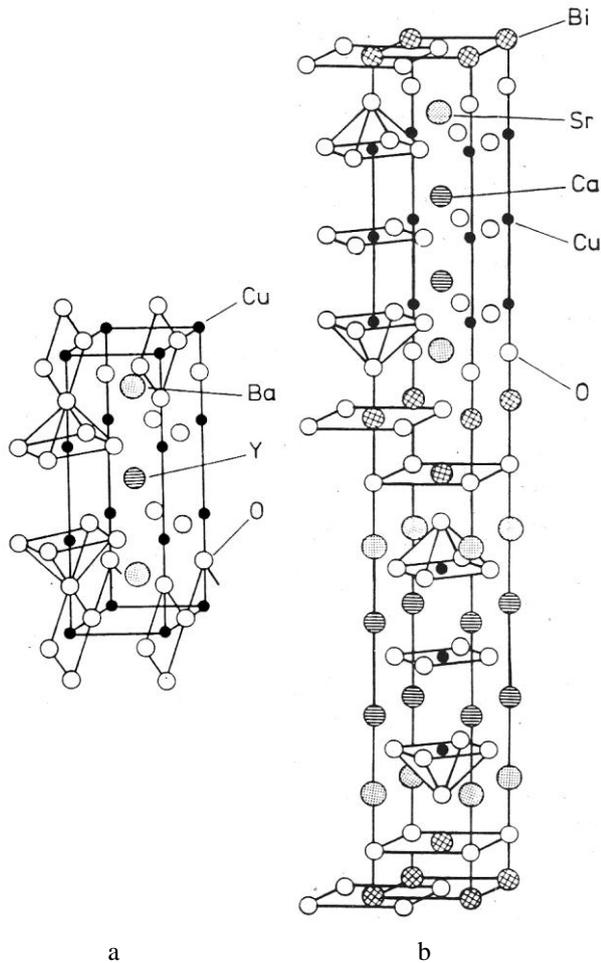


Fig. 1. Crystal structures of elementary cells of HTSC metal-oxide compounds: a)  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , b)  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ .

bond. When the value of  $x \approx 0,5$  is reached, the O ions and oxygen vacancies approximately in the same proportion are distributed along the axes (a) and (b) in the (ab) plane, and at  $x \approx 1$  the basal plane remains without O ions at all, which leads to the transformation of orthorhombic lattice into tetragonal one. The formation of such a specific crystal-chemical structure, the presence of different configurations of Cu and O ions, as well as the phase transformation in the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  compound are experimentally confirmed in many works and, in particular, in the works [13, 14].

It should be noted that the crystal-chemical state and electrical conductivity of this substance are closely interrelated and depend significantly on the concentration of oxygen ions in it, that is, on the value of the parameter  $x$ . With a large deficit of oxygen ions ( $x > 0,5$ ), when the tetragonal crystal structure is realized, the superconductivity does not occur. As the oxygen concentration increases and when the value of the parameter  $x \approx 0,4$  the phase transformation is observed: the tetragonal crystal cell turns into orthorhombic one.

Simultaneously with the phase transformation in the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  compound the superconductivity is appears at temperature  $T_c \approx 50$  K, and when  $x \approx 0$  the superconducting state is realized at the maximum value of the transition temperature for this compound  $T_c \approx 90$  K (see Fig. 2).

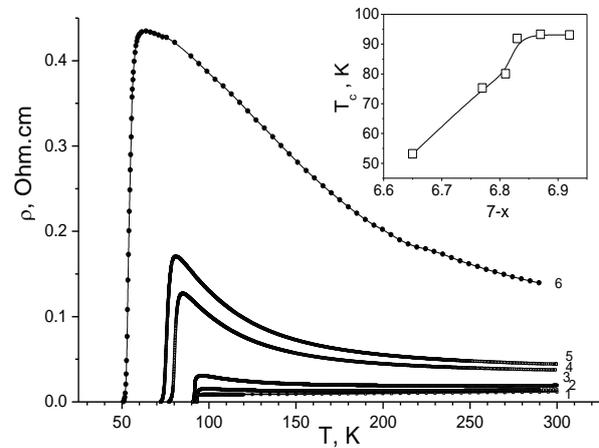


Fig. 2. The dependence of electric resistance of the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  compound on temperature with variation of the parameter  $x$ : 1 – 0,08; 2 – 0,13; 3 – 0,17; 4 – 0,2; 5 – 0,23; 6 – 0,35 [16]. The inset shows the dependence of the transition temperature  $T_c$  on the parameter  $x$ . The same type of dependencies were obtained in [17].

Thus, based on the above analysis, it can be concluded that it is the specific crystal-chemical structure that is the determining factor which causes the anomalous electrical conductivity of the poly-component metal-oxide compounds. More concretely this correlation is discussed in the next section of the paper.

### Crystal-chemical structure of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ compound and the appearance of paired carriers of electric charge

As it already mentioned, according to the concept proposed in the works [8, 9], the main elements of the structure responsible for the generation of electron pairs,

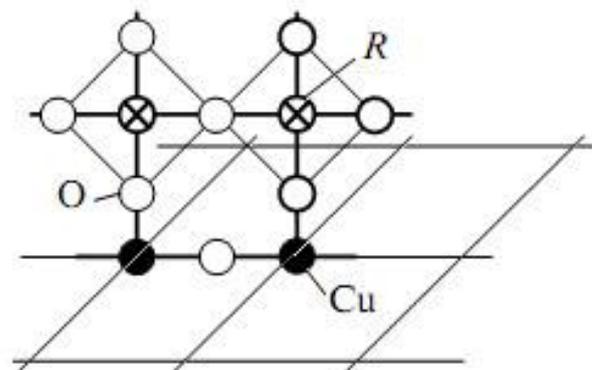


Fig. 3. The scheme of the negative U-center in the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  compound [10].

which cause the anomalous conductivity of metal-oxide compounds, are the clusters formed from negative U-centers. Each separate U-center consists of two neighboring Cu cations embedded in the  $\text{CuO}_2$  plane and of their surrounding O ions (Fig. 3).

The existence of such a configuration of Cu and O ions in the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  compound was confirmed in the works [13,14]. In these studies by the X-ray spectroscopy and by the internal friction methods was found that copper and oxygen ions take part in the formation of specific chemical bonds characterized by different ion valencies. This result provides the additional evidence of the negative U-centers formation in the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  compound.

The U-centers clusters formation causes the appearance in the electrons energy spectrum of a level that allows a local pair transition from an oxygen ion to two neighboring copper ions (Fig. 4) [9]. In this case, separate (not connected to clusters) U-centers cause some "excess" insignificant electric conductivity at temperature  $T^* \gg T_c$  (this is a so-called fluctuation superconductivity). The deviation from the "normal" conductivity at the temperature  $T^*$  is a "messenger" of the transition to the superconducting state, and the temperature  $T^*$  was called the temperature of opening of the "pseudo-gap". In fact, at this temperature the first pair charge carriers appear.

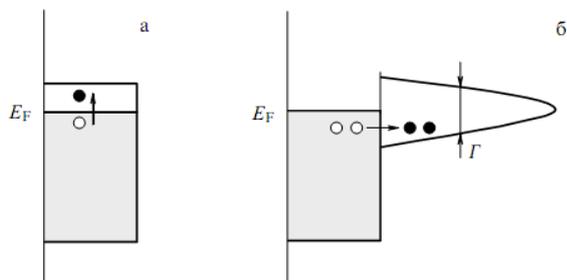


Fig. 4. The scheme of the band structure of the energy spectrum of a) ordinary metal, b) HTSC metal-oxide compound [10]. • – electron; ○ – hole;  $\Gamma$  – the width of the energy level for a pair of electrons

The minimum cluster size that determines the possibility of the pair transition of electrons is determined by the coherence length in the  $\text{CuO}_2$  plane and equal  $\approx 10 \text{ \AA}$ . As the concentration of oxygen ions in the metal-oxide increases, that is when  $x \rightarrow 0$ , the average size of the clusters increases, and the temperature  $T^*$  gradually go up (Fig. 5) [9].

An important experimental fact, which also give evidence to the favor of the above scheme, is the result of the work [15], in which the process of size increasing of U-centers clusters was activated (accelerated) by applying of external hydrostatic pressure  $p \approx 7 \text{ GPa}$ . As it was shown in this study, in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  compound samples

with not complete stoichiometry ( $x \approx 0,4$ ) the pressure intensifies the process of cluster size growth due to their (clusters) diffusion coalescence. The coalescence process is realized as a result of the redistribution of oxygen ions and of decrease in the vacancy concentration in the anion sublattice, which is accompanied by decrease in the parameter  $x \rightarrow 0$ . In accordance with the above described scheme, this process should be accompanied by increase of temperature  $T_c$ , approaching it to the maximum value  $\approx 90 \text{ K}$ , as it was observed in the experiment.

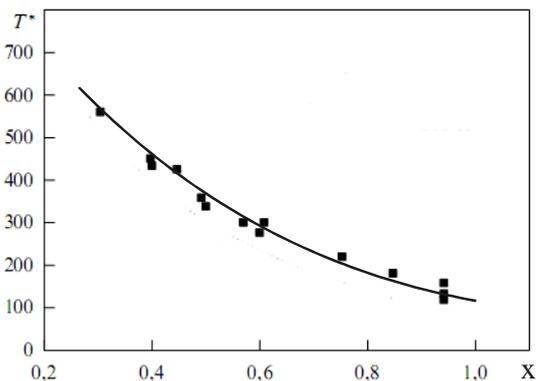


Fig. 5. The dependence of the "pseudogap" opening temperature  $T^*$  in the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  compound on the parameter  $x$  [10].

In addition to the above information, attention should be paid to the following important fact. As mentioned, the  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10-x}$  and the  $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10-x}$  compounds also refer to metal-oxide superconducting substances. They are characterized by the maximum superconducting transition temperatures recorded to date:  $T_c \approx 110$  and  $\approx 125 \text{ K}$  respectively. As the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  compound these oxides are also characterized by the rhombic crystalline cell and by the presence of several "perovskite-like" structural blocks containing planes  $\text{CuO}_2$  (Fig. 1b). Besides, these compounds do not have  $\text{CuO}$  chains in the basal planes (ab), however, in their structure there are solitary copper-oxygen planes of  $\text{CuO}$  separated by Ca planes. This fact once again demonstrates the important role of the crystal structure in formation of pairs of charge carriers in the metal-oxide superconductors: the  $\text{CuO}_2$  planes provide the formation of the negative U-centers which cause the appearance of the paired charge carriers. The presence of  $\text{CuO}$  planes provides anomalous conductivity by the paired electrons in all compounds discussed. At the same time it is the "sandwiching" of solitary  $\text{CuO}$  planes by the planes formed by additionally introducing ions (in this case of "bismuth-thallium" oxides by planes of Ca), increases to a certain limit the value of the superconducting transition temperature. Consequently, an increase in the number of solitary  $\text{CuO}$  planes with metallic conductivity is the

important factor for multi-component metal-oxide "high-temperature" superconductors, which promote in increasing  $T_c$ . The role of the other ions is actually reduced to maintain the required crystal structure.

### Conclusions

Summarizing the above considerations, we can make the following conclusion.

There are no fundamental limitations on increase of the transition temperature  $T_c$  into the superconducting state when using multi-component metal-oxide "high-temperature" superconductors.

When choosing elements of a substance characterized by a higher temperature of transition to the superconducting state, it is necessary to have in mind the realization of the following conditions:

1) the material should have a crystal-isodesmic complex structure, characterized by the orthorhombic unit cell, containing as component elements perovskite-like blocks separated by planes that do not contain oxygen ions;

2) as the ions forming perovskite-like structural unit, in addition to the oxygen ion, it is necessary to use a metal ion which, on the one hand, should be characterized by a "normal" (metallic) electric conductivity, and on the other hand, it must actively react with oxygen and form chemical bonds of various configurations, that is, capable to change its valence state;

3) the metal ions specified in paragraph 2, together with oxygen ions, besides participation in the formation of blocks with a perovskite-like structure, must form either the basal planes (ab) or the solitary "conducting" planes parallel to the basal planes;

4) increase in the number of planes with metallic conductivity when additional ions (cations) are introduced along the axis (c) of the unit cell, promotes in increase the superconducting transition temperature  $T_c$ ;

5) the metal-oxide compound having a "high-temperature" superconductivity with the maximum possible transition temperature  $T_c$  should be characterized by complete stoichiometry in oxygen.

### References

1. J. G. Bednorz, K. A. Mueller, Z. Phys., B64, p. 189, 1986.
2. M. K. Wu, J. R. Ashburn and all, Phys. Rev. Lett., v. 57, p. 908, 1987.
3. J. Bardeen, L. N. Cooper, J. R. Schrieffer, Phys. Rev., v. 108, p. 1175, 1957.
4. B. Batlog, R. G. Cava and all, Phys. Rev. Lett., v. 58 p. 2333, 1987.
5. V. L. Ginzburg, E. G. Maksimov, Phys C, v. 235 – 240, p.193, 1994.
6. M. L. Cohen, S. A. Wolf, V. Z. Kresin, Novel Superconductivity, Plenum Press, London, p. 1095, 1987.

7. O. V. Abramov, O. M. Gradov, A. Yu. Kyrie, Physica Scripta, v. 46, p. 76, 1992.
8. O. V. Abramov, O. M. Gradov, A. Yu. Kyrie, Physica Scripta, v. 48, p. 620, 1993/
9. K. V. Mitsen. O. M. Ivanenko. ZhETF. t. 118. s. 666. 2000.
10. K. V. Mitsen. O. M. Ivanenko. UFN. T. 1744. № 5. s. 545. 2004.
11. R. Evans. Vvedeniye v kristalokhimiyyu. 1948. s. 367.
12. K. Yvon, M. Francois, Z. Phys., v. 76, p. 413, 1989.
13. M. Weller, H. Jaeger, G. Kaiser, K. Schulze, Phys. C, v. 162, p. 953, 1989.
14. H. Jaeger, S. Hofman, G. Kaiser, G. Petzow, Phys. C, v.153, p. 133, 1988.
15. Yu. I. Boyko, V. V. Bogdanov, R. V. Vovk, G. Ya. Khadzhai, S. V. Savich, Low Temperature Physic, v. 44, № 1, p. 63, 2018.
16. R.V.Vovk. M.O.Obolenskiy. A.A.Zavgorodniy. O.V.Bondarenko. M.G.Revyakina. N.N.Chebotaev. Visnik Kharkivskogo universitetu. seriya fizichna. vip. 3 (31). № 744. 2006. s. 94-96.
17. G. Fuchs, A. Gladun and all, Journ. of the Less – Common Metals, v. 151, p.103, 1989.