

## **SUPERCONDUCTING PROPERTIES OF NEGATIVE-U CENTERS MATERIALS: CHALCOGENIDES, CUPRATE OXIDES AND FULLERIDES**

K. D. Tsendin\*

A. F. Ioffe Physico-Technical Institute, Russian Academy of Sciences, 194021,  
Saint-Petersburg, Russia

If the concentration of negative-U centers is enough to create the pair band states, this can lead to superconductivity (negative-U centers model of superconductivity) because Anderson pairs are Bose particles. In the present paper it has been shown that several puzzling superconductivity properties of chalcogenides, high-temperature cuprate superconductors and fullerides are similar for these three groups of materials and can be naturally explained in the frame of negative-U centers model of superconductivity - NUCS model.

(Received May 11, 2005; Accepted July 21, 2005)

*Keywords:* Chalcogenides, High-temperature superconductors, Fullerides, Superconductivity

### **1. Introduction**

Today there are several groups of superconductors for which the nature of superconductivity is unknown. Among them of chalcogenide glassy semiconductors (CGS), high temperature oxide superconductors (HTSC), and fullerides. One of the most interesting applications of negative-U centers conception is superconductivity. In the present work we show very close similarities between some normal and superconducting properties of CGS, HTSC, and fullerides and then consider that this similarities arise exactly because of negative-U centers existing in these materials. The most appeal feature of applying the negative-U centers concept is that it explains both normal and superconducting properties of these various materials from the one point of view. The paper is organized as following: After a brief observation of experimental data on normal and superconducting properties of CGS, HTSC, and fullerides we shortly describe the NUCS model and recent development of the model for applying for CGS, HTSC and fullerides.

### **2. Chalcogenide glassy semiconductors**

Superconductivity has been observed in  $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$  [2],  $\text{Ge}_2\text{Se}_3$  [3] and  $\text{As}_2\text{Te}_3$  [1,4]. In Fig. 1 the dependencies of  $T_c$  and  $2E_a$  on pressure  $p$  have been shown for  $\text{As}_2\text{Te}_3$  [4].  $E_a$  is the energy activation of conductivity:  $\sigma = \sigma_0 \exp(-E_a/kT)$ .

The most interesting features of Fig. 1 data are the following two. Firstly the transitions are not "normal metal state-superconducting state" transitions but "semiconductor state-superconducting state" transitions, which occurs between 65-85 kbar. One can see that superconducting state arises from state with not zero gap, for example  $E_g = 2E_a = 0.07$  eV and  $T_c = 0.75$  K for  $p = 70$  kbar. The optical forbidden gap  $E_g$  approximately equals to  $2E_a$  [1], then in this paper the conclusion has been made that up to the highest pressure the Fermi level in semiconductor state lies at the middle of forbidden gap. The second fact is the very strong pressure dependence of  $T_c$  with large positive

---

\* Corresponding author: tsendin@mail.ioffe.ru

derivative  $dT_c/dp$ . These peculiarities have evidenced that it is very difficult to apply the classical BCS theory for explanation of CGS superconductivity.

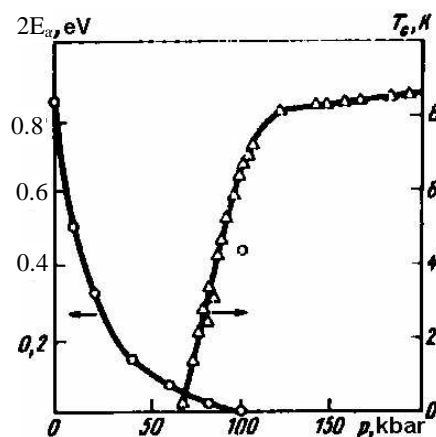


Fig. 1. The dependencies of superconductivity phase transition temperature  $T_c$  and  $2E_a$  on pressure  $p$  for  $As_2Te_3$  [4].

Semiconducting properties at the temperature  $T > T_c$  one can see more transparently from data of Fig. 2a for  $a-Ge_{33}As_{12}Se_{55}$  [5]. The values of  $T_c$  are depicted on Fig. 2b together with values of the energy activation for  $p < 140$  kbar. In the case  $p > 140$  kbar one can only estimate the energy activation of direct current conductivity and these values are shown by dashed line on Fig. 2b.

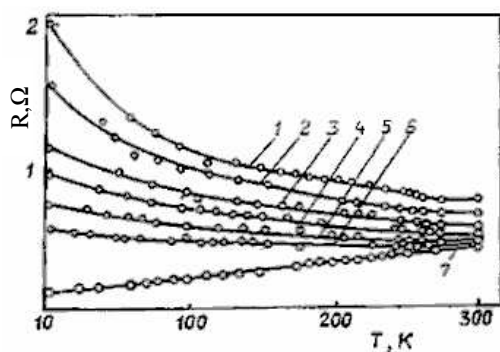


Fig. 2a. Experimental temperature dependence of resistance of  $a-Ge_{33}As_{12}Se_{55}$  for different pressure. Pressure, kbar: 1 – 170, 2 – 173, 3 – 178, 4 – 183, 5 – 190, 6 – 200, 7 – 218 [5]. The transition to superconductivity occurs at temperature lower than 5 K, therefore it is not visible at this scale and shown on Fig. 2b.

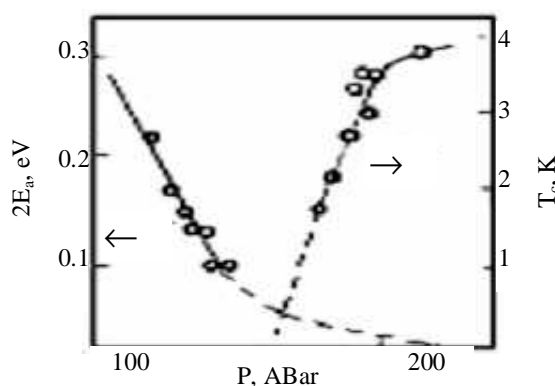


Fig. 2b. Pressure dependence of  $T_c$  and  $2E_a$  for  $a-Ge_{33}As_{12}Se_{55}$  [5].

But without any doubt superconducting transition in  $a-As_2Te_3$  and  $a-Ge_{33}As_{12}Se_{55}$  occurs from not metal but semiconducting state, because the negative values of  $dR/dT$  or  $dp/dT$  are observed.

### 3. High temperature oxide superconductors

Just the same behavior have demonstrated the high temperature oxide superconductors. The values of  $dp/dT$  are negative in the vicinity of  $T_c$  for  $T > T_c$  (see Fig. 3a) and derivative  $dT_c/dp$  is positive (see Fig. 3b).

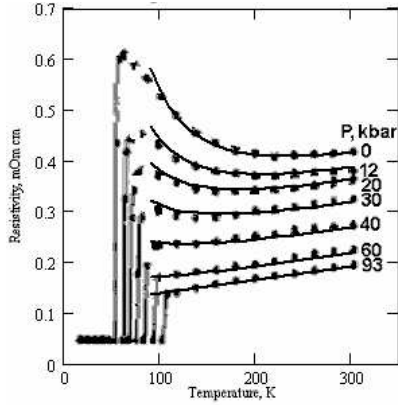


Fig. 3a. Temperature dependence of resistance of  $\text{PrBa}_2\text{Cu}_3\text{O}_{6.6}$  for different pressure. Big dots are experimental data [6], thin lines are theoretical values [7].

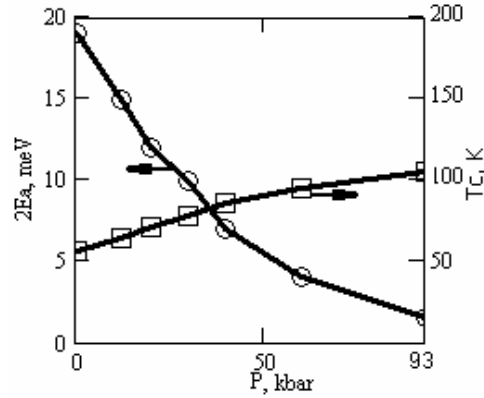


Fig. 3b. Pressure dependence of  $T_c$  and  $2E_a$  for  $\text{PrBa}_2\text{Cu}_3\text{O}_{6.6}$  [6].

#### 4. Fullerides

It is known that pure fullerides do not have superconducting property, but their compounds with alkali metals  $\text{K}_3\text{C}_{60}$  have  $T_c$  about 30 K.  $T_c$  is not as high as 100 K for HTSC but certainly these materials can be considered as high temperature superconductors. The materials are not always metallic — resistances greater than one of normal metal and negative values of  $dp/dT$  are frequently found in them when the superconducting state is destroyed. This situation is similar to that of CGS and underdoped HTSC [8]. Moreover, there is strange behavior of  $T_c$  dependence on lattice parameters for several fullerides. In BCS theory with increasing of lattice parameters the energy bands are narrowing thus leading to increase of density of states on Fermi level and eventually to increasing of  $T_c$ . The picture is completely different for  $(\text{NH}_3)_x\text{NaK}_2\text{C}_{60}$  and  $(\text{NH}_3)_x\text{NaRb}_2\text{C}_{60}$  compounds. In this material the progressive increase of ammonia concentration  $x$  yields an increase in lattice parameter and an unexpected decrease of  $T_c$  [9]. But such dependence of  $T_c$  on pressure can be explained in frame of negative-U center model.

#### 5. Negative U-centers superconductivity model (NUCS model)

The most important differences between classic BCS theory and NUCS model have been shown on Fig. 4. In the BCS theory pairing and coherent state of pairs appears simultaneously at the temperature  $T_c$ . The value of superconducting gap  $\Delta$ , which arises in the vicinity of Fermi level  $E_F$  is governed by both these effects (Fig. 4a). So the superconducting state arises from classic metal state. The second important fact is that according to classic formulae for  $T_c$

$$T_c \sim \exp(-1/\lambda N_F) \quad (1)$$

$T_c$  increases with increasing of density of states on Fermi level ( $N_F$ ).  $\lambda$  is the constant of electron-phonon interaction.

In BCS theory with increasing of lattice parameters the energy bands are narrowing thus leading to increase of density of states on Fermi level and eventually to increasing of  $T_c$ .

The principle of Anderson pairs is basically described as follows: ionization energy  $E_1$  of first outer electron from negative-U center to conduction band is larger than ionization energy  $E_2$  of the second electron (Fig. 4b). Then both electrons form a pair particle and bound energy  $U$  of the pair is  $-U=E_2-E_1$ . The negativity of effective correlation energy  $-U$  means that strong attraction exists between electrons or holes which form pairs. According to [10] negativity of  $-U$  means that reaction (2) is exothermic.



Pairs formed of two electrons or two holes have zero total value of spin, so the pairs are Bose particles. Bosons consisting of two bound electrons are situated on center  $D^-$ , and bosons consisting of two bound holes are situated on center  $D^+$ . If a negative-U centers concentration is low, one has the situation shown on left side of Fig. 4b ( $t=0$ ) with energy levels  $D^-$  and  $D^+$ . The different situation arises in the case of large negative-U centers concentration. In this case single levels split in band states (Fig. 4b ( $t \neq 0$ )). Band states allow to consider superconductivity transition in the collection of bosons, which belong to the negative-U centers system. The energy of binding  $U$  is so high, that bound electrons exist as pairs at temperature higher than several hundreds Kelvin degrees. Due to the pairing of electrons already happened at temperature much higher than temperature of superconducting transition  $T_c$ , only pairs condensation is needed to lead material to superconducting state with superconducting gap which is schematically shown on Fig. 4b as  $\Delta$ . The ideas that preformed bosons form degenerate Bose-gas in superconductors were proposed in early 1946 by Ogg [11] and 1955 by Shafroth [12]. Later such possibilities have been discussed in numerous papers [13-35] and has been reviewed in the papers of Wilson [36], Alexandrov and Mott [37]. The similar plot in all these theories was that preformed bosons already exist at temperature higher than  $T_c$  and non-degenerate Bose-gas becomes degenerate at temperature lower than  $T_c$ . In NUCS model [38,39] we use the assumption that Anderson pairs exist in material and they form not ideal Bose-gas at temperature higher than  $T_c$ . We can apply the results of [13] to calculate the  $T_c$  accordingly:

$$T_c = W \cdot (1 - 2v) / \ln(v^{-1} - 1) \tag{3}$$

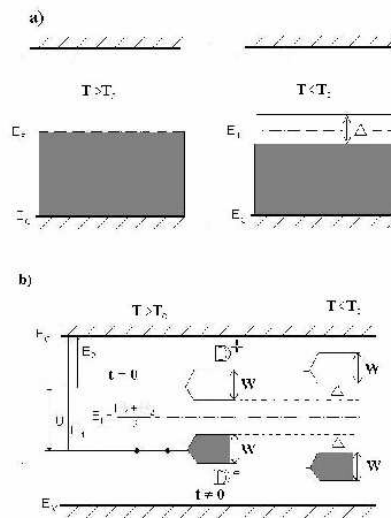


Fig. 4. Superconducting transitions for: a) Classic BCS theory and b) Negative U centers model with bands of preformed electron or hole pairs. Detailed explanations in the text.

Here  $W=2zt^2/U$  – width of the pairs band,  $z$  – number of the nearest neighbors of the given center,  $v$  – relative concentration of electronic pairs ( $v = n/2 \cdot N$ ,  $n$  – electron concentration,  $N$  – concentration of negative-U centers) and  $t$  – matrix element of electron’s transition from negative-U center to the nearest one. Multiplier  $W$  corresponds to the width of  $D^+$  and  $D^-$  energy band, which means that in the NUCS model charge carriers of these bands aren’t single electrons or holes but bounded pairs ( $2t^2/U$  their effective transfer integral from negative-U center to the nearest one).

According to the NUCS model [38, 39] the nature of main charge carriers in the normal and superconducting state is different. Before the condensation of electron pairs in degenerate state, its exist in narrow bands of negative-U centers  $D^+$  and  $D^-$  and take only a little part in the normal state current, which is almost due to charge carriers in wide valence or conduction band as usual. As a result there are two types of charge carriers: one for normal state and second – one for superconducting.

The second important feature of NUCS model is the strong pressure dependence of  $T_c$  with large positive derivative  $dT_c/dp$ , which is due to exponential dependence of transfer integral  $t$  on the distance between the nearest negative-U centers.

## 6. Explanation of CGS, cuprate-HTSC and fullerenes properties.

### 6.1 CGS

In the case of CGS formula (2) was specified in [40], and the most probable reaction which corresponds to the creation of negative-U centers is:



where  $C$  is chalcogen atom, lower index denotes the number of bonds and upper index corresponds to charge state. Fig.5a corresponds to CGS for  $p > 170$  and  $70$  kbar for  $a\text{-Ge}_{33}\text{As}_{12}\text{Se}_{55}$  and  $a\text{-As}_2\text{Te}_3$  correspondingly. It is suggested that high pressure induces large concentration of negative-U centers and  $D^{\pm}$  bands appear

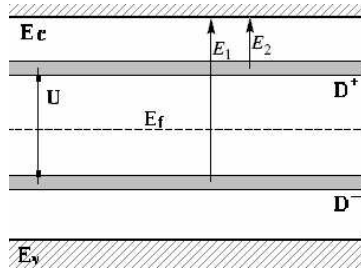


Fig. 5a. Band energy diagram of CGS. The vertical arrow shows the thermal transition of electrons from the negative-U centers. Shaded bands represent the bands of non-localized electron and hole pairs ( $D^-$  and  $D^+$  bands of bosons), whose Bose condensation is responsible for the superconductivity.

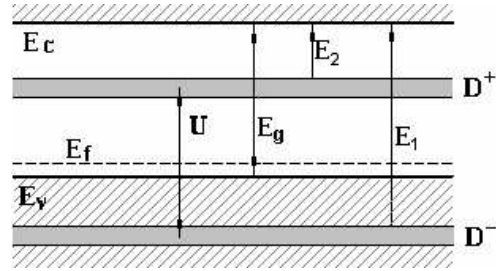


Fig 5b. Band diagram of  $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_x$ .  $D^+$  and  $D^-$  are bands of negative-U centers and they are shaded.  $E_f$  is slightly higher than the top of the valence band.

In the normal state semiconducting current is due to usual wide valence band and “semiconductor state-superconducting state” transitions occurs at the  $T_c$ . The  $T_c$  has positive derivative  $dT_c/dp$  according to NUCS model.

### 6.2 HTSC

In the  $\text{YBaCuO}$  system we think that some amounts of atoms of  $\text{Cu}$  with its oxygen environment are negative-U centers and we can attribute states  $D^-, D^0, D^+$  to  $\text{Cu}^{+1}, \text{Cu}^{+2}, \text{Cu}^{+3}$ . The existence of different  $\text{Cu}$  states was confirmed by experiments, which have been reviewed in [36]. According to [39] the reaction occurring in HTSC, which corresponds to reaction (2), is:



The very presence of negative-U centers in chalcogenides and cuprate-HTSC leads to series of similar properties of these materials. It is known that negative-U centers pin Fermi level in the middle between bands  $D^+$  and  $D^-$  (Fig. 4a).

We suppose that in cuprate-HTSC energy bands of negative-U centers are situated in such position that Fermi level is pinned slightly higher than the top of the valence band (Fig. 5b). Such location of energy levels and bands lead to very low activation energy of electrons from the valence

band (about 10meV). So cuprate-HTSC behaves like metal at near-room temperature, but they become hole semiconductors at the temperature comparable to  $T_c$ . Particularly it is very well emphasized for underdoped samples before superconducting transition [8].

The resistance decreasing under pressure may be explained by decreasing of forbidden gap as in the case of CGS (Fig.5a) or by decreasing of energy gap between the top of valence band and Fermi level, as for cuprate-HTSC (Fig. 5b). Concerning superconducting transition, the situation is rather different. In CGS superconductivity appears only under pressure of magnitude of several kbar and  $T_c$  usually does not rise higher than ten Kelvin degrees (Fig. 1, 2). In cuprate-HTSC superconductivity can occur without applied pressure and temperature of this occurrence is about hundred Kelvin degrees (Fig. 3).

The difference between these materials can be explained in the following way: in cuprate-HTSC negative-U centers are atoms of lattice, their concentration can be equal to  $10^{20}$ - $10^{21}$   $\text{cm}^{-3}$ , in CGS negative-U centers are defects with concentration about  $10^{17}$ - $10^{18}$   $\text{cm}^{-3}$ .

It is obvious that at normal conditions in CGS there is insufficient concentration of negative-U centers for the creation of superconducting cluster in full volume of the material. This concentration rises under pressure (probably because of the appearance of new defects).

When it reaches critical value then percolation superconducting current is possible. It is important both for cuprate-HTSC and chalcogenides that the matrix element  $t$  is rising exponentially under pressure because of decreasing lattice constants. Due to this matrix element  $t$  the exchanging of charge carriers between neighboring negative-U centers occurs. Superconducting transition temperature increases quadratically with rise of  $t$ , as seen in formula (3). This fact has been used in our papers [33,41,42] where it was shown theoretically that replacing oxygen with chalcogens by modification technique may led to significant raising of  $T_c$ .

### 6.3 Fullerides

A semiconducting negative values of  $dp/dT$  are frequently found in fullerides when the superconducting state is destroyed. Then the situation "semiconductor state-superconducting state" transitions is similar to that of CGS and underdoped HTSC [7,8]. The  $T_c$  dependence on lattice parameters for  $(\text{NH}_3)_x\text{NaK}_2\text{C}_{60}$  and  $(\text{NH}_3)_x\text{NaRb}_2\text{C}_{60}$  compounds may be explained in frame of negative-U center model because the matrix element  $t$  rises exponentially under pressure.

Also it was found that the reaction similar to (2) is present not only in CGS and HTSC but also in several fullerides [7,42,43].



## 7. Conclusions

It has been shown that negative-U center model – NUCS model based on assumption that Anderson pairs form the energy bands, in which Bose-particles are condensating in a degenerate state, can explain many properties of superconducting materials including normal state. This model shows that both chalcogenide glassy semiconductors and cuprate-HTSC have many similarities, including the origin of superconductivity. The approach to superconductivity consisting in statement that bound Anderson pairs can exist at temperatures higher than  $T_c$  allows to explain such property as transition from semiconducting to superconducting state. It is also suggested that pre-formed pairs could exist in fullerides, so the application of NUCS model for them would be possible.

### Acknowledgements

The author wish to thank B. P. Popov and D. V. Denisov for their help. This work was supported by Russian Foundation for Basic Researches (RFBR grant 05-03-33113-a).

## References

- [1] N. Sakai, H. Fritzsche, Phys. Rev. B **15**(2), 973 (1977).
- [2] I. B. Berman, N. B. Brandt, V. A. Alekseev, I. E. Kostileva, V. I. Sidorov, O. P. Piatkina, Pis'ma Zhurn. Exp. Teoretich. Fiz. **40**, 472 (1984).
- [3] I. B. Berman, N. B. Brandt, I. E. Kostileva, V. I. Sidorov, V. A. Alekseev, Fiz. Tverd. Tela **27**, 2747 (1985).
- [4] I. B. Berman, N. B. Brandt, I. E. Kostileva, S. K. Pavlov, V. I. Sidorov, S. M. Chudinov, Pis'ma Zhurn. Exp. Teoretich. Fiz. **43**, 48 (1986).
- [5] I. B. Berman, N. B. Brandt, Fiz. Nizkih Temper. **16**, 1227 (1990)
- [6] F. A. Boyko, G. V. Bukin, V. A. Voloshin, A. A. Gusev, Fiz. Nizk. Temp. **28**, 138 (2001).
- [7] K. D. Tsendin, B. P. Popov, D. V. Denisov, Physica C **415** 94 (2004).
- [8] K. D. Tsendin, D. V. Denisov, Supercond. Sci. Technol. **16**, 80 (2003).
- [9] M. Ricco, G. Fumera, T. Shiroka, O. Ligabue, C. Bucci, F. Bolzoni, Phys. Rev. B **68**, 035102 (2003).
- [10] R. F. Street, N. F. Mott, Phys. Lett. **35**, 1293 (1975).
- [11] R. Ogg, Phys. Rev. **69**, 243 (1946).
- [12] M. R. Shafroth, Phys. Rev. B **100**, 460 (1955).
- [13] I. O. Kulik, A. G. Pedan, Zh. Eksp. Teor. Fiz. **79**, 1469 (1980).
- [14] A. Alexandrov, J. Ranninger, Phys. Rev. B **23**, 1796; **24**, 1164 (1981).
- [15] R. Micnas, J. Ranninger, S. Robaszkiewicz, Rev. Mod. Phys. **62**, 113 (1990).
- [16] R. Micnas, S. Robaszkiewicz, A. Bussmann-Holder, Phys. Rev. B **66**, 104516 (2002).
- [17] K. V. Micen, O. M. Ivanenko, Zh. Eksp. Teor. Fiz. **118**, 666 (2000).
- [18] B. Ya. Mojges, S. G. Suprun, Fiz. Tv. Tela **29**, 441 (1987).
- [19] E. Simanek, Sol. St. Commun., **32**, 731 (1979).
- [20] C. S. Ting, D. N. Talwar, K. L. Ngai, Phys. Rev. Lett. **45**, 1213 (1980)
- [21] A. F. Andreev, JETP Letters **79**, 88 (2004)
- [22] K. D. Tsendin, D. V. Denisov, B. P. Popov, JETP Letters **80**, 246 (2004)
- [23] A. S. Alexandrov, S. V. Verhovskiy, I. M. Tsidilkovskiy, Pisma v Zh. Eksp. Teor. Fiz. **46**, 51 (1987).
- [24] A. S. Alexandrov, Abstr. 1<sup>st</sup> Intern. Conf. FPS. Moscow, 4, (2004)
- [25] N. F. Mott, J. Non-Cryst. Sol. **164-166**, 1177 (1993).
- [26] S. D. Savransky, Solid. St. Commun. **79**, 843 (1991)
- [27] S. D. Savransky, J. Non-Cryst. Sol. **83**, 235 (1986).
- [28] S. D. Savransky, J. Non-Cryst. Sol. **94**, 412 (1987).
- [29] S. D. Savransky, J. Non-Cryst. Sol., **164-166**, 1173 (1993).
- [30] B. Ya. Mojges, S. G. Suprun, Fiz. Tv. Tela **27**, 1395 (1985).
- [31] B. Ya. Mojges, Fiz. Tv. Tela **25**, 2805 (1983).
- [32] M. V. Kracinkova, B. Ya. Mojges, Fiz. Tv. Tela **33**, 350 (1991).
- [33] K. D. Tsendin, J. Optoelectron. Adv. Mater. **4**, 763 (2002).
- [34] A. S. Alexandrov, V. V. Kabanov, Phys. Rev. **B59**, 13628 (1999)
- [35] A. S. Alexandrov, Eur. Phys. J. **B39**, 55 (2004)
- [36] J. Wilson, J. Phys.: Cond. Mat. **13**, R945 (2001).
- [37] A. S. Alexandrov, N. F. Mott, Rep. Prog. Phys. **57**, 1197 (1994).
- [38] K. D. Tsendin, B. P. Popov, Supercond. Sci. Technol. **12**, 255 (1999).
- [39] B. P. Popov, K. D. Tsendin, Tech. Phys. Lett. **24**, 265 (1998).
- [40] M. Kastner, D. Adler, H. Fritzsche, Phys. Rev. Lett. **31**, 1504 (1975).
- [41] K. D. Tsendin, D. V. Denisov, J. Optoelectron. Adv. Mater. **3**, 549 (2001).
- [42] K. D. Tsendin, D. V. Denisov, J. Optoelectron. Adv. Mater. **5**(4), 1011 (2003).
- [43] L. Pintschovius, S. L. Chaplot, G. Roth, G. Heger, Phys. Rev. Lett. **75**, 2843 (1995).