

Current carrier localization and Coulomb gap observed in $\text{SrPbO}_{3-\delta}$ by transport measurements and tunnel spectroscopy

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2005 J. Phys.: Condens. Matter 17 7407

(<http://iopscience.iop.org/0953-8984/17/46/024>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 28/05/2010 at 06:48

Please note that [terms and conditions apply](#).

Current carrier localization and Coulomb gap observed in $\text{SrPbO}_{3-\delta}$ by transport measurements and tunnel spectroscopy

Vadim A Drozd¹, Toshikazu Ekino², Alexander M Gabovich^{3,4},
Marek Pękała^{4,6}, Raquel A Ribeiro², Anatoliy D Shevchenko⁵ and
Victor M Uvarov⁵

¹ Department of Chemistry, Kiev State University, 64 Volodymyrs'ka st, 01033, Kiev, Ukraine

² Faculty of Integrated Arts and Sciences, Hiroshima University, 1-7-1 Kagamiyama, Higashi-Hiroshima, 739-8521, Japan

³ Crystal Physics Department, Institute of Physics, prospekt Nauki 46, 03028, Kiev-28, Ukraine

⁴ Department of Chemistry, University of Warsaw, Aleja Żwirki i Wigury 101, PL-02-089 Warsaw, Poland

⁵ Kurdyumov Institute of Metal Physics, Akademician Vernadsky Boulevard 36, 03680, Kiev, Ukraine

E-mail: vdrozd@univ.kiev.ua, ekino@hiroshima-u.ac.jp, gabovich@iop.kiev.ua,
pekala@chem.uw.edu.pl and ribeiro@hiroshima-u.ac.jp

Received 1 May 2005, in final form 7 October 2005

Published 1 November 2005

Online at stacks.iop.org/JPhysCM/17/7407

Abstract

Strontium plumbate $\text{SrPbO}_{3-\delta}$ samples were obtained by means of high pressure synthesis and studied through the temperature (T) dependences of the resistivity ρ and differential thermoelectric power S . Thus prepared samples demonstrate a much steeper increase of ρ for low T than those synthesized by us and other groups without high pressure application. Moreover, the ρ minimum observed earlier and indicating a proximity to the metal state completely disappeared. The sign of $S(T)$ is positive in the whole T range, contrary to what was observed earlier. Tunnel measurements were carried out using the *in situ* break-junction technique, revealing a correlation dielectric gap $\Sigma \approx 1.5\text{--}2$ eV. The data can be explained if one assumes the existence of both holes and electrons in this oxide. The high pressure application during synthesis leads to higher sample disorder, most probably inducing current carrier localization and a Coulomb gap emergence in the quasiparticle spectrum. Electrons do not survive this process, whereas the former minority holes reveal themselves in thermoelectric measurements. Meanwhile, the overall transport behaviour loses its semimetallic features, characteristic of more conventionally produced lead oxide ceramics. Our results show how fragile the electron spectrum of this oxide is, being near the metal–semiconductor phase transition boundary.

⁶ Author to whom any correspondence should be addressed.

1. Introduction

Oxides constitute a very promising class of materials demonstrating electronic properties varying from superconducting [1–4] to magnetic [5–8] ones. They also often show electron spectrum instabilities [9–12], which can drastically influence the desired collective properties of these materials. Therefore, measured transport properties of oxide materials as well as their exciting high critical superconducting temperatures T_c as in the case of Na_xWO_3 [13, 14] or multi-phase ceramics $\text{Cu}_{24}\text{Pb}_2\text{Sr}_2\text{Ag}_2\text{O}_x$ [15, 16] and $\text{Ag}_x\text{Pb}_6\text{CO}_{9+\beta}$ [17] might turn out to be extrinsic due to the granular structure of the samples or a large defect concentration depressing mobility of current carriers. Indeed, synthesis of highly conducting single crystals of $\text{Ag}_5\text{Pb}_2\text{O}_6$ and measurements of their transport and thermodynamic characteristics showed that they do reveal a bulk superconducting transition but at extremely small $T_c \approx 48$ mK [18]. According to band-structure calculations [19], Ag-sub-lattice vacancies crucially influence the inter-atomic interactions and, hence, electronic properties of $\text{Ag}_5\text{Pb}_2\text{O}_6$. At the same time, electrical conductivity studies on a $\text{PbO}_{2-x}\text{Ag}_2\text{O}-0.75\text{C}$ composite do not display any superconductivity but demonstrate a percolation transition from the metallic to variable-range-hopping phase region at $x = 0.275$ [20].

On the other hand, the phenomena appropriate to granularity [21], dielectric electron spectrum gapping [4] or current carrier localization (either weak or strong) [22, 23], competing and sometimes concomitant to ‘useful’ superconductivity and ferromagnetism, are interesting themselves as different kinds of many-body manifestations in solids. Here we present transport and tunnel studies of the lead oxide ceramics $\text{SrPbO}_{3-\delta}$ as one of the basic constituents of the multi-phase ceramics $\text{Cu}_{24}\text{Pb}_2\text{Sr}_2\text{Ag}_2\text{O}_x$ and the mother compound for solid solutions $\text{Sr}_{1-x}\text{K}_x\text{PbO}_{3-\delta}$ and $\text{Sr}_{1-x}\text{La}_x\text{PbO}_{3-\delta}$ studied earlier [24, 25]. These investigations shed some light on the behaviour of more involved materials and demonstrate interesting new features, not observed before in this class of ceramics. In particular, our *in situ* break-junction measurements of the tunnel conductance $G(V) \equiv dI/dV$, where I is the quasiparticle current and V is the bias voltage, revealed the so-called Coulomb gap [21, 22, 26] in the electronic density of states (DOS). We have also shown that the chosen method of synthesis may qualitatively change the electronic properties, which is important while interpreting often conflicting evidence about the compounds concerned.

2. Synthesis and sample characterization

Polycrystalline samples of $\text{SrPbO}_{3-\delta}$ were prepared at ambient pressure by a solid state reaction of stoichiometric amounts of $\text{Sr}(\text{NO}_3)_2$ and PbO . Powders were ground in an agate mortar and annealed at 750°C in air for 48 h with intermediate grinding. We used high pressure synthesis conditions to improve the structural quality of samples, i.e. to reduce the role of granularity, although in the case of polycrystalline ceramics some influence of macro-structural effects is unavoidable [21, 27, 28]. High pressure (HP) samples were obtained from the ambient-pressure phases in a cubic anvil press under 7.5 GPa at 400°C with several minutes of exposure. Oxygen content in the strontium plumbate was determined by the iodometric titration [24]. It was found that the phase $\text{SrPbO}_{3-\delta}$ is slightly oxygen deficient with $\delta = 0.06$ (HP sample).

X-ray investigations were carried out by the powder method using a DRON-3 diffractometer (Cu $K\alpha$ radiation). According to the x-ray diffraction analysis, the samples are single-phase XRD patterns, which were indexed assuming orthorhombically distorted perovskite GdFeO_3 -type structure. The ideal perovskite structure ABO_3 is usually skewed in this way when the ionic radius of the A cation is not large enough to fill the space between BO_6 octahedra. Therefore, the octahedron tilting occurs, reducing the parent $Pm3m$ perovskite

Table 1. Parameters of the orthorhombic crystal lattice, and the lead average valence for SrPbO_{3-δ} samples before and after high pressure treatment.

Sample	a (Å)	b (Å)	c (Å)	V (Å ³)	D (%)	Pb AV
Ambient pressure SrPbO _{3-δ}	5.855(4)	5.951(2)	8.319(5)	289.9(5)	0.624	3.92
High pressure SrPbO _{3-δ}	5.822(8)	5.916(4)	8.297(8)	285.8(9)	0.546	3.88

symmetry to the orthorhombic one $Pbnm$, which leads to significant changes of the physical properties.

Crystal lattice parameters of the ambient and high pressure phases are listed in table 1. They are in good agreement with previously reported values for the SrPbO_{3-δ} phase [29]. High pressure treatment causes appreciable shrinkage of the lattice, with the unit cell volume decreasing from 289.9 to 285.8 Å³. It turns out (see below) that this reduction influences the transport properties significantly. Moreover, the diffraction peaks of the high pressure phase are broader compared to those for the ambient pressure one, attesting the grain size reduction of the high pressure SrPbO_{3-δ} samples. The observed crystal lattice changes provoked by the high pressure treatment are in line with the results of Zhao *et al* [30], indicating that the perovskite ABO₃ response to a high pressure depends on the relative compressibility of the octahedral and dodecahedral cation sites in the perovskite structure. If the BO₆ octahedra are less compressible than the AO₁₂ sites then the resulting perovskite lattice will become more distorted with pressure, but it will be less distorted than the ambient pressure structure if the BO₆ sites are more compressible than the AO₁₂ ones.

The orthorhombic deformation of the perovskite structure, D , which is an indicator of a crystal structure deviation from the ideal cubic perovskite structure, can be calculated by the formula

$$D = \frac{1}{3} \sum_{i=1}^3 \left| \frac{a_i - \bar{a}}{\bar{a}} \right| \cdot 100. \quad (1)$$

Here a_i denotes crystal lattice parameters $a_1 = a$, $a_2 = b$, $a_3 = c/\sqrt{2}$ and $\bar{a} = \sqrt[3]{a_1 a_2 a_3}$. It is worth noting that orthorhombic distortion of the perovskite structure for high pressure samples is smaller than that for ambient pressure samples.

3. Electrical characterization

Electrical resistivity $\rho(T)$ and thermoelectric power $S(T)$ were studied by the same technique as described in [24, 25]. The latter quantity was measured between 20 and 300 K in a closed cycle refrigerator, whereas the former one was investigated in the interval $4.2 \text{ K} \leq T \leq 300 \text{ K}$. Tunnel measurements were carried out by the four-probe *in situ* break-junction technique, which has been proved successful to reveal both superconducting [31] and correlation [32] energy gaps.

4. Results and discussion

A typical dependence $\rho(T)$ measured for a compacted HP sample of SrPbO_{3-δ} is shown in figure 1(a). The absolute values of the resistivity are several orders of magnitude larger than those for the $x = 0$ member of the solid solution series Sr_{1-x}La_xPbO_{3-δ} produced at ambient pressure [25]. Namely, the ambient pressure sample SrPbO_{3-δ} shows $\rho \approx 4 \times 10^{-2} \Omega \text{ cm}$ for

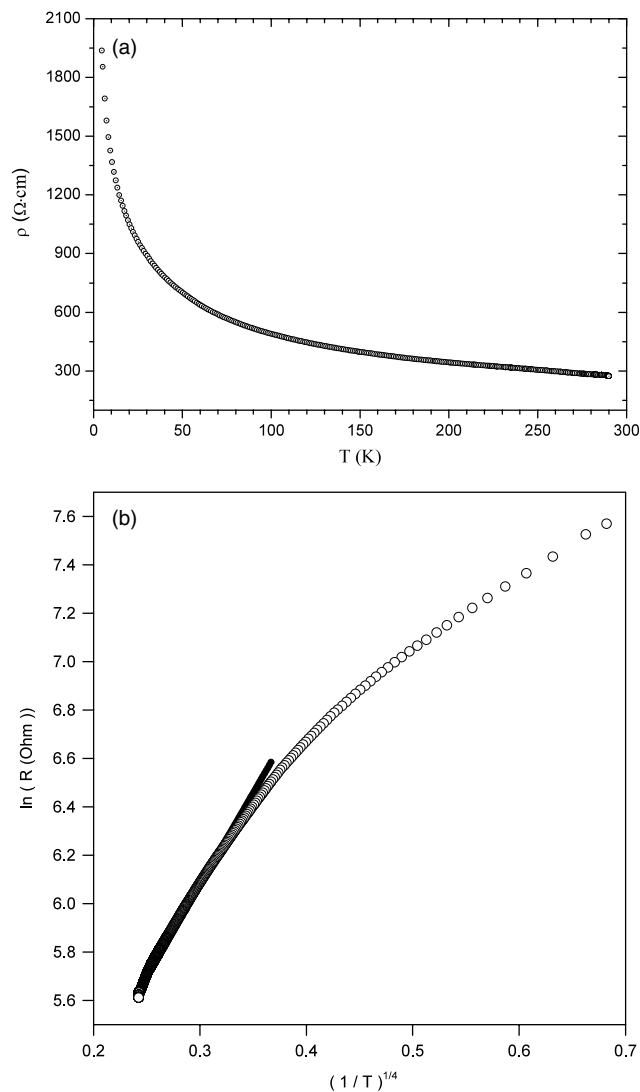


Figure 1. Temperature, T , dependence of the resistivity ρ (a), and resistance, R , on a logarithmic scale versus $T^{1/4}$ (b). Linearization of the sample resistance $\ln R$ versus $T^{-1/4}$ is shown by a solid straight line.

$T \approx 100$ K, whereas for the HP sample of the present work $\rho(100 \text{ K}) \approx 4 \times 10^2 \Omega \text{ cm}$. Moreover, the T -dependence describes an ambient-temperature insulator rather than a semimetal, possessing a shallow $\rho(T)$ minimum in the range $100 \text{ K} < T < 150 \text{ K}$, as was found earlier for more conventionally prepared ceramics (see our publications [24, 25] and references therein). On the other hand, at low T the insulating character of the HP-sample conductivity becomes stronger, which qualitatively agrees with the low- T behaviour obtained in [24] and [25] below a smooth semimetal–insulator transition for specimens synthesized at the ambient pressure. Nevertheless, the apparent absence of any metallic manifestations in the overall curve $\rho(T)$ in figure 1(a) seems rather unexpected in view of the applied treatment designed to improve metallic trends appropriate to the previously investigated basic compound $\text{SrPbO}_{3-\delta}$ or its derivatives obtained by K- [24] and La- [25] doping. We think

that the conspicuous differences in the bulk crystal structure (see table 1) may account for the distinctions in transport properties, although the pressure influence on the inter-grain contacts should be always kept in mind. In the following, various possible scenarios of the apparent non-metallic behaviour are discussed.

As has been already mentioned, the observed semiconducting $\rho(T)$ for ceramics Sr_{1-x}La_xPbO_{3-δ} could be explained by the granular nature of the structures studied [21, 27, 28, 33]. Nevertheless, it is difficult to imagine that the HP synthesis might lead to thicker and less conducting inter-grain areas. Hence, the semiconductor-like $\rho(T)$ displayed in figure 1(a) should most probably be considered as an intrinsic bulk feature. Further still, the observed gap-like non-linearities occur at voltages of the order of several volts (see below), so that the Coulomb gapping apart from the measurements can be attributed to the Ohmic regime, whatever its microscopic nature. On the other hand, the highly non-linear tunnel (Fowler–Nordheim) regime usually reveals itself in oxide granular conductors at voltages ~ 100 V or more, as is inherent, e.g., to ZnO varistors [38]. We did not switch to this regime in order to avoid destroying the samples. Therefore, the Coulomb gaps were the only detected non-linearities.

It should be also noted that various contaminations as well as oxygen vacancies during the synthesis might be, in principle, expelled by the applied pressure to the grain boundaries, thus influencing the transport character. This phenomenon would constitute the basis of the granular conductivity scenario. However, we believe such a possibility to be highly improbable in view of the detected absence of compositional variations between the grain bulk and surface regions in the related ceramics BaPb_{1-x}Bi_xO_{3-δ} [37].

The three-dimensionality and the apparent absence of metallic properties for the investigated ceramics makes unlikely a detectable role of quantum corrections due to weak-localization and Coulomb interaction effects [23] in determining the electrical conductivity. Indeed, as is well known [23], in three-dimensional metallic materials the quantum correction terms are small and proportional to $\sqrt{T/E_F}$, where E_F is the Fermi energy. Such corrections were used, e.g., to fit $\rho(T)$ for perovskite epitaxial SrRuO₃ and LaNiO₃ thin films [34]. However, such objects should instead reveal two-dimensional more pronounced corrections $\sim \ln T$, whereas the square-root extra term might have been taken into account to treat the usually observed non-monotonic behaviour of the plumbate SrPbO_{3-δ} [24, 25]. Nevertheless, the expected small magnitudes of the corrections $\sim \sqrt{T/E_F}$ make such an interpretation hardly convincing.

On the other hand, strong localization precursor phenomena on the metallic side in the neighbourhood of the metal–insulator transition may be crucial. In this case a classification of solid solutions according to the sign of the $d\rho/dT$ would be misleading [26, 35]. Our attempts to fit the curves displayed in figure 1(a) by the Arrhenius law

$$\rho(T) \propto \exp\left(\frac{A}{T}\right), \quad (2)$$

where A is an energy gap appropriate to a definite activation process, failed. This means neither a simple one-body electron band theory nor a charge-density-wave (CDW) one describe the transport properties of SrPbO_{3-δ} at low T . This is also true for samples prepared at ambient pressure [24, 25]. Furthermore, all temperature changes of resistivity are gradual, so that there is no phase transition in the strict sense. One may, however, suggest that the observed semiconductive dependence $\rho(T)$ is governed by the Coulomb interaction in a disordered state of the oxide sample [21, 22, 26]. The intrinsic oxygen nonstoichiometry [36] as a source of the disorder should not be overlooked, since it is known to essentially influence various transport properties of oxides [37, 38].

Coulomb correlations between impurities (defects) in the disordered system $\text{SrPbO}_{3-\delta}$, which cannot be considered as a conventional metal in the one-body Wilson sense [39], must substantially modify the activation law (2), whatever the physical meaning of the constant A . Namely, the conductivity mechanism becomes a variable-hopping one

$$\rho(T) \propto \exp\left(\frac{T_{\text{vh}}}{T}\right)^{1/n}, \quad (3)$$

where the number n equals four when the electron density of states (DOS) of the intrinsic current carriers or those originating from impurities is constant (Mott law [22, 40]), or two if a so-called Coulomb gap appears (Efros–Shklovskii law [21, 22]). In the former case the parameter T_{vh} is inversely related to the DOS, whereas when the DOS at the Fermi level is depleted by the Coulomb interaction the quantity T_{vh} is equal to a certain Coulomb energy value. Real transport measurements for doped semiconductors may demonstrate either $n = 4$ or 2 in different T ranges [21]. In our case we tried to fit the experimental results shown in figure 1(a) for the whole T range using a broad interval of n values. The best agreement according to the correlation coefficients was achieved using the Mott law ($n = 4$) for a rather wide temperature range of 55–290 K. A corresponding linearization of the sample resistance R versus $T^{-1/4}$ is indicated in figure 1(b) by a solid straight line. The respective value of the parameter T_{vh} is about 0.3 eV.

The lack of unambiguous description of experimental data by equation (3) is no great surprise because all formulae of this type are approximate and have been obtained assuming the most probable transport processes only. Nevertheless, all modifications of equation (3) result in n which are always larger than unity. In granular metals Coulomb interaction also transforms the tunnelling inter-grain conductivity, so that the main term is described by the same equation (3) with $n = 2$ [21, 27]. A more sophisticated theory [41] confirms the main trend but leads to another form of the tunnel DOS suppression not covered by the simple formula (3).

We should stress that the apparent localization manifested by equation (3) does not mean that it concerns *all charge carriers*. Some groups of carriers that remain metallic constitute an ordinary Fermi liquid not revealed by bulk $\rho(T)$ measurements in the ceramics $\text{SrPbO}_{3-\delta}$ being on the verge of the metal–insulator boundary. More subtle techniques are needed to remove the veil. This is not so in $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ [37] and cuprates [42], where both free and localized (or gapped) current carriers are relatively easily seen in the normal state, e.g., by electrical and optical means. For instance, a Mott law behaviour, exact within the accuracy of the experiment, was found in transport measurements of the copper oxide samples $\text{Bi}_{1.6}\text{Sr}_{2.4}\text{NdCu}_2\text{O}_{8+x}$ exhibiting a localization of charge carriers in a wide temperature range [43]. In our case such a successful fitting is not possible not only because of the different variable range hopping mechanism but also due to the superposition of itinerant and localized carriers appropriate to $\text{SrPbO}_{3-\delta}$.

To further characterize current carriers of the HP phases we have measured the dependence on T of the differential thermoelectric power (Seebeck coefficient) S in $\text{SrPbO}_{3-\delta}$. Corresponding data are displayed in figure 2. It turns out that values of S are *positive* for all T and the function $S(T)$ is almost linear. This result is puzzling because S for the samples synthesized in a different way are negative in the whole temperature range [24, 25]. At the same time, one should bear in mind that in nominally hole-doped ceramics $\text{Sr}_{1-x}\text{K}_x\text{PbO}_{3-\delta}$ [24] the sign of the curves $S(T)$ is also unexpected, although *negative*. A sign change of $S(T)$ in the variable hopping regime for oxygenated samples as compared to the as-sintered ones was observed for the cuprate $\text{Bi}_{1.6}\text{Sr}_{2.4}\text{NdCu}_2\text{O}_{8+x}$ [43].

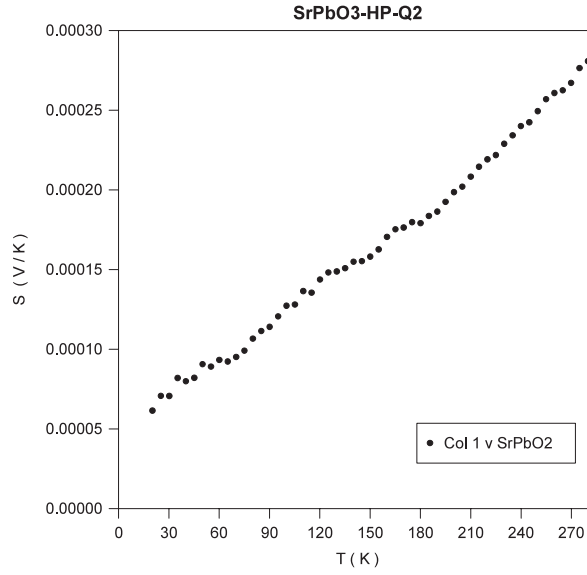


Figure 2. The T dependence for the differential thermoelectric power S .

The observed proportionality between S and T agrees well with the linear T dependences given by the basic theory for conventional metals or semimetals [44] for low T and various dominating types of quasiparticle scattering. For instance, when Coulomb scattering by ionized impurities prevails, the theoretical dependence has the form

$$S(T) = \frac{\pi^2 k_B^2 T}{3e E_F}. \quad (4)$$

Here e is the current carrier charge (negative for electron-like quasiparticles and positive for hole-like ones) and k_B is the Boltzmann constant.

Since the experimental values of $S(T)$ shown in figure 2 are positive, holes apparently dominate in thermoelectricity, which is not the case for the ambient pressure prepared samples [24, 25]. These results, together with the resistivity data (figure 1(a)), clearly indicate that several groups of current carriers are involved in the HP plumbates. Some of them (holes) exhibit properties pertinent to a degenerate Fermi liquid while others (electrons) are to a large extent localized. In the thermoelectric response the contribution of electrons turns out to be negligible against the background of the large Seebeck coefficient of holes. A T -independent value of the localized negative charge carrier contribution to S similar to, e.g., that of [43] can also explain the results displayed in figure 2. It may be estimated as approximately $50 \mu\text{V}$.

To detect the changes in the electronic structure induced by the localization we have made tunnel investigations of HP samples using the *in situ* break-junction technique [31, 32]. The high resistivity of the samples has been the main obstacle to these studies. Nevertheless, we were able to measure tunnel conductance $G(V)$ for SrPbO_{3-δ}. Our data obtained at $T = 4.2$ K are shown in figures 3 and 4. They represent two distinctive groups of results. The first one, depicted in figure 3, reveals clear-cut gap-like peculiarities. The patterns are somewhat asymmetrical but the main features are observed for both polarities. Notwithstanding the apparent gap edges, $G(V) \neq 0$ inside the gapped voltage interval for all those junctions. This confirms our earlier suggestion that localized and itinerant quasiparticle states coexist.

Let us begin with curve (a) as a typical specimen of the tunnel data. Gap-like structures at $V \approx \pm 3$ V should be identified with twice the dielectric, most probably, correlation energy gap

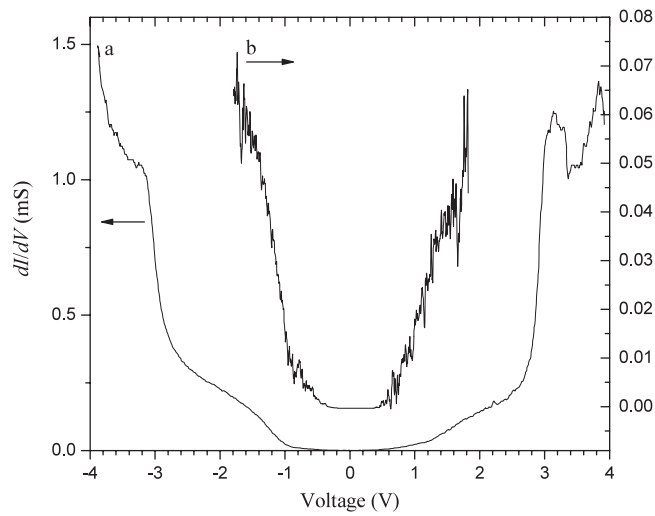


Figure 3. The dependences at $T = 4.2$ K of the differential conductivity $G(V) \equiv dI/dV$ for *in situ* break junctions, where I is the tunnel current. The curves $G(V)$ demonstrate finite-width correlation gaps.

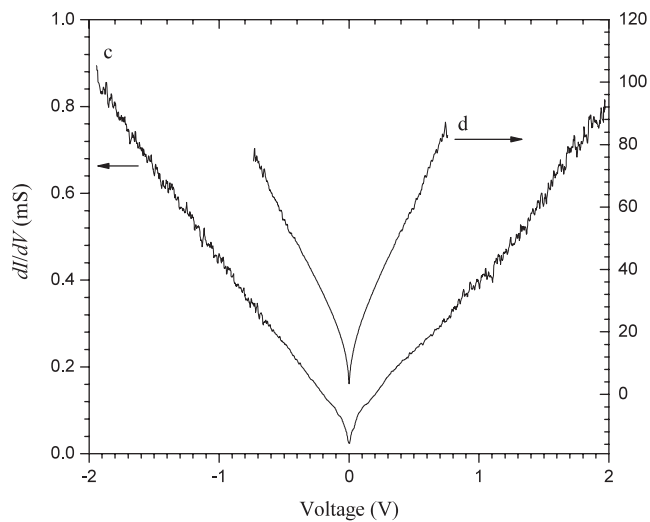


Figure 4. The same as in figure 3. The curves $G(V)$ V-shaped Coulomb gaps.

Σ , the whole pattern corresponding to the semiconductor–insulator–semiconductor junction. At the same time, weak shoulders at 1.5–2 V should be associated with the gap Σ itself. The appearance of $\pm\Sigma$ features is probably caused by partial formation of a semiconductor–insulator–normal metal contact in the *in situ* break-junction area. Such large activation energy 1.5–2 eV substantially exceeds any possible transport activation energy A inferred from resistive measurements, if one tries to fit them by equation (2) in a limited range of temperatures. This circumstance most probably reflects the bulk many-body Coulomb gap effect [21, 26] and, at least partially, the Coulomb blockade effect if tunnelling links one or two small conducting grains [21, 45]. Curve (b) demonstrates the same type of incomplete correlation

gap as its counterpart (a), but the gap edges are located at ± 1 V. It is unclear whether this $G(V)$ corresponds to a semiconductor–insulator–normal metal or a semiconductor–insulator–semiconductor junction.

Other junctions manifest quite different tunnel properties described in figure 4. Not only a true dielectric gap but also a finite-width pseudogap is absent. Instead, a typical Coulomb V-shaped ‘gap’ with a zero-value electron DOS at the Fermi level shows up in the power-law $G(V)$ dependences [21, 22]. Such a behaviour was observed, e.g., for strongly correlated oxides LaNi_xCo_{1-x}O₃ and Na_xTa_yW_{1-y}O₃ on the insulating side of the metal–insulator phase boundary [26]. The emergence of the Coulomb gap in the HP samples qualitatively correlates with the resistivity measurements shown in figures 1(a), (b).

As has been known for decades [46, 47], while studying tunnel junctions made of highly resistive materials, such as oxide ceramics, one should be careful to avoid self-heating. The latter, in principle, can spoil the intrinsic pattern leading to a spurious structure of I – V characteristics that can be misinterpreted as the gap-induced one. Therefore, after a number of groups began investigations of tunnelling in large mesas of high- T_c ceramics with poor thermal conductivity [48], a pulse technique similar to that of [46, 47] was applied [49, 50]. In other studies [51, 52] such precautions were not made. This is why their important results on distinctions between superconducting gaps and pseudogaps were claimed [53] to be artifacts of the self-heating. Fortunately, it turned out that even for such large and highly resistive structures self-heating plays a minor role [54]. In our case the self-heating effects are even less dangerous because the current carrying areas are much smaller. Moreover, the very reason for the Joule-heating-induced nonlinearities of the I – V characteristics, i.e. a minimum of the dependence $\rho(T)$, is absent (see figure 1(a)). Thus, our *in situ* break-junction results have beyond doubt an intrinsic origin.

To summarize, the SrPbO_{3-δ} ceramics synthesized with the help of high pressure demonstrate the coexistence of free holes and highly localized current carriers (predominantly electrons). The Coulomb gap determines resistivity and tunnel conductivity, whereas thermoelectric response is governed by itinerant holes.

Acknowledgments

VAD and AMG are grateful to the Mianowski Foundation and the Polish Science Foundation for support of their visits to Warsaw University. AMG thanks the Japan Society for the Promotion of Science for support of his visit to Hiroshima University (grant ID No S-03204). RAR thanks the Japan Society for the Promotion of Science for support (grant ID No S-03204). The research has been partly supported by the NATO grant PST.CLG.979446 and Grants-in-Aid for COE Research (No 13CE2002) and for Scientific Research (No 15540346) of the Ministry of Education, Culture, Sports, Science and Technology of Japan.

References

- [1] Cava R J 2000 *J. Am. Ceram. Soc.* **83** 5
- [2] Mackenzie A and Maeno Y 2003 *Rev. Mod. Phys.* **75** 657
- [3] Hilgenkamp H and Mannhart J 2002 *Rev. Mod. Phys.* **74** 485
- [4] Gabovich A M, Voitenko A I and Ausloos M 2002 *Phys. Rep.* **367** 583
- [5] Coey J M D, Viret M and von Molnar S 1999 *Adv. Phys.* **48** 167
- [6] Salamon M B and Jaime M 2001 *Rev. Mod. Phys.* **73** 583
- [7] Prellier W, Fouchet A and Mercey B 2003 *J. Phys.: Condens. Matter* **15** R1583
- [8] Coey J M D and Sanvito S 2004 *J. Phys. D: Appl. Phys.* **37** 988
- [9] Tokura Y and Nagaosa N 2000 *Science* **288** 462

- [10] Dumas J, Beierlein U, Drouard S and Schlenker C 2002 *Solid State Sci.* **4** 379
- [11] Gorshunov B, Haas P, R om T, Dressel M, Vuletić T, Hamzić B, Tomić S, Akimitsu J and Nagata T 2002 *Phys. Rev. B* **66** 060508
- [12] Shen K M, Ronning F, Lu D H, Baumberger F, Ingle N J C, Lee W S, Meevasana W, Kohsaka Y, Azuma M, Takano M, Takagi H and Shen Z-X 2005 *Science* **307** 901
- [13] Reich S and Tsabba Y 1999 *Eur. Phys. J. B* **9** 1
- [14] Garif'yanov N N and Vavilova E L 2003 *Physica C* **383** 417
- [15] Djurek D and Manoilovic V 1990 *Croatica Chem. Acta* **63** 1
- [16] Moiseev D P, Pashitskii E A, Boychuk V N, Motuz A A and Uvarova S K 1992 *Ukr. Fiz. Zh.* **37** 1720
- [17] Djurek D, Medunic Z, Tonejc A and Paljevic M 2001 *Physica C* **351** 78
- [18] Yonezawa S and Maeno Y 2004 *Phys. Rev. B* **70** 184523
- [19] Shein I R and Ivanovskii A L 2005 *Fiz. Tverd. Tela* **47** 577
- [20] Li W F, Zhang Z D, Li D and Zhao X G 2004 *J. Phys. D: Appl. Phys.* **37** 1853
- [21] Gantmakher V F 2003 *Electrons in Disordered Systems* (Moscow: Fizmatlit) (in Russian)
- [22] Shklovskii B I and Efros A L 1984 *Electronic Properties of Doped Semiconductors* (Berlin: Springer)
- [23] Lee P A and Ramakrishnan T V 1985 *Rev. Mod. Phys.* **57** 287
- [24] Drozd V A, Gabovich A M, Pekała M, Boychuk V N, Moiseev D P and Nedilko S A 2002 *J. Alloys. Compounds* **346** 17
- [25] Drozd V A, Gabovich A M, Pekała M, Nedilko S A and Gierlowski P 2004 *J. Alloys. Compounds* **367** 246
- [26] Raychaudhuri A K 1995 *Adv. Phys.* **44** 21
- [27] Abeles B, Sheng P, Coutts M D and Arie Y 1975 *Adv. Phys.* **24** 407
- [28] Meilikhov E Z 2001 *Zh. Eksp. Teor. Fiz.* **120** 712
Meilikhov E Z 2001 *JETP* **93** 625 (Engl. Transl.)
- [29] Fu W F and Ijdo D J W 1995 *Solid State Commun.* **95** 581
- [30] Zhao J, Ross N L and Angel R J 2004 *Acta Crystallogr. B* **60** 263
- [31] Takasaki T, Ekino T, Muranaka T, Ichikawa T, Fujii H and Akimitsu J 2004 *J. Phys. Soc. Japan* **72** 1902
- [32] Ekino T, Takabatake T, Tanaka H and Fujii H 1995 *Phys. Rev. Lett.* **75** 4262
- [33] Altland A, Glazman L I and Kamenev A 2003 *Phys. Rev. Lett.* **92** 026801
- [34] Herranz G, Sánchez F, Martínez B, Fontcuberta J, García-Cuenca M V, Ferrater C, Varela M and Levy P 2004 *Eur. Phys. J. B* **40** 439
- [35] Sadovskii M V 1997 *Phys. Rep.* **282** 225
- [36] Collongues R 1971 *La Non-Stoechiométrie* (Paris: Masson) (in French)
- [37] Gabovich A M and Moiseev D P 1986 *Usp. Fiz. Nauk* **150** 599
Gabovich A M and Moiseev D P 1986 *Sov. Phys.—Usp.* **29** 1135 (Engl. Transl.)
- [38] Valeev Kh S and Kvaskov V B 1983 *Nonlinear Metallic Oxide Semiconductors* (Moscow: Energoizdat) (in Russian)
- [39] Wilson A H 1936 *The Theory of Metals* (Cambridge: Cambridge University Press)
- [40] Mott N F and Davis E A 1979 *Electron Processes in Non-Crystalline Materials* (Oxford: Clarendon)
- [41] Beloborodov I S, Lopatin A V, Schwiete G and Vinokur V M 2004 *Phys. Rev. B* **70** 073404
- [42] Bock A 1999 *Ann. Phys., Lpz.* **8** 441
- [43] Henkie Z, Cichorek T, Wojakowski A, Horyń R and Iwasieczko W 1992 *Physica C* **202** 97
- [44] Abrikosov A A 1987 *Fundamentals of the Theory of Metals* (Amsterdam: North-Holland)
- [45] Averin D V and Nazarov Yu V 1992 *Single Charge Tunneling. Coulomb Blockade Phenomena in Nanostructures* ed H Grabert and M H Devoret (New York: Plenum) p 217
- [46] Belous N A, Gabovich A M, Moiseev D P, Postnikov V M and Chernyakhovskii A E 1986 *Sov. Phys.—JETP* **64** 159
- [47] Belous N A, Chernyakhovskii A E, Gabovich A M, Moiseev D P and Postnikov V M 1988 *J. Phys. C: Solid State Phys.* **21** L153
- [48] Ausloos M and Houssa M 1999 *Supercond. Sci. Technol.* **12** R103
- [49] Fenton J C, Thomas P J, Yang G and Gough C E 2002 *Appl. Phys. Lett.* **80** 2535
- [50] Anagawa K, Yamada Y, Shibauchi T, Suzuki M and Watanabe T 2003 *Appl. Phys. Lett.* **83** 2381
- [51] Krasnov V M, Yurgens A, Winkler D, Delsing P and Claeson T 2000 *Phys. Rev. Lett.* **84** 5860
- [52] Krasnov V M, Kovalev A E, Yurgens A and Winkler D 2001 *Phys. Rev. Lett.* **86** 2657
- [53] Zavaritsky V N 2004 *Phys. Rev. Lett.* **92** 259701
- [54] Krasnov V M, Sandberg M and Zogaj I 2005 *Phys. Rev. Lett.* **94** 077003