Comment on “Conduction states in oxide perovskites: Three manifestations of Ti$^{3+}$
Jahn-Teller polaron in barium titanate”

S. A. Prosandeev, 1 I. P. Raevski, 1, 2 and M. A. Bunin 2

1 Physics Department, Rostov State University, 5 Zorge St., 344090 Rostov on Don, Russia
2 Research Institute of Physics, Rostov State University, 190 Stachki ave., 344090 Rostov on Don, Russia

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We have a remark to Sec. 6 were the authors discuss polaron bound to doubly charged oxygen vacancies $V_{O}^{++}$.

By using EPR spectroscopy, Scharfschwerdt et. al. found in reduced BaTiO$_3$ a signal which they attributed to a symmetry broken state of Ti$^{3+}$ bound to $V_{O}^{++}$ ($V_{O}^{++}\text{Ti}^{3+}$). Later on, theoretical studies performed in the framework of a Green function approach considered possible reasons for such symmetry breaking. Within that study the electron’s activation energies were obtained in accordance with data on electroconductivity which we will discuss below.

Theoretical studies did not consider the states of the $F$-center-type (a vacancy centered, symmetric electron density), but, later, computations showed that the states of the $F$-center type, in the single charged oxygen vacancy ($V_{O}^{+}$), can have lower energy than the states of the $V_{O}^{++}\text{Ti}^{3+}$-type. However, the EPR signal of such states has not been found experimentally.

Hence, there is a seemingly contradiction between the experimental results and results of theoretical computations. In order to resolve this contradiction, Lenjer et. al. suggest that the oxygen vacancy $V_{O}$ in BaTiO$_3$ is a negative-U center. This could explain the absence of the EPR signal of $V_{O}^{+}$. The presence in experiment of the EPR signal of a symmetry broken state Lenjer et. al. relate to an overpopulated state of the oxygen vacancy having 3 electrons ($V_{O}\text{Ti}^{3+}$). The third electron, in the authors’ opinion, sits at the Ti site nearest to $V_{O}$ but the source of the existence of this third electron on $V_{O}$ was not discussed, but, probably, it can arise due to Nb doping of BaTiO$_3$ which Scharfschwerdt et. al. employed in their experiment in order to compensate acceptor-type Na impurities.

The main assumption of Lenjer et. al. regarding the negative-U center seems to contradict the theoretical computations which obtained that $V_{O}$ is a positive $U$-center. There can be also contradictions with experimental data on electroconductivity which we want to discuss in more details.

It is well-known that the electroconductivity of perovskites strongly depends on the degree of the reduction of the sample. The crystals in which the donors are nearly fully compensated by acceptors are transparent and have low conductivity. The strongly reduced samples are often dark (and even black) and have a strong conductivity of n-type. Notice that, during the reduction process, only the $V_{O}$ concentration is increased. Hence, the average number of electrons on $V_{O}$ in this experiment cannot be more than 2. However, in order that the room conductivity is high, the electron energy levels of $V_{O}$ should be small, about 0.1 eV. The activation energy of $V_{O}^{+}$ we will discuss below.

In disagreement with these experimental facts INDO computation predicts that the $V_{O}^{+}$ electronic energy level in KNbO$_3$ is about 0.6 eV above the top of the valence band (2.7 eV below the bottom of the conduction band), and the difference between the energies of $V_{O}$ and $V_{O}^{+}$ is positive, and it is about 0.3 eV. This is a mystery, how it is possible to explain the high electric conductivity and black color of the heavily reduced samples of perovskites together with the high activation energy of electrons in $V_{O}$? However this computation is in line with other computations of $V_{O}$ in perovskites showing the presence of deep $V_{O}$ states of the $F$-center type.

This puzzle should be resolved somehow.

Experimental data on electroconductivity in SrTiO$_3$ show that, depending on the degree of reduction, the Fermi energy $E_F$ in the expression $\sigma \sim \exp [(E_F - E)/k_BT]$ changes (here $E$ is the energy of the bottom of the contactance band): there were observed $E - E_F = 0.35$ eV, $0.18$ eV, and $\leq 0.1$ eV. The first value was related to the case when the population of $V_{O}^{+}$ is very small and $E_F$ coincides with the electronic energy level of $V_{O}^{+}$. The second value ($0.18$ eV) corresponds to the case when the population of $V_{O}^{+}$ is high and $E_F$ lies in the middle between the energy level of $V_{O}^{+}$ and the bottom of the conduction band. The final, $\leq 0.1$ eV, small energy was related to the case of $V_{O}$ with 2 electrons. From similar analysis for BaTiO$_3$, the following Fermi energies were obtained: 0.55 eV, 0.28 eV, 0.1 eV. In CaTiO$_3$: 0.15 eV, 0.08 eV, and $\leq 0.1$ eV. From these data it was deduced that, in BaTiO$_3$, the activation energies of $V_{O}^{+}$ are about $E_1 = 0.55$ eV and the activation energy of $V_{O}$ is $E_2 \leq 0.1$ eV; in SrTiO$_3$, $E_1 = 0.35$ eV and $E_2 < 0.1$ eV; and in CaTiO$_3$, $E_1 = 0.15$ eV and $E_2 < 0.1$ eV. Notice that these energies were observed in samples having different degrees of reduction and, in particular, different color, black or gray (very small activation energies) or light-yellow (comparatively deep levels). No other donors besides $V_{O}$ were used (there are no Na and Nb additions in these experiments in contrast to the experiment of Scharfschwerdt et. al.).
In semiempirical theoretical studies, it was obtained that the symmetry broken electronic state $V_{O}^{+}Ti^{3+}$ has the energy about 0.2 eV with respect to the conduction band bottom plus the polaronic energy connected with the interaction of the microscopic dipole with lattice polarization. This is in very good agreement with the data on electroconductivity. However this scheme contradicts the results of modern embedded cluster computations.

In principle, one could connect the first two values of the Fermi energy (for instance, in BaTiO$_3$, 0.55 eV and 0.28 eV with respect to the bottom of the conduction band) with $V_{O}^{+}$ and $V_{O}$ respectively. However, it is not clear again the origin of the value $E - E_F \approx 0.1$ eV as well as the large gain of electroconductivity in heavily reduced samples and their black color. Besides the explanation given above, one could also consider $V_{O}$ clusters, surface conductivity, and a strong decrease of the polaronic energy in reduced samples. In this connection we want to cite reference where in which it was shown that the oxygen vacancies have a tendency to ordering, especially when their concentration increases. The $F$-center state can be destroyed in such pairs and this can help appearing the low-energy electronic states.

Lenjer et al. also argue that, in experimental study, $V_{O}^{+}$ was not found. We stress that $V_{O}^{+}$ exists in a thin interval of the relative donor/acceptor concentration. In order to see these states one should slowly vary the degree of the reduction or oxidation of the sample. At a given donor/acceptor concentration ratio there are vacancies with presumably one charge state because of a strong difference between the electronic energies of $V_{O}$ and $V_{O}^{+}$.

The electroconductivity data are consistent with the existence of three possible states of $V_{O}$ having zero, one or two electrons respectively (the first state having zero electrons does not contribute to the conductivity). The small value of one of the activation energies is connected with the state of $V_{O}$ having two electrons; the electrostatic interaction between these electrons makes this state rather shallow. The comparatively large activation energy is connected with $V_{O}^{+}$. The large difference between these energies in BaTiO$_3$ and CaTiO$_3$ was explained by stronger polaronic effect in BaTiO$_3$ due to softer lattice dynamics. We want also to cite a study in which it was shown that reduced samples of barium titanate exhibit paramagnetic susceptibility. All these experimental findings are consistent with the assumption of the existence of $V_{O}^{+}$ although its appearance requires rather strong inequalities on the donor/acceptor concentration ratio. Other possible explanations of these data and new schemes of computations should be explored in order to understand the origin of the contradiction of this scheme with present time computations.

Unfortunately, it is not clear from the experimental data on EPR if the thermal activation energy of the “third electron on $V_{O}$” is comparable with the activation energy of “$V_{O}^{+}$” obtained from electroconductivity. In any case, it would be helpful to analyze the EPR data together with data on electroconductivity and, perhaps, also on optics (see discussions, for instance, in references). In our opinion, first-principles computations should be also developed further in order to explain the experimentally observed activation energies connected with $V_{O}$ and their tendencies in sequences of perovskites. Finally, the electronic structure of $V_{O}$ and $V_{O}^{+}$ remain a mystery and further studies are necessary.

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