

Research Article

Conventional interactions and the Pr⁴⁺-ion states in PrO₂

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We have pointed out the scientific importance of the experimental clarifying (Phys. Rev. Lett. **86** (2001) 2082) of the electronic state of the Pr ion in PrO₂ and the role of the intermediate valence and the covalent bonding. We have pointed out the substantial applicability of the crystal-field (CEF) model to PrO₂ (the existence of well-defined atomic-like states of the Pr⁴⁺ ion) and that the simple point charge model provides surprisingly good estimates for the sign and the strength of the octupolar CEF interactions.

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Description of electronic and magnetic properties of compounds containing open-shell atoms is one of the long-standing problem of the modern solid-state physics. One can be surprised but the electronic ground state of PrO₂, one of the simplest compound, has been controversial for many years, see Refs 3-6 of Ref. [1]. The experimental paper about PrO₂ [1], just recently published, significantly enlightens the electronic ground state of PrO₂. Of course, it does not fully solve the problem of PrO₂ as now weaker interactions come to the game, but now we know that these weaker interactions play on the electronic Γ_8 ground quartet.

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The aim of the present Letter is to point out the importance of the experimental establishing of the electronic ground state of PrO_2 . In particular, the founding that the Pr ions are almost entirely in a localized $4f^1$ configuration.

We fully agree with authors of Ref. [1] in the conclusion that the observation of the localized low-energy ($E < 730$ meV) excitations, that have been largely predicted [2, 3] and are presently perfectly understood within the atomic-like $4f^1$ configuration, rules out the physical significance of other theoretical models including the intermediate valence model as well as a model with the significant covalent mixing of f and oxygen $2p$ states.

We would like to point out that this conclusion of Ref. [1] is in agreement with the general idea of the Quantum Atomistic Solid State (QUASST) theory [4, 5] that points out the preservation of the discrete atomic-like open-shell $3d/4f/5f$ states also in the case when the paramagnetic atom becomes the full part of the solid.

For the ideal composition PrO_2 one expects within the QUASST theory the existence of the Pr^{4+} ion in the $4f^1$ configuration, states of which are primarily described by the atomic physics. The solid-state physics phenomena are basically going on on low-energy CEF-like states. Thus, the methodology of QUASST is that the description of electronic and magnetic properties of $3d$, $4f$ and $5f$ compounds should start from the evaluation of the atomic-like energy structure with the energy accuracy of the low-lying states, i.e. even below 1 meV. This structure is predominantly determined by the spin-orbit coupling and crystal-field interactions. The latter can be of a quite low symmetry, reflecting the local atomic-scale symmetry of charge surroundings. For the formation of the magnetic state spin-dependent interactions have to be taken into account to break the time reversal symmetry and to split the Kramers-doublet ground state, for instance.

The main message of QUASST can be thought to be quite simple. However, we would like to point out that the appearance of such sophisticated theoretical model involving the intermediate valence and the covalent mixing for PrO_2 , one of the simplest compound, indicates that it is not so. The more, these models appear in quite prestigious physical journals in the recent years and these sophisticated theories have appeared despite of the first experimental evidence for the $4f^1$ configuration in PrO_2 in 1984 [2]. It means that the first-glance quite natural QUASST theory, being somehow an extension of the ionic model, is not so natural for all physicists.

From a scientific point of view very interesting is a fact that the electronic structure is exactly such as predicted by the ionic model - two

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multiplets with the ${}^2F_{5/2}$ -multiplet lower, that is split for the quartet Γ_8 (lower) and doublet Γ_7 by 131 meV; **the Γ_8 ground state results from the cubic 8 oxygen anion surroundings.** We have calculated the Γ_8 – Γ_7 splitting taking into account the first coordination sphere (cube) with the experimental distance of Pr-O^{2-} as $2.334 \text{ \AA} = 4.41 a_o$, a_o is the Bohr radius, resulting from the lattice parameter $a=5.39 \text{ \AA}$, and the octupolar parameters of the f shell of the Pr^{4+} ion, $\beta = +2/315$ and $\langle r^4 \rangle = 4.0 a_o^4$. These values result in the CEF B_4^0 parameter of -3.73 K (z axis along the cube edge) [6]. It is only by 12 % different [7] from the value of -4.22 K coming out from the experimental value of 131 meV. It means that the simple point charge model provides surprisingly good estimates for the strength of the octupolar CEF interactions.

Thus, the solid PrO_2 should be considered as formed by conventional electrostatic interactions among Pr^{4+} and O^{2-} ions. These electrostatic interactions are of the multipolar character. We expect PrO_2 to be an insulator, electric properties of which resembles that of the semiconductor due to not perfect stoichiometry. The O^{2-} anions have complete shells and we expect them not to contribute to the magnetism and to the low-energy electronic structure. Thus we expect the magnetism and the low-energy electronic structure of PrO_2 to be largely determined by Pr^{4+} ions. Properties of the Pr^{4+} ion in the stoichiometric PrO_2 are to large extend described by atomic physics and conventional interactions. We think within QUASST about the Pr^{4+} ion as the $4f^1$ configuration in, say, 99 % - the authors of Ref. 1 on basis of the neutron experiment came out to a conclusion with, at least, 90 %. The main left problems are 1) the way of the removal of the degeneracy of the quartet and 2) the removal of the Kramers degeneracy of the ground state. Obviously, a lattice distortion splits the quartet into two doublets, as then the system can lower the energy by the Jahn-Teller effect, but Nature still have many possibilities to realize this splitting, including the different distortion modes, the differentiation of the Pr ions (the breathing mode) with respect to local lattice distortions and the dynamic Jahn-Teller effect. The removal of the double Kramers degeneracy of the ground state surely undergoes at T_N (of 14 K) what should manifest as a λ -type of peak.

In order to clarify details of the removal of the quartet degeneracy magnetic measurements on the single crystal and the heat capacity measurements are strongly awaited. The magnetic measurements should reveal the anisotropic behaviour whereas the heat-capacity measurements should confirm the presence of the λ peak and enlightens the degeneracy and the quartet energy splitting. The presently available magnetic measurements seem to be largely unreliable in this respect whereas we

are not aware of heat-capacity measurements.

In conclusion, we have pointed out the scientific importance of the experimental clarifying of the electronic state of the Pr ion in PrO₂ and the negligible role of the intermediate valence and the covalent bonding. We point out the applicability of the CEF model to PrO₂ (the existence of well-defined atomic-like states of the Pr⁴⁺ ion) and that the simple point charge model provides surprisingly good estimates for the sign and the strength of the octupolar CEF interactions.

This paper has been written in May 2001 - then this paper was consulted with Prof. A. Furrer. Properties of PrO₂ and other dioxides like UO₂ and NpO₂ are still of current interest [8–10]. The main result of this paper is still valid - the CEF splitting can be calculated from the conventional electrostatic interactions, the point-charge model, taking $\langle r_f^4 \rangle$ for the Pr⁴⁺ ion as 4.5 a_o⁴.

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