# Band or Polaron: The Hole Conduction Mechanism in the p-Type Spinel Rh_2ZnO_4

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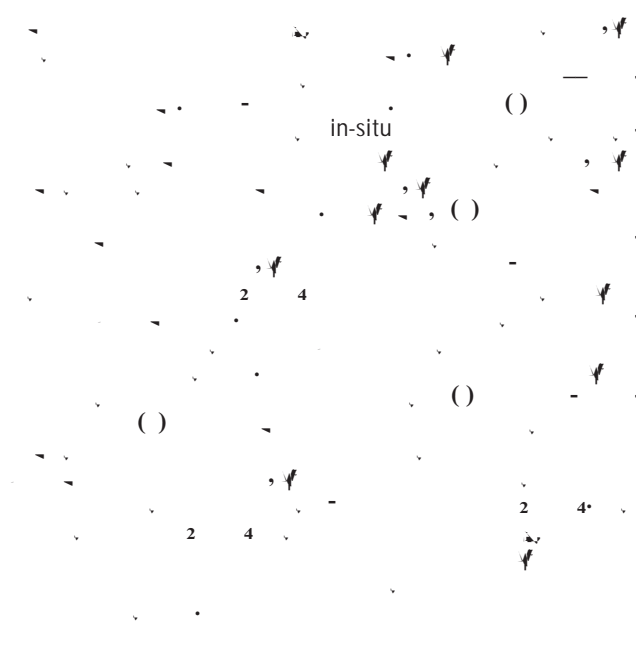
THE A_2BO_4[‡‡] oxide spinels have long been known and utilized for their soft magnetic/ferrimagnetic properties,[1] with more recent attention being given to their magnetoresistive[2] and multiferroic properties.[3] Since the past decade, however, there has been increasing interest in their potential as transparent conductors[4–6] with the possibility for applications in semiconductor devices and photovoltaics. For example, a p–n junction has been demonstrated using a p-type spinel in the amorphous state.[7,8] Determination of the mechanism of conductivity of holes in these potential transparent conducting oxides (TCOs) may be crucial for the future design of better p-type TCOs.

Electrical conductivity in spinel oxides is usually associated with materials that are wide-gap insulators in their stoichiometric and undoped perfect A_2BO_4 structure, but that become conductive owing to specific deviations from stoichiometry leading to generation of excess carriers. Examples of normal spinels that are wide gap insulators in their pristine A_2BO_4 form include systems where the trivalent A atom located on the octahedral site (O_h point group symmetry), as well as the divalent B atom located on the tetrahedral site (T_d), have a closed shell d^0 (e.g., Al, Mg) or d^{10} (e.g., Ga, Zn) configuration. In Rh_2ZnO_4, where the Rh^{+III} ions have an open-shell d^6 configuration (low-spin, S = 0), the insulating gap is formed due to the crystal field splitting: After hybridizing with the O-p states, the fully occupied Rh-t_{2g} forms the valence band, and the unoccupied Rh-e_g state forms the conduction band, as shown in Fig. 1. Along the series of A_2ZnO_4 spinels (A = Co, Rh, Ir), the optical band gaps were measured as 2.26, 2.74, and 2.97 eV, respectively.[4] A recent theoretical work by Scanlon et al.[9] calls into question the magnitudes of these band gaps, but we note that these materials are at least partially transparent to lower energy visible light, making them candidate materials for p-type TCOs.

To obtain p-type conductivity in these otherwise insulating spinels, one must create acceptor-type lattice defects, which can result from o -stoichiometry at finite temperatures. As would-be hole producing cation vacancies require rather high energy to form,[10] the main source of hole
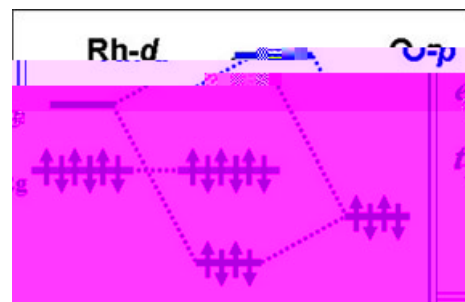
. 1. Nature of the insulating gap in Rh_2ZnO_4 with a low-spin d^6

production in these spinels is the anti-site defect, where a B-cation substitutes for the A-cation on the O_h site, i.e., Zn_{Rh} in Rh_2ZnO_4. In Rh_2ZnO_4, at thermodynamic equilibrium, the calculated maximum number of acceptor-like anti-site defects $N(Zn_{Rh})$ is approximately 10^{20} cm^{-3}, whereas the number of cation vacancies $N(V_{Zn})$ is 10^{17} cm^{-3} and $N(V_{Rh})$ is 10^{14} cm^{-3}. The concentration of donor-like defects $N(Rh_{Zn})$ is 10^{15} cm^{-3}, and $N(V_O)$ is 10^{10} cm^{-3}. Spinel oxides in general can be divided into four "doping

(2) Transport Measurements

Room temperature four-point DC conductivity and thermopower measurements were taken. The specimen was then cut into a bar-shaped geometry with dimensions approximately 10.5 mm 9 4.5 mm 9 1.5 mm, and in-situ electrical measurements were performed from 250 C to 580 C using a previously reported technique.[26,27] For the Hall measurement, the sample was attached to the copper tongue of an 8-pin mount by a thin layer of adhesive grease, which was thermally conductive, but electrically insulating. Four silver stripes were pasted to the four sides of the sample, the width ranging from 1.7 to 3.0 mm, and four indium contacts were soldered onto the stripes. The indium contacts could not be directly soldered to the sample because of its relatively high thermal conductivity. The Van der Pauw method was used to measure Hall resistivity as a function of magnetic field. As the widths of the silver stripes (and hence the e ective contact areas) were large compared with the sample dimensions, the Hall measurement was accurate to within 20%. Hall measurements were carried out in a magnetic field up to 15 T with a 1.7 Hz alternating current source using lock-in techniques, and averaging four up-and-down magnetic field sweeps of both polarities. The data between 0 and 1 T have been removed as they represent purely instrumental noise.

(1) Predictive First-Principles Theory for the Nature of Holes in Rh_2ZnO_4

To predict from electronic structure theory whether a semiconductor (or insulator) shows band- or small polaron conductivity, one needs a method that accurately describes the energy di erence between the delocalized state at the band edge (here, the valence band maximum), and the localized self-trapped state, which can usually be described by a change in the oxidation state (here, Rh^{+IV} instead of Rh^{+III} or O^{-I} instead of O^{-II}). Unfortunately, this requirement is

localize a hole in an O-p orbital at such energies far below the VBM. In the sum, E_{loc}

can be combined to eliminate the carrier density p:

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