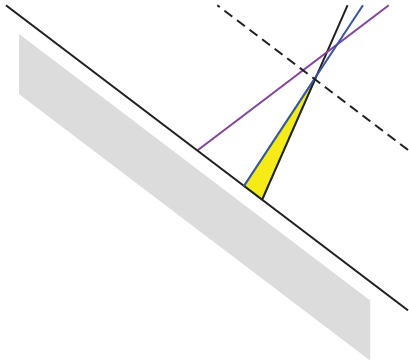






known as self doping. In fact, in the majority of the spinels, this process is the main source of charge carriers.<sup>18</sup>

Experimentally, site occupancy can be measured by several techniques, such as anomalous x-ray diffraction (AXRD), extended x-ray absorption fine structure (EXAFS), neutron diffraction,  $M^{\cdot\cdot}$



of  $\text{Co}/(\text{Zn} + \text{Co}) = 0.633$  were additionally prepared at 390 °C, 450 °C, and 575 °C.] During sintering the pellets were surrounded by sacrificial powder of the same composition and nested inside three concentric crucibles, in order to minimize both contamination and cation volatilization. The extended

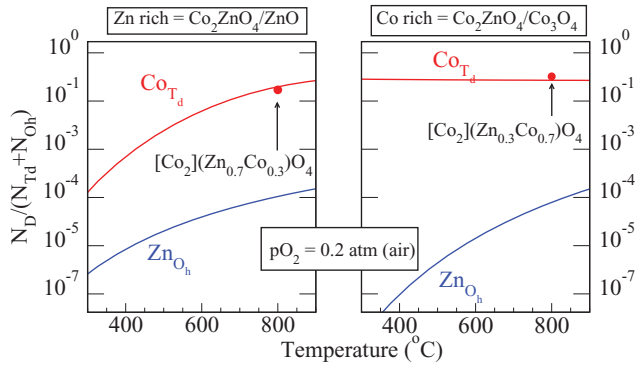


FIG. 6. (Color online) Calculated fraction of antisite defects in  $\text{Co}_2\text{ZnO}_4$  under Zn-rich (left) and Co-rich (right) conditions compared with those (solid circle) measured using AXRD in bulk ceramic sintered samples.

are occupied by Co. The  $T_d$  sites are comprised of all of the Zn and the excess Co (0.3 for the  $\text{Co}_{2.3}\text{Zn}_{0.7}\text{O}_4$  sample and 0.7 for the  $\text{Co}_{2.7}\text{Zn}_{0.3}\text{O}_4$  sample), thus making these samples normal spinels. Figure 6 shows a comparison of the experimentally determined site occupancy to the defect calculations for  $800^\circ\text{C}$  in air. There is excellent quantitative agreement for the Co occupancy on  $T_d$  sites between the measurement and the calculation. A stoichiometry of  $\text{Co}_{2.3}\text{Zn}_{0.7}\text{O}_4$  is calculated at the  $\text{Co}_2\text{ZnO}_4/\text{ZnO}$  boundary at  $800^\circ\text{C}$ , similar to that of the  $\text{Co}_{2.3}\text{Zn}_{0.7}\text{O}_4$  sample, while a stoichiometry of  $\text{Co}_{2.5}\text{Zn}_{0.5}\text{O}_4$  is calculated at the  $\text{Co}_2\text{ZnO}_4/\text{Co}_3\text{O}_4$  boundary at  $800^\circ\text{C}$ ,

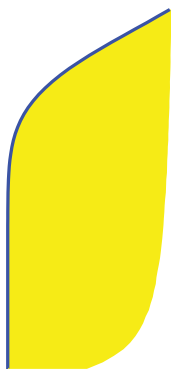


TABLE I. Table shows different  $A_2BO_4$  spinels, corresponding  $A$ -rich and  $B$ -rich phases, and predicted nonstoichiometry deviation. Structure of competing phases that are similar to the host spinel are given in the parentheses. Hausmannite (H) has a distorted spinel structure.



where  $\Delta H(A_{T_d}) \approx 0.0$  eV and  $\Delta H(B_{O_h}) = 0.86$  eV so the system is *B* deficient, by  $\text{Cr}_2\text{MnO}_4$ , where  $\Delta H(A_{T_d}) = 1.98$  eV and  $\Delta H(B_{O_h}) = 0.73$  eV so the system is *A* deficient. However, in compounds such as  $\text{Al}_2\text{MgO}_4$  [ $\Delta H(A_{T_d}) = 0.40$  eV;  $\Delta H(B_{O_h}) = 0.55$  eV] and  $\text{Ga}_2\text{CdO}_4$  [ $\Delta H(A_{T_d}) = 0.28$  eV;  $\Delta H(B_{O_h})$

TABLE III. (*Continued.*)

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Overall specimen<sup>b</sup>

