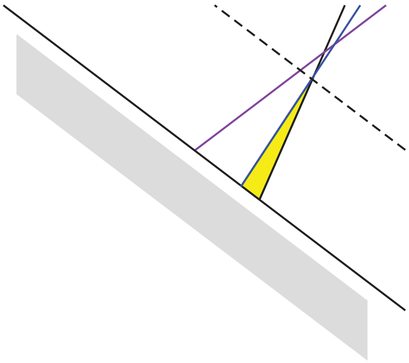
known as self doping. In fact, in the majority of the spinels, this process is the main source of charge carriers.[18]

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¨



of $\mathrm{Co}/(\mathrm{Zn}+\mathrm{Co}) = 0.633$ 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

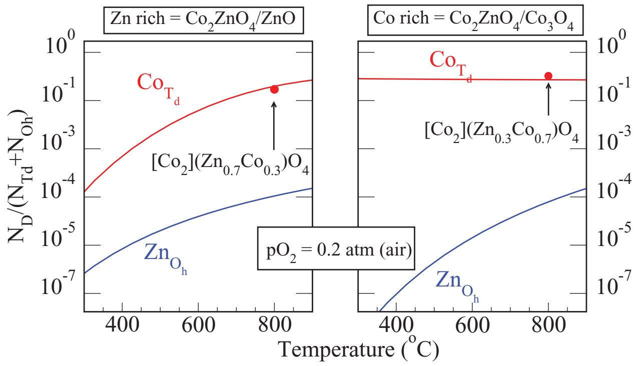


FIG. 6. (Color online) Calculated fraction of antisite defects in Co_2ZnO_4 under Zn-rich (left) and Co-rich (right) conditions compared with those (solid circle) measured using AXRD in bulk ceramic sintered samples.

are occupied by Co. The T_d sites are comprised of all of the Zn and the excess Co (0.3 for the $Co_{2.3}Zn_{0.7}O_4$ sample and 0.7 for the $Co_{2.7}Zn_{0.3}O_4$ sample), thus making these samples normal spinels. Figure 6 shows a comparison of the experimentally determined site occupancy to the defect calculations for 800 °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 $Co_{2.3}Zn_{0.7}O_4$ is calculated at the Co_2ZnO_4/ZnO boundary at 800 °C, similar to that of the $Co_{2.3}Zn_{0.7}O_4$ sample, while a stoichiometry of $Co_{2.5}Zn_{0.5}O_4$ is calculated at the Co_2ZnO_4/Co_3O_4 boundary at 800 °C,4

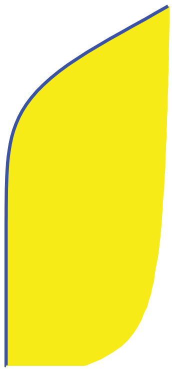


TABLE I. Table shows different A_2BO_4 spinels, corresponding A-rich and B-rich phases, and predicted nonstoichiometry deviation. Structure of competing phases that are similar to the host spinel are given in the parentheses. Hausmannite (H) has a distorted spinel structure. Thus, in the table, if structure of only one competing phase is given, such spinel would deviate toward that cation, whereas if both competing phases have spinel-like structure, the spinel phase would be nonstoichiometric toward the competing phase that is more similar to spinel than the other. In the final column, – means not known.

Compound(S)	A-rich phase	B-rich phase	Predicted nonstoichiometry	Observed nonstoichiometry
Al_2MgO_4	Al_2O_3	MgO	Neither	Both
Ga_2CdO_4	Ga_2O_3	CdO	Neither	Ga
Mg_2TiO_4	MgO	TiO_2	Neither	Neither
Cr_2MnO_4	Mn_3O_4 (H)	Cr_2O_3	Mn	Mn
Co_2ZnO_4	Co_3O_4 (S)	ZnO	Co	Co
Rh_2				

where $\Delta H(A_{\mathrm{T_d}}) \approx 0.0$ eV and $\Delta H(B_{\mathrm{O_h}}) = 0.86$ eV so the system is B deficient, by Cr_2MnO_4, where $\Delta H(A_{\mathrm{T_d}}) = 1.98$ eV and $\Delta H(B_{\mathrm{O_h}}) = 0.73$ eV so the system is A deficient. However, in compounds such as Al_2MgO_4 [$\Delta H(A_{\mathrm{T_d}}) = 0.40$ eV; $\Delta H(B_{\mathrm{O_h}}) = 0.55$ eV] and Ga_2CdO_4 [$\Delta H(A_{\mathrm{T_d}}) = 0.28$ eV; $\Delta H(B_{\mathrm{O_h}}$

TABLE III. (*Continued.*)

	Overall specimen[b]