Resolution of the Ambiguity of Valence States in Spinels Containing Manganese and Iron

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The dilemma of whether $[Fe^{+3}Mn^{+2}]$ or $[Fe^{+2}Mn^{+3}]$ are the stably coexisting species on the octahedrally ligated sites of the spinel structure has been resolved by the application of a crystallographic, rather than a magnetic criterion. The solid solution systems $(Zn[Mn_2]O_4)_{1-x} \cdot (Zn_{0.5}Ge_{0.5}[FeMn]O_4)_x$ and $(Zn[FeMn]O_4)_x \cdot (Zn_{0.5}Ge_{0.5}[Mn_2]O_4)_{1-x}$ were synthesized, and their lattice constants were determined. The compositions in these systems for which cooperative tetragonal distortion occurs, due to the Jahn-Teller effect for Mn^{+3}, depend on whether $[Fe^{+3}Mn^{+2}]$ or $[Fe^{+2}Mn^{+3}]$ are stably coexisting species. The crystallographic findings are in complete agreement with the latter valence assignment. Furthermore, the axial ratios are found to be in quantitative agreement with the theory of cooperative distortions advanced by Wojtowicz, provided that the valence assignment $[Fe^{+2}Mn^{+3}]$ is assumed. The valence behavior observed in the systems studied probably obtains for most other spinels in which iron and manganese coexist on the octahedrally ligated sites.

Unlike magnetic criteria which have been proposed to clarify the valence assignment, the method reported is not subject to ambiguities such as the existence or nonexistence of complex ferrimagnetic coupling schemes (e.g., Yafet-Kittel angular coupling) and "spin quenching."

IT is sometimes impossible to assign, on the basis of stoichiometry, unambiguous valences to the various cations in transition metal compounds. For example, the spinel $CuMn_2O_4$ may have the valence distribution $Cu^{+2}Mn_2^{+3}O_4$, $Cu^{+1}Mn^{+3}Mn^{+4}O_4$, or some distribution intermediate to these. The known oxidation-reduction equilibria in aqueous solutions are generally used as the basis for valence assignments in oxidic compounds, since the crystal field stabilization and other factors influencing the thermodynamic properties are usually nearly the same for both oxides and hydrated ions. A possible exception to this rule has been proposed for the case of manganese ferrite, $MnFe_2O_4$.[1] In order to explain the 0°K saturation moment[2] of 4.6 rather than 5.0 μ_B, it is postulated that all of the manganese on the octahedrally ligated spinel sites (hereafter designated as B sites) exists as Mn^{+3}, and that an equivalent amount of octahedrally ligated iron exists as Fe^{+2}. (In aqueous solutions Fe^{+2} and Mn^{+3} cannot coexist in appreciable concentrations.) Baltzer[3] has pointed out that such a reversal in oxidation-reduction equilibrium may be due to a larger value of the crystal field parameter Dq for ions on the B sites than for hydrated ions. This explanation is reasonable, since the observed moment and ionic distribution data for $MnFe_2O_4$ require that the reversal does not take place on the tetrahedrally ligated sites at room temperature, or on the B sites at temperatures greater than about 1000°K. In each of these cases the value of Dq is lower than what is expected for B sites at room temperature.

The occurrence of reduced moments in ferrimagnetic compounds cannot be used as the sole criterion for the assignment of valence states. Extremely high anisotropy fields which prevent saturation, and departures

from the simple Néel coupling scheme, including Yafet-Kittel angular coupling, could also lower the moment from the usual value. If the Curie constants of paramagnetic compounds containing iron and manganese ions with an average valence of 2.5 are found to correspond to 4, rather than 5 μ_B per paramagnetic ion, then the aforementioned vagaries in ferrimagnetic behavior can be ruled out as causes of the low moment. However, such measurements still cannot be regarded as unequivocal evidence for the coexistence of Fe^{+2} and Mn^{+3}, since the result could be explained by the quenching of spins of some of the Fe^{+3} and/or Mn^{+2} ions to the doublet state.

The results reported here use a crystallographic, rather than a magnetic criterion to establish the valence states, so that the ambiguities mentioned above do not enter. Of the ionic species that can be present in the systems considered, Mn^{+3} is unique in that it possesses a Jahn-Teller effect large enough to cause cooperative tetragonal distortions in spinels. Investigations of numerous systems[4] show that at room temperature, tetragonal distortions from cubic symmetry are observed in spinels when more than about 60% of the B sites are occupied by Mn^{+3}. For appropriately selected solid solutions having the spinel structure the elemental composition corresponding to 60% occupancy of the B sites by Mn^{+3} ions will depend on whether Fe^{+3} and Mn^{+2} (Model I) or Fe^{+2} and Mn^{+3} (Model II) are the stably coexisting valence states. Thus, in the system $(Zn[Mn_2]O_4)_{1-x} \cdot (Zn_{0.5}Ge_{0.5}[FeMn]O_4)_x$ (where the brackets enclose ions occupying the B sites), a tetragonal region in the phase diagram is expected to persist to $x=0.4$ if the coexisting valence states are predominantly Fe^{+3} and Mn^{+2}; to $x=0.8$ if the valence states are predominantly Fe^{+2} and Mn^{+3}, and to a value inter-

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[3] P. K. Baltzer (private communication, 1957).

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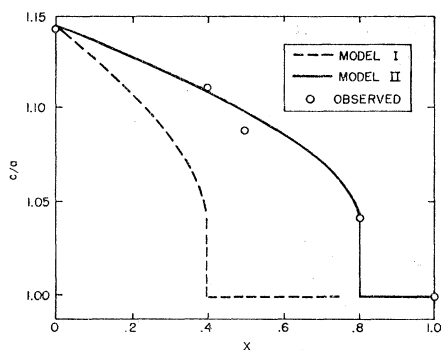
FIG. 1. Calculated and observed c/a ratios in the $(Zn[Mn_2]O_4)_{1-x} \cdot (Zn_{0.5}Ge_{0.5}[FeMn]O_4)_x$ system.

TABLE I. Lattice parameters and valence states in the system $(Zn[Mn_2]O_4)_{1-x} \cdot (Zn_{0.5}Ge_{0.5}[FeMn]O_4)_x$.

| x | Valence distribution of ions on B sites | | a_0 (A) | c_0 (A) | c/a |
	Model I	Model II			
0.0[a]	Mn_2^{+3}	Mn_2^{+3}	8.076	9.225	1.142
0.4	$Fe_{0.4}^{+3}Mn_{0.4}^{+2}Mn_{1.2}^{+3}$	$Fe_{0.4}^{+2}Mn_{1.6}^{+3}$	8.20	9.12	1.11
0.5	$Fe_{0.5}^{+3}Mn_{0.5}^{+2}Mn^{+3}$	$Fe_{0.5}^{+2}Mn_{1.5}^{+3}$	8.238	8.965	1.088
0.8	$Fe_{0.8}^{+3}Mn_{0.8}^{+2}Mn_{0.4}^{+3}$	$Fe_{0.8}^{+2}Mn_{1.2}^{+3}$	8.37	8.724	1.042
1.0	$Fe^{+3}Mn^{+2}$	$Fe^{+2}Mn^{+3}$	8.470	$\cdots$	1.000

[a] The crystallographic data for $Zn[Mn_2]O_4$ are taken from B. Mason, Am. Mineralogist **32**, 426 (1947).

mediate between 0.4 and 0.8 if all four ionic species can coexist in appreciable concentrations.

Representative compounds in this system were prepared by mixing appropriate amounts of ZnO, GeO$_2$, Fe$_2$O$_3$, and Mn$_2$O$_3$ in an agate "buzz mill," pressing the mixtures into pellets, and firing them for 90 minutes in air at 1150°C on a single-crystal MgO plate. The lattice parameters of these preparations are shown in Table I, along with the valence distribution on the B sites consistent with each of the aforementioned models. The occurrence of tetragonal distortion at $x=0.8$ suggests strongly that the ions coexist almost wholly as Fe^{+2} and Mn^{+3} (Model II).

The c/a ratios in spinels have been correlated with the amount of Mn^{+3} on the B sites by a theoretical treatment of cooperative distortions.[5,6] Figure 1 shows a plot of the observed c/a ratios *versus* x, with theoretical curves, I and II, calculated by Wojtowicz for each of the aforementioned models. His calculations assume that at room temperature cooperative distortion occurs when there is 60% or greater occupancy of the B sites by Mn^{+3}, and the c/a ratio for a spinel whose B sites are completely occupied by Mn^{+3} is about 1.144 (which has also been observed in numerous spinel systems). The agreement of the observed values of c/a with the shape of the calculated curve is decisive evidence for the correctness of the second of the alternative models.

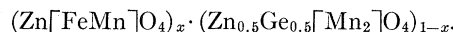[5] P. J. Wojtowicz, J. Appl. Phys. **30**, 30S (1959).
[6] P. J. Wojtowicz, Phys. Rev. **116**, 32 (1959).

Another series of compounds currently being investigated is the system

$$(Zn[FeMn]O_4)_x \cdot (Zn_{0.5}Ge_{0.5}[Mn_2]O_4)_{1-x}.$$

The end points $x=0$ and 1, which should have their B sites 50% occupied by Mn^{+3} regardless of which valence assignment is correct, are found to be cubic spinels with $a_0=8.494$ and 8.37 A, respectively. If Model I were correct, the B sites would be 50% occupied by Mn^{+3} throughout the entire system, and all compositions would be cubic spinels. If Model II were correct, the fraction of Mn^{+3} on the B sites would reach a maximum of 75% at $x=0.5$, and the system would show the unique behavior of having a tetragonal phase domain surrounded by two cubic phase domains. Tetragonality within this system has already been established, since its midpoint is identical to the midpoint of the $(Zn[Mn_2]O_4)_x \cdot (Zn_{0.5}Ge_{0.5}[FeMn]O_4)_{1-x}$ system, with a c/a ratio of 1.088. Further studies of this system should reveal whether the ion pair [Fe^{+2}Mn^{+4}] is more stable than [Fe^{+3}Mn^{+3}].

It can be concluded that in the spinel systems studied, and probably in most other oxidic spinels, Fe^{+2} and Mn^{+3}, rather than Fe^{+3} and Mn^{+2}, are the stably coexisting species on the B sites at room temperatures. If the equilibrium is reversed at higher temperatures, there should be a maximum in the conductivity at an intermediate temperature where all four ionic species coexist. Such measurements are intended at these laboratories.

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