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SUBJECT: AN APPROACH TO A RATIONALE IN FERRITE SYNTHESIS: EVALUATION OF MAGNETIC MOMENTS

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Abstract: A systematic development of broad classes of composite ferrites is given in terms of MO or R_2O_3 addition to a mother spinel under three groupings I-I, N-N, I-N which refer to systems involving two inverse spinels, two normal and one of each. The behavior of the related magnetic moments is examined in terms of composition for certain idealized conditions in the light of antiferromagnetic coupling of spins at the tetrahedral and octahedral sites. The conditions under which the magnetic moment shifts in direction (referred to as a reversal effect already observed in the system $NiO\cdot(Fe_2O_3)_{1-x}\cdot(A\ell_2O_s)_x)$ are established so that predictions can be made as to its general occurrence. Certain departures between theoretical and experimental magnetic moment dependence on composition are pointed out, and in particular, the interesting case of $MgO\cdot(Fe_2O_3)_{1-x}\cdot A\ell_2O_3$ is re-examined by allowance for incomplete inversion in $MgO\cdot Fe_2O_3$ itself--a procedure which still fails to reconcile theory with the reported observation, thus suggesting a closer scrutiny of this system.

Although magnetic spinels have been known for many years,[1] evidently no systematic basis for synthesis, particularly in the meaningful circumstance of mixed ferrites, has been explicitly delineated. Composite ferrites clearly are of special interest since they inherently permit greater variability in the magnetic and electrical properties, both in terms of composition as well as heat treatment.[2] The class of materials of present concern are those preparations adhering to the chemical formula $(MO)_x\cdot(M'O)_{1-x}\cdot(R_2O_3)_y\cdot(R_2'O_3)_{1-y}$;

such variations are possible as stem from single spinels having such formulae as $MO \cdot R_2O_3$ and $2MO \cdot RO_2$.[3] This latter aspect introduces no undue complications in the text to follow.

The systemization scheme for ferrite synthesis is developed from the point of view of characterizing I_s the saturation magnetization. The procedure to be described can readily be extended to other magnetic systems such as the perovskites and ferroxdures. The integrated scheme may be found helpful as a guide for future synthesis, and as will be seen, areas of unusual nature remain to be explored; during the course of this study, researchers at NOL have announced some interesting observations in the system $NiO \cdot (Fe_2O_3)_{1-x} \cdot (A\ell_2O_3)_x$ which fits nicely into our general pattern.[4] An understanding of how reversal of the magnetic moments arises and what critical conditions must be fulfilled for its manifestation is possible on the basis of the elementary treatment given here. Also the general nature of these reversals and the identification of other possible systems which allow such behavior are revealed.

Basic Foundations

To begin with, Néel's classic explanation[5] of the antiferromagnetic alignment of spins at the tetrahedral and octahedral sites serves as the cornerstone for direct and ready calculation of the resultant magnetic moment. Such calculations have indeed appeared in the literature.[6] These data and the simple theory offered here are actually premised on the following idealizations:

1. No upsetting lattice parameter or crystal structure changes occur over the composition range--any such drastic changes will clearly alter the exchange integral and the coupling strength between spins at the two distinct sites.
2. The atoms in the equilibrium state are ordered at the various sites--randomized arrangements are not to be considered in the interest of clarity, although an extension into this domain can be made if desired.
3. No significant departures from stoichiometric oxygen exist in the preparations--modified valencies affecting the normal atomic moments are excluded.
4. The system exhibits complete solid solubility--quantitative treatment for a multi-phase system becomes obscure.

We shall make use of two rather broad classifications of ferrite synthesis that have found their way into practice:

1. $MO \cdot R_2O_3 + x\,M'O \longrightarrow (MO)_{1-x} \cdot (M'O)_x \cdot R_2O_3$

2. $MO \cdot R_2O_3 + xR_2'O_3 \longrightarrow MO \cdot (R_2'O_3)_x \cdot (R_2O_3)_{1-x}$

The first of these conforms to the important ferroxcube series and has of course received considerable attention; the latter pathway, however, is relatively untrammeled and is indeed within the bounds of the NOL work referred to earlier.

In general, a given spinel will prefer a particular arrangement of the atoms so that as a reasonable approximation in the pure state either a normal or inverse structure occurs. That departure can arise is suggested by the observations that ordinarily magnesium ferrite is about 90% inverse.[7] Allowing for this latter possibility, we may still represent three underlying modes of synthesis by

$$\begin{cases} \text{I-I} \text{ --- } MO \cdot R_2O_3 \text{ inverse and } M'O \cdot R_2O_3 \text{ inverse} \\ \text{N-N} \text{ --- } \quad \text{etc.} \\ \text{I-N} \text{ --- } \end{cases}$$

Thus we arrive at the classification scheme within which framework certain elementary deductions are to be formulated.

<u>Group I $(MO)_{1-x} \cdot (M'O)_x \cdot R_2O_3$ Series</u>

Let us consider in turn the three sub-groups as outlined below:

1. I-I ——the atomic arrangements at the tetrahedral and octahedral sites can be represented in such a manner as

T	O
1R	1R (1-x) M x M'

where evidently this is the situation intermediate to either pure spinel, x being the fraction of M' introduced into the preparation. Employing the notation of μ_2, μ_1 and μ', as the individual magnetic moments for the ions R, M and M', respectively, the resultant magnetic moment in units of Bohr magnetons is simply

$$\begin{aligned} \mu_R &= \mu_2 + \mu_1(1-x) + \mu_1' x - \mu_2 \\ &= \mu_1 + x(\mu_1' - \mu_1) \end{aligned}$$

For $\mu_R \neq 0$, R must have an atomic moment and the general appearance of the μ_R vs. composition plot is shown in Figure 1.

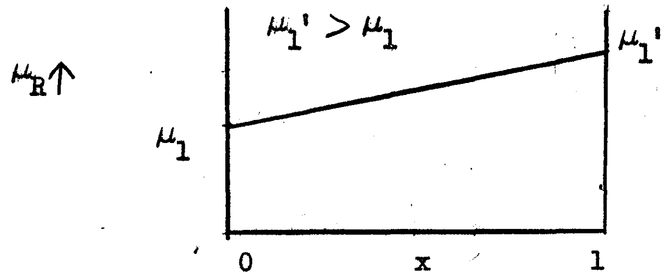
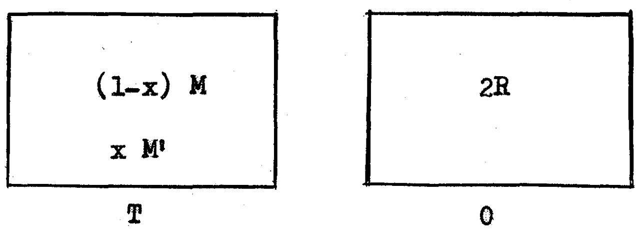


Figure 1

Symmetry allows interchange of μ_1 and μ_1' with $x' = 1-x$ and so a corresponding figure is had for $\mu_1' < \mu_1$. Also either $\mu_1 = 0$ or $\mu_1' = 0$ merely introduces the modification of the line passing through the origin at x = 0 and x = 1, respectively.

2. N-N —— here the sites have the configuration



and so for the net magnetic moment we have

$$\mu_R = 2\mu_2 - \left[\mu_1(1-x) + \mu_1' x\right]$$

$$= 2\mu_2 - \mu_1 + x(\mu_1 - \mu_1')$$

Here $\mu_2 \neq 0$ and only either μ_1 or $\mu_1' = 0$ for a resultant moment. Now two possible kinds of μ_R plots are admitted as Figure 2 shows

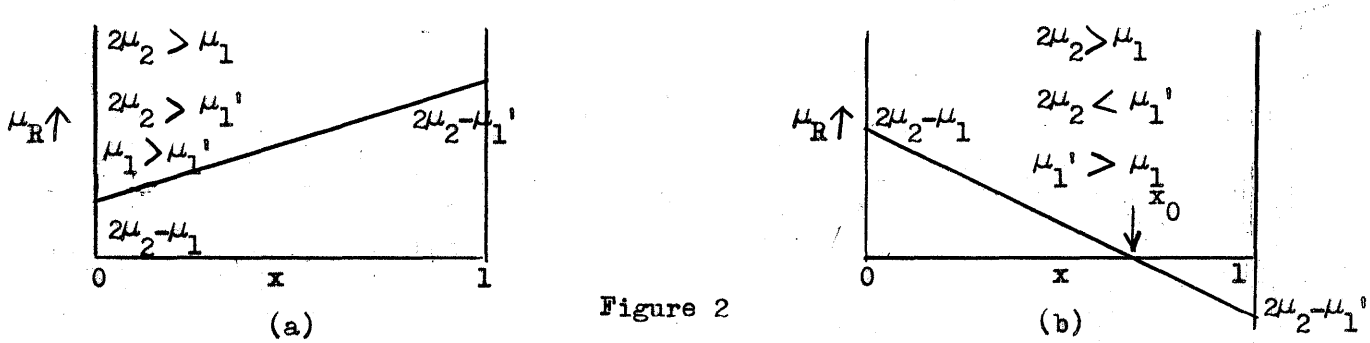


Figure 2

Symmetry considerations flip the slopes in the opposite direction and the special circumstance $2\mu_2 = \mu_1$ makes the line pass through the origin for (2a).

The reversal of the magnetic moment is indicated in (2b) and occurs for the stated conditions at a composition x_0 given by

$$x_0 = \frac{2\mu_2 - \mu_1}{\mu_1' - \mu_1}$$

3. I-N ——— this system entails more involved atomic migrations than the two previous cases considered. The addition of M'O to the inverse spinel $MO \cdot R_2O_3$ tends to shift the R ions from the tetrahedral to the octahedral while at the same time M' itself proportionates over the two sites. Thus for any intermediate state the sites have the appearance as shown

T	O
$(1-y)R$ $y\ M'$	$(1+y)R$ $[1-(z+y)]\ M$ $z\ M'$

where $x = z+y$. The relative proportions of z and y are presumable dependent upon the crystal energies involved and might perhaps be so estimated theoretically; no attempt will be made in this direction, however. Of course the ratio $y/z = f(x)$ can be determined experimentally.

The resultant magnetic moment for this mixed spinel is

$$\begin{aligned} \mu_R &= \mu_2\,(1+y) + \mu_1\left[1-(z+y)\right] + \mu_1' z - \left[\mu_2(1-y) + \mu_1' y\right] \\ &= 2\mu_2 y + \mu_1' z + \mu_1 - \left[\mu_1(z+y) + \mu_1' y\right] \end{aligned}$$

Suppose now we set $y/z = r$, then it follows that

$$\begin{cases} z = \dfrac{x}{1+r} \\[2ex] y = \dfrac{rx}{1+r} \end{cases}$$

and the magnetic moment relation reduces to

$$\mu_R = \mu_1 + x \left\{ \frac{1}{1+r} \left[2\mu_2 r + \mu_1' \ (1-r) \right] - \mu_1 \right\}$$

If we restrict r to a constant, this implies that at $x = 1$ the completely normal spinel does not result but is the limiting case of $r \rightarrow \infty$. In this situation, which clearly is the degenerate case of $z = 0$,

$$\mu_R = \mu_1 + x \left[2\mu_2 - (\mu_1 + \mu_1') \right]$$

one finds two broad groups of μ_R plots as shown in Figure 3

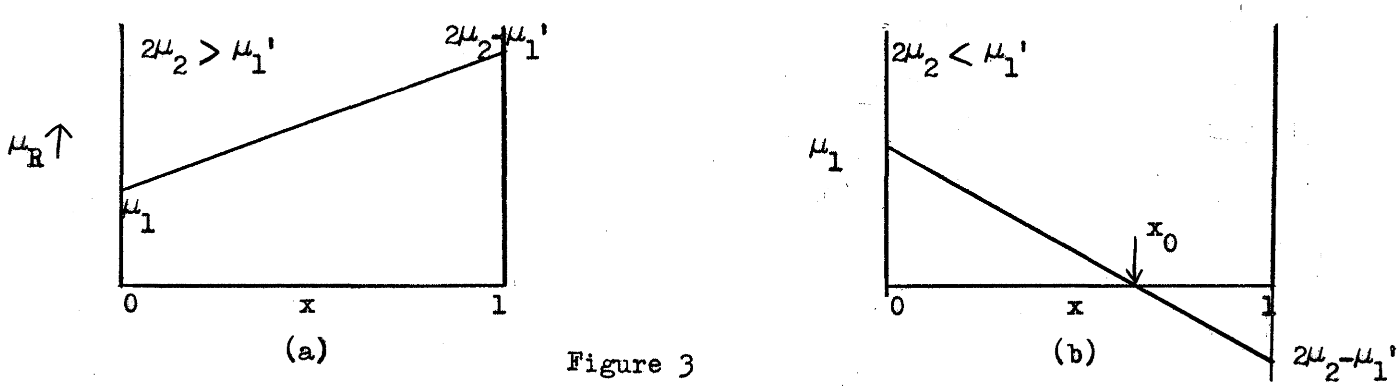


Figure 3

These manifest no essentially new features when compared to Figure 2. Here the reversal composition is

$$x_0 = \frac{1}{1 + \dfrac{\mu_1' - 2\mu_2}{\mu_1}}$$

It is possible to treat the general case of $z \neq 0$ if we deduce trial functions for $y(x)$ and $z(x)$ subject to the following requirements:

1. $y(x) + z(x) = x$
2. at $x = 0$, $y = z = 0$, $x = 1$, $y = 1$, $z = 0$
3. at $x = 0$ $\begin{cases} \dfrac{dy}{dx} = c_1 \\ \dfrac{dz}{dx} = c_2 \end{cases}$; and at $x = 1$ $\begin{cases} \dfrac{dy}{dx} \rightarrow \infty \\ \dfrac{dz}{dx} = c_3 \end{cases}$

   or $\begin{cases} \dfrac{dy}{dx} = c_4 \\ \dfrac{dz}{dx} \rightarrow 0 \end{cases}$

These conditions severely limit the possible functions and as Figure 4 suggests, they must be highly transcendental in nature.

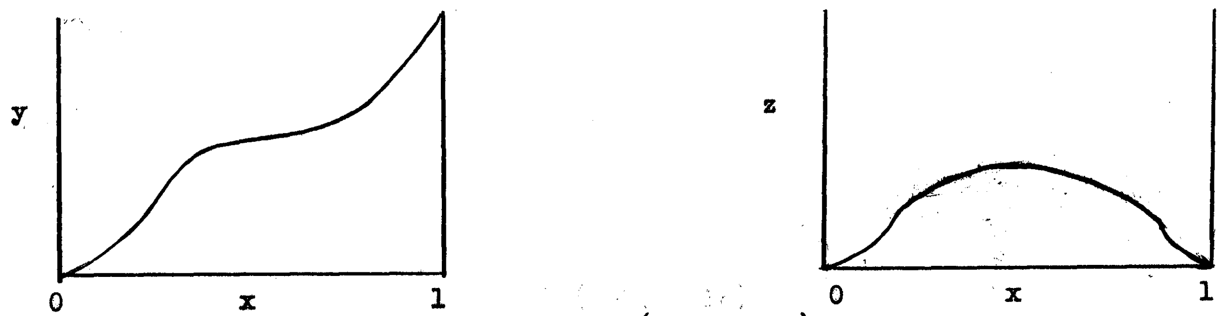


Figure 4 (schematic)

Consequently the dependence of μ_R on composition is intrinsically very complex in this system. Further development in terms of explicit functions does not seem warranted as yet.

Group II. $MO\cdot(R_2O_3)_{1-x}\cdot(R'_2O_3)_x$ Series

In an analogous manner, we proved to deduce the characteristics of mixed ferrites in this category. The sub-groups now take on the following complexions:

1. I-I —— the sites have the atomic distributions

T	O
1R	(1-2x)R 2x R' 1 M

with the resultant moment

$$\mu_R = \mu_2\,(1-2x) + \mu_2'\;2x + \mu_1 - \mu_2$$
$$= \mu_1 + 2x(\mu_2' - \mu_2)$$

Basically, this system is a replica of its Group I companion and Figure 1 applies equally well with allowance made for notation.

2. N-N ——the disposition of the atoms is given below

T	O
1M	2(1-x)R 2x R'

and so

$$\mu_R = \mu_2 \cdot 2(1-x) + \mu_2' \cdot 2x - \mu_1 \;.$$

$$= 2\mu_2 - \mu_1 + 2x(\mu_2' - \mu_2)$$

which is a result reminescent of its Group I analogue. Here the reversal effect occurs at the composition

$$x_0 = \frac{2\mu_2 - \mu_1}{2(\mu_2 - \mu_2')} \quad , \quad \left\{ \begin{array}{l} 2\mu_2 > \mu_1 \\ \mu_2 > \mu_2' \end{array} \right.$$

3. I-N ——the intermediate state is typified by the following distribution of atoms

T	O
$(1-y)R$	$[1-(2x-y)]\ R$
	$2x\ R'$
$y\ M$	$(1-y)M$

$$1 > x > 0$$

for which the corresponding overall magnetic moment is

$$\mu_R = \mu_2 \left[1-(2x-y)\right] + \mu_2' \cdot 2x + (1-y)\,\mu_1 - \left\{\mu_2(1-y) + \mu_1 y\right\}$$

$$= \mu_1 + 2x(\mu_2' - \mu_2) - 2y(\mu_1 - \mu_2)$$

The bifurcation of R over the two sites can be measured in terms of the ratio

$$r = \frac{1-y}{1-(2x-y)}$$

where $r = f(x)$. To express μ_R in terms of x and r we make the substitution

$$y = \frac{1-r+2rx}{1+r}$$

and so derive

$$\mu_R = \mu_1 + 2\,\frac{1-r}{1+r}\,(\mu_2 - \mu_1) + 2x\left[(\mu_2' - \mu_2) + \frac{2r}{1+r}\,(\mu_2 - \mu_1)\right]$$

In general, the functional dependence of r on x can become quite complex. Instead of limiting our discussion to trial functions as was done for the Group I homologue, we can approximate r(x) by

$$r \approx 1-x$$

which clearly becomes questionable at the extreme end where $x \rightarrow 1$; r becomes indeterminate rather than zero for this limiting range. The inferences to be drawn nevertheless serve to depict modes of μ_R behavior as the composition of the mixed ferrite is varied.

Thus there obtains the desired relation

$$\mu_R(x) = \frac{1}{2-x} \left(Ax^2 + Bx + c \right) = -\left[Ax + (B + 2A) \right] + \frac{c + 2(B + 2A)}{2-x}$$

with the definitions

$$A \equiv 2 \left[2\mu_1 - (\mu_2 + \mu_2') \right]$$

$$B \equiv 2 \left(2\mu_2' + \mu_2 \right) - 7\mu_1$$

$$C \equiv 2\mu_1$$

The latent extrema derive from

$$\frac{d\mu_R}{dx} = -A + \frac{c + 2(B + 2A)}{(2-x)^2}$$

whence

$$x^* = 2 - \sqrt{\frac{2(\mu_1 - \mu_2)}{\left[2\mu_1 - (\mu_2 + \mu_2')\right)}} = 2-s$$

Physically meaningful x* require

$$1 \leq s \leq 2$$

and the pairing-off of the following inequalities:

$$\begin{cases} \mu_1 > \mu_2 \\ 2\mu_1 > \mu_2 + \mu_2' \end{cases} \quad \text{or} \quad \begin{cases} \mu_1 < \mu_2 \\ 2\mu_1 < \mu_2 + \mu_2' \end{cases}$$

The extrema values μ_R^*, given by

$$\mu_R^* = \frac{1}{s} \left\{ (2-s) \left[A(2-s) + B \right] + c \right\}$$

correspond to maxima and minima as dictated from

$$\frac{d^2\mu_R}{dx^2} = \frac{2\left[C + 2(2A + B\right]}{(2-x)^3} = \frac{8(\mu_1 - \mu_2)}{(2-x)^3}$$

whereby

$\mu_1 < \mu_2$, μ_{R*} max.

$\mu_1 > \mu_2$, μ_R^* min.

and only one maximum or minimum can occur if no inflection point is possible, i.e. $\mu_1 \neq \mu_2$.

The composition for which reversal of the magnetic moment occurs is evaluable from

$$x_0 = \frac{-B + \sqrt{B^2 - 4AC}}{2A} , \quad 0 \leq x_0 \leq 1$$

Unfortunately the algebra is too messy for explicit expression of x_0 and the determination of conditions for single and double reversal points. However, some qualitative inferences can be made as to the general appearance of the composite magnetic moments as Figure 5 illustrates

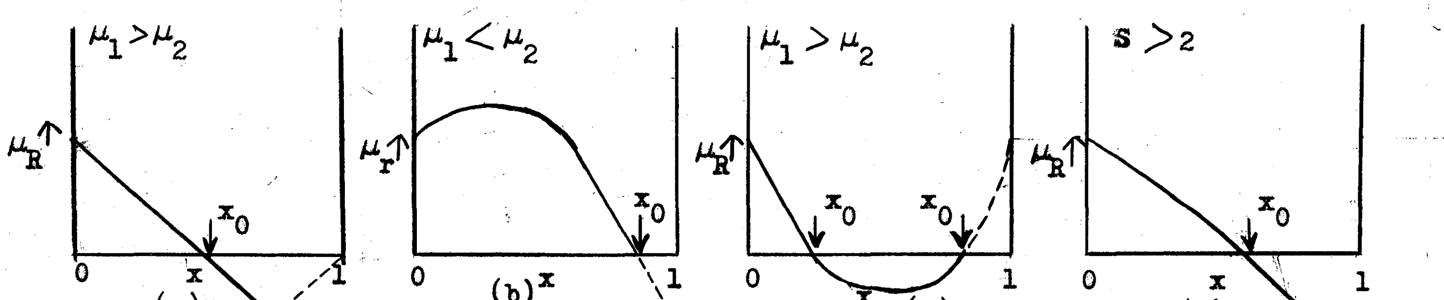


Figure 5 (schematic)

These sketches include some of the more important types of behavior to be anticipated in this system.

<u>Some Practical Considerations</u>

The foregoing somewhat idealized offerings cannot be expected to give strictly quantitative agreement with experiment because of deviations from the assumptions that have been made. There are several other underlying difficulties in that: (1) one may not know precisely what magnetic moments to employ for the ions--for example Ni^{2+} has theoretical $\mu = 2$ while experimental indicates 2.3; (2) strict preference for inverse or normal structures at the terminal points corresponding to x = 0 or 1 may not prevail. These and other possible shortcomings should not, nevertheless, detract from the ability to arrive systematically at the likely general features to be expected in combining certain spinels.

In terms of some specific reported systems, it is interesting to note that idealized behavior in the Ni-Zn ferrite can give agreement with observations only if the zinc ions distribute themselves over both sites rather than exhibit exclusive preference for the tetrahedral sites.[8] Also, while the theory predicts a reversal effect in the addition of $A\ell_2O_3$ to $NiO \cdot Fe_2O_3$ it does not give additional agreement with the NOL observations. Finally, while data given by Roberts[9] show a decrease in resultant magnetic moment for the addition of $A\ell_2O_3$ to $MgO \cdot Fe_2O_3$, theory predicts the contrary and, indeed, suggests a maximum μ_R at approximately $x^* \sim 0.6$. Since it is well known that the magnesium ferrite is about 90% inverse in its normal state, it appears worthwhile to study the influence of such an effect.

A Generalization of Group II I-N System which Allows for Incomplete States

By incomplete state, we mean the pure spinel is neither measurably just normal nor inverse, but is somewhere in between. Thus if the equilibrium of the sites in the isolated spinel appears as follows:

T	O
$(1-a)R$	$(1+a)R$
$a\ M$	$(1-a)M$

where a represents fraction of M ions not in the octahedral sites, then for the mixed ferrite the intermediate state shows the atomic distribution

T	O
$[1-(a+y)]\ R$	$[1+a-2x+y]\ R$
	$2xR'$
$(a+y)\ M$	$[1-(a+y)]\ M$

The net magnetic moment accordingly becomes

$$\mu_R = \mu_2\left[(1+a) + y - 2x\right] + \mu_2' \cdot 2x + \mu_1\left[1-(a+y)\right] - \left\{\mu_2\left[1-(a+y)\right] + \mu_1(a+y)\right\}$$

Now if one introduces the definition of r as

$$r = \frac{1-(a+y)}{[(1+a) - (2x-y)]}$$

the $\mu_R(x,r)$ relation is exactly the same as for the situation where a = 0. However, when the approximate function r(x) is appropriately modified to

$$r \approx \tau - a \quad , \tau = \frac{1-a}{1+a}$$

where τ is a parameter which is a measure of the degree of inversion for the pure spinel, then there obtains

$$\mu_R = \frac{1}{\Delta - x} \; (Ax^2 + Bx + C), \; \Delta = 1 + \tau$$

Here the constants are related to the atomic moments as follows:

$$A \equiv 2 \left[2\mu_1 - (\mu_2 + \mu_2') \right]$$

$$B \equiv 2\mu_2' - 3\mu_1 + 2\tau \, (\mu_2 + \mu_2' - 2\mu_1)$$

$$C \equiv 2\mu_2 - \mu_1 + \tau \, (3\mu_1 - 2\mu_2)$$

The properties of $\mu_R(x)$ are readily deduced by writing it in the form

$$\mu_R = -\left[Ax + (B + A\Delta) \right] + \frac{C + (B + A\Delta)\Delta}{\Delta - x}$$

whereby we have at once

$$\frac{d\mu_R}{dx} = -A + \frac{C + (B+A\Delta)\Delta}{(\Delta - x)^2}$$

and

$$x^* = \Delta \pm \sqrt{\frac{C + (B+A\Delta)\Delta}{A}}, \; 0 \leq x^* \leq 1$$

This can be reduced to

$$x^* = \Delta - \sqrt{\frac{2\tau(\mu_1 - \mu_2)}{\left[2\mu_1 - (\mu_2 + \mu_2')\right]}} = \Delta - S_\tau$$

with S_τ now confined within the limits

$$\tau \leq S_\tau \leq \Delta$$

and the extrema given by

$$\mu_R^* = \frac{1}{S}\left\{(\Delta - S_\tau)\ \left[A(\Delta - S) + B\right] + C\right\}$$

The physical existence of x* is prescribed by exactly the same pairing-off given earlier for the special case $\tau = 1$ and so no new qualitative difference in behavior are introduced by the modified theoretical development. Thus for $MgO \cdot Fe_2O_3$ to which is added Al_2O_3, we have the following data:

$$\mu_1 = \mu_2' = 0, \mu_2 = 5, \ A = -2\mu_2 = -10$$

$$B = 2\tau \cdot \mu_2 = 10\tau, \ C = 2\mu_2 - 2\tau\mu_2 = 2\mu_2(1-\tau) = 10(1-\tau)$$

$$\mu_R = \frac{10}{x - \Delta}\left[x^2 - \tau x + (\tau - 1)\right]$$

We identify the following critical functional dependences on

$$(\mu_R)_{x=0} = 10\,\frac{1-\tau}{1+\tau}$$

$$x^* = 1 + \tau - \sqrt{2\tau}$$

$$\mu_R^* = 5\sqrt{2}\ \left[\sqrt{2}(2+\tau) - 4\sqrt{\tau}\right]$$

whereby in Figure 6 we established the parametric curves as shown below.

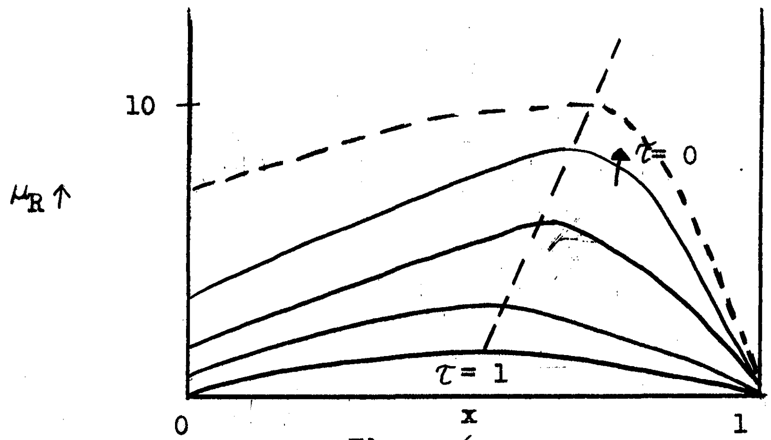


Figure 6

It should be noted that as $\tau \to 0$ and $x \to 1$ the theoretical results become uncertain as described earlier in terms of approximation for $r(x)$.

Signed Louis Gold
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Approved DRB
David R. Brown

LG/jk

cc: Group 63
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