# **Intrinsic Magnetization in Alloys**

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The intrinsic magnetization of alloys among the iron transition group of metals has been explained using a Heitler-London model for the 3d electrons. The magnetic moment associated with each atom is determined by the principle of maximum spin and the sign of the interaction between neighboring pairs from the overlap of the wave functions. It is found that a large number of alloys derive their spontaneous magnetization from an antiparallel arrangement of atomic spins.

OST of the recent attempts to calculate the intrinsic or saturation magnetization of ferromagnetic metals and their alloys (especially in the iron group) have been based upon the collective electron or band concept. This approach was used successfully by Stoner<sup>1</sup> in calculating the magnetization of nickel-base alloys, mainly those containing elements, such as copper with filled 3d shells. The further work of Stoner and Wohlfarth has been adequately summarized.<sup>2,3</sup> Although this work is still in progress, it seems apparent that the alloys such as Ni-Cu were deceptively simple and correct results for some of the other alloys are not readily forthcoming. In particular, the large effect of order on the intrinsic magnetization does not seem to fit naturally into a collective electron picture.

More qualitative calculations have been given by Slater<sup>4</sup> and Pauling.<sup>5</sup> As used by Shockley<sup>6</sup> and Smoluchowski,<sup>7</sup> the Pauling treatment consists in splitting the 3d band, somewhat arbitrarily, into two unequal parts in a way to give agreement with experiment for the points in Fig. 1<sup>8</sup> which fall approximately on two straight lines intersecting between Fe and Co. The



FIG. 1. The average atomic moment in Bohr magnetons as measured by various investigators, plotted against the average number of electrons per atom. The upper point of Ni-Mn is for an ordered alloy (see reference 8).

<sup>1</sup> E. C. Stoner, Phil. Mag. 15, 1018 (1933).
<sup>2</sup> E. C. Stoner, Phys. Soc., Rep. Progr. Phys. 11, 43 (1946-47).
<sup>8</sup> E. C. Stoner, J. phys. et radium 12, 372 (1951).
<sup>4</sup> J. C. Slater, J. Appl. Phys. 8, 385 (1937).
<sup>5</sup> L. Pauling, Phys. Rev. 54, 899 (1938).
<sup>6</sup> W. Shockley, Bell System. Tech. J. 18, 645 (1939).
<sup>7</sup> R. Smoluchowski, J. phys. et radium 12, 389 (1951).
<sup>8</sup> After R. M. Bozorth, *Ferromagnetism* (D. Van Nostrand Company, Inc., New York, 1951.)

remaining points appear to be ignored. Other recent treatments are partly empirical.9,10

In this paper we avoid the band approximation and take the point of view that for the 3d electrons a Heitler-London approximation is closer to reality, and thus the electrons are to be associated with the individual atoms. This viewpoint is in many respects similar to that of Néel.<sup>11</sup> The atomic spins may be aligned parallel or antiparallel and it is proposed that "antiferromagnetism" is more common in the iron transition group of metals than is "ferromagnetism" itself. All the curves in Fig. 1 can be explained in a simple and straightforward manner on the basis of the three following considerations:

(I) The total spin of each ion is determined by using Zener's hypothesis<sup>12</sup> (analogous to Hund's rule for the gaseous state) that the 3d shell has the largest spin possible consistent with the exclusion principle. Hund's rule comes from the fact that electrons on the same atom with parallel spins have a negative exchange energy. For the solid state Zener's hypothesis is tantamount to assuming that the spin coupling between electrons on the same atom is large compared with that between electrons on different atoms and is almost implied by the original assumption that a Heitler-London model is applicable.

Since the d shell has room for 10 electrons, five of each spin, the magnetic moment in Bohr magnetons on an atom A is

$$\mu_A = 10 - n_{dA}, \quad n_{dA} \ge 5 \tag{1a}$$

$$\mu_A = n_{dA}, \qquad n_{dA} \leqslant 5, \qquad (1b)$$

where  $n_{dA}$  is the number of 3d electrons in A. We have the occasion to consider only the case (1a).

As one knows from experiment, the orbital moments (for the iron group of elements) are almost completely quenched in the solid state so that (1a) may be used for the total moment.

(II) The number of electrons in the 3d shell is not the same as that for the free atom. Firstly, some of the 4s electrons of the gaseous state are demoted to the d

<sup>9</sup> R. Forrer, J. phys. et radium 12, 402 (1951).

- T. G. Owe Berg, J. phys. et radium 12, 1051/1017.
   <sup>11</sup> L. Néel, Le Magnétisme, II Ferromagnétisme (Strasbourg 1939),
- p. 65. <sup>12</sup> C. Zener, Phys. Rev. 81, 440 (1951).

shell, as one knows from the number of conduction electrons found in the solids. (For nickel the number of conduction electrons,  $n_c$ , is approximately 0.6, for cobalt  $n_c \simeq 0.7$ . The extrapolated value for iron would be about 0.8.) Secondly, there is the possibility suggested by Zener (see the preceding paper) that a lowering of the energy can be obtained by the transfer of some of the *d* electrons of atom *A* to atom *B*. Such a process would take place in a manner which maximizes the number of pairs of parallel spins and in our examples would result in a tendency for half-filled and completely filled shells.

For example, consider a Mn atom dissolved in the Ni lattice. After the proper contribution to the conduction band, the Mn d shell is somewhat more than half-filled, whereas the Ni shell is almost complete. Such a situation is the most favorable for the Mn atom achieving a halffilled shell of five parallel spins, with the Ni atoms accepting the remainder. Whether phenomena of this type occur generally in alloys need not be discussed here, since in most cases this knowledge is not needed for an approximate calculation of the magnetic moment.

(III) Of the interactions of an atom A in a lattice of B atoms, the combinations Ni-Ni, Ni-Co, Co-Co, Ni-Fe, Co-Fe, and Ni-Mn among the iron group of elements tend to give a parallel alignment of atomic spins for all the cases in Fig. 1. All other interactions in this transition group tend towards an antiparallel alignment in our examples, the principal reason being that for a fixed interatomic distance the 3d shells of the above atoms overlap the least, and thus either on Zener's or Heisenberg's theory of ferromagnetism would be most likely to tend towards a parallel orientation.

For qualitative purposes we have listed in Table I the sum of the radii of various 3d shells as given by Slater.<sup>13</sup> These "radii" will give an indication of the overlap, assuming the interatomic distance to be about the same for all the alloys to be considered. Going from nickel to the left on the periodic chart one finds that the 3d radii of the transition elements get bigger as the nuclear charge decreases since this decrease, as a result of incomplete screening, is not fully compensated by the decrease in 3d electrons.

Thus taking the demarcation between positive and negative interaction, on the basis of experiment, to be just below Ni—Mn, one has a ready interpretation from Table I why the interactions listed above should be positive. This listing, of course, has neglected such things as variations in interatomic distance, number of d electrons as mentioned in II, and in Zener's theory, differences in the interaction of conduction electrons with the d shells, all of which are probably important in some cases. It evidently is possible to overlook them among the alloys of Fig. 1.

TABLE I. Qualitative estimate of the overlap of 3d shells for various pairs of nearest neighbors from the sum of the 3d "radii." Those pairs above the line are assumed to tend toward parallel alignment of spins, those below toward antiparallel alignment.

Interaction	Sum of 3d radii
$egin{array}{ccc} { m Ni-Ni} & { m Ni-Co} & { m Co-Co} & { m Ni-Fe} & { m Co-Fe} & { m Ni-Mn} & { m Ni-Nn} $	0.68 0.70 0.72 0.73 0.75 0.76
Fe-Fe Co-Mn	0.78 0.78

### 1. The Case of Parallel Spins

For simplicity only binary alloys will be considered, although for this particular case the result would be the same for any number of components. If  $f_A$  and  $f_B$  are the atomic fractions of atoms A and B, then the average number of Bohr magnetons per atom is

$$\mu = f_A \mu_A + f_B \mu_B$$
  
= 10- f\_A n\_{dA} - f\_B n\_{dB}. (2)

One can write (2) in terms of the average number of electrons per atom, N, which is given for elements in the iron group by  $N=18+f_An_{dA}+f_Bn_{dB}+n_c$ , where  $n_c$  is the average number of conduction electrons per atom. Thus (2) becomes

 $\mu = 28 + n_c - N$ 

and

$$d\mu/dN \simeq -1,$$
 (4)

(3)

where it is assumed that the number of conduction electrons remains practically constant, independent of composition for a given alloy system.

According to the sign of the interactions given in III, one would definitely expect points for Ni-Co alloys to fall along a line with slope of minus unity since all three types of interactions involved (Ni-Ni, Co-Co, and Ni-Co) tend toward a parallel alignment. Also copper and zinc with complete d shells, when alloyed with cobalt or nickel, should fall on this curve since in these cases only Ni-Ni or Co-Co interactions are involved and the outer electrons of the copper or zinc would go into the conduction band and into filling up the d shells of the cobalt or nickel.

Other alloys which fit this curve over a limited range of composition will be discussed separately.

### 2. Antiparallel Spins

When the atomic spins of A are aligned antiparallel to those of B, the expression for the average magnetic moment is not as simple as (3). Assuming the B atoms contribute the greater part to the magnetization, one has

$$\mu = f_B(10 - n_{dB}) - f_A(10 - n_{dA}). \tag{5}$$

<sup>&</sup>lt;sup>13</sup> J. C. Slater, Introduction to Chemical Physics (McGraw-Hill Book Company, Inc., New York, 1939), p. 349.

We shall fix our attention on the case where  $n_{dA}$  is independent of composition in a given alloy system, but we shall not overlook the possibility mentioned previously that, in the solid, some of the electrons of atom A will go into the 3d shell of atom B. The average



FIG. 2. Calculated atomic moment versus electron concentration.

number of electrons in the d shell of atom B can be obtained from

$$n_{dB} = (N - 18 - n_c - f_A n_{dA}) / f_B.$$
(6)

Since the number of electrons per atom can be written in terms of the atomic numbers as  $N = f_B Z_B + f_A Z_A$  and since  $f_A + f_B = 1$ , one can express (5) as

$$\mu = 28 - Z_B + n_c + [(N - Z_B)/(Z_B - Z_A)] \times [Z_A - Z_B + 2(10 - n_{dA})]. \quad (7)$$

Again assuming the variation of  $n_c$  with composition to be small, one has

$$d\mu/dN \simeq [2(10 - n_{dA})/(Z_B - Z_A)] - 1,$$
 (8)

where B is the dominant element.

Thus when the spins of A are antiparallel to those of B, the points for various compositions in a given alloy AB can fall upon a straight line of positive slope, but not necessarily the same line for each alloy system.

As an example, we cite the case of  $Cr(Z_A=24)$ alloyed in  $Co(Z_B=27)$ . The Co-Co interaction is positive whereas Co-Cr and Cr-Cr are negative. The measured points in Fig. 1 are in the region where  $f_{Cr}$ is small. Thus the Cr-Cr interactions make only a small contribution to the energy and the other two interactions, which predominate, will insure that the cobalt atoms point in the plus direction and the chromium in the minus. Since a free chromium atom has six electrons outside of closed shells, it will very likely exhibit five 3d electrons in the solid. Equation (8) gives  $d\mu/dN=2.3$  as compared with the observed value of 2.28.

The Co-Mn, Ni-Cr, and Ni-V alloys in Fig. 1 fit this same pattern. The agreement with experiment for the nickel alloys is not as exact, but nevertheless reasonably correct. The calculated curves are shown in Fig. 2.

The results are really not based on the assumption of five electrons in the 3d shell of the A atoms (Mn, Cr, V),

but rather, only on the assumption of five or less, since for this case of atomic spins oppositely directed, if  $n_{dB} \ge 5$  and  $n_{dA} \le 5$ , the average moment by (1a) and (1b) is easily shown to be

$$\mu = 18 + n_c - [10Z_A/(Z_B - Z_A)] + [N(Z_A - Z_B + 10)/(Z_B - Z_A)].$$
(7a)

### 3. Nickel-Manganese

The Ni-Mn alloys come under a case in which two types of interaction (Ni-Ni and Ni-Mn) are positive, whereas one Mn-Mn is negative. Thus one would expect the following behavior: For a small percentage of manganese the Mn-Mn interactions can be neglected, so to this approximation all spins should be parallel and the points should fall upon the curve with slope minus one. As the manganese composition increases, there are still no Mn-Mn nearest neighbors if the alloy is ordered, such as Ni<sub>8</sub>Mn, and consequently, the points should continue to fall on the same line (assuming the number of conduction electrons to be approximately constant). This behavior is qualitatively observed in Fig. 1.

For a disordered alloy with an appreciable percentage of manganese atoms, the Mn-Mn interaction begins to outweigh the weaker Ni-Mn interactions, and one eventually finds the manganese spins start to cancel one another. This behavior becomes clearer in the energy calculations which follow and which indicate that the bending over of the curve as observed in Fig. 1 should occur for a relatively small fraction of manganese. Beyond this point, the magnetic moment is derived principally from the nickel ions and diminishes with increasing manganese content because of the replacement of nickel and to the filling up of the nickel dshell. Assuming the manganese ions to have five electrons in the 3d shell, one finds from (6) that the nickel shells become completely filled at about 30 percent manganese. The moment thus goes to zero at this composition in approximate agreement with experiment.

# 4. Cobalt-Iron and Nickel-Iron

As far as the interactions are concerned, these alloys are of the same type as nickel-manganese. Iron alloys, in the iron-rich region, however, are somewhat of a special case, for the apparent reason as postulated by Zener that the arrangement in the pure metal is an antiparallel one (in agreement with the scheme of Table I) between ions with different magnitudes of spin. Thus for the body centered cubic lattice in the iron rich region one has two types of iron ions as well as the solute ions, a somewhat more difficult case to treat. Since this case is discussed in reference 12, we shall not consider iron base alloys in the region near the pure metal.

In the cobalt-rich or nickel-rich regions the negative Fe-Fe interactions are overpowered by the Fe-Co or Fe-Ni so the magnetization falls on the line with

negative slope, all spins being parallel. At some composition, however, the Fe–Fe interactions should become sufficiently numerous to be predominant and the curves should bend over as the nickel-manganese curve does. In the Ni–Fe alloy a tendency to bend over occurs just before the phase change from f.c.c. to b.c.c. Likewise, the slope of the Co–Fe curve eventually changes sign.<sup>14</sup>

#### 5. Iron-Chromium and Iron-Vanadium

For these alloys all interactions are negative. For appreciable fractions of Cr or V, however, the Cr-Cr or V-V will dominate since they are the largest interactions individually. Thus the Cr or V will largely cancel itself, consistent with the energy calculations in the next section.

The six electrons of the chromium atoms will supply five to the d shell in addition approximately to their correct share for the conduction band, leaving the moment of the iron unchanged. Thus chromium to a first approximation will act only as a diluent, and the magnetic moment of the alloys will approach zero as the fraction as iron approaches zero.

The points for the Fe–V alloys in Fig. 1 are mostly well within the iron-rich region and so will not be discussed here in detail. However, in a qualitative way Fe-V should behave as Fe–Cr, although V with only five electrons will not act as well as a diluent since it would be expected to change the moment of the iron ions somewhat.

## 6. Energy Considerations

In order to determine whether (a) all spins will align parallel, (b) all A spins antiparallel to B spins, or (c) some intermediate situation, one must determine which arrangement in the particular alloy makes the energy a minimum. It is assumed the dipoles point only to the right or to the left (Ising approximation).

In the Heisenberg theory of ferromagnetism, one would write the average energy per atom as

$$E = \frac{1}{2n} \sum_{i \neq j} \alpha_{ij} S_{di} S_{dj}, \qquad (9)$$

for *n* atoms in the solid with  $S_{dj}$  the spin in Bohr magnetons of the *i*th ion and  $a_{ij}$  the exchange interaction between the *i*th and *j*th ions. We shall assume the summation to be over nearest neighbors.

In the framework of Zener's theory<sup>12</sup> the energy is

$$E = \frac{1}{2n} \sum_{i \neq j} \alpha_{ij} S_{di} S_{dj} - \frac{1}{n} \sum \beta_j S_{dj} S_c + \frac{\gamma}{2} S_c^2, \quad (10)$$

where  $S_c$  is the excess number of positive over negative spins per atom of the conduction electrons, and  $\alpha_{ij}$ ,  $\beta_j$ , and  $\gamma$  positive coupling constants giving, respectively, the direct exchange coupling between ions, the exchange coupling between ions and conduction electrons, and the coupling between conduction electrons.

In the Appendix I it is shown that (10) can be put into the same form as (9), and the average energy per atom for a random distribution of ions in an alloy of two components A, B is

$$E = -\frac{1}{2} \{ (2f_{A+} - f_A)^2 W_{AA} S_{dA}^2 + (2f_{B+} - f_B)^2 W_{BB} S_{dB}^2 + 2(2f_{A+} - f_A)(2f_{B+} - f_B) W_{AB} | S_{dA} S_{dB} | \}.$$
(11)

Here, W is a constant which determines the sign of the interaction,  $f_A$  is the atomic fraction of A, and  $f_{A+}$  the atomic fraction of positive A spins  $(f_{A+}+f_{A-}=f_A)$ . The W's are given by  $W_{AA}=(\beta_A\beta_A/\gamma)-\alpha_{AA}z$ , with z the number of nearest neighbors for the particular type lattice. For different atoms the principal change in the expression for W is in  $\alpha$ , which depends upon the overlap of nearest neighbor wave functions (see Table I).

For a fixed composition  $f_A$ ,  $f_B$ , one must find what fraction of the atoms A and B must possess positive spins to minimize the energy. By using the average energy (11) one neglects the effect of statistical fluctuations in the environment of the various atoms. Consider the following cases:

# (a) $W_{AA}$ , $W_{BB}$ , $W_{AB}$ positive

If  $W_{AA}$  and  $W_{BB}$  have the same sign,  $W_{AB}$  will probably have that sign too. When the sign is positive, it is obvious that  $f_{A+}=f_A$  and  $f_{B+}=f_B$  for minimum energy, i.e., all the spins are parallel and the average magnetic moment per atom is given by (2).

# (b) $W_{AA}$ , $W_{BB}$ , and $W_{AB}$ negative

If  $W_{AA}W_{BB} > W_{AB}^2$ , then  $f_{A+} = \frac{1}{2}f_A$  and  $f_{B+} = \frac{1}{2}f_B$  or, in other words, each of the components has a net moment of zero. This classification should contain a group of alloys, but our attention at the present is focused on the other cases which exhibit a net magnetization.

If  $W_{AA}W_{BB} < W_{AB}^2$ , from Appendix II

for

for

$$\mu = \left| f_B S_{dB} \left[ 1 - (W_{AB} / W_{AA}) \right] \right|$$

$$|S_{dB}W_{AB}/S_{dA}W_{AA}| \le f_A/f_B.$$
(12)

This equation gives only one end of the curve between A and B but suffices for our purpose. Iron-chromium apparently fits this case in the chromium rich region, if one lets  $f_A$  be the fraction of chromium. Since one might expect  $|W_{AB}/W_{AA}| \ll 1$  for this case, Eq. (12) shows that the moment should result almost entirely from the iron atoms.

(c) 
$$W_{AA}$$
 negative and  $W_{BB}$  positive  

$$\mu = |f_B S_{dB} [1 - (W_{AB}/W_{AA})]|$$

$$|S_{dB} W_{AB}/S_{dA} W_{AA}| \leq f_A/f_B \qquad (13)$$

<sup>&</sup>lt;sup>14</sup> This does not occur until after the lattice has become b.c.c. and an alternative explanation is given by C. Zener, Phys. Rev. 85, 324 (1951).

and for  $|S_{dB}W_{AB}/S_{dA}W_{AA}| \geq f_A/f_B$ ,

$$\mu = f_B |S_{dB}| + f_A |S_{dA}| \tag{14}$$

if  $W_{AB}$  is positive and

$$\mu = |f_B|S_{dB}| - f_A|S_{dA}|| \tag{15}$$

for  $W_{AB}$  negative. These results come from Appendix II.

Equation (14) is the same as (2), and (15) the same as (5). The equations confirm the qualitative statements made previously. If A represents the solute atoms, then for small fractions of A the A-A interactions can be neglected, and one has either parallel or antiparallel spins between A and B depending upon the sign of  $W_{AB}$ .

For larger fractions of A (13) applies and if  $|W_{AB}/W_{AA}| \ll 1$ , the magnetization is caused almost entirely by the *B* ions, i.e., the *A* cancel. For the Ni-Mn alloys (13) should apply down to a relatively small fraction of manganese since  $S_{dB}/S_{dA}$  is small (less than 0.12).

# 7. Discussion

According to the ideas presented here, it will be observed that there are more metals which derive a spontaneous magnetization from an antiparallel arrangement of unequal spins than from a parallel arrangement of spins. Nickel and cobalt are the prototypes of the parallel spins.

Although the calculations made are generally in good agreement with experiment (compare Fig. 2 with Fig. 1), several corrections could be applied in the interest of exactness. For example, the small contribution of the orbital moment could be subtracted from the measured moment to give the spin-only values. Also in Zener's ferromagnetic theory one must subtract out the small contribution of the conduction electrons. In addition, statistical fluctuations in atomic environment could be taken into account.<sup>7</sup> Most of these corrections appear futile, however, since there is an uncertainty in the number of conduction electrons.

The present calculations have been confined to metals of the iron transition group, since these have seemed to be the most puzzling. The intrinsic magnetization of nonmetals such as ferrites has been considered rather extensively by Néel and others.

#### APPENDIX I

The value of  $S_c$  which makes (10) a minimum is  $(1/\gamma n)\Sigma\beta_j S_{dj}$ , so the last two terms on the right in (10) become  $-(1/2\gamma n^2)\Sigma\beta_j S_{dj}\Sigma\beta_i S_{di}$ .

Let there be several types of ions in the solid, designated by A, B, C, etc. Each of these can exist at absolute zero with plus or minus spin which we designate by  $A^+$ ,  $A^-$ ,  $B^+$ ,  $B^-$ , etc. The sum  $(1/n)\Sigma\beta_jS_{dj}$  may be replaced by  $\Sigma' f_a\beta_aS_{da}$ , where the prime indicates a summation over all the types  $A^+$ ,  $A^-$ ,  $B^+$ ,  $B^-$ , and  $f_a$  is the atomic fraction of that type. Likewise, we assume only nearest neighbors to be important in the first summation in (10) and write

$$(1/2n)\Sigma S_{di}\Sigma \alpha_{ij}S_{dj} = \frac{1}{2}\Sigma' f_a S_{da}\Sigma' \bar{n}_{ab}\alpha_{ab}S_{db}, \quad (16)$$

where  $\bar{n}_{ab}$  is the average number of nearest neighbors an atom of type *a* has of type *b*. Thus the energy becomes

$$E = \frac{1}{2} \Sigma' \Sigma' (f_a \bar{n}_{ab} \alpha_{ab} - \gamma^{-1} f_a f_b \beta_a \beta_b) S_{da} S_{db}$$
  
=  $-\frac{1}{2} \Sigma' \Sigma' \xi_{ab} S_{da} S_{db}.$  (17)

For qualitative purposes we consider a distribution for which  $\bar{n}_{ab} = f_b z$  with z being the number of nearest neighbors. Thus  $\xi_{ab} = f_a f_b W_{ab}$ , where  $W_{ab} = (\beta_a \beta_b / \gamma) - \alpha_{ab} z$ and is independent of the sign on the spins.

In a binary alloy with components A, B there will be four types of spins in (17) to sum over, i.e.,  $S_{dA}$ ,  $-S_{dA}$ ,  $S_{dB}$ ,  $-S_{dB}$ . Therefore,

$$E = -\frac{1}{2} \{ (f_{A+} - f_{A-})^2 S_{dA}^2 W_{AA} + (f_{B+} - f_{B-})^2 S_{dB}^2 W_{BB} + 2(f_{A+} - f_{A-})(f_{B+} - f_{B-}) | S_{dB} S_{dA} | W_{AB} \}.$$
(18)

Making use of  $f_{A+}+f_{A-}=f_A$  and  $f_{B+}+f_{B-}=f_B$ , one obtains (11).

### APPENDIX II

One can transform (11) to the following form

$$\epsilon = Y^2 + CX^2, \tag{19}$$

where

$$\epsilon = \frac{-2E}{f_A{}^2S_{dA}{}^2W_{AA}}, \quad C = \frac{f_B{}^2S_{dB}{}^2}{f_A{}^2S_{dA}{}^2} \left(\frac{W_{BB}}{W_{AA}} - \frac{W_{AB}{}^2}{W_{AA}{}^2}\right),$$
$$W = Y' + \frac{f_B{}|S_{dB}|}{f_A{}|S_{dA}|} \frac{W_{AB}}{W_{AA}}X, \quad X = \frac{2f_{B+}}{f_B} - 1, \quad Y' = \frac{2f_{A+}}{f_A} - 1,$$

and  $1 \ge X \ge -1$ ,  $1 \ge Y' \ge -1$ . We shall always consider  $W_{AA}$  to be negative so  $\epsilon$  must be a minimum.

It is immediately apparent that for C positive  $\epsilon$  is a minimum when X = Y = 0, i.e.,  $f_{A+} = \frac{1}{2}f_A$  and  $f_{B+} = \frac{1}{2}f_B$ . This includes the case where all three interactions are negative and  $W_{AA}W_{BB} > W_{AB}^2$ .

The constant C can be negative if  $W_{BB}$  is positive and  $W_{AA}$  negative, or if both  $W_{AA}$  and  $W_{BB}$  are negative and the additional condition  $W_{AA}W_{BB} < W_{AB}^2$  applies. It is obvious that for  $|(f_BS_{dB}/f_AS_{dA})(W_{AB}/W_{AA})| \le 1$ ,  $\epsilon$  is minimum when Y=0, and  $X^2=1$ . The average magnetic moment is  $|f_AY'|S_{dA}|+f_BX|S_{dB}||$  so

$$\mu = |f_B S_{dB} [1 - (W_{AB} / W_{AA})]|.$$
(20)

If for a given value of X,  $|(f_B S_{dB} W_{AB}/f_A S_{dA} W_{AA})X| > 1$ , then Y will wish to be as small as possible, having the magnitude  $|(f_B S_{dB} W_{AB}/f_A S_{dA} W_{AA})X| - 1$ . (For positive X, Y'=1 if  $W_{AB}$  is positive and -1 if  $W_{AB}$  is negative.) Putting this magnitude into (19) and solving for the minimum  $\epsilon$ , one finds that for the case  $W_{BB}$ positive and  $W_{AA}$  negative |X| = 1.

These results are collected in Eqs. (12) to (15).

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