

Comments on "Molecular-Field Theory for Randomly Substituted Ferrimagnetic Garnet Systems" by I. Nowik

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THE Nowik paper¹ claims that "The proposed model [his] is capable of reproducing, with no adjustable parameters, the substitution dependence of the magnetic moment at 0°K of various substituted rare-earth iron garnets. Maxima in the temperature dependence of the moments are predicted and agree with experimental prediction." I propose to show that neither claim is justified by the evidence, and that, in addition, his thesis contains logical flaws and in places is misleading.

To begin, we look at the molecular-field equations for the substituted ferrimagnetic garnet proposed by Nowik. He writes

$$\sigma_i(T) = \frac{\langle S_i^z \rangle}{S_i} = \frac{N_{1i}N_{2i}N_{3i}N_{4i}}{\sum_{m_1 m_2 m_3 m_4=0} P(N_{1i}, m_1) P(N_{2i}, m_2) \times P(N_{3i}, m_3) P(N_{4i}, m_4) B_{S_i}(z_i)}, \quad (2)$$

with

$$kTz_i = 2 \sum_{j=1}^4 m_j J_{ij} S_j \sigma_j(T) + g\beta S_i H. \quad (3)$$

(The symbols are the same as those used in Nowik's paper.) His Ref. 10 states that "At high substitution the solution of Eqs. (2) will depend on the exact values of J_{ij} ." This seems to mean that, contrary to the claim, the J_{ij} must be adjusted to make the fit.

As these equations stand, they require a self-consistent calculation (as also implied in his Ref. 10). Nowik, however, puts some simple conditions on the J_{ij} :

$$\begin{aligned} -8J_{aa} &< -J_{ad}, \\ -4J_{ad} &< -J_{ad}. \end{aligned}$$

These conditions lead to the conclusion that the 0°K moments of the diamagnetic-ion-substituted garnets are field-independent. None of the systems²⁻⁶ discussed by Nowik has this behavior. (For example, see the large differences between the $H=0$ and $H=\infty$ data in Nowik's Fig. 2.) Apparently, all the data except those

¹ I. Nowik, Phys. Rev. **171**, 550 (1968).

² S. Geller, H. J. Williams, G. P. Espinosa, and R. C. Sherwood, Bell System Tech. J. **43**, 565 (1964).

³ S. Geller, H. J. Williams, R. C. Sherwood, and G. P. Espinosa, J. Appl. Phys. **36**, 88 (1965).

⁴ S. Geller, J. Appl. Phys. **37**, 1408 (1966).

⁵ S. Geller, R. M. Bozorth, M. A. Gilleo, and C. E. Miller, J. Phys. Chem. Solids **12**, 111 (1959).

⁶ S. Geller, H. J. Williams, R. C. Sherwood, and G. P. Espinosa, J. Phys. Chem. Solids **26**, 443 (1965).

of the $\text{Eu}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_{12}$ system⁷ came from papers by myself and my colleagues.

One of the important points of our papers is²⁻⁴: In all the diamagnetic-ion-substituted iron garnets that are discussed by Nowik, to a certain concentration (x), the garnets are saturated magnetically at moderate fields, while above these particular concentrations they are not saturated to fields of 80 kOe. Further, above these critical compositions dn_B/dH increases with increasing diamagnetic-ion substitution.

A representation of our model^{2,4} is given in Fig. 1. Starting with the ideal Néel ferrimagnet, $\{\text{Y}_3\}[\text{Fe}_2](\text{Fe}_3)\text{O}_{12}$, substitution of diamagnetic ions for Fe^{3+} ions ultimately leads to an antiferromagnet. The critical values of x are 0.70 and 1.92 for octahedral and tetrahedral ion substitution, respectively. Our model is based on *random* canting of moments in the sites in which no substitution is made or, when substitution is made in both sites, canting still occurs only in one set of sites, the one in which the average intrasublattice interaction is stronger; e.g., in the $\text{Y}_3[\text{Mg}_x\text{Fe}_{2-x}](\text{Fe}_{3-x}\text{Si}_x)\text{O}_{12}$ system, the canting occurs in the d sites. (While the canting is yet to be proved, 180° flipping of spins would not change the model substantially. There are good reasons to expect canting rather

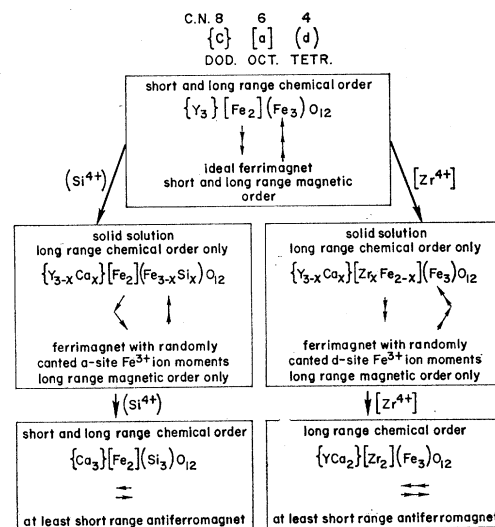


FIG. 1. Summary of proposed explanation for the magnetic behavior of the system $\{\text{Y}_{3-x}\text{Ca}_x\}[\text{Fe}_2](\text{Fe}_{3-x}\text{Si}_x)\text{O}_{12}$ and $\{\text{Y}_{3-x}\text{Ca}_x\}[\text{Zr}_x\text{Fe}_{2-x}](\text{Fe}_3)\text{O}_{12}$.

⁷ The data seem to be taken from R. C. LeCraw, J. P. Remeika, and H. Matthews, Phys. Letters **12**, 9 (1964).

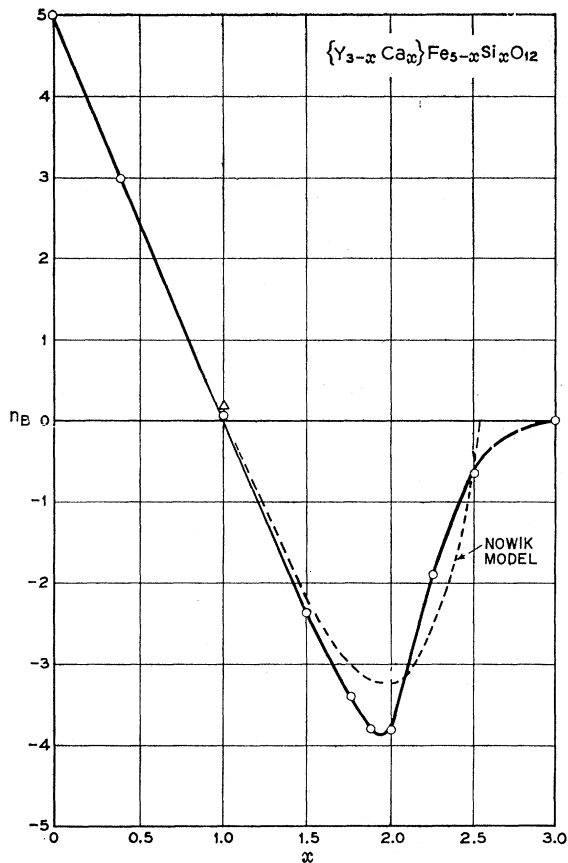


Fig. 2. Spontaneous moment at 0°K versus composition for silicon-substituted yttrium iron garnet.

than flipping. However, it is true that Mössbauer spectroscopy, but not coherent neutron diffraction,² can decide this issue, and we intend to do the experiments.)

At concentrations of diamagnetic ions below the critical one for each system, the $a-d$ interactions dominate and the anisotropy is low. Thus, alignment of domains is accomplished easily, that is, with moderate fields. At concentrations above the critical one, there is indication of a significant increase in anisotropy: The curves of moment versus applied field do not become linear until about 40 kOe are applied (see Figs. 3 and 8 of Ref. 2). In the antiferromagnetic ground state, the dominance of the intrasublattice interactions² in the magnetic structure probably causes the increased anisotropy. (It is also probable that there is a change in the long-range magnetic structure at the critical composition.) As in the case of an antiferromagnet itself, the moment versus field of garnets having an antiferromagnetic ground state is field-dependent, the more so, the weaker the *average* interaction (i.e., the greater the concentration of diamagnetic ions).

In Fig. 2, we show the data for the system $\{Y_{3-x}Ca_x\}[Fe_2](Fe_{3-x}Si_x)O_{12}$.² For $x=2.50$, there is still a spontaneous moment of $-0.65\mu_B$ and a T_c of 86°K. We

were not able to make a single-phase specimen with $x=2.75$ because it was too close in composition to $Ca_3Fe_2Si_3O_{12}$, which, as is well known, cannot be made by solid-state reaction. (See note added in proof.) However, it is clear that the curve for the system is as we showed it and that spontaneous moments might be expected for compositions very close to that of $Ca_3Fe_2Si_3O_{12}$. Nowik's curve gives a zero moment for x just slightly greater than 2.50. A viable theory must fit the algebraic minimum (Nowik's does not), because this is where there is a transition from dominance of the $a-d$ to that of the $a-a$ interactions. (The fit for the Ge^{4+} ion substitution is not really better; see Nowik's Fig. 1. In this case, it should be emphasized that some of the Ge^{4+} ions enter octahedral sites.)

A plot of the 0°K zero-field moments of the systems $\{Y_{3-x}Ca_x\}[Fe_2](Fe_{3-x}Si_x)O_{12}$ and $\{Y_{3-x}Ca_x\}[Fe_{2-x}Zr_x](Fe_3)O_{12}$ ² is shown in Fig. 3. Clearly, the two are intimately connected. In our paper,² we presented arguments as to why the zero-field moments are the most plausible. While Nowik compares the calculations from his model with the zero-field data for all other systems, for octahedral substitution he plots our data² extrapolated to infinite field as well as those we plotted that were obtained by extrapolation to zero field. The fit of Nowik's model to the $H = \infty$ data is hardly adequate, but because there is no good reason for making such a comparison, Fig. 4 shows only curves through our $H=0$ data with which the comparison *should* be made. It is easily seen that no fit can be claimed. The data for tin-substituted garnets have been omitted, because, as we have indicated elsewhere,^{5,6} some Sn^{4+} ions enter tetrahedral sites especially at high substitution. It should be emphasized that below $x \leq 0.70$ the garnets belonging to the systems of Fig. 4 saturate readily, while for $x > 0.70$ they do not saturate to fields of 80 kOe.²

Nowik claims that his model predicts average sublattice magnetizations that can be less than unity. Our

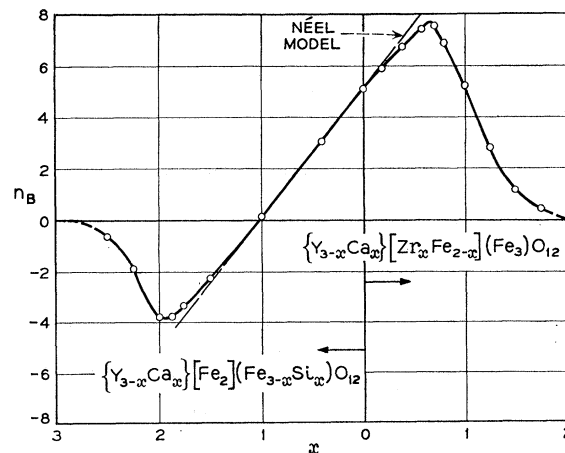


Fig. 3. Continuous relation between the systems $\{Y_{3-x}Ca_x\}[Fe_2](Fe_{3-x}Si_x)O_{12}$ and $\{Y_{3-x}Ca_x\}[Zr_xFe_{2-x}](Fe_3)O_{12}$.

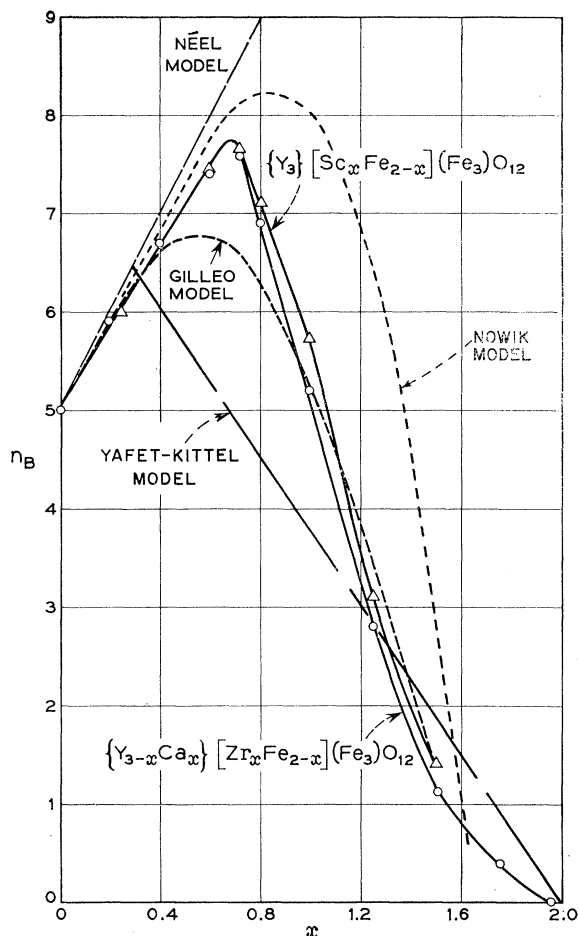


FIG. 4. Spontaneous moment at 0°K versus composition for the zirconium- and scandium-substituted yttrium iron garnets.

model, of course, shows this quite clearly, as do those of Gilileo⁸ and of Yafet and Kittel⁹; the observations require that this be part of any model. Figure 5 gives the "effective" moment² of the Fe³⁺ ions in the sites where, according to our model, random canting occurs. Not only does this figure show that the resultant moment is less than $5\mu_B$ per Fe³⁺ ion for the sublattice in which the random canting occurs, but it also gives additional important results:

(i) It shows (more directly than by any other model) that the $d-d$ interactions are far stronger than the $a-a$ interactions.

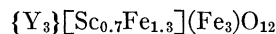
(ii) At the point of transition to the antiferromagnetic ground state, there is a rapid change in $(-dn_B/dx)$ from a small to a large value, demonstrating the rapidly increasing dominance of the intrasublattice interactions.

(iii) Introduction of the Si⁴⁺ ions in d sites as against the substitution of the Mg²⁺ ions in a sites raises the value of x for this transition, even though x implies

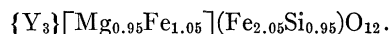
⁸ M. A. Gilileo, J. Phys. Chem. Solids 13, 33 (1960).

⁹ Y. Yafet and C. Kittel, Phys. Rev. 87, 290 (1952).

twice the amount of substituent ion compared with substitution exclusively in a or d sites. This shows that the presence of Si⁴⁺ ions weakens the average $d-d$ interaction substantially to raise the required amount of octahedral ion substitution for the transition. A look at the comparable formulas may be enlightening:



and



In total, there is 2.7 times the substitution of diamagnetic ions in the latter than in the former, and 1.36 times the octahedral substitution: Our model gives an understanding of these results. (It should be kept in mind, as we demonstrated elsewhere,^{2,3} that in the $Y_3[Mg_xFe_{2-x}](Fe_{3-x}Si_x)O_{12}$ system, below the transition composition, $x=0.95$, the garnets saturate magnetically at moderate fields, while for $x>0.95$, they do not saturate. Thus, for $x>0.95$, the $d-d$ intrasublattice interactions dominate.)

For the $\{Y_3\}[Mg_xFe_{2-x}](Fe_{3-x}Si_x)O_{12}$ system, we had plotted both the $H=0$ and $H=\infty$ data, the *only* system for which we did this. Yet in this case, comparison is made by Nowik with only the $H=0$ data (as it should be). However, the fit is quite poor, especially for the ends of the system, and there is no indication of the transition discussed above and clearly shown in Fig. 11 of Ref. 2 or Fig. 3 of Ref. 3. Thus Nowik's theory does not sharply delineate these transitions in all the systems where the data do so.

Nowik says that I came to the conclusion that the Gd³⁺ ion moments in the system $\{Gd_3\}[Fe_{2-x}Sc_x](Fe_3)O_{12}$ are canted "because the behavior of the magnetic moment was not that of three times the Gd moment minus the moment of $\{Y_3\}[Fe_{2-x}Sc_x](Fe_3)O_{12}$." In our paper on the refinement of the yttrium iron

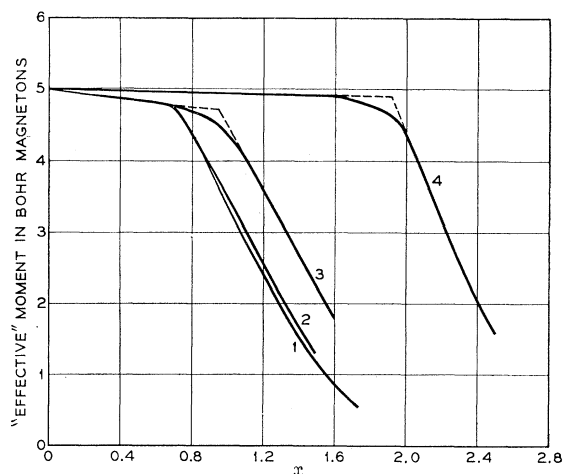


FIG. 5. "Effective" moment (see Ref. 2) per Fe³⁺ ion in (1) d sites for $\{Y_{3-x}Ca_x\}[Fe_{2-x}Zr_x](Fe_3)O_{12}$, (2) d sites for $\{Y_3\}[Fe_{2-x}Sc_x](Fe_3)O_{12}$, (3) d sites for $\{Y_3\}[Fe_{2-x}Mg_x](Fe_{3-x}Si_x)O_{12}$, (4) a sites for $\{Y_{3-x}Ca_x\}[Fe_2](Fe_{3-x}Si_x)O_{12}$.

TABLE I. Comparisons of σ_i for GdIG and YIG (data from Refs. 14 and 17).

T°K	σ_a (GdIG)	σ_a (YIG)	σ_d (GdIG)	σ_d (YIG)	$15\sigma_d-10\sigma_a$		Measured in YIG
					GdIG	YIG	
0	1.0000	1.0000	1.0000	1.0000	5.000	5.000	5.01
10	0.9995	0.9997	0.9995	0.9997	5.000	5.000	5.00
20	0.9988	0.9992	0.9984	0.9991	4.988	4.995	5.00
30	0.9980	0.9984	0.9968	0.9983	4.972	4.991	5.00
40	0.9971	0.9974	0.9952	0.9972	4.957	4.984	4.99
50	0.9961	0.9963	0.9935	0.9958	4.941	4.974	4.99
60	0.9950	0.9950	0.9916	0.9942	4.924	4.963	4.98
70	0.9937	0.9936	0.9895	0.9923	4.906	4.949	4.96
80	0.9922	0.9921	0.9871	0.9900	4.885	4.929	4.93
90	0.9906	0.9901	0.9843	0.9873	4.859	4.909	4.92
100	0.9889	0.9880	0.9810	0.9839	4.826	4.879	4.88
110	0.9868	0.9867	0.9772	0.9800	4.790	4.833	4.84
120	0.9846	0.9832	0.9731	0.9757	4.751	4.804	4.80
140	0.9792	0.9775	0.9635	0.9656	4.661	4.709	4.70
160	0.9726	0.9706	0.9520	0.9531	4.554	4.591	4.59
180	0.9648	0.9621	0.9392	0.9396	4.444	4.473	4.47
200	0.9557	0.9524	0.9247	0.9251	4.314	4.353	4.34
220	0.9453	0.9415	0.9085	0.9091	4.175	4.222	4.21
240	0.9336	0.9292	0.8919	0.8916	4.043	4.082	4.08
260	0.9210	0.9156	0.8741	0.8727	3.902	3.935	3.93
280	0.9070	0.9007	0.8549	0.8525	3.754	3.781	3.79
300	0.8910	0.8842	0.8347	0.8313	3.611	3.627	3.64

garnet (YIG) structure,¹⁰ Gilleo and I pointed out that the strong interaction involving a rare earth in the *c* sites would be with the *d*-site ions and that the *c*-*a* interaction should be negligibly small—all on structural grounds and based on ideas of superexchange interaction formulated earlier by Anderson.¹¹ The paper³ on the substituted gadolinium iron garnets was the first to prove this *experimentally*. It shows unequivocally that the behavior of the Gd³⁺ ion moments is tied to that of the *d*-site Fe³⁺ ions. If our model is correct, and there is random canting of moments on the *d* sites resulting from substitution in the *a* sites, then the Gd³⁺ ion moments must also be canted. The interaction between the Gd³⁺ ion and *d*-site Fe³⁺ ion moments tends to maintain this canting against an applied field. If it turned out that instead of causing random canting, substitution in the *a* sites would cause 180° flipping of moments in the *d* sites, it must also cause an equal number of Gd³⁺ ion moments to flip. While such a proposal would give fair agreement in the region of *a*-*d* interaction dominance, it would not do so in the region of *d*-*d* interaction dominance.

Nowik argues that the Gd³⁺ ion moments prevent the Fe³⁺ ion moments, which according to his model would line up antiparallel to the average *d*-sublattice moment, from doing so. This thesis gives the rare-earth ions an importance that is not supported by the experimental results. For example, (1) if an Y atom replaces one Gd atom as in the system {Gd₂Y}[Fe_{2-*x*}Sc_{*x*}](Fe₃)O₁₂, the remaining Gd³⁺ ion moments still follow the Fe³⁺ ion moment behavior³; (2) the Curie temperatures of all the rare-earth iron garnets are within a few degrees of that of YIG; (3) the compensation points of the system

{Gd_{3-*x*}Y_{*x*}}[Fe₂](Fe₃)O₁₂ are directly predictable from a knowledge of the magnetization curves of GdIG and YIG¹²; (4) the strong dependence of the Eu³⁺ ion moment on the *d*-site Fe³⁺ ion concentration.¹³ Of course, there are other examples.

Indeed, the results of Nowik's own theory dispose of his statement because his curve for the {Gd₃}[Fe_{2-*x*}Sc_{*x*}](Fe₃)O₁₂ system fits fairly well the data where there is very little canting, but it does not fit at all where there is the substantial canting we proposed. Further, his curve for the {Gd₂Y}[Fe_{2-*x*}Sc_{*x*}](Fe₃)O₁₂ system shows at the very least an inflection or tendency to a minimum which is unexplained and, of course, does not occur in the system. Another consequence of Nowik's argument is that, as his curve for the system indicates, a hypothetical specimen such as {Gd₃}[Sc₂](Fe₃)O₁₂, with the octahedral sites filled with diamagnetic ions, should be ferrimagnetic, in this case, with a 0°K moment of ~6μ_B. This is in disagreement with the clear indication³ that it would be a weak ferromagnet or an antiferromagnet.

Myers *et al.*¹⁴ (and others^{15,16}) have found that the temperature behavior of the *a* and *d* sublattice magnetizations in GdIG differ from those in YIG. However, the effects are *extremely* small. Myer *et al.*¹⁴ plot $(1-\sigma_i)_{\text{GdIG}}/(1-\sigma_i)_{\text{YIG}}$ against *T*, where $\sigma_i = M_i(T)/$

¹² S. Geller, J. Phys. Chem. Solids **16**, 21 (1960); E. E. Anderson, in *Proceedings of the International Conference on Magnetism, Nottingham, 1964* (The Institute of Physics and The Physical Society, London, 1965), p. 660.

¹³ S. Geller, J. A. Cape, G. P. Espinosa, and D. H. Leslie, Phys. Letters **21**, 495 (1966).

¹⁴ S. M. Myers, R. Gonano, and H. Meyer, Phys. Rev. **170**, 513 (1968).

¹⁵ E. L. Boyd, V. L. Moruzzi, and J. S. Smart, J. Appl. Phys. **34**, 3049 (1963).

¹⁶ Le Dang Kuoi and M. Buyle-Bodin, Compt. Rend. **253**, 2514 (1961).

¹⁰ S. Geller and M. A. Gilleo, J. Phys. Chem. Solids **3**, 30 (1957); **9**, 235 (1959).

¹¹ P. W. Anderson, Phys. Rev. **7**, 350 (1950).

$M_i(0^\circ\text{K})$ and $i=a$ or d . This magnifies the effect considerably, especially at low temperatures, where the values of $1-\sigma_i$ are very small indeed. Listed in Table I are the values of σ_i converted from $1-\sigma_i$ of Table I of the paper of Myers *et al.*¹⁴ These are compared with the analogous values for YIG taken from the paper by Gonano *et al.*¹⁷

At no temperature do the analogous σ_i 's differ by more than 0.8% and usually by much less. A calculation of the net moments from the Fe^{3+} ion sublattices in GdIG and YIG (see Table I) shows that at no temperature do the values differ by more than 1.2%. Table I shows also that a comparison of the net moments of YIG calculated from the σ_i 's is in excellent agreement with the measured values¹⁸ (some are interpolated). Comparisons made with the results of Myers *et al.*¹⁴ for TmIG and for LuIG show again that the differences in the σ_i 's are very small. (A more graphic comparison may be obtained from the paper by Kuoi and Buyle-Bodin.¹⁶) Thus, Nowik's argument that "GdIG is not just YIG plus Gd in a passive role" is not substantiated.

The small differences probably have nothing to do with the magnetic moment of the Gd^{3+} ion but rather with its small effect on the "geometry" of the $\text{Fe}^{3+}(a)$ - O^{2-} - $\text{Fe}^{3+}(d)$ interactions.^{2,19,20} In fact, the *largest* known effect of c -site substitution on the thermal behavior of the a and d sublattice magnetizations occurs on the replacement of the Y^{3+} by the diamagnetic Bi^{3+} ion. A substitution of one Bi^{3+} ion for one Y^{3+} ion, i.e., $\{\text{BiY}_2\}[\text{Fe}_2](\text{Fe}_3)\text{O}_{12}$, results in an increase of 38°K in the Curie temperature.¹⁹ The Bi^{3+} ion prefers a somewhat different kind of coordination from that of the rare-earth ions even though it can readily replace Y^{3+} and rare-earth ions. We have found also that replacement of 13% of the d -site Fe^{3+} ions in the YIG by the *diamagnetic* V^{5+} ions causes an increase of 6° in the Curie temperature.²⁰ The V^{5+} ion does not usually "like" tetrahedral coordination and must have a favorable effect on the interaction geometry. This effect is considerable because it must more than overcome the replacement of 0.4 Fe^{3+} ion per formula unit by diamagnetic ions. In fact, the garnet $\{\text{Ca}_3\}[\text{Fe}_2](\text{Fe}_{1.5}\text{V}_{1.5})\text{O}_{12}$ has a T_C of 493°K ,²⁰ which is 126°K higher than that of $\{\text{Y}_{1.5}\text{Ca}_{1.5}\}[\text{Fe}_2](\text{Fe}_{1.5}\text{Si}_{1.5})\text{O}_{12}$,² a garnet with equivalent diamagnetic-ion substitution for Fe^{3+} ion and with very nearly the same 0°K moment as $\{\text{Ca}_3\}[\text{Fe}_2]\times(\text{Fe}_{1.5}\text{V}_{1.5})\text{O}_{12}$.

For the $\{\text{Eu}_{3-x}\text{Ca}_x\}[\text{Fe}_2](\text{Fe}_{3-x}\text{Si}_x)\text{O}_{12}$ system,¹⁸ Nowik's theory again predicts a minimum, the location

¹⁷ R. Gonano, E. Hunt, and H. Meyer, *Phys. Rev.* **156**, 521 (1967).

¹⁸ S. Geller, H. J. Williams, R. C. Sherwood, J. P. Remeika, and G. P. Espinosa, *Phys. Rev.* **131**, 1080 (1963).

¹⁹ S. Geller, H. J. Williams, G. P. Espinosa, R. C. Sherwood, and M. A. Gilleo, *Appl. Phys. Letters* **3**, 21 (1963).

²⁰ S. Geller, G. P. Espinosa, H. J. Williams, R. C. Sherwood, and E. A. Nesbitt, *Appl. Phys. Letters* **3**, 60 (1963); *J. Appl. Phys.* **35**, 570 (1964).

of which is not in accord with the data. In fact, the same holds true for the $\text{Eu}_3\text{Ga}_x\text{Fe}_{5-x}\text{O}_{12}$ system.⁷ In both systems, the situation in regard to the Eu^{3+} moment differs markedly from that of the other paramagnetic rare-earth ions. In the Eu^{3+} ion case, there is, of course, an actual reduction of the intrinsic Eu^{3+} ion moment as a result of the reduction of the d -site Fe^{3+} ion concentration.^{7,13}

We have already discussed in our papers some points raised by Nowik about other theories. The graphs of the results of these theories given in Nowik's paper seem to have been taken from our papers.^{2,4} In discussing de Gennes's treatment of the data of the tin-substituted garnets (Nowik's Ref. 7), Nowik apparently used our results,² which corrected an arithmetic error in de Gennes's calculation. Another point previously made is that the use of exchange parameters of an unsubstituted garnet to predict behavior of substituted garnets is incorrect. An extreme example is given in Ref. 2.

Gilleo made an important contribution, as we have indicated elsewhere,⁴ in demonstrating the statistical nature of the problem. Nowik uses such ideas himself. Further, we have already shown that there are no ions remaining paramagnetic down to 0°K ; in fact, our model precludes this. But, of course, Gilleo himself recognized that his model was not the last word. It did show a tentative agreement, not much worse than Nowik's in general and much better for octahedral substitution. Further, as we have shown, Gilleo's model allows one to calculate rather accurately many of the Curie temperatures; Nowik's theory does not. However, neither theory is adequate, while our proposed model accounts logically for the observations, and then allows a variety of accurate predictions to be made.

Because the magnetic behavior of the rare-earth ion sublattice is almost completely dependent on the magnetic behavior of the d sublattice, it is surprising that the agreement Nowik's theory shows with the $\{\text{Gd}_{3-x}\text{Ca}_x\}[\text{Fe}_2](\text{Fe}_{3-x}\text{Si}_x)\text{O}_{12}$ system (see his Fig. 3) can be so good when it is so poor for the $\{\text{Y}_{3-x}\text{Ca}_x\}[\text{Fe}_2](\text{Fe}_{3-x}\text{Si}_x)\text{O}_{12}$ system.

Now we look at the explanation given by Nowik of the peaks seen in some of the magnetic moment versus temperature curves of some of the substituted yttrium iron garnets. It is correct that we have found a number of these. In *every* case illustrated in our paper,² these occur for *high* substitution, that is, *far* into the regions where we believe that the intrasublattice interactions dominate. Nowik did not show the data for $\{\text{Y}_{0.75}\text{Ca}_{2.25}\}[\text{Fe}_2](\text{Fe}_{0.75}\text{Si}_{2.25})\text{O}_{12}$; therefore, for the sake of clarity and convenience, the data are shown again here (Fig. 6). The striking feature of these particular data is that the behavior of n_B versus T is field-dependent. At 5.0 kOe there is no peak at all. At 9.6 kOe, there is a peak which becomes more apparent when the field is increased to 14.24 kOe. Thus, at the very least, Nowik's theory would require adjustment of parameters to account for this field dependence.

But let us suppose that the Nowik theory could be adjusted to account for the field dependence of the peak. Nowik points out that the maximum occurs at 37°K. This is about where the peak occurs for the higher field curves in Fig. 6. But compare the shapes of the curves with the Nowik curve. Observe the predicted moments: At 0°K, n_B is about 2.7; at the peak it is about 3.8. These are almost a factor of 2 higher than those observed in a field of 14.2 kOe. Is Nowik's curve that for the zero field? If so, it cannot be easily obtained from the data at moderate fields as indicated in Fig. 3 of Ref. 2. For those garnets which are not saturated magnetically at moderate fields, the linear portion of n_B versus H_a occurs above 30–40 kOe. This is how we obtained a 0°K moment for this garnet of $-1.9\mu_B$, which is not what one would get from Fig. 6. The garnets which are in the antiferromagnetic ground state appear to have high anisotropy. In any case, it would seem that Nowik's statement that "In fact, the sample $\{Y_{0.75}Ca_{2.25}\}[Fe_2](Fe_{0.75}Si_{2.25})O_{12}$ has exactly the behavior predicted by our model . . ." is rather uncritical.

The explanation of the rise in moment must include the effects of a change in field as well as of temperature. We did not obtain the zero-field data over the entire temperature range. To obtain them, it would seem necessary to make measurements to very high fields over this temperature range and extrapolate to $H=0$. I do not find Nowik's explanation acceptable in any case, especially because it is difficult to see how the *magnetic moments* of some Fe^{3+} ions could decrease much more rapidly than those of other Fe^{3+} ions. It is probable that anisotropy and perhaps field-dependent differences in thermomagnetic behavior of the two sublattice magnetizations are involved. This matter can probably be settled by investigations on single crystals, and we hope to do this in the future.

After first rejecting the Yafet-Kittel (YK) theory, Nowik later indicates that there might be canting after all "like that in the YK model." But the reasons he gave earlier in his paper for rejecting it are correct. (The words differ from those we gave,² but the result is

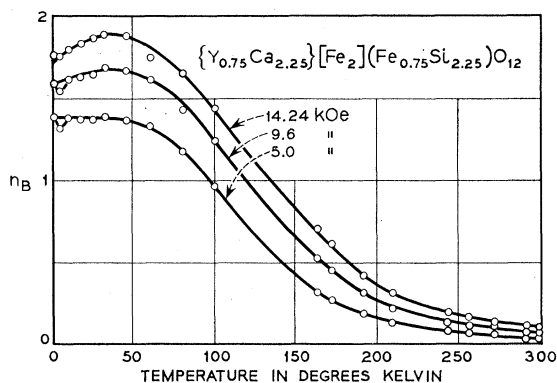


FIG. 6. n_B versus T at different magnetic fields for $\{Y_{0.75}Ca_{2.75}\}[Fe_2](Fe_{0.75}Si_{2.25})O_{12}$.

the same.) If there is canting, it should not be that of the YK model but of ours, namely, *random canting*.

I have little doubt but that all the accumulated data, including those from NMR investigations, indicate that an adequate *mathematical* formulation must include detailed consideration of the intrasublattice interactions, especially in the regions where they appear to dominate the intersublattice interactions. These are undoubtedly linked with the details of the crystal structure and the changes in distances and angles brought about by substitutions. Further, the statistical nature of the problem must be treated adequately. No theory will be adequate if it does not show consistency over the wide range of results which, as our own model shows, are consistent.

Note added in proof. I have recently been informed by Yoder²¹ that pure $Ca_3Fe_2Si_3O_{12}$ garnet may be synthesized at atmospheric pressure by long annealing of a glass of appropriate composition.

I wish to thank M. Sparks for discussions of many aspects of this paper, especially those pertaining to the various models.

²¹ H. G. Huckenholz, J. F. Schairer, and H. S. Yoder, Am. Min. Soc. Special Paper No. 2 (to be published).