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Structure and ferrimagnetism of yttrium and rare-earth–iron garnets.*

By S. Geller and M. A. Gilleo, *Bell Telephone Laboratories, Inc., Murray Hill, New Jersey, U.S.A.*

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Ferrimagnetism in rare-earth–iron garnets was discovered independently by the authors, though at a later date and in a way different from that of Bertaut & Forrat (1956). The observations leading to our synthesis of these new magnetic materials are given below.

In the course of work on the crystallographic and magnetic properties of $A^{3+}B^{3+}O_3$ compounds with perovskite-like structure we observed (1) that most of these compounds have an orthorhombic structure (D_{2h}^{16}–$Pbnm$) (Geller, 1955, 1956, 1957; Geller & Wood, 1956; Geller & Bala, 1956) with all B^{3+} (magnetic transition metal) ions in identical (4*b*) positions; and (2) that spontaneous magnetization had not been observed when these B^{3+} ions are identical (same valence and atomic number) (Gilleo, 1955, 1956, 1957). Spontaneous magnetization does occur when identical magnetic ions occupy different crystallographic sites (e.g. $MgFe_2O_4$).

Although steric considerations appeared to be most important to the prediction of the occurrence of perovskite-like phases we found that these considerations were not sufficient. Perovskite-like phases of $YGaO_3$, $GdGaO_3$ and $SmGaO_3$ could not be obtained even though such phases were made without difficulty for the corresponding compounds of Sc^{3+}, Fe^{3+}, V^{3+}, Cr^{3+} and Al^{3+} (except YVO_3 and $SmScO_3$ which were not tried) and for $NdGaO_3$, $PrGaO_3$ and $LaGaO_3$. However, one of the phases which did form in the reaction of Ga_2O_3 with Y_2O_3, Sm_2O_3 and Gd_2O_3 was of the garnet type,† e.g. $Y_3Ga_2(GaO_4)_3$, as was first established through comparison with the work of Keith & Roy (1954). In a garnet-like compound (see Menzer, 1929) $(GaO_4)^{5-}$ represents three Ga^{3+} ions tetrahedrally surrounded by O^{2-}; the two remaining Ga^{3+} ions are in octahedral positions and the three Y^{3+} ions are in C.N.(8) positions. The garnet structure was obviously conducive to ferrimagnetism with Fe^{3+} substituted for Ga^{3+}. A net moment of $5\mu_B$ per formula unit would result from dominant antiferromagnetic interaction between iron ions in these different positions since the tetrahedral Fe^{3+} ions outnumber the octahedral Fe^{3+} ions by one.

In our first trial we fired a pressed pill of $3Y_2O_3+5Fe_2O_3$ at 1400° C. in air for 4 hr. We obtained a strongly magnetic material of pure garnet phase, $Y_3Fe_2(FeO_4)_3$. Subsequently, we obtained garnet phases of $Sm_3Fe_2(FeO_4)_3$ and $Gd_3Fe_2(FeO_4)_3$. These results were in accord with those of Yoder & Keith (1951), who were first to show that a silicon-free garnet could be synthesized, namely $Y_3Al_2(AlO_4)_3$.

The spontaneous magnetization of the above sample at zero temperature and infinite field, $\sigma_{\infty,0}$, was determined by extrapolation from measurements down to 1·4° K. and with fields up to 8000 oersteds by Miss D. E. Walsh and A. J. Williams of these Laboratories; the value is $4{\cdot}69\mu_B$ per formula unit with a precision of $\pm 1\%$. A Curie temperature of 272·5±0·5° C. was determined by F. B. Humphrey for the disappearance of the hysteresis loop. These data are in agreement with those of Aléonard, Barbier & Pauthenet (1956). Pauthenet (1956) has also reported magnetic data for gadolinium–iron garnet which greatly clarify the interpretation of data previously in disagreement with our work on $GdFeO_3$ (Gilleo, 1955, 1956).

Single-crystal data have been obtained for yttrium–iron garnet with the purpose of confirming the most probable space group and of determining accurately the positions of the O^{2-} ions. The crystal was produced by Nielsen (1956) of these laboratories. A spherical specimen which had been prepared by J. F. Dillon for ferromagnetic resonance experiments was used.

The symmetry of the single-crystal photographs is O_h–$m3m$. Only the following types of reflections appear to be present: (hkl), $h+k+l=2n$; $(hk0)$, $h=2n$, $k=2n$; (hhl), $l=2n$, $2h+l=4n$. Thus the most probable space group for yttrium–iron garnet is O_h^{10}–$Ia3d$.

Fortunately, a substantial number of reflections have no contribution from the metal ions, all of which are in highly specialized positions. These reflections are of the type (hkl) with any two of the indices odd and the third divisible by 4. There is also a substantial number of reflections which have no contribution from the octahedral Fe^{3+} ions; the contribution from the remaining ions is eight times the difference between the scattering of yttrium and iron. These reflections have two indices odd and the third equal to $4n+2$. Thus we expect to obtain fairly accurate positions for the oxygen ions.

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† These reactions took place during experiments in the growth of perovskite-like crystals by Remeika (1956). Subsequent solid–solid reaction experiments substantiated the compositions of these garnet phases.