

for values of $x \geq 1.80$. In a recent attempt to make the garnet with $x = 1.95$, the specimen obtained was clearly not single phase and the garnet phase present had $a = 12.517 \text{ \AA}$, 0.004 \AA higher than our previous value. ESPINOSA's work⁶³, indicated that the Nd_2O_3 we had used must have contained an impurity ion smaller than Nd^{3+} . He obtained a value of 12.488 as opposed to 12.485 \AA for the $x = 1.5$ specimen. The new maximum a value is in line with this difference and still indicates maximum $x = 1.88$.

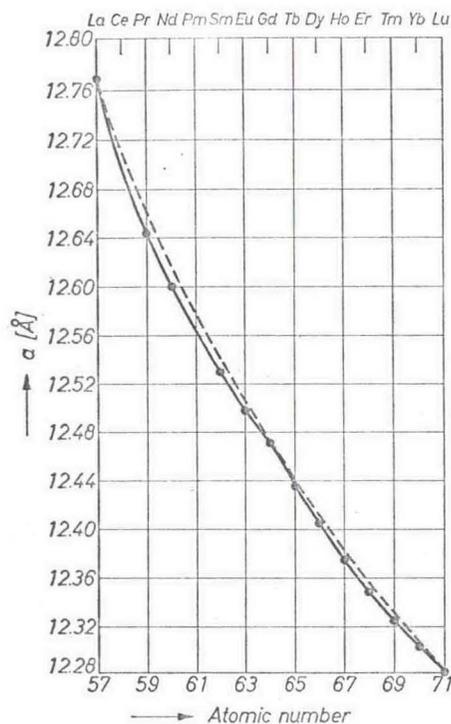


Fig. 4. Lattice constant vs atomic number for rare-earth iron garnets. Dashed curve passes through values for the trivalent rare earths with spherical electronic configuration (after ESPINOSA⁶³)

ESPINOSA also determined maximum x for $M \equiv \text{Pr}$ and La in the systems $\{\text{Y}_{3-x}\text{M}_x\}\text{Fe}_2\text{Fe}_3\text{O}_{12}$ to be 1.33 and 0.45, respectively. He also determined the maximum substitution of Pr for Lu , Gd and Sm in their iron garnets. The results are shown in Fig. 3 taken from ESPINOSA's paper. It is seen that a maximum lattice constant for any iron garnet, obtained by extrapolation is 12.538 \AA in good agreement with 12.540 \AA obtained by GELLER *et al.*⁶⁴ who first determined this

value from their work with Nd substituted iron garnets. This value is just about 0.02 \AA too small to allow the existence of $\text{Pm}_3\text{Fe}_2\text{Fe}_3\text{O}_{12}$. It is just about realized by the garnet $\{\text{Pr}_{0.25}\text{Sm}_{2.75}\}\text{Fe}_2\text{Fe}_3\text{O}_{12}$ ⁶³.

A plot of a vs atomic number taken from ESPINOSA's paper is given in Fig. 4. It shows the small crystal-field effects on the rare-earth ions not having spherical electronic configurations and the expected cusp at the Gd^{3+} ion.

BERTAUT and FORRAT⁶² predicted a value of 12.57 \AA for a PmFe garnet, we obtained⁶⁴ 12.561 \AA . The latter value is also obtained from the curve in ESPINOSA's paper. For a hypothetical $\{\text{Ce}_3\}\text{Fe}_2\text{Fe}_3\text{O}_{12}$, a value of 12.699 \AA would be obtained from the same curve.

In the case of the gallium garnets, while there have been numerous investigations involving Tb and Tm garnets, I have not been able to find a report of the lattice constants of these with ideal stoichiometry. The lattice constants of the others have been mainly determined first by BERTAUT and FORRAT⁵⁸ and then by SCHNEIDER *et al.*⁵⁷ and by SWANSON *et al.*^{67,68} on the materials made by SCHNEIDER *et al.* Because those of SWANSON *et al.* are insignificantly different from those of SCHNEIDER *et al.*, only the averages of the two (which in no case differ by more than 0.002 \AA) are listed. For YGa garnet, there are several values, the best seeming to be $12.274 \pm 0.001 \text{ \AA}$.

In the early work on a few of the gallium and aluminum garnets done by KEITH and ROY⁵⁶, it was found that excess yttrium or rare-earth oxide was soluble in the garnet. No proof was given, but it was postulated that the large ions were replacing the Ga^{3+} or Al^{3+} ions in octahedral sites. Some of the gallium-garnet crystals grown by REMEIK (see Ref. 4) showed solid-solution ranges within the same batch. Subsequently, SCHNEIDER *et al.*⁵⁷ explored these solid solutions in the rare earth and yttrium gallium garnet systems. They found that the "solubility" and lattice constant increase with decreasing rare earth ion radius until Tm^{3+} is reached, then both decrease. For Y^{3+} , both the range of solid solution and lattice-constant difference were substantially larger than those for Ho^{3+} with the same size.

SCHNEIDER *et al.*⁵⁷ also believe that in these solid solutions, the Ga^{3+} ions in a sites are replaced by the excess rare-earth ions. They mention that I said, in private communication, that the solid solution may be of the "interstitial and/or vacancy types instead of substitutional and thus results in a defect structure". I cannot remember exactly what I said but surely there are no interstitial sites in the garnet structure to be occupied. However, I did think it probable