

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  $a = 12.517 \text{ \AA}$ ,  $0.004 \text{ \AA}$  higher than our previous value. ESPINOSA's work<sup>63</sup>, indicated that the  $\text{Nd}_2\text{O}_3$  we had used must have contained an impurity ion smaller than  $\text{Nd}^{3+}$ . He obtained a value of  $12.488 \text{ \AA}$  as opposed to  $12.485 \text{ \AA}$  for the  $x = 1.5$  specimen. The new maximum  $a$  value is in line with this difference and still indicates maximum  $x = 1.88$ .

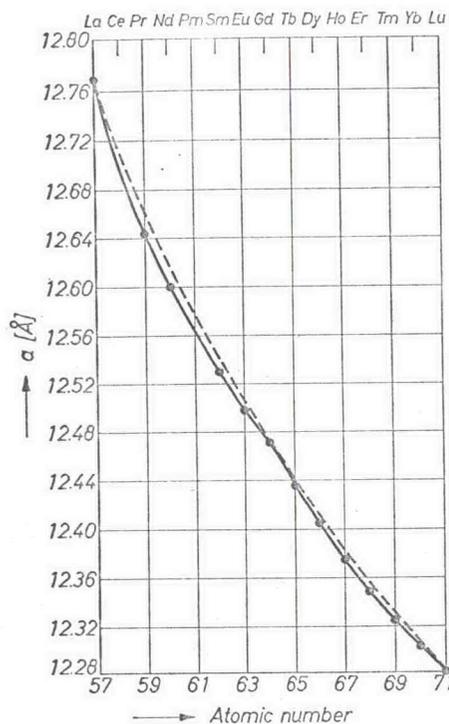


Fig. 4. Lattice constant vs atomic number for rare-earth iron garnets. Dashed curve passes through values for the trivalent rare earths with spherical electronic configuration (after ESPINOSA<sup>63</sup>)

ESPINOSA also determined maximum  $x$  for  $M \equiv \text{Pr}$  and  $\text{La}$  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  $\text{Pr}$  for  $\text{Lu}$ ,  $\text{Gd}$  and  $\text{Sm}$  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  $12.538 \text{ \AA}$  in good agreement with  $12.540 \text{ \AA}$  obtained by GELLER *et al.*<sup>64</sup> who first determined this

value from their work with  $\text{Nd}$  substituted iron garnets. This value is just about  $0.02 \text{ \AA}$  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  $\{\text{Pr}_{0.25}\text{Sm}_{2.75}\}\text{Fe}_2\text{Fe}_3\text{O}_{12}$ <sup>63</sup>.

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  $\text{Gd}^{3+}$  ion.

BERTAUT and FERRAT<sup>62</sup> predicted a value of  $12.57 \text{ \AA}$  for a  $\text{PmFe}$  garnet, we obtained<sup>64</sup>  $12.561 \text{ \AA}$ . 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  $12.699 \text{ \AA}$  would be obtained from the same curve.

In the case of the gallium garnets, while there have been numerous investigations involving  $\text{Tb}$  and  $\text{Tm}$  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 FERRAT<sup>58</sup> and then by SCHNEIDER *et al.*<sup>57</sup> and by SWANSON *et al.*<sup>67,68</sup> 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  $0.002 \text{ \AA}$ ) are listed. For  $\text{YGa}$  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 ROY<sup>56</sup>, 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  $\text{Ga}^{3+}$  or  $\text{Al}^{3+}$  ions in octahedral sites. Some of the gallium-garnet crystals grown by REMEKA (see Ref. 4) showed solid-solution ranges within the same batch. Subsequently, SCHNEIDER *et al.*<sup>57</sup> 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  $\text{Tm}^{3+}$  is reached, then both decrease. For  $\text{Y}^{3+}$ , both the range of solid solution and lattice-constant difference were substantially larger than those for  $\text{Ho}^{3+}$  with the same size.

SCHNEIDER *et al.*<sup>57</sup> also believe that in these solid solutions, the  $\text{Ga}^{3+}$  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