

## Detection of $\text{Al}_2\text{O}_3 : \text{Fe}^{2+}$ by EPR Relaxation-Time Measurements of $\text{Cr}^{3+}$ Ions in Corundum

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Angular-dependence experiments of relaxation times  $T_1$  for the  $\text{Cr}^{3+}$  ion have already been reported in a ruby sample doped with silicon. They showed minima in  $T_1$  which could not be interpreted in terms of harmonic cross relaxation. The presence of  $\text{Fe}^{2+}$  ions in the specimen may explain these minima. Ruby samples doped with both iron and silicon have been made to increase the  $\text{Fe}^{2+}$  concentration by charge compensation with  $\text{Si}^{4+}$  ions. The minima in relaxation time for  $\text{Cr}^{3+}$  are enhanced in these crystals and they occur at all the crossing points of the  $\text{Cr}^{3+}$  and  $\text{Fe}^{2+}$  lines. The variation of  $T_1$  vs angle for  $\text{Cr}^{3+}$  is studied and the temperature dependence of  $T_1$  is investigated from 4.2 to 1.2°K. Further work is in progress to see if our results are in agreement with the sign of the zero-field splitting parameter  $D$  found by Lewiner *et al.* or with the one obtained by Ganapol'skii. Theoretical work by Stevens and Walsh and the acoustical-paramagnetic-resonance experiments by Lewiner *et al.* and Ganapol'skii on  $\text{Fe}^{2+}$  in corundum are inconsistent.

### I. INTRODUCTION

A number of investigations have been reported on the spectra and the spin-lattice relaxation times of iron-group ions in alumina by electron paramagnetic resonance. However, the ferrous ion has never been observed in  $\text{Al}_2\text{O}_3$  by this method.

We have reported experiments<sup>1</sup> of the angular dependence of the relaxation time  $T_1$  for the  $\text{Cr}^{3+}$  ion in a ruby sample doped with  $\text{Si}^{4+}$  ions. It was shown that the observed minima in  $T_1$  could not be interpreted in terms of harmonic cross relaxation. One explanation could be the presence of an unknown fast-relaxing ion or defect which cross relaxes the  $\text{Cr}^{3+}$  ions at specific directions of the magnetic field, thus causing a marked reduction in the observed value of  $T_1$ . We have drawn approximate isofrequency resonance charts of this fast-relaxing ion for a large range of angles. We have also observed the same minima in  $T_1$  in some rubies doped with iron.<sup>2</sup> However, the presence of  $\text{Fe}^{3+}$  could not explain these results, and a paper by Lewiner *et al.*<sup>3</sup> led us to the conclusion that the ferrous ion might be the unknown fast-relaxing ion. The isofrequency chart of  $\text{Fe}^{2+}$  given by Lewiner *et al.* is the same as the one we obtained, and iron can often be found as an impurity in ruby crystals. If a charge compensation occurs with  $\text{Si}^{4+}$ , iron is likely to be in the  $\text{Fe}^{2+}$  state.

To verify the assumption that the observed minima of  $T_1$  in a ruby sample doped with  $\text{Si}^{4+}$  may be attributable to  $\text{Fe}^{2+}$ , we have made and investigated ruby samples doped with iron and silicon to increase further the concentration of the ferrous ions.

### II. $\text{Fe}^{2+}$ IN ALUMINA

$\text{Fe}^{2+}$  has six electrons in its outer  $3d$  shell and

spin  $S = 2$ . The ground state and the spin-lattice relaxation time of  $\text{Fe}^{2+}$  replacing  $\text{Al}^{3+}$  in corundum have been studied theoretically by Stevens and Walsh.<sup>4</sup> They found that the lowest level is a non-Kramers doublet with  $\Delta M_s = 4$ , and the excited states are  $\sim 100 \text{ cm}^{-1}$  above the ground doublet. Also, they deduced that the relaxation time of the ferrous ion in alumina is quite long.

Using acoustical paramagnetic resonance (APR), Lewiner *et al.*<sup>3</sup> and Lewiner and Meijer<sup>5</sup> have observed an asymmetric line having a sharp high-field edge on a crystal of corundum doped with ferric ions. They deduce that this resonance is due to a  $\Delta M_s = 2$  transition of  $\text{Fe}^{2+}$ , where the effective "spin"  $S' = 1$ , and that the sign of the zero-field splitting parameter  $D$  is negative. They find  $g_{\parallel} = 3.40 \pm 0.04$  and  $|D| > 6 \text{ cm}^{-1}$ . Similar results were found, using APR, by Ganapol'skii.<sup>6</sup> However, a different temperature dependence of the spectrum was obtained, and it is concluded that the lower level is the  $M_s = 0$  singlet which lies at a distance of  $D = 4.2 \pm 0.1 \text{ cm}^{-1}$  from the  $M_s = \pm 1$  doublet. Both sets of experimental results are inconsistent with the calculation of Stevens and Walsh.<sup>4</sup>

TABLE I. Chromium and iron concentrations in the specimens, and silicon concentration in the original alumina powders.

Ruby Sample	Concentration (at. % $\text{Cr}^{3+}$ ) (crystal)	Concentration (at. % $\text{Fe}^{3+}$ ) (crystal)	Concentration (at. % $\text{Si}^{4+}$ ) (powder)
I	0.023	0.0025	0.0625
II	0.023	0.0050	0.125
III	0.023	0.0080	0.250

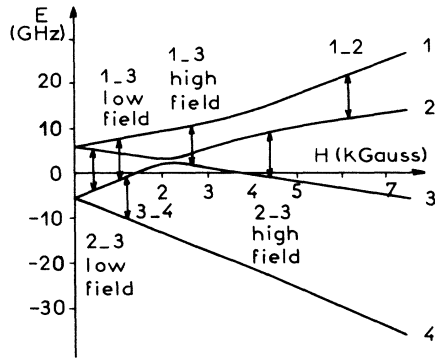


FIG. 1. Energy levels in ruby.  $\theta = 20^\circ$ .

### III. EXPERIMENTAL DETAILS

We have made three rubies doped with iron and silicon, having the same chromium concentration (approximately 0.023 at.%), by the Verneuil process. Their iron and silicon contents are different (Table I), but the silicon concentration in the crystals is unknown and only the concentration of  $\text{Si}^{4+}$  in the original alumina powder can be given.

Relaxation-time measurements have been carried out at 9.3 GHz by pulse-saturation techniques at liquid-helium temperatures.

### IV. ANGULAR VARIATION OF RELAXATION TIMES FOR $\text{Cr}^{3+}$ ION IN RUBIES DOPED WITH IRON AND SILICON

The notation used for the energy levels and the different transitions of the  $\text{Cr}^{3+}$  ion in ruby is shown in Fig. 1.  $\theta$  is the angle between the magnetic field

and the crystal  $c$  axis. The isofrequency resonance chart for ruby at 9.3 GHz is drawn in Fig. 2 with a solid curve, while the broken curve represents magnetic field vs angle for the ferrous ion reported by both Lewiner *et al.* and Ganapol'skii.

The variations of relaxation times  $T_1$  with crystal orientation for different transitions of the  $\text{Cr}^{3+}$  ion have been investigated at 4.2°K for the three specimens. Figures 3-7 give the results obtained with the 1-3 high-field, 1-3 low-field, 1-2, 2-3 high-field, and 3-4 transitions. When the recoveries are not of the form of a single exponential,  $T_1$  is the longest time constant measured from the tail of the relaxation signal.

Comparison of these curves with those obtained from a pure ruby sample having the same chromium concentration<sup>1</sup> shows that a decrease in  $T_1$  for  $\text{Cr}^{3+}$  occurs in rubies doped with iron and silicon for almost all orientations.

We have already observed such effects in rubies doped only with iron or only with silicon and in rubies doped with other impurities such as vanadium, nickel, and magnesium.<sup>7,8</sup>  $T_1$  decreases further when the impurity concentration increases.

Furthermore, when the frequencies of  $\text{Cr}^{3+}$  and  $\text{Fe}^{2+}$  are equal, we observe a minimum in  $T_1$ . Figure 2 shows the points of intersection of the lines for chromic and ferrous ions. They occur, within about 1°, at 21° for the 1-3 low-field transition, 62.5° for the 1-2 transition, 71° for the 2-3 high-field transition, and 79° for the 3-4 transition.

At these four angles there are marked minima for corresponding transitions of  $\text{Cr}^{3+}$  (Figs. 4-7). They are strongly emphasized in these three specimens doped with both iron and silicon. Further,

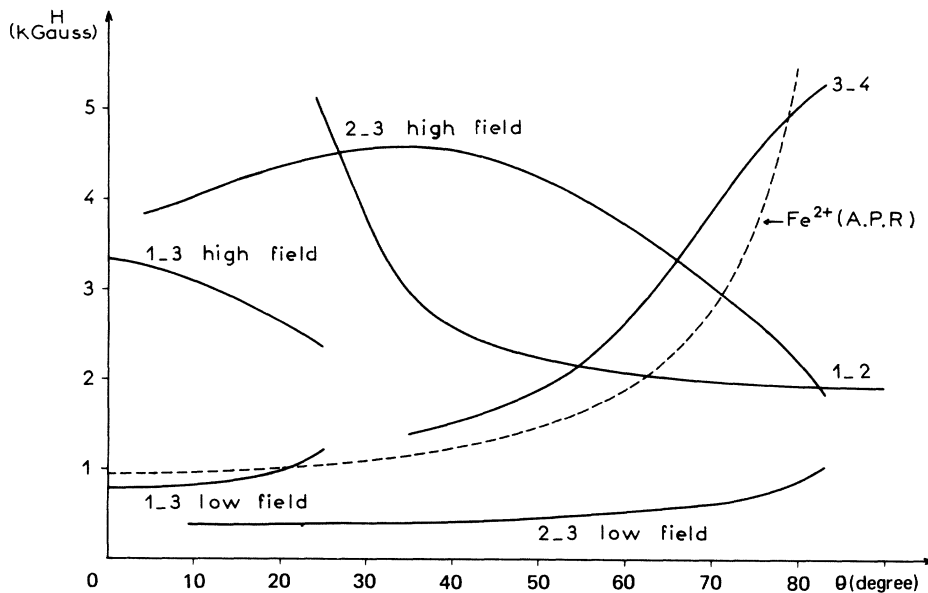


FIG. 2. Isofrequency resonance chart showing crossing points of  $\text{Cr}^{3+}$  and  $\text{Fe}^{2+}$  lines in corundum at 9.3 GHz.

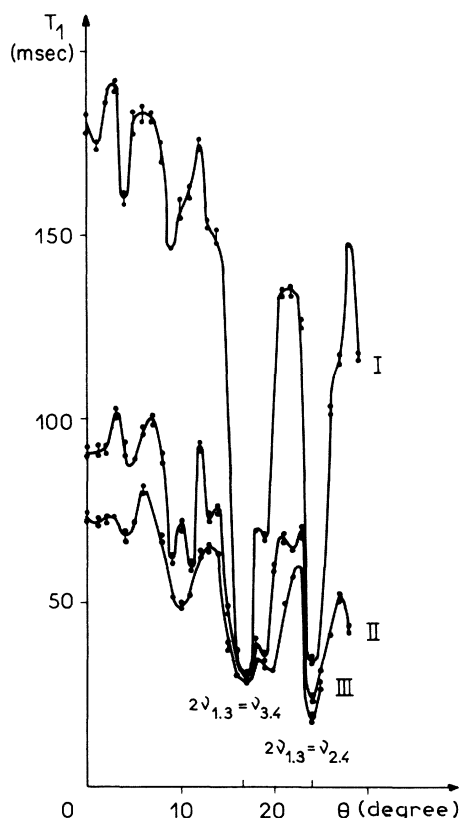


FIG. 3. Angular dependence of relaxation time for 1-3 high-field transition of  $\text{Cr}^{3+}$ .

each minimum has a definite asymmetric shape which agrees with the sharper high-field edge of the  $\text{Fe}^{2+}$  line.

At the points of intersection,  $T_1$  seems to vary with the concentration of  $\text{Fe}^{2+}$  as shown in Table II. Corresponding values of  $T_1$  are given for a pure ruby sample with the same chromium concentration for comparison.

Preliminary results of this work have been published elsewhere.<sup>9</sup>

#### Harmonic Cross Relaxation of $\text{Cr}^{3+}$ and Cross Relaxation with $\text{Fe}^{3+}$

$\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$  cross relaxation has been investigated in ruby samples doped with iron.<sup>2</sup> It is evident that the effect of the  $\text{Fe}^{3+}$  ion on the relaxation time of  $\text{Cr}^{3+}$  is not so important as is the effect of  $\text{Fe}^{2+}$ . Therefore, the four asymmetric minima described here are really due to the effect of  $\text{Fe}^{2+}$ , even though they lie in the neighborhood of some crossing points of the lines of  $\text{Cr}^{3+}$  and  $\text{Fe}^{3+}$  for the 1-2, 2-3 high-field, and 3-4 transitions.

For the 3-4 transition there is also, at about  $80^\circ$ , an harmonic cross-relaxation process  $2\nu_{34} = \nu_{12}$  (where  $\nu_{mn}$  is the frequency difference between the

levels  $m$  and  $n$ ) which we have observed in pure rubies. This process apparently masks the interaction of  $\text{Cr}^{3+}$  with  $\text{Fe}^{2+}$  in our first sample doped only with silicon. It seems that its effect is much less important than cross relaxation of  $\text{Cr}^{3+}$  and  $\text{Fe}^{2+}$  in the three ruby samples doped with both iron and silicon.

There are many extrema on the curves of  $T_1$  vs angle for the different transitions of  $\text{Cr}^{3+}$ . Some of them can be explained in terms of harmonic cross relaxation or crossing of the lines of  $\text{Cr}^{3+}$  and  $\text{Fe}^{3+}$ . The more obvious are given below.

#### 1-3 high-field transition:

$\theta \approx 17^\circ$  minimum,  $2\nu_{13} = \nu_{34}$  for  $\text{Cr}^{3+}$

$\theta \approx 19^\circ$  minimum,  
crossing point with a line of  $\text{Fe}^{3+}$

$\theta \approx 24^\circ$  minimum,  $2\nu_{13} = \nu_{24}$  for  $\text{Cr}^{3+}$ .

#### 1-2 transition:

$\theta \approx 39^\circ$  minimum,  $2\nu_{12} = \nu_{24}$  for  $\text{Cr}^{3+}$

$\theta \approx 54.7^\circ$  maximum,  $\nu_{12} = \nu_{34}$  for  $\text{Cr}^{3+}$

$\theta \approx 82.5^\circ$  maximum,  $\nu_{12} = \nu_{23}$  for  $\text{Cr}^{3+}$ .

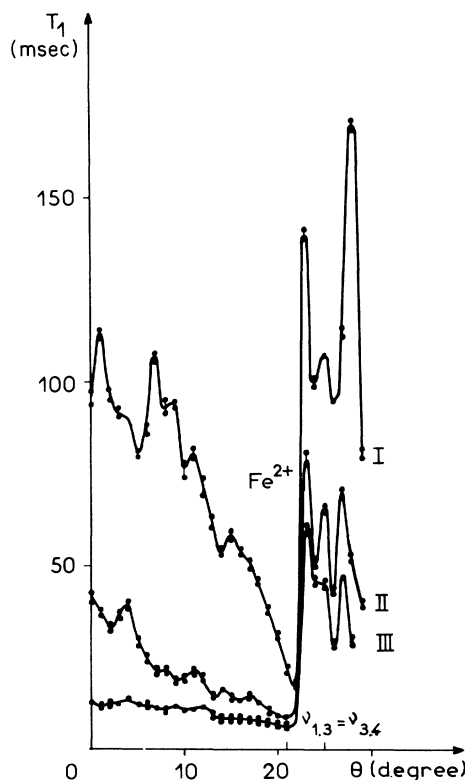


FIG. 4. Angular dependence of relaxation time for 1-3 low-field transition of  $\text{Cr}^{3+}$ .

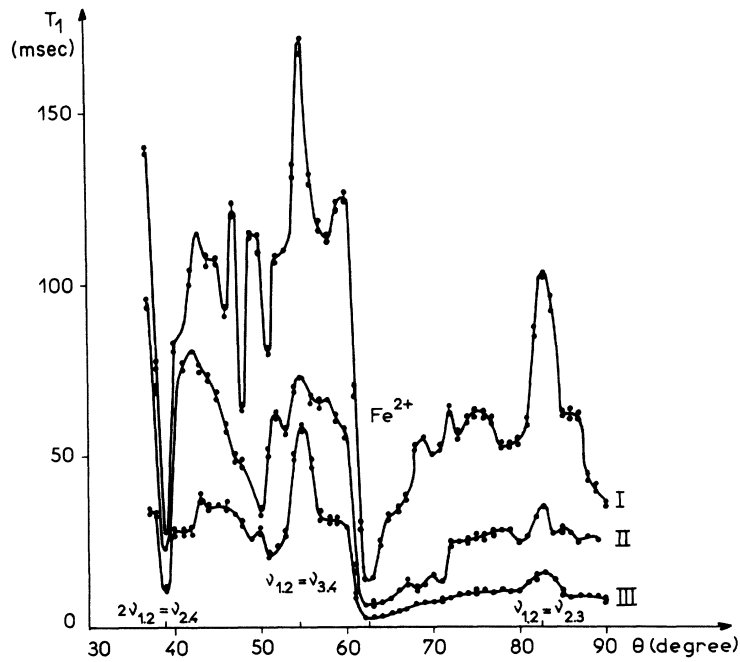


FIG. 5. Angular dependence of relaxation time for 1-2 transition of  $\text{Cr}^{3+}$ .

*2-3 high-field transition:*

$\theta \approx 29^\circ$  minimum ,

crossing point with a line of  $\text{Fe}^{3+}$

$\theta \approx 42^\circ$  minimum ,  $2\nu_{23} = \nu_{34}$  for  $\text{Cr}^{3+}$

$42^\circ < \theta < 50^\circ$  minima ,

crossing points with lines of  $\text{Fe}^{3+}$

$\theta \approx 66^\circ$  { minimum for I ,  $\nu_{23} = \nu_{34}$  for  $\text{Cr}^{3+}$   
maximum for II and III .

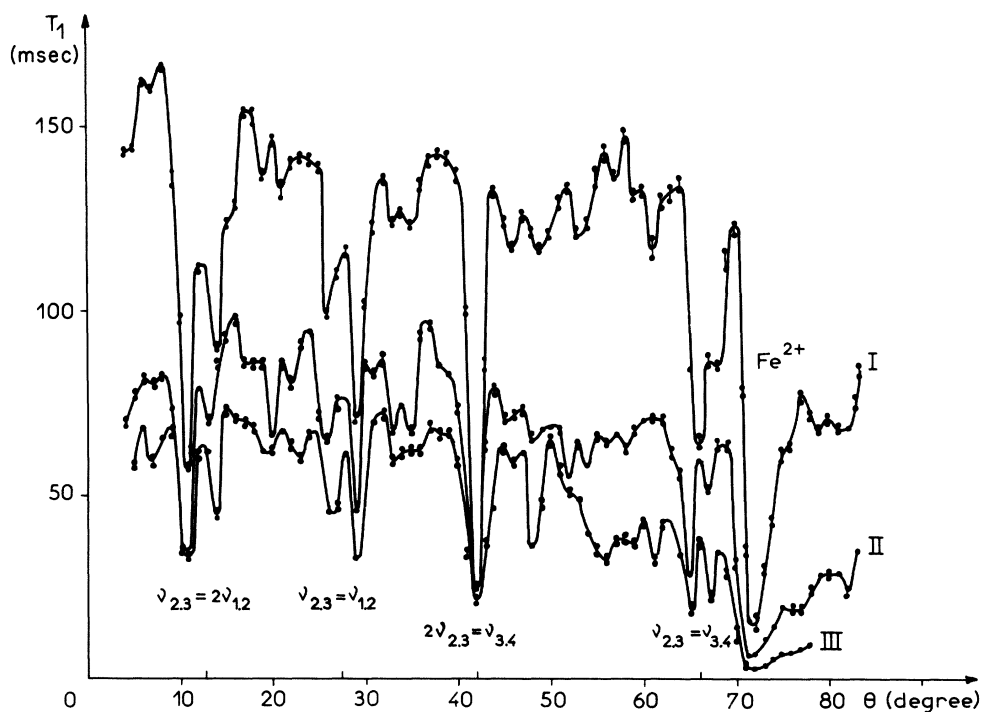


FIG. 6. Angular dependence of relaxation time for 2-3 high-field transition of  $\text{Cr}^{3+}$ .

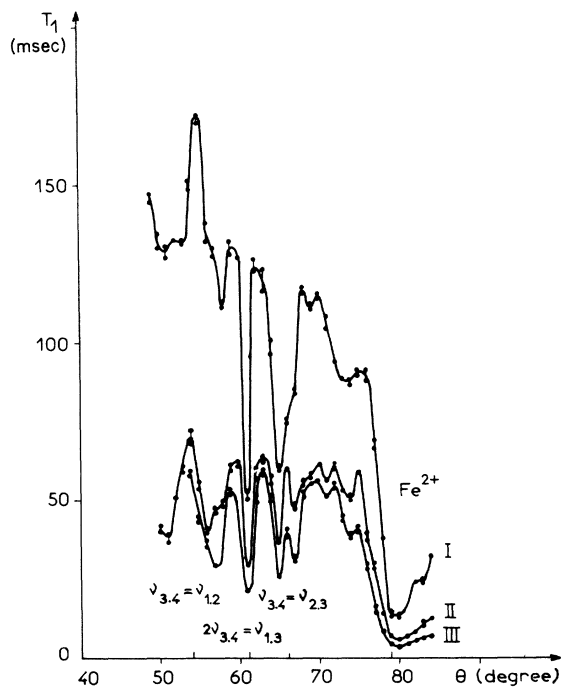


FIG. 7. Angular dependence of relaxation time for 3-4 transition of  $\text{Cr}^{3+}$ .

#### 3-4 transition:

$$\begin{aligned} \theta \approx 54.7^\circ \text{ maximum,} & \quad \nu_{34} = \nu_{12} \text{ for } \text{Cr}^{3+} \\ \theta \approx 61^\circ \text{ minimum,} & \quad 2\nu_{34} = \nu_{13} \text{ for } \text{Cr}^{3+} \\ \theta \approx 74^\circ \text{ minimum,} & \\ & \text{crossing points with lines of } \text{Fe}^{3+} \end{aligned}$$

#### V. TEMPERATURE DEPENDENCE OF RELAXATION TIME FOR $\text{Cr}^{3+}$ ION IN RUBIES DOPED WITH IRON AND SILICON

The temperature dependence of the relaxation time  $T_1$  for the  $\text{Cr}^{3+}$  ion in ruby samples doped with iron and silicon I, II, and III has been investigated from 4.2 to 1.2°K.

When  $\text{Cr}^{3+}$  has no particular frequency relation with  $\text{Fe}^{2+}$  we observe a one-phonon process dependence for the three specimens. However, when the

TABLE II. Comparison of relaxation times for  $\text{Cr}^{3+}$  in a "pure" ruby and in the three rubies doped with iron and silicon, when the frequencies of  $\text{Cr}^{3+}$  and  $\text{Fe}^{2+}$  are equal.

Transition	"Pure" ruby $T_1$ (msec)	Sample I $T_1$ (msec)	Sample II $T_1$ (msec)	Sample III $T_1$ (msec)
1-3 low field	240	18.5	9	6
1-2	150	14.5	7	3
2-3 high field	165	14.5	6	2.5
3-4	180	13	5.5	3.5

frequencies of  $\text{Cr}^{3+}$  and  $\text{Fe}^{2+}$  are equal,  $T_1$  varies more rapidly. It increases almost exponentially with decreasing temperature, but is rather slower than  $e^{\delta/T} + 1$ . This may suggest that  $T_1$  depends upon the population of the  $M_s, = \pm 1$  levels of  $\text{Fe}^{2+}$  and tends to support the conclusions of Ganapol'skii, but further work is in progress to check this assumption. There is perhaps an analogy with the case of our rubies doped with vanadium at the crossing points of the lines of  $\text{Cr}^{3+}$  and  $\text{V}^{3+}$ .<sup>7,8</sup> We are trying to explain the cross-relaxation process of  $\text{Cr}^{3+}$  and  $\text{Fe}^{2+}$  and the disagreement between the results of Stevens and Walsh, Ganapol'skii, and Lewiner *et al.*

#### VI. CONCLUSION

We have detected  $\text{Fe}^{2+}$  in corundum by an EPR method. Our results agree with the isofrequency chart of the line observed by Ganapol'skii and Lewiner *et al.*  $\text{Fe}^{2+}$  seems to be more strongly coupled to the lattice than Stevens and Walsh have expected. But Stevens and Walsh consider  $\text{Fe}^{2+}$  ions which are replacing  $\text{Al}^{3+}$  ions in  $\text{Al}_2\text{O}_3$  lattice. The observed line may be due to  $\text{Fe}^{2+}$  ions situated at vacant sites in alumina. These sites have almost cubic symmetry and would account for the results obtained.<sup>10</sup>

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