

The influence of titanium on the e.s.r. behaviour of Cr^{3+} in alumina

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Electron spin resonance techniques have been used to study the effects of double doping alumina with chromium and titanium. Measurements were made as a function of polar angle on the peak-to-peak derivative linewidths of the three Cr^{3+} transitions at room temperature for a range of samples containing about 0.02% chromium and between zero and 0.024% titanium. Theoretical linewidth variations, calculated from Van Vleck's dipolar broadening theory, were compared with experiment. For crystals singly doped with Cr^{3+} the theory fitted well qualitatively but gave values too great by a factor of seven, in agreement with previous studies. On addition of titanium, marked changes were seen experimentally in the Cr^{3+} linewidth polar plots. These showed a pronounced minimum near $\theta = 55^\circ$ in complete contrast to the behaviour of singly doped ($\text{Cr}/\text{Al}_2\text{O}_3$) crystals. This has been attributed to the formation of (Cr—Ti) complexes by some of the titanium ions.

1. Introduction

Recently the properties of glasses, and in particular nucleation and crystallization processes in glasses and glass ceramics, have been subject to increasing investigation [1]. As a method of further study, work has been started to establish a series of single crystal reference standards corresponding to the crystallization products of certain glasses. The central theme was to incorporate a paramagnetic monitor ion and titanium (which is added to glasses as a nucleating agent) into known crystal lattices in order to study titanium induced crystallization using electron spin resonance techniques. One system under investigation is the magnesia-alumina-silica system ($\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$), primarily because it forms the basis of many commercial glasses and also because large doped crystals of both the primary constituent oxides and several of the binary and tertiary crystallization products can be grown by Czochralski techniques. Initially crystals of alumina (Al_2O_3) have been doped with chromium ions and also with titanium. The main objectives are to determine the factors governing the resonance linewidths of chromium ions in the singly doped crystals and to assess the influence of the addition of titanium on the linewidths.

2. Experimental

The double doped single crystals of alumina used for the linewidth measurements were grown by the Czochralski technique at I.R.D., Newcastle-on-Tyne. The aim was for the samples to be doped with 0.025% chromium and have titanium concentrations varying between 0.025 and 0.25%. For ease of comparison with theory the concentration figures reported in this paper refer to the percentage of aluminium sites occupied by chromium or titanium ions; for alumina these percentages are approximately equal to the weight percentages and to half the atomic percentages. However, analysis by Imperial College, University of London, showed that the chromium concentration varied from 0.015 to 0.023% and the titanium concentration from less than 0.01 to 0.024% (see Table I). As a comparison, the linewidths of two ruby samples were also investigated; one was an I.R.D. ruby (sample 1) grown by the Czochralski technique and the other a vapour phase ruby (sample 2), grown by Thermal Syndicate Ltd of Wallsend, both containing around 0.02% chromium. In alumina the impurity ions enter the lattice substitutionally for the aluminium ions. The aluminium ion is small, with a radius of 0.51 Å and while Cr^{3+} (0.63 Å) is only slightly larger,

TABLE I Chromium and titanium concentrations in the alumina samples.

Sample	Nominal concentration (%)		Actual concentration (%)	
	Cr	Ti	Cr	Ti
1	0.02	—	0.02	—
2	0.025	—	0.025	—
3	0.025	0.025	0.015	< 0.01
4	0.025	0.05	0.02	0.015
5	0.025	0.25	0.23	0.024

Ti^{3+} has a radius of 0.76 Å. This suggests that the lattice surrounding the impurity ion must undergo some strain and distortion to accommodate the impurity [2].

The ground state of the free ion Cr^{3+} is $(3d^3)^4F_{3/2}$ and in the crystal field of alumina two doublets lie lowest; in a magnetic field these are resolved to give an electron spin resonance spectrum of three resonance lines. Ti^{3+} in Al_2O_3 gives a spectrum consisting of a single resonance line which cannot be seen above 9 K [3]; also, due to the small g -values, the line occurs at high magnetic fields of between 2.3 and 24 T, at the frequency of 34 GHz used in these experiments. Hence the Ti^{3+} spectrum was never detected directly because the available field was limited.

The chromium resonance lines were detected using a spectrometer, working at 34 GHz. A phase-sensitive detection system at 160 KHz was used to record the first derivative of the absorption line; thus the actual linewidth measurements involved the peak-to-peak derivative width, ΔH_{ms} . Samples were placed on the short-circuiting plunger, which terminated a section of thin walled stainless steel waveguide, such that they fitted within the modulation loop on the plunger. The c -axis was placed in the plane of rotation of the magnetic field, with the direction of c parallel to one of the plunger sides so that the polar angle, θ , between the c -axis and the magnetic field could be determined directly; a check on the orientation was made from the symmetry of the e.s.r. spectrum.

Measurements of the absorption linewidths (ΔH_{ms}) were made on all the Cr-Ti doped samples and the two ruby samples at room temperature (293 K) for all three Cr^{3+} transitions. Fig. 1 shows the linewidth polar plot for the transition $(-\frac{1}{2} \leftrightarrow -\frac{3}{2})$ as the amount of titanium was increased. The important features observed were that sample 1 had the narrowest lines and

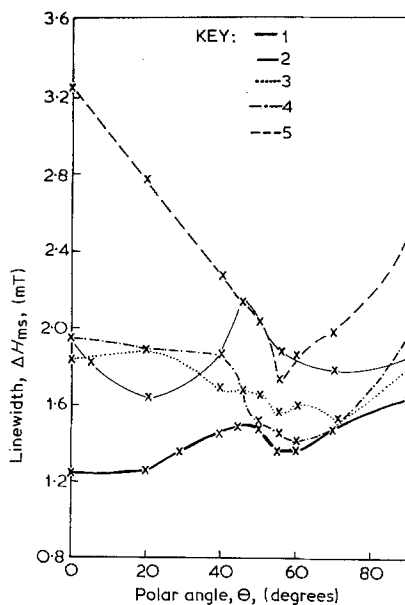


Figure 1 Variation of Cr^{3+} linewidth with polar angle in $Cr/Ti/Al_2O_3$; 34 GHz, room temperature ($-\frac{1}{2} \leftrightarrow -\frac{3}{2}$) transition.

very little angular dependence; sample 2 had much broader lines and a definite peak, probably due to inhomogeneous broadening [4] and the effect of the titanium on the chromium linewidths was to produce a definite "dip" in the polar plot at 55 to 60°, the dip becoming more pronounced as the Ti concentration increased. Similar minima were present in the other two transitions, though to a lesser extent in the transition $(-\frac{1}{2} \leftrightarrow +\frac{1}{2})$; this is shown in Fig. 2 for the highest concentration titanium sample (sample 5). The variation of width with angle for the different samples was quite large, for example in sample 5 the variation was 1.2 to 3.2 mT. Investigation of the linewidths at low temperatures (4.2 K) showed that for the double doped samples the pronounced dip noticed at room temperature was still present and had in fact split to give two distinct minima at 45 and 55 to 60°; this was true for all three transitions.

The presence of titanium ions in the ruby samples did not greatly affect the magnitude of the spin lattice relaxation times. For titanium the relaxation time at 4.2 K, 9 GHz is 0.1 msec [3] and over the temperature range 1.55 to 9 K, T_1 varies as T^{-7} [5]. It is well known that for Cr^{3+} in alumina at these temperatures $T_1 \propto T^{-1}$ [6]. Here, in all the titanium doped samples T_1 varied as T^{-1} and the magnitude of T_1 (25 msec

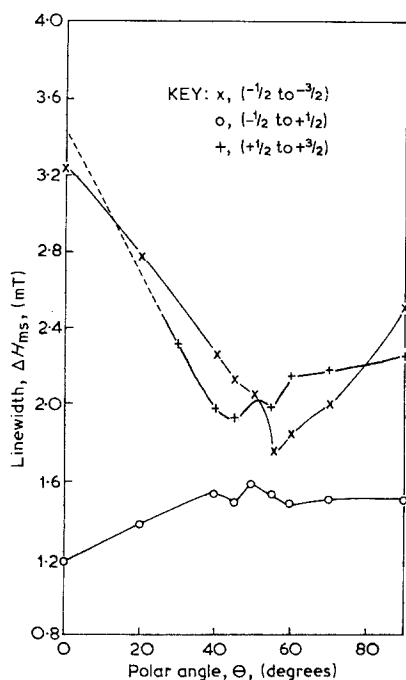


Figure 2 Cr³⁺ linewidths in sample 5; room temperature, 34 GHz.

at 4.2K, $\theta = 90^\circ$) indicated that cross-relaxation had not significantly reduced T_1 below the values to be expected for singly doped Cr/Al₂O₃ [6]. This is not really surprising as the titanium and chromium spectra never overlap at 34 GHz and transitions have to be very close in field value for cross relaxation to take place. Since it is known that the spin lattice interaction of the chromium itself only contributes about 1% to the linewidth at room temperature [7] it may be assumed that the extra broadening of the linewidth is negligible.

3. Theory of linewidth broadening

3.1. Introduction

In the theory presented here it has been assumed that of the homogeneous line broadening mechanisms (i.e. those which act on every spin in the system), dipolar broadening will play a major part; this follows from the work of Grant and Strandberg [7] on Cr/Al₂O₃ and that of Kurkin and Shekun [8] on Nd/CaMoO₄. Making use of more recent work on Nd/CaWO₄ [9], Van Vleck's second moment theory [10] has been applied to the dipolar interactions in the double doped alumina, namely the Cr-Al, Cr-Cr and Cr-Ti interactions.

Two different types of dipolar interaction must be considered; for like atoms the second moment, $\langle \Delta\omega^2 \rangle$ can be written:

$$\langle \Delta\omega^2 \rangle = \frac{3}{4} S(S+1) (g^2 \beta^2 / \hbar)^2 \cdot n \sum_k [r_{jk}^{-6} (3 \cos^2 \theta_{jk} - 1)^2] \quad (1)$$

where ω is measured in radians per second; n is the concentration of atoms; g is the Landé g -factor of the atoms of spin S ; β is the Bohr magneton; r_{jk} is the radius vector from the reference atom j to all the neighbouring atoms labelled over k ; θ_{jk} is the angle between the radius vector and a crystallographic reference axis.

For unlike atoms:

$$\langle \Delta\omega^2 \rangle = \frac{1}{3} S(S+1) (gg' \beta^2 / \hbar)^2 \cdot n \sum_k [r_{jk}^{-6} (3 \cos^2 \theta_{jk} - 1)^2] \quad (2)$$

where g refers to the reference atom and g' to the surrounding atoms; n is the concentration of the second species.

In the case of transition metals the magnetic moment is characterized by $g\sqrt{S(S+1)}$ where $g = 2$ (due to orbital quenching). The term $(3 \cos^2 \theta_{jk} - 1)^2$ may be evaluated using spherical harmonics, $Y_{l,m}$ [9].

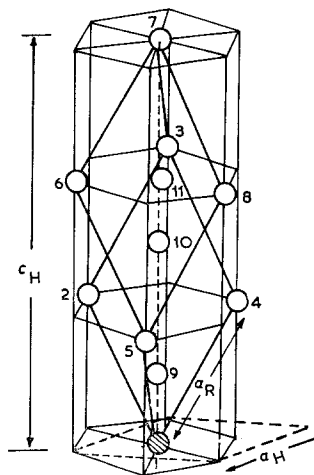


Figure 3 Unit cell of Al₂O₃. (a) Rhombohedral unit cell (oxygen sites omitted); (b) referred to hexagonal lattice.

3.2. Alumina unit cell

The unit cell of corundum, or α -Al₂O₃, is a rhombohedron (Fig. 3a) having three equal edges ($a_R = 5.1374 \text{ \AA}$) and three equal interaxial angles ($\alpha = 55^\circ 17'$) [11]. However, it is more

convenient to refer the unit cell to the hexagonal system with $a_H = 4.7664 \text{ \AA}$ and $c_H = 13.0146 \text{ \AA}$ [12], as indicated in Fig. 3b. Both chromium and titanium are expected to substitute at the aluminium sites so a complete tabulation of these sites is needed; as with Nd/CaWO₄ [9] eight unit cells are considered with the chromium reference ion as a common corner. The r , θ , ϕ values for all the sites are given in the Appendix; it is found that the aluminium sites lie on the surface of fifteen spheres.

Since the crystal has three-fold symmetry the values which m can take are 0 and ± 3 giving equations:

$$\langle \Delta\omega^2 \rangle = \frac{3}{4} S(S+1) (g^2 \beta^2 / \hbar)^2 \cdot n \times 10^{45} [12.826 + 0.107 Y_{2,0}^* (\theta_H, \phi_H) + 4.814 Y_{4,0}^* (\theta_H, \phi_H) - 4.025 Y_{4,3}^* (\theta_H, \phi_H) + 4.025 Y_{4,-3}^* (\theta_H, \phi_H)] \quad (5a)$$

for unlike atoms

$$\langle \Delta\omega^2 \rangle = \frac{1}{3} S(S+1) (gg' \beta^2 / \hbar)^2 \cdot n \times 10^{45} [12.826 + 0.107 Y_{2,0}^* (\theta_H, \phi_H) + 4.814 Y_{4,0}^* (\theta_H, \phi_H) - 4.025 Y_{4,3}^* (\theta_H, \phi_H) + 4.025 Y_{4,-3}^* (\theta_H, \phi_H)] \quad (5b)$$

All the results are for the plane containing the

$$(a) \langle \Delta\omega^2 \rangle = \frac{3}{4} S(S+1) (g^2 \beta^2 / \hbar)^2 \cdot n \left\{ \left[\frac{4}{5} \sum_k r_{jk}^{-6} + \frac{32\pi}{21} Y_{2,0}^* (\theta_H, \phi_H) \sum_k r_{jk}^{-6} Y_{2,0} (\theta_k, \phi_k) \right. \right. \quad (3)$$

$$\left. \left. + \frac{32\pi}{35} Y_{4,0}^* (\theta_H, \phi_H) \sum_k r_{jk}^{-6} Y_{4,0} (\theta_k, \phi_k) + \frac{32\pi}{35} Y_{4,3}^* (\theta_H, \phi_H) \sum_k r_{jk}^{-6} Y_{4,3} (\theta_k, \phi_k) + \frac{32\pi}{35} Y_{4,-3}^* (\theta_H, \phi_H) \sum_k r_{jk}^{-6} Y_{4,-3} (\theta_k, \phi_k) \right] \right\}$$

$$(b) \langle \Delta\omega^2 \rangle = \frac{1}{3} S(S+1) (gg' \beta^2 / \hbar)^2 \cdot n \left\{ \left[\frac{4}{5} \sum_k r_{jk}^{-6} + \frac{32\pi}{21} Y_{2,0}^* (\theta_H, \phi_H) \sum_k r_{jk}^{-6} Y_{2,0} (\theta_k, \phi_k) \right. \right.$$

$$\left. \left. + \frac{32\pi}{35} Y_{4,0}^* (\theta_H, \phi_H) \sum_k r_{jk}^{-6} Y_{4,0} (\theta_k, \phi_k) + \frac{32\pi}{35} Y_{4,3}^* (\theta_H, \phi_H) \sum_k r_{jk}^{-6} Y_{4,3} (\theta_k, \phi_k) + \frac{32\pi}{35} Y_{4,-3}^* (\theta_H, \phi_H) \sum_k r_{jk}^{-6} Y_{4,-3} (\theta_k, \phi_k) \right] \right\}$$

θ_k and ϕ_k refer the radius vector to the crystal axes while θ_H and ϕ_H refer the static magnetic field to the same axes. Comparison with Nd/CaWO₄ indicates that the only difference lies in the last two terms where ± 4 are replaced by ± 3 . The equation:

$$Y_{l,-m} = (-1)^m Y_{l,m}^* \quad (4)$$

shows that $Y_{4,-3} = -Y_{4,3}^*$. On consideration of the aluminium sites one finds that at any given radius the θ values are supplementary, which for $Y_{2,0}$ and $Y_{4,0}$ produce the same values. For $Y_{4,3}$ these give a difference in sign but in this case one also has a term $\exp(j3\phi)$ which is always found to have the value ± 1 , giving the same final value for $Y_{4,3}$; since the imaginary terms are always zero $Y_{4,-3} = -Y_{4,3}$.

3.3. The dipolar interactions

Since both chromium and titanium substitute at the aluminium sites all three dipolar interactions Cr-Al, Cr-Cr and Cr-Ti have the same values for the spherical harmonics; using the data in Table II one finds that:

for like atoms

c -axis, i.e. variation of θ_H with $\phi_H = 0$, and thus the spherical harmonics related to the static magnetic field are always totally real. Only the first part of the equation is different, dependent on the atomic parameters of the actual species involved. For the Cr-Cr interaction one needs the dipolar broadening between like atoms; since Cr³⁺ is a transition metal ion, $g = 2$ and with $S = 3/2$:

$$\frac{3}{4} S(S+1) (g^2 \beta^2 / \hbar)^2 \cdot n = 2.989 \times 10^{-25} \cdot n (\text{rad sec}^{-1})^2 \text{ cm}^6 \quad (6)$$

For both the Cr-Al and Cr-Ti Equation 3b is used; however, there is a difference in these interactions since in the former the chromium reference ion is interacting with the nuclear spin of Al³⁺ while that between chromium and titanium is an electronic interaction. Thus the parameters for the Cr-Ti interaction parallel those for Cr-Cr, except that this is an interaction between unlike atoms. The value of $g' = 2$ due to orbital quenching and $S = \frac{1}{2}$, giving:

$$\frac{1}{3} S(S+1) (gg' \beta^2 / \hbar)^2 \cdot n = 0.266 \times 10^{-25} \cdot n (\text{rad sec}^{-1})^2 \text{ cm}^6 \quad (7)$$

In the case of Cr-Al, the isotope ²⁷Al has a

TABLE II Trigonometrical parameters for the aluminium sites in eight unit cells of Al₂O₃, the origin of coordinates being the common corner.

r (Å)	θ_k (degrees)	ϕ_k (degrees)	N	$Y_{2,0}$ (θ_k, ϕ_k)	$Y_{4,0}$ (θ_k, ϕ_k)	$Y_{4,\pm 2}$ (θ_k, ϕ_k)	Nr^{-6} ($\times 10^{45}$ cm ⁻⁶)	$Nr^{-6} Y_{2,0}$ ($\times 10^{45}$ cm ⁻⁶)	$Nr^{-6} Y_{4,0}$ ($\times 10^{45}$ cm ⁻⁶)	$Nr^{-6} Y_{4,\pm 2}$ ($\times 10^{45}$ cm ⁻⁶)
2.730	0.00	—	1	0.6308	0.8463	0.0000	2.4156	1.5238	2.0443	0.0000
2.809	78.48	0	3	-0.2778	0.1967	∓ 0.2352	6.1068	-1.6965	1.2012	∓ 1.4363
3.187	120.30	60	3	-0.0745	-0.3054	∓ 0.4064	2.8634	-0.2133	-0.8744	∓ 1.1636
3.504	51.76	60	6	0.0471	-0.3550	± 0.3754	3.2417	0.1527	-1.1508	± 1.2169
	128.24	0								
3.777	180.00	—	1	0.6308	0.8463	0.0000	0.3443	0.2172	0.2914	0.0000
4.766	90.00	30	6	-0.3154	0.3174	0.0000	0.5117	-0.1614	0.1624	0.0000
5.137	32.29	0	6	0.3593	-0.0630	∓ 0.1625	0.3263	0.1172	-0.0206	∓ 0.0530
	147.61	60								
5.619	29.32	60	3	0.4039	0.0445	± 0.1281	0.0953	0.0385	0.0042	± 0.0122
6.507	0.00	—	2	0.6308	0.8463	0.0000	0.0263	0.0166	0.0223	0.0000
6.552	155.17	0	3	0.4639	0.1764	± 0.0841	0.0379	0.0176	0.0067	± 0.0032
7.008	51.76	60	6	0.0471	-0.3550	± 0.3754	0.0507	0.0024	-0.0180	± 0.0190
	128.24	0								
9.102	17.60	60	6	0.5443	0.4904	± 0.0330	0.0105	0.0057	0.0051	± 0.0003
	162.40	0								
9.237	0.00	—	1	0.6308	0.8463	0.0000	0.0016	0.0010	0.0014	0.0000
10.285	180.00	—	1	0.6308	0.8463	0.0000	0.0009	0.0006	0.0008	0.0000
13.015	0.00	—	2	0.6308	0.8463	0.0000	0.0004	0.0003	0.0003	0.0000
						Sum	16.0331	0.0224	1.6763	± 1.4013

100% abundance, with a nuclear spin $S = 5/2$. From n.m.r. tables the nuclear g is 1.455, but for inclusion in the equation it must be multiplied by the ratio of the nuclear magneton to the Bohr magneton, i.e. $1/1836$, giving $g' = 7.926 \times 10^{-4}$. This results in:

$$\frac{1}{3} S(S+1) (gg'\beta^2/\hbar)^2 \quad (8)$$

$$.n = 4.869 \times 10^{-32} \text{ (rad sec}^{-1}\text{)}^2 \text{ cm}^6 .$$

The total dipolar broadening is given by the square root of the sum of the second moments of the three individual dipolar interactions; this means square width is then converted into the peak to peak derivative linewidth, ΔH_{ms} using the equation:

$$\Delta H_{\text{ms}} = \frac{\sqrt{\langle \Delta\omega^2 \rangle}}{\pi} \cdot \frac{\partial H}{\partial \nu} \times 10^3 \text{ mT} \quad (9)$$

where $\partial H/\partial \nu = h/g\beta$ and the experimental g -values may be calculated from the isofrequency plots of the three Cr³⁺ transitions.

4. Discussion

The aim of this discussion is to attempt correlation of the theoretical and experimental values of the linewidth. This is done by considering the various dipolar interactions, first in the singly

doped alumina and then in the double doped Cr/Ti/Al₂O₃.

4.1. Singly doped Cr/Al₂O₃

Consideration of Equation 8 shows that the chromium-aluminium broadening is less than the Cr-Cr interaction. The component of ΔH_{ms} due to Cr-Al broadening varies between 0.2 and 0.5 mT in the θ plane for the three transitions. However, in Cr/Al₂O₃ the experimental linewidths are of the order of 1.2 mT and thus only a small part of the total width is due to the Cr-Al broadening. The magnitudes calculated are in agreement with previous work [7, 13]. However, both these references note the fact that there is a residual width of 1.2 mT at vanishing chromium concentrations, of which the Cr-Al broadening is only part, and the remainder remains unexplained; one suggestion is that covalent bonding may be the answer [7].

In deriving the linewidth polar plot for the Cr-Cr interaction the value of concentration (n), used for substitution in Equations 5 and 6 was taken as 0.02%. The angular variation of transition ($-\frac{1}{2} \leftrightarrow -\frac{3}{2}$), shown in Fig. 4, is comparable with the plot for sample 1 in Fig. 1. Quantitatively the theoretical linewidths are about a factor of seven too great, and this is

neglecting the effect of the Cr-Al interaction which would have increased the theoretical width slightly. This type of discrepancy has been found before [14]; the suggestion is that exchange interactions due to exchange coupled pairs of ions play a major role in determining the linewidth. Another source of error is that the theory was originally intended for the transition across an isolated Kramer's doublet. The theory has been adapted for the two Kramer's doublets in Cr/Al₂O₃ [7, 13] by replacing *S* in Equation 3a for Cr-Cr with its projection operator, which slightly reduced the linewidths. However, the answers were still too large and again exchange interactions were suggested. From the present point of view the important result is that the overall agreement between dipolar broadening theory and experiment indicates the validity of the assumption that Cr substitutes at Al sites.

4.2. Double doped Cr/Ti/Al₂O₃

If titanium substitution takes place at the Al sites the predicted form of the angular variation of the linewidth due to the Cr-Ti interaction will be exactly the same as for Cr-Cr. However, consideration of Figs. 1 and 2 shows that experimentally this was not found to be true. It was, therefore, concluded that the assumption of complete Ti substitution at Al sites could not be valid. Consequently, in order to see whether agreement between experiment and theory for the linewidth variation in the doubly doped samples could be obtained various interstitial sites for Ti were considered. In all of these possible interstitial sites the Cr-Ti spacing was less than that corresponding to substitution at Al sites. The best fit was obtained by assuming that some of the titanium ions, instead of substituting at the aluminium sites along the *c*-axis closest to the chromium reference ion (i.e. *r* = 2.73 or 3.777 Å; Fig. 3 and Table II) take up positions at the closest distance of approach to the reference ion in the *c*-direction (i.e. *r* = 1.4 Å). This gives two extra sites which in turn add an extra component to the linewidth equation:

$$\langle \Delta\omega^2 \rangle = 0.266 \times 10^{21} \cdot n [21.25 + 80.21 Y_{2,0}^* (\theta_H \phi_H) + 64.56 Y_{4,0}^* (\theta_H \phi_H)] \quad (10)$$

which together with Equations 5 and 7 results in:

$$\begin{aligned} \langle \Delta\omega^2 \rangle = & 0.266 \times 10^{21} \quad (11) \\ & \cdot n [22.53 + 80.22 Y_{2,0}^* (\theta_H, \phi_H) \\ & + 65.04 Y_{4,0}^* (\theta_H, \phi_H) \\ & - 0.403 Y_{4,3}^* (\theta_H, \phi_H) \\ & + 0.403 Y_{4,-3}^* (\theta_H, \phi_H)] \end{aligned}$$

for the Cr-Ti broadening. The angular variation of Δ*H*_{ms} thus calculated is found to produce a definite minimum.

To find the total broadening effect of Cr-Cr and Cr-Ti interactions (neglecting Cr-Al) one must add Equations 5, 6 and 11, and calculate Δ*H*_{ms} from the resultant. For Cr³⁺ the concentration lay between 0.015 and 0.023% while for titanium the concentration varied between zero and 0.024%. The theoretical angular variation of transition (-½ ↔ -¾) for increasing amounts of titanium in the double doped samples is shown in Fig. 4 and this compares

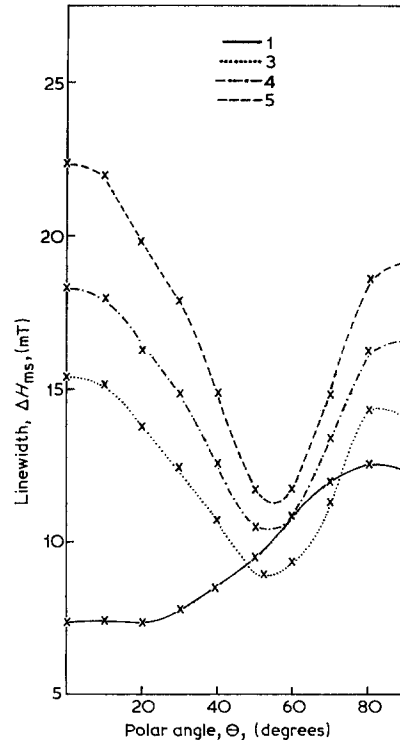


Figure 4 Effect of increasing the titanium concentration on the theoretical Cr³⁺ linewidth; transition (-½ ↔ -¾).

well with Fig. 1, showing a pronounced minimum for sample 5 at 55° and a broader, shallower dip for sample 3. Fig. 5 shows the angular variation of the three chromium transitions in sample 5; this compares favourably with Fig. 2

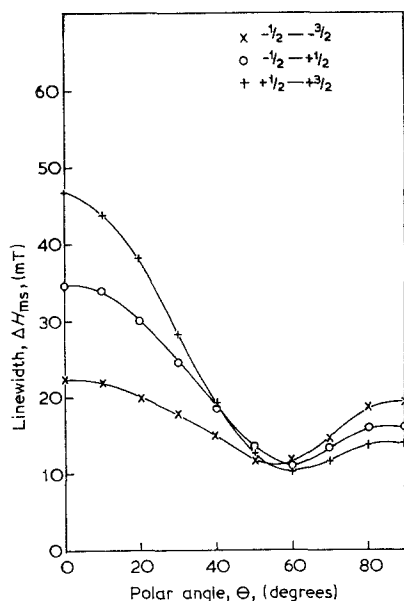


Figure 5 Theoretical angular variation of linewidth for Cr—Ti doped alumina; sample 5.

for transitions other than the $(-\frac{1}{2} \leftrightarrow +\frac{1}{2})$ transition. Again the linewidths are a factor of seven greater than experiment. Experimentally, in order to eliminate inhomogeneous broadening effects, one must measure the linewidth at angles where $dH/d\theta = 0$, i.e. $\theta = 0$ or 90° . For transition $(-\frac{1}{2} \leftrightarrow -\frac{3}{2})$ at $\theta = 90^\circ$ a comparison of the experimental and theoretical linewidth re-

sults versus concentration of titanium is given in Fig. 6, taking into account the factor of seven in the theory. If the dependence were only on the titanium concentration then the theoretical curve would vary as \sqrt{n} ; since the chromium concentration is not constant this does not hold exactly. Qualitatively then the variation for transition $(-\frac{1}{2} \leftrightarrow -\frac{3}{2})$ is quite close to the theory; this is also true for transition $(+\frac{1}{2} \leftrightarrow +\frac{3}{2})$ while transition $(-\frac{1}{2} \leftrightarrow +\frac{1}{2})$ seems to be quite insensitive to changes in concentration.

5. Conclusions

The e.s.r. linewidths of a chromium monitor ion in singly doped crystals of alumina were measured and then the influence of titanium on these linewidths was assessed. Use was made of the dipolar broadening theory of Van Vleck to correlate the theoretical values of the linewidths with those obtained from experimental measurements. It was discovered that the theory explained qualitatively the angular variation of the linewidth for chromium in alumina. However, difficulties arose over the addition of titanium since the large effect of titanium on the Cr³⁺ linewidths could only be explained by allowing some titanium ions to approach closer to a chromium ion than the nearest neighbour aluminium sites in a specific direction. This resulted in good qualitative agreement with experiment for transitions $(-\frac{1}{2} \leftrightarrow -\frac{3}{2})$ and $(+\frac{1}{2} \leftrightarrow +\frac{3}{2})$ but not for transition $(-\frac{1}{2} \leftrightarrow +\frac{1}{2})$

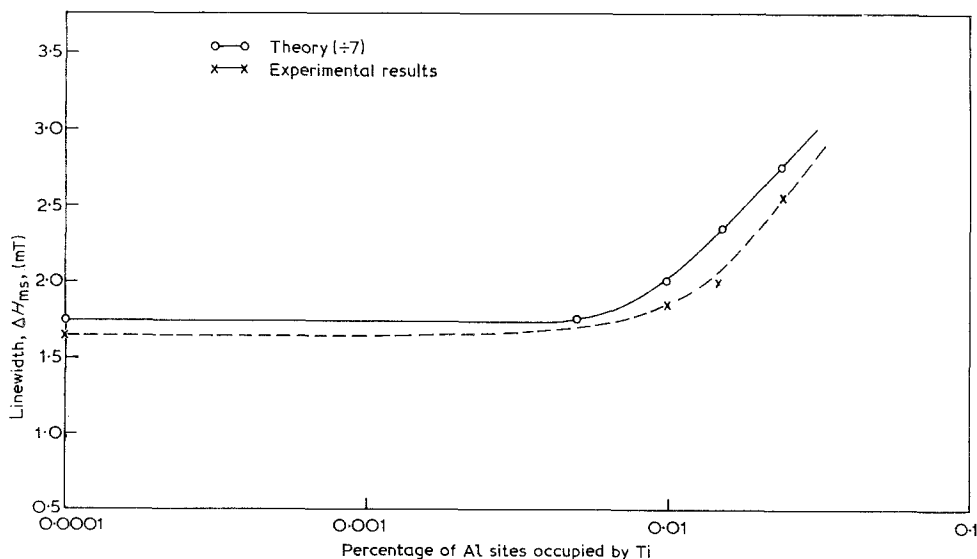


Figure 6 Variation of Cr³⁺ linewidth with titanium concentration; transition $(-\frac{1}{2} \leftrightarrow -\frac{3}{2})$, $\theta = 90^\circ$.

which experimentally was insensitive to changes in titanium concentration. Thus the changes in Cr^{3+} linewidth on addition of titanium are attributed to the formation of Cr—Ti complexes, showing that the resonance behaviour of chromium is quite sensitive to local changes in its environment.

Appendix

Taking eight unit cells of Al_2O_3 the aluminium sites can be indexed (see Fig. 3).

r (Å)	θ°	ϕ°	r (Å)	θ°	ϕ°
2.73	0.00	—	5.619	29.32	60
			5.619	29.32	180
2.809	78.48	0	5.619	29.32	300
2.809	78.48	120			
2.809	78.48	240	6.5073	0.00	—
			6.5073	180.00	—
3.187	120.30	60			
3.187	120.30	180	6.552	155.17	0
3.187	120.30	300	6.552	155.17	120
			6.552	155.17	240
3.504	51.76	60			
3.504	51.76	180	7.008	51.76	60
3.504	51.76	300	7.008	51.76	180
3.504	128.24	0	7.008	51.76	300
3.504	128.24	120	7.008	128.24	0
3.504	128.24	240	7.008	128.24	120
			7.008	128.24	240
3.777	180.00	—			
			9.102	17.60	60
4.766	90.00	30	9.102	17.60	180
4.766	90.00	90	9.102	17.60	300
4.766	90.00	150	9.102	162.40	0
4.766	90.00	210	9.102	162.40	120
4.766	90.00	270	9.102	162.40	240
4.766	90.00	330			
			9.237	0.00	—
5.137	32.39	0			
5.137	32.39	120	10.285	180.00	—
5.137	32.39	240			
5.137	147.61	60	13.015	0.00	—
5.137	147.61	180	13.015	180.00	—
5.137	147.61	300			

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References

1. R. P. HUNT and K. N. R. TAYLOR, *J. Mater. Sci.* **8** (1973) 203.
2. C. A. BATES, J. P. BENTLEY, B. F. JONES and W. S. MOORE, *J. Phys. C* **3** (1970) 570.
3. L. S. KORNIENKO and A. M. PROKHOROV, *Sov. Phys. J.E.T.P.* **11** (1960) 1189.
4. D. A. CURTIS, C. J. KIRKBY and J. S. THORP, *Brit. J. Appl. Phys.* **16** (1965) 1681.
5. S. A. AL'TSHULER and M. M. ZARIPOV, *Sov. Phys. J.E.T.P.* **13** (1961) 257.
6. J. H. PACE, D. F. SAMPSON and J. S. THORP, *Proc. Phys. Soc.* **76** (1960) 697.
7. W. J. C. GRANT and M. W. P. STRANDBERG, *Phys. Rev.* **135A** (1964) 727.
8. I. N. KURKIN and L. YA. SHEKUN, *Sov. Phys. Sol. Stat.* **9** (1967) 339.
9. G. BROWN, C. J. KIRKBY and J. S. THORP, *J. Mater. Sci.* **9** (1974) 65.
10. J. H. VAN VLECK, *Phys. Rev.* **74** (1948) 1168.
11. R. W. G. WYCKOFF, "Crystal Structures" (Interscience, New York, 1957).
12. W. H. BRAGG and W. L. BRAGG, "X-rays and Crystal Structure" (Bell and Sons, London, 1924).
13. A. A. MANENKOV and V. B. FEDEROV, *Sov. Phys. J.E.T.P.* **11** (1960) 751.
14. D. N. KLYSHKO, *Sov. Phys. Sol. Stat.* **5** (1964) 2066.

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