

ESR OF Ti(III) IN LiCl-KCl EUTECTIC

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INTRODUCTION

Study of corrosion phenomena associated with the use of molten salts as coolants raised interest in the behaviour of various metal ions in such melts. Gruen & McBeth<sup>1</sup>, in the early sixties, studied various transition metal ions in LiCl/KCl eutectic. The purpose of the present letter is an attempt to correlate ESR data with data derived from optical spectroscopy, in particular with respect to the equilibrium between hexa- and tetra-coördinate species of Ti(III) with chlorine ions.

EXPERIMENTAL

High-purity  $TiCl_3$  was prepared according to the literature<sup>2</sup> by reduction of  $TiCl_4$  with hydrogen on a tungsten wire, and subsequent purification by sublimation. The tungsten content of the final sample was below the detection limit of conventional chemical tests.

The eutectic was prepared from lithiumchloride and potassiumchloride, p.a. grade of Merck Darmstadt, and used without further purification. Trace amounts of  $Mn^{2+}$  were interfering with all measurements. Mixing calculated amounts of the components was followed by powdering in a ball mill. It was dried in a vertical tube, fitted at the bottom with a sintered glass filter through which dry HCl gas was passed, at a temperature of  $300^{\circ}C$ . This system behaves as a crude form of a fluid bed. Through a 6 mm cock the dry eutectic could be transferred to a roundbottom flask which had been heated and evacuated previously in order to remove adhering water vapour to a considerable extent, and purged with dry argon gas.

Via a ground glass joint the vessel containing the  $\text{TiCl}_3$  was connected to the flask with eutectic; the  $\text{TiCl}_3$  was then introduced by gentle shaking. Dosation of a known amount by this procedure is hardly feasible. A part of the mixture thus obtained was admitted to a short ESR sample tube of fused silica (special quality with no observable paramagnetic impurity) that had been attached before to the round bottom flask by means of a ground glass joint and a stopcock. Final mixing was achieved by heating above the melting point. When the liquid appeared homogeneous to the eye the sample tube was molten off the stopcock/joint assembly.

ESR spectra were recorded with a VARIAN V4500 Spectrometer operating at X-band. A temperature of  $-180^\circ\text{C}$  was obtained by the use of a Varian Low Temperature Accessory.

Using conventional sample tubes it is impossible to carry out measurements on the molten samples due to the high electric conductivity. Therefore samples were kept on the chosen temperature for about one hour and then quenched by dropping the tube in liquid nitrogen.

The spectra were recorded at  $-180^\circ\text{C}$ .

#### RESULTS AND DISCUSSION

All spectra (150) that were recorded during this study exhibit impurity signals, designated  $O_1$ ,  $O_2$  and  $O_3$  in the figures.

$O_1$  is at  $g = 2.00$ , possibly originating from stopcock grease or pump oil.

$O_2$  and  $O_3$  are respectively at  $g = 1.95$  and  $1.87$ , presumably arising from metal impurities.

A  $\text{Mn}^{2+}$  signal is always disturbingly present. Its hyperfine lines are numbered  $M_1$  through  $M_6$ .

Representative spectra are shown in Figures 1-6. Of these, Figure 1 clearly shows the presence of a broad signal centered at  $g = 1.73$ , with superimposed on that an intense, rather sharp signal (T), 65 Gauss peak-to-peak, and the impurity signals including the manganese lines.

Since it is a well-known fact that for octahedral  $\text{Ti(III)}$ -species the relaxation time  $T_1$  is very short, it is assumed that the broad signal should be attributed to octahedrally coordinated  $\text{Ti(III)}$  and the sharper signal at  $g = 1.95$  to tetrahedrally coordinated  $\text{Ti(III)}$ . Both signals are absent in eutectic without added  $\text{TiCl}_3$ .

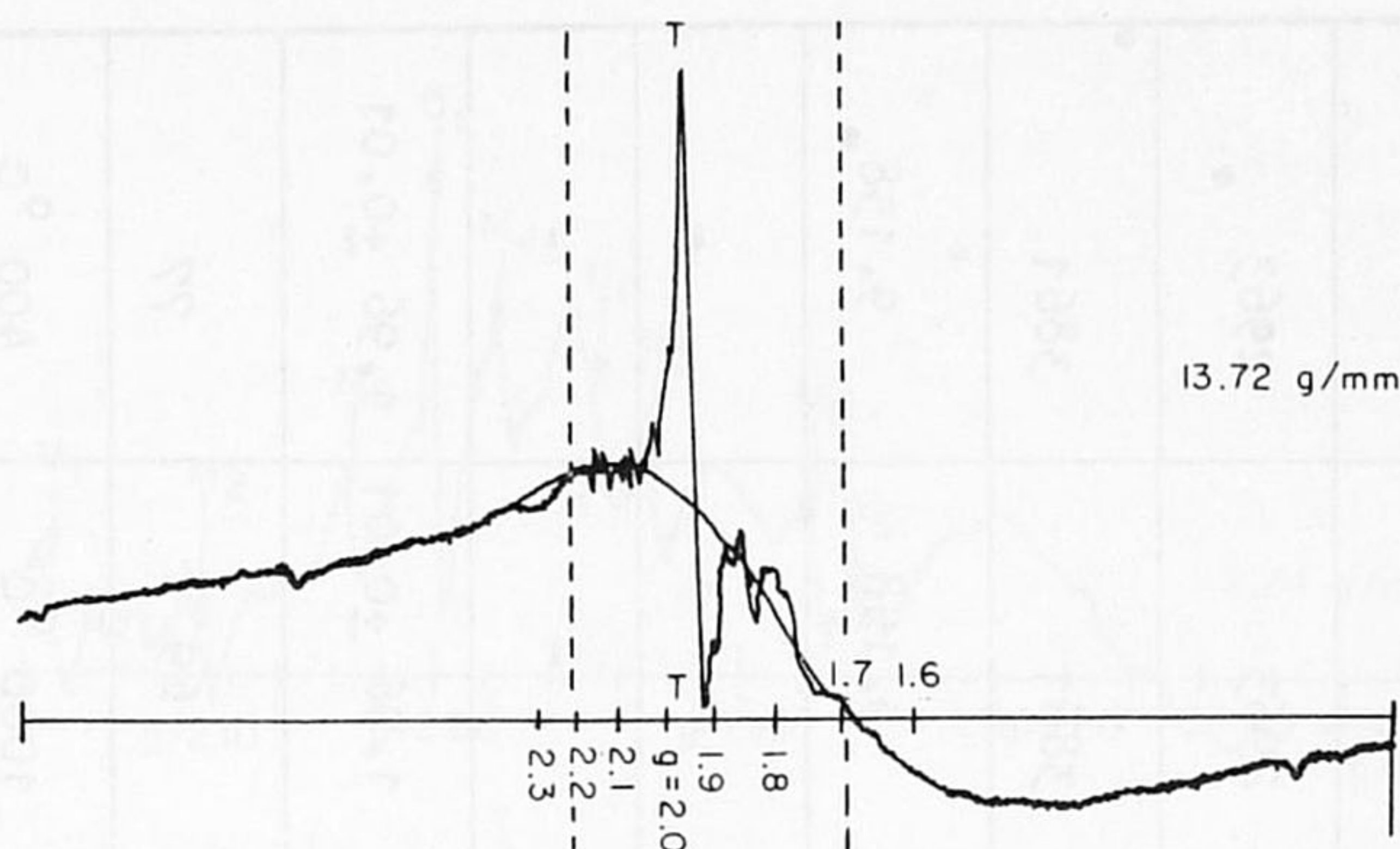


FIG. 1

General shape of ESR spectrum of Ti(III) in LiCl/KCl. Broad signal (partially hand drawn) of oct. with tetr. signal T superimposed. Impurities not indicated.

It is possible to make a crude estimate of the ratio  $N_{\text{oct}}/N_{\text{tetr}}$  (where  $N$  = number of molecules of a type given by the subscript) by putting  $N = cc'(\Delta H_{\text{pp}})^2 A_{\text{pp}}$  with  $\Delta H_{\text{pp}}$  = peak-to-peak line width,  $A_{\text{pp}}$  = peak-to-peak amplitude and  $c$  = proportionality factor depending on line shape and  $c'$  on relative intensity respectively.

Taking  $c_{\text{oct}} = c_{\text{tetr}}$  this relation leads in Fig. 1 to  $N_{\text{oct}}/N_{\text{tetr}} = 247$ . This is not very remarkable in view of the large excess of chloride ions in the melt.

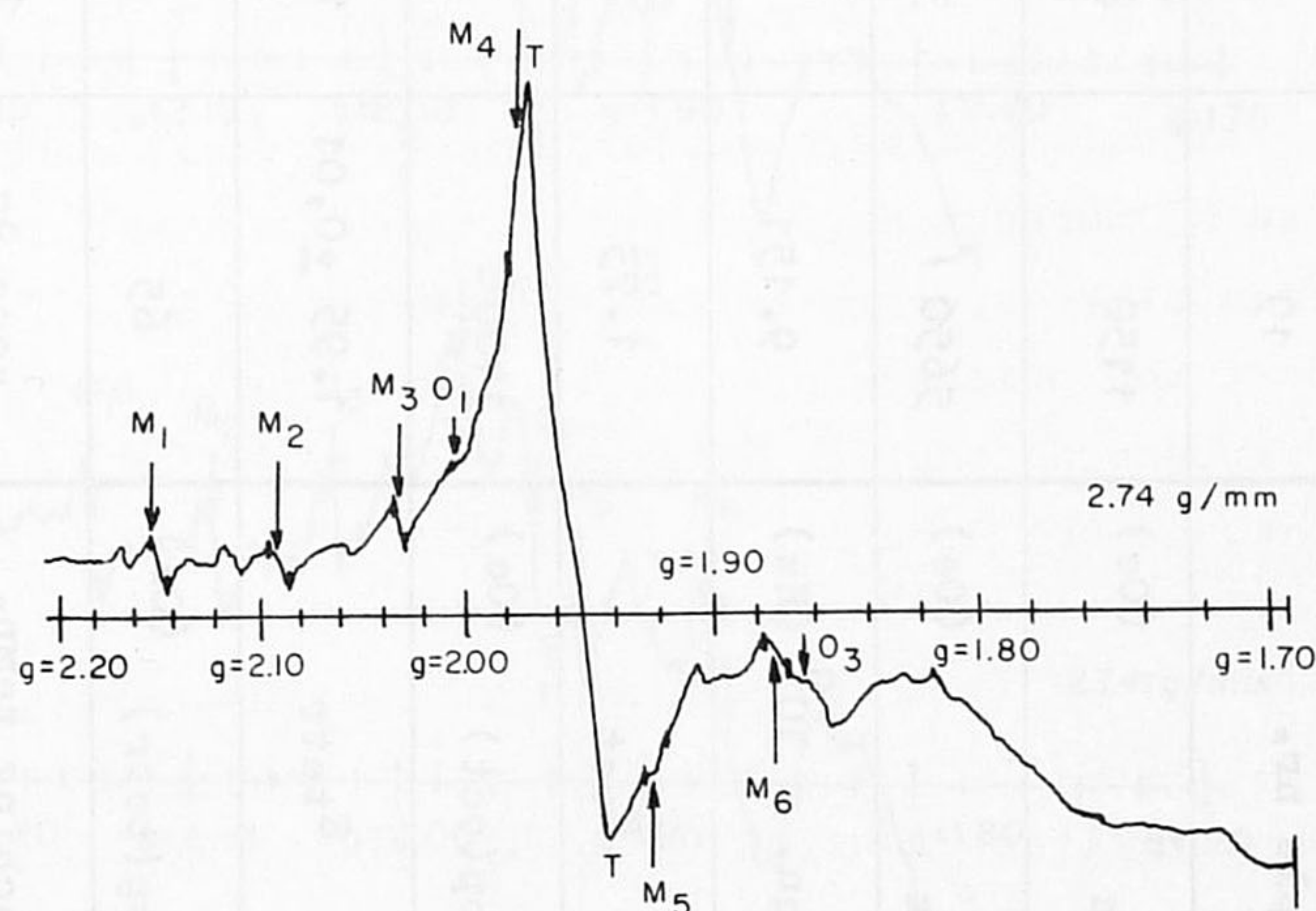
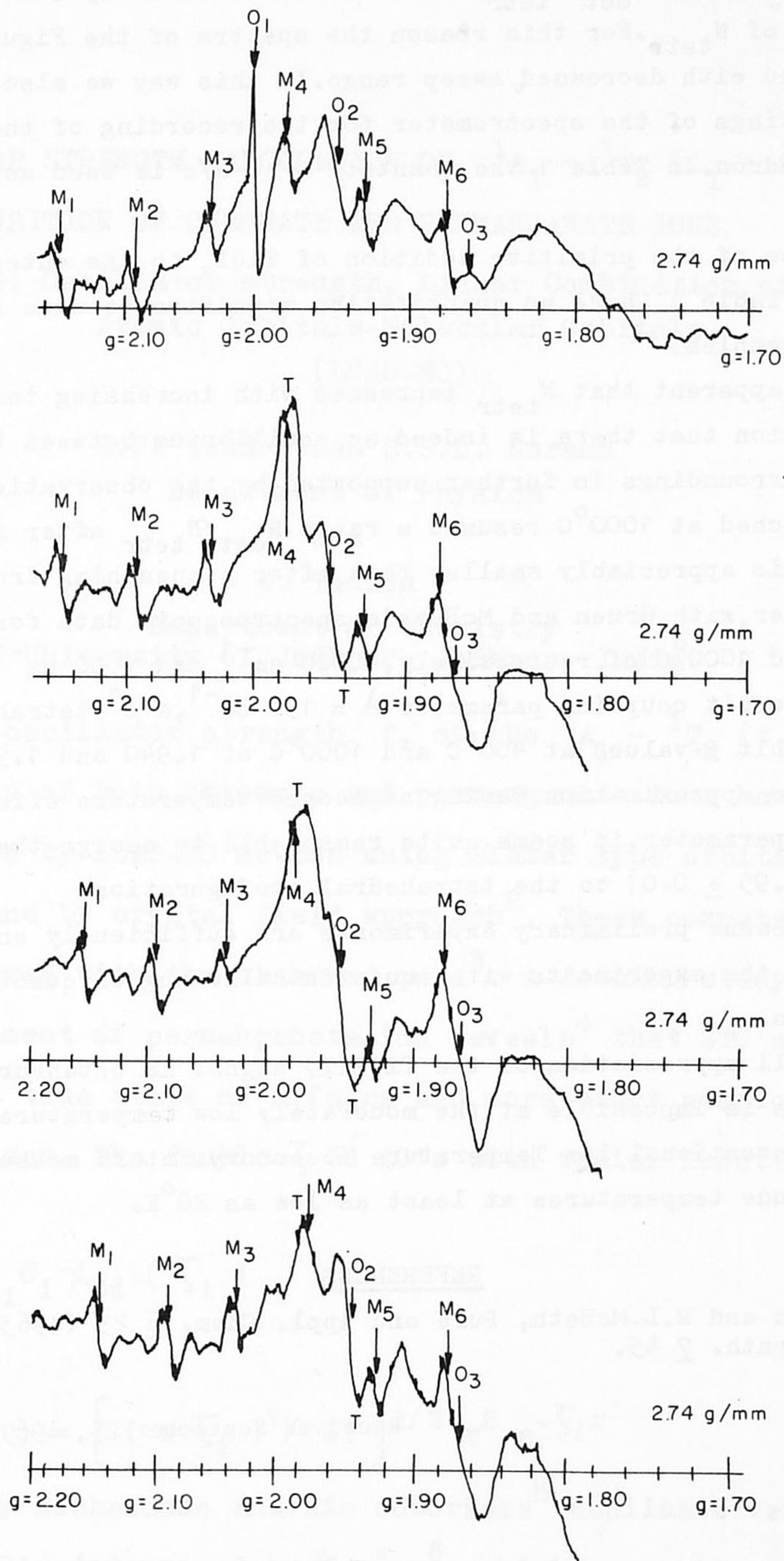


FIG. 2

Central region (indicated by vertical dotted lines) of Fig. 1

TABLE 1

Figure	1	2	3	4	5	6
Sample nr.	19	19	18	18	18	18
$H_{\min}$ (Oe)	1150	2963	2963	2963	2963	2963
$H_{\max}$ (Oe)	5650	3861	3861	3861	3861	3861
Frequ. $\times 10^9$ (Hz)	9.151	9.151	9.157	9.156	9.158	9.158
$g_{\text{oct}}$	1.73	-	-	-	-	-
$\Delta H_{\text{pp(oct)}}$ (Oe)	1400	-	-	-	-	-
$g_{\text{tetr}}$	1.95 $\pm 0.01$	1.96 $\pm 0.01$	-	1.96 $\pm 0.01$	1.96 $\pm 0.01$	1.96 $\pm 0.01$
$\Delta H_{\text{pp(tetr)}}$ (Oe)	65	58	-	60	69	77
Quenching temp.	1000 °C	1000 °C	-	800 °C	1000 °C	400 °C
Measuring temp.	- 180 °C	- 180 °C	- 180 °C	- 180 °C	- 180 °C	- 180 °C
$N_{\text{tetr}}^*$	(see text)	3430	0	830	950	500



FIGURES 3 (TOP) - 6 (BOTTOM)

Variations in  $N_{\text{oct}}/N_{\text{tetr}}$  are then almost entirely due to variations of  $N_{\text{tetr}}$ . For this reason the spectra of the Figures 2-6 are recorded with decreased sweep range. In this way we also obtained better settings of the spectrometer for the recording of the peak of the tetrahedron. In Table 1 the quantity  $N^* = N/c$  is used as a measure of  $N_{\text{tetr}}$ .

Because of the primitive addition of  $\text{TiCl}_3$  to the eutectic, the entries in Table 1 have no quantitative significance when related to different samples.

It is apparent that  $N_{\text{tetr}}$  increases with increasing temperature. The conclusion that there is indeed an equilibrium between two different kinds of surroundings is further supported by the observation that a sample quenched at  $1000^\circ\text{C}$  resumed a ratio  $N_{\text{oct}}/N_{\text{tetr}}$  after reheating at  $400^\circ\text{C}$  that is appreciably smaller than after a quenching from  $800^\circ\text{C}$ .

Moreover, with Gruen and McBeth's spectroscopic data for  $\Delta_{\text{tetr}}$  at  $400^\circ\text{C}$  and  $1000^\circ\text{C}$  of, respectively,  $10000\text{ cm}^{-1}$  and  $7000\text{ cm}^{-1}$ , and assuming a spin-orbit coupling parameter  $\lambda = 150\text{ cm}^{-1}$ , a  $d^1$ -tetrahedron should exhibit  $g$ -values at  $400^\circ\text{C}$  and  $1000^\circ\text{C}$  of 1.940 and 1.914 resp. in the ionic approximation. Having neglected temperature effects on the spin-orbit parameter, it seems quite reasonable to assign the measured value  $g = 1.95 \pm 0.01$  to the tetrahedral configuration.

The present preliminary experiments are sufficiently encouraging to continue the experiments with equipment allowing of quantitative manipulation.

The full appreciation of the  $\text{Ti(III)}$  signal in octahedral surroundings is impossible at the moderately low temperature obtainable with the conventional Low Temperature Accessory. Future measurements should include temperatures at least as low as  $20^\circ\text{K}$ .

#### REFERENCES

1. D.M.Gruen and R.L.McBeth, Pure and Appl. Chem. 6 23 (1963)
2. Inorg. Synth. 7 45.

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