Electron Spin Resonance of Divalent Titanium Ions Doped into a Magnesium Chloride Host Lattice

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Abstract

Magnesium chloride crystals homogeneously doped with titanium ions can be prepared by crystal growth from the melt. The electronic spectrum taken along the *c*-axis indicates that the titanium ions are six coordinate and divalent. The *x* band electron spin resonance consists of a series of sharp lines and the nuclear hyperfine due to ^{47}Ti and ^{49}Ti can be observed. The peaks are assigned to a forbidden $M_s = 2$ double quantum transition and orientation studies indicate that the environment is trigonally distorted. These measurements make it possible to interpret the powder spectrum. The powder along with an aluminium alkyl is a catalyst for the polymerization of ethene and a comparison is made between the powder ESR and ESR signals observed in the polymerization of ethene using a conventional Ziegler–Natta catalyst of titanium tetrachloride, magnesium chloride and aluminium triethyl.

Introduction

Magnesium chloride is a particularly effective substrate for the polymerization of ethene using titanium tetrachloride and aluminium alkyl-based catalysts [1–3]. In the conventional process, the magnesium chloride is milled with the catalyst components before use and it is generally believed that the active site is likely to be titanium(III) in a specific environment at the surface of the crystals, although there is some evidence that reduction to titanium(II) may occur [2, 3]. Magnesium chloride doped with titanium ions can be produced by the growth of a polycrystalline material from a melt of the halide containing titanium ions [4]. These materials are active catalysts, although they do not compete with current commercial systems in their present state of development.

However, it is possible to grow single crystals of this material in which the titanium ion is in a well defined environment which can be studied in detail. The impurity site studied is representative of the bulk of the crystal and not the active surface site, but since the titanium ion is in a reduced and isolated environment, this system provides a good opportunity to study a better defined alternative to conventional mixtures. ESR measurements have proved to be of particular interest, not only because they provided information on the ion site but also because they rather surprisingly consist of a set of relatively sharp bands at room temperature.

Experimental

Materials and Methods

Reagent-grade magnesium chloride was placed in a silica crucible and melted at 800 °C in a muffle furnace for 1 h. A top layer of magnesium oxychloride and a bottom layer containing black impurities formed. The crucible was allowed to cool in a dry box and the middle layer of polycrystalline magnesium chloride was recovered. A sample of this middle layer was placed in a silica ampoule and the ampoule sealed under vacuum. It was suspended in a furnace heated to 800 °C. A single crystal of magnesium chloride was grown from the melt by the Bridgman process. The product consisted of clear, well-formed single crystals with a definite cleavage plane. The ampoule was broken open in the dry box and the top and bottom of the crystal were discarded. Part of the middle section of the crystal was crushed, and a weighed amount of it was added along with a weighed amount of anhydrous cadmium chloride and pure titanium metal to a second ampoule. This was sealed, melted and a crystal grown as before. In the melt, the cadmium chloride reacted with the titanium, which was present in slight excess:

$$CdCl_2 + Ti \longrightarrow Cd\uparrow + TiCl_2$$

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The cadmium metal sublimed out of the melt and condensed on the neck of the ampoule [4–6]. Crystals prepared in this manner were blue or green depending on the titanium doping level. Titanium concentrations in the crystal samples used for the ESR experiments were determined at the conclusion of the experiment by Atomic Absorption Spectrometry using flame atomisation. For single crystal measurements, a sample was cleaved from the middle section of the crystal with a razor blade. The *z* axis of the crystal is expected to be perpendicular to the parallel cleaved faces and this was confirmed by precession of X-ray photographs and by examination with a polarizing microscope.

ESR spectra were measured in a Jeol JES FE-IX, X band spectrometer, equipped with a cooled nitrogen gas flow unit which can produce sample temperatures between room temperature and 100 K. Spectra below this temperature were obtained by mounting the sample in a Displex closed-cycle refrigerator system which was specially modified to enable it to be used in the Jeol system. The lower optical port of the Displex was removed and replaced with a short ESR tube to complete the vacuum shroud. The sample was mounted on a screwed copper rod attached to the Displex cold-head and was placed in the cavity by inserting the tube through the normal sample port in the top. Single-crystal orientation studies were carried out by mounting the sample in an ESR tube attached to a protractor and suspending the closed tube in the nitrogen flow in the conventional way. Magnesium chloride is extremely hygroscopic and care was taken to keep the sample in anhydrous condition at all times.

Results and Discussion

Since the co-ordination sphere of transition-metal ions in chloride melts are kinetically labile, the oxidation state of titanium in a particular melt will be determined largely by thermodynamic factors and by the acid-base character of the melt. In a crystal grown from such a melt, the oxidation state of the titanium ions trapped in it depends both on the oxidation state of the ion in the melt above the growing crystal and on properties of the crystal such as the size and number of the holes, the degree of polar character, etc. Further, in many ionic crystals the percentage of ions that can be dispersed to form a solid solution in the host without aggregation, precipitation or separation of the components is quite small. For example, it has been possible so far to replace only about 1% of the sodium ions in sodium chloride with titanium(II) or vanadium(II) [6]. However, both magnesium chloride and titanium dichloride are layer lattices which have a more covalent character and some analogous systems such as the cobalt chloride/cadmium chloride system can produce a very wide range of solid solutions [7, 8]. Magnesium chloride crystals belong to the space group $R\bar{3}m$ and consist of a distorted cubic close-packed array of chlorides, with magnesium ions occupying every second layer of octahedral holes, producing a cleavage plane along the chloride layers. Since the crystals are evenly doped, with no evidence of a concentration gradient of titanium ions and since the sections appear homogeneous under the microscope, it seems that the system is analogous to cobalt chloride, cadmium chloride one, with the titanium ions in solid solution and occupying octahedral positions either on magnesium sites or in the octahedral holes in the layers between them.

The electronic spectra taken along the *C* axis of a crystal doped with 1% of titanium indicate that the titanium is present as a divalent (d^2) ion in an octahedral environment. The peaks at 9090 cm^{-1} and 15,748 cm^{-1} are assigned to the ${}^3T_{1g} \rightarrow {}^3T_{2g}({}^3F)$ and ${}^3T_{1g} \rightarrow {}^3T_{1g}({}^3P)$ transitions, respectively, and Dq and B values of 1000 cm^{-1} and 505 cm^{-1} are reasonable for an octahedral chloride environment round a divalent titanium ion [6]. There is no evidence of trivalent titanium in the spectrum. The molar absorptivity for a titanium(III) ion will be greater than for titanium(II) and it is possible from the spectrum to estimate that the titanium(III) content of the crystal is below 5% of the titanium present. Further, magnesium chloride melts at 714 °C and hence the equilibrium between titanium(II) and titanium(III) will be well towards the titanium(I) side in the molten phase unless there is a very significant chlorine overpressure:

$$TiCl_3 \rightleftharpoons TiCl_2 + 1/2Cl_2$$

In our experiments, an excess of titanium metal was used, so that no such overpressure would be expected nor was any observed when the ampoule was opened. Attempts to add titanium(III) ions to the crystal by using an excess of zinc metal produced a purple colouration in a polycrystalline melt but no single crystal could be grown which contained the purple colouration. Thus, it would seem that in the high quality magnesium chloride crystals used, the amount of titanium(III) is very low, certainly below 5% and probably well below 1% of the ions doped into the lattice. Powder ESR spectra of heavily doped material produced weaker signals than low doped material, presumably because of exchange interactions between titanium ions and, consequently, the doping levels used in single crystals were kept below a 3% substitution of magnesium ions by titanium.

The ESR spectrum with the z axis parallel to the field direction has a single dominant peak with side bands due to titanium hyperfine interactions (Fig. 1). The half band width of the major peak at room temperature (298 K) is about 32 gauss. On cooling to 20 K the spectra sharpened somewhat to give a half band width of 14 gauss but no new features were resolved in the spectrum. The major peak is due to ^{48}Ti which has a nuclear spin of 0. The more intense side bands are due to a combination of ^{47}Ti($I = 5/2$) and ^{49}Ti($I = 7/2$). The two less intense bands are from ^{49}Ti only. Other side bands are obscured by the ^{48}Ti signal.

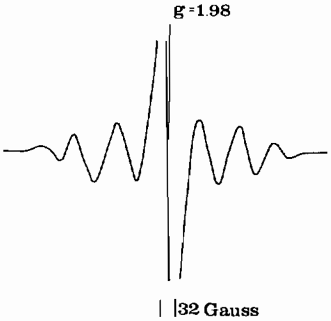

Fig. 1. ESR spectrum of a single crystal of $MgCl_2$:Ti(II) with the z axis of the crystal parallel to the field direction. The titanium ion concentration corresponds to a 1% replacement of magnesium ion by titanium.

The ratio of the intensities of the ^{48}Ti, ^{47}Ti and ^{49}Ti signals is difficult to calculate exactly due to band overlap but it is in reasonable agreement with that expected on the basis of the natural abundance of the isotopes. The hyperfine splitting is as expected for titanium in a chloride lattice. Thus, it would seem that the signal is due to titanium and not to a spurious impurity. Further, magnesium chloride purified as described previously gave no ESR signal under the conditions used to obtain the spectrum in Fig. 1 and the substitution of Analar zinc chloride for cadmium chloride in the presence of titanium-doped samples produced crystals with signals similar to those in Fig. 1.

A major problem with the assignment of the spectra is to decide which oxidation state is responsible for the spectrum which could in principle be due to titanium(III) impurities. A comparison of the ESR signals from $TiCl_3$ with that from 0.5% and 5% titanium-doped magnesium chloride is shown in Fig. 2. The allowed transition in $TiCl_3$ can be observed readily, whereas no such transition can be observed in the doped samples. An approximate estimation of the total number of spins observed was obtained by comparing the integrated area under the peaks with that obtained from a standard. It was found to be difficult to obtain a standard of the correct dilution and homogeneity but an acceptable standard was eventually prepared from hydrated cupric sulphate dissolved in methanol and absorbed into magnesium oxide powder. The product was dried and ground before use. The titanium signal strength in the doped samples corresponded to about 1/10 of the spins expected for an allowed transition. Therefore, since less than 5% of titanium ions are present as titanium(III), the ESR signal is too intense to be assigned to a titanium(III) signal from an allowed transition, and since there was no evidence of the band usually associated with octahedral titanium(III), the spectra observed are due to the octahedral titanium(II) species identified by UV-visible spectroscopy.

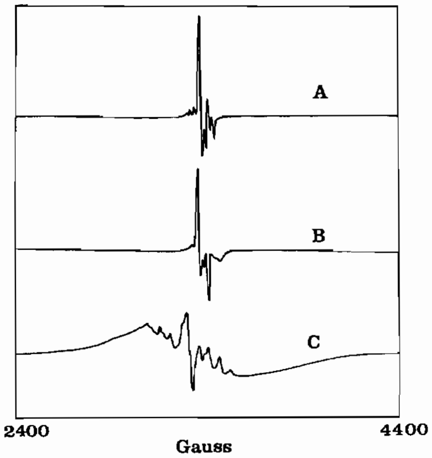

Fig. 2. ESR of powders of 0.5% titanium-doped magnesium chloride (A); 5% titanium-doped magnesium (B) and titanium trichloride (C). A similar spectrum has been reported for tetrahedral titanium(II) [14–16].

The most likely assignment of the absorption in lightly doped magnesium chloride is to a double quantum forbidden $M_s = 2$ transition of octahedral titanium(II) (Fig. 3). The $^3T_{1g}$ octahedral ground

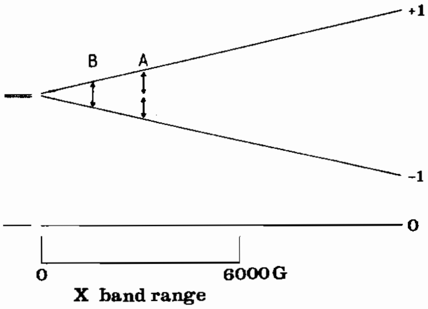

Fig. 3. Likely transitions in the ESR spectrum of octahedral titanium(II). The zero field splitting is likely to be larger than the microwave energy throughout the X-band region but a double quantum $M_s = 2$ transition (A) may appear at about $g = 1.962$ and a single quantum $\Delta M_s = 2$ transition (B) at $g \simeq 4$.

state is split by the known trigonal distortion of the magnesium chloride and by zero field splitting. The field strength for resonance to occur is dependent on the zero field splitting and it may be outwith the X band range. Thus, the allowed transitions, which were not observed in this investigation, may either be unobservable or too broad to be detected. Forbidden transitions with $M_s = 2$ are well known for titanium(III) [10–12] tetrahedral titanium(II) [13–15] and for other transition-metal ions such as nickel(II) in magnesium oxide [16]. In these cases, allowed bands are also observed but the mechanism by which the forbidden bands are postulated to occur is equally applicable in the present case and the bands should appear between $g = 1.9$ and $g = 2.0$.

This simple, intense and sharp band system has not previously been observed for octahedral titanium(II). Titanium signals from doped hafnium sulphide may arise from a similar site but neither the site geometry nor oxidation state has been clearly defined for that system [17].

Rotation of a single-crystal sample about the *z* axis, with the *z* axis perpendicular to the plane of the magnetic field and microwave directions, produced a series of spectra in which the pattern of lines at 15° intervals between a pattern of three lines of equal intensity and one with two lines, one twice the intensity of the other. A plot of the *g* values obtained indicates that there is a regular periodicity of 60° (Fig. 4). g_{xx} and g_{yy} can be assigned from this diagram as shown. No *g* value lower than 1.94 was observed in any plane or in the powder spectrum. A drawing was made of the crystal and the apparent positions of the axis were marked on it. An X-ray precession photograph was used to determine the position of the crystallographic axis and, within experimental error, the two sets of axes coincide.

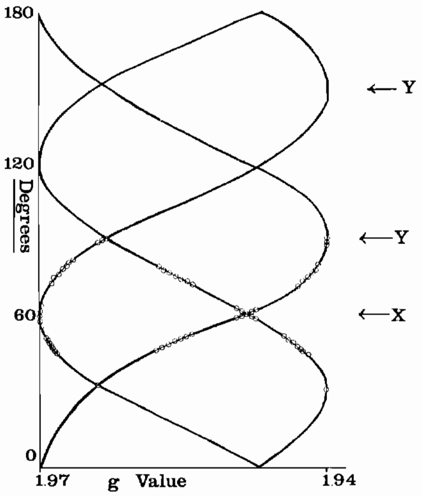

Fig. 4. *g* values for each peak observed as the crystal is rotated about the *z* axis with the *z* axis perpendicular to the plane containing the magnetic field and the incident microwave directions. Experimental points are shown between 30° and 90° as open circles. *g* values at X and Y give g_{xx} and g_{yy} respectively.

The polycrystalline material used as a catalyst and a powder prepared by grinding down some of the single crystal material used in this study produced identical ESR spectra. The spectrum is a complex one which can be seen to be due to an addition of the components of the single-crystal spectrum (Fig. 5).

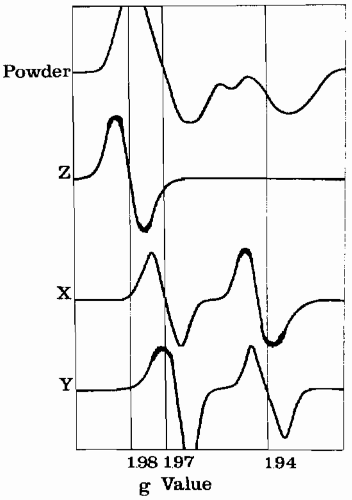

Fig. 5. Relationship between the spectrum recorded along each axis of the crystal and the powder spectrum. Z, X and Y correspond to single-crystal spectra taken with the *z*, *x* and *y* axis of the crystal parallel to the field direction.

Somewhat similar sharp bands have been observed in studies of Ziegler–Natta catalysts based on $TiCl_3$ and aluminium alkyls. *g* values of 1.95 and 1.93 [17, 18] and of 1.97 and 1.94 [19] and band widths of about 20 gauss were reported. It was suggested that these bands arise from weak, ill-assigned lines often seen in the spectrum of $TiCl_3$ [20]. However, these lines in $TiCl_3$ are a very weak feature compared to the allowed transition, whereas the sharp bands found in the $TiCl_3$/aluminium alkyl solutions are the major peaks in the spectrum. There is a close similarity between these bands and the titanium(II) spectrum which, together with the fact that the titanium(II) system is a good catalyst, suggests that a better assignment of the spectra from catalyst mixtures may be to an octahedral titanium(II) site produced by the reduction of the surfaces of $TiCl_3$ by the aluminium alkyl. The appearance of this ESR signal is not a prerequisite for catalysis, and the role of titanium(II) in the catalysis process is not clearly understood, but it seems likely that the ESR spectrum of divalent titanium may prove to be a useful probe of structure and oxidation state, both in studies of catalytic mixtures and in studies of the chemistry of divalent titanium compounds.

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