# PRECIPITATION AND AGEING OF IRON SULPHIDES

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## ABSTRACT

The oxidations of zinc and lead sulphides are important reactions in the extractive metallurgy of these metals. Their sulphide ore concentrates contain significant amounts of iron sulphides, which affect the oxidation behaviour of ores. For oxidation studies, iron sulphides have been prepared by precipitation from aqueous solution under different conditions of pH, temperature, concentration and time of ageing. The effect of these factors on the surface and solid-state properties of the products has been studied.

Precipitations were carried out with iron (III) chloride and iron (II) sulphates of varying concentrations using hydrogen sulphide gas and aqueous sodium sulphide as the precipitants. The precipitations were carried out at room temperature ($20^\circ$C) as well as at elevated temperatures ($85^\circ$C). The products were aged for different lengths of time.

The phase compositions and crystallinity of the products were examined by X-ray powder diffraction. The specific surface areas of selected samples were determined by the BET method from the nitrogen adsorption isotherms recorded gravimetrically at $-196^\circ$C on a CI Mark II vacuum microbalance. Preliminary studies of their oxidation were made on a Stanton-Redcroft mass flow balance.

Results will be presented for a selection of precipitated iron sulphides and commercially available materials.

## INTRODUCTION

In the extraction of zinc and lead, the sulphide ores are oxidised. Significant amounts of iron sulphides in the ore concentrates influence the oxidation processes (1). Thus for oxidation studies, iron sulphides have been precipitated from aqueous solution at different conditions of pH, temperature, concentration and time of ageing, so that comparison can be made ultimately with commercial materials. Resultant variations in surface and solid-state properties of the products have been correlated, using vacuum balance techniques

(for surface area and porosity determination by gas sorption) in conjunction with X-ray diffraction, optical- and electron-microscopy. Preliminary oxidation studies have been made, using a mass-flow balance.


EXPERIMENTAL

The surface areas of the iron sulphide samples were determined by a gravi-metric B.E.T. method (2), using nitrogen gas sorption at $-196^{\circ}C$ recorded on a vacuum microbalance, CI Microforce Mark 2B, which gave µg to mg sensitivity using samples of 0.25 g or less. The adsorption isotherms also indicated any porosity present (from hysteresis) and pore size ranges. Average crystallite sizes deduced from the specific surfaces of the less porous materials were compared with aggregate sizes observed by optical- and scanning electron-microscopy, (Jeol SEM 35).

Preliminary TG and DTA studies of the oxidation of some of the iron sulphide samples were made, using a Stanton-Redcroft Mass-flow Balance.


RESULTS AND DISCUSSION

### Iron sulphide precipitated at lower pH levels

When iron sulphide is precipitated by addition of sodium sulphide to ferric chloride, the products are liable to contain appreciable amounts of hydrous ferric oxide. Comparison of pH curves for the additions of sodium sulphide and sodium hydroxide to ferric chloride (Fig. 1) shows that hydrous ferric oxide can precipitate at pH levels as low as 2-3, whereas levels of over 5 are required for iron sulphides to be precipitated.

Therefore the particles of iron sulphide precipitated by addition of $M.Na_2S$ to $0.5M.FeCl_3$ contain porous cores of hydrous ferric oxide coated with iron sulphide and have specific surfaces of 3-6 $m^2g^{-1}$, even though the overall sizes of the particles are several microns (which would correspond to specific surfaces of below 1 $m^2g^{-1}$ for non-porous material). The 2 samples shown in Fig. 2 have been precipitated and aged for 1 h and 72 h at room temperature. The specific surface decreases from 5.7 to 3.3 $m^2g^{-1}$ on ageing, while the porosity decreases somewhat, as evidenced by the areas of the hysteresis loops of the nitrogen adsorption isotherms. Application of the Kelvin equation to the hysteresis loops indicates that the fresher sample has a full range of mesopore sizes (widths 20-500 A), while the smaller pores of the older (3 days aged) sample have been removed, leaving a mesopore range of only about 50-500 A.

Purer iron sulphide samples are obtained by addition of $M.Na_2S$ to more dilute $0.1M.FeCl_3$. It is essential that the pH is raised as quickly as possible by rapid addition of the sodium sulphide solution to reach the levels
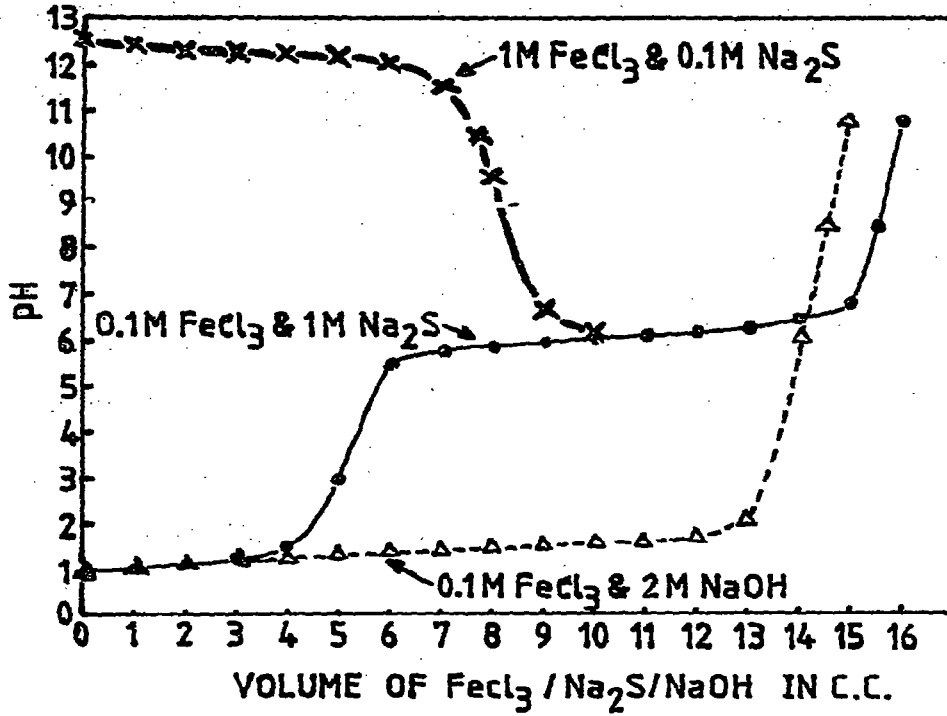
Fig. 1. pH curves for the precipitation of iron sulphides and hydrous iron oxide.
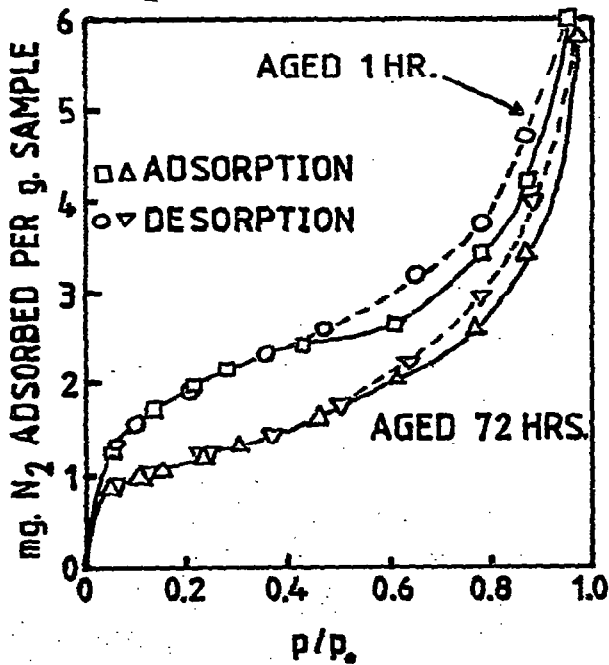


Fig. 2. Adsorption of nitrogen on iron sulphide.
1M.$Na_2S$ added to 0.5M.$FeCl_3$.

at which sulphide precipitation can occur in preference to hydrous oxide precipitation. Also a slight excess of sodium sulphide is preferable to prevent any unreacted ferric chloride from hydrolysing, cf. the purer 1 h aged sample ($\underline{S}$ = 0.7 m$^2$g$^{-1}$, average crystallite size $\sim$2 µm) with the 24 h aged sample separately prepared ($\underline{S}$ = 5.0 m$^2$g$^{-1}$) in Fig. 3 and 4.
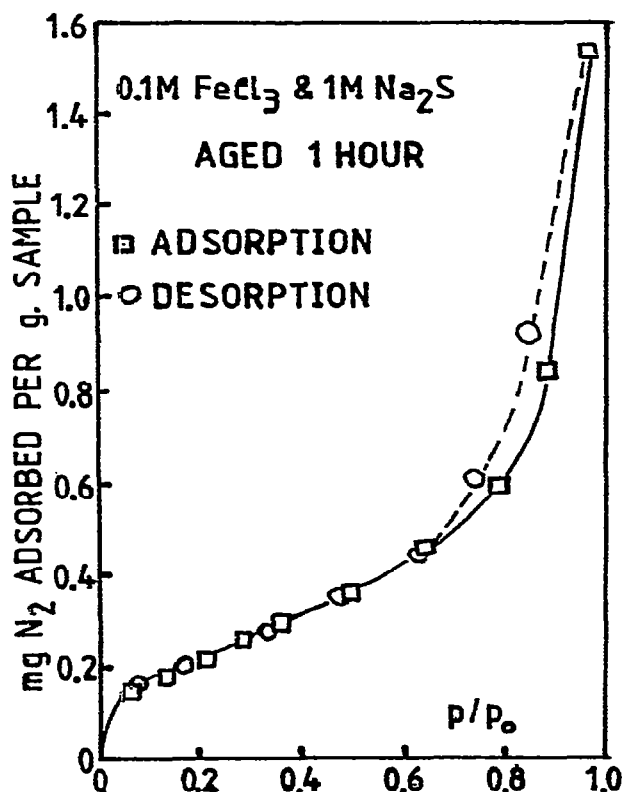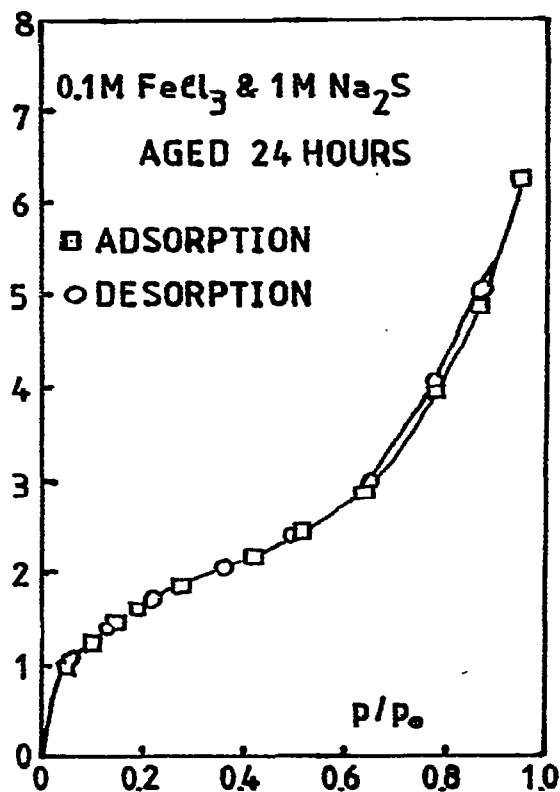


Fig. 3.     Fig. 4.

Fig. 3 and 4. Adsorption of nitrogen on iron sulphide.

The pore structure of the hydrous ferrice oxide is analogous to that obtained when ferrous hydroxide is precipitated from ferrous chloride and subsequently oxidised by dissolved oxygen in the water (3). This is in contrast to the hydrous ferric oxide obtained by direct hydrolysis of ferric chloride which has a restricted upper and lower mesopore size range, giving a markedly different shaped adsorption hysteresis loop (3,4). There is evidently some reduction of $FeCl_3$ to $FeCl_2$ by the reaction:-
$2FeCl_3$ + $Na_2S$ = $2FeCl_2$ + $2NaCl$ + S, which can occur best at pH 0-1; also research here on precipitation of iron sulphide from ferric sulphate has shown that the products contain small amounts of free sulphur (removed when washing

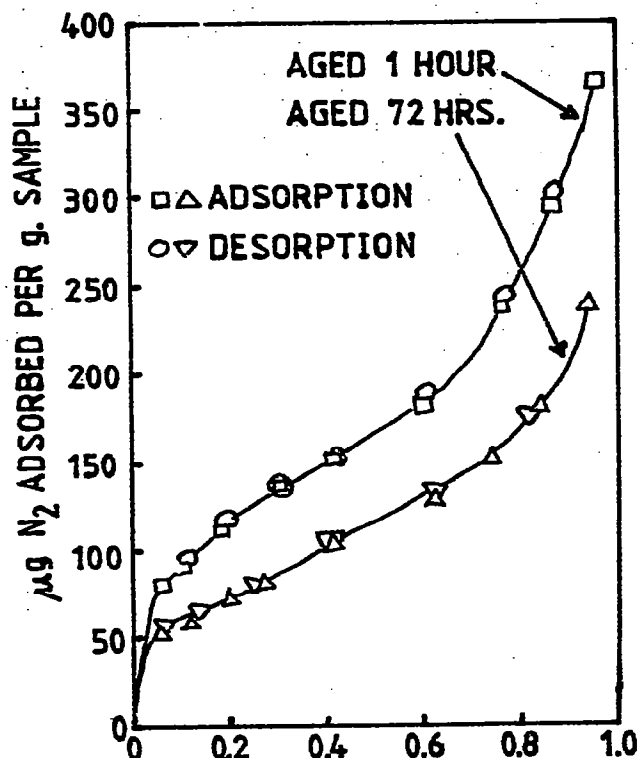ADSORPTION OF N$_2$ ON IRON SULPHIDE

1M FeCl$_3$ ADDED TO 0.1M Na$_2$S

AGED 1 HOUR
AGED 72 HRS.

□△ ADSORPTION
○▽ DESORPTION

Fig. 5.

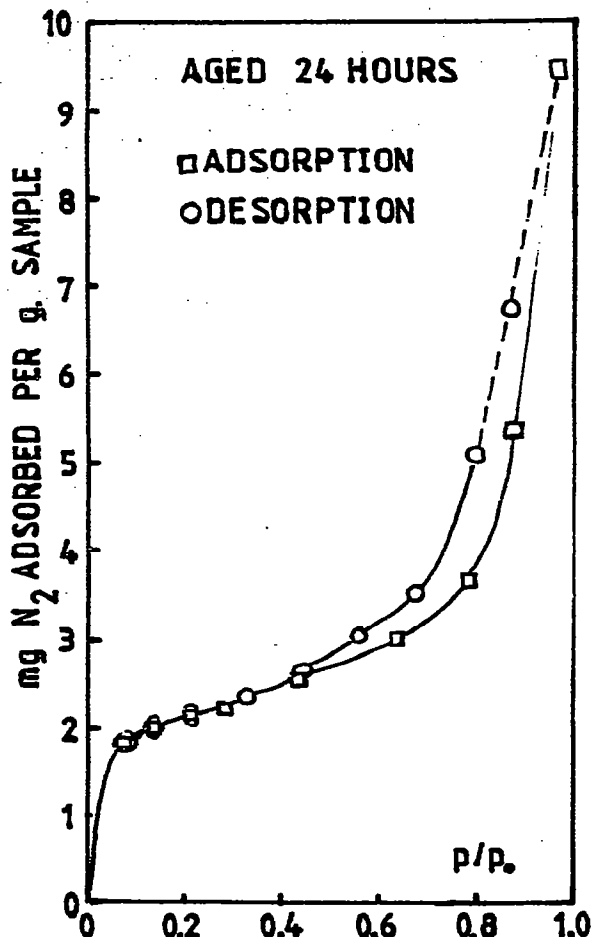AGED 24 HOURS

□ ADSORPTION
○ DESORPTION

p/p$_•$

Fig. 6.

Fig. 5 and 6.  Adsorption of nitrogen on iron sulphide.

with alcohol/either or acetone to arrest ageing.) and that the FeS$_2$ formed is sulphur deficient, viz., FeS$_x$ where $\underline{x}$ = 1.8 to 2.0, and the crystal lattice constant $\underline{a}$ of the cubic pyrite structure falls from 5.42 to 5.36 A.

Iron sulphide precipitated at higher pH levels

The purest iron sulphide samples are precipitated by addition of M.FeCl$_3$ to O.1M.Na$_2$S.  The adsorption isotherms (Fig. 5) show no hysteresis (as would be caused by any hydrous oxide present) and the specific surfaces of 0.3 and 0.2 m$^2$g$^{-1}$ correspond to average crystallite sizes of 4-6 μm for non-porous material, consistent with optical microscopic observations.  Nevertheless, addition of any excess ferric chloride must be avoided.  Otherwise the iron sulphide particles become coated with porous layers of hydrous ferric oxide. This is shown by a sample which has been allowed to age for 24 h (Fig. 6), where the specific surface has become as high as 5.8 m$^2$g$^{-1}$, even though the
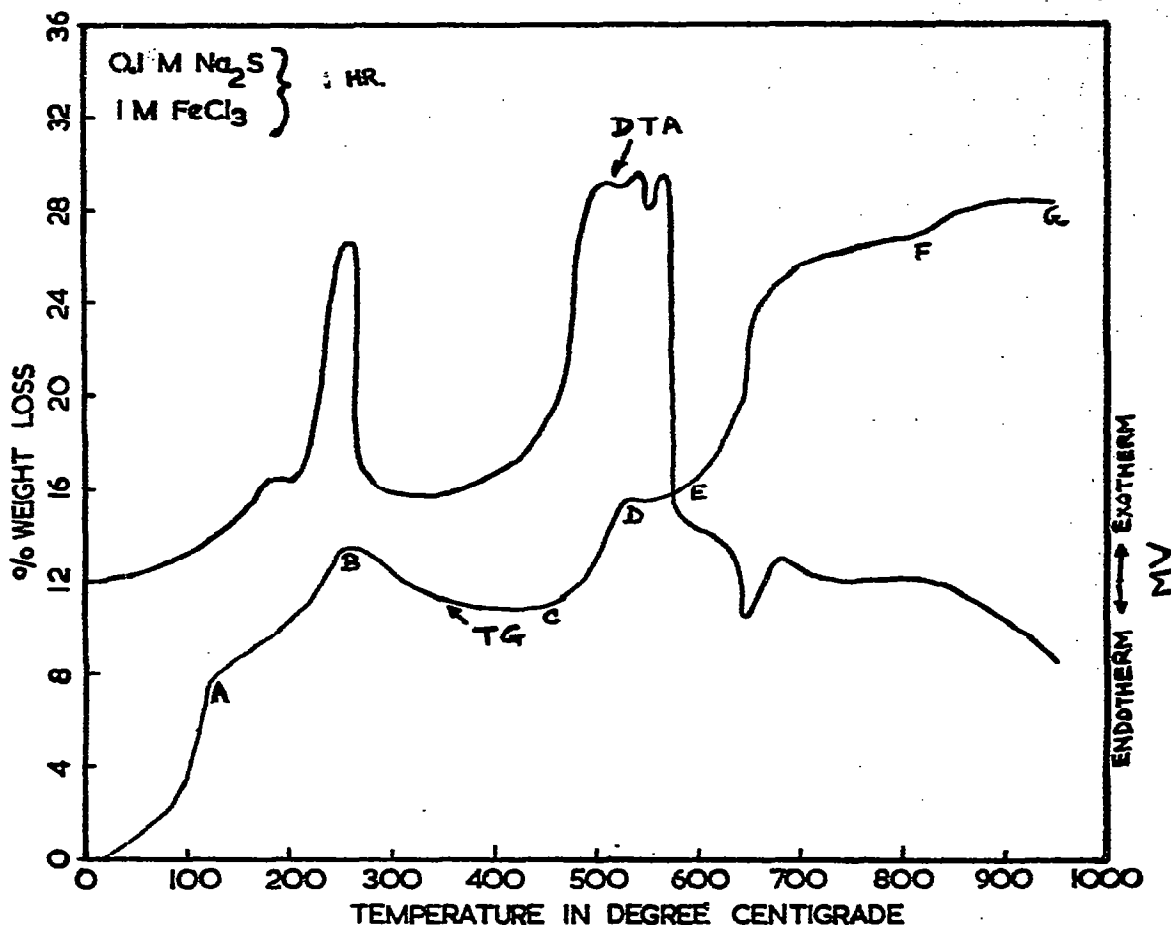
Fig. 7.  Oxidation of iron sulphide (TG and DTA data)

overall size of the particles is several microns like the uncoated samples.
Other research here has shown that precipitated hydrous ferric oxide samples have
specific surfaces of over 100 $m^2g^{-1}$ (3) and the porous nature of the coating
on the iron sulphide particles has been observed microscopically.

Oxidation of iron sulphides

TG and DTA data on the oxidation of an iron sulphide sample are presented
in Fig. 7.  The sample was the one precipitated by addition of $M.FeCl_3$ to
$0.1M.Na_2S$ and aged for 1 h.

The TG data is interpreted on the following basis.  The weight loss at A
represents removal of moisture (7.8%), while further loss, AB, is caused by
desulphurisation of $FeS_2$, viz., $FeS_2 + O_2 \rightarrow FeS + SO_2$, (1).  The subsequent
weight gain, BC, is due to oxidation of the original and newly-formed FeS to
$FeSO_4$, viz., $FeS + 2O_2 \rightarrow FeSO_4$, (2).  This is followed by a weight loss, CD,
at higher temperature as the $FeSO_4$ decomposes, viz., $4FeSO_4 \rightarrow 2Fe_2O_3 + 4SO_2 + O_2$,
(3).  At certain temperatures, some of the $FeSO_4$ is oxidised to $Fe_2(SO_4)_3$ before

finally decomposing to $Fe_2O_3$, viz., $12FeSO_4 + 3O_2 \rightarrow 4Fe_2(SO_4)_3 + 2Fe_2O_3$, (3a), or when sufficient $SO_2$ is present from reaction (3) at higher temperatures, more $Fe_2(SO_4)_3$ can be formed by $2FeSO_4 + SO_2 + O_2 \rightarrow Fe_2(SO_4)_3$. (3b). Since these reactions (3a,b) involve weight gains, then the decrease in weight is temporarily arrested, DE, until still higher temperatures are reached when the $Fe_2(SO_4)_3$ decomposes. There is probably no $FeSO_4$ remaining when F is reached and the remaining $Fe_2(SO_4)_3$ decomposes to $Fe_2O_3$ along FG, viz., $2Fe_2(SO_4)_3 \rightarrow 2Fe_2O_3 + 6SO_2 + 3O_2$.

Quantitatively, the total sulphur content of the original material can be determined from the net overall weight loss between A and G (20.5%) when all of the iron sulphide has been converted to $Fe_2O_3$. This indicates that the initial material consists of approximately equimolecular proportions of FeS and $FeS_x$ where $\underline{x} = 1.77$, i.e., the $FeS_2$ is sulphur-deficient, as discussed earlier. Nevertheless complete desulphurisation of the $FeS_{1.77}$ to FeS by reaction (1) should give a total weight loss corresponding to 19.5% compared with 13.5% experimentally (B). Thus some of the FeS (10.3%) oxidises to $FeSO_4$ by reaction (2) before (1) is complete. The full oxidation of the FeS to $FeSO_4$ would correspond to a net weight gain of 39.0%, but this is not reached (cf. point C at 10.9% weight loss), since some of the $FeSO_4$ already decomposes so that at D (15.6% net weight loss) 81.5% of the $FeSO_4$ has decomposed, when the temperature has reached $540^{\circ}C$. Above this temperature, some of the remaining 18.5% $FeSO_4$ evidently oxidises to $Fe_2(SO_4)_3$, so that the weight loss is temporarily arrested. Complete conversion of this $FeSO_4$ to $Fe_2(SO_4)_3$ would leave point E 1.4% below D but experimentally it is only 0.4% below, so that there is only partial conversion and most of the remaining $FeSO_4$ decomposes to $Fe_2O_3$ along EF before the remaining $Fe_2(SO_4)_3$ decomposes to $Fe_2(SO_4)_3$ along FG. The magnitude of the weight loss along FG of 1.4% is consistent with the amount of $Fe_2(SO_4)_3$ expected to have been formed earlier.

The DTA data in Fig. 7 shows exotherms which evidently correspond to desulphurisation of the higher sulphide at about $270^{\circ}C$ and decomposition of the $FeSO_4$ mainly between $400^{\circ}C$ and $600^{\circ}C$. The wide temperature range for this decomposition suggests that it may involve several stages with possible intermediate formation of basic sulphates and is the subject of further investigation.

REFERENCES

1 D.R. Glasson and S.A.A. Jayaweera, "Thermoanalytical studies of the effect of additives on the oxidation of zinc sulphide", Proc. 2nd European Symposium on Thermal Analysis (Ed. D. Dollimore) 1981 in press.
2 D.R. Glasson, J. chem. Soc., 1956, pp. 1506-10
3 S.A. Crosby, D.R. Glasson and G.E. Millward, (to be published)
4 S.J. Gregg and K.J. Hill, J. chem. Soc., 1953, 3945 – J.F. Goodman and S.J. Gregg, J. chem. Soc., 1956, 3612.