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**Changes of the Electronic State and the Electrical Resistance of  
Some Iron Compounds at High Pressures**

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## Changes of the Electronic State and the Electrical Resistance of Some Iron Compounds at High Pressures

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The electrical resistance of some iron compounds has been measured at high pressures. In Fe(III) compounds, the resistance decreases with increasing pressure, by means of electron transfer from Fe(II), which is formed from Fe(III) under pressure, to Fe(III). A pressure-induced chemical reaction was observed for potassium ferricyanide and ferric oxalate. The resistance vs. pressure curve for these two compounds has a resistance minimum. The pressure-induced spin changes observed in Fe(II) compounds make only a small contribution to a decrease in resistance.

### Introduction

A great deal of knowledge on a pressure-induced electronic transition of iron compounds has been accumulated from measurements of Mössbauer effect and optical absorption.<sup>1</sup> Champion et al.<sup>2</sup> first observed that the electronic transitions involving the reduction of ferric ions or the spin flip of ferrous ions are induced with various iron compounds by applying a wide range of pressures.

In a previous paper,<sup>3</sup> the effect of pressures up to 50 kbars was measured on the absorption spectra in some ferric and ferrous compounds by the authors, who observed pressure-induced bands at the lower energy side of the original one in both ferric and ferrous compounds. It was thought that such bands might decrease the electrical resistance. These bands are due to the thermal occupation of the excited states, which leads to a formation of new oxidation and spin states.

In this paper, the results presented will be divided into three sections: (1) the resistance and the Fe(III) → Fe(II) reduction in five ferric compounds with oxygen ligands at high pressures, (2) the resistance and the chemical reaction in two ferric compounds at high pressures, and (3) the resistance and the changes of the spin states in three ferrous compounds at high pressures. All the phenomena mentioned above involve electronic transitions and therefore electrical resistance surveys will be helpful to get some information concerning the electron-transport mechanism.

### Experimental Section

In order to eliminate the difficulties in the near-ultraviolet region involved in a high-pressure diamond optical cell, a new apparatus was made, using a single crystal of sapphire instead of diamond. This sapphire single crystal is transparent up to ~350 nm (~28 kK). In the present experiments, the authors used it without a gasketing device; they simply placed the sample in a KBr disk between two sapphire windows, compressed it axially, and then clamped pressure up to ~15 kbars by screwing the bolt up until it did not rotate any more. The quasi-hydrostatic pressures were generated by means of a high-pressure optical bomb using a NaCl medium up to 50 kbars.<sup>4</sup> The infrared spectra of the samples were observed in a KBr disk. These optical measurements were performed with a Bausch-Lomb grating spectrometer, with a Shimadzu double-beam spectrometer and with a

Table I. Materials Studied

Compd	Formula
Ferric phosphate hydrate (FPH)	FePO <sub>4</sub> ·nH <sub>2</sub> O
Ferric acetylacetonate (FAA)	Fe(C <sub>5</sub> H <sub>7</sub> O <sub>2</sub> ) <sub>3</sub>
Ferric citrate (FCT)	Fe(C <sub>6</sub> H <sub>5</sub> O <sub>7</sub> ) <sub>3</sub> ·3H <sub>2</sub> O
Ferric oxide (FOD)	Fe <sub>2</sub> O <sub>3</sub>
Basic ferric acetate (BFA)	Fe <sub>3</sub> (CH <sub>3</sub> CO <sub>2</sub> ) <sub>6</sub> (OH) <sub>2</sub> ·CH <sub>3</sub> CO <sub>2</sub> ·H <sub>2</sub> O
Potassium ferricyanide (PFIC)	K <sub>3</sub> Fe(CN) <sub>6</sub>
Ferric oxalate (FIOL)	Fe <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ·5H <sub>2</sub> O
Ferrous oxalate (FOOL)	FeC <sub>2</sub> O <sub>4</sub> ·2H <sub>2</sub> O
Potassium ferrocyanide (PFOC)	K <sub>4</sub> Fe(CN) <sub>6</sub>
Ferrous chloride hydrate (FCH)	FeCl <sub>2</sub> ·nH <sub>2</sub> O
Ferrous phosphate (FP)	Fe <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>

Table II. Fraction of Fe(II) Formed under Pressure

Compd	Pressure, kbars				
	25	50	75	100	125
FPH	22 <sup>a</sup>	32	39	43	46
FAA	0	10	17	24	31
BFA	0	5	6	7	8
FCT	35	46	50	54	56

<sup>a</sup> Expressed in percent.

Nihonbunko IR-S Type infrared spectrometer.

The electrical resistance has been measured as a function of pressure up to 130 kbars at room temperature, using a supported-taper piston apparatus.<sup>5</sup> The resistance was observed by the two-probe method. The pellet of the sample was made by the compression of about 5 kbars and was set between two Cu electrodes.

In this study, seven ferric and three ferrous complexes were studied. Ferric acetylacetonate was prepared as described in the literature.<sup>6</sup> The other materials used were all of a commercially available reagent grade quality. Ferric oxalate was handled in the dark to prevent photoreduction.

The materials studied are listed in Table I.

### Results and Discussion

**Resistance and Fe(III) → Fe(II) Reduction.** In Figure 1, the resistances of various ferric compounds are shown as a function of pressure. The five compounds in Figure 1 are FPH, FAA, FCT, FOD, and BFA, in all of which Fe(III) is sur-



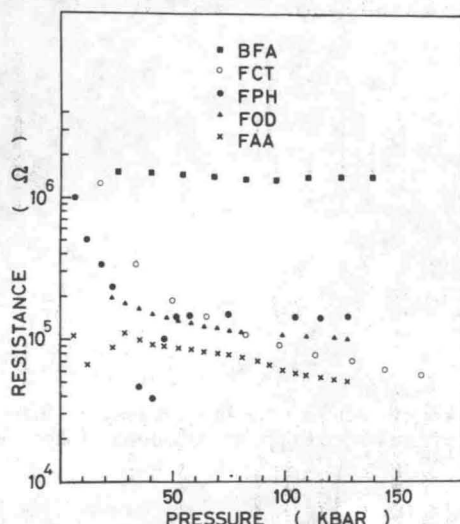


Figure 1. Resistance of various ferric compounds as a function of pressure—basic ferric acetate, ferric citrate, ferric phosphate hydrate, ferric oxide, and ferric acetylacetonate.

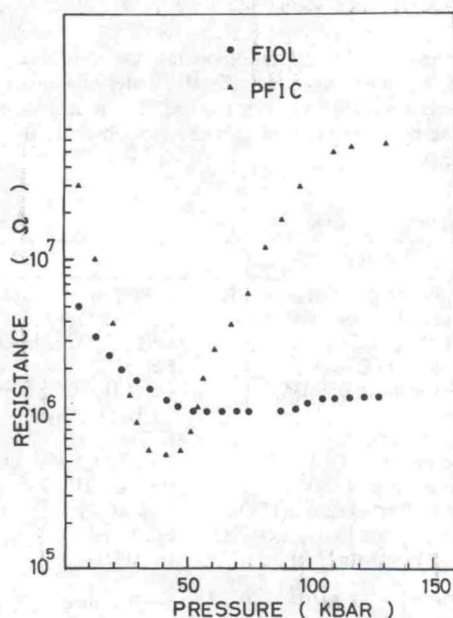


Figure 2. Resistance of potassium ferricyanide and ferric oxalate as a function of pressure.

rounded by the oxygen ligands. FCT decreases in the resistance continuously by a factor of  $10^{-2}$  up to 160 kbars. FPH has a resistance minimum at 40 kbars. FAA has the resistance minimum and maximum at 15 and at 30 kbars, respectively. Both BFA and FOD seem to be rather insensitive to pressure in their resistance.

Table II shows the fraction of Fe(II) formed under pressure for FCT, FPH, FAA, and BFA.<sup>2</sup> FOD has not been detected to reduce to Fe(II) up to 125 kbars.<sup>2</sup> At the outset, it can be inferred that the amounts of the fraction of Fe(II) formed under pressure are closely related to decreasing resistance in these five ferric compounds. In the resistance measurements for the ferric compounds, Kaneko and Inoue<sup>7</sup> attributed the electrical conduction to the hopping of excess d electrons in Fe(II) to Fe(III). In insoluble Prussian Blue,  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ , both Fe(II) and Fe(III) are present at 1 atm. At 46 kbars, the d electron in the  $t_{2g}$  orbital of the Fe(II) stays in the  $t_{2g}$  orbital of the Fe(III) about 3 times longer than at 1 atm.<sup>8</sup>

By using the high-pressure diamond optical cell, the color of FPH up to ~50 kbars was observed. A color change from yellow to yellowish green at around 40 kbars was observed.

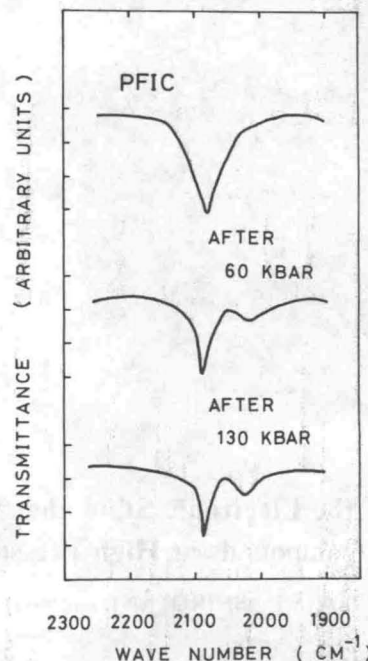


Figure 3. Infrared spectra of potassium ferricyanide and pressure products at 60 and 130 kbars.

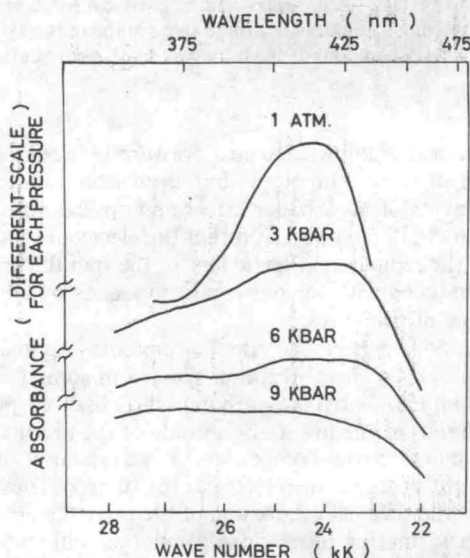


Figure 4. Electronic spectra of potassium ferricyanide as a function of pressure.

This was a reversible change. This range of pressure is compatible with that observed for the resistance minimum. FAA exceptionally exhibits an increase in isomer shift up to 30 kbars,<sup>9</sup> and above about 30 kbars the behavior is normal. Champion and Drickamer attributed the behavior to the changes in the hybridization in the  $\beta$ -diketone rings. These are closely reflected by the increase in the resistance vs. pressure curve of FAA up to about 30 kbars. As can be seen from Table I, above ~30 kbars the Fe(III) begins to reduce. Fe(II) formed under pressure can supply one of the adjacent Fe(III) atoms with an electron and cause the resistance to decrease.

**Resistance and Chemical Reaction.** Figure 2 shows the resistance of PFIC and FIOL as a function of pressure up to 130 kbars. As for PFIC, above 40 kbars the resistance tends to drift upward; this tendency accelerates with increasing pressure. By 130 kbars the resistance has increased by a factor of  $\sim 10^2$ .

As for FIOL, in the pressure range of 50–90 kbars the resistance appears to be rather insensitive to pressure and



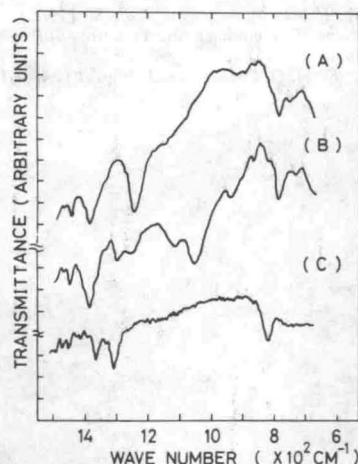


Figure 5. Infrared spectra of ferric oxalate (A), the high-pressure product from 130 kbars (B), and ferrous oxalate (C).

gradually tends to drift upward with increasing pressure.

Pressure products were recovered for both PFIC and FIOL. Three pressure products of PFIC were recovered at 7, 60, and 130 kbars.

In Figure 3 the infrared spectra of these three samples at 1 atm are exhibited. In PFIC there is only a single peak at  $2090\text{ cm}^{-1}$  assigned to the  $\text{C}\equiv\text{N}$  stretching vibration. The pressure products exhibit the band with a doublet appearance. The higher frequency peak in each spectrum corresponds to the  $\text{C}\equiv\text{N}$  stretching vibration of  $\text{Fe(III)}$  and the lower one to that of  $\text{Fe(II)}$ , since in PFOC there is an intense band at  $2025\text{ cm}^{-1}$ . With increasing pressure, the  $\text{Fe(III)}$  band decreases in intensity, while the  $\text{Fe(II)}$  band increases in intensity. These results show that the chemical reaction from PFIC to PFOC proceeded with increasing pressure.

It is possible to follow the course of the reaction for PFIC by observing the ligand ( $\text{CN}^-$ )-to-metal ( $\text{Fe(III)}$ ) charge-transfer peak, which lies near  $24.1\text{ kK}$  ( $\sim 3\text{ eV}$ ) at 1 atm, in the high-pressure sapphire optical cell. Figure 4 exhibits spectra at several pressures. The most obvious features are the fading of intensity of the original peak, starting at 3 kbars, and the increase of intensity of the band around  $27\text{ kK}$  ( $\sim 3.4\text{ eV}$ ). This pressure-induced band around  $27\text{ kK}$  is due to PFOC which was produced as a result of the chemical reaction under pressure, since the electronic spectrum of the water solution of the recovered sample at 10 kbars shows a weak band at  $23.7\text{ kK}$ , which is assigned to the spin-forbidden transition of  $\text{Fe(CN)}_6^{4-}$ ,  $^1\text{A}_{1g} \rightarrow ^3\text{T}_{1g}$ .<sup>10</sup> The spectrum run after release of pressure shows that the peak does not recover intensity. This is, of course, consistent with the irreversible nature of the chemical reaction as discussed above.

The pressure product of FIOL was recovered at 130 kbars. The infrared spectra of FIOL were measured. It was found that the spectrum was the superimposition of FIOL and FOOL by examining the  $750\text{--}850\text{ cm}^{-1}$  ( $\text{O--C--O}$  bending) and  $1250\text{--}1350\text{ cm}^{-1}$  ( $\text{C--O}$  stretching) regions as shown in Figure 5. It should be noted that there are three pressure-induced unknown peaks at  $1120$ ,  $1055$ , and  $940\text{ cm}^{-1}$  in the high-pressure product at 130 kbars.<sup>11</sup> It has been pointed out that both PFIC and FIOL reduce photochemically at 1 atm.<sup>12,13</sup> It has also been shown that a combination of pressure and shear is very effective in reducing PFIC in an irreversible manner.<sup>14</sup>

**Resistance and Changes in the Spin States of Ferrous Compounds.** The pressure effect on the absorption spectra of PFOC at quasihydrostatic pressure up to 50 kbars was measured. The result is shown in Figure 6. The band around  $24\text{ kK}$  at 7 kbars which appears as a shoulder showed a blue shift, about  $500\text{ cm}^{-1}$  at 37 kbars, drastically increasing in intensity with pressure. At 26 kbars another pressure-induced

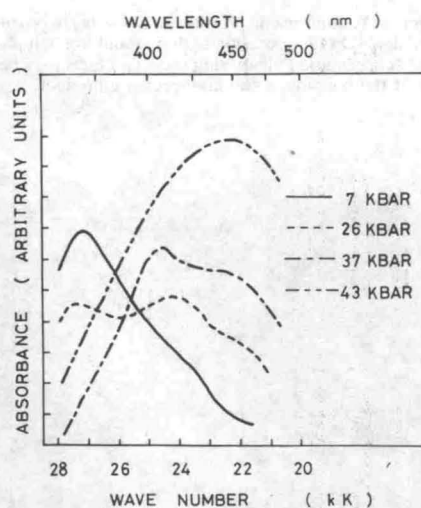


Figure 6. Electronic spectra of potassium ferrocyanide as a function of pressure.

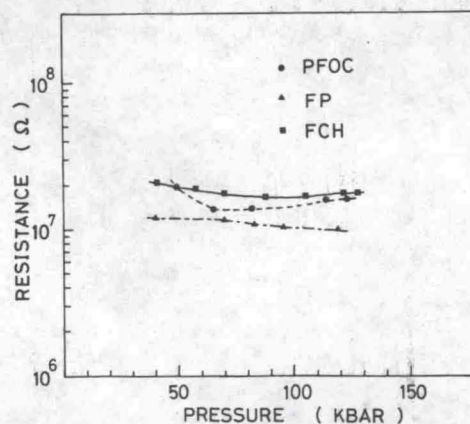


Figure 7. Resistance of various ferrous compounds as a function of pressure—potassium ferrocyanide, ferrous phosphate, and ferrous chloride hydrate.

band was observed around  $22\text{ kK}$ . This band also exhibited a blue shift, drastically increasing in intensity with pressure. The behaviors were reproducible. The electronic spectrum of  $\text{Fe(CN)}_6^{4-}$  shows a weak band at  $23.7\text{ kK}$  assigned as  $^1\text{A}_{1g} \rightarrow ^3\text{T}_{1g}$ . The bands at  $21\text{--}26\text{ kK}$  which drastically increased in intensity seem to be related to this transition.

In Figure 7, we show the resistance of PFOC, FCH, and FP as a function of pressure up to 130 kbars. The spin changes in the ground state apparently do not contribute to decreasing the resistance, since the resistance changes with pressure of these ferrous compounds are small.

**Registry No.** FPH, 51833-68-2; FAA, 14024-18-1; FCT, 17217-76-4; FOD, 1309-37-1; BFA, 21007-42-1; PFIC, 13746-66-2; FIOL, 15155-21-2; FOOL, 6047-25-2; PFOC, 13943-58-3; FCH, 23838-02-0; FP, 14940-41-1.

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and  $950\text{ cm}^{-1}$ . At atmospheric pressure, it is possible to produce trioxane from oxalic ion. On that occasion both iron and iron ion play a role as a catalyst. A speculation identifying these two facts may be somewhat indicative of the bonding in the high-pressure product.

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