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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.[1] Champion et al.[2] 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,[3] 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 quasihydrostatic pressures were generated by means of a high-pressure optical bomb using a NaCl medium up to 50 kbars.[4] 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 Shimazu double-beam spectrometer and with a 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.[5] 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.[6] 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.

Table I. Materials Studied

Compd	Formula
Ferric phosphate hydrate (FPH)	$FePO_4 \cdot nH_2O$
Ferric acetylacetonate (FAA)	$Fe(C_5H_7O_2)_3$
Ferric citrate (FCT)	$Fe(C_6H_5O_7) \cdot 3H_2O$
Ferric oxide (FOD)	Fe_2O_3
Basic ferric acetate (BFA)	$Fe_3(CH_3CO_2)_6(OH)_2 \cdot CH_3CO_2 \cdot H_2O$
Potassium ferricyanide (PFIC)	$K_3Fe(CN)_6$
Ferric oxalate (FIOL)	$Fe_2(C_2O_4)_3 \cdot 5H_2O$
Ferrous oxalate (FOOL)	$FeC_2O_4 \cdot 2H_2O$
Potassium ferrocyanide (PFOC)	$K_4Fe(CN)_6$
Ferrous chloride hydrate (FCH)	$FeCl_2 \cdot nH_2O$
Ferrous phosphate (FP)	$Fe_3(PO_4)_2$

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

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

[a] Expressed in percent.

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-

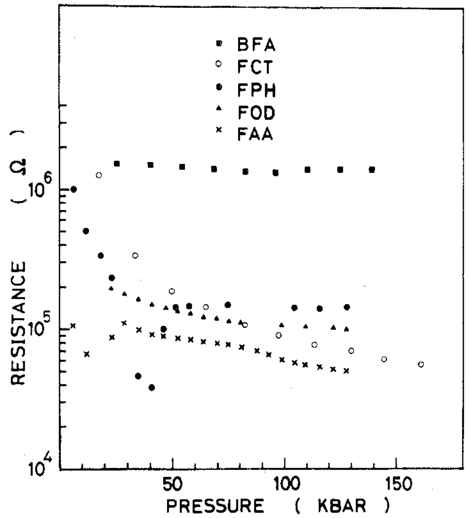

Figure 1. Resistance of various ferric compounds as a function of pressure–basic ferric acetate, ferric citrate, ferric phosphate hydrate, ferric oxide, and ferric acetylacetonate.

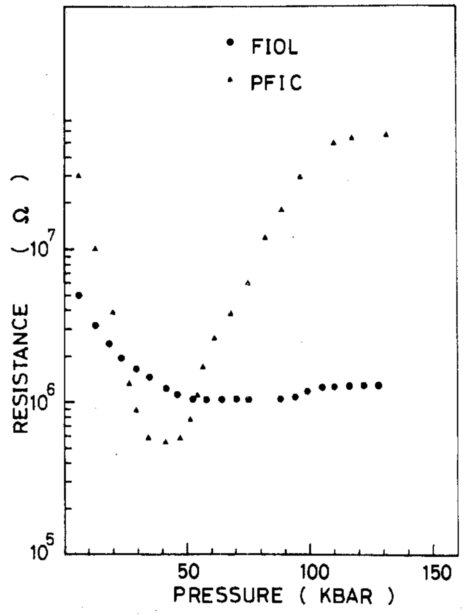

Figure 2. Resistance of potassium ferricyanide and ferric oxalate as a function of pressure.

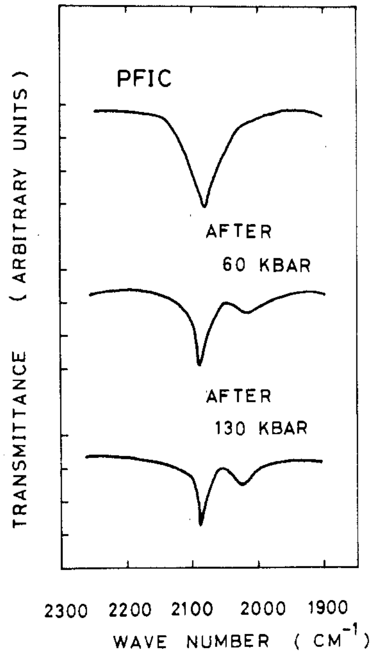

Figure 3. Infrared spectra of potassium ferricyanide and pressure products at 60 and 130 kbars.

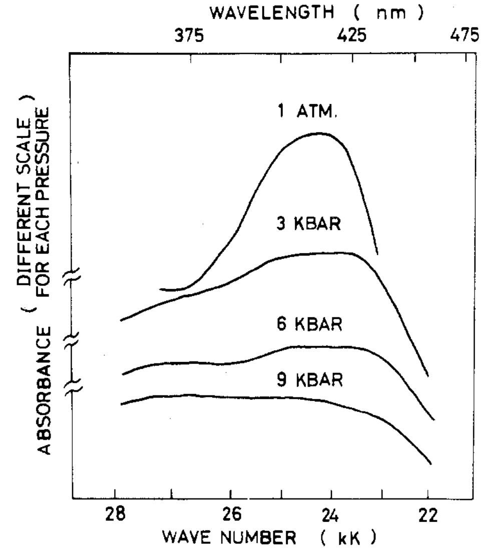

Figure 4. Electronic spectra of potassium ferricyanide as a function of pressure.

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.[2] FOD has not been detected to reduce to Fe(II) up to 125 kbars.[2] 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[7] attributed the electrical conduction to the hopping of excess d electrons in Fe(II) to Fe(III). In insoluble Prussian Blue, $Fe_4[Fe(CN)_6]_3$, 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.[8]

By using the high-pressure diamond optical cell, the color of FPH up to $\sim$50 kbars was observed. A color change from yellow to yellowish green at around 40 kbars was observed. 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,[9] and above about 30 kbars the behavior is normal. Champion and Drickamer attributed the behavior to the changes in the hybridization in the β-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 $\sim$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

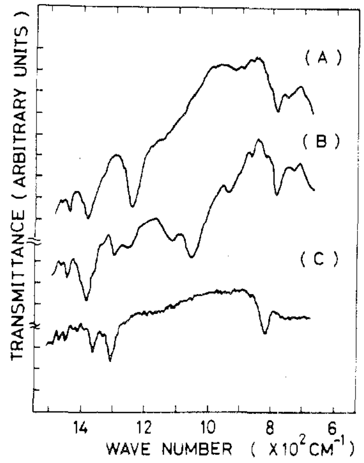

Figure 5. Infrared spectra of ferric oxalate (A), the high-pressure product from 130 kbars (B), and ferrous oxalate (C).

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 cm^{-1} assigned to the C≡N stretching vibration: The pressure products exhibit the band with a doublet appearance. The higher frequency peak in each spectrum corresponds to the C≡N stretching vibration of Fe(III) and the lower one to that of Fe(II), since in PFOC there is an intense band at 2025 cm^{-1}. With increasing pressure, the Fe(III) band decreases in intensity, while the 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 (CN$^-$)-to-metal (Fe(III)) charge-transfer peak, which lies near 24.1 kK (~3 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 kK (~3.4 eV). This pressure-induced band around 27 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 kK, which is assigned to the spin-forbidden transition of $Fe(CN)_6^{4-}$, $^1A_{1g} \rightarrow {}^3T_{1g}$.[10] 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 750–850-cm^{-1} (O–C–O bending) and 1250–1350-cm^{-1} (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 cm^{-1} in the high-pressure product at 130 kbars.[11] It has been pointed out that both PFIC and FIOL reduce photochemically at 1 atm.[12,13] It has also been shown that a combination of pressure and shear is very effective in reducing PFIC in a irreversible manner.[14]

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 kK at 7 kbars which appears as a shoulder showed a blue shift, about 500 cm^{-1} at 37 kbars, drastically increasing in intensity with pressure. At 26 kbars another pressure-induced band was observed around 22 kK. This band also exhibited a blue shift, drastically increasing in intensity with pressure. The behaviors were reproducible. The electronic spectrum of $Fe(CN)_6^{4-}$ shows a weak band at 23.7 kK assigned as $^1A_{1g} \rightarrow {}^3T_{1g}$. The bands at 21–26 kK which drastically increased in intensity seem to be related to this transition.

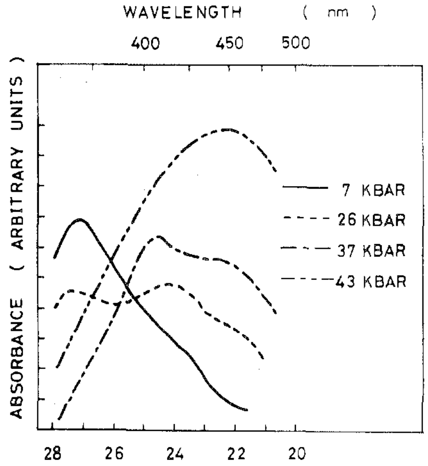

Figure 6. Electronic spectra of potassium ferrocyanide as a function of pressure.

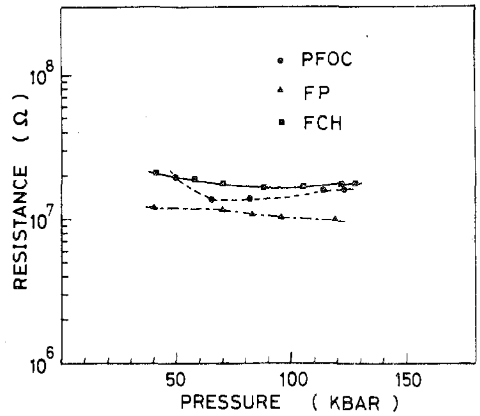

Figure 7. Resistance of various ferrous compounds as a function of pressure–potassium ferrocyanide, ferrous phosphate, and ferrous chloride hydrate.

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 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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Fourier Transform Carbon-13 Nuclear Magnetic Resonance of Aqueous Nickel(II)–Acetic Acid Solutions. I. Equilibrium Quotients from Relative Abundances of Solution Species[1]

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The complex formation reaction between nickel(II) and acetate ions in aqueous solution has been studied by Fourier transform carbon-13 nuclear magnetic resonance. Equilibrium quotients for the formation of monoacetatonickel(II) complex were calculated from the relative areas of distinct coordinated and bulk acetate signals over the temperature range –5 to +20° and were found to be constant over this range. Equilibrium quotients determined over the ionic strength range 1.2–4.0 *m* were found to be smaller than previously reported values. A minimum in the equilibrium quotient was observed at approximately 2 *m* ionic strength.

Introduction

The weak complex formation reaction between nickel(II) ion and acetate ion in aqueous solution has been investigated by various physical methods.[3–14] It has been generally assumed that only the monoacetatonickel(II) species is formed appreciably, although formation constants for higher acetato species have been reported.[11–14] Wide scatter of the reported formation constants in the ionic strength range 0–1 *M* possibly reflects a high sensitivity of the formation constant to ionic strength or, instead, a high sensitivity to the widely varying reaction conditions required by each method. In addition, no results are available for this reaction at ionic strengths higher than 1 *M*.[15] We report here equilibrium quotients obtained from carbon-13 nuclear magnetic resonance (^{13}C NMR) studies of aqueous solutions of nickel(II) and 90 atom % ^{13}C-enriched carboxyl-labeled acetic acid, $CH_3{}^{13}COOH$, for the formation of monoacetatonickel(II) over the ionic strength range 1.2–4.0 *m*.

The combination of selective high ^{13}C enrichment and proton-decoupled Fourier transform ^{13}C NMR is sufficient to overcome inherent experimental difficulties arising from the low natural abundance and small magnetic moment of carbon-13, as well as paramagnetic line broadening from nickel(II). Simultaneous observation of ^{13}C acetate signals in bulk solution and acetate bound to nickel(II) is possible below 20°, the bound acetate signal appearing upfield from that of bulk acetate. Relatively few such systems[16–21] have been studied because the experimental conditions necessary for detection of distinct coordinated and bulk signals are often not attainable.[16,20]

Experimental Section

Materials. $Ni(ClO_4)_2{\cdot}6H_2O$ and anhydrous $NaClO_4$ were purchased from the G. F. Smith Chemical Co. and used without further purification. The nickel salt was analyzed by titration with ethylenediaminetetraacetic acid and Murexide indicator, according to Welcher.[22] Acetic acid enriched to 90.0 atom % ^{13}C in the carboxyl position was a gift from D. G. Ott and V. Kerr of the Los Alamos Scientific Laboratory. All samples were prepared by weight in 99.5% D_2O and used without further analysis. Samples were adjusted to pH 5.5–6.0 with a 6 *m* solution of NaOD in D_2O. The pH recorded was that observed with an Orion 700 pH meter equipped with a combination electrode. In general, the pD correction (pH = pD – 0.4) and the p*K* correction for deuterium isotope effects essentially offset each other.[23,24] Because the differences resulting from these corrections are small for the specific case of acetic acid, no attempt was made to record pD values.

Magnetic Resonance Methods. Proton-decoupled ^{13}C NMR Fourier transform spectra were obtained at 25.2 MHz with a Varian Associates XL-100-15-FT spectrometer interfaced to a Data General Supernova computer. The magnetic field was stabilized by locking to the 15.4-MHz deuterium resonance of internal D_2O. Free induction decays of 40-μsec radiofrequency pulses were accumulated as 8192 data points in the time domain and transformed as 4096 data points in the frequency domain. In some cases, when the highest resolution capability was not required, 4096 time domain and 2048 frequency domain data points were used. Samples were contained in 12-mm (o.d.) Pyrex glass tubes spinning at 14–16 revolutions/sec in the probe. Temperature was varied by flowing heated or cooled nitrogen gas through the probe and around the sample tube. The sample temperature was checked before and after individual measurements with a copper–constantan thermocouple inserted into an NMR tube filled with a standard solution. Sample temperatures were found to be constant within ±1.0°.

Relative signal areas were obtained from transformed spectra by various manual integration methods and by analog curve fitting with a Du Pont 301 curve analyzer adjusted to fit lorentzian lines.

Treatment of Data and Results

The spectrum of a representative solution at 0° is shown in Figure 1. The strong alternating magnetic field due to nickel(II) ion's two unpaired electrons broadens the bound acetate resonance, which appears 111.3 ppm upfield in Figure 1. Relative intensities of the separate bound and free acetate signals remain essentially constant in the temperature range –5 to +20°, for a given solution composition. No evidence for other carbon-13 resonances was observed in the spectra, although broad peaks representing less than 10% of total acetate are probably not observable.

Assuming formation of only one complex species, $[Ni(OAc)(H_2O)_5{}^+]$, molal concentrations of the various solution components were calculated directly from P_M and P_L, the fractions of bound and free acetate, respectively, according to eq 1, where $(m_{Ni})_0$ and $(m_{HOAc})_0$ are the stoichiometric molal concentrations of $Ni(ClO_4)_2$ and $[1\text{-}^{13}C]$acetic acid; m_{HOAc} and m_{OAc^-} are the molal concentrations of undissociated acetic acid and bulk acetate, respectively; and $m_{Ni^{2+}}$ and m_{NiOAc^+} are the molal concentrations of uncomplexed nickel ion and monoacetatonickel(II) complex, respectively. The