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Pressure Effect on the Absorption Spectra of Iron Compounds

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The effect of pressures up to 50 kbar has been measured on the absorption spectra in five ferric compounds, two ferrous compounds, and one mixed valence compound. In six compounds, but not in basic ferric acetate and soluble prussian blue, we observed pressure-induced bands which were assigned to the d-d transition of the converted Fe(II) for the ferric compounds and to the spin-forbidden d-d transition for the ferrous compounds. The absorption spectra for single crystals of potassium ferri- and ferrocyanide were studied at hydrostatic pressures up to 5 kbar. The band-peak intensity decreased with an increase in the pressure in both cases. The charge-transfer band from Fe(II) to Fe(III) of soluble prussian blue showed a blue shift (69 cm^{-1}/kb) at hydrostatic pressures up to 7.2 kbar.

A great deal of knowledge on the pressure-induced electronic transitions of iron compounds has been accumulated from measurements of the Mössbauer effect and of optical absorptions. Drickamer *et al.*¹⁾ first observed that 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.

The reduction or spin flip initially increases with the increase in the pressure and exhibits a reversible process, sometimes with hysteresis. This behavior can be explained in terms of such basic effects of the pressure on the electronic structures as the increasing overlap and the relative displacement between adjacent electronic orbitals. In this paper, we wish to present data on the effects of pressures up to 50 kbar on the absorption spectra of some ferric, ferrous, and mixed-valence iron compounds.

The changes in the oxidation states of ferric and ferrous ions with pressure are discussed in connection with the results of the Mössbauer effect reported by Drickamer *et al.*

Experimental

The ferric and ferrous compounds used in this experiment were all of a commercially-available, reagent-grade quality. The absorption spectra were measured as a function of the pressure. The pressures were generated by means of an intensifier using a white gasoline medium up to 8 kbar and a high-pressure optical bomb using a NaCl medium up to 50 kbar.²⁾ The optical measurements were performed with a Shimadzu double-beam spectrometer and also with a Bausch-Lomb grating spectrometer.

The materials studied are listed in Table 1.

Table 1. Materials studied

Compounds	
Potassium ferricyanide	$K_3Fe(CN)_6$
Potassium ferrocyanide	$K_4Fe(CN)_6$
Ferric phosphate hydrate	$FePO_4 \cdot nH_2O$
Basic ferric acetate	$Fe_3(CH_3CO_2)_6(OH)_2 \cdot CH_3CO_2 \cdot H_2O$
Ferric citrate	$Fe(C_6H_5O_7) \cdot 3H_2O$
Ferric chloride	$FeCl_3$
Ferrous chloride hydrate	$FeCl_2 \cdot nH_2O$
Soluble prussian blue	$KFeFe(CN)_6$

Results and Discussion

Potassium Ferricyanide. Potassium ferricyanide and ferrocyanide are low-spin complexes. Figure 1 shows the pressure effect on the absorption spectra with a single crystal of potassium ferricyanide at hydrostatic pressures up to 4.5 kbar. Basu *et al.* assigned the broad band to the charge transfer from a ligand to the central metal ion.³⁾ The absorption intensity decreases with the increase in the pressure. This behavior was reproducible. Gardiner *et al.* have examined the visible spectrum of a $K_3Fe(CN)_6$ (potassium ferricyanide) solution in water under hydrostatic pressures up to 2 kbar.⁴⁾ They found no measureable change (>1/2%) in the absorbance.

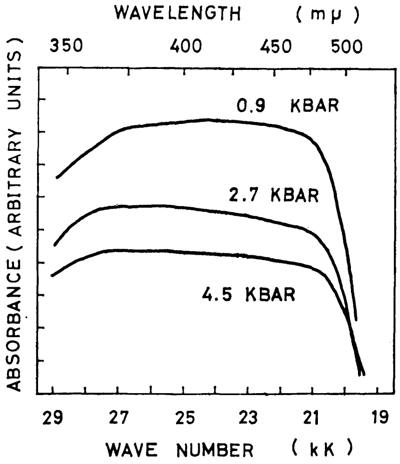

Fig. 1. Absorption spectra of a single crystal of potassium ferricyanide at various hydrostatic pressures.

In our experiment, however, a decrease of about 25% in the band peak intensity was observed upon a change from 0.9 kbar to 4.5 kbar. The decrease was over twice as much as that expected from the Mössbauer data of Champion and Drickamer.⁵⁾ This discrepancy may be interpreted as showing the remarkable dependence of the reduction on the samples. Therefore, in the first place, a reduction of the central $Fe(CN)_6^{3-}$ seems to be closely related to the direct interaction with the surrounding K^+ ions and $Fe(CN)_6^{3-}$. In the second place, the reduction can be explained in terms of the influence of the lattice distortion introduced by a kind of increasing local deformation with pressure near vacancies or dislocations in the

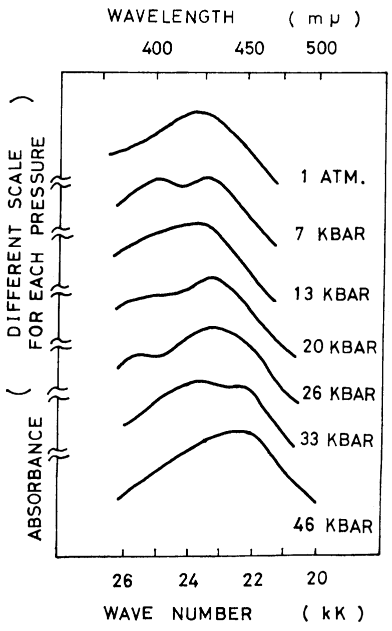

Fig. 2. Absorption spectra of polycrystalline potassium ferricyanide at various pressures.

crystal. The relationship between the reduction and the shearing stress of the sample has already been pointed out.[4,6] The absorption spectrum of a polycrystalline $K_3Fe(CN)_6$ sample diluted with NaCl was measured up to 46 kbar under quasi-hydrostatic pressure. The results are shown in Fig. 2. When the pressure was released, the original spectrum was obtained again. The band at 23.8 kK was assigned to the charge transfer from (CN^-) to the central Fe(III).[7] The intensity of the peak was found to decrease gradually up to 33 kbar, but was found to increase a little at 39 kbar. At 7 kbar, a doublet band appeared. The pressure-induced band at 25 kK exhibited a shift to the higher frequencies (blue shift) of about 500 cm^{-1} at 26 kbar, decreasing in intensity with pressure. By 33 kbar this band has been almost swamped by the lower energy bands. Another pressure-induced band was observed around 22.5 kK at 20 kbar; it was found to swamp the charge-transfer band at 46 kbar, increasing in intensity. These two pressure-induced bands seem to be due to the converted Fe(II).

Potassium Ferrocyanide. Figure 3 shows the pressure effect on the absorption spectra of a single crystal of potassium ferrocyanide at hydrostatic pressures up to 4.5 kbar. In an octahedral environment, the five d orbitals of the metal split into a threefold degenerated t_{2g} level and a doubly-degenerated e_g with the t_{2g} lying lowest.

In a low-spin case such as ferrocyanide, the six d electrons are in the t_{2g} orbital, with their spins paired; this is the ground state ${}^1A_{1g}$. The spectral assignment $K_4Fe(CN)_6$ in an aqueous solution shows that the band can be assigned to the expected d-d transition, ${}^1A_{1g} \rightarrow {}^1T_{1g}$.[8] The absorption peak showed a definite blue shift with an increase in the pressure, at the rate of 83 cm^{-1}/kb. The band-peak intensity decreased about 28% upon the pressure change from 0.9 kbar to 4.5 kbar.

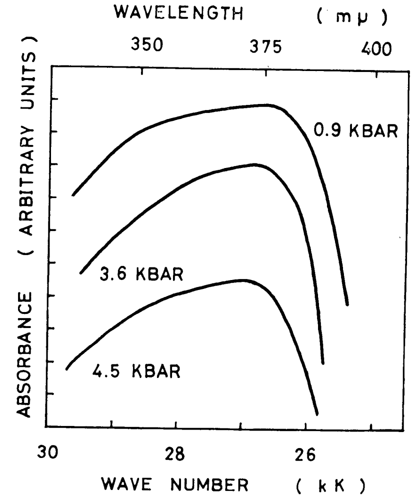

Fig. 3. Absorption spectra of a single crystal of potassium ferrocyanide at various hydrostatic pressures.

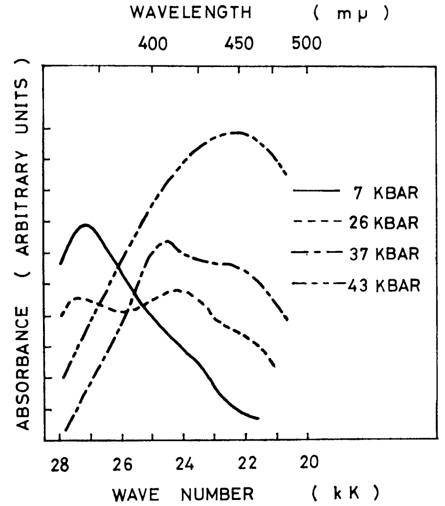

Fig. 4. Absorption spectra of polycrystalline potassium ferrocyanide at various pressures.

The blue shift and the decrease in the intensity continue at higher pressures, as is illustrated in Fig. 4, where the fade-out of the band is exhibited at 37 kbar. A reasonable explanation for the decrease from 2.7 kbar to 4.5 kbar in the absorbance around 27 kK of the single crystal $K_3Fe(CN)_6$, as is illustrated in Fig. 1, presents itself when one considers the decrease in the band intensity due to the converted Fe(II), as is shown in Fig. 3.

The pressure effect on the absorption spectra at quasi-hydrostatic pressures up to 50 kbar was measured. The results are shown in Fig. 4. The band around 24 kK at 7 kbar which appears as a shoulder showed a blue shift, about 500 cm^{-1} in 37 kbar, increasing in intensity drastically with pressure. At 26 kbar, another pressure-induced band was observed around 22 kK. This band also exhibited a blue shift, increasing in intensity drastically with pressure. This behavior was reproducible. The electronic spectrum of $Fe(CN)_6{}^{4-}$ shows a very weak band at 23.7 kK; this band can be assigned to the first spin-forbidden transition, ${}^1A_{1g} \rightarrow {}^3T_{1g}$.[8] Thus, the band at 21~26 kK which increased in intensity drastically seem to be related to this transition. We obtained samples after 50 kbar and measured their infrared with a KBr pellet. No reasonable spectral change in the Fe(II)–C stretching frequency was observed.

Ferric Phosphate Hydrate. The absorption spectra of ferric phosphate hydrate at various pressures are given in Fig. 5. The spectra at 1 atmosphere and 6.3 kbar were measured with a KBr pellet under hydrostatic pressures. When the spectrum at 6.3 kbar was compared with that at 1 atmosphere, a swelling around 24 kK due to a pressure-induced band was found. The band peak at 1 atmosphere showed a red shift, about -700 cm^{-1} at 38 kbar. In 13 kbar a definite pressure-induced band around 24 kK was observed. This band increased in intensity relatively with that at higher wave numbers, exhibiting a slight shift. The spectra were reversible with some hysteresis. The electronic spectrum of ferrous phosphate, Fe$_3$(PO$_4$)$_2$, shows a band at about 23 kK at 1 atmosphere. This band corresponds to the pressure-induced band in ferric phosphate hydrate.

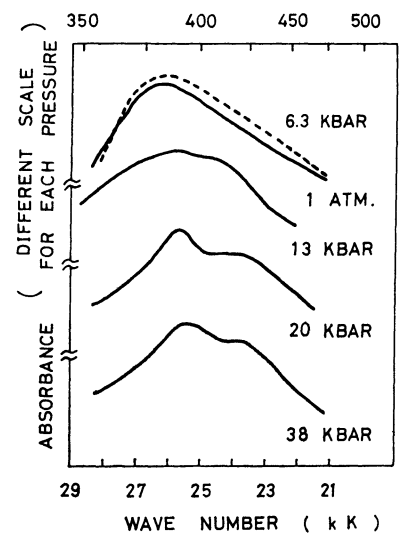

Fig. 5. Absorption spectra of polycrystalline ferric phosphate hydrate at various pressures; The spectra at 1 ATM. and 6.3 KBAR are at hydrostatic pressures.

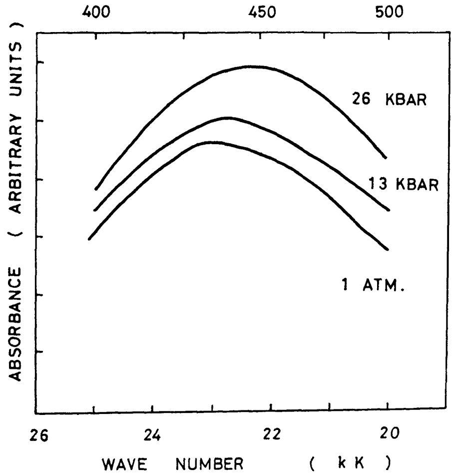

Fig. 6. Absorption spectra of polycrystalline basic ferric acetate at various pressures.

Basic Ferric Acetate. Figure 6 shows the absorption spectra measured with basic ferric acetate at various pressures up to 26 kbar. The measurement of the Mössbauer by Drickamer *et al.* showed evidence of only a trace of any reduction up to 150 kbar.9,10) The band peak showed a red shift of -1100 cm^{-1} in 26 kbar, increasing in peak intensity about 30%. Basic ferric acetate is a tri-nuclear complex of ferric ions which are joined with each other by a strong linkage of the (CH$_3$CO$_2^-$) ions.11)

Therefore, it may be inferred that the complex is difficult either to distort and to reduce because of less influence of a vacany and/or a dislocation.

Ferric Citrate. Figure 7 shows the effect of the hydrostatic pressure on the absorption spectra of ferric citrate with the KBr pellet. The band-peak intensity decreased by about 17% upon the pressure change from 0.9 to 5.4 kbar. This behavior was reproducible. The band shift may be small. According to the experiment which was carried out under quasi-hydrostatic pressures up to 26 kbar, this band shows a red shift, at the rate of -15 cm^{-1}/kb. At about 21.5 kK, a pressure-induced band was observed at 7 kbar, showing a blue shift, at the rate of 37 cm^{-1}/kb up to 26 kbar.

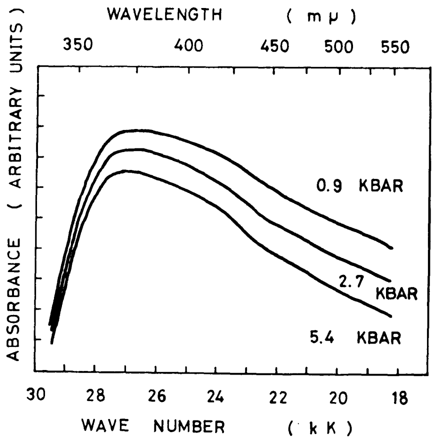

Fig. 7. Absorption spectra of polycrystalline ferric citrate at various hydrostatic pressures.

Ferric Chloride. The pressure effect on the absorption spectra of ferric chloride up to 46 kbar is illustrated in Fig. 8. The absorbance of the peak maximum decreased about 30% up to 46 kbar. The maximum of the broad band is 22.6 kK at 1 atomosphere. Pressure-induced bands were observed around 24.1 and 22 kK in 13 kbar. Judging from the results for ferrous chloride hydrate, these two bands should be assigned to the spin-forbidden bands of Fe(II). The peak around 23 kK due to Fe(III) was left. The band at 24.1 kK was swamped by the lower-energy bands by 20 kbar but was found to appear again at 39 kbar. The shift was approximately 200 cm^{-1} up to 39 kbar. The maximum absorption irregularly exhibited a red shift of about -800 cm^{-1} from 26 to 33 kbar; this is too great to be ascribed to the normal absorption due to Fe(III). A possible explanation of the irregular shift is that a pressure- induced band around 22 kK increases

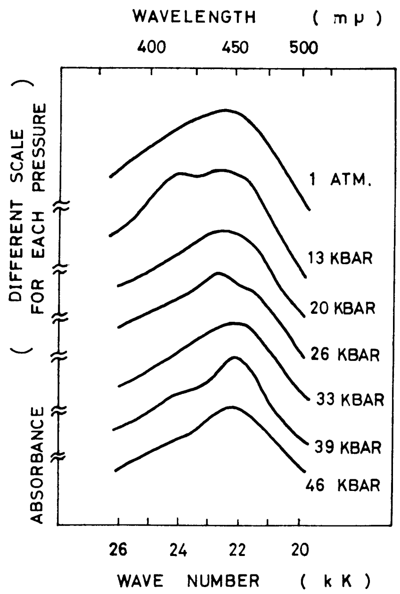

Fig. 8. Absorption spectra of polycrystalline ferric chloride at various pressures.

in intensity relative to the band which corresponds to Fe(III), located around 23 kK.

Ferrous Chloride Hydrate. Four d electrons are in the t_{2g} orbital and two are in the e_g orbital, which is the ground state $^5T_{2g}$. The two spin-forbidden d-d bands, $^5T_{2g}\rightarrow{}^3T_{1g}$ and $^5T_{2g}\rightarrow{}^3T_{2g}$, may be expected in the visible region. Figure 9 shows the pressure effect on the absorption spectra of ferrous chloride hydrate up to 36 kbar. No band was found in the 21∼25 kK region of the spectrum at 1 atm. At 7 kbar, pressure-induced bands were observed, increasing in intensities drastically with pressure. The shifts of the two bands from 13 to 36 kbar were small. The spin-forbidden bands generally show a slight shift upon pressure.[12] Therefore, these new pressure-induced bands should be assigned to the expected d-d spin-forbidden transition.

Soluble Prussian Blue. The absorption spectra of polycrystalline soluble prussian blue at hydrostatic pressure are shown in Fig. 10. The structure of prussian blue has been elucidated by Robin.[13] A low-spin Fe(II) is coordinated to the carbon, and a high-spin Fe(III) to the nitrogen. The intermetallic charge-transfer band from the Fe(II) to the Fe(III) site assigned to $t_{2g}(\pi)\rightarrow t_{2g}(\pi)$ appears at 14.3 kK for the soluble prussian blue. The band exhibited a shift to higher frequencies of about 69 cm^{-1}/kb with pressure.

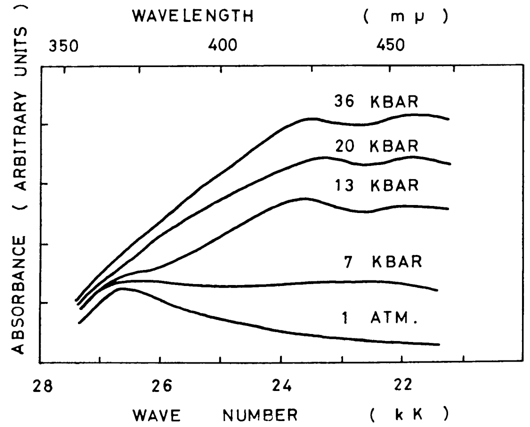

Fig. 9. Absorption spectra of polycrystalline ferrous chloride hydrate at various pressures.

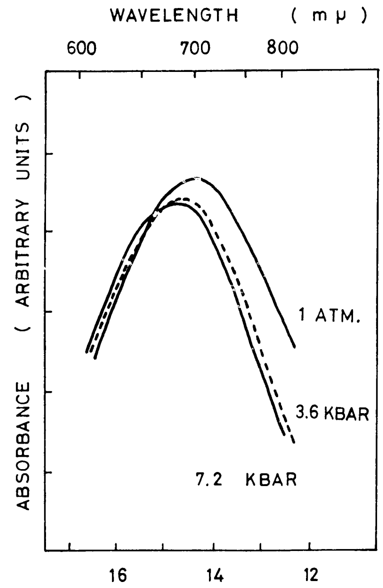

Fig. 10. Absorption spectra of polycrystalline soluble prussian blue at various hydrostatic pressures.

The absorbance at the band decreased by about 5% up to 7.2 kbar. This value is almost the same as that (about 5%) extrapolated from the result for Fe[Fe(CN)$_6$]$_3$ given by Mössbauer measurements by Drickamer *et al.*[14] who measured the transference of an electron from a low-spin Fe(II) site to a high-spin Fe(III) site at low pressure. The decrease in the absorbance at high pressure might be related to results of the Mössbauer spectra.

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