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BONDING NATURE AND SEMICONDUCTIVITY OF  
COORDINATION POLYMERS OF THE TYPE  
 $\text{KM}[\text{Fe}(\text{CN})_6]$

BY

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# BONDING NATURE AND SEMICONDUCTIVITY OF COORDINATION POLYMERS OF THE TYPE $KM[Fe(CN)_6]$

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## ABSTRACT

A series of coordination polymers of the type  $KM[Fe(CN)_6]$  ( $M=Mn, Fe, Co, Ni, Cu$  or  $Zn$ ) have the face-centered cubic unit cell characteristic of Prussian blue analogs. The lattice parameter and magnetic susceptibility data have indicated that these compounds consist of carbon-coordinated low-spin  $Fe(III)$  ion and nitrogen-coordinated high-spin  $M(II)$  ion. The  $C\equiv N$  stretching,  $Fe-C$  stretching and  $Fe-CN$  bending frequencies are shifted to the higher frequency side compared with those of corresponding potassium hexacyanoferrates. This shift provides an evidence for the existence of the linkage structure  $Fe-C\equiv N-M$ . The conductivity-temperature curves have the characteristics of semiconductor in the range from room temperature to about  $170^\circ C$ . This property could be interpreted in terms of weak metal-metal interaction through the bridged cyanide group.

## Introduction

Prussian blue, a well-noted blue dye, is known in soluble and insoluble forms, the compositions of which are  $KFe[Fe(CN)_6]$  and  $Fe_4[Fe(CN)_6]_3$  respectively. The former is obtained on adding an excess of potassium hexacyanoferrate(II) to ferric salt and the latter is obtained by the use of the excess amount of ferric salt. On the other hand, two types of compounds formulated as  $KM[Fe(CN)_6]$  and  $M_3[Fe(CN)_6]_2$  are obtained by the reaction of potassium hexacyanoferrate(III) with divalent first row transition metal ion  $M(II)$  ( $M(II)=Mn, Fe, Co, Ni, Cu$  or  $Zn$ ). There have been numerous structural investigations on Prussian blue (KEGGIN and MILES, 1936) and the compounds of the type  $M_3[Fe(CN)_6]_2$  (VAN BEVER 1938; WEISER, MILLIGAN, *et al.* 1942), whereas the studies on the  $KM[Fe(CN)_6]$ -type compounds seem to be relatively few.

It has been evidenced that these compounds are of an infinite three-

dimensional polymer complex based on the linking of  $\text{Fe-C}\equiv\text{N-M}$ . Iron and another metal ions are located in face-centered cubic arrangement in the compounds. The electronic spectrum of Prussian blue was interpreted on the basis of ligand field theory by ROBIN (1962). He assigned its intense blue color to charge-transfer transition between  $\text{Fe}^{\text{II}}(\text{CN})_6^{4-}$  and  $\text{Fe}(\text{III})$  and pointed out that the optical electron is mostly localized on  $\text{Fe}^{\text{II}}(\text{CN})_6^{4-}$  in the ground state. BRATERMAN (1966) extended ROBIN's model of Prussian blue to the compounds of the type  $\text{KM}[\text{Fe}(\text{CN})_6]$ . A number of charge-transfer bands were observed in  $\text{KM}[\text{Fe}(\text{CN})_6]$  by CSÁSZÁR and FELVÉGI (1966). The existence of metal-metal interaction through bridged cyanide ligands is suggested by the studies on the electronic structure of these compounds. This metal-metal interaction between Fe and M prompts us to study the electrical property of these compounds. FIELDING and MELLOR (1954) measured the electrical conductivity of Prussian blue and indicated that complexes containing metal atoms in different oxidation states, though lying in crystallographically equivalent positions, are capable of acting as intrinsic semiconductor. However, there have been relatively few systematic studies on the electrical property of  $\text{KM}[\text{Fe}(\text{CN})_6]$  except for conductivity measurements by DADIC (1959).

It is the purpose of the present work to study the relationship between the chemical bonding nature and the semiconductive property  $\text{KM}[\text{Fe}(\text{CN})_6]$  on the basis of X-ray powder diffraction, infrared spectra and conductivity measurements.

## Experimental

*Preparation of Compounds.* Iron compound  $[\text{KFe}[\text{Fe}(\text{CN})_6]]$  was prepared by the following conventional method. A 0.1M solution of ferrous sulfate was added stoichiometrically to a 0.1M solution of potassium hexacyanoferrate(III). The precipitate obtained was allowed to stand overnight. After decantation it was centrifuged or filtered, and washed by distilled water until the reaction of sulfate ion turned out negative in the filtrate. Finally, the precipitate was dried to constant weight in an oven at  $130^\circ\text{C}$ . A series of compounds of the type  $\text{KM}[\text{Fe}(\text{CN})_6]$  were obtained in the same way as in the case of the iron compound, i.e., by adding an aqueous solution of potassium hexacyanoferrate(III) to an aqueous solution of the adequate metal chlorides. The compounds obtained were analyzed by the usual method and the following results were obtained. Found: Fe, 18.1; Mn, 18.3%. Calcd for  $\text{KMn}[\text{Fe}(\text{CN})_6]$ : Fe, 18.25; Mn, 17.95%. Found: Fe, 36.0%. Calcd for  $\text{KFe}[\text{Fe}(\text{CN})_6]$ : Fe, 36.39%. Found: Fe, 18.1; Co, 19.3%. Calcd for  $\text{KCo}[\text{Fe}(\text{CN})_6]$ : Fe, 18.02; Co, 19.01%. Found: Fe, 16.2; Ni, 19.3%. Calcd for  $\text{KNi}[\text{Fe}(\text{CN})_6]$ : Fe, 18.03; Ni, 18.95%. Found: Fe, 17.1; Cu, 20.0%. Calcd for  $\text{KCu}[\text{Fe}(\text{CN})_6]$ : Fe, 17.74; Cu, 20.20%. Found: Fe, 17.4; Zn, 24.4%. Calcd for  $\text{KZn}[\text{Fe}(\text{CN})_6]$ : Fe, 17.65; Zn, 20.02%.

*X-ray powder diffraction.* The X-ray powder diffraction patterns were measured with a Rigak-Denki X-ray diffractometer. The lattice constants were determined using  $\text{Fe K}\alpha$  radiation ( $\lambda=1.937 \text{ \AA}$ ) and sodium chloride as a standard.

*Magnetic measurements.* The magnetic susceptibilities were measured by the

Gouy method with  $\text{Hg}[\text{Co}(\text{NCS})_4]$  ( $16.44 \times 10^{-6}$  cgs units at  $20.0^\circ\text{C}$ ) (FIGGIS and NYHOLM, 1958) as a standard at room temperature. The diamagnetic corrections were calculated with the Pascal constants (LEWIS and WILKINS, 1960).

*Infrared spectra.* The infrared spectra were recorded in the range  $350$  to  $4000\text{cm}^{-1}$  by the KBr disk method with a Hitachi EPI-2 infrared spectrophotometer. The wavenumbers recorded here were calibrated with a polystyrene film. The accuracies are estimated to be  $\pm 3.5\text{cm}^{-1}$  in the NaCl region and  $\pm 4.0\text{cm}^{-1}$  in the KBr region.

*Conductivity measurements.* The precipitates obtained above were powdered and pressed under vacuum to a disk with a diameter of  $1\text{cm}$  and a thickness of  $2\sim 3\text{mm}$  at pressure of  $5\sim 6\text{t/cm}^2$ . Silver paste was used as electrodes, which could give good ohmic contacts. Measurements were carried out by the two- and four-probe methods, but in the latter case it was difficult to balance the potentiometer due to its high sensitivity. Therefore, ordinary current-voltage method was mainly used, in which voltage was maintained constant throughout the run. The electrometer was highly sensitive to be capable of reaching to  $2 \times 10^{-12}\text{A}$  with a sufficient accuracy. Temperature was recorded with an automatic potentiometric recorder connected with carefully calibrated copper-constantan thermocouples. The cryostat which consisted of glass tube, copper block attached to electric heater and sample specimen holder, and Dewar vessel was employed to control the temperature in the range from room temperature to about  $170^\circ\text{C}$ . All measurements were carried out at pressure below  $10^{-2}\text{mmHg}$  to reduce the effect of atmosphere.

## Results and Discussion

*Structure and magnetic moment.* The crystal structure of the  $\text{KM}[\text{Fe}(\text{CN})_6]$ -type compounds was first reported for Prussian blue and its related compounds by KEGGIN and MILES (1936). According to them this series of compounds belong to space group  $O_h^2-F_{m\bar{3}m}$  and have the face-centered cubic unit cell as shown in Fig. 1. The cyanide ligand of these so-called coordination polymers plays a role of bridged group. Namely, both carbon and nitrogen ends of cyanide ligand are linked to iron and other metal atoms, building up the three-dimensional network. This polymeric nature is qualitatively acceptable through the formation of colloidal or peptized gel in aqueous solution. On the other hand, four potassium ions, which are not shown in Fig. 1., occupy the interstitial sites (8c position) to maintain electroneutrality.

The lattice constants of the  $\text{KM}[\text{Fe}(\text{CN})_6]$ -type compounds have not been studied in detail, though these compounds are isomorphous with  $\text{M}_3[\text{Fe}(\text{CN})_6]_2$ . The lattice constants of  $\text{KM}[\text{Fe}(\text{CN})_6]$  have been systematically measured in the present work and the typical results are shown in Fig. 2. The lattice constants of this series of compounds show a different tendency from that observed in the  $\text{KM}[\text{Fe}(\text{CN})_6]$ -type compounds (INOUE and YANAGISAWA, 1972) and many other Prussian blue analogs (SHRIVER 1966; INOUE, WADA, *et al.* 1973). They are no smooth function of the number of d-electrons in M(II) ion. In other words, the

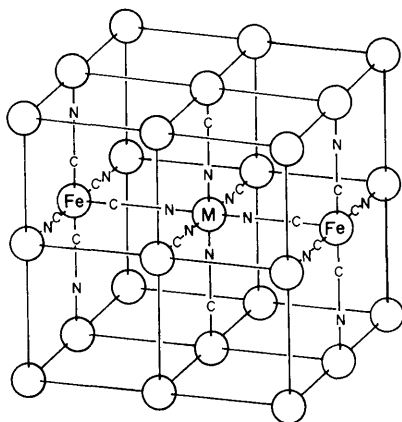


Fig. 1. The unit cell of the compounds of the type  $KM[Fe(CN)_6]$ . Potassium ions and most of the  $C\equiv N$  groups are not shown for brevity.

increasing order of lattice constants could not be associated directly with the crystal field stabilization energy (c. f. s. e.) of the  $M(II)$  ion which is located in the octahedral weak field. As may be seen from Fig. 2., the values of  $KFe[Fe(CN)_6]$  and  $KCo[Fe(CN)_6]$  deviate from the smooth curve which has been observed in other Prussian blue analogs. This is drawn by a broken line in Fig. 2. The deviation of iron and cobalt compounds is ascribed to difference in their electronic

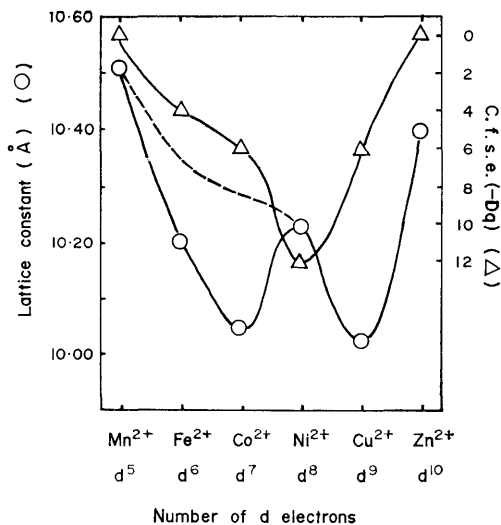


Fig. 2. Lattice constants as compared with crystal field stabilization energies (c. f. s. e.).

structures from the other compounds of this series. This is compatible with the results of magnetic moments and infrared spectra which will be described below.

The value of atomic distances between Fe-C, C-N and M-N gives valuable informations on the bonding nature of  $\text{KM}[\text{Fe}(\text{CN})_6]$ . However, unfortunately it is difficult to obtain the atomic distances directly from the X-ray diffraction analysis because the peaks observed in the X-ray diffraction patterns of  $\text{KM}[\text{Fe}(\text{CN})_6]$  are diffuse owing to their poor crystallinity and/or polymeric nature. Here we assume that the atomic distances in  $\text{K}_4[\text{Fe}(\text{CN})_6]$ ; Fe-C (1.85 Å) and C-N (1.16 Å) (POSPELOV and ZHDANOV, 1947), and in  $\text{M}_3[\text{Fe}(\text{CN})_6]_2$ ; Fe-C (1.88 Å) and C-N (1.15 Å) (BEASLEY 1968), are also kept in  $\text{KM}[\text{Fe}(\text{CN})_6]$ . This assumption makes it possible for us to estimate the atomic distances in  $\text{KM}[\text{Fe}(\text{CN})_6]$  from the lattice constants. The calculated M-N distance which ranges from 1.98 to 2.23 Å is comparable with that reported on analogous compounds, e.g., Ni-N (2.11 Å) in  $\text{Ni}(\text{CN})_2 \cdot \text{NH}_3 \cdot \frac{1}{2} \text{H}_2\text{O}$  (RAYNER and POWELL, 1958) and M-N (2.08~2.21 Å) in  $\text{M}_3[\text{Co}(\text{CN})_6] \cdot x\text{H}_2\text{O}$  (LUDI, GÜDEL, *et al.* 1970). Accordingly it is proved that the atomic distance M-N is short enough to expect a coordination bonding between them.

Table 1. Lattice Parameters and Magnetic Moments.

Compound	Lattice constant (Å)	M-N distance Å	Magnetic moment (BM)
$\text{KMn}[\text{Fe}(\text{CN})_6]$	$10.51 \pm 0.01$	2.23	6.31
$\text{KFe}[\text{Fe}(\text{CN})_6]$	$10.20 \pm 0.03$	2.15	5.23
$\text{KCo}[\text{Fe}(\text{CN})_6]$	$10.05 \pm 0.02$	2.00	3.51
$\text{KNi}[\text{Fe}(\text{CN})_6]$	$10.25 \pm 0.01$	2.10	4.30
$\text{KCu}[\text{Fe}(\text{CN})_6]$	$10.02 \pm 0.04$	1.98	3.04
$\text{KZn}[\text{Fe}(\text{CN})_6]$	$10.40 \pm 0.05$	2.17	2.13

The effective Bohr magneton  $\mu_{\text{eff}}$  per formula unit  $\text{KM}[\text{Fe}(\text{CN})_6]$  was calculated from the magnetic susceptibilities measured at room temperature and the results are listed in Table 1. Except for  $\text{KFe}[\text{Fe}(\text{CN})_6]$  and  $\text{KCo}[\text{Fe}(\text{CN})_6]$ , the calculated values are in good agreement with the assumption that the carbon-coordinated iron ion is in the low spin state and that the nitrogen-coordinated metal ion is in the high spin state. The electronic structure of  $\text{KFe}[\text{Fe}(\text{CN})_6]$  cannot be determined only from the magnetic data, because both  $\text{KFe}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]$  and  $\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]$  in which the carbon-coordinated iron is, of course, in the low spin state have the same number of unpaired electrons. However, the electronic structure  $\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]$  has been substantiated by the results of Mössbauer spectra (FLUCK, KERLER, *et al.* 1963; DUNCAN and WIGLEY, 1963). The magnetic moment of cobalt compound is quite low as compared with that expected for the electronic structure  $\text{KCo}^{\text{I}}[\text{Fe}^{\text{III}}(\text{CN})_6]$  which consists of high spin cobaltous and low spin ferric ions. The observed moment, 3.51 BM, suggests that nitrogen-coordinated cobaltous ion is not in the high spin state but in the low spin state. This peculiarity of iron and cobalt compounds must be connected with the deviation of the lattice constants from the smooth curve.

*Infrared spectra.* The infrared spectra of  $\text{KM}[\text{Fe}(\text{CN})_6]$  are reproduced in Fig. 3. where the spectra of potassium hexacyanoferrate(II) and -ferrate(III) are also shown for comparison. There are two types of  $\text{C}\equiv\text{N}$  stretching bands; the first type of absorption pattern is similar to that of potassium hexacyanoferrate(II) and the second is similar to that of potassium hexacyanoferrate(III). Simply viewed from the pattern of absorption, iron and copper compounds belong to the first type and the other compounds do to the second type. However, it is not apprehensible that the copper compound falls into the first type in which carbon-coordinated iron should be divalent. This may be due to the fact that the copper compound has an abnormally small lattice constant compared with that of the other compounds.

The  $\text{C}\equiv\text{N}$  stretching frequencies of  $\text{KM}[\text{Fe}(\text{CN})_6]$  are shifted to the higher frequency side as compared with those of corresponding potassium salts. This phenomenon has been also observed in other Prussian blue analogs (INOUE, MORIOKA, *et al.* 1973) and pointed out as an evidence for the existence of linkage structure  $\text{Fe}-\text{C}\equiv\text{N}-\text{M}$ . Dows *et al.* (1961) explained this shift in  $\text{C}\equiv\text{N}$  stretching frequency by the following mechanism: The presence of a second metal ion  $\text{M}(\text{II})$  at the nitrogen end of cyanide ligands constrains the motion of cyanide group, so

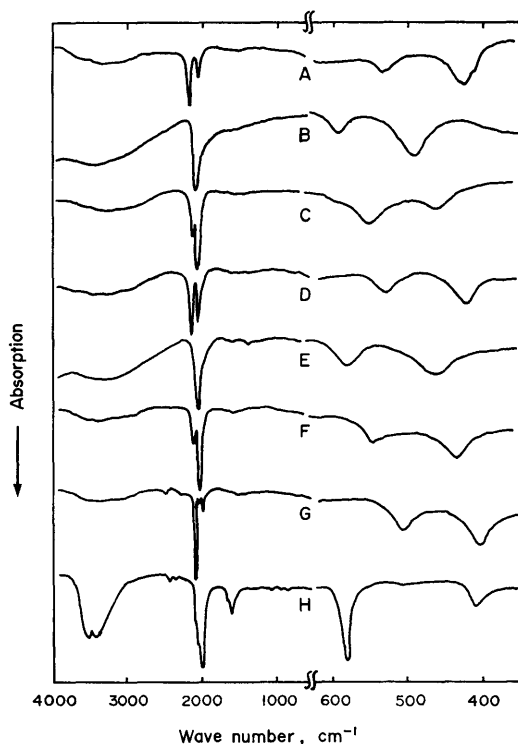


Fig. 3. Infrared spectra of  $\text{KM}[\text{Fe}(\text{CN})_6]$ . A,  $\text{KMn}[\text{Fe}(\text{CN})_6]$ ; B,  $\text{KFe}[\text{Fe}(\text{CN})_6]$ ; C,  $\text{KCo}[\text{Fe}(\text{CN})_6]$ ; D,  $\text{KNi}[\text{Fe}(\text{CN})_6]$ ; E,  $\text{KCu}[\text{Fe}(\text{CN})_6]$ ; F,  $\text{KZn}[\text{Fe}(\text{CN})_6]$ .



that the bridged cyanide groups exhibit a higher absorption frequency as compared with terminal cyanide groups. In addition, probably an inductive effect contributes to the shift of  $C\equiv N$  stretching frequency, that is, the  $M(II)$  ion coordinated by the nitrogen ends of cyanide ligands withdraws electric charge accumulated on the central  $Fe(III)$  ion through the cyanide group and consequently the  $C\equiv N$  stretching is increased.

On the other hand, two relatively broad bands are observed in the far infrared region where are usually expected a variety of metal-ligand stretching and bending vibrations. The spectra of this region are similar to those of corresponding potassium hexacyanoferrates. Consequently, it is very convenient to make use of the results of the normal coordinate analysis carried out with potassium hexacyanoferrate(II) and -ferrate(III) (NAKAGAWA and SHIMANOCHI, 1962; JONES 1971). According to them the broad bands observed in the range from 450 to 500  $cm^{-1}$  and from 535 to 600  $cm^{-1}$  are assigned to  $Fe-C$  stretching and  $Fe-CN$  bending vibrations, respectively. This assignment is not definite because  $M-N$  stretching vibrations might be appear in this region. However, no such  $M-N$  stretching vibrations have been reported on Prussian blue analogs. It is probable that they are located out of our spectral region, i.e., below 350  $cm^{-1}$ . Both  $Fe-C$  stretching and  $Fe-CN$  bending vibrations are shifted to the higher frequency side compared with those of the corresponding potassium hexacyanoferrates. This shift is ascribed to the formation of the linkage structure  $Fe-C\equiv N-M$ . In conclusion, we can safely say that the results of the infrared spectra in both  $NaCl$  and  $KBr$  regions are favor of the idea that coordination bonding is existent between the  $M(II)$  ion and the nitrogen ends of cyanide ligand.

*Conductivity.* The conductivity-temperature curves of  $KM[Fe(CN)_6]$  showed the characteristics of semiconductor in the range from room temperature to about 170°C, but some of them exhibited a thermohysteresis phenomenon. Probably this comes out from the evolution of gases confined in the sample specimen or water molecules lying in the interstitial sites of the lattice; they are guest molecules in the clathrate structure, the host of which is the three-dimensional infinite lattice bridged by cyanide ligands. Actually, this thermohysteresis property disappeared when the run of measurements was repeated several times. The type of conduction is clearly not ionic but electronic, because there was neither metal deposit on the electrodes after electric current was passed for a long time, nor was change of resistivity detectable on inverting the passage of current. In ordinary semiconductors the relationship

$$\sigma = \sigma_0 \exp(-E_a/kT)$$

holds between observed conductivity  $\sigma$  and absolute temperature  $T$ , where  $\sigma_0$ ,  $E_a$  and  $k$  are a constant, the activation energy for electric conduction and Boltzmann constant, respectively. The plots of  $\log \sigma$  vs.  $1/T$  fall on a straight line as shown in Fig. 4. The linear plot for  $KFe[Fe(CN)_6]$  breaks at about 100°C, which is probably due to impurity levels or phase transition. However, it is impossible to make an unambiguous interpretation of this break point only from a conductivity measurement without magnetic or X-ray diffraction data around 100°C.

As for conduction mechanism of these semiconductors "hopping mechanism" has been accepted since FIELDING and MELLOR (1954) started first the study on

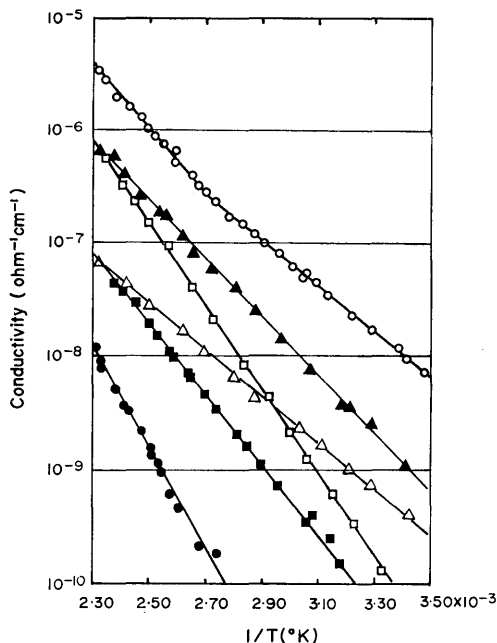


Fig. 4. Conductivity-temperature dependence of  $\text{KM}[\text{Fe}(\text{CN})_6]$ .  
 $\text{M} = \text{Mn}$  (▲),  $\text{Fe}$  (○),  $\text{Co}$  (■),  $\text{Ni}$  (●),  $\text{Cu}$  (□), and  $\text{Zn}$  (△).

Prussian blue from the viewpoint of hopping. For example, the conduction mechanism for the soluble Prussian blue can be described by the following oxidation-reduction reaction:



This hopping mechanism was extended to the Prussian blue analogs by BRATERMAN *et al.* (1965). The conduction mechanism in the other compounds of the type  $\text{KM}[\text{Fe}(\text{CN})_6]$  also can be well described by the hopping mechanism. In this case electrons or holes produced through the delocalization of electrons from the  $\text{M(II)}$  ion play a role of carrier. The electron in the  $\text{Fe(II)}(\text{CN})_6^{4-}$  moiety is distributed over the whole complex ion by so-called back donation from metal  $d_\pi$  to ligand  $\pi^*$  orbitals (GRAY and BEACH, 1963) and consequently are quite easy to flow out of that ion moiety. In addition, the bonding between  $\text{Fe-C}$  in  $\text{KFe}[\text{Fe}(\text{CN})_6]$  is characteristic not only of covalent bond but also of double bond. Though the atomic distance  $\text{Fe-N}$  is larger than  $\text{Fe-C}$ , it is not so long as to expect some interaction between them. Accordingly, the  $d_\pi$  orbitals of  $\text{Fe(III)}$  coordinated by the nitrogen end of cyanide ligand can be partly overlapped with ligand anti-bonding  $\pi^*$  orbitals. Under these conditions conduction electrons or holes can move to the direction of electric field through the partly overlapped orbitals which have to some extent  $\pi$ -bonding nature. As a result the compound  $\text{KFe}[\text{Fe}(\text{CN})_6]$  behaves as a semiconductor. On the other hand, the conduction mechanism for the compounds other

than the iron compound is somewhat different from that of the iron compound because of their difference in the electronic configuration of ground state. Nevertheless the overlapping of orbitals analogous to that in the iron compound is expected and this must cause a significant contribution to electric conduction.

The activation energies for electric conduction have been calculated from the plots of  $\log \sigma$  vs.  $1/T$  and are given in Table 2 together with the conductivities at

Table 2. Conductivities and Activation Energies

Compound	Conductivity ( $\text{ohm}^{-1}\text{cm}^{-1}$ )	Activation energy (eV)
KMn[Fe(CN) <sub>6</sub> ]	$1.70 \times 10^{-9}$ (30°C)	0.49
KFe[Fe(CN) <sub>6</sub> ]	$1.50 \times 10^{-8}$ (30°C)	0.40, 0.59
KCo[Fe(CN) <sub>6</sub> ]	$5.88 \times 10^{-9}$ (100°C)	1.00
KNi[Fe(CN) <sub>6</sub> ]	$1.05 \times 10^{-8}$ (100°C)	0.61
KCu[Fe(CN) <sub>6</sub> ]	$3.43 \times 10^{-8}$ (100°C)	1.00
KZn[Fe(CN) <sub>6</sub> ]	$1.00 \times 10^{-9}$ (30°C)	0.36

certain temperatures. BRATERMAN *et al.* (1965) have studied the conductivity-temperature characteristics of divalent transition metal hexacyanocobaltates(III). They have reported the general relationship between the activation energy and either the charge transfer band or the ionization potential from M(II) to M(III). However, such clear-cut relationship could not be found in the present work. Since the compounds of the type KM[Fe(CN)<sub>6</sub>] are relatively amorphous owing to their polymeric nature, the activation energy seems too complicated to be explained only by

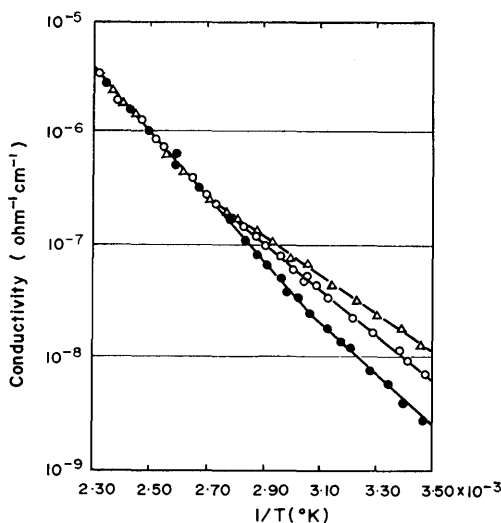


Fig. 5. The effect of atmosphere on conductivity.  $\circ$ , under vacuum;  $\triangle$ , in an atmosphere of  $\text{SO}_2$  (30 mm Hg);  $\bullet$ , in an atmosphere of  $\text{NH}_3$  (40 mmHg).

such a simple factor as the ionization potential.

The gas adsorption on semiconductor has been employed as a conventional method to determine the carrier which contributes to conductivity (SCHNEIDER and WADDINGTON, 1956; MEIER 1959). This method is based on the fact that the action of electron donor gases on semiconductivity is essentially different from that of electron acceptor gases. Here, ammonia acting as electron donor and sulfur dioxide as electron acceptor were selected and used as representative gases. Figure 5 shows a typical result obtained for  $\text{KFe}[\text{Fe}(\text{CN})_6]$ . Its conductivity decreases in an atmosphere of ammonia and slightly increases in that of sulfur dioxide. Consequently, Prussian blue behaves as a p-type semiconductor. On the other hand, a series of compounds of the type  $\text{KM}[\text{Fe}(\text{CN})_6]$  gave also similar results to that obtained for Prussian blue. The effect of these gases on semiconductivity leads to the conclusion that the major carriers of manganese, iron, cobalt and zinc compounds are positive holes (p-type semiconductor) while those of the other compounds are electrons (n-type semiconductor). This conclusion is consistent with the conduction mechanism explained in the preceding section.

### Conclusions

- (1) All the coordination polymers of the type  $\text{KM}[\text{Fe}(\text{CN})_6]$  have the face-centered cubic unit cell characteristic of Prussian blue analogs. Their lattice constants have been related to the crystal field stabilization energy of  $\text{M}(\text{II})$  ion in the octahedral weak field. The magnetic moments and the dependence of the lattice constants on the crystal field stabilization energy have indicated that the carbon-coordinated iron ion is in the low spin state and that the nitrogen-coordinated metal ion is in the high spin state.
- (2) The shifts of the  $\text{C}\equiv\text{N}$  stretching,  $\text{Fe}-\text{C}$  stretching and  $\text{Fe}-\text{CN}$  bending vibrations to the higher frequency side as compared with those of corresponding potassium salts have been explained in terms of the linkage structure  $\text{Fe}-\text{C}\equiv\text{N}-\text{M}(\text{II})$ . This phenomenon is in favor of the existence of coordination bonding between the  $\text{M}(\text{II})$  ion and the nitrogen ends of cyanide ligand.
- (3) The plots of  $\log \sigma$  vs.  $1/T$  have shown a typical semiconductive property in the range from room temperature to about  $170^\circ\text{C}$ . This property could be elucidated on the basis of the  $\pi$ -bonding nature resulting from the overlapping of the metal  $d\pi$  orbitals with the ligand anti-bonding  $\pi^*$  orbitals. The major carriers contributing to electric conduction are electrons in the nickel and copper compounds, while in the other compounds they are positive holes.

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