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Electrical Conductivity of the Complex Cyanides of the Prussian Blue Type

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The specific electrical resistivity of the complex cyanides of the Prussian blue type was measured. It was established that these compounds belong to the group of intrinsic semiconductors, their own specific resistivity varying from 10^3 to 10^6 ohm \times cm. The compounds were prepared as coloured crystalline powders and the measurements carried out by means of a press. Specific resistivity—pressure dependence was measured in the pressure interval from about 2000 atmospheres to about 6000 atmospheres.

INTRODUCTION

In the present paper some investigations of the electrical conductivity of the Prussian blue type complex cyanides are described. Keggin and Miles¹ have found, by a preliminary *x*-ray investigation, that in Prussian blue there is an arrangement of Fe atoms on a cubic face-centred lattice. One half the atoms are Fe^{II} and the others Fe^{III}, and alkali atoms are taken up to maintain electrical neutrality. These latter are at the centres of the alternate small cubes. It must be remembered that we cannot distinguish between ferric and ferrous atoms by *x*-ray methods nor are the CN groups definitely located. It is reasonable, however, to assume that in the iron compounds the CN groups lie along the cube edges.

The investigation of the electrical properties of complex cyanides was started by P. E. Fielding². With D. P. Mellor³ he examined the possibility that some complex cyanides, having a metal atom in different oxidation states and in equivalent crystallographic positions, could act as intrinsic semiconductors. They found that insoluble Prussian blue, Fe.₃[Fe(CN)₆]₃, was an intrinsic semiconductor with a negative temperature coefficient of 7% per degree. Except this, however, no further data have been published so far.

The present investigation was undertaken with the aim to check previous findings on a much greater variety of complex cyanides.

Prussian blue itself appears in soluble and insoluble form. Both of them were prepared. The total iron amount of insoluble Prussian blue was found to correspond to the composition of Fe.₃[Fe(CN)₆]₃ and that of the soluble form to the composition of KFeFe(CN)₆. The insoluble form of Prussian blue is produced by adding an excess of Fe^{III}-salt to K₄Fe(CN)₆, but if the latter

is in excess the soluble Prussian blue is produced.⁴ The same Prussian blue structure is encountered with the following complex cyanides: KNiFe(CN)_6 , KMnFe(CN)_6 , KCoFe(CN)_6 , KCuFe(CN)_6 and KRuFe(CN)_6 . All of them — except the so called Ruthenium purple — were prepared analogously to the soluble Prussian blue i. e. by addition of a slight excess of $\text{K}_4\text{Fe(CN)}_6$ to the trivalent metallic salt. The complex cyanides thus obtained represent coloured crystalline powders.

EXPERIMENTAL

The preparation of the samples

Insoluble Prussian blue was prepared according to Weiser et al.⁶: 100 ml. of 0.4 N $\text{K}_4\text{Fe(CN)}_6$ was mixed with 100 ml. of 0.3 N FeCl_3 (stoichiometrical excess of Fe^{III} -salt). The blue reaction mixture was centrifuged and a blue gel obtained.

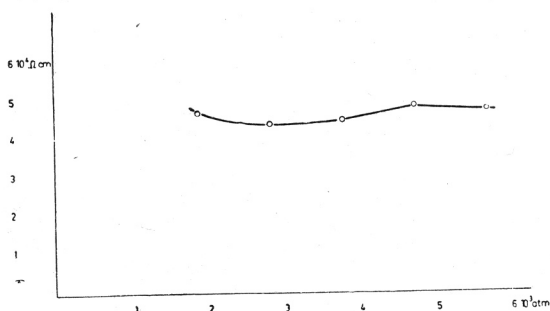


Fig. 1. Specific resistivity-pressure dependence for insoluble Prussian blue.

It was washed with water until the chloride ion reaction became negative and dried to constant weight in a thermostat at $110^\circ\text{--}120^\circ\text{C}$ during 2 hours. Thus a blue violet crystalline powder was obtained. If the powder is further pulverized in a mortar this violet colour disappears and an intensive blue colour remains. Obviously the colour depends on the size of the particles. The substance was evaporated with

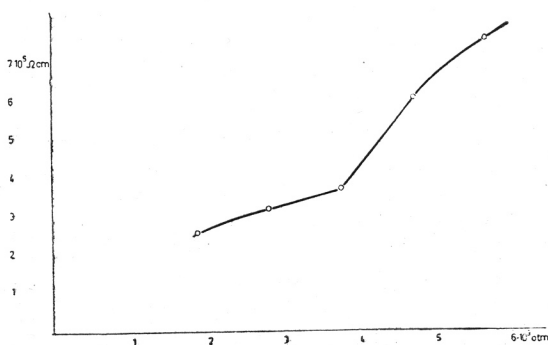


Fig. 2. Specific resistivity-pressure dependence for iron blue ex HCl.

fuming sulphuric acid in a porcelain dish, the sulphates turned to chlorides and the total iron amount determined by the Zimmermann-Reinhardt method. The presumed formula $\text{Fe}_4[\text{Fe(CN)}_6]_3$ was thus confirmed.

Soluble Prussian blue was prepared by adding a slight stoichiometrical excess of $\text{K}_4\text{Fe(CN)}_6$ solution (0.015 moles) to the FeCl_3 solution (0.010 moles). A blue

colloidal solution was obtained from which the soluble Prussian blue was precipitated by adding large quantities of rock salt. The precipitate was washed until the chloride ion reaction became negative, the blue gel centrifuged from the mother liquor and dried to constant weight in a thermostat at 120°C. A dark blue crystalline powder was obtained. The determination of the total iron confirmed the formula $KFeFe(CN)_6$, proposed also by Keggin and Miles¹.

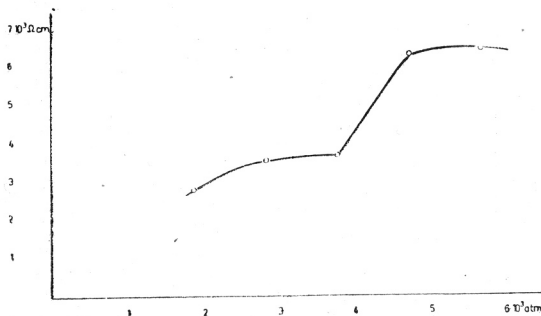


Fig. 3. Specific resistivity-pressure dependence for soluble Prussian blue.

In the same way as the soluble Prussian blue the following analogous complex cyanides were prepared: $KCoFe(CN)_6$, $KNiFe(CN)_6$, $KMnFe(CN)_6$ and $KCuFe(CN)_6$. The ratio of the soluble alkali cyanide to the metallic chloride used was (in moles) 1.1:1, hence, a slight stoichiometrical excess of the former was added. In all cases coloured powders were obtained. Cobalt complex was reddish-brown, nickel complex green, manganese complex brownish and copper complex dark red.

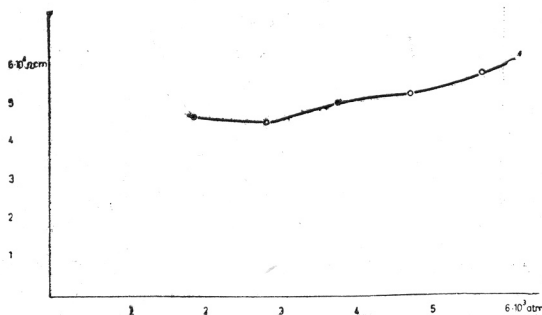


Fig. 4. Specific resistivity-pressure dependence for $KNiFe(CN)_6$.

A particular product was obtained by recrystallization of the insoluble Prussian blue from the concentrated hydrochloric acid heated to 100°C⁸. It was prepared while attempting to increase the size of the Prussian blue particles. When washed with water and dried in a thermostat at 120°C it is of a light-blue colour and still in the form of crystalline powder. The iron blue *ex HCl*⁶ exhibits a slight odour characteristic of cyanides which is indicative of its decomposition.

Specific resistivity measurements

The assembly in use at the Structural — Inorganic Department of the Institute »Ruder Bošković« consists of a hand-operated press and a Siemens RLC-type Wheatstone bridge supplied from a stabilized power source (22±1 V, 50 Hz) with a magic eye serving as null-indicator. The press has been constructed after the one described by Brentano and Goldberg⁷, but with some essential alterations, the details of which will be published elsewhere⁸. We mention briefly here that it had

a calibrated pressure gauge (for values of: 1887, 2830, 3773, 4717 and 5660 atmospheres) and device for measuring the thickness of the pressed pellet accurately to 0.1 mm and to 0.02 mm by estimation. From the known cross section of the pressed

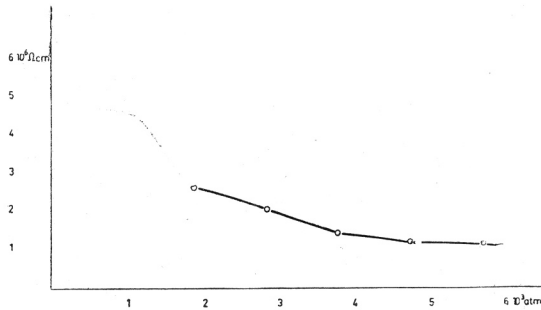


Fig. 5. Specific resistivity-pressure dependence for KCoFe(CN)_6 .

pellet and its thickness the specific resistivity was calculated according to Ohm's law and using the bridge readings.

The overall accuracy of this assembly was checked by making measurements on powdered germanium obtained from a single crystal of known specific resistivity

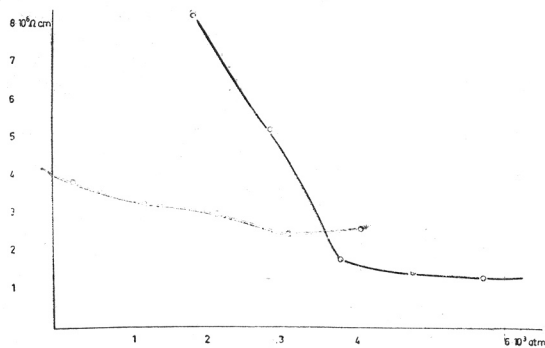


Fig. 6. Specific resistivity-pressure dependence for KMnFe(CN)_6 .

and on polycrystalline silicon of known specific resistivity. The results given in Table I show a very good agreement for this type of measurements.

TABLE I

Sample	specific resistivity in $\text{ohm} \times \text{cm}$	
	standard values	measured values
1. Ge (P.A.N.)	33	39
2. Ge (Eagle-Picher)	5—15	13
3. Si (Sylvania C)	6—30	35

All the measurements of the cyanide samples were performed at room temperature. The actual temperature inside the press was measured and found to vary between 19.5° and 20.5°C.

No attempt was made to define partial errors of the method, but the precision of the measurements (*maximum error*) on the cyanide samples was found to range from 5–32% at 5660 atmospheres and 11–42% at 1887 atmospheres, irrespective of the absolute value of the resistivity.

RESULTS AND DISCUSSION

Figs. 1–6 show graphically the specific resistivity—pressure dependence of the measured complex cyanides within the range of pressure changes from 1887 to 5660 atmospheres. The resistivity of the copper complex could not be measured by means of the bridge applied because its resistivity lay beyond the scale of the bridge. The measurements were repeated several times and the means of the obtained values were used in constructing the figures.

It may be noted that there are no remarkable changes of specific resistivity with pressure. The changes within a pressure set of measurements are not larger than one order of magnitude. Nevertheless, in three cases (Figs. 2, 3 and 6) there is a definite abrupt change which is real in view of the fact that the error of measurements is more than ten times smaller than the discussed effect. It is interesting to note that, whatever the nature of the resistivity/pressure curve, the knick occurs at about 4×10^3 atmospheres.

Another interesting point is the change of the specific resistivity—pressure dependence when going from the insoluble Prussian blue (Fig. 1) to the one obtained *ex HCl* (Fig. 2) and to the soluble Prussian blue (Fig. 3).

At present it would be difficult to relate each of these effects to a particular cause. Rather strange as they might seem, such effects have already been encountered in similar measurements.

D. H. Davis⁹, experimenting with pressed semiconducting oxides, reported that in a general way the conductivity of the powder increases with pressure. J. C. Brentano and C. Goldberg⁷ have given detailed information about the electrical conductivity of some semiconducting powders in particular ZnO. The real existence of the contact area between the particles was proved. According to R. Holm¹⁰ the actual contact area increases with pressure. This increase is less marked at higher pressures, so that the contact area may be considered to be approximately constant at higher pressures. In this way the resistance is gradually reduced with increasing pressure to a more or less constant value, a situation found in this work with the insoluble Prussian blue (Fig. 1), $\text{KCoFe}(\text{CN})_6$ (Fig. 5) and $\text{KMnFe}(\text{CN})_6$ (Fig. 6).

There is also evidence^{11, 12, 13} that an increase in resistivity may be caused by the pressure applied, which is ascribed to the change in the band structure of semiconductors. There is a certain resemblance to this effect in our measurements on insoluble Prussian blue *ex HCl* (Fig. 2), soluble Prussian blue (Fig. 3) and to a less extent with $\text{KNiFe}(\text{CN})_6$ (Fig. 4). Such changes could also be related to the effects of cleaving crystals.

CONCLUSION

It was established on the basis of these measurements that all the complex cyanides investigated are intrinsic semiconductors, their specific resistivity varying from 10^3 to 10^6 ohm \times cm. The method for measuring the electrical conductivity of the powdered complex cyanides, described in this paper, can be applied for a quick determination of the order of magnitude of the specific

resistivity of a given powdered material. However, some further improvements of the method would be desirable, especially in respect of measuring the dimensions of the pellets and the actual determination of the resistivity.

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IZVOD

Električna vodljivost kompleksnih cijanida tipa berlinskog modrila

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U ovome radu izmjeren je specifični otpor kompleksnih cijanida tipa berlinskog modrila. Ustanovljeno je da ti spojevi pripadaju području poluvodiča sa vlastitom vodljivošću, s rasponom od 10^3 do 10^6 $\text{ohm} \times \text{cm}$. Spojevi su priređeni u formi kristalnoga praha, a električna mjerenja izvedena su uz pomoć posebnoga tijeska i Wheatstonova mosta. Grafički je prikazana promjena vodljivosti (recipročne) praha s promjenom tlaka u intervalu tlakova od cca 2000 do 6000 atmosfera.

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