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ELECTRICAL AND PHYSICAL PROPERTIES OF SYSTEMS COMPRISING POWDERED METALS AND ORGANIC SEMICONDUCTORS

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It has been shown [1-3] that systems comprising powdered metals and organic polymers exhibit semiconductor properties, the nature of which depends greatly on the conditions of preparation of these systems. In most cases powdered iron and polymeric organic dielectrics were employed. The present study deals with systems consisting of powdered nickel and cobalt in combination with phthalocyanine, which exhibits semiconductor properties and is very stable; much work has been done on the properties of this material [4,5].

The compositions were prepared by allowing phthalonitrile vapour to act on the surface of the powdered metal at temperatures between 250° and 400°C. The reaction of phthalonitrile vapour with the surface atoms of the metal results in the formation of a film of the metal phthalocyanine. The reaction was carried out in a vacuum-sealed tube, which was rotated in an electric furnace heated to the required temperature†. After the reaction had been completed, the contents of the tube were removed, ground, and evacuated at 250°C to remove the unreacted phthalonitrile. The powder remaining after evacuation was pressed into rectangular pellets (1.4 × 0.5 cm) under a pressure of 6×10^3 atm.

All the measurements of electrical conductivity σ and Seebeck coefficient α were made in a vacuum (10^{-6} mmHg). In the measurement of α the temperature gradient in the specimen varied from 15 to 30 deg.

Figs. 1 and 2 show the temperature variation of the conductivity of the nickel–nickel phthalocyanine and cobalt–cobalt phthalocyanine systems. The data for all the specimens are described satisfactorily by the equation $\sigma = \sigma_0 \exp(-\Delta E/kT)$. The increase of electrical conductivity with temperature, which is typical for semiconductors, may have different mechanisms: involving the exponential growth of the number of current carriers or exponential growth of the mobility of the current carriers [6,7]. The temperature variation of the Seebeck coefficient may serve as a criterion for the determination of the mechanism [7,8]. Fig. 3 shows that the Seebeck coefficient for the nickel–nickel phthalocyanine and cobalt–cobalt phthalocyanine systems is virtually independent of temperature, which shows that the conductivity is activated by an increase in the mobility of the current carriers. Similar observations were made on single-crystal phthalocyanines of copper, nickel, and cobalt [9] and the phthalocyanines of copper, zinc, and magnesium in film form [10]. In a number of investigations with other organic semiconductors the same temperature variation of the Seebeck coefficient was found [5,7,8,11].

Figs. 1 and 2 and Table 1 show that the electrical conductivity σ of our specimens is much higher and the activation energy ΔE lower than for the nickel and cobalt phthalocyanines obtained from our systems by sublimation at 450°C.

† The technique has been described in detail elsewhere [3].

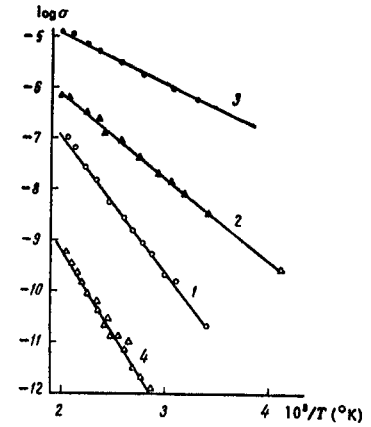

Fig. 1. Variation of $\log\sigma$ with $1/T$. 1)–3) For the nickel–nickel phthalocyanine system at different preparation temperatures (°C): 1) 250; 2) 350; 3) 400. 4) For nickel phthalocyanine obtained by sublimation at 450°.

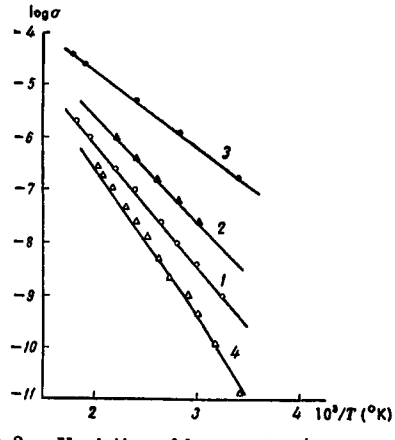

Fig. 2. Variation of $\log\sigma$ with $1/T$. 1)–3) For the cobalt–cobalt phthalocyanine system at different preparation temperatures (°C): 1) 250; 2) 350; 3) 400. 4) For cobalt phthalocyanine obtained by sublimation at 450°.

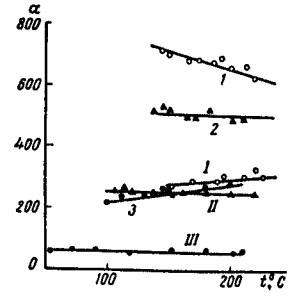

Fig. 3. Temperature variation of the Seebeck coefficient of the system: I)–III) nickel–nickel phthalocyanine system prepared at 250°, 350°, and 400°; 1)–3) cobalt–cobalt phthalocyanine system prepared at 250°, 350°, and 400°C.

TABLE 1.

System	t, °C	σ at 20°C, Ω^{-1} cm^{-1}	ΔE, eV	α, μV deg^{-1}	Type of conductivity
Nickel–nickel phthalocyanine	250	$1\cdot10^{-10}$	0.52		p
	300	$1\cdot10^{-10}$	0.52	300	p
	350	$1\cdot10^{-8}$	0.34	250	n
	400	$1\cdot10^{-6}$	0.20	60	p
Nickel phthalocyanine (sublimed at 450°C)		$1\cdot10^{-12}$	0.7		
Cobalt–cobalt phthalocyanine	250	$1\cdot10^{-9}$	0.46	650	n
	350	$1\cdot10^{-8}$	0.40	550	n
	400	$4\cdot10^{-7}$	0.29	270	n
Cobalt phthalocyanine (sublimed at 450°C)		$2\cdot10^{-11}$	0.59		

Elemental chemical microanalysis showed that the substances obtained under these conditions are indeed the phthalocyanines of nickel and copper.

Comparison of the curves shows that increase in the preparation temperature results in an increase of the electrical conductivity, both with cobalt and with nickel. The conductivities of pure nickel and cobalt phthalocyanines are in good agreement with literature data[9].

In the preparation of the specimens usually 0.3 g of phthalonitrile was used with 0.3 g of metal. Experiment showed that, when the same component ratio is employed in the reaction with nickel at 400°C metal-type conductivity results; in order to obtain semiconductor-type conductivity at 400°C it was necessary to take 0.5 g of phthalonitrile with 0.3 g of metal. In the case of nickel at 350°C a study was made of the composition prepared using 0.3 g of nickel and 0.5 g of phthalonitrile in addition to the composition obtained with 0.3 g of nickel and 0.3 g of phthalonitrile. The results were the same in both cases, i.e. the temperature variation was characteristic of an n-type semiconductor.

The observed semiconductor-type temperature variation of conductivity suggests that the electric current flowing from one metallic grain to another passes through a thin layer of metal phthalocyanine which closely covers the grains. It was shown that, when relatively small amounts of phthalonitrile are used in the reaction or when the surface area of the metal grains is very large, it is possible to obtain systems with a wide range of conductivities, from several units to 10^{-4} Ω^{-1} cm^{-1}. Such systems exhibit low temperature variation of the conductivity, a negative temperature coefficient as with metals (Fig. 4), and their conductivity is of n-type. Clearly in these systems current flows through metal grains which come into direct contact with one another when the specimen is compressed.

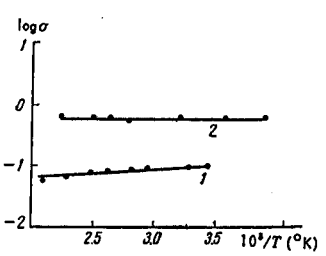

Fig. 4. Variation of $\log\sigma$ with $1/T$:
1) nickel–nickel phthalocyanine system;
2) cobalt–cobalt phthalocyanine system.

The experimentally observed increase of conductivity with the preparation temperature of the specimens may be explained by the fact that the contribution to the conductivity of the thinnest layers of both copper and nickel phthalocyanines greatly increases with preparation temperature. At higher temperatures phthalonitrile vapour diffuses more readily into difficultly accessible channels and pores and very thin phthalocyanine films are thereby formed. Under these conditions individual metal grains probably break down.

When the system is prepared at 400°C, i.e. close to the sublimation temperature of phthalocyanine (450°C), particularly favourable conditions are established for the formation of nickel phthalocyanine at difficultly accessible sites and also for the diffusion of nickel atoms through layers of phthalocyanine which have already formed.

The above hypotheses concerning the mechanism of conductivity are confirmed by measurements of the true surface area of the powdered metal, both initial and in the systems prepared at different temperatures. The metal phthalocyanines sublime at about 700°C. Measurements of the surface area of the metal remaining after the phthalocyanine had been sublimed were made by the BET method.

The average thickness of the phthalocyanine layers in systems obtained at different temperatures may be estimated from the true surface area of the metal and the amount of metal phthalocyanine formed (found from elemental chemical microanalysis) (Table 2). Table 2 shows that the reaction between phthalonitrile vapour and the metals investigated increases the surface area of the latter to an extent which is greater the higher the temperature, the phthalocyanine layers being thinner at higher temperatures.

Although the estimate of the thickness of the layers is approximate, it permits certain definite conclusions. The decrease in the thickness of the phthalocyanine layers with temperature is greater in the nickel–nickel phthalocyanine system than in the similar systems with cobalt. Fig. 1 shows that the electrical conductivity of the nickel system increases by more than four powers of ten when the reaction temperature is raised from 250° to 400°C. In the same

TABLE 2.

System		Surface area, m^2 g^{-1}	Average thickness of phthalocyanine layer*, cm
Initial nickel		1.5	
Nickel after sublimation of phthalocyanine from systems obtained at different temperatures	250°C	3.5	$2.1\cdot10^{-5}$
	400°C	18.3**	$6.0\cdot10^{-5}$
Initial cobalt		0.6	
Cobalt after sublimation of phthalocyanine from systems obtained at different temperatures	250°C	4.1	$2.1\cdot10^{-5}$
	400°C	6.8**	$1.5\cdot10^{-5}$

* The thickness of the layer A was calculated from the expression $A = M/dS$, where M is the amount of metal phthalocyanine in grammes, S the surface area in cm^2, and d the density of the metal phthalocyanine. The values of d, which are 1.59 and 1.53 for nickel and cobalt phthalocyanines respectively, have been taken from Linstead and Robertson[12].

** These determinations were kindly made by O. A. Golovina.

range of reaction temperatures for the cobalt system (Fig. 2) the change is only by two powers of ten. Thus the increase in the conductivity of our systems with temperature is greater the thinner the phthalocyanine layers become.

The data in Table 2 show that in the systems current is conducted through metal phthalocyanine layers whose thickness is of the order of 10^{-5}–10^{-6} cm. The conductivity of such thin layers[7,13,14] may be much greater than that of the corresponding massive specimen.

According to the literature[4,5,7], phthalocyanine without metal and metal phthalocyanines exhibit *p*-type conductivity. In view of their high resistivity, the type of conductivity of our systems was determined only from the sign of the Seebeck coefficient. Table 1 shows that in the cobalt–cobalt phthalocyanine system the conductivity is of *n*-type regardless of the preparation temperature. The reason for this is as yet unkown. The conductivity of the nickel–nickel phthalocyanine system was of the *p*-type in all cases, except for specimens obtained at 350°C. The reason for this behaviour is also still obscure.

Experiments are now being carried out on the electrical and physical properties of very thin phthalocyanine films both on massive nickel and copper supports and supports produced by the sublimation of the metals. These studies should provide an answer to the problems, which are not as yet entirely clear, associated with the mechanism of the electrical conductivity of systems comprising powdered metals and organic semiconductors.

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SUMMARY

1. Systems comprising powdered nickel and cobalt covered with a thin layer of the phthalocyanine of the corresponding metal were obtained by the action of phthalonitrile vapour on the surface of the metal at 250°, 350°, and 400°C.
2. It has been shown that, as the reaction temperature is raised from 250° to 400°C, the specific conductance of the system increases by four powers of ten and the activation energy falls by 0.3 eV.
3. The formation of a layer of phthalocyanine causes extensive loosening of the metal surface and the thickness of the phthalocyanine film on the metal becomes progressively reduced. This effect is greater the higher the reaction temperature.

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THERMODYNAMIC ANALYSIS OF THE COMBUSTION OF MONOSILANE

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The combustion of many organosilicon compounds is known to yield SiO_2 of high purity, and when these compounds are burned with a deficiency of oxygen, the final products may contain also Si and SiO. It is interesting to elucidate in terms of thermodynamics the purity attainable for SiO_2 on combustion of silicones and to determine whether the preparation of SiO by this method is possible. The present paper presents the results of a thermodynamic study of the combustion of monosilane.

Combustion of SiH_4 results in the formation of a multicomponent mixture:

$$SiH_4 + \alpha 2O_2 \rightarrow SiO_2(solid) + SiO_2(gas) + SiO + SiH + Si + H_2O + OH + H_2 + H + O_2 + O \ldots$$

The equilibrium composition of a system comprising k elements and l components at constant temperature and pressure is described by k linear material balance equations and $l - k$ equilibrium equations. If the system is not homogeneous, it can be shown that, in the presence of n different phases, the number of unknowns may be reduced by $n - 1$. The methods of calculation of the equilibrium composition of multicomponent systems have been described in numerous monographs and papers (see, for example, Refs. 1–4).

In order to find the thermodynamic conditions for the combustion of SiH_4 which would permit the selective synthesis of highly pure SiO_2 or SiO, the equilibrium position of the system comprising the elements Si, H, and O was calculated for the temperature range 1900–3000°K at different monosilane-oxidant ratios and different pressures. The calculations were made by means of a BESM-2M electronic computer. The heat of formation of SiH_4 determined by Brimm and Humphreys[5] was used in the calculations. All the remaining thermodynamic quantities required for the calculations were taken from Ref. 4. The thermodynamic functions for SiO have been determined very approximately, which reduces the precision of the calculations as a whole, but the data do suggest where the optimum conditions should be sought.