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Correlation between π-orbital overlap and conductivity in bis-phthalocyaninato lanthanides

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Abstract

Conductivity measurements on praseodymium, neodymium, gadolinium, holmium, erbium and lutetium phthalocyanine sandwich compounds of the general formula $H[M(Pc)_2]$ taken with both d.c. and a.c. techniques on pressed pellet samples show a direct correlation with the intraplanar separation between the phthalocyanine ligands. Conductivity measurements on the iodine-doped bis-phthalocyaninato lanthanides, $H[M(Pc)_2I_x]$, show an average increase of four orders of magnitude when measured with d.c. techniques, and two orders of magnitude when measured with a.c. techniques. The high-temperature conductivity behavior may be explained by using the mobility model. The low-temperature data show hopping conduction behaviour.

Introduction

Shortly after the bis-phthalocyaninato lanthanide sandwich compounds were synthesized [1], electrical resistivity measurements were carried out [2]. After partial oxidation with iodine, like their transition metal analogues [3], they show a substantial decrease in electrical resistivity. However, discrepancies as large as five orders of magnitude in the resistivity values reported by different authors for the same compound are found in the literature [4–9].

There are possible explanations to account for the discrepancies. (i) It is difficult to control the purity of the samples; the impurities include dopants, defects, vacancies and grain boundaries. (ii) Ambient conditions, especially while the measurements are being taken, play a major role. (iii) Different authors have used different techniques to measure the conductivities (two-probe technique versus four-probe technique).

For the above reasons, it has not been possible to find correlations between the electrical properties of bis-phthalocyaninato lanthanide sandwich compounds and their structural features. It is clear, however, that in order to make meaningful comparisons, it is essential that systematic measurements be made on a series of compounds prepared under the same conditions. Therefore, we have measured the electrical resistivities of praseodymium, neodymium, gadolinium, holmium, erbium and lutetium phthalocyanines, and their iodine-doped analogues throughout the 20–300 K range, using d.c. and a.c. techniques. To avoid adsorption of gases, the resistivities of all the samples were measured under vacuum [10].

Experimental

The samples were synthesized as published in a preliminary communication [10]. The electrical resistivities were measured on pellets, and they were checked for cracks under a microscope to assure integrity. Valdes [11] and Van der Pauw's [12, 13] techniques were used, and equivalent results were obtained with both methods.

With the Valdes technique the electrical connection was accomplished with four equally spaced spring-loaded electrodes; unfortunately, at low temperatures, the pellets become rigid and brittle, plus they tend to contract. As a consequence, due to the pressure exerted by the spring-loaded electrodes, the pellets crack rather easily. For this reason, the resistivity measurements reported on this study are the ones obtained using the Van der Pauw technique.

The a.c. resistivity measurements were taken on the same pellets used for d.c. measurements. After

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carefully pulling out the four probes, both sides of the pellets were covered with a thin film of silver paste, and the paste was allowed to dry completely. Afterwards, the pellets were mounted between two square platinum electrodes of approximately the same size as the pellets. The temperature dependence measurements were taken at 20 kHz.

Instrumentation

The four probe d.c. resistivity measurements were carried out using a model 21SC cryodine cryocooler from CTI-Cryogenics, which consists of an air-cooled model 21SC compressor unit, and a model 21 cold head. The temperature was measured with a DT-500K silicon diode located a few milimeters from the sample pellet, and connected to a model DRC 80C temperature controller from Lake Shore Cryotronics, Inc. The temperatures are estimated to be accurate to ±5 K. The current source used is the model 227 from Keithley and was monitored with a digital multimeter model 8600A from Fluke. The voltage across the probes was measured with a multimeter model 8502A from Fluke. All the instruments were interfaced through an HP scanner model 3495A to a Tektronix computer model 4052.

The a.c. resistivity measurements were carried out using a GenRad 1688 Precision LC Digibridge digital impedance meter interfaced to a Tektronix computer model 4052. The digibridge responds to frequencies between 240 Hz and 20 kHz, inclusive. Temperature dependence measurements were made at 20 kHz because the capacitance versus frequency curve is flatter at high frequencies. In all the samples the resistivity was found to be frequency dependent, as has been observed in low mobility materials.

Results and discussion

Room temperature resistivities

The trend observed in the room temperature resistivities for undoped bis-phthalocyaninato lanthanides is (Table 1)

$$\rho(\mathrm{Pr}) > \rho(\mathrm{Nd}) > \rho(\mathrm{Gd}) > \rho(\mathrm{Ho}) \cong \rho(\mathrm{Er}) > \rho(\mathrm{Lu})$$

which is the same trend observed for the ionic radii of the respective lanthanide, i.e. as the ionic radius decreases, the resistivity decreases as well. This relationship had not been pointed out before because of the lack of a systematic study of a series of sandwich lanthanide phthalocyanines, prepared and measured under the same conditions.

When the ionic radius decreases, the separation distance between the phthalocyanine macrocycles also decreases, favoring a greater overlap between the π-orbitals of both macrocycles. This result is significant because it strongly suggests that the overlap of π-orbitals plays a major role in the resistivity behavior.

In addition, this finding indirectly provides an explanation for the enhanced conductivity of lanthanide phthalocyanines with respect to their transition metal analogues. For example, nickel phthalocyanine shows a room temperature resistivity of 10^{12} Ω cm [14]. As shown in Table 2, the closest intermolecular distance between adjacent molecules in the lattice is 3.38 A [15]. By contrast, in lanthanide phthalocyanines, the lanthanide ion keeps the two macrocyclic rings closer together, which results in shorter intramolecular distances.

Thus far, there is no evidence that points to the lanthanide ion as directly responsible for the enhanced conductivity. For example, the metal-free phthalocyanine shows a room temperature resistivity of about 10^{12} Ω cm [14], quite similar to typical transition metal phthalocyanines, and so it has been argued that the transport of charge carriers is through the ligands, and not through the metal ions.

When the resistivity of lanthanide phthalocyanines is measured by using a.c. techniques (Table 3), the trend observed is essentially the same found for d.c. resistivities:

$$\rho(\mathrm{Pr}) \cong \rho(\mathrm{Nd}) > \rho(\mathrm{Gd}) > \rho(\mathrm{Ho}) \cong \rho(\mathrm{Er}) > \rho(\mathrm{Lu})$$

The values however differ as much as two orders of magnitude. In general, a.c. resistivities are not

TABLE 1. Room temperature d.c. electrical resistivities for lanthanide phthalocyanines

Compound	ρ (Ω cm)	Compound	ρ (Ω cm)
H(Pc)Pr(Pc)	$> 1.0\times10^{8}$	H(Pc)Pr(Pc)$I_{1.2}$	2.3×10^{2}
H(Pc)Nd(Pc)	1.3×10^{7}	H(Pc)Nd(Pc)$I_{1.8}$	1.5×10^{1}
H(Pc)Gd(Pc)	6.7×10^{6}	H(Pc)Gd(Pc)$I_{1.2}$	1.0×10^{3}
H(Pc)Ho(Pc)	1.7×10^{5}	H(Pc)Ho(Pc)$I_{1.8}$	1.7×10^{0}
H(Pc)Er(Pc)	2.4×10^{5}	H(Pc)Er(Pc)$I_{1/4}$	3.2×10^{2}
H(Pc)Lu(Pc)	6.7×10^{3}	H(Pc)Lu(Pc)$I_{2.0}$	1.7×10^{2}

TABLE 2. Room temperature d.c. resistivities and interplanar spacings for a series of phthalocyanines

Compound	ρ (Ω cm)	Interplanar spacing (Å)	Reference
(Pc)Pt	$\approx 10^{12}$	3.41	17
(Pc)H_2	10^{11-13}	3.38	16
(Pc)Ni	$\approx 10^{12}$	3.38	15
β-(Pc)Pr(Pc)	$> 10^{8}$	3.0	18
β-(Pc)Nd(Pc)	1.3×10^{7}	2.94	19
γ-(Pc)Lu(Pc)	6.7×10^{3}	2.7	20

TABLE 3. Room temperature a.c. electrical resistivities for the lanthanide phthalocyanines

Compound	ρ (Ω cm)	Compound	ρ (Ω cm)
H(Pc)Pr(Pc)	$>5.1\times10^6$	H(Pc)Pr(Pc)$I_{1.2}$	9.3×10^3
H(Pc)Nd(Pc)	5.4×10^6	H(Pc)Nd(Pc)$I_{1.8}$	7.6×10^3
H(Pc)Gd(Pc)	1.3×10^6	H(Pc)Gd(Pc)$I_{1.2}$	5.9×10^4
H(Pc)Ho(Pc)	2.1×10^5	H(Pc)Ho(Pc)$I_{1.8}$	1.1×10^3
H(Pc)Er(Pc)	4.7×10^5	H(Pc)Er(Pc)$I_{1.4}$	1.2×10^4
H(Pc)Lu(Pc)	1.1×10^4	H(Pc)Lu(Pc)$I_{2.0}$	3.6×10^3

equal to d.c. resistivities. There are several competing factors that may affect the results. In a.c. techniques, the resultant current-flow depends not only on the resistance of the sample, but also on the capacitance. The a.c. resistivity equals the d.c. resistivity when the impedance of the sample is purely resistive. This condition is met when the reactance is zero. If this were the only factor, the a.c. resistivity would always be greater than the d.c. resistivity.

On the other hand, a.c. techniques have the advantage of eliminating certain resistances at the contacts between particles, because such resistances, if large, are electrically shorted by the capacitance of the contacts [21].

Compared with the undoped samples, iodine-doped lanthanide phthalocyanines show an average of four orders of magnitude decrease in resistivity when measured by using d.c. techniques, and an average of two orders of magnitude decrease by using a.c. techniques. However, the same trends are not observed with the undoped materials because the doping level is not the same for all the compounds studied here, even though the same molar ratios were used during the preparations.

Although it is not possible to compare the resistivities of undoped and iodine-doped lanthanide phthalocyanines, because of the difficulty of doping them by the same amount, the trend observed between d.c. and a.c. resistivities for doped samples is essentially the same:

$$\rho(\mathrm{Gd})>\rho(\mathrm{Er})>\rho(\mathrm{Pr})>\rho(\mathrm{Lu})\cong\rho(\mathrm{Nd})>\rho(\mathrm{Ho})$$

This is not an unexpected result since the a.c. measurements were carried out on the same pellets used for d.c. measurements.

Low-temperature resistivities

The low-temperature resistivity data were collected through the entire range (20–300 K) only for iodine-doped lanthanide phthalocyanines. For undoped samples, the resistivity at low temperatures increases beyond the voltage compliance limit of the current source used, and it was not possible to hold a constant current. Therefore, only the temperature dependence of doped samples will be analyzed here.

The temperature dependence of the resistivity for iodine-doped lanthanide phthalocyanines may be explained qualitatively according to the theory for doped semiconductors.

At low temperatures most of the electronic properties of semiconductors are determined by impurities. The iodine may be considered as an impurity acting as a p-type acceptor that creates a narrow band of acceptor levels. In a p-type semiconductor, these levels are close to the top of the valence band. Thus, the iodine content determines the number of acceptor levels and the temperature behavior of extrinsic conduction.

The acceptor impurity may be comparatively easily ionized by accepting one electron from the valence band, leaving a positive charge (hole) on the phthalocyanine molecule (electron donor species). These holes may then participate in transport processes while the impurity centers become negatively charged. If the impurity concentration is not large, electrons may be captured by the valence band at sufficiently low temperatures, and the charge neutralized (the so-called ‘freezing-out’ of conduction carriers [22]).

The most important characteristic of a p-type impurity is its electron affinity, i.e. the energy necessary to move one electron from the valence band to the acceptor level. The ‘freeze-out’ temperature is mainly determined by this energy.

At high temperatures, semiconductors possess an intrinsic electrical conductivity due to thermal activation of carriers across the gap separating the valence and the conduction bands. The intrinsic carrier concentration of holes are exponential functions of temperature.

Due to the large activation energy, the intrinsic carrier concentration decreases very rapidly with temperature. At sufficiently low temperatures it becomes less than the concentration contributed by impurities. In this region, the conduction is entirely determined by the nature and concentration of impurities.

Figure 1 shows the inverse temperature dependence of the resistivity of iodine-doped praseodymium phthalocyanine. Four separate regions labeled A, B, C, and D are seen, as is the case for iodine-doped gadolinium phthalocyanine, but the other samples show only two or three well-defined regions.

The temperature range A, with the slope nearly vertical, corresponds to intrinsic conduction, while ranges B, C and D correspond to extrinsic conduction. When dealing with shallow impurities whose ionization energy is much lower than the energy gap,

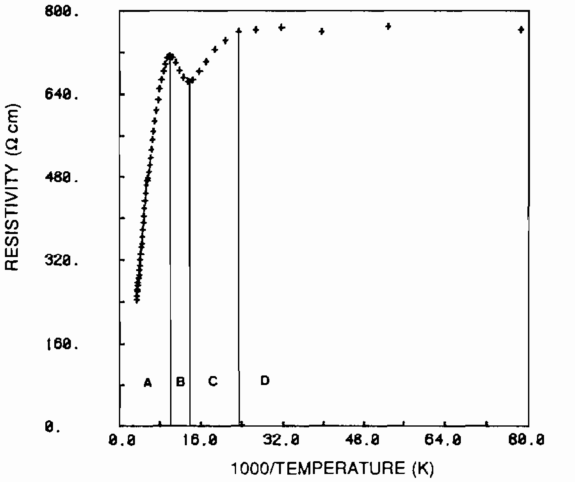

Fig. 1. Plot of the resistivity vs. 1000/temperature for $H(Pc)Pr(Pc)I_{1.2}$ under d.c. conditions. Range A = intrinsic conduction. Range B = saturation. Range C = freezing-out. Range D = hopping conduction.

there exists a saturation range, B, in which all the impurities are ionized, and hence the carrier concentration in the band is independent of temperature. In this range, the temperature dependence of the resistivity is entirely determined by that of the mobility, and the decrease in resistivity with a lowering of the temperature is associated with a weaker phonon scattering [22].

A further decrease in temperature (range C) leads to a gradual freezing-out of impurity electrons, i.e. they are recaptured by the valence band. In this region, the temperature dependence of the electrical resistivity is entirely due to a rapid decrease in the free electron concentration. The temperature dependence of the concentration in this region depends on the relation between the number of empty donor positions due to compensation, and the number of empty positions due to thermal excitation of electrons into the acceptor levels [22].

Range C is generally narrow, and does not exist at all unless the compensation is low enough. Experimentally, only praseodymium and gadolinium phthalocyanines show a well-defined region C. These two compounds are precisely the ones with the lowest compensation.

The gradual freezing-out of conduction electrons with decreasing temperature eventually leads to a situation in which the main contribution to the electrical conductivity comes from electrons hopping directly in the acceptor levels without any excursion to the conduction band (range D). Electrons jump from occupied acceptors to empty ones, and therefore the presence of empty positions on acceptors is a necessary condition. At low temperatures, this condition can be fulfilled only by compensation.

The hopping mechanism of conduction corresponds to a very low mobility, since the electron jumps are associated with a weak overlap of wavefunctions tails from neighboring acceptors. Nevertheless, this mechanism prevails in the competition with band conduction because only an exponentially small number of free carriers can participate in the latter.

High-temperature fittings

The high-temperature behavior of the resistivity of organic semiconductors may be explained using the mobility equation, $\rho = eC_0\eta\mu$, where ρ is the resistivity, C_0 is a proportionality constant, η is the concentration of charge carriers, and μ is the mobility of charge carriers.

The mobility model has been used to explain the high-temperature behavior of a variety of inorganic and organic low-dimensional materials, such as tetracyanoplatinates (KCP) [23], *N*-methylphenazinium-tetracyanoquinodimethane (NMP-TCNQ) [24], quinolinium-$(TCNQ)_2$ [25], tetrathiofulvalene (TTF) halides [26], pseudohalides [27] and octamethyltetrabenzoporphyrins [28].

The high-temperature experimental data of iodine-doped lanthanide phthalocyanines were fitted to the mobility equation using a non-linear Simplex fitting routine [29]. The best-fit parameters are listed in Table 4. It is important to emphasize that only the high-temperature data were fitted since the low-temperature resistivity follows a different conduction mechanism. The values obtained for the energy gaps are quite comparable to those found in the literature [2, 6, 7]. The values for the parameter α are similar to those found in low-dimensional materials. For example, typical values for TCNQ salts are around 1.8 [30].

Low-temperature behavior

There are two mechanisms that have been proposed to explain the low-temperature behavior of doped semiconductors; namely, tunneling [14] and hopping [31].

TABLE 4. Best-fit parameters for iodine-doped lanthanide phthalocyanines using the mobility equation

Compound	C_0	α	E_g (eV)
$H(Pc)Pr(Pc)I_{1.2}$	1.7×10^8	2.2	0.035
$H(Pc)Nd(Pc)I_{1.8}$	1.2×10^5	1.4	0.011
$H(Pc)Gd(Pc)I_{1.2}$	1.8×10^{14}	4.3	0.068
$H(PcHo(Pc)I_{1.8}$	4.1×10^5	2.1	0.032
$H(Pc)Er(Pc)I_{1.4}$	9.8×10^7	2.3	0.020
$H(PcLu(Pc)I_{2.0}$	3.0×10^6	1.6	0.025

Tunneling is a quantum mechanical phenomenon in which a charge carrier passes through a potential barrier without acquiring enough energy to pass over the top of the barrier. At the absolute zero of temperature, the hopping probability is zero; any charge transfer then must occur by tunnelling. As the temperature is raised the tunnelling probability, which is virtually temperature independent, remains substantially constant while the hopping probability, being a thermally activated process, increases exponentially [30].

Hopping occurs when a charge carrier jumps over the potential barrier that separates two molecules, via an activated state. Experimental evidence for thermally activated hopping has been deduced for several TCNQ complexes [32, 33]. Charge carriers can hop isoenergetically from one site to another only if the energy levels on both sides of the intervening potential barrier coincide [30]; this is made possible by thermal fluctuations, leading to a decreasing activation energy as the temperature drops [34, 35].

Attempts to fit the resistivity data to Mott's law [36] were not satisfactory. One of the reasons is that the low-temperature hopping behavior can be strongly affected by various effects, such as electron–electron correlation, or long-range potential fluctuations [31]. The hopping equation rests upon the one-electron approximation. However, electron–electron interactions may also be important in disordered systems. For instance, in impurity bands the electron–electron interaction energy is of the order of the disorder energy, except for very large and very small compensations [22, 31]. The iodine-doped lanthanide phthalocyanines prepared in this study do not have either a very large or a very small compensation, but the compensation is at an intermediate level, and so the electron–electron interaction cannot be neglected. Unfortunately, the problem of taking into account the electron–electron interaction is very difficult, and it cannot be solved analytically in general [22, 31].

On the other hand, long-range potential fluctuations may be calculated with the help of a self-consistent field method, which is not applicable to the intermediate compensation problem [22]. Currently, the only approach to tackle this problem is through computer simulations of the impurity band, but that goes beyond the scope of this work.

Conclusions

A definite correlation has been found between the electrical resistivities of sandwich-like lanthanide phthalocyanines of the general formula $H[M(Pc)_2]$ and their structural features. In particular, it has been found that the trends in resistivities are correlated with the intra-ring spacing between phthalocyanine rings, but the problem of the correlation of conductivity properties with the inter-ring spacing can not be addressed because of a lack of adequate experimental structural data, although the limited data available suggest that a trend is emerging.

The low-temperature data indicate that hopping conduction occurs at very low temperatures, as evidenced by the strong dependence of the specific resistivity on the dopant concentration, and the weak dependence on temperature.

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