NEW MEMBERS OF THE SERIES OF QUASI-ONE-DIMENSIONAL METALS $(PERYLENE)_2[M(mnt)_2]$, M=Ni AND Cu

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ABSTRACT

Electrocrystallisation techniques afford the preparation of single crystals $(Per)_2M(mnt)_2$ M=Ni and Cu. Systematic transport properties measurements give evidence for the existence of two phases, one " α-phase" metallic and one other " β-phase" with semiconducting properties. These results are compared with other compounds in this series with M= Au, Pd, Pt, Fe and Co.

INTRODUCTION

The compounds $(Per)_2[M(mnt)_2]$ (mnt= maleonitriledithiolate) with M=Ni and Cu were the first compounds to be prepared in this series of low dimensional conductors, and they were reported to be semiconductors by Alcácer and Maki [1] more than 15 years ago. Later compounds with M=Pd, Au and Pt were obtained as single crystals and reported as metals at room temperature with Metal-Insulator (M-I) transitions at lower temperatures (at 29 and 7 K in case of M=Pd and Pt respectively) [2,3]. These compounds have an unusual behaviour [4,5], of conducting Perylene chains and magnetic $M(mnt)_2$ chains that undergo a dimerisation at the M-I transition [3].

In order to achieve a better overall understanding of the physical properties of the different members of this series, together with the preparation of new members with M=Fe and Co, we recently reinvestigated the Ni and Cu compounds. In this paper we present results of a systematic investigation of the transport properties of these compounds, and the results are compared with those obtained in other members of this series.

EXPERIMENTAL

Single crystals (up to $\simeq 3x0.05x0.03\ mm^3$) of the compounds with M=Cu and Ni were obtained by electrocrystallisation from dichloromethane solutions of Perylene and TBA $M(mnt)_2$ on platinum electrodes. The best crystals were obtained employing galvanostatic conditions. For M=Ni a current density of 10-15 $\mu A/cm^2$ during 3 to 5 days was used while for M=Cu larger current densities 100-200 $\mu A/cm^2$ were employed for 2 to 3 hours.

Electrical resistivity ρ and thermopower S were measured in the range 10-300K in a closed cycle refrigerator. Resistivity was measured using four electrodes and an a.c. current (≃1 A) at 70Hz, the voltage being measured with a lock-in amplifier. Thermopower was measured using a slow a.c.

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technique (≃0.01Hz) and gradients of ≃1K. Contacts to the sample were made with platinum paint. In a large number of crystals, after thermopower measurements, two extra voltage contacts were placed on the sample, without removing it from the cryostat, so that both resistivity and thermopower measurements were performed in the same crystal.

RESULTS AND DISCUSSION

Elemental analysis of C, H and N performed in different batches of both M=Ni and M=Cu gave results consistent with a stoichiometry of $(Per)_2[M(mnt)_2]$. Resistivity and thermopower measurements performed in a large number of samples from different preparations gave evidence for two distinct behaviours occuring in both the compounds with M=Ni and Cu, as shown in Fig. 1 and 2.

One set of samples (denoted as β-phases) show a semiconducting behaviour that is similar to the one reported earlier in these compounds [1], with $\sigma_{RT} \simeq 50\text{-}100\ \Omega^{-1}cm^{-1}$. At lower temperatures resistivity increases with an aparent activation energy that increases smoothly at lower temperatures reaching 45 meV at 100K. This semiconducting behaviour is confirmed by the thermopower that increases upon cooling from a value of 22 μVK^{-1} at room temperature to 60-80 μVK^{-1} at 100K.

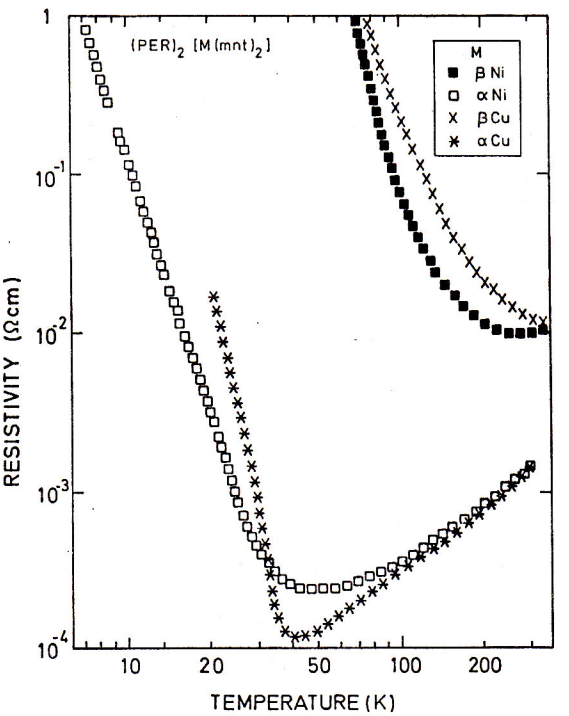

Fig. 1- Temperature dependence of the electrical resistivity along the chain axis of $(Per)_2[M(mnt)_2]$ for α and β phases, with M=Ni and Cu.

One other set of samples (denoted α-phases) have higher room temperature conductivity $\sigma_{RT}=700\ \Omega^{-1}cm^{-1}$ with metallic behaviour ($d\rho/dT>0$) down to lower temperatures where a M-I transition, better seen as a sharp maximum of $d\sigma/dT$, occurs at 25K for M=Ni and at 32K for M=Cu. Thermopower measurements on these crystals confirm the metallic behaviour and the M-I transition. At room temperature, thermopower is positive, 35 μVK^{-1} for M=Ni and 38 μVK^{-1} for M=Cu, with a behaviour approximately linear in T down to 120K where it reaches constant values before starting to increase again near the M-I transition. The metallic behaviour of these phases is very similar to the one observed in other compounds of this family, except for the clear M-I transition absent in the gold compound that instead seems to undergo a gradual localisation at low temperatures [3]. The positive thermopower observed in these compounds indicates hole type carriers, consistent with conduction via the 3/4 filled band of the perylene chains. From the linear regime at high temperature in α-phases and as previously done for the Au, Pt and Pd analogues [6], it is possible to estimate the bandwidth to be 0.55eV for M=Cu and ≃ 0.60eV for M=Ni.

Although minor variations on the resistivity results of different β-samples were detected, in the large number of samples tested, coming from different batches, we never observed any intermediate behaviour between those of α and β samples. The evidence for two similar phases was previously reported in the analogue with M=Co [7]. In the other compounds of this series previously studied in our laboratory with M= Fe, Pd, Pt and Au we have only observed the metallic behaviour characteristic of the phases. A comparison of the transport properties of the different α and β phases of the compounds of this series, so far studied in our laboratory is summarized in Table I. The occurrence of both α and β phases is present at least in compounds with 3 different transition metals. While the metallic phases (α) are associated with regular chains of closed packed perylene

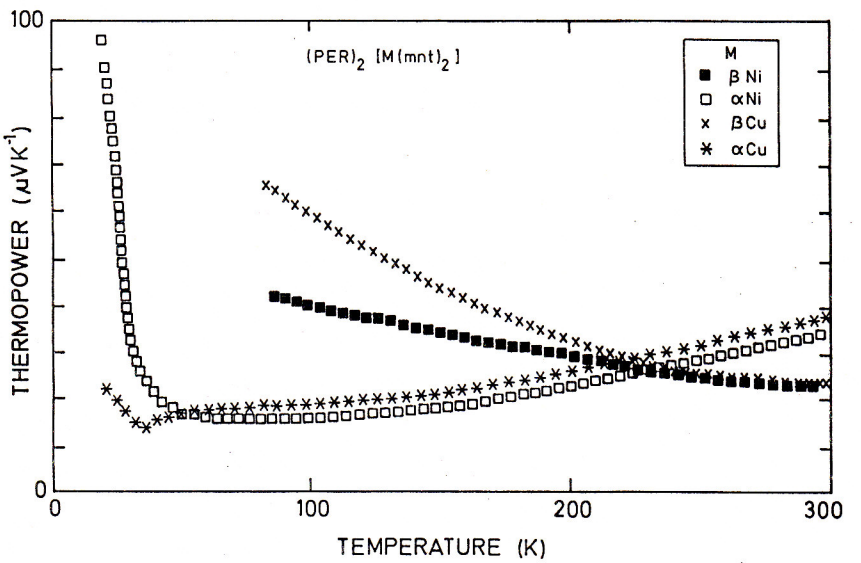

Fig. 2- Temperature dependence of the thermoelectric power along the chain axis of $(Per)_2[M(mnt)_2]$ for α and β phases with M=Ni and Cu.

Table I- Transport properties parameters of different phases of $(Per)_2[M(mnt)_2]$ T_{M-I}-metal insulator transition temperature, Δ-low temperature gap derived from resistivity.

Compound M	$(d\rho/dT)_{RT}$	σ_{RT} $(\Omega cm)^{-1}$	S_{RT} (μVK^{-1})	T_{M-I} (K)	Δ (meV)
α-Au	>0	700	32		
α-Cu	>0	700	38	32	20
β-Cu	<0	80	22	----	90
α-Pt	>0	700	32	7	10
α-Pd	>0	300	32	28	
α-Ni	>0	700	35	25	15
β-Ni	<0	100	22	----	90
α-Co	>0	150	42	73	60
β-Co	<0	80	22	----	90
α-Fe	>0	150	42	58	50

molecules.. [8], the structural origin for the semiconducting properties of β phases is not yet known. Further X-ray diffraction studies are in progress in order to clarify the structural differences between α and β-phases.

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