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THE INTERPLAY BETWEEN CONDUCTION ELECTRONS AND CHAINS OF LOCALISED SPINS IN THE MOLECULAR METALS $(Per)_2M(mnt)_2$, M=Au, Pt, Pd, Ni, Cu, Co and Fe.

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Abstract The properties of the compounds of the family $Per_2M(mnt)_2$ with α phases are reviewed taking into account recent experimental results. The perylene chains, responsible for electronic conduction undergo Peierls transitions at low temperatures. In the cases of M= Pt, Pd and Ni, the chains of $M(mnt)_2^-$ units with localised spins have exchange interactions with the conduction electrons and undergo spin-Peierls transitions at the same temperatures. In the Fe compound only the Peierls transition occurs as the localised spins stacks are already in the ground state.

INTRODUCTION

The α-phases of the $(Per)_2M(mnt)_2$ (where Per= perylene and mnt= maleonitriledithilolate) compounds have been studied in our laboratory since the preparation of the first compounds with M=Pt, Au and Pd more than 10 years ago [1-6]. It was early realised that these compounds had unique features among the low-dimensional solids [5]. In fact, in addition to stacks of perylene molecules that provide quasi-one-dimensional metallic behaviour, the $M(mnt)_2$ chains, for some metals M, can have localised magnetic moments. These two types of chains in the same solid can, a priori, present Peierls and spin-Peierls instabilities, which could be either coupled or uncoupled in a situation whose description still remains a challenge to the theoretical models presently available.

In this paper, the properties of this family of compounds will be reviewed taking into account recent work which includes the preparation of the Ni and Cu compounds in the α-phase [7] and the M=Fe and Co compounds with dimerised $[M(mnt)_2]_2^{2-}$ units [8].

Special attention will be paid to the nature of the phase transitions and of the coupling between the two types of chains.

STRUCTURE

The crystal structures of these compounds are very similar [1,7,8,9]. In the unit cell there are two chains of perylene for each chain of $M(mnt)_2^-$. All these chains are uniform with the exception of the M=Fe and Co derivatives where there is a doubling of the unit cell along the chain axis, **b**, for which, although a full structure is not yet available, there is strong evidence, namely from Mössbauer spectroscopy and magnetic susceptibility [8], that the $M(mnt)_2^-$ units are dimerised with the metal M having a temperature independent distorted square pyramidal coordination. The overlap mode of the perylene molecules is the same in all compounds and minor changes are detected in the overlap of the metal-bis-dithiolenes.

TRANSPORT PROPERTIES

The behaviour of the electrical conductivity of these compounds as a function of temperature is shown in Fig. 1, where a similar metallic behaviour can be observed in all the derivatives, at high temperatures. In the Fe and Pt compounds for which larger single crystals can be obtained, the anisotropy of conductivity determined by the Montgomery method is ≅900, and almost temperature independent in the metallic regime. A more recent and careful reinvestigation of the Au compound [10] showed that this compound, as all the other members of this family, also undergoes a clear metal to insulator (M-I) transition at 12K, which was not detected in earlier works. The electrical conductivity (as well as

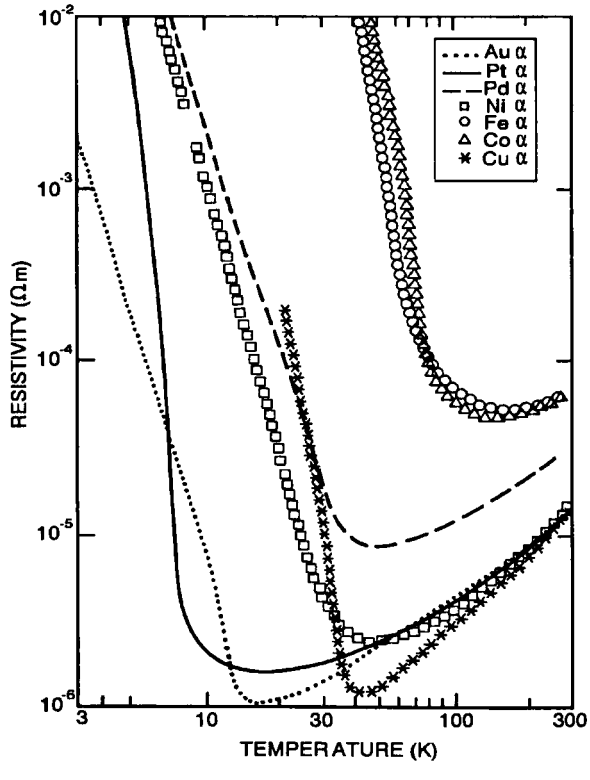

Fig. 1- Electrical resistivity as a function of temperature for α–$Per_2M(mnt)_2$ compounds.

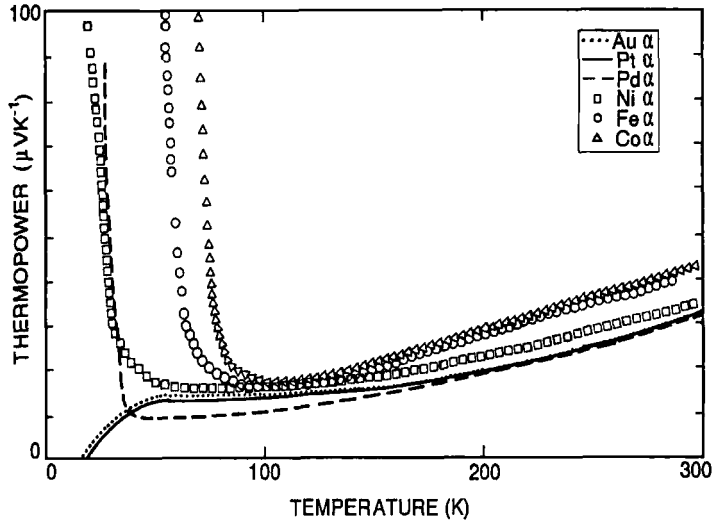

Fig. 2- Thermopower as a function of temperature for α-$Per_2M(mnt)_2$ compounds.

thermopower) does not appear to depend on the magnetic nature of the $M(mnt)_2^-$ units. The slightly smaller conductivty of the Pd compound can be due to the poorer quality of the samples. This compound can only be prepared by iodine oxidation, which tends to lead to iodine contaminations and poorer crystal quality than the electrocrystallisation route used with better results in all other cases. The compounds with dimerised $M(mnt)_2^-$ units (M=Fe and Co) have a significantly smaller conductivity but still present the same metallic behaviour, with however M-I transitions at significantly higher temperatures.

The metallic regime at high temperatures and the metal to insulator transitions are confirmed by thermopower measurements [6,7,8] shown in Fig. 2. Thermopower results indicate that conduction takes place in the 3/4 filled band of the perylene chains with relatively small electronic correlations, and of bandwidths in the range 0.5-0.65 eV. The similar behaviour of the thermopower in the case of the Fe and Co compounds further indicates that the dimerisation potential felt by the conduction perylene chains is relatively small and the slight variations in absolute values correlate well with the observed changes in intermolecular perylene distances.

MAGNETIC PROPERTIES

As opposed to the transport properties, the magnetic properties are very sensitive to the existence of unpaired electrons in the $M(mnt)_2^-$ units. These have been carefully

investigated recently both by static susceptibility measurements [8,11] and by EPR spectroscopy [11,12]. As shown in Fig 3. in the cases of M=Au, Cu and Co, where the $M(mnt)_2^-$ unit is closed shell, the magnetic susceptibility is very small ($1.5\text{-}3\times10^{-4}$ emu mol^{-1}) and weakly temperature dependent, while in cases of $M(mnt)_2^-$ paramagnetic species (M= Ni, Fe, Pd and Pt) the susceptibility is significantly larger due to the extra contribution of the chain of localised spins. Furthermore, this contribution vanishes at the same temperature at which the M-I transition takes place, indicating that the instabilities of both chains are coupled, with the exception of the Fe derivative, where the $Fe(mnt)_2^-$ units are already chemically dimerised at room temperature, giving rise to a contribution typical of antiferromagnetically coupled pairs of spins 3/2 [8]. Magnetisation measurements made both with field parallel and perpendicular to the chain axis **b** in the larger single crystals of the Pt compound, show for both field directions an exponential decrease below T_{MI}, as expected for a spin-Peierls transition. Further evidence for this type of transition is given by X-ray scattering studies presented in the next section.

The spin magnetism of the Au [13], Cu [13] and Co [8] compounds, vanishing at the M-I transition is closely followed by the intensity of the EPR line [12], which is in these cases relatively narrow ($<$1G for Cu and Au and 6G for Co at room temperature and $<$ 1G below 150 K) and isotropic ($g\cong2.004$) showing that it is due to a Pauli type contribution of the conduction electrons of the perylene chains. As in many other molecular metals, this Pauli type contribution is found to be enhanced due to Coulomb correlations (by a factor of $\cong 1.5$) when compared to the one calculated from the bandwidth, 4t, estimated from thermopower. From this enhancement the ratio of the on site Coulomb repulsion to the bandwidth can be estimated as $U/4t \cong 0.5$.

In the cases of the compounds with unpaired electrons in the $M(mnt)_2^-$ units, the EPR lines are significantly broader (30-95 G) [5,11-13]. Furthermore, for the Pt, Ni and Pd compounds, these lines present temperature dependent g-values [11, 13, 17] which are between those of the perylene cation and the $M(mnt)_2^-$ units, denoting the existence of spin exchange between the spins in the two types of chains. It is interesting to remark that in the case of the Fe compound, although the EPR line is wider (32 G at room temperature), it presents g-values ($g\cong2.004$) and intensity temperature dependence quite similar to the observed for the compound with diamagnetic $M(mnt)_2^-$ units. This indicates that this line is only due to the perylene chain spins without evidence for strong spin exchange with the $Fe(mnt)_2^-$ chains.

Additional evidence for interchain coupling between spins was provided by the study of ^1H NMR spin lattice relaxation time[15] in the Pt compound, whose temperature dependence differs substantially from the Au analogue and from traditional one chain

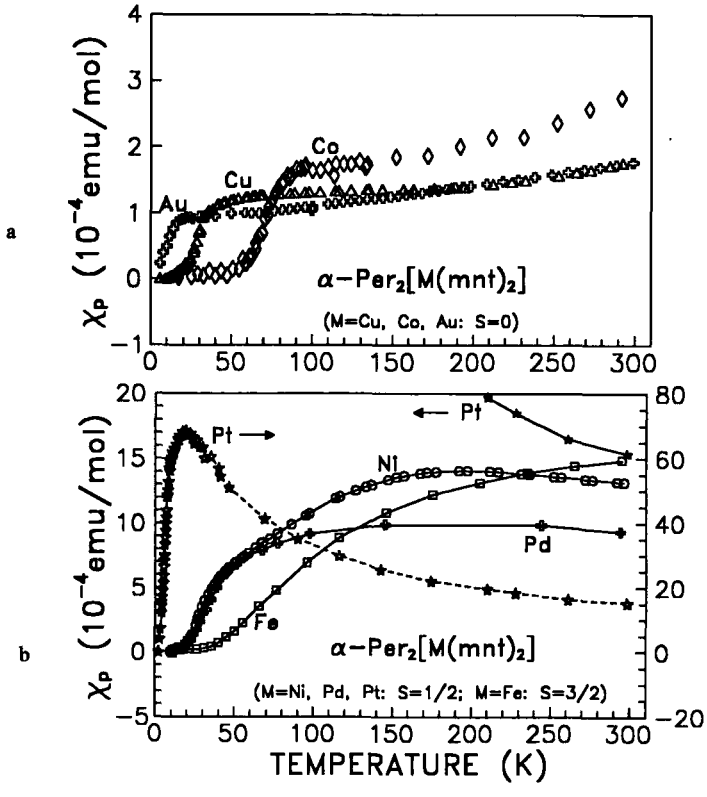

Fig. 3- Paramagnetic susceptibility as a function of temperature for α-Per$_2$M(mnt)$_2$.
a- M= Cu, Au and Co (diamagnetic anionic complexes)
b- M= Ni, Pd, Pt (S=1/2) and Fe (S=3/2) (paramagnetic anionic complexes)

conductors. These results and the above quoted averaging of EPR g-values, underline the possible existence of a RKKY interaction between the localised spins via the exchange coupling to the conduction electrons in the perylene chains. No such evidence exists for the Fe compound in spite of the relaxation being also dominated by dipolar interchain interactions with Fe(mnt)$_2^-$ localised spins [16].

STRUCTURAL ASPECTS AND THE NATURE OF THE PHASE TRANSITIONS.

The first X-ray investigation of the phase transitions in the Au, Pt, Pd compounds [2] showed, for the two latter compounds, that they are associated with a lattice doubling along the chain axis, **b**, having strong 1D precursor effects detected as early as $3T_{MI}$. No signs of any structural effect could be observed in the Au compounds, in which, at that time, a clear M-I transition could not be detected. The doubling of the unit cell was

ascribed to the $M(mnt)_2^-$ chains, explaining in a spin-Peierls fashion the decrease of susceptibility of the Pt salt from a Curie-Weiss behaviour at higher temperatures. At that time it was thought that, due to electronic correlation effects, the M-I transition could be induced on the perylene chains by the dimerisation of the magnetic chains.

Recent work on the Ni, Cu, Fe and Co compounds showed that this picture is not correct. Not only the compounds with diamagnetic $M(mnt)_2^-$ species (M=Cu, Co and Au) showed clear M-I transitions as well, but also the dimerised compounds of Fe and Co were metallic, demonstrating that the dimerisation of the $M(mnt)_2^-$ units alone could not induce a M-I transition on the perylene chains and suggesting that this transition would require the $2k_F$ distortion (tetramerisation) of the perylene chains. More recently this hypothesis has been clearly demonstrated by the X-ray study of Fe, Co and Cu compounds [14, 16] showing that in these cases the transition is due to a tetramerisation ascribed to the perylene chains. In case of the Ni compound, having localised spins in the $Ni(mnt)_2^-$ units, both types of distortions (dimerisation and tetramerisation) could be detected at the transition [14]. However, more probably due to lack of experimental sensitivity, the 1D precursor effects characteristic of a Peierls transition have not been detected so far for the tetramerisation critical wave vector.

Table I- Properties of α-phases of $(Per)_2M(mnt)_2$

M	n	S	σ_{RT} Ωcm^{-1}	S_{RT} μVK^{-1}	T_{MI} K	Tρ K	2Δ meV	Distortions Dim.	Tetram.
Au	8	0	700	32	12	16	3.5		
Cu	8	0	700	38	32	40	20		X
Pt	7	1/2	700	32	8	18	8.6	X *	
Pd	7	1/2	300	32	28	80		X *	
Ni	7	1/2	700	35	25	50	15	X *	X
Co	6	0	200	42	73	160	60	⊗	X
Fe	5	3/2	200	42	58	180	50	⊗	X

n- number of d electrons; S-spin on $M(mnt)_2^-$ unit; T_{MI}- metal insulator transition temperature; Tρ- minimum electrical resistivity temperature; 2Δ- low temperature gap derived from resistivity; X- distortion observed below T_{MI}; *- 1D precursor effects above T_{MI} up to $\cong 3T_{MI}$; ⊗- distortion is present in all the temperature range

In view of these results, summarised in Table I, it is believed that the tetramerisation, ascribed to the perylene chains, is responsible for the M-I (Peierls) transition and its detection was missed in the earlier works on the Au, Pt and Pd compounds, which will

be reinvestigated soon. The dimerisation, is ascribed to the $M(mnt)_2^-$ units with localised magnetic moments (M=Ni, Pd, Pt) and it is due to a spin-Peierls transition coupled to the Peierls transition on the perylene chains. Due to the "chemical" dimerisation of the $Fe(mnt)_2^-$ units, this compound clearly shows, that the tetramerisation transition could also be decoupled from the magnetic chain behaviour.

However the most interesting effect to be explained in this family of compounds, is the exact mechanism of coupling leading to a simultaneous distortion of the two chains in the Ni, Pd and Pt compounds. The magnetic field dependence of the M-I transition temperature for the Pt and Au compounds is similar, both following the same type of law, typical of a Peierls transition [10], in spite of the extra chain of localised S=1/2 spins in case of Pt. This indicates that the role of the magnetic chains in the transition is relatively small. Therefore the interesting feature to understand is how a quasi-1D dimerisation instability in the $M(mnt)_2^-$ chains is induced by a tetramerisation ($2k_F$ instability, on the perylene stacks). A possible mechanism could be based on the observed exchange interaction between the localised and the itinerant spins. A possible coupling between the two entities could be achieved via non-negligible correlation effects on the conducting chains leading to a weak $4k_F$ instability, but detailed theoretical investigation of such a coupling is clearly missing at present. In this respect it is interesting to notice that by comparing the transition temperatures of the different compounds with elements M in neighbouring columns and on the same row of the periodic table, a systematic decrease of T_{MI} is observed whenever the $M(mnt)_2^-$ units is paramagnetic, together with a relative increase of the difference ($T\rho$ - T_{MI}). Specific heat studies of these transitions under a magnetic field, are expected to enlighten this interesting problem.

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