

Modification of the magnetic-field dependence of the Peierls transition by a magnetic chain

Manuel Matos

*Departamento de Química, Instituto Tecnológico e Nuclear, P-2686 Sacavém Codex, Portugal
and Departamento de Química, Instituto Superior de Engenharia de Lisboa, P-1900 Lisboa, Portugal*

Gregoire Bonfait

*Departamento de Química, Instituto Tecnológico e Nuclear, P-2686 Sacavém Codex, Portugal
and Departamento de Física, Faculdade de Ciências e de Tecnologia, Universidade Nova de Lisboa, P-2825, Monte de Caparica,
Portugal*

Rui T. Henriques

*Departamento de Química, Instituto Tecnológico e Nuclear, P-2686 Sacavém Codex, Portugal
and Departamento de Engenharia Química, Instituto Superior Técnico, P-1096 Lisboa Codex, Portugal*

Manuel Almeida

Departamento de Química, Instituto Tecnológico e Nuclear, P-2686 Sacavém Codex, Portugal

(Received 5 June 1996)

The magnetic-field dependence of the metal-to-insulator transition temperature, $T_c(B)$, in the quasi-one-dimensional systems $(\text{Per})_2M(\text{mnt})_2$, with $M=\text{Au}$ and Pt , was studied by magnetoresistance measurements under fields up to 18 T. In the Pt compound, our results show that $T_c(B)$ is anisotropic: $T_c(B)$ decreases as B^2 up to 18 T with a slope similar to that found in the Au compound when the magnetic field is applied parallel to the chain axis, while $T_c(B)$ decreases faster and does not follow a pure B^2 dependence when the magnetic field is applied perpendicular to the chain axis. This anisotropy of the field dependence denotes the coupling of the Peierls transition in the perylene chains to a spin-Peierls-like transition in the $\text{Pt}(\text{mnt})_2^-$ chains, correlated with an anisotropic magnetic susceptibility, while in the Au compound a pure Peierls transition takes place. [S0163-1829(96)08445-7]

I. INTRODUCTION

In the past twenty years the physics of quasi-one-dimensional (1D) solids has experienced significant advancements. Many 1D metals have been studied and quite accurate models to explain their properties, namely the charge and spin density wave instabilities, have been developed. Several one-dimensional magnetic systems have been also studied and the instability of the spin chains toward a lattice distortion, the so-called spin-Peierls instability, is also well known, both theoretically and experimentally in some of these solids. However, the possible situation of solids containing both delocalized conducting chains and localized spin chains in the same lattice is much more rare and their physics has remained almost unexplored.

The molecular compounds $(\text{Per})_2M(\text{mnt})_2$, where Per =perylene and mnt =maleonitriledithiolate with $M=\text{Pt}$ and Au , first prepared more than 15 years ago, are one-dimensional metals undergoing metal to insulator (MI) transitions at low temperatures.¹⁻⁵ These compounds are isostructural and their unit cell contains four equivalent perylene molecules and two $M(\text{mnt})_2^-$ units, both stacking regularly along the \mathbf{b} axis.^{1,5} Their metallic properties are due to the regular stacking of partially oxidized perylene molecules, $(\text{Per})_2^+$, giving rise to a 3/4 filled one-dimensional band.^{3,6} Early since their first studies, it was recognized that, in addition to the delocalized conduction electrons in the perylene stacks, the $M(\text{mnt})_2^-$ units can also have a localized spin

depending on the metal M [e.g., $S=1/2$ for $\text{Pt}(\text{mnt})_2$ and $S=0$ for $\text{Au}(\text{mnt})_2$] and therefore these solids can present unique properties derived from the coexistence in the same structure of magnetic chains and conducting chains.⁶ In the $M=\text{Au}$ compound, the $\text{Au}(\text{mnt})_2^-$ units are diamagnetic ($S=0$) and the magnetic susceptibility is just due to a small Pauli-like contribution (1.7×10^{-4} emu/mole at room temperature)⁶ down to the MI transition [$T_c(0) \approx 12$ K]. In the $M=\text{Pt}$ compound, the magnetic susceptibility is dominated by the much larger contribution of the paramagnetic $\text{Pt}(\text{mnt})_2^-$ units (18×10^{-4} emu/mole at room temperature). This contribution reaches a maximum ($\approx 70 \times 10^{-4}$ emu/mole) between 10 and 20 K and sharply decreases at the temperature where the metal to insulator transition is observed⁷ [$T_c(0) \approx 8$ K]. This last result as well as the results obtained from specific heat measurements⁸ prove that a magnetic order occurs simultaneously with the MI transition indicating a coupling between the two types of chains.

The structural investigation of the transitions in these compounds has been limited by both the low transition temperatures and the relatively small sample dimensions. In the $M=\text{Pt}$ compound ($S=1/2$), one-dimensional precursor effects, as diffuse lines at $\mathbf{b}^*/2$ whose intensity diverges as T_c is approached, have been observed.² These lines have been attributed to a dimerization of the $\text{Pt}(\text{mnt})_2^-$ units, as in a spin-Peierls (SP) transition² and in agreement with the exponential decrease of the magnetic susceptibility below T_c .⁷ A $2k_F$ tetramerization of perylene chains, as expected for a

Peierls transition in a 3/4-filled band, could not yet be observed in these compounds mainly due to the low temperature of the transitions and the small single crystal size. However, from the comparison with other members of this family, namely the Ni and Cu compounds,⁹ it becomes clear that the MI transition is due to a simultaneous tetramerization of the Perylene chains and a dimerization of the $M(\text{mnt})_2$ units.⁶ Further evidence of a CDW transition in these compounds has been provided by the nonlinear transport observed below their transitions.^{10,11} The competitions effects between the Peierls and SP mechanisms as well as the origin of the coupling between the two types of chains in these solids, i.e., why and how they both experience different wave vector distortions at the same critical temperature, have remained so far unclear.

In this paper, we address the study of these transitions by magnetoresistance and namely by the determination of the magnetic field dependence of the MI transition temperature under fields up to 18 T. As already denoted in our previous measurements,⁵ the rather low temperature at which occurs the Peierls transition in the Au compound provides an rare opportunity for an experimental study of the behavior of such a transition over a large range of $\mu_B B/kT_c(0)$ [for $T_c(0)=12$ K, $\mu_B B/kT_c(0)\approx 1$ for $B=18$ T, μ_B : magnetic moment of the conduction electrons]. The first measurements up to 8 T showed a similar field dependence for T_c in the Pt and Au compounds.⁵ More recently, we reported measurements in the Au compound up to 18 T providing the first experimental measurements of a Peierls transition under such a high magnetic field.¹² However, since in the Pt compound, the $\text{Pt}(\text{mnt})_2$ magnetic chains are coupled to the perylene conducting chains, the $T_c(B)$ is expected to present under higher magnetic fields a different behavior, similar to that of the SP transition as experimentally studied in TTF-MBDT ($M=\text{Au}$ and Cu) and MEM(TCNQ)₂,¹³ or even to present a possible decoupling of the different transitions in the two types of chains. In this paper the study of the Pt compound under fields up to 18 T is reported and compared to the Au analogue. At variance with the Au compound, the field dependence of T_c in the Pt compound is anisotropic and present a complex behavior at high field.

II. EXPERIMENT

The needle shaped $(\text{Per})_2\text{Pt}(\text{mnt})_2$ single crystals used in this work, with typical dimensions $5\times 0.5\times 0.01$ mm³, were obtained by electrocrystallisation using galvanostatic conditions in a standard procedure for these materials.¹

Electrical resistivity measurements were performed with the current flowing along the **b** axis, corresponding to the needle long axis and by the usual four probes technique; four 25 μm gold wires, used as current and voltage leads, were attached with platinum paint (Demetron 308 A) to four evaporated gold pads covering all sides around the crystal. The electrical resistivity was measured at low frequency (17 Hz) using currents in the range 1–100 μA and the voltage was measured with a lock-in amplifier. Samples with un-nested to nested voltage ratio, as defined by Schaffer *et al.*,¹⁴ larger than 5% were rejected. Measurements were performed in a helium cryostat equipped with a 18 T superconducting magnet, the samples being in exchange gas. By rotation of

the sample holder, the results were obtained, in the same samples, for the **b** axis either parallel or perpendicular to the magnetic field **B**. For the perpendicular configuration it was not possible to ascribe a precise orientation of the magnetic field in the (**a,c**) plane. However possible anisotropy effects in the (**a,c**) plane were tested by 90° sample holder rotation around the **b** axis.

Due to the low temperature range of the measurements and the high magnetic fields used, special care was dedicated to the thermometry. Both a calibrated carbon glass resistance and a capacitance thermometer were used. The latter one is virtually field independent but exhibits relaxation phenomena at low temperature leading to a poor reproducibility over an extended temperature or time range. On the other hand, the carbon glass resistance, much more reproducible, presents a magnetic field dependence not negligible in respect to the expected temperature shifts. In order to overcome these two limitations, the procedure previously described¹² was followed. Before each measurement of a $\rho(T)$ curve under magnetic field, a few thermal cycles with amplitudes of 2 K above and below the transition were made under zero field in order to ensure minimum capacitance drifts. In the last cycle (cycle I) the capacitance C was calibrated as a function of the temperature T , determined by the carbon glass thermometer. Then the magnetic field was raised to the desired value and the electrical resistivity $\rho(C)$ were recorded during a similar thermal cycle (cycle II) together with the capacitance C . Finally the field was removed and during a third thermal cycle (cycle III) the capacitance $C(T)$ was again calibrated as a function of the temperature given by the carbon glass thermometer. If the two calibrations $C(T)$ obtained during the cycles I and III showed no significant differences (less than 50 mK) their data was used to determine the temperature in the $\rho(C)$ measurements of cycle II.

The magnetization of several crystals bounded along their **b** axis (needle direction) was measured in a SQUID magnetometer under a magnetic field of 1 T either in the **B**||**b** or **B**⊥**b** configurations.

III. RESULTS AND DISCUSSION

As shown in Fig. 1 for the **B**||**b** configuration, the temperature dependence of the electrical resistivity measured along the **b** axis of a $(\text{Per})_2\text{Pt}(\text{mnt})_2$ crystal, under different magnetic fields, clearly denotes a large magnetic field dependence of the MI transition temperature. As usual in this type of transition, the transition temperature, $T_c(B)$, is defined by the maximum in the derivative $d \log \rho/d(1/T)$. This maximum, although tending to become less pronounced under larger magnetic fields, is much sharper than in the Au samples¹² and, as shown in the inset to the Fig. 1, it clearly shifts to lower temperatures as the magnetic field is increased.

The transition temperatures determined in this way for the different configurations and in two samples under fields up to 18 T are displayed in Fig. 2. For the parallel configuration the transition temperature shift, $\Delta T_c/T_c = [T_c(B) - T_c(0)]/T_c(0)$, is proportional to B^2 up to 18 T, with the same slope for the two samples. For the **B**⊥**b** configuration, $T_c(B)$ decreases faster than in the **B**||**b** configuration. From the crystal shape, we were not able to specify the orientation

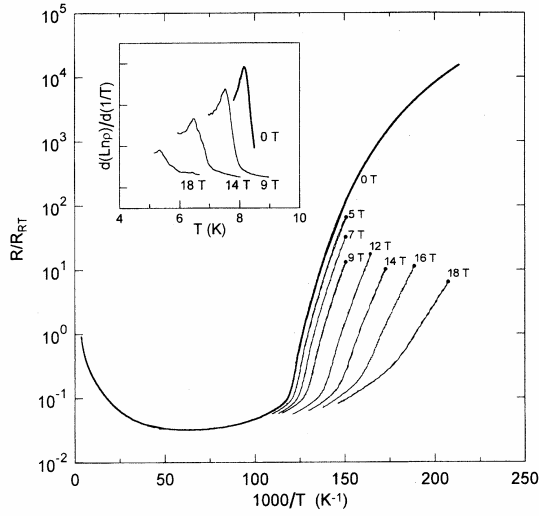


FIG. 1. Electrical resistivity of $(\text{Per})_2\text{Pt}(\text{mnt})_2$ ($I \parallel \mathbf{b}$, $\mathbf{B} \parallel \mathbf{b}$), normalized to the room temperature value R_{RT} , as a function of the reciprocal temperature and under different magnetic fields (indicated on the figure). The inset shows the logarithmic derivative of the resistivity, $d \ln \rho d(1/T)$, with the maximum used to define $T_c(B)$.

of the magnetic field in the (\mathbf{a}, \mathbf{c}) plane, referred in the figures as α . However, a significant anisotropy of $T_c(B)$ towards the magnetic field orientation in the (\mathbf{a}, \mathbf{c}) plane is demonstrated by the two different curves obtained with the same sample

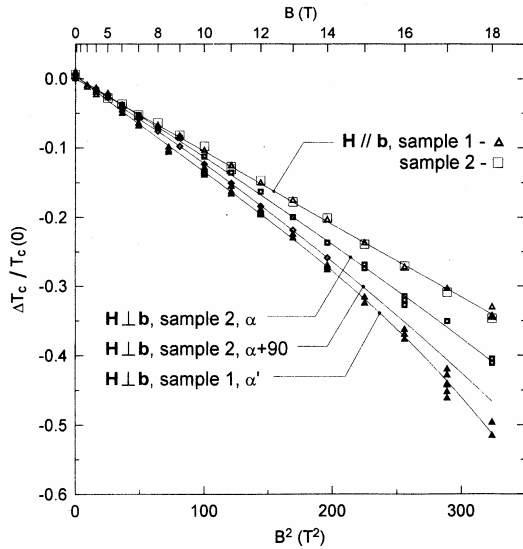


FIG. 2. Transition temperature shift, $\Delta T/T_c = [T_c(B) - T_c(0)]/T_c(0)$, plotted as a function of B^2 for different $(\text{Per})_2\text{Pt}(\text{mnt})_2$ samples and configurations. For sample 2 in the $\mathbf{B} \perp \mathbf{b}$ configuration, two sets of measurements with a 90° degree rotation of the sample holder around the \mathbf{b} axis (α angle) are shown. The lines are guides to the eye.

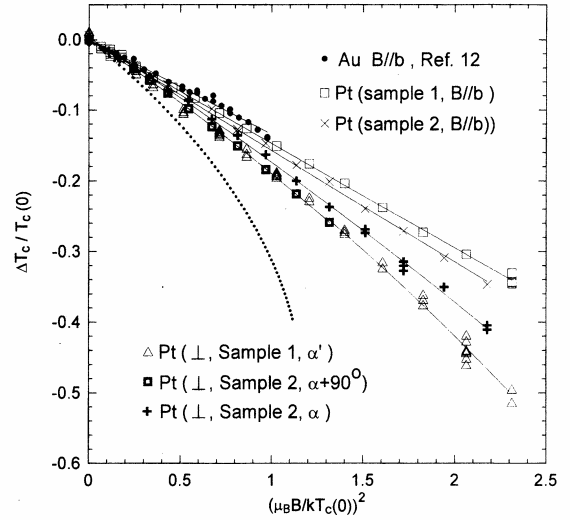


FIG. 3. Comparison of the MI transition temperature shift, $\Delta T/T_c(0)$, in $(\text{Per})_2\text{Pt}(\text{mnt})_2$ and $(\text{Per})_2\text{Au}(\text{mnt})_2$ using reduced units [$T_c(0) \cong 8.2$ and 12.2 K, respectively]. This figure illustrates the identical field dependence of $T_c(B)$ for the Au (in the parallel and perpendicular configuration) and for the Pt samples in the parallel configuration. The dotted line is Eq. (1) and the solid lines are guides to the eye.

rotated 90° around the \mathbf{b} axis (sample 2, $\mathbf{B} \perp \mathbf{b}$, α and $\alpha + 90^\circ$). This result indicates that the different field dependencies of T_c for samples 1 and 2 are due to a different orientations of \mathbf{B} in the (\mathbf{a}, \mathbf{c}) plane. It is also worth noting that while for the $\mathbf{B} \parallel \mathbf{b}$ configuration $T_c(B)$ varies proportionally to B^2 in the whole field range, for the transverse configuration, a more complex behavior is followed above 12 T.

These results in the Pt compound contrast with those found for the Au analogue, where the field dependence is isotropic.¹² A comparison between the field dependence of transition in the two compounds is made in Fig. 3, where the results $\Delta T_c(B)/T_c(0)$ are plotted in reduced units of magnetic field, $\mu_B B/kT_c(0)$. There it becomes evident that the main differences are observed for the $\mathbf{B} \perp \mathbf{b}$ configuration, while for $\mathbf{B} \parallel \mathbf{b}$ the behavior of the two compounds is quite similar.

These results should be compared with the theoretical predictions for both a Peierls and a SP transition under magnetic field as well as with experimental data in a few SP systems. Within the mean field approximation and taking into account the Zeeman energy of the spin-up and spin-down energy bands, the following magnetic field dependence of the Peierls transition temperature was obtained by Dietrich and Fulde:¹⁵

$$\ln[T_c(0)/T_c(B)] = \text{Re}\{\psi[1/2 + i\mu_B B/2\pi kT_c(B)]\} - \psi(1/2), \quad (1)$$

where $\psi(x)$ is the digamma function. For low fields [$\mu_B B \ll 2\pi kT_c(0)$], this gives a relation linear in B^2 as first applied to TTF-TCNQ.¹⁶

$$\begin{aligned} \Delta T(B)/T_c(0) &= [T_c(B) - T_c(0)]/T_c(0) \\ &= -\gamma[\mu_B B/k_B T_c(0)]^2, \end{aligned} \quad (2)$$

TABLE I. Summary of the low field behavior of $T_c(B)$ in the Au and Pt compounds. The γ_{expt} is obtained by a fit of Eq. (2) to the experimental data for $B \leq 10$ T. γ_{th} is the value predicted by Eq. (1) at low field ($\gamma_{\text{th}}=0.21$).

Sample (Ref.)	Configuration	γ_{expt} (Experimental, $B < 10$ T)	$(\gamma_{\text{expt}} - \gamma_{\text{th}})/\gamma_{\text{th}}$
Au (Ref. 12)	\parallel and \perp	0.135 ($B \leq 18$ T)	-0.36
Pt 1 (This work)	\parallel	0.147	-0.30
Pt 2 (This work)	\parallel	0.157	-0.25
Pt 1 (This work)	\perp	0.190	-0.10
Pt 2 (This work)	\perp, α	0.166	-0.21
Pt 2 (This work)	$\perp, \alpha + 90^\circ$	0.185	-0.12
Pt (Ref. 5)	\perp	0.21	
Pt (Ref. 26)	\perp	0.21	

with $\gamma \approx 0.21$. For higher fields, higher order terms must be added to this last equation.

For a SP transition, the problem becomes formally equivalent to the Peierls transition^{13,17} by converting the localized spin operators to pseudofermions operators. In the same mean field approximation, the field dependence of the transition temperature is given by Eq. (1) in which $\mu_B B$ must be replaced by the Fermi level of the pseudofermions band, ε_F , measured from the center of the band.¹⁷ In lower order of field, for $g=2$ and $S=1/2$, $\varepsilon_F = -1.44\mu_B$.^{17,18} Then Eq. (1) gives a field dependence of $T_c(B)$ twice that predicted above in the same approach for a Peierls system. For both types of transition, a quadratic dependence of $T_c(B)$, like Eq. (2), is expected at low fields and a faster dependence given by Eq. (1), or its corresponding one for the spin Peierls, should be observed at higher fields (dotted lines of Fig. 3). A change of the wave vector of the distortion, with possible discommensuration phenomena, are also expected to take place in the high field regime.¹⁹ While for Peierls systems, besides $(\text{Per})_2\text{Au}(\text{mnt})_2$ there are no clear data on the field dependence of the transition temperature, in a few SP systems as in TTF-MBDT (with $M=\text{Au}$ and Cu)^{20,21} and MEM(TCNQ)₂,²² Eq. (2) has been used to fit experimental data with success.^{13,23}

For the Pt compound in the $\mathbf{B}\parallel\mathbf{b}$ configuration, as well as for the Au compound in the two configurations, the results gives the B^2 dependence as predicted by Eq. (2) but with a slope γ significantly smaller (see Table I) than the expected value. The observed γ value smaller than the prediction could be explained by the strong fluctuation effects existing in quasi-1D systems. For instance, $T_c(0)$ as $T_c(B)$ in Eq. (1) and Eq. (2) are mean field values which, due to fluctuations, are expected to be larger²⁴ than the actual transition temperature as defined by the maximum in the derivative $d \log \rho/d(1/T)$.^{12,25} Such type of corrections are not unexpected in these compounds since the fluctuations are known to be of major importance, as clearly denoted by the large temperature range between the minimum resistance temperature (circa 17 and 16 K for the Au and Pt compounds, respectively) and the actual transition temperature. For some perpendicular configurations (sample 1, and sample 2, $\alpha+90^\circ$), the initial slopes γ_{expt} are found significantly higher than in the parallel configuration and not so far of the theoretical prediction in the low field range (Fig. 4). These configurations correspond probably to configurations closed to

that of Ref. 5 in which Eq. (2) was found in agreement with the experimental results. Equation (2) is then found in quantitative agreement with the experimental results only in some special perpendicular configurations in the Pt compound and never in the Au compound or in the Pt compound in the parallel configuration.

For the Pt compound at 18 T, the value of the argument of Eq. (1) reaches 1.5 and therefore the full Eq. (1) should be used (dotted lines of Figs. 3 and 4): However, this equation cannot fit the experimental data in the high field regime, predicting a curvature much higher than observed. Equation (1) was recently claimed to agree with the magnetic field dependence of the transition temperature in $(\text{Per})_2\text{Pt}(\text{mnt})_2$ obtained by high frequency conductivity measurements

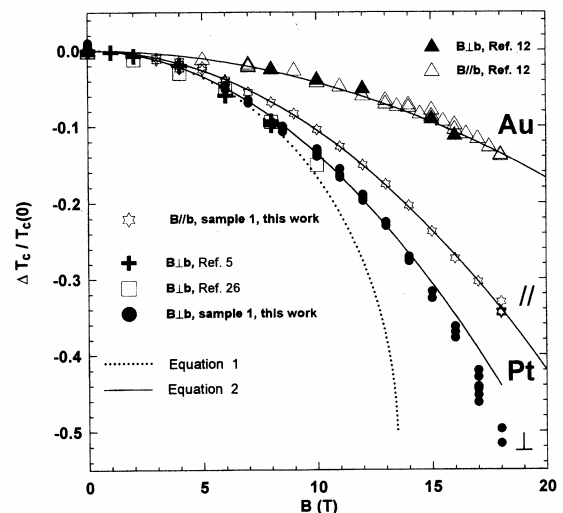


FIG. 4. Transition temperature shift, $\Delta T/T_c(0)$, as a function of the magnetic field in order to clarify the low field behavior. The triangles are experimental data of Ref. 12 obtained on the Au compound (closed triangle: $\mathbf{B}\perp\mathbf{b}$; open triangles: $\mathbf{B}\parallel\mathbf{b}$). The other symbols represent the results obtained on Pt samples in this work and the results of Refs. 5 and 26. The solid lines represent the \mathbf{B}^2 behavior [Eq. (2)] with the γ_{expt} of Table I. The dotted line represents Eq. (1).

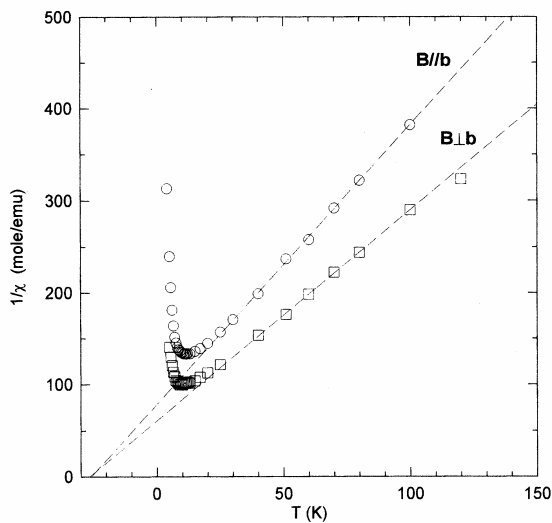


FIG. 5. Inverse magnetic susceptibility, χ^{-1} , of $(\text{Per})_2\text{Pt}(\text{mnt})_2$ single crystals with the field parallel (\parallel) and perpendicular (\perp) to the chain axis \mathbf{b} as a function of temperature T .

along the \mathbf{b} axis under smaller fields (up to 10 T)²⁶ applied perpendicular to this axis. As shown on the Fig. 4, measurements up to 10 T with the accuracy obtained in this experiment are not enough to clearly distinguish between Eq. (1) (dotted line) and a pure B^2 dependence of $T_c(B)$ (solid lines) as in Eq. (2). Our results demonstrate that the $T_c(B)$ behavior obtained in that work, equal to that of Ref. 5, agrees with Eq. (2) as a result of a special perpendicular configuration and of the anisotropy in the (\mathbf{a}, \mathbf{c}) plane.

Besides the importance of the fluctuations neglected in the above mean field model, it is clear that it cannot explain the $T_c(B)$ anisotropy found for the Pt compound. Magnetization measurements in SP systems^{13,23} indicate a field dependence of $T_c(B)$ in agreement with the above model, i.e., about twice faster than that predicted for a Peierls system. Therefore it is tempting to ascribe the faster and anisotropic field dependence of the MI transition temperature in the Pt compound to a coupling of the perylene conducting chains to the magnetic $\text{Pt}(\text{mnt})_2$ chains that enter a SP state below T_c . The anisotropy of the magnetization was measured in the Pt compound and the results, shown in Fig. 5, support this picture.

In the magnetization measurements of several $(\text{Per})_2\text{Pt}(\text{mnt})_2$ crystals aligned, either for the $\mathbf{B}\parallel\mathbf{b}$ or $\mathbf{B}\perp\mathbf{b}$ configurations, the MI transition is associated with an anomaly, as a knee at T_c , followed by an exponential decrease upon cooling that is typical of the SP systems.^{7,13,23} At higher temperatures, the data follow a Curie-Weiss law with the same Curie temperature ($\cong 25$ K) for both configurations (Fig. 5). However, an anisotropy is observed corresponding to a Curie constant 30% smaller for the $\mathbf{B}\parallel\mathbf{b}$ configuration, for which a smaller field dependence of $T_c(B)$ is observed. This result is in agreement with the specific data above T_c which were not described by the isotropic Heisenberg Hamiltonian.⁸

While in the organic based SP systems so far studied, as MEM(TCNQ)₂ or TTF-MBDT (with $M=\text{Au}$ and Cu), the magnetic susceptibility was found essentially isotropic,¹³ the

inorganic SP system CuGeO_3 , more recently studied, presents a significant magnetic anisotropy²⁷ due to the g factor,²⁸ leading to an anisotropic field dependence of the SP transition temperature in agreement with Eq. (2), taking into account the field dependence of the Fermi level.¹⁷ In our case, the anisotropy of the Curie constant (30%) would lead to 70% change of the slope between the two configurations, which is clearly too high to explain the $T_c(B)$ anisotropy.

The fact that the field dependence of the transition temperature in the Au compound, in which there is no chain of localised spins, is approximately the same than that in the $(\text{Per})_2\text{Pt}(\text{mnt})_2$ for the parallel configuration, indicates that the main driving force for the transition in these two compounds is the e -phonon interaction in the perylene chains. For the Au compound, no anisotropy effects in the magnetic field dependence of the transition temperature were detected, and therefore the anisotropy effects for $T_c(B)$ in the Pt compound must be ascribed to the magnetic chains. The stronger field dependence of T_c , for $\mathbf{B}\perp\mathbf{b}$, is probably a consequence of the larger magnetic susceptibility along this direction and the observed anisotropy of the field dependence of $T_c(B)$ in the (\mathbf{a}, \mathbf{c}) plane (α and $\alpha+90^\circ$ configurations) also corresponds to a magnetic anisotropy in this plane.

In other words, to describe the transitions in these quasi-one-dimensional compounds, two kinds of terms, corresponding to the two different chains, must be used in the free energy. The first one describes the conduction electron energy with the e -phonon energy, leading to the Peierls transition, and, under magnetic field, the Zeeman energy of the conduction bands which modifies the Peierls transition temperature. In the Au compound, only this kind of term exists and a more careful treatment could explain the slope smaller than calculated by mean field theory. The second kind of terms describes the localized spins energy with the exchange interaction ($\approx -\sum J_{i,i+1} \mathbf{S}_i \cdot \mathbf{S}_{i+1}$) and the Zeeman energy ($\approx -\sum g \mu_B \mathbf{S}_i \cdot \mathbf{H}$). This second kind of terms leads to the SP transition and its dependence under magnetic field. In the Pt compound, the two kinds of terms exist and the evolution of their respective weights on an increase of the magnetic field must be taken into account. As already mentioned, the fact that the low field slope γ for the Pt compound varies only between 10% ($\mathbf{B}\parallel\mathbf{b}$) and 40% ($\mathbf{B}\perp\mathbf{b}$) in respect to the Au compound shows that the first kind of terms is dominant and the localized spins chains acts as a perturbation leading to the higher slope. Therefore, the SP state of the magnetic chain is a consequence of the distortion of the conducting chain. This result is coherent with the similar transition temperature for the two compounds. An alternative explanation would require the two kinds of chains to have independently the same transition (Peierls or SP) temperature, which is very unlikely. At higher fields, the problem is more complex. The effect of the magnetic chain on the instability increases as shown by the emergence of an anisotropic dependence of $T_c(B)$. Under high magnetic field, the Zeeman energy of the localized spins can become rapidly comparable with the exchange energy, and the spin-Peierls state is progressively modified or destroyed, leading, for instance, to the so-called "intermediate state" as in the canonical SP compounds.^{13,23} In $\text{Per}_2(\text{Pt})\text{mnt}_2$, this modification of the magnetic chain can induce some consequences on the distortion of the adjacent perylene chains: the Peierls state is modified and with it, the

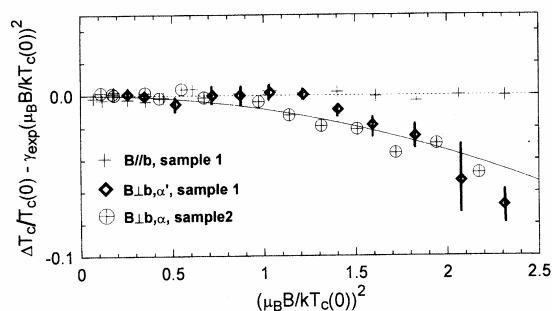


FIG. 6. Differences between the experimental results and Eq. (2): These data are obtained by subtracting from the mean experimental results of $\Delta T_c/T_c(0)$ the term $-\gamma_{\text{exp}}[\mu_B B/kT_c(0)]^2$ fitted for $B < 10$ T (cf. Table I).

temperature dependence of the Peierls transition. In the framework of this description, it is natural to obtain stronger effects of the magnetic field when it is applied along a direction of higher susceptibility ($\mathbf{B} \perp \mathbf{b}$). When the field is applied parallel to the \mathbf{b} axis, the effect of the magnetic field on the localized spins is smaller and a higher magnetic field would be necessary to modify significantly the magnetic and conducting chains and, consequently, the B^2 law.

If our explanation is correct, it is not simple to obtain the theoretical $T_c(B)$ law. However, it is clear that two regimes will be obtained: a low field regime where the Peierls mechanism is dominant and an high field regime where the magnetic chains strongly affect the Peierls state. In order to characterize this crossover, we display in Fig. 6 the difference between the $\Delta T_c(B)/T_c(0)$ experimentally measured on all the magnetic field range and the low field behavior [$\Delta T_c/T_c(0) = -\gamma(\mu_B B/kT_c(0))^2$, γ given by Table I]. In spite of the error bars of our data, this figure suggest that the $T_c(B)$ behavior is badly described by a simple additional fourth order term (solid lines on Fig. 6). In agreement with our previous considerations, a new regime seems to appear for $\mu_B B/kT_c(0) > 1$. Let us note that this description does not explain why, for the Pt compound in the parallel configuration, a B^2 behavior is followed on such extend range of

magnetic field. It is not clear if this behavior is induced by the interaction between the two kinds of chain and therefore characteristic of $(\text{Per})_2\text{Pt}(\text{mnt})_2$ or is specific to the Peierls transition.

IV. CONCLUSION

By measurements of the electrical resistivity of $(\text{Per})_2M(\text{mnt})_2$ ($M = \text{Au}$ and Pt) compounds in high fields, we showed that the magnetic field dependence of the Peierls transition is not yet fully understood. For the Au compound, the B^2 dependence predicted by mean field approach is followed up to $\mu_B B/kT_c(0) \approx 1$ but with a slope almost twice smaller than expected. For the Pt case and for B parallel to the chain axis, the B^2 dependence, with the same discrepancy on the value of the slope γ , subsists up to $\mu_B B/kT_c(0) \approx 1.3$ in clear contradiction with Eq. (1). A more careful treatment of the effects neglected above, such as fluctuations, electron-electron interactions or possible discommensuration, should be dedicated to this problem to allow a complete description of the Peierls transition behavior under high magnetic field.

At low magnetic field, the slope γ for the Pt ($S=1/2$) compound in the $\mathbf{B} \parallel \mathbf{b}$ configuration is almost equal to that of the Au compound (diamagnetic), and we take this result as a proof that the SP state of the magnetic chain is induced by the distortion of the whole lattice due to the Peierls transition of the conducting chain. The $T_c(B)$ anisotropy ($\leq 30\%$) measured in our experiment gives the order of magnitude of the perturbation caused by the magnetic chain on the Peierls mechanism. At high magnetic field, the coupling of the localized spins to the magnetic field becomes important in respect to the exchange energy and to the e -phonon energy and the Peierls state is modified as shown by the stronger dependence of $T_c(B)$. Our results suggest that this crossover occurs for $\mu_B B/kT_c(0) \approx 1$.

ACKNOWLEDGMENTS

We thank Margarida Godinho for the access to the SQUID used at the Faculdade de Ciências da Universidade de Lisboa. This work was partially supported by JNICT under Contract No. PRAXIS/2/2.1/QUI/203/94.

- ¹L. Alcácer, H. Novais, F. Pedroso, S. Flandrois, C. Coulon, D. Chasseau, and J. Gaultier, *Solid State Commun.* **35**, 945 (1980).
- ²R. T. Henriques, L. Alcácer, J. P. Pouget, and D. Jérôme, *J. Phys. C* **17**, 5197 (1984).
- ³R. T. Henriques, M. Almeida, M. J. Matos, L. Alcácer, and C. Bourbonnais, *Synth. Met.* **19**, 379 (1987).
- ⁴A. Domingos, R. T. Henriques, V. Gama, M. Almeida, A. Lopes Vieira, and L. Alcácer, *Synth. Met.* **27**, B411 (1988).
- ⁵G. Bonfait, E. B. Lopes, M. J. Matos, R. T. Henriques, and M. Almeida, *Solid State Commun.* **80**, 391 (1991).
- ⁶V. Gama, R. T. Henriques, G. Bonfait, M. Almeida, S. Ravy, J. P. Pouget, and L. Alcácer, *Mol. Cryst. Liq. Cryst.* **234**, 171 (1993).
- ⁷C. Bourbonnais, R. T. Henriques, P. Wzietek, D. Kongeter, J. Voiron, and D. Jérôme, *Phys. Rev. B* **44**, 641 (1991).
- ⁸G. Bonfait, M. J. Matos, R. T. Henriques, and M. Almeida, *J. Phys. IV (Paris)* **3**, 251 (1993).

- ⁹V. Gama, R. T. Henriques, M. Almeida, and J. P. Pouget, *Synth. Met.* **56**, 1677 (1993).
- ¹⁰E. B. Lopes, M. J. Matos, R. T. Henriques, M. Almeida, and J. Dumas, *Europhys. Lett.* **27**, 241 (1994).
- ¹¹E. B. Lopes, M. J. Matos, R. T. Henriques, M. Almeida, and J. Dumas, *Phys. Rev. B* **52**, R2237 (1995).
- ¹²G. Bonfait, M. J. Matos, R. T. Henriques, and M. Almeida, *Physica B* **211**, 297 (1995).
- ¹³J. W. Bray, L. V. Interrante, I. S. Jacobs, and J. C. Bonner, in *Extended Linear Chain Compounds* edited by J. S. Miller (Plenum, New York and London, 1983), Vol. 3.
- ¹⁴P. E. Schaffer, F. Wudl, G. A. Thomas, J. P. Ferraris, and D. O. Cowan, *Solid State Commun.* **14**, 347 (1974).
- ¹⁵W. Dietrich and P. Fulde, *Z. Phys.* **265**, 239 (1973).
- ¹⁶T. Tiedje, J. F. Carolan, A. J. Berlinsky, and L. Weiler, *Can. J. Phys.* **53**, 1593 (1975).

- ¹⁷J. W. Bray, *Solid State Commun.* **26**, 771 (1978).
- ¹⁸ μ_B represents the magnetic moment of a conduction electron and μ represents the magnetic moment of a localized spin. Nevertheless, in the case of the Pt compound, $S=1/2$ and $g=2$ for the localized spins, therefore μ_B and μ are equal and the same reduced variable $\mu_B B/kT_c(0)$ can be used for the two transitions in spite of their different origins.
- ¹⁹D. Zanchi, A. Bjelis, and G. Montambaux, *Phys. Rev. B* **53**, 1240 (1996).
- ²⁰J. A. Nortby, H. A. Gorenendijk, L. de Jongh, J. C. Bonner, I. S. Jacobs, and L. V. Interrante, *Phys. Rev. B* **25**, 3215 (1982).
- ²¹D. Bloch, J. Voiron, J. C. Bonner, J. W. Bray, I. S. Jacobs, and L. V. Interrante, *Phys. Rev. Lett.* **44**, 2049 (1984).
- ²²D. Bloch, J. Voiron, J. W. Bray, I. S. Jacobs, J. C. Bonner, and J. Kommandeur, *Phys. Lett.* **28A**, 21 (1981).
- ²³D. Bloch, J. Voiron, and L. J. de Jongh, in *High Field Magnetism*, edited by M. Date (North-Holland, Amsterdam, 1983), p. 19.
- ²⁴D. C. Johnston, *Phys. Rev. Lett.* **52**, 2049 (1984).
- ²⁵P. H. Nguten, G. Paasch, W. Brüttig, and W. Riess, *Phys. Rev. B* **49**, 5172 (1984).
- ²⁶S. Allen, J.-C. Piéri, C. Bourbonnais, M. Poirier, M. Matos, and R. T. Henriques, *Europhys. Lett.* **32**, 663 (1995).
- ²⁷M. Hase, I. Terasaki, and K. Uchinokura, *Phys. Rev. Lett.* **70**, 3651 (1993).
- ²⁸K. Uchinokura, M. Hase, and Y. Sasago, *Physica B* **211**, 175 (1995).