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# Nuclear and electronic resonance approaches to magnetic and lattice fluctuations in the two-chain family of organic compounds (perylene)$_2$[$M$(S$_2$C$_2$(CN)$_2$)$_2$] ($M$=Pt,Au)

C. Bourbonnais
*Laboratoire de Physique des Solides, Université de Paris–Sud, Bâtiment 510, Orsay, F-91405, France*
*and Centre de Recherche en Physique du Solide, Département de Physique, Université de Sherbrooke, Sherbrooke, PQ, Canada J1K 2R*

R. T. Henriques
*Laboratoire de Physique des Solides, Université de Paris–Sud, Bâtiment 510, Orsay, F-91405, France*
*and Laboratório Nacional de Engenharia e Tecnologia Industrial, Departamento de Química, P-2685 Sacavém, Portugal*

P. Wzietek and D. Köngeter
*Laboratoire de Physique des Solides, Université de Paris–Sud, Bâtiment 510, Orsay, F-91405, France*

J. Voiron
*Laboratoire Louis Néel, Centre National de Recherche Scientifique, 166X, F-38042 Grenoble CEDEX, France*

D. Jérôme
*Laboratoire de Physique des Solides, Université de Paris–Sud, Bâtiment 510, Orsay, F-91405, France*

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In this work we present and analyze the temperature dependence of the $^1$H nuclear-spin-lattice relaxation rate and of the magnetic susceptibility of the two-chain organic compound (Per)$_2$[Pt(mnt)$_2$]. [Here, "Per" is perylene; "mnt" stands for maleonitriledithiolate, which is the same as *cis*-(2,3-dimercapto-2-butenedinitrile).] The analysis confirms the existence of localized spins on the Pt(mnt)$_2$ chains and their dominant influence on the relaxation through an interstack dipolar coupling. A scaling relation of the form $T_1^{-1} \propto T\chi_s(T)$ is found to exist in the entire temperature domain, including the regime of one-dimensional spin-Peierls Pt(mnt)$_2$ lattice fluctuations observed by x-ray experiments below 30 K. The magnetic-field dependence of the relaxation is also found to qualitatively agree with one-dimensional spin diffusion which is cut off in the low-field region. A comparison is made to data obtained for (Per)$_2$[Au(mnt)$_2$], which have a completely different $T_1^{-1}$ temperature dependence. This is demonstrated to be a characteristic of itinerant electrons. Finally we analyze the existing EPR data on (Per)$_2$[Pt(mnt)$_2$] and show that the observed low-temperature linear temperature profile of the EPR linewidth results from the existence of an exchange coupling between the itinerant and the localized spins of different stacks. Similar conclusions previously made for Per$_2$[Pd(mnt)$_2$] allow one to study such two-chain compounds as realizations of a one-dimensional Kondo lattice. We discussed several puzzling questions raised by the analysis concerning possible mechanisms that can lead to a spin-Peierls distortion.

## I. INTRODUCTION

Among the large variety of organic conductors, the family based on perylene and some metal *bis*-dithiolates has gotten its own reputation due to the possibility of having a metal-like conductivity over a wide temperature range in the presence of a stack of localized magnetic moments. This occurs within the series of compounds (Per)$_2$[$M$(mnt)$_2$], where "Per" is perylene, "mnt" stands for maleonitriledithiolate, a common name for the ligand *cis*-(2,3-dimercapto-2-butenedinitrile), and $M$ is a transition metal (Pt,Au,Pd,Ni,Cu,Fe,Co), for several members of the series (e.g., $M$=Pt,Pd).[1]

The consequences of this particular feature for the electronic properties related to the Fermi level and the role that they play in the one-dimensional instabilities that occur in organic conductors can be revealed by a comparison with isostructural systems with diamagnetic counterions (e.g., $M$=Au). The first assertion that can be made is that the transport properties do not differ substantially for (Per)$_2$[Pt(mnt)$_2$] or (Per)$_2$[Au(mnt)$_2$], as both present identical room-temperature values for the electrical conductivity, typically $\sigma = 700\ \Omega^{-1}\ \mathrm{cm}^{-1}$, and for the thermoelectric power, $S = 32\ \mu\mathrm{V\,K}^{-1}$, indicating that they are primarily governed by the band parameters due to the perylene stacking.[2,3] On the contrary, the x-ray study revealed lattice instabilities of one-dimensional character for the Pd and Pt compounds and none for (Per)$_2$[Au(mnt)$_2$].[2] In agreement with this observation, the temperature dependence of the electrical resistivity of the Au compound evolves from the metallic regime to a situation with a negative temperature derivative through a broad minimum, whereas for the Pt and Pd compounds, well-defined metal-to-insulator transition temperatures of 7 and 28 K, respectively, can be ascribed by sharp anomalies in the derivative $d\ln\rho/dT$. The transition temperature for $(\mathrm{Per})_2[\mathrm{Pt(mnt)}_2]$ was not attained at the time of the x-ray diffuse scattering experiment, but for the Pd compound condensation of Bragg satellites is observed at the same temperature, at half distance between the main reflexions along the stacking direction **b**.

The microscopic mechanism for these transitions cannot be simply described within the framework of electron-phonon coupling (Peierls) or spin-phonon coupling (spin-Peierls), as discussed previously.[4] Besides the role played by lattice instabilities, spin-exchange interactions between the perylene and the $\mathrm{Pt(mnt)}_2$, put into evidence by EPR experiments[1,5] must also be considered. In other organic conductors with arrays of localized moments coupled to itinerant electrons, such as the copper phthalocyanine iodide[6] or the copper triazatetrabenzporphyrinato iodide,[7] the exchange interaction play an important role in their singular properties. The theory developed thereby[8] is not, however, applicable to the present case as lattice instabilities are also present.

As we faced a somewhat singular situation, we decided to make use of the NMR spin-lattice relaxation time ($T_1$) experimental tool, which proved to be useful for getting information about the electronic correlations that are involved in organic conductors that undergo phase transitions.[9] The pair of isostructural compounds with $M$=Pt and Au in the series $(\mathrm{Per})_2[M(\mathrm{mnt})_2]$ was chosen because the first contains chains of local moments and the second does not. In both, the studied nucleus with spin-$\frac{1}{2}$ $^1H$ belongs only to the perylene moieties, whose stacking are mainly responsible for the conducting properties of the compounds.

## II. EXPERIMENTAL RESULTS

The magnetic susceptibility of $(\mathrm{Per})_2[\mathrm{Pt(mnt)}_2]$ was measured on a powder sample of 100 mg using a vibrating sample magnetometer, under a static magnetic field of 70.5 kOe, in the temperature range $2.5 < T < 40$ K. The results after correction of the constant diamagnetic contribution, are displayed in Fig. 1. They exhibit a maximum in the range 15–20 K, followed at lower temperature by a steep decay.

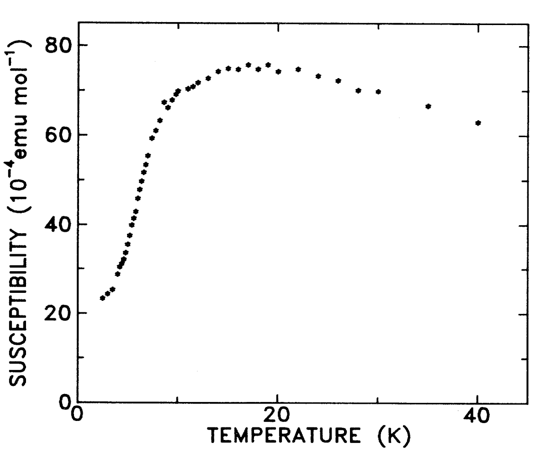

FIG. 1. Paramagnetic susceptibility $\chi_s$ of $(\mathrm{Per})_2[\mathrm{Pt(mnt)}_2]$ for $T < 40$ K.

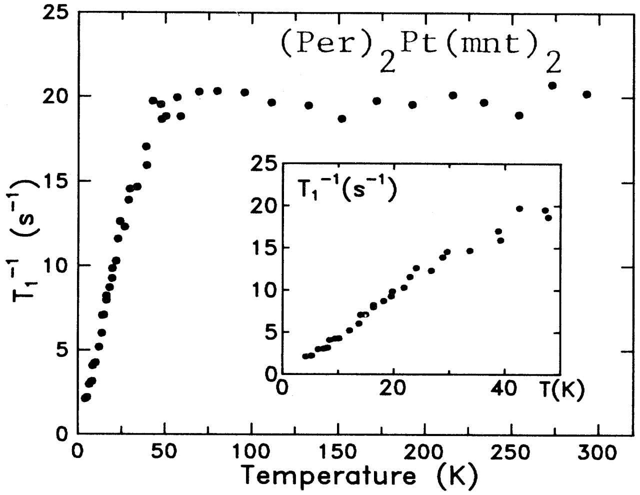

FIG. 2. $^1$H nuclear-spin-lattice relaxation rate ($T_1^{-1}$) as a function of temperature for $(\mathrm{Per})_2[\mathrm{Pt(mnt)}_2]$. Note in the inset the decrease of $T_1^{-1}$ with temperature for $T \leq 40$.

The relaxation-time measurements of the nuclear spin of proton in $(\mathrm{Per})_2[\mathrm{Pt(mnt)}_2]$ and $(\mathrm{Per})_2[\mathrm{Au(mnt)}_2]$ were performed with a Clark-type NMR spectrometer, using a standard relaxation-recovery technique. For both compounds powder samples were used, 66 mg for $(\mathrm{Per})_2[\mathrm{Pt(mnt)}_2]$ and 52 mg the Au compound. For the temperature dependence of the relaxation time $T_1$, all the measurements were made at 36.4 MHz (magnetic field of 8.55 kG). The results for the Pt compound are shown in Fig. 2. The most remarkable feature is that there is no $T_1$ dependence on temperature over a wide temperature range (40–300 K). For $T < 40$ K, a noticeable decrease of $T_1^{-1}$ with temperature is observed (inset of Fig. 2).

At $T = 300$ K, we performed some measurements of $T_1$ at different values of the magnetic field, in order to detect one-dimensional spin diffusion. In spite of the few points obtained (Fig. 4), a rough estimate of a threshold field of 15 kG can be made for the Pt compound.

The temperature dependence of $T_1^{-1}$ for $(\mathrm{Per})_2[\mathrm{Au(mnt)}_2]$ exhibits a behavior reminiscent of one-dimensional conductors, with deviations to the Korringa law ($T_1^{-1} \propto T$), clearly shown by the upward curvature in the high-temperature range, with a similar profile to the corresponding data for $(\mathrm{TMTTF})_2\mathrm{PF}_6$ (Ref. 10) or $\mathrm{TTF[Ni(dmit)}_2]_2$ (Ref. 11), where dmit is 4,5-dimercapto-1,3dithiole-2-thione, TTF is tetrathiofulvalene, and TMTTF is tetramethyltetrathiofulvalene.

## III. THEORETICAL ASPECTS AND ANALYSIS

### A. Magnetic susceptibility

According to the x-ray data reported by Henriques *et al.*,[2] it has been clearly established that the lattice instabillity of $(\mathrm{Per})_2[M(\mathrm{mnt})_2]$ occurs on the $M(\mathrm{mnt})_2$

chains for $M$=Pt,Pd. It is characterized by a one-dimensional (1D) phonon softening, which becomes apparent below $T^0_{\text{sp}} \simeq 25$ K (Pt) and 100 K (Pd). Owing to the localized nature of the spins degrees of freedoms, as shown by the Curie-Weiss susceptibility profile above $T^0_{\text{sp}}$ (Ref. 12; see also Fig. 1), the lattice softening can be considered as a spin-Peierls instability. The tendency to form dimers will then strongly affect the response of spin degrees of freedom owing to their singlet nature. We will disregard for the moment the problems of the microscopic modeling of the spin-Peierls instability, which presents anomalous characteristics (see Sec. IV). Nevertheless, it is rather easy to illustrate using simple arguments how the spin susceptibility is depressed by 1D thermodynamical fluctuations in the lattice dimerization. Our approach is strictly 1D and will thus be applicable in the temperature range of x-ray experiments where there is no transverse component for the lattice fluctuations above the true phase transition.[2]

Assuming that the spins satisfy an adiabatic condition with respect to the lattice, large thermodynamical 1D fluctuations of the lattice will break the dimerization corresponding to large spin fluctuations. For a chain that consists of $N/2$ dimers, long-range order will be broken at finite temperature due to the formation of thermally excited lattice kinks. These consist of isolated Pt(mnt)$_2$ molecules separated by ordered regions of opposite phases. By a standard argument, the change in free energy for the kink-antikink pair formation in a chain of $N$ molecules with boundary conditions is given by

$$\Delta F = \Delta - k_B T \ln N \ . \tag{1}$$

Here $\Delta$ is the effective cost exchange energy to break a singlet dimer, whereas $k_B \ln N$ is the associated entropy. For an infinite system, $\Delta F$ is always negative whenever $T \neq 0$, and then no long-range order can be stabilized at finite temperature. The value $N_c$ for which $\Delta F = 0$, namely,

$$N_c = \exp(\Delta / k_B T) \ , \tag{2}$$

determines the average size of ordered regions. This quantity can be identified as the correlation length $\xi = N_c b$ of the system, with $b$ as the lattice spacing. For each kink one can associate a localized free spin, and the average number of such spins will be

$$N_s(T) = N \exp(-\Delta / k_B T) \ . \tag{3}$$

Assuming that each isolated spin will respond to a uniform magnetic field according to a Curie law, the uniform and static magnetic susceptibility per site will take the singlet-doublet form

$$\chi_s(T) = \frac{n g_s^2 \mu_B^2}{4 k_B T} \exp(-\Delta / k_B T) \ . \tag{4}$$

Here $g_s$ stands for the Lande factor of localized spins, and $n$ is the number of spins per site. At very low temperature ($T \ll \Delta$), the susceptibility will then be thermally activated due to the spin-Peierls pseudogap. At large temperature ($T \gg \Delta$), however, one recovers a Curie-Weiss type of behavior

$$\chi_s(T \gg \Delta) \approx \tfrac{1}{4} n g_s^2 \mu_B^2 k_B^{-1} (T + \Theta)^{-1} \ , \tag{5}$$

with $\Theta = \Delta / k_B$. Using expression (4) for the data of Fig. 1, one obtains $\Theta \approx 20$ K, which essentially coincides with the temperature of the maximum of $\chi_s(T)$, which is in turn of the order of $T^0_{\text{sp}}$ seen in x-ray experiments.[2] Here, the maximum of the susceptibility is uniquely due to the onset of strong lattice fluctuations. This should not be confused with a Bonner-Fisher type of susceptibility obtained from a 1D Heisenberg antiferromagnet.[13] In that case, the maximum of $\chi_s$ reveals the onset of quantum spin dynamics for temperatures of the order of the nearest-neighbor antiferromagnetic coupling constant $J$. Therefore, here the $M$(mnt)$_2$ chains present essentially no spin dynamics when the phonon softening occurs at $T^0_{\text{sp}}$. This is quite unusual in the spirit of the theory of the spin-Peierls phase transition in quasi-1D systems. Indeed, according to the work of Cross and Fisher,[14] one should have $k_B T^0_{\text{sp}} \ll J$ as a necessary condition for spin dynamics to be able to induce a lattice softening. The characteristic energy found for $\Delta$ in (Per)$_2$[Pt(mnt)$_2$] shows that this condition is not satisfied. This will have puzzling consequences when one tries to identify the microscopic origin of the lattice instability. This will be discussed in more detail in Sec. IV. Before ending this section, one should note that the total susceptibility,

$$\chi(T) = \chi_s(T) + \chi_e(T) \ ,$$

includes $\chi_e(T)$ as the contribution of conduction electrons of the Perylene stacks. The latter is shown to be much smaller than $\chi_s(T)$ (Ref. 15) and weakly temperature dependent so that $\chi(T) \approx \chi_s(T)$ for (Per)$_2$[Pt(mnt)$_2$] and (Per)$_2$[Pd(mnt)$_2$].

### B. Nuclear relaxation

#### *1. (Per)$_2$[Pt(mnt)$_2$]*

The $^1$H nuclear relaxation-rate data presented in Fig. 2 for the (Per)$_2$[Pt(mnt)$_2$] compound are found to be temperature independent down to 40 K or so. There, $T_1^{-1}$ starts to become significantly depressed as the temperature is lowered. This temperature range essentially coincides with the one found for the deviations of $\chi(T)$ to the Curie-Weiss behavior[12] (see also Fig. 1). This would suggest that the protons of the perylene chains probe the fluctuating fields produced by the localized spins of the neighboring Pt(mnt)$_2$ chains. This is also supported by the values of $T_1^{-1}$ and $\chi$ observed for the platinum compound, which are much higher than those observed for the gold compound[15] (see also Fig. 5), which has no localized spins. For the latter, the protons can then only relax through their coupling to the spins of itinerant electrons of the perylene chains. Two intrachain contributions, the dipolar $T^{-1}_{1,d_\parallel}$ and the contact $T^{-1}_{1,c_\parallel}$ can be considered for the conducting chains. As we will see, this unique source of nuclear relaxation for (Per)$_2$[Au(mnt)$_2$] allows us to explain the quite different temperature dependence observed in these compounds for $T_1^{-1}$ (see Figs. 2 and 5).

Owing to the rather large anisotropy in conductivity[2] and in the band structure,[16] the contribution $T_{1,c_\perp}^{-1}$ coming from the interchain contact term will be considered as small in comparison to a *dipolar* type of coupling between both spins. From the sum of all the contributions to $T_1^{-1}$ namely,

$$T_1^{-1}=T_{1,d_\parallel}^{-1}+T_{1,c_\parallel}^{-1}+T_{1,d\perp}^{-1}+T_{1,c_\perp}^{-1}$$

and the data of Fig. 2, only the transverse dipolar part $T_{1,d_\perp}^{-1}$ will be taken as relevant for the (Per)$_2$[Pt(mnt)$_2$] compound. The influence of dipolar interaction on the molecular relaxation has been studied in several contexts for many years,[17,18] including the study of low-dimensional magnetic systems.[19] For the present particular two-chain problem, we have thought it useful to give some details of the derivation of $T_{1,d_\perp}^{-1}$.

The dipolar Hamiltonian $H_d$ is commonly expressed in terms of the following six contributions:

$$H_d=\tfrac{1}{2}\sum_{i\neq j}\zeta(r_{ij})(D_0+D_0'+D_{-1}+D_1+D_{-2}+D_2)\ , \tag{6}$$

where

$$\zeta(r_{ij})=-\hbar^2\gamma_e\gamma_N/r_{ij}^3 \tag{7}$$

and

$$\begin{aligned}
&D_{=}(3\cos^2\theta_{ij}-1)S_{zi}I_{zj}\ ,\\
&D_0'=-\tfrac{1}{4}(3\cos^2\theta_{ij}-1)(S_{+,i}I_{-,j}+S_{-,i}I_{+,j})\\
&D_{\pm1}=\tfrac{3}{2}\sin\theta_{ij}\cos\theta_{ij}e^{\pm i\varphi_{ij}}(S_{\pm,i}I_{z,j}+S_{z,i}+I_{\pm,j})\ ,\\
&D_{\pm2}=\tfrac{3}{4}\sin^2\theta_{ij}e^{\pm 2i\varphi_{ij}}S_{\pm,i}I_{\pm,j}\ .
\end{aligned} \tag{8}$$

Here $\theta_{ij}$ and $\varphi_{ij}$ are the polar angles of the unit vector $\mathbf{r}_{ij}/r_{ij}$ joining the electronic spin ($S$) to the one of the nucleus ($I$) at sites $i$ and $j$ respectively, while $\gamma_e$ and $\gamma_N$ stand for the gyromagnetic ratios of the electronic and the nuclear spins. In the usual way,[20] the expression for the nuclear-spin-lattice relaxation rate follows from the master equation of the full nuclear magnetization $m_z$ parallel to the applied static magnetic field $\mathbf{H}_0\|\hat{\mathbf{z}}$ and it is written as

$$dm_z/dt=-T_1^{-1}(m_z-m_0)\ , \tag{9}$$

where $m_0$ is the equilibrium nuclear magnetization. $T_1^{-1}$ is related to the nuclear spin-flip probability per unit of time ($W$) at the fixed nuclear site $j$. For $T_{1,d_\perp}^{-1}$, one will have

$$\begin{aligned}
T_{1,d_\perp}^{-1}=2W=2\sum_{i,i'\neq j}\hbar^{-2}\zeta(r_{ij})\zeta(r_{i'j})[&A_0(\theta_{ij},\theta_{i'j})G_+(i,\omega_N-\omega_e)+A_1(\theta_{ij},\varphi_{ij};\theta_{i'j}\varphi_{i'j})G_z(i,\omega_N)\\
&+A_2(\theta_{ij},\varphi_{ij};\theta_{i'j}\varphi_{i'j})G_-(i,\omega_N+\omega_e)]\ ,
\end{aligned} \tag{10}$$

where the Fourier transforms of the spin-correlation functions are defined as follows

$$G_{\pm(z)}(i,\omega)=\int_{-\infty}^{+\infty}dt\,\langle S_{\pm(z),0}(0)S_{\mp(z),i}(t)\rangle e^{i\omega t}\ . \tag{11}$$

The geometrical factors are given by

$$A_0(\theta_{ij},\theta_{i'j})=\tfrac{1}{16}(3\cos^2\theta_{ij}-1)(3\cos^2\theta_{i'j}-1)\ , \tag{12a}$$

$$\begin{aligned}
A_1(\theta_{ij},\varphi_{ij};\theta_{i'j},\varphi_{i'j})=&\tfrac{9}{4}\sin\theta_{ij}\cos\theta_{ij}\\
&\times\sin\theta_{i'j}\cos\theta_{i'j}e^{i(\varphi_{ij}-i\varphi_{i'j})}
\end{aligned} \tag{12b}$$

$$A_2(\theta_{ij},\varphi_{ij};\theta_{i'j}\varphi_{i'j})=\tfrac{9}{16}\sin^2\theta_{ij}\sin^2\theta_{i'j}e^{i2(\varphi_{ij}-\varphi_{i'j})}\ . \tag{12c}$$

The NMR experiments reported here have been performed on powder samples so that the evolution in time of the nuclear magnetization and in turn of $T_{1,d_\perp}^{-1}$ must be averaged over all the possible directions.[21] Actually powder averaging of $T_{1,d_\perp}^{-1}$ will eliminate most of the nonlocal spatial dependence of the dynamical correlators with the result

$$T_{1,d_\perp}^{-1}\simeq\tilde{\xi}^2(r_0)\left[\tfrac{3}{5}G_z(\omega_N)+\tfrac{3}{5}G_-(\omega_e)+\sum_i\tfrac{1}{8}G_+(i,\omega_e)\right]. \tag{13}$$

$G_z(\omega_N)$ and $G_-(\omega_e)$ are spatially local dynamic correlation functions. Here, we have taken $\omega_e\pm\omega_N\simeq\omega_e$ and we have neglected the fact that protons occupy different positions on the periphery of the perylene molecule[12,22] by identifying $r_{ij}$ in (10) to the average distance $r_0$ between the perylene and the Pt(mnt)$_2$ molecules. Taking $r_0\approx10$ Å for example, gives

$$\tilde{\xi}^2(r_0)=\hbar^{-2}\zeta^2(r_0)=\hbar^2\gamma_e^2\gamma_N^2/r_0^6=2.5\times10^{11}\ \text{sec}^{-2}\ .$$

The second and the third terms of (13) are related to a spin-flip transition of both the nucleus and the electron. These will then require an energy $\sim\omega_e$, which is much higher than for the process related to the first term where only the nuclear spin is flipped with an energy $\omega_N\ll\omega_e$. Consequently, it is the latter process that we will consider to dominate the relaxation for a dipole source of hyperfine coupling.[17,18] In the following, we will then concentrate on the expression

$$T^{-1}_{1,d_\perp}=\tfrac{3}{5}\tilde{\xi}^2(r_0)G_z(\omega_N)\ . \tag{14}$$

The important quantity to evaluate is the dynamic correlator $G_z(\omega_N)$. For a quite large nuclear Larmor precession period with respect to the collision time $\tau$ ($\omega_N\tau \ll 1$), spin fluctuations modes of wavelength larger than the mean free path $l$ ($ql \ll 1$) become diffusive. If one assumes that the diffusion is limited by the intrachain exchange interaction,[23] then $l \sim b$, and only the hydrodynamic limit can be taken for $G_z(\omega_N)$. We can write

$$\begin{aligned}\langle S_z(0)S_z(t)\rangle &\simeq N^{-1}\sum_{q\ll l^{-1}}\langle S_z(q,t)S_z(-q,0)\rangle\\ &\simeq k_BT(g\mu_B)^{-2}\chi_s(T)N^{-1}\sum_{q\ll l^{-1}}\exp[-(Dq^2+\tau_c^{-1})|t|]\ ,\end{aligned} \tag{15}$$

where $D \sim Jb^2$ is the spin diffusion constant,[23] $\tau_c$ is the characteristic lifetime cutoff due to processes that do not conserve the spin along the chain. Interchain transfer of spin fluctuation is usually considered the main contribution to $\tau_c$.[11,19,24] The Fourier transform of (15) and the wave-vector integration then lead, for $T_1^{-1}$,

$$T^{-1}_{1,d_\perp}=\frac{6}{5\sqrt{2}}k_BT\tilde{\xi}^2(r_0)(g\mu_B)^{-2}\chi_s(T)(D\omega_N)^{-1/2}\mathscr{g}(\omega_N)\ , \tag{16}$$

with

$$\mathscr{g}(\omega_N)=(\omega_N\tau_c)^{1/2}\{1+[1+(\omega_N\tau_c)^2]^{1/2}\}^{-1/2}+\omega_N\tau_c[1+(\omega_N\tau_c)^2]^{-1}(\{[1+(\omega_N\tau_c)^2]^{1/2}-1\}/[1+(\omega_N\tau_c)^2]^{1/2})^{1/2}\ . \tag{17}$$

As a function of the temperature at fixed $H_0$ one then has

$$T^{-1}_{1,d_\perp}\propto T\chi_s(T)\ . \tag{18}$$

At high temperature, where $T \gg T^0_{\text{sp}}$, the Curie-Weiss spin susceptibility of the platinum chains[12] will essentially lead to a temperature-independent $T^{-1}_{1,d_\perp}$ as precisely shown by the data of Fig. 2 above 40 K. This behavior is typical of weakly interacting localized spins. At lower temperature the observed $T_1^{-1}$ is sizably depressed due to lattice fluctuations. In order to check whether relation (17) holds in this domain, we have plotted in Fig. 3 the $T_1^{-1}$ versus $T\chi_s(T)$ data, and one finds that the scaling between the two quantities is again well satisfied down to lowest temperature above the true phase transition estimated to be around 7 K (see Sec. III C). The observation of this dependence confirms the influence of lattice fluctuations as well as diffusion on spin fluctuations. One must note that the hydrodynamic regime of spin dynamics is commonly checked through the frequency dependence of the nuclear relaxation. This is especially true in one dimension, where the expression (16) in the limit $\omega_N\tau_c \gg 1$ leads to the 1D characteristic square-root frequency dependence:

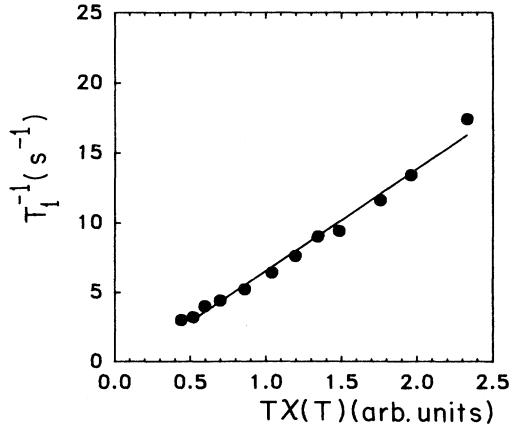

FIG. 3. Scaling of $T_1^{-1}$ with $T\chi_s$ for (Per)$_2$[Pt(mnt)$_2$].

$$T^{-1}_{1,d_\perp}\approx\frac{6}{5\sqrt{2}}k_BT\tilde{\xi}^2(r_0)(g\mu_B)^{-2}\chi_s(T)(D\omega_N)^{-1/2}\ . \tag{19}$$

However, the diffusion-induced increase of the relaxation rate when the field is decreasing is cutoff by the lifetime $\tau_c$ of spin fluctuations along the chain.[19] Indeed, in the opposite frequency limit $\omega_N\tau_c \ll 1$, one has

$$T^{-1}_{1,d_\perp}\approx\frac{6}{5\sqrt{2}}k_BT\tilde{\xi}^2(r_0)(g\mu_B)^{-2}\chi_s(T)(D/\tau_c)^{-1/2}\ , \tag{20}$$

which is field independent. The data of Fig. 4 for the frequency dependence, though taken in a limited field domain, give some indication of a saturation of $T_1^{-1}$ at $H_0 \approx 15$ kG, which implies a value of $\tau_c \approx 2.5\times10^{-9}$ sec. One must note here that in both limits only the first term of (17) matters.

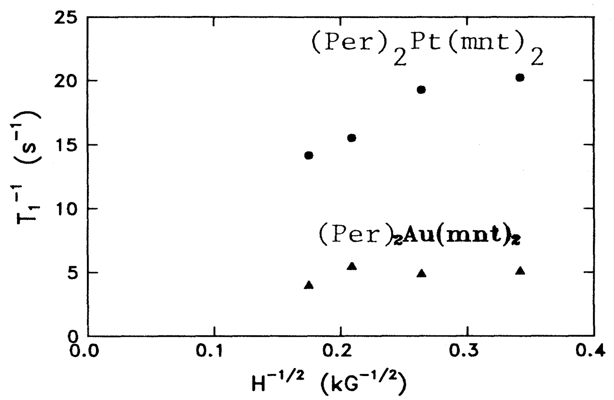

FIG. 4. Field dependence of the $^1$H nuclear-spin-lattice relaxation rate of (Per)$_2$[Pt(mnt)$_2$] (circles) and (Per)$_2$[Au(mnt)$_2$] (triangles) at room temperature.

### 2. *(Per)$_2$[Au(mnt)$_2$].*

For the case of (Per)$_2$[Au(mnt)$_2$] compound, there are no localized spins on the dithiolate chains and the relaxation of the protons comes from the fluctuating field produced by the spins of itinerant electrons along the perylene stacks. No Knight-shift measurements have been performed on the protons of perylene, and therefore the amplitude of the contact term for the relaxation is not known. Furthermore, the $T_1^{-1}$ field dependence for the gold compound in Fig. 4 is quite weak in the range of field available so that it is difficult to estimate the importance of the dipolar source of relaxation with respect to the contact source of relaxation. In the following we will, therefore, be interested in the contributions

$$T_1^{-1}=T_{1,d_{\parallel}}^{-1}+T_{1,c_{\parallel}}^{-1} . \tag{21}$$

For the intrachain dipolar term only an expression of the form (14) is important by taking $r_{o_{\parallel}}\simeq 4$ Å as the average distance between the protons and the center carbons of the perylene molecule.[22] The evaluation of the dynamic response functions for a 1D interacting electron gas has been done in several contexts,[11,24] and some of the previous results can be transposed to the present discussion. Starting from expression (14), which can be written as

$$T_{1,d_{\parallel}}^{-1}=\frac{3}{5\pi}k_B T(g\mu_B)^{-2}\xi^2(r_{0_{\parallel}})b\int dq\,\chi_z''(q,\omega_N)/\hbar\omega_N . \tag{22}$$

As for the contact term, it is related to the transverse spectral function $G_{\perp}(\omega_e)$, and it will involve an electronic spin flip in the applied magnetic field. It is then useful for $T_{1,c_{\parallel}}^{-1}$ explicitly to put the dependence on the electronic Larmor frequency $\omega_e$ so that

$$T_{1,c_{\parallel}}^{-1}=k_B T(g\mu_B)^{-2}|A|^2\gamma_N^2\pi^{-1}\int dq\,\chi_{\perp}''(q,\omega_e)/\omega_e . \tag{23}$$

Here $\chi_{z(\perp)}''$ is the imaginary part of the retarded spin susceptibility along the $z\,(\perp)$ direction, and $A$ is the hyperfine local coupling constant.[25]

The spectral weight of interest for spin fluctuations in one dimension is concentrated near $q\sim 0$ and $q\sim 2k_F$, where $k_F$ is the Fermi wave vector.[11,24] At small $q$ ($ql\ll 1$) and $\omega$ ($\omega\tau\ll 1$), however, spin fluctuations will become diffusive. Since $\omega_e\gg\omega_N$, we will consider the particular but realistic situation where the condition $\omega_N\tau\ll 1$ makes the dipolar term sensitive to the diffusive spin fluctuations, whereas, for the contact term, the condition $\omega_e\tau\gg 1$ allows us to prove only nondiffusive fluctuations. When electron-electron interaction is included, the expression for $\chi_z(q,\omega)$ at small $q$ and $\omega$ in the random-phase approximation is given by[11,26]

$$\chi_z(q,\omega_N)=\hbar\mu_B^2 E_F^{*\,-1}\tilde{\chi}_z^0(q,\omega_N)/[1-\tfrac{1}{2}g_1(T)(\pi v_F\hbar)^{-1}\tilde{\chi}_z^0(q,\omega_N)] \tag{24}$$

where

$$\tilde{\chi}_z^0(q,\omega_N)=(D_0q^2+\tau_c^{-1})/[(D_0q^2+\tau_c^{-1})-i\omega_N] \tag{25}$$

is the impurity-averaged bare susceptibility[26–28] in the presence of an intrachain lifetime $\tau_c$ for uniform spin fluctuations. $\tilde{\chi}_z^0(q,\omega_N)$ has been normalized to the Pauli susceptibility, and $D_0=v_F^{*2}\tau$ is the diffusion constant in one dimension. $v_F^*=v_F(1-g_4/2\pi\hbar v_F)$ is the effective velocity for spin excitations, and $g_4$ is the small momentum-transfer part of the electron-electron interaction. $g_1(T)$ is the electron-electron backward-scattering coupling constant, which is logarithmically screened from its bare value $g_1$ by 1D many-body effects according to[28]

$$g_1(T)=g_1/[1+(\pi\hbar v_F^*)^{-1}g_1\ln(E_F^*/k_BT)] , \tag{26}$$

with $E_F^*=\hbar v_F^* k_F$ ($k_F=\pi/2b$) for a quarter-filled band. Therefore the static magnetic susceptibility is enhanced by $g_1$ when the temperature is increased. The expression of the relaxation (20) in the diffusive sector then becomes

$$T_{1,d_{\parallel}}^{-1}(0\le|q|\ll l^{-1})=\frac{6\pi}{5\sqrt{2}}\hbar k_B T\xi^2(r_{0_{\parallel}})E_F^{*\,-2}[1-g_1(T)(2\pi\hbar v_F^*)^{-1}]^{-3/2}(\omega_N\tau)^{-1/2}\mathcal{g}(\omega_N) , \tag{27}$$

where the diffusion constant in $g(\omega_N)$ is replaced by $D_0$. The diffusion dynamics for itinerant electrons imposes a temperature dependence of the form $T^{-1}_{1,d_\parallel} \propto T\chi_z^{3/2}(T)$, which is different than the one found in (16) in the localized case. The increase with temperature of the short-range effective electron-electron interaction in (23) will enhance the relaxation rate with respect to an ideal metal Korringa law ($T_1^{-1} \propto T$). This is consistent with the $T_1^{-1}$ versus $T$ profile of Fig. 5, which clearly shows an upward curvature in the high-temperature domain. It is worthwhile to mention, however, that the enhancement of the relaxation is less important than the one found for the Bechaard salt series.[29,30] This must be put together with the observation for (Per)$_2$[Au(mnt)$_2$] of a weak enhancement of $\chi_s$ with temperature.[15] Another remark concerns the thermal dilatation, which also contributes to the increase of $\chi$ and of $(T_1T)^{-1}$ with $T$. This effect is not included in the constant volume of theory presented here. This further reduces the effects of interactions and then indicate that the coupling constant $g_1/\pi\hbar v_F$ is indeed small.

In contrast to uniform spin fluctuations, which grow in amplitude with the temperature, the contribution of $2k_F$ spin fluctuations in the 1D metallic system with Coulomb interaction is well known to become singular at low temperature. Near $2k_F$, their nondiffusive character can be considered dominant. First-order renormalization-group calculations have shown that the auxiliary $2k_F$ spin-density wave response function[28]

$$\bar{\chi}(q-2k_F,T,\omega)=\{1-g_1(\pi\hbar v_F^*)^{-1} \times\ln[\max(k_BT,\hbar v_F^*q,\hbar\omega)/E_F^*]\}^{1/2} \times[\max(k_BT,\hbar v_F^*q,\hbar\omega)/E_F^*]^{-\gamma} \qquad (28)$$

has a power-law singularity with an exponent

$$\gamma=(2\hbar\pi v_F^*)^{-1}(2g_2-g_1)>0\ ,$$

which is a function of the bare forward- ($g_2$) and the backward- ($g_1$) scattering coupling constants. For small $\omega$, $\bar{\chi}(q-2k_F,T)$ is related to $\chi''(q-2k_F,\omega)$ in the following way:[31]

$$\chi_z''(q-2k_F,\omega)\rightarrow\bar{\chi}(q-2k_F,T)\chi_{0z}''(\omega),\ \text{as } \omega\rightarrow 0\ , \qquad (29)$$

where

$$\chi_{0z}''(\omega)=(g\mu_B)^2\pi\hbar^2\omega/(32E_F^*k_BT) \qquad (30)$$

is the imaginary part of the bare $2k_F$ spin-density wave response function at small $\omega$ for a quarter-filled band. The $q$ integration of (22) in the range $\hbar v_F^*|q|<k_BT$ around $2k_F$ leads to

$$T^{-1}_{1,d_\parallel}(q\sim 2k_F)=\frac{3}{40\pi}\hbar k_BT\tilde{\xi}^2(r_{0_\parallel})E_F^{*\,-2}\bar{\chi}(2k_F,T) \qquad (31)$$

for $\hbar\omega_N \ll k_BT$. This form leads to a nonuniversal power-law enhancement of the quantity $(T_{1,d_\parallel}T)^{-1}$ at low temperature.[32]

If we now focus on $T^{-1}_{1,c_\parallel}$ in (23) coming from the contact term, we first remark that in the absence of diffusion ($\omega_e\tau \gg 1$) for the small $q$ spin fluctuations the magnetic susceptibility is dominated by paramagnons type of excitations. In RPA, one has[11,30]

$$\chi_\perp(q,\omega)=\chi_\perp^0(q,\omega)/[1-\tfrac{1}{2}g_1(T)\chi_\perp^0(q,\omega)]\ . \qquad (32)$$

where $\chi_\perp^0$ is the bare transverse susceptibility. For a linearized spectrum, the imaginary part of $\chi_\perp^0$ is

$$\chi_\perp^{0\,\prime\prime}(q,\omega)=\tfrac{1}{2}(g\mu_B)^2\hbar v_F^*q/E_F^*\delta(\omega-v_F^*q)\ , \qquad (33)$$

and one gets from (23)

$$T^{-1}_{1,c_\parallel}(q\sim 0)=\tfrac{1}{4}\hbar k_BT\gamma_N^2|A|^2 \times E_F^{*\,-2}[1-(2\pi\hbar v_F^*)^{-1}g_1(T)]^{-2}\ , \qquad (34)$$

for $\hbar\omega_e \ll k_BT$. One then recovers the characteristic $T^{-1}_{1,c_\parallel}(q\sim 0)\propto T\chi_\perp^2(T)$ scaling form in presence of nondiffusive 1D paramagnons, which enhance the relaxation rate in the high-temperature domain.[30] Comparing (34) and (27), it is the contact term that gives the strongest deviations to a noninteracting linear temperature dependence. However, since the amplitude of the hyperfine coupling constant $A$ is not known together with the observation of a relatively weak enhancement of the magnetic susceptibility at high temperature and the absence of field dependence of the relaxation (see Fig. 4), we are not in a position to single out which contribution, diffusive or nondiffusive, dominates the relaxation rate at high temperature for (Per)$_2$[Au(mnt)$_2$].

Near $2k_F$, the power-law enhancement of $T^{-1}_{1,c_\parallel}$ is obtained in a way similar to the one leading to (31), and it is given by[33]

$$T^{-1}_{1,c_\parallel}(q\sim 2k_F)=\frac{\pi}{16}\hbar\gamma_N^2k_BT|A|^2E_F^{*\,-2}\bar{\chi}(2k_F,T)\ , \qquad (35)$$

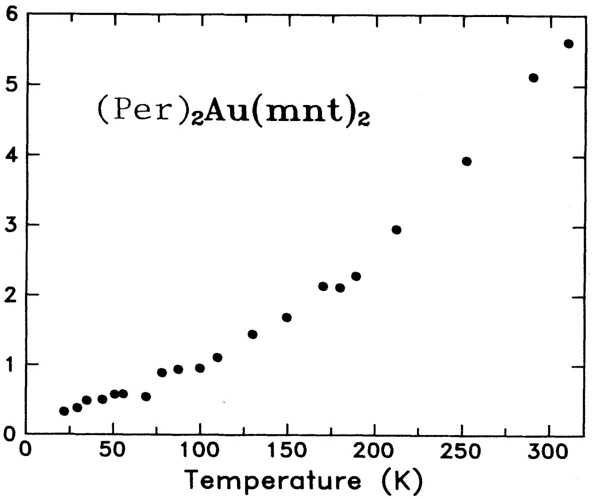

FIG. 5. Temperature dependence of $^1$H nuclear-spin-lattice relaxation rate ($T_1^{-1}$) for (Per)$_2$[Au(mnt)$_2$]. Note the upwards deviation to the Korringa law ($T_1^{-1} \propto T$).

which is valid for $\hbar\omega_e \ll k_B T$. Otherwise, one replaces $k_B T$ by $\hbar\omega_e$ in (26) and (28), and in this high-field domain the two contributions of $T^{-1}_{1,c_\parallel}$ are depressed by the magnetic field.

From the data of Fig. 5, no enhancement of $(T_1 T)^{-1}$ is seen down to the lowest temperature reached. Assuming that the assembly of perylene chains still remain one dimensional, this indicates that the value of exponent $\gamma$ should be small. Owing to the weak high-temperature enhancement of the susceptibility[15] and of $T_1^{-1}$ (Fig. 5), one can infer that the values of the coupling constants $g_1$ and $g_2$ are relatively small. This is not so surprising if one considers that the perylene molecule is large and highly polarizable. This is known to favor a weak electron-electron coupling constant. Very precise $T_1^{-1}$ measurements in the low-temperature domain are, however, needed to confirm the weakness of $g_2$.[11,30]

### C. Electron paramagnetic resonance

The first detailed EPR measurements performed by Alcacer and Maki[33] on (Per)$_2$[Pd(mnt)$_2$] already showed some rather nice peculiarities of the magnetic properties of this type of compound. The EPR spectra, taken between room temperature and 77 K, shows that the three principal values of the **g** tensor are temperature dependent with a growing anisotropy that evolves toward those of magnetically dilute [Pd(mnt)$_2$]$^-$ complexes[34] as the temperature is lowered. Actually, no superimposed line at $g_e = g_{\text{Per}} \sim 2.003$ of magnetically diluted perylene$^+$, was found. Therefore the observed temperature dependence of the **g** tensor was interpreted as the signature of sizable exchange interaction between the two different Pd(mnt)$_2$ and the perylene spin systems.

Direct consequences on the thermal dependence of the EPR spin-lattice relaxation rate $T_1'^{-1}$ are to be expected. $T_1'^{-1}$ and the linewidth $\Delta H$ are essentially proportional to each other when small spin anisotropy is present. One is therefore confronted to a problem similar to the one encountered in dilute magnetic alloys in higher-dimensional systems where the exchange interaction between the localized spins of magnetic ions and those of conduction electrons imposes very characteristic features to the EPR spectra as well as to its temperature dependence.[35] Actually, exchange interaction will lead to interchain spin-flip processes between the two different stacks. The resulting exchange of angular momentum is sufficiently rapid that the relaxation and the thermal line broadening of the two coupled spin systems can only be achieved through the lattice. This particular situation is well known as the "bottleneck" regime of relaxation.[35] Using a molecular-field-like treatment for the coupled equations of motion of both spin systems in presence of the different channels of relaxation, the "bottleneck" regime is characterized by[35]

$$T_1'^{-1} = T_{\text{sl}}'^{-1} + (\chi_e^0/\chi_s^0) T_{\text{el}}'^{-1} \ . \tag{36}$$

Here $T_{\text{el}}'^{-1}$ and $T_{\text{sl}}'^{-1}$ are the conduction electron and the localized spin-lattice relaxation rates, respectively, while $\chi_e^0$ and $\chi_s^0$ stand for the related bare susceptibilities. $T_{\text{el}}'^{-1}$ and $T_{\text{sl}}'^{-1}$ are small quantities because of the slow mechanisms involved for the relaxation imposed by the lattice. In the case of (Per)$_2$[Au(mnt)$_2$], for example, the absence of localized spins makes the EPR signal directly accessible to $T_{\text{el}}'^{-1} \sim \gamma_e \Delta H_{\text{el}}$. From the EPR data of Henriques *et al.*[5] obtained on the gold compound, it turns out that $\Delta H_{\text{el}}$ is indeed quite small ($\sim$0.5 G) and very weakly temperature dependent. Therefore, in the above conditions, the temperature dependence of the EPR linewidth for the two coupled spin subsystems is expected to be linear:

$$\Delta H = \Delta H(0) + cT \ , \tag{37}$$

where $\Delta H(0) = \gamma_e^{-1} T_{\text{sl}}'^{-1}$, $c = k_B (g_e^2/g_s^2) \Delta H_{\text{el}} n^{-1} N(0)$, with $n$ as the number of localized spins per unit cell distance $b$ and $N(0) = (\hbar\pi v_F^*)^{-1}$ as the density of electronic states at the Fermi level. We have reproduced in Figs. 6 and 7, the EPR susceptibility data for (Per)$_2$[Pt(mnt)$_2$] for 6 K $< T <$ 50 K as obtained by Henriques *et al.*[5] In the geometry used in this experiment, a single line at $g_e < g \simeq 2.016 < g_s$ was observed. From Fig. 6, we first note that the EPR intensity temperature profile is clearly consistent with the susceptibility data of Fig. 1 obtained by the Faraday method, thereby indicating that the spin of the platinum chains dominate the EPR signal. The data also show that a phase transition takes place at $T_{\text{sp}} \simeq 7$ K, where the EPR intensity drops off abruptly. The disappearance of the spin degrees of freedom is thus compatible with a spin-Peierls type of ordering. As for $\Delta H$, Fig. 7 shows that it is linear with $T$ above the critical spin-Peierls domain, and this is highly suggestive of a

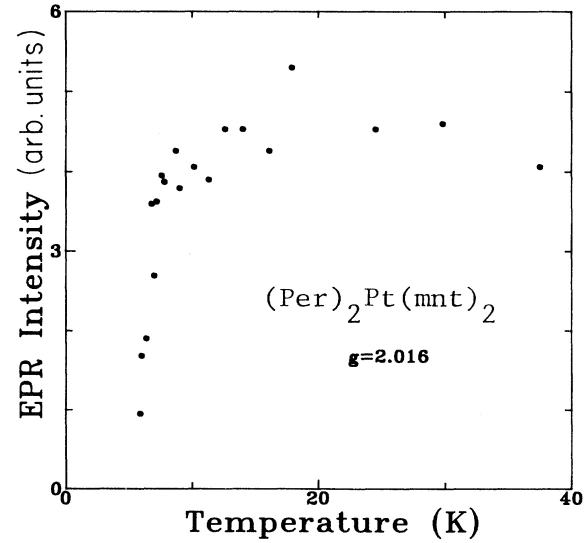

FIG. 6. The integrated intensity of EPR signal for (Per)$_2$[Pt(mnt)$_2$], after Ref. 5.

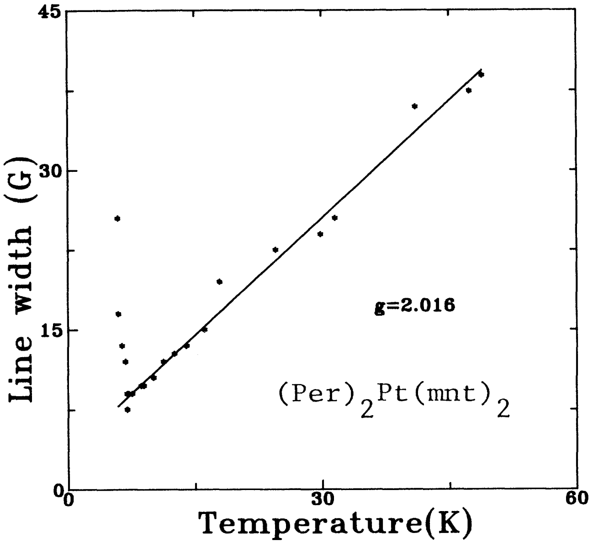

FIG. 7. EPR linewidth as a function of emperature for $(Per)_2[Pt(mnt)_2]$, after Ref. 5.

"bottleneck" regime of spin relaxation characterized by $\Delta H(0) \simeq 3.5$ G and $c \simeq 0.74$ G/K. The abrupt increase of the linewidth as we approach $T_{sp}$ is also interesting. Indeed, since a "bottleneck" type of EPR relaxation is dependent on the concentration of spin degrees of freedom ($c \propto n^{-1}$), a vanishing $n$ at $T_{sp}$ would then imply a singular increase of $\Delta H$, as observed. However, the data of figure do not show any 1D precursors for $T \leq T_{sp}^0 \simeq 20$ K, where deviations to the Curie-Weiss are clearly seen for the susceptibility (Figs. 1 and 6). One should point out, however, that the macroscopic approach leading to (38) is mean field like and does not include fluctuations effects. In this respect, it is not ruled out that lattice fluctuations will affect both $n$ and $N(0)$. For the latter, the observation of an upturn of resistivity below $T_{sp}^0$ (Ref. 2) can originate to some extent from a decrease of the density of states at the Fermi level. An obvious shortcoming of the fluctuation-free expression (38) resides in the value of $\Delta H_{el} \simeq 6 \times 10^3$ G obtained from the apparent slope of $\Delta H$ versus $T$ when the maximum value $nb = 1$ is taken for the spin density with the value $bN(0) \simeq 1.3$ states/eV obtained from the thermoelectric power data of Ref. 3. Therefore $\Delta H_{el}$ is almost four orders of magnitude higher than $\Delta H(0) \simeq \Delta H_{sl}$ and the observed linewidth for the gold compound.[5] The discrepancy can be reduced to some extent if one takes the effective and smaller value of $n$ deduced from the susceptibility data.[1,32] The agreement remains only qualitative, however.

## IV. DISCUSSION

The existence of an exchange coupling between localized spins and itinerant electrons would allow us to look at $(Per)_2[M(mnt)_2]$ compounds with $M$=Pt and Pd as realizations of a two-chain 1D Kondo lattice. The corresponding total Hamiltonian can be written as

$$H = H_{\mathrm{Per}}(g_1, g_2) + H_M(J) + H_\perp \ , \tag{38}$$

where $H_{\mathrm{Per}}$ is the Hamiltonian for the interacting conduction electrons and $H_M$ is the localized spin part that contains the direct spin-spin exchange term. The interchain Kondo-like coupling can be expressed in the form

$$H_\perp = \int \sum_{\langle i,j \rangle} J_{\perp i,j} \mathbf{S}_i(x) \cdot \mathbf{s}_j(x) dx \ . \tag{39}$$

Here $\mathbf{S}_i(x)$ and $\mathbf{s}_j(x)$ are the electronic spin operators for nearest-neighbor platinum ($i$) and perylene ($j$) chains, and $x$ is the position along the $\hat{\mathbf{b}}$ direction. $J_\perp$ is the exchange coupling taken as antiferromagnetic ($J_\perp > 0$). Depending on its amplitude and the band filling, a Kondo lattice is well known to present either a Kondo scattering or a magnetic modulation instability of the localized spins.[36–38] The latter is induced by the so-called Ruderman-Kittel-Kasuya-Yosida (RKKY) indirect exchange coupling $J_{\mathrm{RKKY}}(2k_F, T)$. In the present case, this spin-spin interaction is generated by the $2k_F$ spin-density wave instability of the perylene stack, which is singular in one dimension [$J_{\mathrm{RKKY}}(2k_F, T) \propto J_\perp^2 \chi(2k_F, T)$, see Ref. 37]. As far as the Kondo screening is concerned, one should note that for a Kondo lattice like $(Per)_2[M(mnt)_2]$, which has a quarter-filled band for the conduction electrons and one localized spin per $[M(mnt)_2]^-$ molecule, there are not enough conduction electrons to achieve a perfect Kondo screening.[37,38] It is worth pointing out, however, that the actual value of $n$ as deduced from the susceptibility data[1,32] was found to be smaller than 1. This effect can then be interpreted as a result of a partial screening of the localized spins. Although the amplitude of $J_\perp$ can be sizably renormalized and increased, the Kondo effect, being incomplete, gives place to the RKKY instability. The latter is obviously not observed either. Instead, one has the remarkable experimental fact that the coupling phonons make such a system unstable towards a lattice distortion.

As already mentioned, despite the clear confirmation by NMR and EPR of the existence of localized spins on the dithiolate stacks, the microscopic origin of this apparent spin-Peierls phase transition is not so clear. Indeed, from x-ray experiments 1D lattice correlations are found to be already well developed, whereas the antiferromagnetic correlations of localized spins do not show any evidence for quantum dynamics and, in turn, no spatial extension ($T_{sp}^0 \gtrsim \Theta$). For $(Per)_2[Pd(mnt)_2]$, the situation is even worse, since, from x ray,[2] $T_{sp}^0 \simeq 100$ K and $T_{sp} \simeq 28$ K, while the Curie-Weiss temperature estimated from the high-temperature data of Alcacer and Maki[32] is found to be only $\Theta \sim 20$ K. This would imply for example, that at $T_{sp}$, the one-chain correlation length for dimerization becomes macroscopic, while the magnetic one is still of the order of the unit cell distance $b$!. It follows that the standard approaches[14,39] to the spin-Peierls transition, which are all fixed to the condition $T_{\mathrm{sp}}^{0} \ll \Theta$, cannot be applied in a straightforward way. It is known that the only prerequisite to stabilize a dimerized ground state for a linear chain of spins is its capacity to develop quantum spin dynamics,[39] although this condition would be satisfied in the present isotropic spin case with $S=\frac{1}{2}$ for thermal energies $k_B T$ smaller than the characteristic energy scale $J \simeq k_B \Theta$. Therefore, it is not so clear how strong 1D lattice softening precursors can appear in a temperature domain where thermal magnetic fluctuations apparently dominate. Yet, NMR and EPR results show clear evidence for the localized spins to be involved in the transition.

It is thus of interest to look for other possible contributions to quantum spin dynamics and more specifically for the possible role played by the neighboring perylene stacks in the transition. Two scenarios with their respective relevance will be discussed. First, the 1D metallic conditions that prevail along the perylene stacks will favor the development of $2k_F$ and even $4k_F$ density-wave correlations. This is known to occur below the highest-energy cutoff of $H_{\mathrm{Per}}$ in (37), namely, the Fermi energy $E_F \sim 0.5$ eV. Of course the amplitude of the singularities for the related response functions are strongly dependent on the electron-electron interaction[28] [c.f. (29)]. One can infer that, in order to observe x-ray diffuse scattering at $q_0 = \pi/b$, the bond charge correlations of the dithiolate stacks would be precisely coupled via the direct Coulomb interaction to the $4k_F$ charge-density-wave fluctuations of neighboring perylene stacks. This in turn, can give rise to a large temperature domain of 1D lattice softening precursors. The weakness of this scenario, however, resides in the complete absence of diffuse scattering for $(\mathrm{Per})_2[\mathrm{Au(mnt)}_2]$ at both $2k_F$ and $4k_F$.[2] This shows that these density wave fluctuations are either small or their coupling to the perylene lattice is extremely weak.

Another interesting possibility emerges if one considers the influence of the spin-spin interaction $J_{\mathrm{RKKY}}$ mediated by the conduction electrons. Being proportional to $J_\perp^2 \chi(2k_F, T)$, this interaction, though small at high temperature, will grow under the influence of the singular behavior of $\chi(2k_F, T)$ [see (29)] and to some extent from the effect of the partial Kondo screening on $J_\perp$. Although we have no idea of the net amplitude of $J_{\mathrm{RKKY}}$, there is no doubt that this will bring additional quantum fluctuations for the localized spins degrees of freedom. A difficulty arises, however, when one tries to match the perylene spin-density modulation wave vector $2k_F = \pi/2b$ with the one of the lattice modulation $q_0 = \pi/b$, which is twice as large.

The RKKY interaction will therefore weaken antiferromagnetic correlations at $q_0 = \pi/b$. Moreover, according to a recent work,[8] it turns out that this mismatch is sufficient to give rise to a *negative* or *ferromagnetic* contribution to the Curie-Weiss constant $\Theta$. Therefore, this suggests that the *direct* antiferromagnetic exchange $J$ between spins is likely to be larger than the estimated $\Theta$ from the susceptibility data. The consequences of this on the stability of the lattice at $q_0 = \pi/b$ is not clear at the present time.

At this point it is important to emphasize that the rather puzzling properties of $M(\mathrm{mnt})_2$ spin chains are apparently peculiar to the $(\mathrm{Per})_2[M(\mathrm{mnt})_2]$ type of compound. In this respect, it is worthwhile to mention that the one-chain compound $\mathrm{Li}_{0.82}(\mathrm{H_2O})_2[\mathrm{Pt(mnt)}_2]$ presents metallic properties at high temperature and is followed by the observation of 1D diffuse x-ray scattering at $2k_F$ located above a regular *incommensurate* Peierls distortion at $T_p = 215$ K.[40] The metallic properties of the dithiolate chains occur despite an intermolecular distance along the stacking axis that is essentially the same as the one found for $(\mathrm{Per})_2[M(\mathrm{mnt})_2]$.[34,40] Furthermore preliminary band calculations[16] made for $(\mathrm{Per})_2[\mathrm{Pd(mnt)}_2]$ show that the lowest unoccupied molecular (LUMO) orbitals of the dithiolate molecules overlap to form a band dispersion of 0.4 eV, which is not too far from the 0.75 eV previously found for the lithium compound.[40] No doubt that the fact that the band is not half-filled in this case should play a major role in the existence of metallic properties. Actually, in contrast to the lithium compound there is one negative charge transferred for each $M(\mathrm{mnt})_2$ complex so that the dithiolate bands are half-filled, which is known to lead to a Mott-Hubbard type of localization. As the temperature scale of the insulating properties depends on the value of the one-site repulsion $U$, the Curie-Weiss type of susceptibility data shows that the value of $U$ must exceed the bandwidth. Taking the standard expression $J = 2t^2/U$ for the intermolecular exchange in the large-$U$ limit and the estimated value of $\Theta \sim J/k_B \simeq 20$ K, one finds a ration $t/U \sim 10^{-2}$, which thus implies a quite large value for the one-site repulsion $U$. This puzzling result is somewhat surprising if one considers that the LUMO orbitals for $M(\mathrm{mnt})_2$ (Ref. 34) have a sizable polarizability.

In conclusion, this work has shown that the low-temperature susceptibility and the nuclear relaxation rate data of $(\mathrm{Per})_2[\mathrm{Pt(mnt)}_2]$ give firm evidence for a 1D spin-Peierls instability on $\mathrm{Pt(mnt)}_2$ stacks of localized spins below 40 K, in agreement with previous x-ray studies. In contrast, a weakly enhanced metalliclike $T_1^{-1}$ temperature profile has been found for $(\mathrm{Per})_2[\mathrm{Au(mnt)}_2]$, which has no localized spins. The linear scaling relation between $T_1^{-1}$ and $T\chi_s$ found for all temperatures of the 1D regime for $(\mathrm{Per})_2[\mathrm{Pt(mnt)}_2]$ has emphasized the diffusive and the weakly correlated character of the localized spin degrees of freedom. The absence of quantum spin dynamics, however, was found to raise some basic and unanswered questions about the microscopic driving force of the spin-Peierls instability. From the analysis of the existing data for the EPR linewidth temperature dependence, which confirms, at least in a qualitative way, the existence of a Kondo-like interstack exchange coupling between localized spins and itinerant electrons, it was conjectured that the RKKY-induced interaction between localized spins can play an important role in the dynamics of the transition. It is clear that additional experimental works on other members of this family, which are now under way, are needed in order to get a more complete understanding of this interesting family of compounds.

## ACKNOWLEDGMENTS

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[1] L. Alcacer, Mol. Cryst. Liq. Cryst. **120**, 221 (1985).

[2] R. T. Henriques, L. Alcacer, J. P. Pouget, and D. Jérôme, J. Phys. C **17**, 5197 (1984).

[3] R. T. Henriques, M. Almeida, M. J. Matos, L. Alcacer, and C. Bourbonnais, Synth. Met. **19**, 379 (1987).

[4] R. T. Henriques, L. Alcacer, D. Jérôme, C. Boubonnais, and C. Weyl, J. Phys. C **19**, 4663 (1986).

[5] R. T. Henriques, L. Alcacer, M. Almeida, and S. Tomic, Mol. Cryst. Liq. Cryst. **120**, 237 (1985).

[6] M. Y. Ogawa, B. M. Ogawa, S. Lee, M. Yudkowsky, and W. P. Halperin, Phys. Rev. Lett. **57**, 1177 (1986).

[7] G. Quirion, M. Poirier, K. K. Liou, M. Y. Ogawa, and B. M. Hoffman, Phys. Rev. B **37**, 4272 (1988).

[8] B. Guay, L. G. Caron, and C. Bourbonnais, Synth. Met. **29**, F557 (1989).

[9] D. Jérôme and H. J. Schulz, Adv. Phys. **31**, 299 (1982).

[10] F. Creuzet, C. Bourbonnais, L. G. Caron, D. Jérôme, and K. Bechgaard, Synth. Met. **19**, 289 (1987).

[11] C. Bourbonnais, P. Wzietek, D. Jérôme, F. Creuzet, L. Valade, and P. Cassoux, Europhys. Lett. **6**, 177 (1988).

[12] L. Alcacer, H. Novais, F. Pedroso, S. Flandrois, C. Coulon, D. Chasseau, and J. Gaultier, Solid State Commun. **35**, 945 (1980).

[13] J. C. Bonner and M. E. Fisher, Phys. Rev. **135**, A640 (1964).

[14] M. C. Cross and D. S. Fisher, Phys. Rev. B **19**, 402 (1979).

[15] S. Flandrois (unpublished).

[16] E. Canadel (unpublished).

[17] N. Bloembergen, Physica **15**, 386 (1949).

[18] A. Abragam, Phys. Rev. **98**, 1729 (1955).

[19] J. P. Boucher, F. Ferrieu, and N. Nechtschein, Phys. Rev. B **9**, 3871 (1974); J. P. Boucher, M. Ahmed Bakheit, M. Nechtschein, M. Villa, G. Bonera, and F. Borsa, *ibid.* **13**, 4098 (1976).

[20] A. Abragam, *Principles of Nuclear Magnetic Resonance* (Clarendon, Oxford, 1961), Chaps. VIII–IX.

[21] F. Devreux, J. P. Boucher, and M. Nechtschein, J. Phys. (Paris) **35**, 271 (1974).

[22] A. Domingos, R. T. Henriques, V. Gama, M. Almeida, A. Lopes Veira, and L. Alcacer, Synth. Met. **27**, B 411 (1988).

[23] N. Lurie, D. Huber, and M. Blume, Phys. Rev. B **9**, 2171 (1974).

[24] G. Soda, D. Jérôme, M. Weger, J. Alizon, J. Gallice, H. Robert, J. M. Fabre, and L. Giral, J. Phys. (Paris) **38**, 931 (1977).

[25] T. Moriya, J. Phys. Soc. Jpn. **18**, 516 (1963).

[26] P. Fulde and A. Luther, Phys. Rev. **170**, 570 (1968).

[27] P. A. Lee and T. V. Ramakrishnan, Rev. Mod. Phys. **57**, 287 (1985).

[28] J. Solyom, Adv. Phys. **28**, 201 (1979).

[29] M. Miljak and J. R. Cooper, Mol. Cryst. Liq. Cryst. **119**, 141 (1985).

[30] C. Bourbonnais, P. Wzietek, F. Creuzet, D. Jérôme, P. Batail, and K. Bechgaard, Phys. Rev. Lett. **62**, 1532 (1989).

[31] C. Bourbonnais, P. Stein, D. Jérôme, and A. Moradpour, Phys. Rev. B **33**, 7608 (1986).

[32] L. Alcacer, and A. H. Maki, J. Phys. Chem. **80**, 1912 (1976).

[33] C. Bourbonnais, F. Creuzet, D. Jérôme, K. Bechgaard, and A. Moradpour, J. Phys. Lett. (Paris) **45**, L755 (1984).

[34] L. Alcacer and H. Novais, in *Extended Linear Compounds,* edited by J. S. Miller (Plenum, New York, 1983), Vol. 3, p. 319.

[35] S. E. Barnes, Adv. Phys. **30**, 801 (1981).

[36] R. Jullien, J. N. Fields, and S. Doniach, Phys. Rev. B **16**, 4889 (1977).

[37] L. G. Caron and C. Bourbonnais, Europhys. Lett. **11**, 473 (1990).

[38] P. Nozieres, Ann. Phys. (Paris) **10**, 19 (1985).

[39] J. N. Bray, L. V. Interrante, I. S. Jacobs, and J. C. Bonner, in *Extended Linear Compounds,* edited by J. S. Miller (Plenum, New York, 1983), Vol. 3, p. 353.

[40] M. M. Ahmad, D. J. Turner, A. E. Underhill, C. S. Jacobsen, K. Mortensen, and K. Carneiro, Phys. Rev. B **29**, 4796 (1984).