

Strong Electronic Correlations in Li_xZnPc Organic Metals

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Nuclear magnetic resonance, electron paramagnetic resonance and magnetization measurements show that bulk Li_xZnPc are strongly correlated one-dimensional metals. The temperature dependence of the nuclear spin-lattice relaxation rate $1/T_1$ and of the static uniform susceptibility χ_S on approaching room temperature are characteristic of a Fermi liquid. Moreover, while for $x \approx 2$ the electrons are delocalized down to low temperature, for $x \rightarrow 4$ a tendency towards localization is noticed upon cooling, yielding an increase both in $1/T_1$ and χ_S . The x dependence of the effective density of states at the Fermi level $D(E_F)$ displays a sharp enhancement for $x \approx 2$, at the half filling of the ZnPc lowest unoccupied molecular orbitals. This suggests that Li_xZnPc is on the edge of a metal-insulator transition where enhanced superconducting fluctuations could develop

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Organic molecular crystals have been the subject of intensive research activity for decades in view of their complex electronic properties and several technological applicabilities [1]. In these crystals the bandwidth W is narrow (0.1–1 eV) and they are usually insulators, as charge delocalization can be achieved only when W is larger than the on site Coulomb repulsion U . Nevertheless, when $U/W \approx 1$ and the local energy scales become relevant, it is still possible to observe unexpected phenomena as the enhancement of superconducting fluctuations. In this respect alkali-doped fullerenes $A_x\text{C}_{60}$ are paradigmatic. For $x = 3$ the π lowest unoccupied molecular orbital (LUMO) band is half filled and, despite the significant correlations, they are metals featuring a superconducting transition at a surprisingly high critical temperature [2]. The unconventional superconductivity in $A_x\text{C}_{60}$ has been ascribed to the competition between the Jahn-Teller (JT) coupling of the electrons with the intramolecular phonon modes [3] and the local exchange J (Hund coupling), representing the relevant energy scales when $U/W \approx 1$. In this limit the system behaves as if it had a reduced bandwidth W^* and, as far as the effective exchange $J_{\text{eff}} = J - E_{\text{JT}}/4$ remains of the order of W^* , even in the presence of a high Coulomb repulsion an attractive electron pairing can arise [3]. Recently it was pointed out that also the electronic properties of the insulating transition metal phthalocyanines [(MPc) where $\text{Pc} = \text{C}_{32}\text{H}_{16}\text{N}_8$] thin films can be affected by alkali ions intercalation [4]. MPc molecules consist in a planar organic macrocycle hosting a metal ion in the central cavity and form typical slipped-stacked chains. Along the stacking direction b the Pc antibonding π^* LUMOs have the strongest overlap and form a nearly one-dimensional (1D) narrow band [5]. The results reported in Ref. [4] indicate that $A_x\text{MPc}$ s become metallic when the doubly degenerate $2e_g$ LUMO is half filled for $x \approx 2$ and become insulating again when the band is completely filled for $x = 4$. The possibility that super-

conductivity could develop in $A_x\text{MPc}$ was suggested by Tosatti *et al.* [6]. In fact, they pointed out that $A_x\text{MPc}$ should be at the edge of a metal-to-insulator transition (MIT) [3]. Then $U/W \sim 1$ and the $2e_g$ electrons could strongly couple with the intramolecular B phonon modes [7] to yield $J_{\text{eff}} \sim W^*$, as in fullerenes. Nevertheless, recent photoelectron spectroscopy results [8,9] seem to indicate that K -doped MPc thin films are insulating, questioning the results reported in Ref. [4].

In this work we present an experimental study of the electronic properties of bulk $\beta\text{-Li}_x\text{ZnPc}$ by means of nuclear magnetic resonance (NMR), electron paramagnetic resonance (EPR), and squid magnetometry. The synthesis of $\beta\text{-}A_x\text{MPc}$ powder samples was attained recently by means of liquid-phase methods [10]. These compounds form molecular crystals in which the cell parameters of the pure β form are modified in order to accommodate the alkali ions in intrastack positions, bound to the pyrrole bridging nitrogens of adjacent Pc rings [10]. The β form is preferred by MPc in the bulk state to the α form typical of thin films. It must be remarked that the liquid phase synthesis is a low energy and slow process, yielding a better control of homogeneity and defects than the higher energy ionic implantation processes adopted to dope thin films. Thus, the properties of the powder samples produced by means of the liquid-phase process used in this work are definitely reproducible.

Li_xZnPc powders were synthesized under inert atmosphere, following the procedure published by Taguchi *et al.* in Ref. [10] with a few modifications. ZnPc powders were freshly synthesized, repeatedly filtered, and purified by sequential vacuum sublimation. The blueish residue of Li_xZnPc , obtained by dissolving ZnPc in 1.6 M $n\text{-BuLi}$ in hexane of the appropriate molarity, was dried and underwent annealing procedure into NMR tubes with heating at 240 °C under vacuum (6.8×10^{-2} mbar) for 3–4 days. This heating procedure ensures formation of the β poly-

morph. The NMR tubes were then sealed to avoid oxidation. A small fraction (a few percent) of LiPc was found to be present in some samples. The air sensitivity and the powder morphology prevent one from performing standard transport measurements.

NMR measurements were performed by using standard radio frequency (rf) pulse sequences. The lithium content x was determined from the relative intensity of ${}^7\text{Li}$ and ${}^1\text{H}$ NMR signals, namely, from the echo intensity $E(2\tau)$ extrapolated to a delay $\tau \rightarrow 0$. The values of x derived were consistent with the doping estimated by induced coupled plasma analysis. ${}^7\text{Li}$ NMR spectra were obtained from the Fourier transform of half of the echo signal after a $\pi/2 - \tau - \pi/2$ pulse sequence. They showed the typical features of a $I = 3/2$ powder spectrum (see the inset of Fig. 1) with a quadrupole coupling frequency $\Delta\nu_Q \approx 44$ kHz. The quadrupole frequency and the line shape are temperature (T) independent up to room temperature (RT); namely, the local electric-field gradient does not change upon varying T . This is a neat indication that lithium does not diffuse and that it is rather strongly bound to the Pc molecules.

Nuclear spin-lattice relaxation rate $1/T_1$ was estimated from the recovery of nuclear magnetization $m(\tau)$ after a saturating rf pulse sequence. ${}^7\text{Li}$ recovery law was observed to be a stretched exponential, namely, $y(\tau) \equiv 1 - m(\tau)/m(\tau \rightarrow \infty) = \exp[-(\tau/T_1)^\beta]$, with $\beta \approx 0.65$ over the entire T range. The stretched character of the recovery laws indicates a distribution of relaxation rates with an average relaxation $1/T_1$ [11]. This likely originates from the anisotropic hyperfine coupling tensors or from some disorder in Li distribution.

${}^7\text{Li}$ $1/T_1$ in Li_xZnPc powders was found to be about two orders of magnitude smaller than in Li_xMnPc , which is insulating [12]. Since ${}^7\text{Li}$ hyperfine coupling A in Li_xZnPc (≈ 2 kG, see later on) is much larger than that in Li_xMnPc (~ 100 G), the significant decrease of ${}^7\text{Li}$ $1/T_1$ in Li_xZnPc

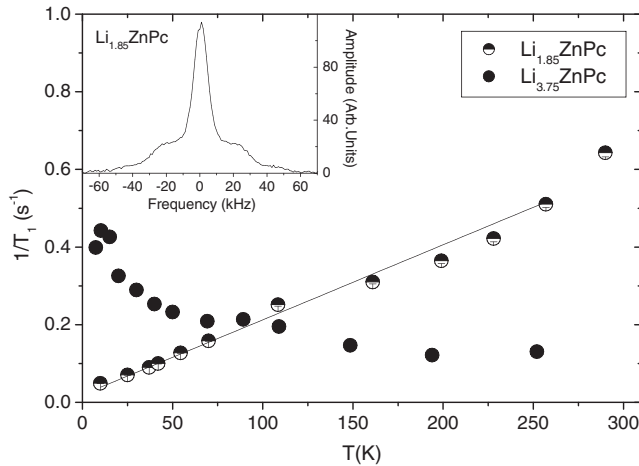


FIG. 1. ${}^7\text{Li}$ $1/T_1$ in Li_xZnPc as a function of T . The solid line is the fit according to Eq. (1). In the inset ${}^7\text{Li}$ NMR powder spectrum in $\text{Li}_{1.85}\text{ZnPc}$, for $T = 293$ K, is reported.

must reflect an increase in the frequencies of the spin fluctuations by several orders of magnitude, as one would expect when the electrons become delocalized. The T dependence of ${}^7\text{Li}$ $1/T_1$ relaxation rates in $\text{Li}_{1.85}\text{ZnPc}$ and $\text{Li}_{3.75}\text{ZnPc}$ powder samples is shown in Fig. 1. $1/T_1(T)$ shows significant changes upon varying the lithium content owing to the evolution of the electronic correlations. In $\text{Li}_{1.85}\text{ZnPc}$ ${}^7\text{Li}$ $1/T_1(T)$ is linear down to the lowest T , as expected for a Fermi liquid [13]

$$\frac{1}{T_1} = \frac{\gamma_N^2}{2} A^2 k_B \hbar D(E_F)^2 T = C_0 \chi_S^2 T, \quad (1)$$

where $D(E_F)$ is the density of states at the Fermi level and χ_S the static uniform spin susceptibility. On the contrary, in $\text{Li}_{3.75}\text{ZnPc}$ $1/T_1$ deviates from Eq. (1) on decreasing T and rather diverges at $T \approx 10$ K. The rise in $1/T_1$ below $T = 150$ K recalls the one observed in other 1D strongly correlated metals as the Bechgaard salts [14]. In a quasi-1D metal, owing to the Fermi surface topology, the low-energy excitations contributing to nuclear spin-lattice relaxation are essentially the ones at $\vec{q} \approx 0$ and at $\vec{q} \approx 2\vec{k}_F$, then one can write [15]

$$\frac{1}{T_1}(T) = C_0 \chi_S(T)^2 T + C_1 (2\vec{k}_F) T \chi(2\vec{k}_F, \omega_L). \quad (2)$$

In Eq. (2) the first term corresponds to Eq. (1), where the static uniform susceptibility $\chi_S(T)$ is in general T dependent due to the strong electronic correlations, whereas in a weakly correlated metal $\chi_S(T)$ should be Pauli-like, i.e., nearly constant. Hereafter we will show that, even if in Li_xZnPc $U/W \rightarrow 1$, as far as the electrons remain delocalized $\chi_S(T)$ is almost T independent.

$\chi_S(T)$ for Li_xZnPc powders was estimated from the area of the EPR spectra, recorded with an X-band spectrometer.

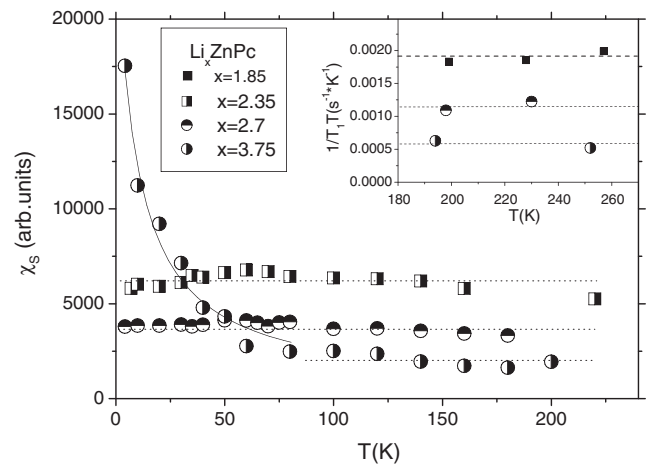


FIG. 2. Spin susceptibility, derived from the integral of the EPR spectra, in Li_xZnPc compounds as a function of T . The dotted lines are guides to the eye marking the high T limit of the susceptibility. The solid line is a Curie-Weiss fit. The inset shows the ${}^7\text{Li}$ $1/T_1 T$ values at high T marked by the dotted lines.

The spectra were characterized by an asymmetric line shape with a broadening of a few hundreds Gauss. Further details on the EPR spectra will be reported elsewhere. Figure 2 shows that χ_S for $x \approx 2$ is nearly constant over all the explored T range; namely, it is Pauli-like and arises from the delocalized electrons filling the LUMO band, in agreement with what was found from NMR $1/T_1$ measurements. Moreover, it is noticed that upon increasing x χ_S decreases, exactly as $1/T_1 T$ in the high T limit (see the inset of Fig. 2). Eventually, for $x \approx 3.75$, χ_S grows on cooling below $T \sim 150$ K. This rise can be interpreted either as a consequence of electron localization or can be simply due to a few percent of impurities [16]. Nevertheless, the precise origin of this localization is still uncertain. Magnetization (M) measurements performed in $\text{Li}_{1.85}\text{ZnPc}$ using an MPMS-XL7 Quantum Design SQUID magnetometer are consistent with the EPR measurements. The macroscopic susceptibility, defined as $\chi = M/H$ with H the intensity of the applied magnetic field (inset of Fig. 3), is practically constant, except for a low- T Curie tail ascribable to impurities. Now, one can compare the $1/T_1 T$ data of the different Li_xZnPc samples with χ_S data to evaluate the evolution of the spectral weight of $\vec{q} = 0$ and $\vec{q} = 2\vec{k}_F$ excitations on cooling. At high T $1/T_1 T$, in all compounds, is dominated by the first term of Eq. (2) and the curves tend to a constant nonzero value proportional to χ_S^2 (inset of Fig. 2), decreasing with increasing x , for $x > 1.85$. Remarkably, in all Li_xZnPc compounds the electrons are delocalized at RT. In fact, if in $\text{Li}_{3.75}\text{ZnPc}$ the electrons were localized, one would expect $1/T_1 T \rightarrow 0$ on increasing T , as $1/T_1$ is constant in a paramagnetic insulator [17]. $1/T_1 T$ in $\text{Li}_{1.85}\text{ZnPc}$ remains practically constant on cooling (Fig. 3) with a trend similar to the one of χ , which indicates that the $\vec{q} = 0$ excitations are dominant down to

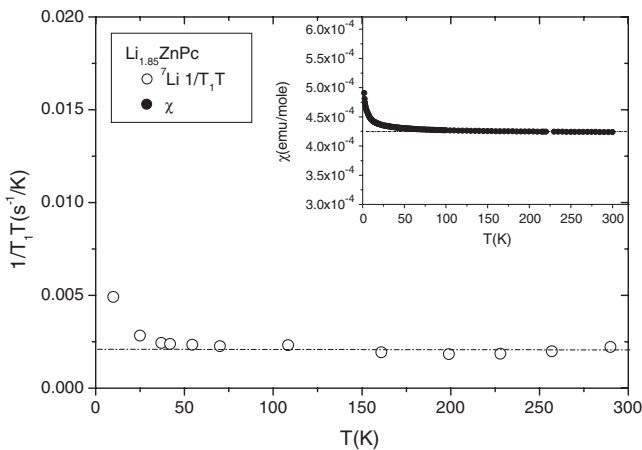


FIG. 3. ${}^7\text{Li}$ $1/T_1 T$ in $\text{Li}_{1.85}\text{ZnPc}$ as functions of T . The dash-dotted line is a guide to the eye. Inset: T dependence of the molar magnetic susceptibility of $\text{Li}_{1.85}\text{ZnPc}$ powders, measured with a SQUID magnetometer in a field of 1000 G. The diamagnetic contributions have already been subtracted from the raw data.

low T . On the contrary, the growth observed in $1/T_1$ for $\text{Li}_{2.7}\text{ZnPc}$ and $\text{Li}_{3.75}\text{ZnPc}$ has rather to be associated with the enhancement of the $\vec{q} = 2\vec{k}_F$ fluctuations leading to $\chi(2\vec{k}_F) \propto (T/E_F)^{K_\rho - 1} \gg \chi(q \approx 0)$ [18,19], with K_ρ an exponent characterizing both charge and spin correlation functions. In particular, since $1/T_1$ is constant for $T \geq 150$ K, $K_\rho \rightarrow 0$ for $x \approx 3.75$, i.e., $U/W \gg 1$. The low- T dynamics observed by ${}^7\text{Li}$ NMR in $\text{Li}_{3.75}\text{ZnPc}$ could then originate from localized electrons, which eventually give rise to a spin density wave as in the Bechgaard salts [14].

Now, the results obtained by means of the different techniques can be conveniently combined to derive the effective $D(E_F)$ as a function of Li content. Since at high T the behavior of χ_S is Pauli-like, $\chi_S = N_A \mu_B^2 D(E_F)$, and since $1/T_1$ follows Eq. (1), one can quantitatively derive $D(E_F)$. However, although all EPR measurements were performed in the same experimental conditions, the absolute value of the EPR susceptibility was not calibrated and, moreover, to derive $D(E_F)$ from $1/T_1$ the knowledge of the hyperfine coupling A is required. For $x = 1.85$ A can be calculated by resorting to Eq. (1), on the basis of $1/T_1$ data and from the susceptibility estimated with the SQUID magnetometer. One finds $A(x = 1.85) \approx 2$ kG and $D(E_F) \approx 3.6$ states/eV. Upon increasing x one finds that $C_0 = 1/T_1 \chi_S^2$ [see Eq. (1)] slightly increases. The variation of this constant is related to the variation of the hyperfine coupling A with x . In particular, one has $A(x = 3.75) = 1.32A(x = 2.7) = 1.27A(x = 1.85)$. Now that the hyperfine constants are known, $D(E_F)$ can be derived from $1/T_1$ or, alternatively, by scaling the absolute value of χ_S determined by EPR with $\chi_S(x = 1.85) = N_A \mu_B^2 D(E_F)$.

The doping dependence of $D(E_F)$ per electron derived from the high T data is finally reported in Fig. 4. It is noticed that $D(E_F)$ shows a marked peak for $x = 2$, while it diminishes almost symmetrically for $x \rightarrow 0$ and $x \rightarrow 4$.

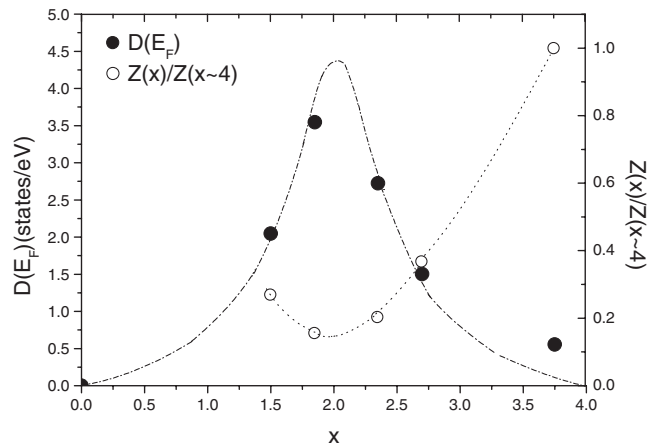


FIG. 4. Density of states at the Fermi level per electron in Li_xZnPc , obtained from susceptibility data, and the quasiparticle residue $Z(x)$, normalized to the value $Z(x \sim 4)$. The lines are guides to eye.

Remarkably, $D(E_F)$ is finite for every $x \neq 0$ or 4, indicating that electron injection in the $2e_g$ band always drives the system towards metallicity. This is to our knowledge the first clear indication that bulk MPCs become metallic upon alkali doping despite the significant Coulomb repulsion, in agreement with the conductivity measurements in K_x MPC thin films [4]. The increase by almost an order of magnitude in the effective $D(E_F)$ at half-band filling cannot be justified in light of the bare $D(E)$. Recent band structure calculations for K_x CuPc [20] show an asymmetric shape for the $D(E)$ in the e_g bands. On the other hand, Li_x ZnPc behave as a Fermi liquid with an effective bandwidth W^* which is sizably reduced for $x \approx 2$. This narrowing was explained by Capone *et al.* within the dynamical mean field theory [3]. These authors have shown that in the strong correlation limit, $0.8 < U/W < 0.9$, these systems are characterized by an effective renormalized bandwidth $W^*(x) = Z(x)W$, with W the bare bandwidth and Z the free fermionlike quasiparticle residue which should vanish for $U/W \rightarrow 0.8$, i.e., close to the MIT. The doping dependence of Z derived from the one of $D(E_F)$ is reported in Fig. 4 for comparison. One notices that Z is significantly reduced for $x \approx 2$. Now, since A_x MPC shows analogies with A_x C₆₀, one could envisage the onset of strongly correlated superconductivity for $x \approx 2$, with an effective coupling $J_{\text{eff}} = J - E_{JT}/4$. So far, for $x \approx 2$ no evidence of a superconducting transition emerges from the experimental data down to liquid helium T . Nevertheless, it has to be remarked that this transition could be suppressed either by a certain disorder or by the small interchain coupling typical of these quasi-1D systems. Finally we point out that recent infrared spectra show an increase in the reflectivity of Li_x ZnPc powders upon Li doping, with a minimum around 0.6 eV for $x \approx 2.35$, possibly marking the plasma frequency.

In conclusion, from a series of NMR, EPR, and magnetization measurements we have evidenced that bulk Li_x ZnPc become metallic upon Li doping. The T dependence of the nuclear spin-lattice relaxation rate $1/T_1$ and of the static uniform susceptibility χ_S on approaching RT are characteristic of a Fermi liquid, with an effective $D(E_F)$ markedly peaked at half-band filling. While for $x \approx 2$ the electrons are delocalized down to low T , for $x \rightarrow 4$ a tendency towards localization is noticed upon cooling. The x dependence of $D(E_F)$ shows that for $x \approx 2$ Li_x ZnPc is close to a metal-insulator transition where enhanced superconducting fluctuations could develop, suggesting that in A_x MPCs a phenomenology analogous to the one observed in A_x C₆₀ could develop.

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