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Physical properties and the Peierls instability of $Li_{0.82}[Pt(S_2C_2(CN)_2)_2]\cdot 2H_2O$

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The infrared reflectivity, the temperature-dependent conductivity, and thermopower of the one-dimensional conductor $Li_{0.82}[Pt(S_2C_2(CN)_2)_2]\cdot 2H_2O$, LiPt(mnt), is presented. It undergoes a simple Peierls transition at $T_c = 215$ K, which is not influenced by correlations or by cation ordering. The metallic LiPt(mnt) is characterized by a transfer integral $|t_{\parallel}| \approx 0.1$ eV. When $155\text{ K} < T < T_c$ it behaves as an intrinsic Peierls semiconductor with $\Delta \approx 36$ meV. At lower temperatures the thermopower indicates extrinsic behavior due to the presence of donor impurities. Our results agree with those obtained from magnetic-susceptibility studies.

The recent report that the compound $Li_{0.82}[Pt(S_2C_2(CN)_2)_2]\cdot 2H_2O$, LiPt(mnt), is a synthetic metal in which the metallic conductivity is associated with columnar stacks of anions consisting of Pt complexes of maleonitriledithiolate, mnt, is an interesting development for several reasons.[1] $[M(\mathrm{mnt})_2]$ (M = Ni, Pd, or Pt), shown in Fig. 1, is a well studied anion most often found in nonconducting salts with two exceptions. One is $(\mathrm{perylene})_2[M(\mathrm{mnt})_2]$ where the conduction stems from overlap between perylene ions[2] and the other as indicated by some preliminary studies in salts of $[M(\mathrm{mnt})_2]$, with small cations and M = Ni or Pd.[3] LiPt(mnt) is therefore the first example of a well characterized conductor based on this type of molecule. Compared to other molecules which contain sulfur as hetero atoms and form conducting stacks, such as tetrathiofulvalene TTF, one might expect that the central metal ions give rise to an increased electron delocalization in $[Pt(\mathrm{mnt})_2]$ by tying the two symmetric parts of the molecule more closely together than in TTF. This approach is opposite to the one applied in designing the two "superconducting" molecules TMTSF (tetramethyltetraselenafulvalene)[4] and BEDT-TTF (bis-ethylene-di-thiolate-TTF)[5] where delocalization is presumably achieved by expanding the TTF molecule. These molecules are also shown in Fig. 1.

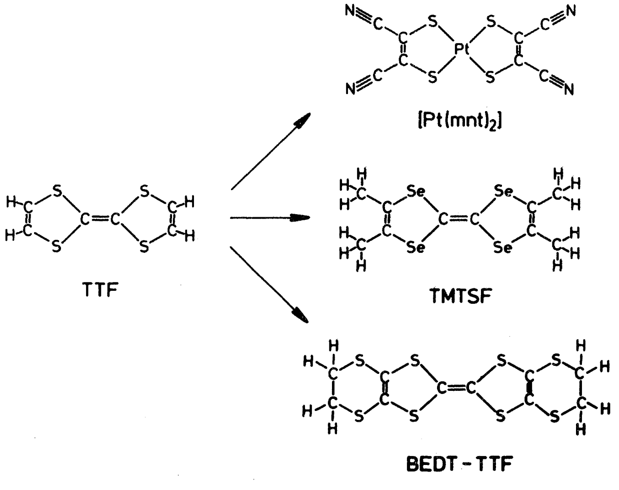

FIG. 1. Schematic representations of the molecules TTF, $[Pt(\mathrm{mnt})_2]$, TMTSF, and BEDT-TTF.

X-ray studies by Kobayashi *et al.* show that the room-temperature structure of LiPt(mnt) consists of stacks of nearly eclipsed $[Pt(\mathrm{mnt})_2]$ moieties along the c axis, with $c = 3.639$ Å.[6] The unit cell is triclinic (volume $V_c = 355$ Å^3, space group $P\bar{1}$) and the stacks form sheets along b separated along a by Li^+ and H_2O. In common with the structures of $(\mathrm{TMTSF})_2X$ compounds and the superconducting salt $(\mathrm{BEDT\text{-}TTF})_2ReO_4$ there are short chalgogen contacts between chains within the sheets as well as within the chain, suggesting a relatively two-dimensional network.[4,7]

Later crystallographic studies show a superstructure, below $T_c = 215$ K preceeded by one-dimensional diffuse scattering above T_c typical of a Peierls transition.[8] The position of the diffuse lines along c^* determines the fermivector to be $2k_F = 0.82(2\pi/c)$, so that the nominal oxidation state of Pt is +3.18 or +2.82. We interpret this as an indication that the concentration x of Li is greater than 0.75 suggested by chemical analysis.[1] But we cannot exclude that H_3O^+ is incorporated in the lattice to give the measured $2k_F$. Finally, it is noteworthy that the thermal expansion is unusually large for a one-dimensional conductor in particular along b, a feature also found in the $(\mathrm{TMTSF})_2X$ series.[7]

In this paper we report on the physical properties of LiPt(mnt), which appears to display in an unusually clear way the characteristics of a one-dimensional conductor as originally proposed by Peierls.[9]

The infrared reflectivity $R_{\parallel}(\omega)$ of LiPt(mnt) was measured in the region from 3500 to 14 000 cm^{-1} at room temperature using a single beam spectrometer as described elsewhere.[10] The results shown in Fig. 2 demonstrate a high reflectance at low frequencies but the small size of the crystals

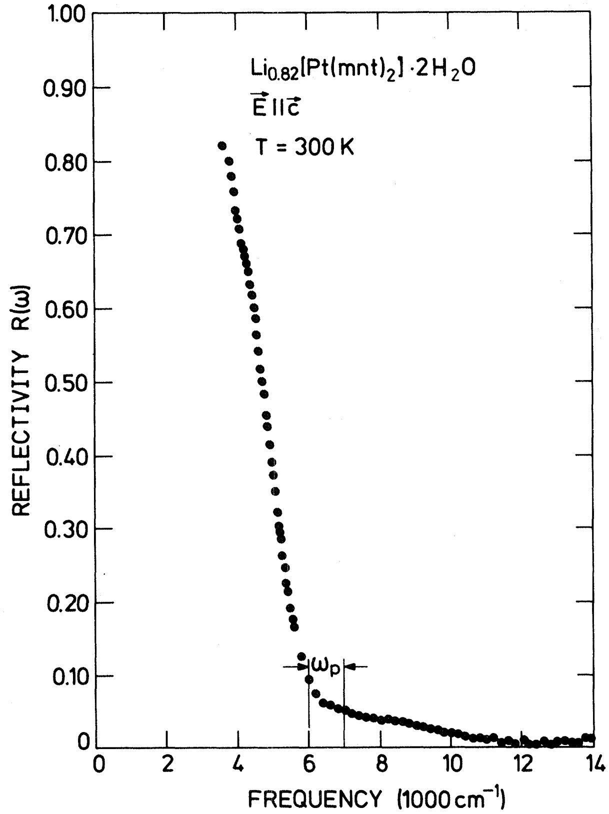

FIG. 2. Room-temperature reflectivity $R(\omega)$ of LiPt(mnt) with the light polarized in the conducting direction. The region of the estimated plasma frequency is indicated.

made it impossible to see whether $R(\omega)$ approaches unity according to Drude theory. From the drop in $R(\omega)$ we deduce a lower estimate of 6000 cm^{-1} for the plasma frequency ω_p; but again, an accurate Drude fit is not possible, partly because there is no minimum in $R(\omega)$ just above ω_p and hence the value of the background dielectric constant $\epsilon(\infty)$ is not well determined. Most one-dimensional conductors have $\epsilon(\infty) = 2.0$–2.5.[11-14] With $\epsilon(\infty) = 2.5$ the data of Fig. 2 yield $\omega_p \approx 7000$ cm^{-1} which we consider an upper limit.

Assuming a one-dimensional tight-binding approximation to model the electronic structure of LiPt(mnt), the plasma frequency is related to the bandwidth $W_\parallel (=4|t_\parallel|)$ in the following way:

$$\omega_p^2 = \frac{e^2c^2\sin(k_F c)}{\pi\epsilon_0\hbar^2 V_c} W_\parallel \ , \qquad (1)$$

from which we get $W_\parallel = 0.3$–0.4 eV. As pointed out by Cooper *et al.* this is an astonishing result since they find a Pauli susceptibility χ corresponding to $W_\parallel = 0.66 \pm 0.05$ eV.[15] The relation between $W_\parallel$'s derived from the two kinds of experiments is the opposite of what would be expected if Coulomb correlations were important. Hence these results suggest that correlations are not important and we conclude that a reasonable value for the bandwidth is $W_\parallel = 0.4 \pm 0.1$ eV at room temperature. With respect to the difference between susceptibility and reflectivity, it may relate to the fact that when electron-phonon coupling is of importance (as is always the case in one-dimensional metals) then the effective electronic mass m^* is not necessarily the same in different experiments. Indeed one finds[16] that $m_{\rm ir}^* = (1+\lambda_{\rm ir}) m_\chi$, consistent with the deduced bandwidths.

The dc conductivity of LiPt(mnt) was measured using four probe techniques as described previously.[10] At room temperature the conductivity along c is $\sigma(\mathrm{RT}) = 30$ –200 $\Omega^{-1}\mathrm{cm}^{-1}$, a typical value for synthetic metals. The temperature dependence shown in Fig. 3 indicates a metal-insulator transition around 200 K with a low-temperature activation energy $\Delta(0) = (\frac{1}{2}E_g =)$ 36 meV. The characteristics of $\sigma(T)$, of the susceptibility $\chi(T)$, and of the diffuse x-ray scattering suggest that the transition is due to a straightforward Peierls instability without complications either due to electronic Coulomb correlations or due to counterion ordering. The former effect is often of importance in organic conductors giving $4k_F$ x-ray scattering, enhanced Pauli susceptibility, and a decreased activation energy [compared to $\Delta(0)$] for the susceptibility below T_c. The latter effect, counterion ordering, has been seen in some of the $(\mathrm{TMTSF})_2X$ compounds[4] and bis-oxalatoplatinates[17,18] and it interferes profoundly with the Peierls instability. In LiPt(mnt) no such complications are found and we therefore conclude that the low-temperature semiconductor is a simple charge-density-wave state with period $2k_F$ along c.

It is usual to deduce the critical temperature T_c from

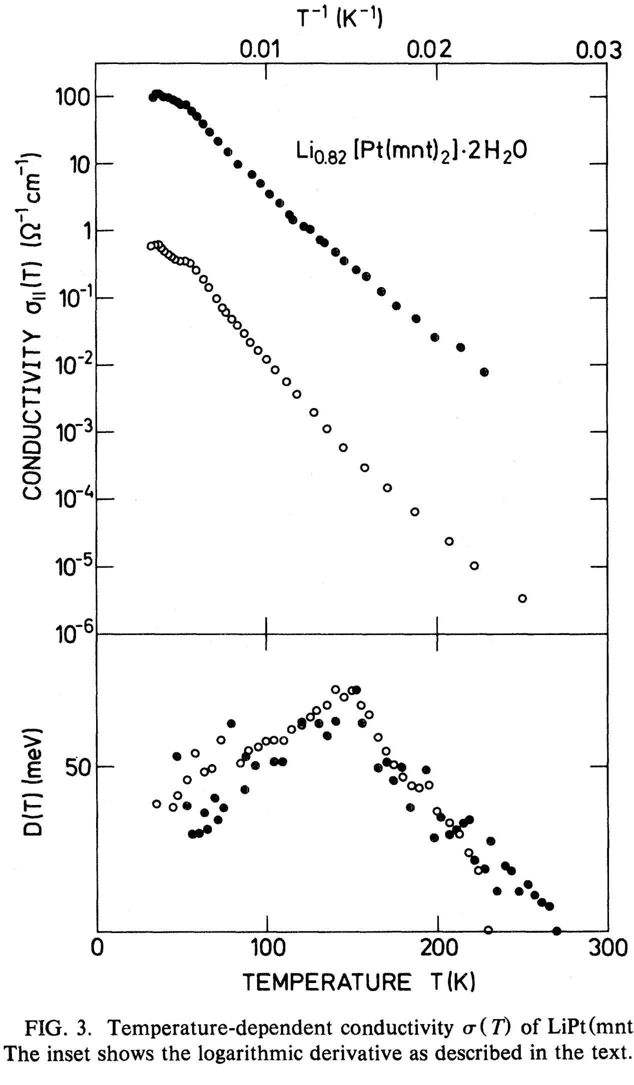

FIG. 3. Temperature-dependent conductivity $\sigma(T)$ of LiPt(mnt). The inset shows the logarithmic derivative as described in the text.

$\sigma(T)$ by locating the maximum in its logarithmic derivative $D(T) = -\partial[\ln\sigma(T)]/\partial(1/T)$.[19] As shown in Fig. 3, $D(T)$ for LiPt(mnt) has its maximum around 180 K somewhat lower than T_c as measured by x rays. To explain this apparent discrepancy it should be noted that the temperature dependence of the conductivity is determined both by the temperature-dependent gap $\Delta(T)$ as well as by the temperature-dependent mobility $\mu(T)$. If $\mu(T)$ varies as $T^{-\beta}$ then $D(T)$ has the following form:

$$D(T) = \Delta(T) - T\frac{d\Delta(T)}{dT} - \beta T \ , \tag{2}$$

so that the maximum in $D(T)$ does not occur at T_c where the second term in (2) is biggest, but at a lower temperature owing to the third term. This latter term is usually small in Pt-chain conductors. For LiPt(mnt), however, a combination of a relatively small $\Delta(0)$, a relatively big T_c, as well as a big β caused by the large thermal expansion, may explain the apparent suppression of the measured critical temperature in the conductivity results.

Assuming from the above that the low-temperature gap is caused by the Peierls instability we may deduce the dimensionless electron-phonon coupling constant λ from the following relation:[20]

$$\Delta(0) = 2W_{\parallel}[1-\cos^2(k_F c)]e^{-1/\lambda} \ . \tag{3}$$

With $W_{\parallel} = 0.4 \pm 0.1$ eV this gives $\lambda = 0.34 \pm 0.02$. This value for λ is typical for both organic and inorganic one-dimensional conductors but the microscopic origin is quite different in the two cases. In Pt-chain conductors only acoustic phonons seem to contribute to λ, whereas their contribution in organic conductors is typically 0.1 and intramolecular vibrations (vibrons) play an important role. We have looked for direct evidence of this electron-vibron coupling in the reflectivity $R(\omega)$, but our results are unfortunately inconclusive due to the small size of the crystals.

A comparison of the observed transition temperature $T_c = 215$ K with the mean-field transition temperature $T_p = \Delta(0)/(1.76k_B) = 237$ K yields information about the transverse coupling between chains. Following the theory of Horovitz, Guffreund, and Weger[21] the fact that T_c is rather close to T_p leads to the conclusion that the anisotropy of the electronic overlap is rather small and that one-dimensional fluctuations should not be seen far away from T_c. The first conclusion is in accordance with the short S-S distances between the stacks and the second is in agreement with all the observed temperature-dependent properties. Hence LiPt(mnt) appears to be the case of a quasi-one-dimensional conductor with sufficient coupling between the chains, so that the Peierls instability gives rise to relatively mean-field-like behavior.

The thermoelectric power S of LiPt(mnt) was also measured using the setup described earlier.[10,22] The results are shown in Fig. 4. Above T_c, $S(T)$ is approximately constant at $+10\ \mu$V/K. Below T_c it increases to a maximum of about 35 μV/K at $T = 155$ K before it goes to negative values at low temperatures.

The fact that S is positive above T_c implies hole characteristics of the carriers in the metallic region. Hence the band structure of LiPt(mnt) in the nearest neighbor tight-binding approximation has the form

$$\epsilon(k_{\parallel}) = 2t_{\parallel}(1-\cos k_{\parallel}c) \tag{4}$$

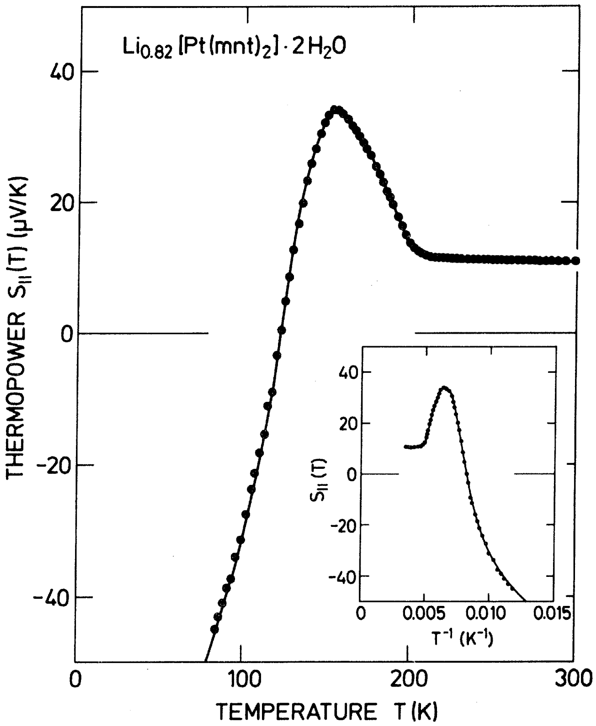

FIG. 4. Temperature-dependent thermopower $S(T)$ of LiPt(mnt). The inset shows S vs $1/T$.

as shown in Fig. 5. We can of course not exclude (1) that $\epsilon(k)$ has a more complicated form than (4), and it would therefore be interesting to do a molecular-orbital calculation for the compound or (2) that the energy dependence of the scattering dominates over the band contribution to $S_{\parallel}$ (which would explain the lack of temperature dependence). Finally, it should be noted, that the room-temperature value of S corresponds to a bandwidth consistent with the results mentioned above.

Below T_c one would expect the thermopower to reflect the intrinsic properties of the charge-density-wave semiconductor. In this case we have

$$S_{\parallel}(T) = \frac{k_B}{e}\left[\frac{\mu^*\Delta}{k_B T} + \text{const}\right] \ , \tag{5}$$

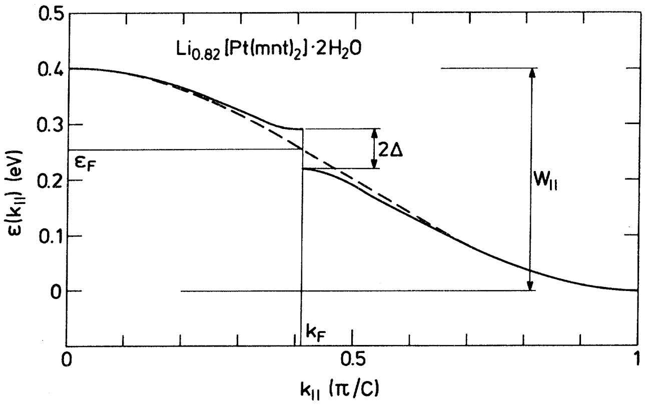

FIG. 5. Proposed band structure of LiPt(mnt) at high temperatures (dashed line) and at low temperature (solid line). $\epsilon(k_{\parallel})$ is drawn for $t_{\parallel} < 0$ although it cannot be excluded that $t_{\parallel} > 0$.

where μ^* is determined by the ratio between the mobilities of electrons and holes, above and below the gap 2Δ. Conwell and Banik have shown that for the intrinsic Peierls semiconductor one gets[24]

$$\mu^* \approx 3 \frac{\Delta}{W_{\parallel}} \frac{\cos(k_F c)}{\sin^2(k_F c)} , \tag{6}$$

which with the values given above gives $\mu^* \approx 0.1$. Hence $S(T)$ below T_c should behave according to (5) with an effective half-gap $\mu^*\Delta \approx 4$ meV which compares reasonably well to a slope of S vs $1/T$ (cf. inset of Fig. 4) of 10–16 meV between 160 and 200 K.

The deviation from intrinsic behavior below $T \approx 155$ K is ascribed to the existence of impurity levels, which must be donors since $S(T)$ eventually becomes negative. These defect levels are probably related to the paramagnetic defects seen at low temperatures in the magnetic susceptibility. It should be noted that these defects are not to be thought of as chemical impurities but rather as defects occurring in the conducting stacks, since the electronic g value from electron-spin resonance does not change significantly with temperature.[25] In our interpretation the peak in $S_{\parallel}(T)$ at 155 K marks the onset of extrinsic behavior, whereas we interpreted the conductivity $\sigma_{\parallel}(T)$ as predominantly intrinsic at appreciably lower temperatures. In order to justify this we estimate the density of impurities relative to the intrinsic carrier density from the thermopower at the temperature where it goes through zero. This in turn allows an estimate of the impurity contribution to the conductivity. From this we conclude that intrinsic behavior prevails in $\sigma_{\parallel}(T)$ at least down to 120 K and that the simultaneous occurrences of peaks in $D(T)$ and $S_{\parallel}(T)$ at 150 K are therefore accidental.

The experimental data presented here strongly suggest that the compound $Li_{0.82}[Pt(S_2C_2(CN)_2)_2] \cdot 2H_2O$ behaves like a simple quasi-one-dimensional conductor, where the Peierls instability gives rise to a mean-field-like transition because of high transverse coupling. Infrared reflectivity, electrical conductivity, and thermopower studies consistently indicate that the electronic structure is of the tight-binding nature with a bandwidth of $W_{\parallel} = 0.4 \pm 0.1$ eV stemming from a p-type overlap integral $|t| \approx 0.1$ eV, that the charge-density-wave state is characterized by a gap parameter $\Delta = 36$ meV corresponding to an electron-phonon coupling $\lambda = 0.34 \pm 0.02$, and that the transition temperature is 215 K. Below 155 K the thermopower changes from intrinsic to extrinsic behavior due to the presence of donor levels. Our results are in reasonable agreement with magnetic susceptibility studies.

The consistent lack of signatures from Coulomb correlations is a peculiar feature for an organic material with a bandwidth as narrow as we observe for LiPt(mnt). Although the role of the Pt atom in the center of the (mnt) appears rather minor for the properties of LiPt(mnt), the crucial effect may be that Pt aids delocalization of electrons on the mnt's as suggested from chemical arguments. The increased delocalization within the $[Pt(mnt)_2]$ molecule is then responsible for the decrease of electron correlations along the stack.

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