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HIGHLY CONDUCTING PERYLENE RADICAL SALTS⁺

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Temperature dependent dc and microwave conductivity data together with EPR and optical reflectance measurements on the "mixed" system $(pe)_2(AsF_6)_{0,75}(PF_6)_{0,35} \times 0,85 CH_2Cl_2$ are described. The data prove metallic behaviour of this organic solid down to 200 K.

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INTRODUCTION

Recently electrochemically prepared single crystals of quasi one-dimensional organic conductors have caused considerable interest because of a number of exciting electronic properties. Specially crystals of the series of tetramethyltetraselenafulvalene (TMTSF) salts $[(\text{TMTSF})_2\text{X}]$ with typical anions $\text{X} = \text{PF}_6^-, \text{AsF}_6^-, \text{ClO}_4^-$ etc.] show a variety of fascinating properties and are the first organic solids which became superconducting¹. On the other hand also simple hydrocarbons such as naphthalene², perylene (pe), coronene, anthracene, pyrene, triphenylene³ and fluoranthene⁴ were used to generate quasi one-dimensional crystals by electrochemical methods. It was found that perylene $[(\text{pe})_2(\text{PF}_6)_{1,1} \times 0,8 \text{CH}_2\text{Cl}_2 \text{ and } (\text{pe})_2(\text{AsF}_6)_{1,1} \times 0,7 \text{CH}_2\text{Cl}_2]$ is specially well suited to form highly conducting organic metals with up to $1200 (\Omega\text{cm})^{-1}$ room temperature conductivity³.

Here we report electronic properties of electrochemically prepared single crystals of $(\text{pe})_2 \cdot (\text{AsF}_6)_{0,75}(\text{PF}_6)_{0,35} \times 0,85 \text{CH}_2\text{Cl}_2$. Some of these crystals show strongly increasing conductivities with decreasing temperature. In addition to the temperature dependent conductivities EPR- and optical reflectance data confirm a metallic behaviour of these crystals at temperatures above 200K.

EXPERIMENTAL

Crystals were prepared in a 100 ml electrochemical cell of 3 compartments separated by two glass filters from each other. Platinum wires with platinum plates ($1,5 \times 1,5 \text{ cm}^2$) at the end were used as electrodes. 0,1 g perylene, 0,39 g Bu_4NPF_6 (Bu_4N^+ = tetrakis(n-butyl)ammonium ion) and 0,43 g Bu_4NAsF_6 were dissolved in 100 ml CH_2Cl_2 and saturated with dry nitrogen. Equimolar mixtures of the electrolyte salts were used. The crystals were grown using a constant current of 10 μA resulting in a potential of about 1,9 V, at a temperature of 300 K and under exclusion of light. Crystals of the following composition were obtained.

Analysis: $(\text{pe})_2(\text{AsF}_6)_{0,75}(\text{PF}_6)_{0,35} \times 0,85 \text{ CH}_2\text{Cl}_2$
 $(\text{C}_{40,85} \text{H}_{25,7} \text{As}_{0,75} \text{P}_{0,35} \text{Cl}_{1,7} \text{F}_{6,6})$

Calc.: C 63,78%; H 3,36%; As 7,31%; P 1,41%; Cl 7,83%;
 F 16,30%

Found: C 63,98%; H 3,44%; As 6,9 %; P 1,41%; Cl 7,82%;
 F 16,6 %

C 64,13%; H 3,41%; As 7,1 %; P 1,33%; Cl 7,85%;
 F 16,4 %

The crystals have typical dimensions as described earlier³ but in addition very "thin" crystals (cross sections $< 10\mu \times 10\mu$) of a few millimeter length were obtained. Conduction measure-

ments were performed on "thick" and "thin" crystals.

The dc-conductivity was measured by the standard four-probe method⁵ along the needle axis, while for the conductivity perpendicular to the perylene stacks the method of Montgomery⁶ was used. The samples were mounted on gold wires in a teflon block and measured with the same apparatus as described recently³.

In addition to the dc-conductivity the microwave conductivity was studied. The temperature dependent conductivity $\sigma = 2\pi f \epsilon_0 \epsilon''$ (f = frequency, $\epsilon_0 = 8,854 \times 10^{-12}$ As/Vm dielectric constant of free space, ϵ'' = imaginary part of the complex dielectric constant $\epsilon = \epsilon' - i\epsilon''$) was measured in the range from 80 to 300 K at both 9,3 and 23,5 GHz using cavity perturbation technique. The frequency generator was controlled by the resonance frequency of the cavity in a feedback loop (frequency accuracy $\approx 10^{-7}$). The qualities of the cavities at room temperature are 6000 and 4700 at 9,3 and 23,5 GHz, respectively. The single crystals were brought into the maximum of the electric field inside a rectangular TE_{103} transmission cavity with the needle axis parallel to the field. The relative change in halfwidth and the normalized frequency shift were used to calculate σ with the perturbation formula⁷ in the quasi-static regime $|\sqrt{\epsilon} \cdot k \cdot d/2| \ll 1$ (k wave vector, d sample diameter) and with the surface impedance formula⁸ in the skin effect regime $|\sqrt{\epsilon} \cdot k \cdot d/2| \gg 1$. A general formula⁹ valid in both cases can be

used to calculate σ in the difficult region between both approximations.

Temperature dependent EPR spectra were taken on a Varian spectrometer E-101 equipped with a Varian NMR-Gauss-meter for field calibration. Spectral reflectance measurements were performed and analyzed by a Drude model similar as described for $(pe)_2(PF_6)_{1,1} \times 0,8 CH_2Cl_2^{10}$.

RESULTS AND DISCUSSION

"Thick" crystals

The temperature dependence of the dc-conductivity of "thick" specimens of the "mixed system" $(pe)_2 \cdot (AsF_6)_{0,75} (PF_6)_{0,35} \times 0,85 CH_2Cl_2$ is very similar to the characteristics of $(pe)_2 (PF_6)_{1,1} \times 0,8 CH_2Cl_2$ and of $(pe)_2 (AsF_6)_{1,1} \times 0,7 CH_2Cl_2^3$. The room temperature conductivity σ_{rt}^{dc} ranged typically between 200 and 1200 $(\Omega cm)^{-1}$ along the needle axis but is reduced by a factor of at least 400 perpendicular to this axis.

The room temperature microwave conductivity σ_{rt}^{mw} was in the average smaller than the σ_{rt}^{dc} values. Nevertheless, a very similar temperature dependence was observed. Typical microwave conductivity data on $(pe)_2 (AsF_6)_{0,75} (PF_6)_{0,75} \times 0,85 CH_2Cl_2$ single crystals are shown in fig. 1. With decreasing temperature the mw-conductivity reaches (similar to the dc-conductivity) a flat maximum σ_{max} at temperature T_{max} and passes

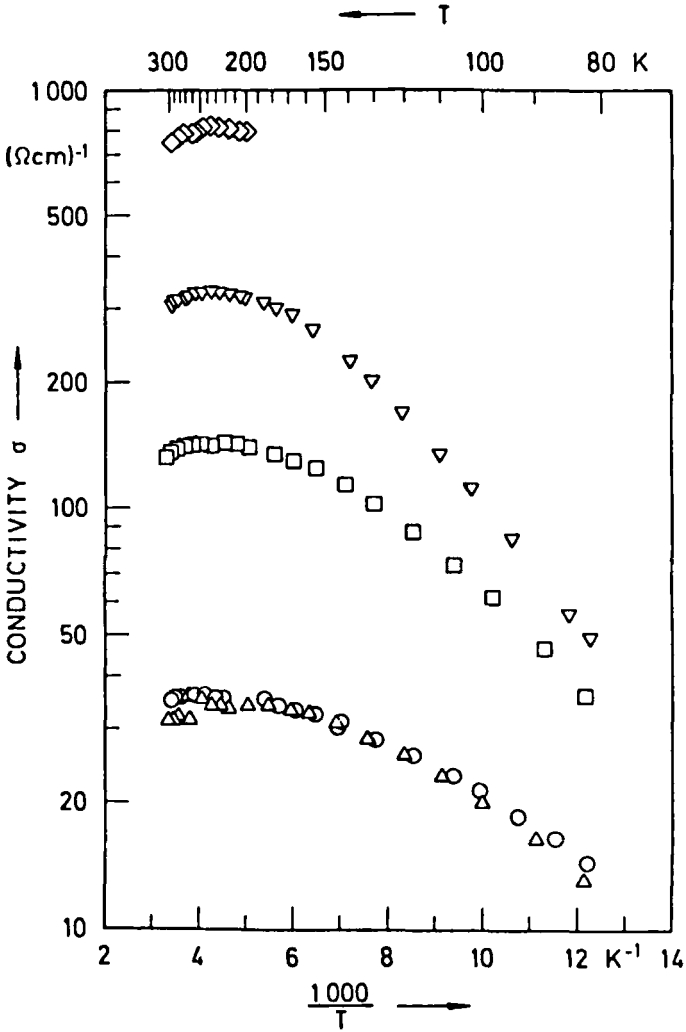


FIGURE 1 Microwave conductivity of $(pe)_2 \cdot (AsF_6)_{0.75}(PF_6)_{0.35} \cdot 0.85 CH_2Cl_2$ single crystals vs. reciprocal temperature (three different crystals at (\diamond) 9.3 and (∇, \square) 23,5 GHz, one crystal at (Δ) 9,3 and (O) 23,5 GHz).

through a smooth transition into a semiconducting region at lower temperatures. Values for $\sigma_{\max}/\sigma_{\text{rt}}$ range between 1,0 and 1,1 at a T_{\max} between 200 and 250 K. From sample to sample there are considerable variations of $\sigma_{\text{rt}}^{\text{mw}}$ (20 ... 750 (Ohm cm)⁻¹) and of the activation energy E_a^{mw} in the semiconducting range. Crystals with a larger $\sigma_{\text{rt}}^{\text{mw}}$ have larger E_a^{mw} too. $(\text{pe})_2(\text{AsF}_6)_{0,75}(\text{PF}_6)_{0,35} \times 0,85 \text{ CH}_2\text{Cl}_2$ crystals usually have a larger E_a^{mw} (14 to 27 me V) than $(\text{pe})_2(\text{PF}_6)_{1,1} \times 0,8 \text{ CH}_2\text{Cl}_2$ or $(\text{pe})_2(\text{AsF}_6)_{1,1} \times 0,7 \text{ CH}_2\text{Cl}_2$ samples ($E_a = 8$ to 17 me V). The crystal with the highest conductivity in Figure 1 [$\sigma_{\text{rt}}^{\text{mw}} = 750 \text{ (Ohm cm)}^{-1}$] belonged to the class of "thin" crystals (cross section 14 x 8 μ) and was not cooled below 200 K in order to avoid its destruction by thermal tension and to preserve it for other measurements. The same crystal was used earlier for temperature dependent EPR-measurements.

The frequency dependent mw-conductivity was measured on the same samples at both frequencies thus avoiding quality effects of different crystals. All crystals (see fig. 1) do not exhibit a significant frequency dependence of the conductivity between 9,3 and 23,5 GHz.

The spectral reflectance data confirm a metallic like behaviour of the "mixed" $(\text{pe})_2(\text{AsF}_6)_{0,75} \cdot (\text{PF}_6)_{0,35} \times 0,85 \text{ CH}_2\text{Cl}_2$ system. Figure 2 shows the reflectance spectra with the direction of the polarization of the incident light parallel (R_{\parallel}) and perpendicular (R_{\perp}) to the (a-)axis of the perylene stacks. The R_{\parallel} -spectrum is typi-

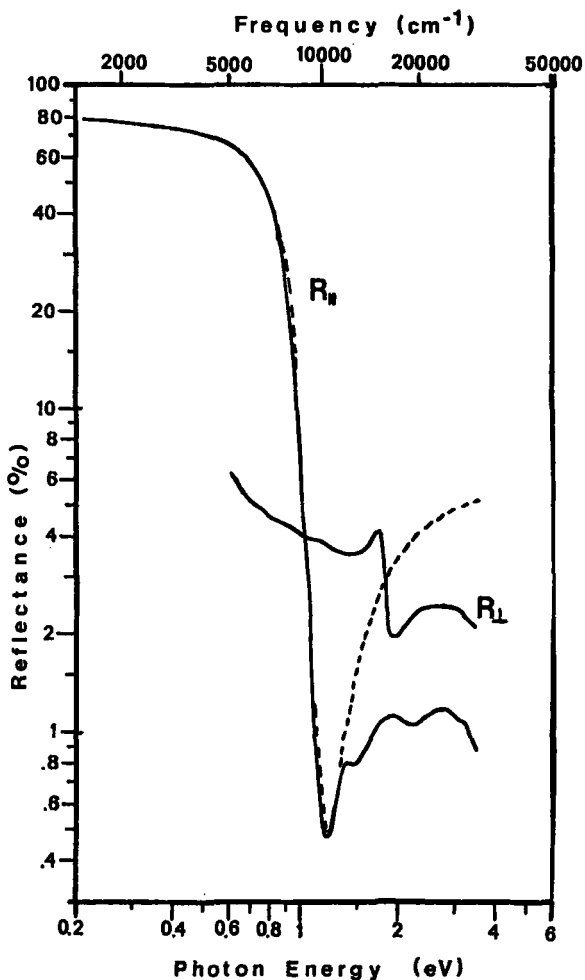


FIGURE 2 Polarized reflectance spectra of a "thick" $(pe)_2(AsF_6)_{0.75}(PF_6)_{0.35} \times 0.85 CH_2Cl_2$ single crystal. $R_{||}$ and R_{\perp} refer to the polarization direction with respect to the axis of the molecular stacks, full line: experimental curve, dotted line: Drude fit.

cal for a solid with free charge carriers. The values of the reflectance reach almost 80 % at low photon energies and exhibit a steep plasma edge with a pronounced minimum. At higher photon energies the spectral distribution of the reflectivity is dominated by the electronic transition in the organic molecules. If the direction of polarization is perpendicular to the stack axis (R_{\perp}), the crystal behaves optically as a non-conducting organic compound. Probably due to larger scattering losses at the surface above 1,3 eV the reflectivity here is smaller than for $(pe)_2 \cdot (PF_6)_{1,1} \times 0,8 CH_2Cl_2$ crystals¹⁰. The R_{\parallel} -spectrum was fitted by a Drude model (dashed curve). Therefore in this case a somewhat larger error must be assumed than in the case of the $(pe)_2 \cdot (PF_6)_{1,1} \times 0,8 CH_2Cl_2$ crystals, where a Lorentz-Drude model could be used¹⁰.

With the Drude parameter $\hbar\omega_p = 0,95$ eV, $\tau = 3,3 \times 10^{-15}$ sec and $\epsilon_{\infty} = 2,7$ an optical value for the electrical dc-conductivity of $\sigma_0 = 1700$ (Ohm cm)⁻¹ was calculated. This value is about 40 % larger as the largest value obtained from dc-measurements. Such differences are common¹⁰.

From the charge carrier concentration $N = 1,40 \times 10^{+21}$ cm⁻³ and the plasma frequency ω_p the effective mass of the free charge carriers can be calculated to $m^* = 0,77 m_0$. On the basis of a tight binding model for the band structure these effective mass value can be translated into a band-width¹⁰ of $t = 1,22$ eV. A repeating distance of 429 Å was used for this calculations.

A Fermi vector $k_F = 0,275 \pi/a$ was calculated. This value of the bandwidth is about 10 % larger as the one for $(pe)_2(PF_6)_{1,1} \times 0,8 CH_2Cl_2$ crystals¹⁰.

"Thin" crystals

The dc-conductivity of "thin" $(pe)_2(AsF_6)_{0,75}(PF_6)_{0,35} \times 0,85 CH_2Cl_2$ crystals shows a somewhat different temperature characteristic. With respect to their conductivities at least two types of "thin" crystals can be discerned.

One type whose conductivity characteristic is shown for a typical example in figure 3, $[\sigma_{rt}^{dc} = 1240 \text{ (Ohm cm)}^{-1}]$ shows an increase in conductivity by a factor of 5 to 10 and a maximum value of about $10000 \text{ (Ohm cm)}^{-1}$ around 200 K. There is a phase transition between 200 and 180 K to a semiconducting state.

A second, more seldom type of "thin" crystals has a sharp increase in dc-conductivity in a small temperature range with a sudden decrease at lower temperatures. After the sharp decrease in conductivity a weak increase before the transition to the semiconducting state is observed by lowering the temperature. Figure 4 shows the temperature dependence of an extreme example of such a second type "thin" crystal $[\sigma_{rt}^{dc} = 1400 \text{ (Ohm cm)}^{-1}]$. Within a temperature range of 15 K the conductivity increases by a factor of 50 having a maximum value of about $70000 \text{ (Ohm cm)}^{-1}$. After the sharp decrease in conductivity the crystal has a further plateau and a weak increase in con-

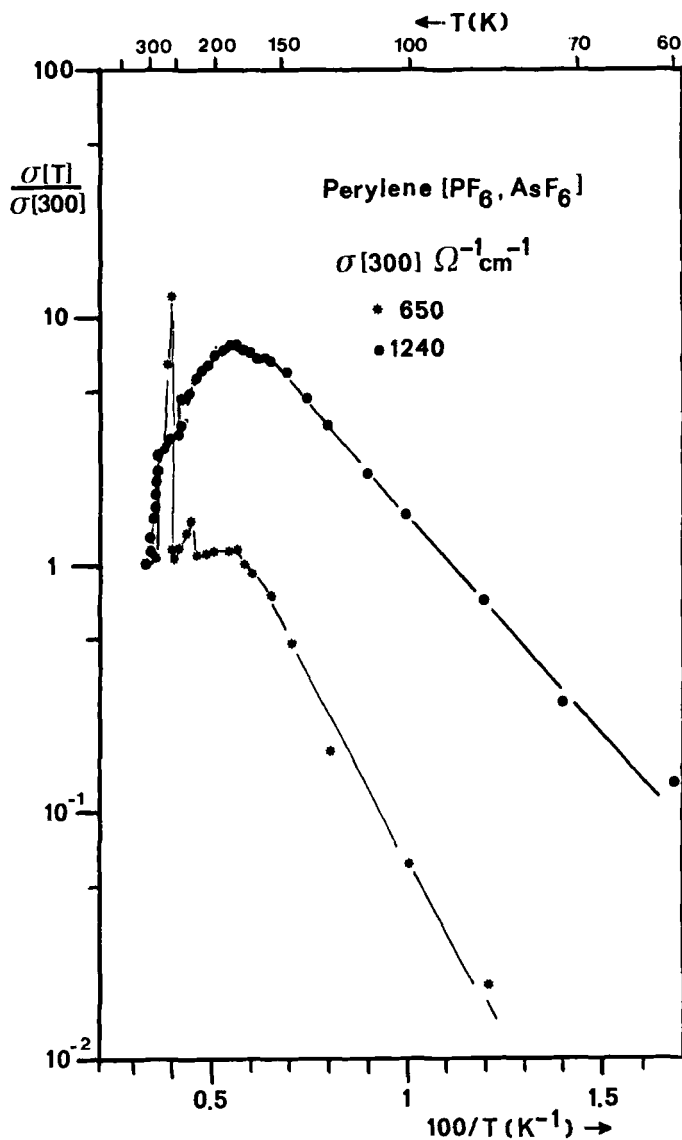


FIGURE 3 Normalized dc-conductivity of "thin" $(\text{pe})_2 \cdot (\text{AsF}_6)_{0,75}(\text{PF}_6)_{0,35} \times 0,85 \text{CH}_2\text{Cl}_2$ crystals vs. reciprocal temperature (see text)

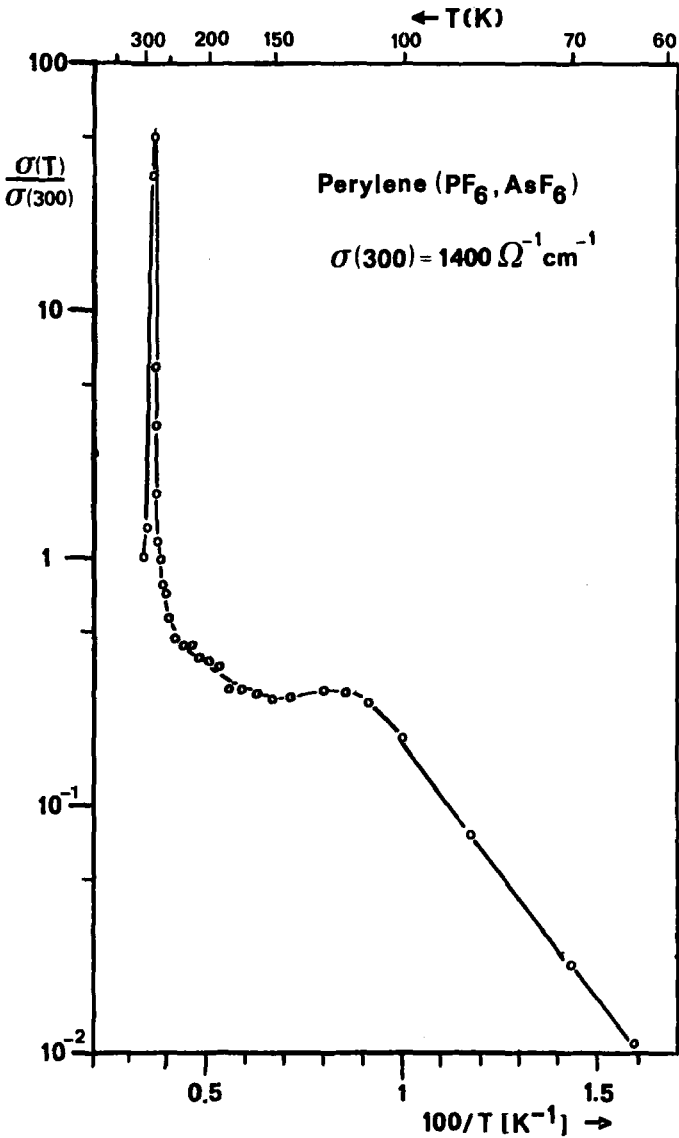


FIGURE 4 Normalized dc-conductivity of an extreme example of a "thin" $(\text{pe})_2(\text{AsF}_6)_{0.75}(\text{PF}_6)_{0.35} \times 0.85 \text{ CH}_2\text{Cl}_2$ crystal vs. reciprocal temperature (see text)

ductivity at around $300 \text{ (Ohm-cm)}^{-1}$. In a second temperature cycle with a reduced "starting" conductivity of $\sigma_{rt}^{dc} = 350 \text{ (Ohm cm)}^{-1}$ the sharp conductivity increase disappeared ($\sigma_{rt}^{dc}/\sigma_{max}^{dc}$ only 3).

There is experimental evidence that the disappearance of the huge conductivity peak after temperature cycling is connected with the 200 K transition. The technical problems with dc-conductivity measurements on such "thin" crystals with cross sections of the order of $10 \mu \times 7 \mu$ may explain the so far limited experimental data.

Comparison of "thick" and "thin" crystals

The question arises:

What is the difference between the "thin" and the "thick" crystals? An elementary analysis could not be done because of the small amount of "thin" crystals available. Furthermore, up to now it was not possible to investigate the crystal structure of the "thin" specimens by x-ray methods, because of their small cross section. Nevertheless, EPR-data show a clear difference between both types which indicate that the "thin" crystals might be more "one-dimensional" than the "thick" ones. For all crystals, "thick" and "thin" ones, only one EPR-line was observed with an isotropic g-value of 2.0022. All crystals show the same small anisotropy range with a maximum value $g_{max} = 2.0025$ and a minimum value of $g_{min} = 2.0019$ by turning the crystals around the needle (a-)axis and with the magnetic field perpendicular

to this axis. But the EPR-lines of "thick" and "thin" $(\text{pe})_2(\text{AsF}_6)_{0,75}(\text{PF}_6)_{0,35} \times 0,85 \text{CH}_2\text{Cl}_2$ crystals differ appreciably in their linewidth. The EPR linewidth of the "thick" crystals ranges between 0,5 and 1,2 Gauss depending on the individual crystal, while the "thin" crystals have a linewidth of only 95 mGauss. In all cases the EPR linewidth and the intensity of the signal is temperature independent in the metallic range down to 200 K. This is also true for those "thin" crystals which have the sharp dc-conductivity peak.

To clarify the difference between "thin" and "thick" $(\text{pe})_2(\text{AsF}_6)_{0,75}(\text{PF}_6)_{0,35} \times 0,85 \text{CH}_2\text{Cl}_2$ crystals further experiments are necessary. Additional information might be obtained by varying the concentrations of the AsF_6^- and PF_6^- anions in the preparation.

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