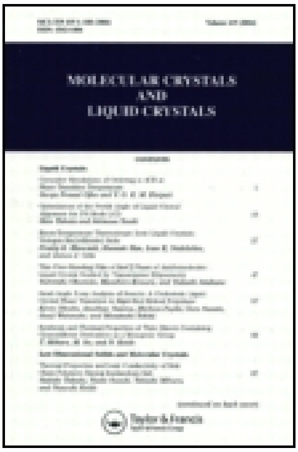

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Electron Energy Loss Investigation of Palladium Containing Liquid Crystals†

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Electron Energy Loss Spectroscopy was used for the first time to investigate collective properties of metal-containing liquid crystals: the applicability of this experimental technique to investigate electronic properties of liquid crystals is proved. Loss data were collected versus temperature and primary beam energy. Present results show that temperature can change the orientation of molecules with respect to the surface and that the studied material, after few thermal cycles up to 135°C becomes conductor and keeps its electrical conductivity from the solid state up to the isotropic phase.

INTRODUCTION

Metal-containing liquid crystals form a new class of thermotropic compounds obtained by complexation of mesogenic molecules with metals.[1] Previously we reported on Shiff bases copper complexes[2] and on *p*-alkoxy-*p*′-alkylazobenzenes complexed to palladium.[3] Such compounds are formed by two mesogenic molecules and one (copper case) or two (palladium case) metallic centers.

More recently, another example of palladium-mesogen whose molecule contains a thermotropic ligand and a palladium atom was prepared. The formula of this metallorganic molecule, Pd-complexed 4-4′-Bis(hexyloxy)-azoxybenzene, thereafter called AZPAC, is $C_{29}H_{33}N_2O_5Pd$. It is featured by a planar rigid core formed by the palladium atom and three aromatic rings and by two aliphatic chains which create an elongated molecular structure.[4] Figure 1 shows the most feasible structure of the molecule.

The AZPAC transition temperatures and the mesophases are:

$$(K \rightarrow 90°C\ (N) \rightarrow 105°C\ (I)$$

where K, N and I are respectively for Solid, Nematic and Isotropic phases.

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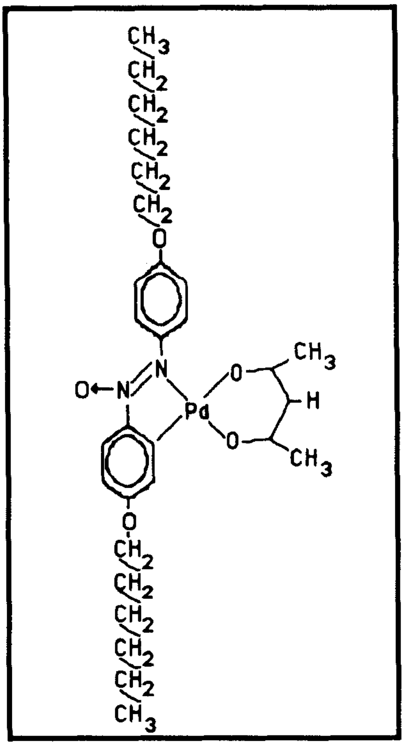

FIGURE 1 Formula of AZPAC.

The structures of liquid crystalline compounds are currently studied by Nuclear Magnetic Resonance, Electron Paramagnetic Resonance, X-Ray Diffraction, Small Angle X-ray Scattering, Neutron Scattering techniques.[5-9] Recently Extended X-Ray Absorption Fine Structures (EXAFS) were detected for the first time at the K-edge of copper mesogen liquid crystal.[10] In the metallo-mesogens case, because of the metal presence, other techniques, typical of research in semiconductors and metals (i.e. Electron Energy Loss, Auger or Photoemission Spectroscopies) can be used if the compound has a proper thermal stability.

In this paper we present the first electron energy loss results on Pd-containing liquid crystal with the aim to prove the applicability of this technique to liquid crystal studies and to provide information on their electronic and structural properties. Being the electron probe surface sensitive because of its short penetration length, free surface induced effects on the orientation of liquid crystal molecules can also be studied.

Electron Energy Loss Spectroscopy (EELS)[11] allows us to investigate collective properties of AZPAC. As it is known,[11,12] each EEL feature is the evidence of a longitudinal excitation created by the impinging electron. For small transferring moments, as it is the case,[13] EEL spectra can be also interpreted as an optical-like response[14] and compared to optical absorptions.[15]

We observed a temperature dependence of EEL spectra showing an insulating to conductive transition and an orientation change of the molecules of liquid-crystal uppermost surface layers.

EXPERIMENTAL

The AZPAC liquid crystal was first melt from powder under high vacuum (10^{-9} Torr) and then investigated by the EELS technique. The measurements were highly reproducible and much more resolved after several thermal cycles up to 135°C.

The partial pressure of the chamber was continuously monitored by a mass spectrometer and thermal desorptions, which might be due to H_2O and CO_2 trapped in the sample, were detected only during the first few thermal cycles. The chemical and physical stability of the so treated samples was confirmed through microanalytical data and optical observations with a polarizing optical microscope Zeiss Axioskop of the nematic phase texture. Auger technique did not show any other element than Pd, C, N and O on the surface.

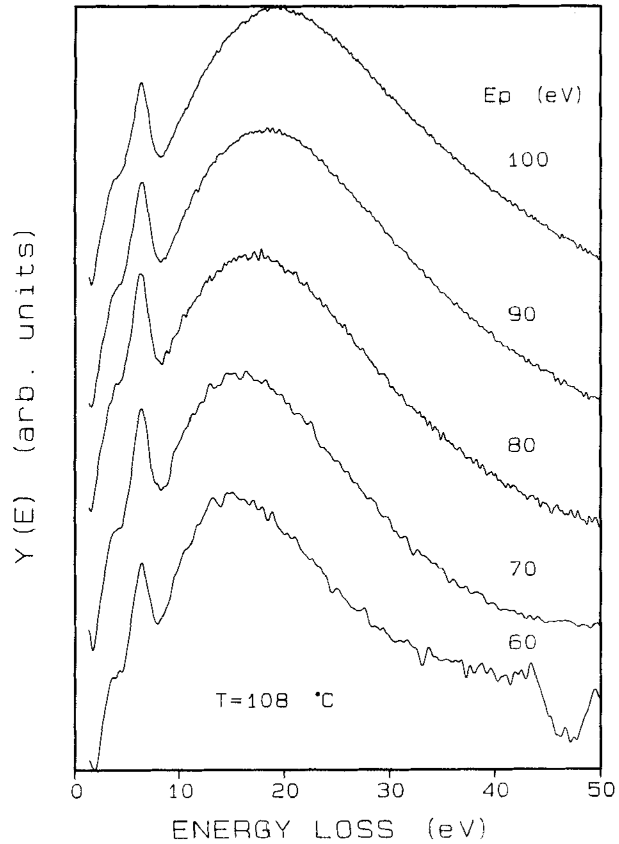

FIGURE 2 Electron energy loss spectra of AZPAC taken at T = 108°C for increasing *Ep* from 60 eV up to 100 eV. The shift of the broad feature from 14.7 eV (for *Ep* = 60 eV) to 20 eV (for *Ep* = 100 eV) is shown.

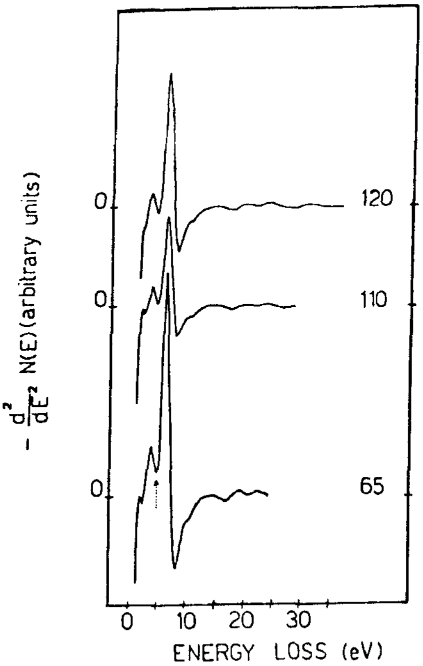

FIGURE 3 Electron Energy Loss spectra of polycrystalline Pd in the second derivative form. Note that each peak corresponds to a loss peak recorded in the integral form.

The surface exposed to the electron beam was supposed to be clean from possible contaminations because of the thermal cycles itselves. In fact they should give rise, each time, to new surfaces via convection of internal vortexes driven by the temperature gradient from the hidden to the free surface of the liquid crystal. Above 90°C the spectrum of the electrons backscattered from the sample showed the typical well-shaped electron secondary peak with a cut-off at only few ten's eV. That was the best evidence of the occurrence of electrical connections between the free surface and the sample holder through the liquid crystal. Once switched-on, this status was persistent even at room temperature for several minutes as expected because of the slow sample response to any thermal perturbation. The insulating to conductive transition was very clear and reproducible. Such a big change in the electrical conductivity of AZPAC allowed us to take EEL data without any use of experimental tricks to avoid charging effects.

DISCUSSION

Figure 2 shows EEL spectra taken at about 108°C for several primary beam energies (i.e. $Ep = 60$ eV, 80 eV, 90 eV and 100 eV). Although each loss feature of the same spectrum has different bulk and surface contributions, the spectrum taken at 60 eV is mainly bulk-like while that taken at 100 eV is mainly surface-like.

Comparing them with the EEL spectrum on pure Pd-polycrystalline sample[16] of

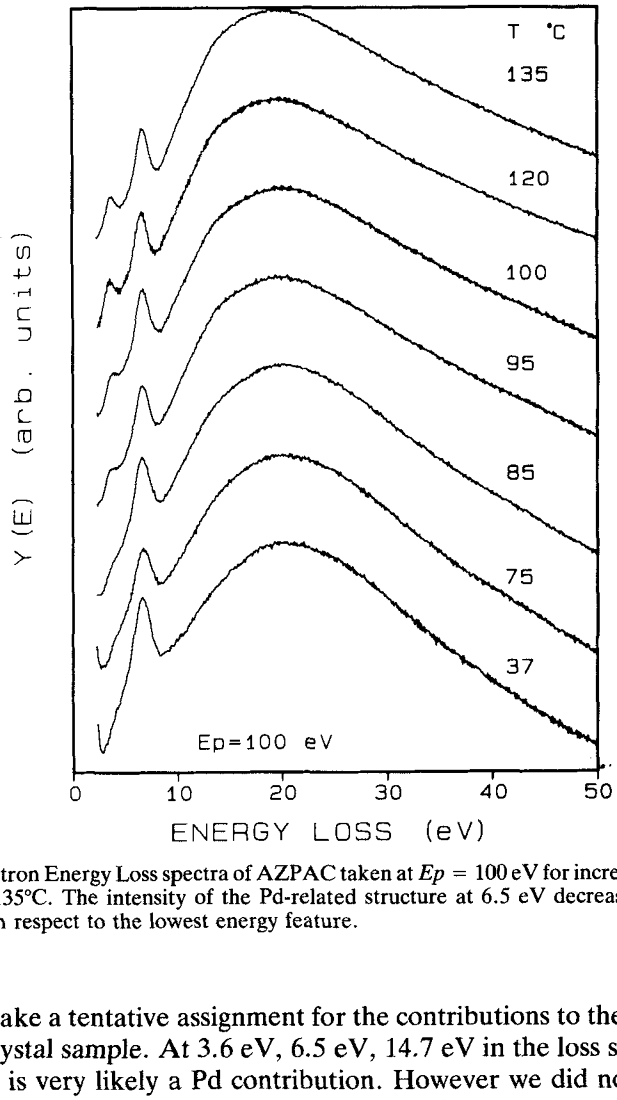

FIGURE 4 Electron Energy Loss spectra of AZPAC taken at $Ep = 100$ eV for increasing temperature from 37°C up to 135°C. The intensity of the Pd-related structure at 6.5 eV decreases on going from 37°C to 135°C with respect to the lowest energy feature.

Figure 3, we make a tentative assignment for the contributions to the EEL features of the liquid crystal sample. At 3.6 eV, 6.5 eV, 14.7 eV in the loss spectrum taken at 60 eV there is very likely a Pd contribution. However we did not observe any higher loss energy, probably because of the lack of long range order[16] in liquid crystals at this temperature.

On the contrary, the surface-like EEL spectrum ($Ep = 100$ eV) partially turns to the graphite EEL spectrum because the main plasmon moves from 14.7 eV up to 20 eV. In this respect the features at 3.6 eV and 6.5 eV might also have contributions from graphite-like signals[17] related to aromatic rigid cores. The above findings suggest a surface orientation of liquid crystal molecules with aromatic cores sticking out from the surface at a small angle. According to this picture we expect to observe both Pd-like and graphite-like contributions even if Pd atoms are deeper inside the volume.

The results of Figure 4 confirm the above interpretation because the EEL spectra taken at $Ep = 100$ eV (surface-like contributions) for several temperatures from

37°C up to 135°C are indicative of a change in the molecule orientation with respect to the surface.

At 37°C the EEL spectrum reproduces both Pd and graphite energy loss excitations; on increasing the temperature the ratio between the intensities of the two low energy losses changes and the main plasmon becomes more structured. Within the proposed picture, at $T = 37°C$, the molecules lie, indeed, almost parallel to the surface with the palladium-containing planar core floating on the surface, while at $T = 135°C$ a more intense surface contribution comes from aromatic rings and aliphatic chains. The change of the low energy loss features at about 85°C is probably to be related to the phase transition from solid to nematic. In the nematic phase, molecules are free to respond to the orientational strength provided from the vacuum-sample interface and change slightly their orientation with respect to the surface. As already said, such palladium-containing liquid crystal is insulating at room temperature, but few cycles up to 135°C, clearly ensure a good electrical connection to ground. The above model of the AZPAC liquid crystal texture seems to suggest an electrical connection provided by Pd-atoms from the surface down to the substrate. This finding is also supported by the comparison of EEL spectra on AZPAC with bulk-Pd EEL spectra. Pd-atoms in the liquid crystal must see each other so that bulk-like electronic properties are installed and observed.

From Figure 4 is also possible to locate interband transitions where minima of EEL spectra occur (see the arrow in Figure 3).[14,16] We suggest optical absorptions at 2 eV, 4 eV and 9 eV in agreement with optical transmission studies on dilute solutions of AZPAC liquid crystals.[15]

CONCLUSIONS

Electron energy loss spectra were carried out on AZPAC liquid crystals versus temperature and primary beam energies.

The rigid molecular aromatic core appears to form a small angle with the surface. The temperature can change the orientation of the molecules with Pd atoms being nearest to the surface at $T = 37°C$. Interband transitions are foreseen and located at 2 eV, 4 eV and 9 eV of photon energy.

Samples occur to be conducting after several thermal cycles up to 135°C: such property is observed fro the first time. Remarkably, the rise of electrical conductivity is itself an important finding to be used to understand transport properties and opens several possible technological applications.

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