EPR OF RADICALS TRAPPED IN IRRADIATED CYANIDE-DOPED KCl SINGLE CRYSTALS

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In the present work we studied one radical formed by irradiation at 77 K. We suggest that the radical contains C, N and other elements in its structure.

EXPERIMENTAL

Crystals of KCl doped with $2x10^{-3}$ parts of KCN was grown from the melt. The KCN used as a dopant was 90% enriched with the isotope ^{13}C. The crystals were irradiated at 77 K with ultraviolet light, using a high-pressure mercury arc lamp, Osram HBO, 500 W. The irradiation time was variable between 2 and 4 hours. The samples were in the form of rectangular parallelopipeds of 0.5x0.5x1.0 cm and each was located on a cold finger inside the resonant cavity. The research was carried out with a locally assembled X-band EPR spectrometer. The cylindrical cavity was a Varian V-4535 and the magnetic field was produced by a Varian 12-in. magnet. The infrared spectra was obtained with a Perkin-Elmer Model 180 spectrophotometer.

RESULTS AND CONCLUSIONS

Before irradiation, the crystals exhibited infrared bands in the range from 2100 to 2500 cm^{-1}. The CNO^- band shows greater intensity relative to CN^- band and was attributed to the presence of oxygen in the sample. No infrared spectral lines arising from hydroxyl (OH) or HCN^- vibrations were observed. On the other hand, other radicals without H, such as CNO^{2-}, CNN^- and $CNON^-$, are detected.

The EPR isotropic spectrum at 77 K consisted of two quintuplets with line intensities in the ratios 1:2:3:2:1 as shown in Fig.1.

The quintuplet splitting is evidence that they are due to the hyperfine interaction with the nuclear spin $I=\frac{1}{2}$ attributed to ^{13}C, with a relative large isotropic hyperfine coupling constant A_o^C. The splitting of five lines with variable intensities is due to the hyperfine interaction with two equivalent nuclei of nuclear spin I=1, attributed to N, with a relatively small isotropic coupling constant A_o^N.

The radical ion EPR spectrum exhibit the following Hamiltonian parameters at 77 K

$g_o = 2.0060$, $A_o^C = 53.3G$, $A_o^N = 10.0G$.

By annealing experiments the radical ion was observed to be stable below 179 K. The isotropic EPR spectrum disappeared and a second isotropic spectrum appeared above 179 K(1).

The spectrum in Fig.1 is attributed to a radical ion that contains in its structure C,N and other unidentified atoms. Measurements of EPR made at 13 K showed an anisotropic spectrum when the orientation of the external magnetic field on the (100) and (110) crystallographic planes was varied, a result to be reported elsewhere.

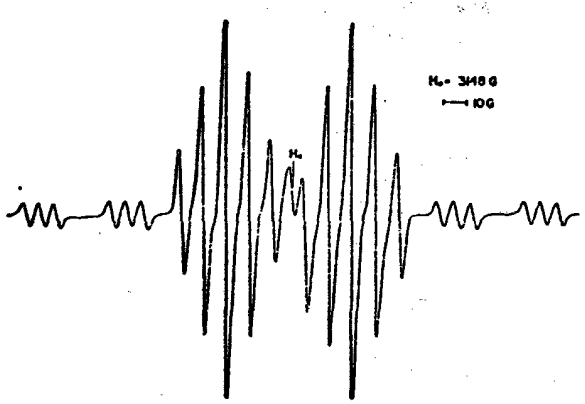

Fig.1 EPR spectrum of the radical ion at 77 K in KCl after irradiation at 77K

1. J.E.RODAS DURAN and H.PANEPUCCI, in Bull.Magn.Reson.(1986).