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ESR AND MAGNETIC SUSCEPTIBILITY STUDIES OF GRAPHITE INTERCALATED WITH TRANSITION METAL HEXAFLUORIDES

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ESR signals attributed to intercalated paramagnetic species in HOPG/MF_6 (M=Os, Ir) for stage I compounds were observed for the first time. A single metallic ESR line exhibiting significant field anisotropy was observed. The field dependence could be fitted to $g^2 = g_{\parallel}^2\cos^2\theta+g_{\perp}^2\sin^2\theta$ with $g_{\parallel} = 1.73\pm0.05$ and $g_{\perp} = 3.23$ for HOPG/OsF_6 and $g_{\parallel} = 2.4\pm0.1$ and $g_{\perp} = 3.23$ for HOPG/IrF_6 at $T = 6K$. These g values are temperature independent above 6K. Signal intensities diminish with temperature roughly according to the Curie Law and are practically unobservable above 40K for both systems. No resonance associated with conduction carriers could be observed.

A strong anisotropy of the g value can be attributed to (1) co-operative magnetic phenomena, (2) crystal field effects, or (3) exchange with conduction carriers. The first possibility was eliminated by magnetic susceptibility measurements performed over a range of 2-150K using a squid magnetometer. Susceptibility data obey Curie-Weiss behaviour except for deviations below 10K. In this lower temperature range they differ significantly from those reported by Bartlett. The magnetic moments (and Weiss temperatures) are $2.7\mu_B(\theta = -15K)$ and $2.3\mu_B(\theta = 0)$ for stage I and II HOPG/OsF_6, respectively. For stage I HOPG/IrF_6, $\mu_B \sim 0.7\mu_B(\theta = 0)$.

Susceptibility data as well as the temperature dependence of the ESR line intensity strongly support crystal field effects as the main mechanism accounting for the g values. Following Bartlett, we assume the intercalated species is $OsF_6^-(5d^3)$ in HOPG/OsF_6. The crystal field is mainly due to fluorines in the OsF_6^- anion. For the $5d^3$ configuration perturbation theory by Griffith yields $g_{\perp} \sim 2g_{\parallel}$, in rough agreement with our results. The ratio of spin-orbit coupling to overall crystal field splitting, ζ/Δ, is estimated to be ~ 0.1. Possibly the most important consequence of the ESR study is the existence of a well-defined symmetry and uniform orientation within the graphite planes leading to well defined crystal field effects.

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