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Origin of ESR linewidth for polypyrrole

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Abstract

ESR measurements were performed for a two-fold stretched film of PF_6^- doped polypyrrole (PPY-PF). Linewidths were observed as functions of temperature and the angle between the static magnetic field and the stretched direction. From the temperature dependence of the anisotropy amplitude, the linewidth of spins responsible for metallic properties in the crystalline region was deduced to be proportional to T^n, n ≈ 0.6. The g-shift was independent of temperature within the experimental errors.

Keywords: Electron spin resonance, Polypyrrole and derivatives

Magnetic susceptibility of PPY-PF comprises Pauli-like and Curie-like components. The former is attributed to spins in the crystalline region and the latter in the amorphous region. In order to elucidate the temperature variation of ΔH_{pp} of spins in the crystalline region, we measured the dependence of ΔH_{pp} on the angle between the static magnetic field and the aligned direction for a two-fold stretched PPY-PF. The angle dependence is reproduced by a relation, $a + b{\bullet}\cos^2(\theta+\alpha)$ at each temperature. b is defined as the anisotropy amplitude (A_{aniso}). α is a parameter originating in the uncertainty of the angle.

In Fig. 1, temperature dependence of A_{aniso} is shown by the open circles together with ESR linewidth (ΔH_{pp}) (the closed circles). One can see that at T > 50 K both of them show the same dependence on temperature, namely, $A_{aniso}/\Delta H_{\mathrm{pp}}$ = constant.

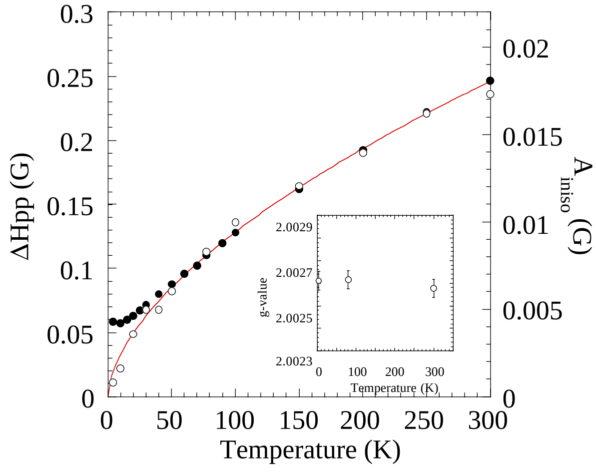

Fig.1 Temperature dependence of ESR linewidth (closed circles) and anisotropy amplitude of ESR linewidth (open circles) of PPY-PF. The solid curve is reproduced by $c{\bullet}T^n$, n ≈ 0.6. The inset: The g-values measured at 22.3 GHz.

Since ΔH_{pp} is dominated by Elliott mechanism, [1] the following relation is valid: [2]

$$\Delta H_{\mathrm{pp}} \propto \alpha(\Delta g)^2/\tau$$

where α is a numerical factor, Δg the g-shift, τ the relaxation time of electron momentum. Since the g-value is independent of temperature as given in the inset of Fig.1, $\Delta H_{\mathrm{pp}}(T) \propto 1/\tau(T) \propto \rho(T)$ can be deduced. As a result, the observed relation, $A_{aniso}/\Delta H_{\mathrm{pp}}$ = constant means that A_{aniso} is proportional to the electrical resistivity, $\rho(T)$. The positive slope of the temperature dependence of $\rho(T)$ suggests the metallic state in the crystalline region.

Below 50 K ΔH_{pp} slightly broadens probably due to Curie-like spins growing in this temperature range. This broadening is probably caused isotropic hyperfine interaction in the amorphous region. $A_{aniso} \propto \rho(T)$ decreases monotonically down to 4.2 K. This implies that by studying A_{aniso} of anisotropic Elliott broadening, the temperature dependence of $\rho(T)$ in the crystalline region can be investigated even at low temperatures in spite of the broadening of ΔH_{pp} contributed from the amorphous region. The temperature dependence in the range 4.2 K < T < 300 K turns out to be proportional to $c{\bullet}T^n$, n ≈ 0.6 (the solid curve in Fig.1).

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