Shallowly Trapped Electrons in Silver Halide Microcrystals: an Electron Spin Resonance Study

H. Vercammen†, D. Schoemaker, D. Vandenbroucke
Physics Department, University of Antwerp (UIA)
B-2610 Antwerp, Belgium

Abstract

Electron spin resonance experiments on AgCl emulsions doped with $[Ru(CN)_6]^{4-}$ are performed. This transition metal complex acts as a shallow trap for electrons.

The effective mass model is used to explain the electron spin resonance spectral changes, i.e., intensity and line width, after *uv*-illumination. Changes in line width are explained in terms of exchange and motional narrowing. These effects are studied as a function of concentration, temperature and *uv*-irradiation.

Finally, the concentration dependence of the stability of shallowly trapped electrons was studied using thermal anneal experiments.

1. Introduction

Electron traps are widely employed in conventional AgX (X=halide) photography. These traps are typically transition metal complexes substituted in the AgX lattice. Their properties can be classified in terms of electron release time. If the lifetime of the trapped electron state is larger than the typical time scale of latent image formation (1 ms – 1 s), i.e., the formation of silver clusters, the trap is deep or permanent. Examples[1-4] are $[RhCl_6]^{3-}$, the aquated derivates[3,4], or $[RuCl_5NO]^{3-}$ [5]. When the time scale of electron release becomes comparable with latent image formation, trapping is undeep, e.g.[6,7], $[IrCl_6]^{4-}$. In both cases, the electron is localized in one of the metal or ligand molecular orbitals. Shallow electron traps (SETs), on the other hand, are characterized by fast detrapping rates.

The behavior of the aforementioned SETs can be compared with shallow donor centers in semiconductors like Ge and Si, doped with P, As, Bi, or Sb[8,9]. Since the dielectric constant is rather large for AgX, electrons will be loosely bound in these centers. The effective-mass theory (EMT), as a model to describe

the wave function of the shallowly trapped electrons, was used by Bennebroek *et al.*[10], to describe their pulsed electron nuclear double resonance results at 95 GHz for the intrinsic SET in AgCl as well for the Pb^{2+} and Cd^{2+} SETs[11]. More recently, the $[Fe(CN)_6]^{4-}$ SET in AgCl was investigated[12] and the hydrogen-like wave function model is now firmly established. Application of the EMT gives a value for the binding energy for the intrinsic SET center[10], which is (45.4 ± 2.2) meV, compared to 45.0 meV, obtained experimentally[13].

The electron spin resonance (ESR) spectrum of SETs reveals only a single, structureless line, centered at about $g = 1.878$[12,14] for AgCl and $g = 1.489$[14] for AgBr. These values are independent of the nature of the metal complex involved, due to large delocalization of the loosely bound electron. As a consequence the g value is shown to be dependent on lattice composition[14].

2. Experimental

2.1. Sample preparation

The AgCl microcrystals were prepared using a *p*Ag controlled double-jet precipitation technique. Crystal growth was done at low *p*H and *p*Ag= 7.5. The dopants were introduced in a third jet between 5 and 95 % of the grain volume. The concentration of the traps was varied between $1 \cdot 10^{-6}$ and $150 \cdot 10^{-6}$ mol per mol Ag. Samples of these emulsions were coated on a film base at approximately 25 mmol AgX/m^2 and 4 g gel/m^2.

2.2. Methods

The ESR spectra were recorded using an X-band ESR spectrometer (BRUKER) operated at 9.4 GHz. A continuous-flow helium cryostat (Oxford Instruments) was mounted in the cavity, so that ESR measurements

could be performed in a temperature-range from 1.5 K to 300 K.

The coated AgCl and AgBr emulsion strips were irradiated in an optical transmission cavity. The irradiation source was a Xenon lamp, equipped with an interference filter, transmitting around 366 nm.

The ESR spectra of SETs, obtained in this work, were carefully fitted with a Gaussian line shape. By this procedure the integrated intensity, line width and position are determined in a reproducible manner.

3. ESR Results

The ESR signal of SETs consists of a single resonance line. As an example, for the SET in 100 ppm $Ru(CN)_6^{4-}$ doped AgCl emulsion the average g value at 1.6 K and is 1.8785 ± 0.0002, with a line width of 0.55 ± 0.05 mT. This information was obtained by fitting the experimental spectrum with a Gaussian line. This indicates that the line is inhomogeneously broadened, which means that, due to the delocalized nature of the SET, the line width at very low temperatures is uniquely determined by superhyperfine-interactions with neighboring ions, mostly Ag^+ and Cl^-. On the other hand, mechanisms such as exchange and hopping, will also influence the line width. Figures 1 and 2 show the ESR signals and their behavior at different temperatures.
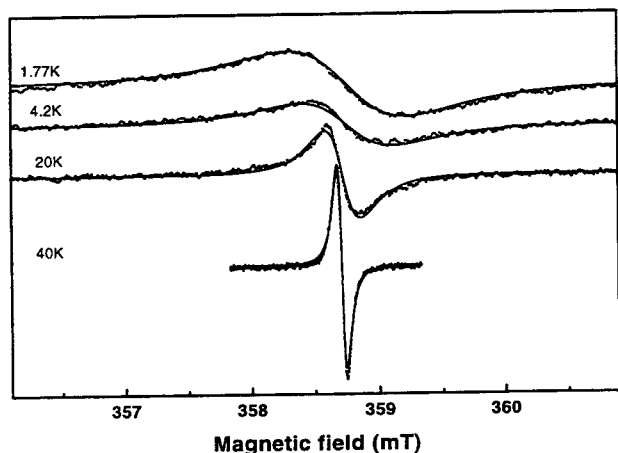
a thermally activated process and the influence on the line width, δH_{hop}, can be described[16] as a function of temperature T and average distance between complexes R, as $\delta H_{hop} \sim \exp{(2R/r_0)} \cdot \tanh{(\Delta/2k_B T)}$. This formula will be discussed further on in the text. The curves in figure 2 are simulated for the three different concentrations. The activation energies E, obtained by this method lie between $1.1 - 1.5$ meV, and appear to be slightly dependent on concentration. The change in line width as a function of concentration can be understood from the inset and the functional dependency on concentration, or equivalently, the average distance between SETs, R: $\exp{(2R/r_0)}$. This property not only results from hopping, but also of exchange narrowing of the line, due to the increasing concentration. It will be discussed later on that changes in line width related to exchange narrowing can be described by an almost similar functional dependence.
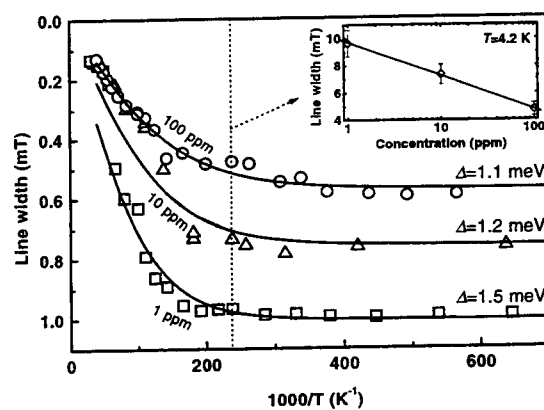
Figure 2: Temperature dependence of the SET line widths in $[Ru(CN)_6]^{4-}$ doped AgCl emulsions. The concentrations are 1, 10 and 100 ppm. The AgCl emulsions are uv-illuminated at 1.6 K. The inset shows the line width at 4.2 K plotted against the logarithm of the concentration.

Figure 1: Example of the ESR spectra of the SET in 150 ppm $Ru(CN)_6^{4-}$ doped AgCl emulsions after uv-excitation at 1.8 K, measured at different temperatures. The solid curves represent simulations with a Gaussian line shape.

The temperature dependence of the ESR signals in figure 2 can be explained by the process of motional narrowing, caused by hopping motion. This is

The thermal stability of the SETs appears dependent upon concentration. Figure 3 shows that the thermal stability of filled SETs is enhanced to higher temperatures with increasing dopant concentration. During successive thermal anneals, the electrons become mobile and the concentration of filled SETs will be lowered. This implies, that the average distance between trapped electrons r_{av}, is increased, causing an increase in line width. Nevertheless, at the lowest temperatures there is a small decrease in line width for the 10 ppm, and more pronounced for 100 ppm sample. This could indicate that between 20 K and 40 K,

where the 1 ppm signal is already decaying, there is some sort of reorganization: electrons, released from SETs in accidentally lower concentration regions (e.g., near the surface), can move to higher concentration regions (e.g., to the inside). These regions appear more stable. During this process the *local* concentration of electrons grows, while the *global* concentration remains the same, and at all times the concentration of metal complexes remains the same. The above might explain the small decrease in line width.
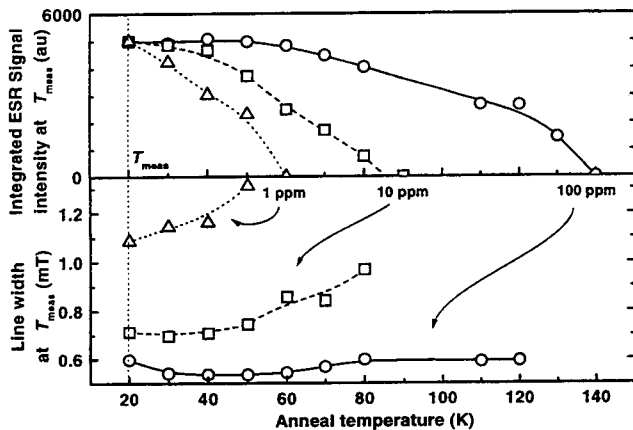

Figure 3: Thermal anneal experiments for 1, 10 and 100 ppm $[Ru(CN)_6]^{4-}$ doped AgCl emulsion. The ESR measuring temperature (T_{meas}) is 20 K for all points, and anneal durations are 1 min. The SET ESR signal decays at lower temperatures for lower concentrations. In the lower figure, the line width at T_{meas} during the experiment is displayed.

Filled SETs are created by *uv*-excitation in the band gap of the AgCl. Due to the low time response of conventional ESR spectrometers, only a resolution in the order of seconds is obtained with low intensity irradiations.

4. Application of the hydrogenic model for SETs in the ESR analysis

Experimental evidence for the hydrogen-like orbital of the SET is well established[10,12]. The spin density $|\Psi(\alpha)|^2$ on a particular nucleus α is proportional to a density function $|\Phi(\alpha)|^2$. The analysis shows –on the basis of EMT– that at large distances[12] from the center, the envelope function $\Phi(r)$ can be described by a hydrogen-like $1s$ wave function[8],
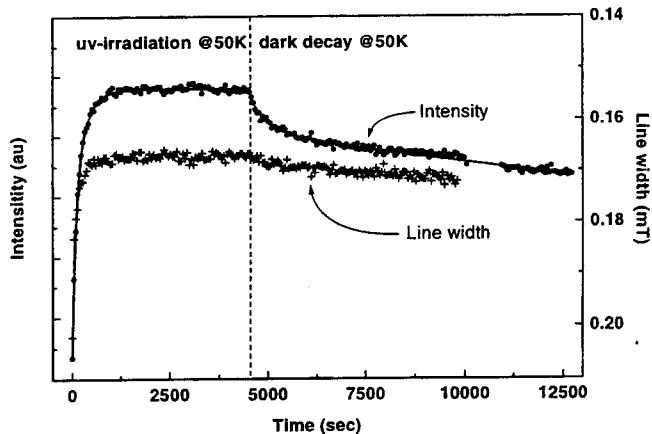
$$\Phi(r) \sim \exp(-r/r_0), \tag{1}$$

Figure 4: Example of the ESR signal of SETs for 100 ppm doped $[Ru(CN)_6]^{4-}$ doped AgCl emulsion, during continuous uv-irradiation, as a function of time at 50 K. Both intensity and line width of the signal are represented.

where r_0 is the effective Bohr radius of the SET (e.g., $r_0 = (18.5\pm1.1)$ Å for $[Fe(CN)_6]^{4-}$ in AgCl[12]). From this envelope function, the inhomogeneously broadened line width can be calculated, and as a result of the large delocalization, only a single structureless line is observed. This approximation is only valid for dilute systems, where –on average– no wave function overlap exists between different centers.

At higher concentrations this approximation is no longer valid, and overlap between nearby trapped electrons cannot be neglected. Anderson[15] has shown that the line width δH_{ex} of the ESR line is inversely proportional to the exchange energy J: $\delta H_{ex} \sim J^{-1}$. When $r_{av} \gg r_0$, where r_{av} is the average distance between trapped electrons, the exchange energy can be approximated[18] by $J(r_{av}, r_0) = J_0 \exp(-r_{av}/r_0)$, and the effect on the line width can be expressed as:

$$\delta H_{ex} \sim \exp(r_{av}/r_0). \tag{2}$$

The concentration of trapped electrons can be raised in two ways: increasing the number of traps ($r_{av} \uparrow$ and $R \uparrow$) or increasing the incident uv-irradiation ($r_{av} \uparrow$). The number of traps should in principle be the upper-limit of trapped electrons. When the concentration of trapped electrons is raised during uv-irradiation, the exchange will increase, but the line width due to exchange, δH_{ex}, will decrease. In this way not only the intensity of the resonance line is indicative for the number of centers, but also the line width, δH_{ex}, is a function of the concentration of shallowly trapped electrons. The overlap between two shallowly trapped electrons is expected to be more or less independent

on temperature, confirming that exchange narrowing is not a function of temperature.

Below about 4.2 K, the electrons are confined in hydrogen-like states. Above 4.2 K, phonon-induced hopping[9,19] will cause conduction. The effect on the line width can only be observed if the hopping rate becomes comparable or larger than the dominant superhyperfine splittings in the inhomogeneously broadened line. The effect on line width as function of temperature T, average distance between the $[Ru(CN)_6]^{4-}$ centers R and Bohr radius r_0 can now be written as[17]:

$$\delta H_{hop} \sim \exp(2R/r_0) \cdot \tanh(\Delta/2k_BT), \qquad (3)$$

where Δ is the activation energy for hopping[9,16]. The experimental value for Δ, that is determined in this work, is situated around $1.1 - 1.5$ meV. The validity of this approach has recently supported by Clerjaud et al.[20], applied to conduction-electron spin resonance data on n-type InP. Their value for Δ lies between $1.0 - 1.6$ meV, and can be compared with our values. Equation (3) demonstrates the temperature dependence of the ESR line width: due to the hopping process, which is favored at higher temperature, the line will narrow with increasing temperature. Furthermore if the concentration of traps is increased (decrease of R) hopping is promoted, and the line will further narrow.

5. Conclusions

We have shown that, through the behavior of the line width, two physical properties of SETs –hopping and exchange– can be examined. The variation in line width is studied as a function of temperature, and dopant and electron concentration, and is, in this sense, an excellent indicator for various physical processes.

The stability of the SETs is dependent on dopant concentration. This indicates that the concentration of traps is a parameter, easily accessible, for changing the performance of a given photographic AgX system.

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References

† Address: Universiteitsplein 1, B-2610 Antwerpen, Belgium, fax 32-3-8202245, telephone 32-3-8202454,

e-mail: *hansver@uia.ua.ac.be.*

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