

**Electron Spin Relaxation in Solid Metal–Ammonia Solutions
Evidence for Highly Mobile Electron Pairs near the Metal–Non-
metal Transition**

By R. CATTERALL

Department of Chemistry and Applied Chemistry,
University of Salford, Salford M5 4WT, Lancs.

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ABSTRACT

The existence of a very narrow, homogeneously broadened electron spin resonance signal in frozen metal–ammonia solutions requires rapid modulation of electron–nuclear hyperfine interactions. Previously proposed models of unpaired electron motion in fluid solutions depend on viscous motion and so are not applicable to the solid state. The mobile electron pair model proposed by Catterall and Mott (1969) to describe the metal–non-metal transition in fluid solutions provides a natural explanation for the high mobility in the solid state.

§ 1. INTRODUCTION

Catterall and Mott (1969) have proposed that the metal–non-metal (MNM) transition in fluid alkali metal–ammonia solutions accompanies an increase in concentration of highly mobile e_2 centres, i.e. pairs of electrons trapped at single cavities in the liquid structure. Although the number of these carriers is only a small fraction of the total number of e_1 centres, their high mobility is responsible for the very rapid increase of conductivity in this region. Unfortunately most physical properties of metal–ammonia solutions are dominated by the high concentrations of e_1 centres and no direct evidence for the existence of highly mobile e_2 centres was available. The purpose of this note is to present evidence for the existence of these mobile centres in frozen (vitreous) metal–ammonia solutions.

We first examine electron motion in very dilute liquid metal–ammonia solutions. The diffusion coefficient for electrons

$$D(e^-) = 2.66 \times 10^{-4} \text{ cm}^2 \text{ sec}^{-1}$$

is much higher than expected for ionic diffusion, e.g.,

$$D(\text{Na}^+) = 4.66 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$$

(Catterall and Dye 1970) and all electron–nuclear interactions are rapidly modulated in a random fashion by this motion, resulting in time-averaged electron spin resonance spectra. Electron spin relaxation in dilute liquid metal–ammonia solutions (Catterall 1969, 1970, O'Reilly 1969) is dominated

by two processes: a rapid modulation of scalar electron–nitrogen hyperfine interactions, T_{1e}^{-1} (scalar), and a spin–orbit coupling term, T_{1e}^{-1} (s.o.),

$$T_{1e}^{-1} = T_{1e}^{-1} (\text{scalar}) + T_{1e}^{-1} (\text{s.o.}).$$

These terms are clearly distinguished by their different dependences on the correlation time, τ , for electron motion

$$T_{1e}^{-1} = H\tau + S\tau^{-1},$$

where H and S are hyperfine and spin–orbit coupling constants. For very dilute solutions relaxation by the spin–orbit mechanism makes only a minor contribution (Catterall 1969) to T_{1e}^{-1} . However, as either metal concentration or temperature is increased (O'Reilly 1961, 1969, Catterall 1969) τ decreases and eventually the spin–orbit interaction dominates and causes strong broadening of the electron resonance line. At room temperature the onset of this broadening (Catterall 1965) and a characteristic asymmetry occur at concentrations an order of magnitude lower than for the MNM transition (see Catterall and Mott 1969, fig. 4) so that the ESR in the MNM region is uninformative. However, the onset of broadening shifts strongly to higher concentration as the temperature is lowered and the possibility arises of studying the MNM transition by electron spin resonance at low temperature where spin–orbit broadening is not significant. An estimate of the spin–orbit coupling constant was given by Lloyd and Pake (1954):

$$S = (\Delta g)^2 \bar{\delta}^2 / (\Delta E)^2.$$

For dilute fluid solutions $\tau \propto \eta/T$ over a wide range (Cutler and Powles 1963, Catterall 1969) while optical line widths ($\simeq \bar{\delta}$) are independent of temperature (Burow and Lagowski 1965) so that using optical transition energies (ΔE) (Catterall and Symons 1965, Burow and Lagowski 1965), measured g -factor shifts (Δg) (Catterall and Symons 1964, 1965), and viscosities (η) (O'Reilly 1955, Krynicki and Hennel 1963, Wa She Wong 1966) at 300 and 195 K we find (see table)

$$T_{1e}^{-1} (\text{s.o.}) (195 \text{ K}) / T_{1e}^{-1} (\text{s.o.}) (300 \text{ K}) \simeq 0.05.$$

Over the same temperature interval T_{1e}^{-1} (scalar) $\propto \eta/T$ increases by a factor of seven, and it is obvious that there is no appreciable contribution from spin–orbit coupling to the total electron relaxation rate at temperatures near the freezing point. Therefore, a study of the glass, which also removes narrowing by diffusive motion, can give evidence for the presence of mobile electrons.

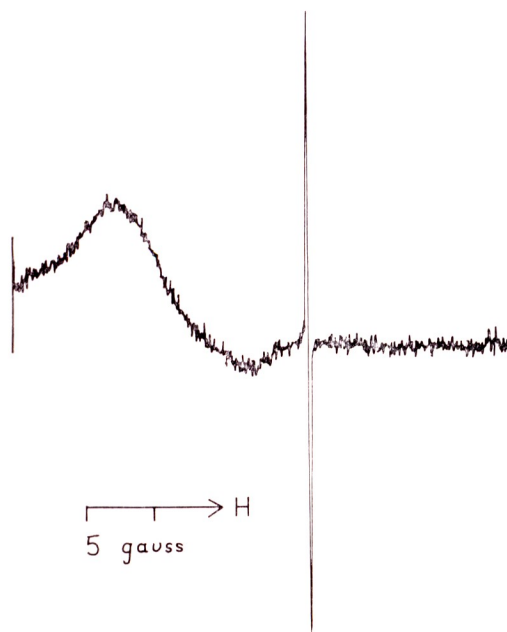
T (K)	$10^3 \Delta g (\text{K-NH}_3)$	ΔE (cm $^{-1}$)	$10^2 \eta$ (g cm $^{-1}$ sec $^{-2}$)	$10^{-4} (\Delta g / \Delta E)^2 (T / \eta)$
300	1.7	5500	0.126	2.27
195	1.4	7500	0.570	0.12

§ 2. RESULTS

Metal-ammonia solutions freeze at ~ 195 K with a very strong tendency to separate into crystalline phases of pure ammonia and pure metal. By adding high concentrations (up to 1 mol l^{-1}) of structure-breaking salts and quenching very rapidly to 77 K, we have been able to obtain vitreous blue beads of sodium- and potassium-ammonia solutions in the concentration region (0.1 to 0.8 mol l^{-1}) just below the MNM transition ($\sim 1.0 \text{ mol l}^{-1}$). Attempts to glassify more dilute solutions have been unsuccessful.

Electron spin resonance spectra (9.3 GHz) of these samples at 77 K contained very narrow singlet resonances (see figure) with power saturation behaviour characteristic of homogeneous broadening (i.e. time-averaged signals). Line widths ($\Delta H_{\text{ms}} < 0.1$ gauss) and g factors (1.9992 ± 0.0002) were independent of metal or salt concentration for sodium solutions containing sodium chloride (3 samples), sodium bromide (4), sodium iodide (1), and potassium solutions containing potassium bromide (6), and potassium iodide (8). Salt concentrations varied from 0.1 to 1.0 mol l^{-1} and metal concentrations from 0.1 to 0.5 mol l^{-1} with one sample (K/KBr) of 0.8 mol l^{-1} . Accurate determinations of line widths ($\Delta H_{\text{ms}} \lesssim 0.035$ gauss) using superheterodyne detection were made for two K/KBr samples and one K/KI sample.

Spectra at 150 K were unchanged and irradiation with light in the visible region had no effect. Fluid solutions at 195 K gave the normal solution



Electron spin resonance spectrum (9.3 GHz , 77 K) of a rapidly quenched potassium-ammonia solution containing 0.4 mol l^{-1} potassium and 1.0 mol l^{-1} potassium bromide.

line but slow cooling to 77 K (with obvious crystallization of ammonia) did not regenerate the narrow line which could only be regained by very rapid quenching.

Unpaired electron spin concentrations giving rise to the singlets were determined relative to the colloidal sodium resonance obtained after slow freezing. The fraction of unpaired electron spins was only $\sim 0.1\%$.

Other, much broader spectra from radical species were always present (see figure) but did not interfere. These will be discussed elsewhere (Catterall, Cronenwett, Egland and Symons 1970).

§ 3. DISCUSSION

3.1. *Identification of the Singlet*

The electron spin resonance was independent of the nature or concentration of metal or salt and was only present after rapid quenching. The line width and saturation behaviour strongly support a time-averaged situation, and the signal is quite recognizably not that of expected impurities: O_2^- , O_3^- , N_2^- , CO_2^- , and nitrogen oxide radicals (Atkins and Symons 1967). Very narrow resonances have been observed for precipitated lithium metal particles at room temperature (Kaplan and Bray 1963), but are precluded for higher alkali metals by enhanced spin-orbit coupling. Line widths at 77 K for colloidal lithium (~ 1.5 gauss), sodium (~ 2 gauss) and potassium (~ 13 gauss) in frozen metal-ammonia solutions have been reported by Levy (1956).

Accordingly the singlet is taken to arise from transitions of solvated electrons which have been frozen-in by rapid quenching.

3.2. *Spin Concentration*

Long-range spin exchange interactions (Catterall and Mott 1969, Catterall and Dye 1970, Dye 1969) between e_1 centres lead to strong electron spin-pairing in fluid metal-ammonia solutions. The extent of the pairing is dependent upon concentration and temperature (Freed and Sugarman 1943, Huster 1938, 1948, Hutchison and Pastor 1953) and an analysis of the heats of dilution yielded an enthalpy change on spin pairing (ΔH) of -2.4 kcal mol $^{-1}$, i.e. spin pairing is exothermic to the extent of about $4kT$ at room temperature (Dye 1969, Catterall and Dye 1970). Using a simple model of a perfect classical gas Hill (1948) expressed the temperature dependence in terms of

$$K = (\text{concentration of unpaired electrons})^2 / (\text{concentration of electron pairs})$$

by

$$K = \text{constant } T^{3/2} \exp(-\Delta H/kT)$$

and from spin concentration measurements at 300 K we calculate a fraction of unpaired spins, $\alpha = 5 \times 10^{-3}$ at 77 K, which is in order of magnitude agreement with the observed fraction ($\sim 10^{-3}$).

Furthermore, Hill (1948) found that the transition from a classical system to a quantized one in which the assemblies of unpaired and paired spins obey Fermi-Dirac and Bose-Einstein statistics respectively tended to decrease the fraction of unpaired spins still further.

We conclude, therefore, that the low concentrations of unpaired electron spins which we observed are quite consistent with the temperature dependent spin pairing observed in fluid metal-ammonia solutions.

3.3. *Modulation of Electron-Nuclear Interactions*

In view of the evidence discussed above, we treat the electron spin resonance line width in frozen solutions as arising from rapidly modulated electron-nuclear interactions. Furthermore, since formation of the vitreous state requires major retention of fluid structure, we describe electron relaxation in the solid state solely in terms of rapidly modulated scalar hyperfine interactions between electrons and nitrogen nuclei just as for fluid solutions and with the same total coupling constant, na_N . The relaxation rate is related to the observed line width and the hyperfine coupling constant by (Catterall 1969)

$$T_{1e}^{-1} = T_{2e}^{-1} = A_N na_N^2 \tau = \sqrt{3} g_e \beta_e \Delta H_{ms} / 2\hbar,$$

where

$$A_N = 2x_N I_N (I_N + 1) / 3\hbar^2,$$

g_e is the electronic g factor, β_e the Bohr magneton, I_N the nitrogen nuclear spin in units of Planck's constant \hbar , and each electron has a coupling constant a_N to each of the x_N nitrogen nuclei in the n equivalent ammonia molecules solvating the electron.

Using $na_N = 2.04 \times 10^{-18}$ ergs from the nitrogen Knight shift (O'Reilly 1964) we obtain

$$\tau/n(\text{fluid}) = 0.69 \times 10^{-13} \text{ sec at } 300 \text{ K},$$

$$\tau/n(\text{solid}) \leq 1.06 \times 10^{-13} \text{ sec at } 77 \text{ K},$$

or, for $n = 7$ (Catterall 1969, 1970),

$$\tau(\text{fluid}) = 4.9 \times 10^{-13} \text{ sec at } 300 \text{ K},$$

$$\tau(\text{solid}) \leq 7.4 \times 10^{-13} \text{ sec at } 77 \text{ K}.$$

3.4. *Source of Modulation Rates*

Up to the present time the mechanism responsible for the rapid modulation rates has only been discussed for fluid solutions. In this section the various mechanisms are outlined and shown to be dependent on viscous motion which must be severely reduced by freezing.

Kaplan and Kittel (1953) explained the rapid modulation of the scalar electron-nuclear coupling by a random rotation of ammonia molecules on the periphery of the electron's cavity. Pollak (1961) introduced the concept of modulation by electron tunnelling between vacant sites in the

solvent structure (Dewald and Lepoutre 1956), whilst Newmark, Stephenson and Waugh (1967) and Cutler and Powles (1963) showed that the correlation time for unpaired electron motion is an order of magnitude shorter than the Debye correlation time for molecular rotation. Modulation by solvent exchange between bulk solvent and the electron's solvation shell should be slower than by molecular rotation. Farkas (1932) and Arnold and Patterson (1964) have considered electron hopping between cation sites to explain conductivity, but electron spin resonance studies of europium-ammonia solutions (Catterall and Symons 1965) have demonstrated the absence of strong electron-cation interactions.

Electron tunnelling by electrons in cavities (e_1) can only occur when another suitably preformed but empty cavity is in the close vicinity of a solvated electron. The motion has a high probability only when the polarization potentials around the empty cavity and the electron are equal. Unless the concentration of empty cavities is extremely high, tunnelling is only feasible when normal diffusion processes bring an e_1 centre and an empty cavity into fortuitous proximity. Mobility of cavities in fluids is very high and the collision of empty cavities and electrons (with a collision radius $\gtrsim 10 \text{ \AA}$) would be the rate-controlling step determining unpaired electron mobilities. Such a process is viscosity-dependent and substantially slower in frozen solutions. Since the correlation time for modulation of electron-nuclear interactions is nearly unchanged on freezing, we conclude that electron tunnelling to empty cavities is not the dominant mode of electron motion. Similarly the viscosity-dependent solvent rotation and exchange processes are ruled out.

In the discussion at the Colloque Weyl II (1969) there was considerable support for an 'amoeba-like' motion: the electron-in-a-cavity drifting through the ammonia lattice without appreciable mass transport of solvent. Such a process requires continual orientation polarization and depolarization of solvent along the path of the electron together with some translational motion to allow cavity motion. It is difficult to see how electron mobility by this mechanism could remain unchanged on freezing.

Random molecular motions within solvation shells in fluid solution (Swift 1969) could modulate electron-nuclear interactions, particularly if solvent density in these regions is low, but it is difficult to see them maintained without change in rate into the solid state.

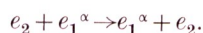
We must conclude, therefore, that none of the mechanisms proposed so far for electron motion is compatible with the almost unchanged rates of modulation of electron-nuclear interactions which we have observed in frozen solutions.

3.5. *Mobile e_2 Centres*

Catterall and Mott (1969) proposed that near the MNM transition fluid metal-ammonia solutions contained a sub-lattice of e_1 centres together with a small fraction of doubly occupied centres, e_2 . The mobility of the

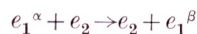
e_2 centres was high because hopping of an extra electron between e_1 centres required only a relatively small polarization change and no translational motion of solvent.

We propose that this situation is maintained in rapidly quenched metal-ammonia solutions since very little solvent reorientation is required, and that the modulation of electron-nuclear interactions occurs by random migration of a small fraction† of e_2 centres which limits the lifetime of an unpaired electron in any particular nuclear site but does not limit the lifetime of any given electron spin state α :



The migration of an e_2 centre in one direction is formally identical to e_1 migration in the opposite direction.

Exchange processes which interrupt the electron spin state



would lead to uncertainty broadening of the electron spin resonance and no exchange narrowing.

3.6. Pressure Dependence of the MNM Transition

The decrease in conductivity with increased pressure in the MNM region was tentatively explained (Catterall and Mott 1969) by an increase in cavity volume when an e_1 centre traps a second electron: in fact we proposed

$$2V(e_1) < V(e_2).$$

This cavity expansion requires appreciable solvent reorientation and should be inhibited on freezing. If this cavity expansion were a necessary prerequisite for electron motion, freezing would result in decreased mobility of e_2 centres since thermal fluctuations in the rigid solution are unlikely to lead to large expansions of cavities. However, high mobility *is* observed and we must conclude that the formation of e_2 centres does not necessarily require the relaxation of solvent shells, i.e. an attractive potential for a second electron is a property of e_1 centres, whilst solvent relaxation in the fluid medium provides only an additional stabilization. If this is the case, we suppose that the probability of freezing out electron pairs in large cavities is less than for smaller e_1 centres, with a resulting tendency for electron pairs to be trapped in smaller cavities with a correspondingly lower activation energy for the conduction process. In fact, there does appear to be a discontinuous decrease in resistance of metal-ammonia solutions at the freezing point (Ogg 1946, Hodgins 1946, Giulotto and Gigli 1947, Birch and MacDonald 1947, Nabauer 1949), although it is not clear how much of this arises from the formation of highly conducting channels of precipitated metal, supercooled eutectic mixtures, or solid metal-ammoniates (Jaffe 1948, Birch and MacDonald 1948).

† We stress that these are not the prime cause of electron spin-pairing which is dominated by the long-range spin exchange coupling.

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