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CONDUCTIVITY ELECTRON SPIN RESONANCE OF LITHIUM AMMONIA SOLUTIONS IN THE RANGE OF THE METAL TO NON METAL TRANSITION

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INTRODUCTION

It is well established that solutions of alkali metals in liquid ammonia display a continuous transition, when the metal concentration is increased, from an electrolytic to a metallic state. This non-metal to metal transition is well displayed by experimental quantities like the electrical conductivity. Theoretical description of the transition has been a matter of controversy during the past years, and is still a subject of interest. 1, 8, 9, 10, 11. A microscopic description of this transition requires knowledge of experimental properties with a strong local character. Electron spin resonance has been observed for a long time in the solutions of alkali metals in liquid ammonia 2. The linewidth of the ESR signal for the dilute solutions (when the mole ratio ammonia/metal is larger than about 200, i.e. when the metal concentration is smaller than about 0.5 Mole per Cent of Metal (M PM) is of the order of 30 m G and is one the narrowest known ESR lines. For very concentrated solutions (mole ratio smaller than approximately 10, i.e. metal concentration larger than about 9 MPM), this line is a few Gauss wide, depending upon the alkali metal in the solution. For these very concentrated solutions, the electrical conductivity is larger than about 10^3 n m^-1 cm^-1, and therefore for the X-band frequency range of a typical ESR experiment the skin depth is smaller than the diameter of the sample. Consequently the electrons diffuse into or out of the skin depth. In these conditions typical of metals, a distortion of the ESR signal is observed 3, 4, 5, 6.

In the present paper, we report a detailed experimental study of ESR in lithium ammonia solutions in the concentration range of the non-metal to metal transition. In this concentration range the linewidth of the ESR signal increases rapidly with the lithium concentration, and the electrical conductivity increases rapidly too. Therefore the lineshape is strongly concentration dependent. The variations of the lineshape have been analyzed versus the lithium concentration between 0 and -80°C. The relaxation time T2 and the diffusion time T0 have been obtained. The shift has also been measured as a function of lithium concentration and temperature. Parameters related to the ESR lineshape in presence of skin effect, experimental procedure and results are successively presented.

PARAMETERS OF THE ESR SIGNAL

In lithium ammonia solutions, the electrical conductivity increases quite rapidly with the lithium concentration, and also with the temperature. Consequently the skin depth varies and the ESR signal lineshape is concentration and temperature dependent. The parameters which characterize the lineshape are hereby given. Also the first and the second derivatives of the spin resonance absorption signal have been recorded and analyzed. The theory of ESR in metals was first given by Dyson 3, and detailed by Feher and Kip 4. Another formulation of the theory was given by Kaplan 5 and de Gennes 6. The usefulness of the second derivative was detailed by Glaunsinger and Sienko 7. It appears from the theory that the basic parameter which determines the lineshape is the ratio R = (T2/T0)^2 where T0 is the diffusion time of an electron through the skin depth, and T2 is the spin relaxation time. All the usual parameters of the first derivative (i.e. the asymmetry parameter A(1)/B(1), line width at half maximum AH(1) for the peak to peak linewidth AHPP, displacement S(1) of the resonance with the apparent resonance position, are defined in ref. 7. The quantities A(1)/B(1), γT2 AHPP, γT2 AH(1) have been expressed in the literature versus R. Therefore the measurement of A/B gives the
value of R for a given sample and \( \gamma T_2 \) can then be deduced. As the electron gyromagnetic ratio \( \gamma \) value of R for a given sample and \( \gamma T_2 \) can then be deduced. As the electron gyromagnetic ratio \( \gamma \) can be determined quite accurately with the free electron \( g \) value, \( T_2 \) can then be obtained, and also \( T_D \).

The same procedure has been used for the second derivative. The parameters are labelled with index \( 2 \),

rate measurements of \( A^{(2)}/B^{(2)} \), and then \( T_2 \) and \( T_D \) can be extracted by the measurement of either \( \Delta H^{(2)} \) or \( \Delta H^{(2)} \).

Therefore, the basic physical quantities \( T_2 \), \( T_D \), and also the \( g \) shift, can be obtained from either the first or the second derivative of the spin resonance absorption signal. However the determination of these quantities from both derivatives assures the coherence of experimental results and can confirm or infirm the Dysonian character of the lineshape. \( \Delta H^{(2)} \) is also more well defined experimentally than \( \Delta H^{(2)} \), due to the fact that the second derivative is more compact than the first.

**EXPERIMENTAL**

Samples of lithium in liquid ammonia have been prepared in quartz or pyrex cylindrical tubing of 4 mm outer diameter and 2 mm inner diameter. Samples were about 8 cm high, and the solution inside was about 3 cm high. The lithium was cut under argon in a glove bag, and weighed under vacuum or argon atmosphere. The amount of ammonia condensed on the lithium was determined by the volumetric determination of ammonia gas therefore the concentrations of the samples were known very accurately. It must be noted that in this study a relatively narrow concentration range is sampled, which requires an accurate knowledge of the lithium concentration.

For a few samples, the concentration was not known a priori, and was then determined by the value of \( \Delta H^{(1)} \), on the curve \( \Delta H^{(1)} \) versus the lithium concentration. The experiments have been performed on a Varian Spectrometer E 109. The field sweep was controlled via the Varian Fieldlock Unit which locks the field on the resonance of a sample of dpdph. In this way accurate determination of \( g \) value can be obtained. The temperature is stabilized by means of a flow of nitrogen cooled in liquid nitrogen using the varian temperature control unit.

The two modulation frequencies for determining the first and second derivative of the signal were respectively 100 k Hz and 1 kHz. Usual response times were 8 or 4 milliseconds.

The relative uncertainty for the determination of \( \Delta H^{(1)} \) for the first derivative is less than one per cent. The absolute error for the temperature coefficient \( \frac{\Delta \Delta H^{(1)}}{dT} \) is \( \pm 2 \times 10^{-4} \times \Delta H^{(1)} \) per degree. After preparation, the samples were stored in liquid nitrogen. Before the experiments the samples were homogenized at room temperature.

Measurements were taken every five degrees, from room temperature down to -60°C. For most of the samples, the full runs have been carried out at least another time. Results were found perfectly reproducible.

**RESULTS**

The variation of the linewidth \( \Delta H^{(1)} \) is reported on Fig. 1 versus the lithium concentration.

![Fig. 1: Peak to Peak linewidth \( \Delta H^{(1)} \) of the first derivative (Gauss) versus the lithium concentration (Mole Per Cent of lithium) at -35°C.](image)

Points on this curve are related to samples of known concentration. This curve was used to determine the concentration of some samples for which the concentration was previously unknown. This curve shows that the linewidth increases rapidly during the non metal to metal transition. The linewidth should still increase for more concentrated solutions, but with a smaller slope. This curve relative to the linewidth contains of course the information relative to the spin - spin relaxation time \( T_2 \), which is continuously decreasing when the metal concentration increases.
be equal to one. For the most dilute sample we have studied, the concentration of which was close to 1 M P M the asymmetry is already important, and is increasing with the lithium concentration up to about 3 M P M and then decreases and becomes a constant close to 2.55 for concentrations larger than about 6 M P M. The value of the asymmetry ratio of 2.55 is the value predicted by Dyson theory for very large values of $R$, i.e., when the diffusion time $T_D$ through the skin depth is much larger than the spin relaxation time. Note that the maximum of the curve of $A/B$ versus the lithium concentration implies a minimum in the curve of $R$ versus the lithium concentration. This will be the cause of a minimum in the variations of $T_D$ versus the lithium concentration. On Fig. 3, an experimental point at about 3.5 M P M is apparently out of the curve. There was no reason for us to drop this value, because the corresponding experiment is seemingly perfectly precise. Therefore other samples of concentration close to 3.5 M P M should be made to confirm the variations of $A/B$ in this region.

As was explained previously, from the values of $A/B$ the values of $R$ can be obtained from Fig. 4 of reference 7 for the first derivative and from Fig. 7 of the same reference for the second derivative. With the values of $R$ and $\Delta H$, $T_2$ is obtained from the values of $\gamma T_2 \Delta H$ plotted versus $R$ on Fig. 5 and 8 of reference 7. From the values of $R$ and $T_2$, $T_D$ is then directly obtained.

Fig. 2: Temperature coefficient $\frac{\Delta H^{(1)}}{dT}$ (m G per degree) versus the lithium concentration at -35°C.

The asymmetry ratio $A/B$ of the first derivative of the E S R absorption line is plotted on Fig. 3 versus the lithium concentration. For extremely dilute solutions the asymmetry ratio should
The values of $T_D$ and $T_2$ are plotted on Fig. 4 versus the lithium concentration. $T_2$ decreases smoothly when the lithium concentration increases, while $T_D$ has a deep minimum at about $3 \text{ M P M}$.

Fig. 4: $T_D$ and $T_2$ versus the lithium concentration.

The g values obtained as indicated in the experimental section are reported in Fig. 5 versus the lithium concentration. There is a well defined increase of $g$ when the lithium concentration increases. For the most concentrated sample (about $10 \text{ M P M}$) the $g$ value is still lower than the free electron $g$ value or than the $g$ value of pure lithium metal. There is no value of $g$ in the literature for very dilute lithium ammonia solutions.

DISCUSSION - CONCLUSION

Our results have been analyzed within the framework of the Dyson theory - for concentrations between 6 and $10 \text{ M P M}$, lithium ammonia solutions are in the limiting case of $R$ large, i.e. a diffusion time $T_D$ large compared to $T_2$. For solutions of concentration lower than $1 \text{ M P M}$, the asymmetry ratio goes below 2.5 toward unity, which is not predicted by the Dyson theory, valid when the size of the sample is large compared to the skin depth. It must also be noted that when the asymmetry ratio $A/B$ is smaller than about 3, it is not very accurate to read $R$ on Fig. 4 and 7 of reference 7. Therefore a more accurate numerical tabulation of $R$ versus $A/B$ should be made to obtain a precise value of $R$ in this region. Such calculations are required to ascertain without ambiguity the Dysonian character of the lineshape below $10 \text{ M P M}$. This is important because the Dyson theory is based on a single diffusion constant and this could possibly be incorrect in the non-metal to metal transition when the delocalization of electrons happens. It must be noted that the important variations of $A/B$ occur below $6 \text{ M P M}$. In the same concentration range, large variations are displayed by the temperature coefficient of $A/B$. Near $2 \text{ M P M}$, the temperature coefficient of the linewidth shows a rather deep minimum which is reminiscent of the extremum of the temperature coefficient of the electrical conductivity.

These ESR experiments provide detailed microscopic information about the non-metal to metal transition in lithium-ammonia solutions - Large and unexpected variations of several quantities ($A/B$, i.e. $R$, $dA(1)/dT$) oblige us to complete the set of our experiments to confirm and detail the observed variations before discussing the physical parameters which are deduced from these experiments.

BIBLIOGRAPHY