

Electron Spin Resonance Studies of the Onset of Metallic Character in Metal-Ammonia Solutions*

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Asymmetric electron spin resonance spectra are described for moderately concentrated solutions of the alkali metals in liquid ammonia as functions of temperature, metal concentration, and concentration of added electrolytes. Both the asymmetry and the linewidth increase markedly above a critical temperature, corresponding to a thermal promotion of electrons from trapping sites to a conduction band. The g factor of the asymmetric resonance is strongly dependent on the concentration of added iodides.

INTRODUCTION

IN a recent communication, Kyser and Thompson have reported results of their measurements of the Hall effect in metal-ammonia solutions.¹ They find that the free-electron concentration increases rapidly in the region of 1.2 molal (at -40° to -80°C). No obvious temperature effect was observed. One purpose of the present paper is to draw attention to the similar, equally drastic, change in structure with varying temperature. Although dilute solutions of sodium and potassium in liquid ammonia have very narrow (~ 20 mG) electron spin resonance spectra, those of more concentrated solutions ($> 0.3m$) are asymmetrically broadened² in the manner found for bulk alkali metals.³ The line shape was interpreted in terms of freely diffusing metallic conduction electrons in particles large compared to the microwave skin depth.^{3,4}

EXPERIMENTAL METHODS

Preparation of Solutions

Solutions of known concentration of salts and metal were prepared using conventional high-vacuum techniques and the procedure described elsewhere.² Samples for measurement at 9400 Mc/sec were contained in 1-mm capillaries; those for 340 Mc/sec in 4-mm tubes.

Electron Spin Resonance Spectra

Spectra at 9400 Mc/sec were obtained using the apparatus described previously.² The temperature of the sample was maintained in the region -78° to 0°C by surrounding the microwave cavity with a wet-alcohol-solid-carbon-dioxide bath. Temperatures above 0°C were obtained using warm water baths.

Spectra at 340 Mc/sec and room temperatures were measured on an Alpha Scientific Laboratories, Inc., AL.340 SYH spectrometer.

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¹ D. S. Kyser and J. C. Thompson, *J. Am. Chem. Soc.* **86**, 4509 (1964).

² R. Catterall and M. C. R. Symons, *J. Chem. Soc.* **1964**, 4342.

³ G. Feher and A. F. Kip, *Phys. Rev.* **98**, 337 (1955).

⁴ F. J. Dyson, *Phys. Rev.* **98**, 349 (1955).

RESULTS AND DISCUSSION

The effect of temperature on the asymmetry of the electron spin resonance signal from metal solutions is reported in terms of the parameters A/B (the asymmetry ratio, see Fig. 1) and ΔH_{ms} (the linewidth between points of maximum slope on the first derivative of the

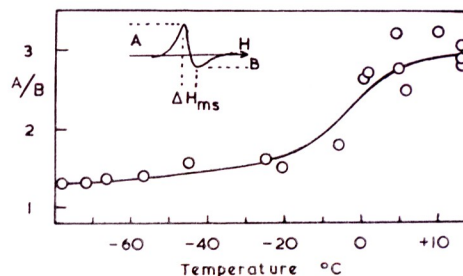


FIG. 1. The asymmetry ratio of the ESR at 9400 Mc/sec from a 0.51*m* solution of Cs in liquid ammonia.

absorption signal). We find

(i) ΔH_{ms} and A/B decrease markedly over the temperature range $+30^\circ$ to -78°C ;

(ii) ΔH_{ms} and A/B increase with increasing concentration of metal;

(iii) the asymmetry and line broadening are most marked for Rb and Cs solutions;

(iv) A/B is independent of frequency in the range 340–9400 Mc/sec. The results given in Table I for solutions containing added salts show similar trends.

The temperature dependence of the ESR from a 0.51*m* Cs solution is shown in Figs. 1 and 2. A drastic change occurs in the vicinity of 0° , and in addition, the blue color characteristic of dilute, ionic solutions changes to the bronze color of concentrated, metallic solutions in the same region. The region of sudden change shifts to 20° and 30° for 0.3 and 0.13*m* solutions, respectively.

In the presence of added salts Δg ($= 10^4\{g - 2.0012\}$, see Fig. 2) is dependent on metal concentration (Table II) but it has been pointed out² that this dependence is, at least in part, due to difficulty in locating the true g factor of the resonance. Since this value ap-

proaches Δg_{LF} (Fig. 2) as A/B increases,³ we compare (Table II) at constant salt concentration the shift ($\Delta g_{m(0)}$) for solutions $<10^{-2}m$ in metal with Δg_{LF} and Δg for the more concentrated solutions. At room temperature, iodide solutions showing marked asymmetry without excessive line broadening have $-\Delta g_{m(0)}$ significantly lower than $-\Delta g_{LF}$. The additional g shift is most reasonably attributed to spin-orbit coupling between delocalized electrons and ions in the solution, and since solutions without added salt (Fig. 2) do not show such large shifts, coupling to the anion is probably the predominant interaction. It is significant that the additional g shift has largely disappeared at -78° (Table II). For bromide solutions $\Delta g_{m(0)} \approx \Delta g_{LF}$, but it seems possible from the shift in Δg that a less marked effect might occur. We have shown that bromide, unlike iodide, does not give a measurable g shift in dilute metal solutions.²

Although asymmetric lines are observed for solutions concentrated in both metal and salt, the effect of

TABLE I. Linewidths and asymmetry ratios at 9400 Mc/sec for alkali-metal-ammonia solutions containing added alkali halides.

Sample	Solution (molalities)	Room temperature		-78°	
		ΔH_{ms} (G)	A/B	ΔH_{ms} (G)	A/B
64	Na: 0.20	1.20	2.45	0.2	1
	NaI: 0.392				
63	Na: 0.30	1.21	2.60	0.2	1
	NaI: 0.201				
34	K: 0.20	1.25	1.37	1.21	1
	KI: 2.500				
47	Rb: 0.10	6.62	2.65	1.03	1.27
	RbI: 0.199				
53	Rb: 0.10	4.54	1.64	7.1	1
	RbI: 2.517				
50	Rb: 0.20	29.6	2.59	1.22	1.25
	RbI: 1.082				
49	Rb: 0.30	54.9	3.13	5.0	2.19
	RbI: 0.726				
58	Rb: 0.10	0.90	2.86	0.2	1.1
	RbBr: 1.010				
59	Rb: 0.10	1.50	2.32	0.33	1.36
	RbBr: 1.490				
56	Rb: 0.15	1.51	3.65	0.2	1
	RbBr: 0.396				
55	Rb: 0.25	5.0	3.02	0.97	2.56
	RbBr: 0.200				
85	Cs: 0.10	2.29	1.54	0.98	1
	CsI: 0.750				
89	Cs: 0.10	9.6	1.51	4.06	1.42
	CsI: 2.513				
62	Cs: 0.20	11.0	6.67	1.27	1.87
	CsI: 0.504				
43	Cs: 0.30	17.8	3.68	0.69	1.67
	CsI: 0.206				

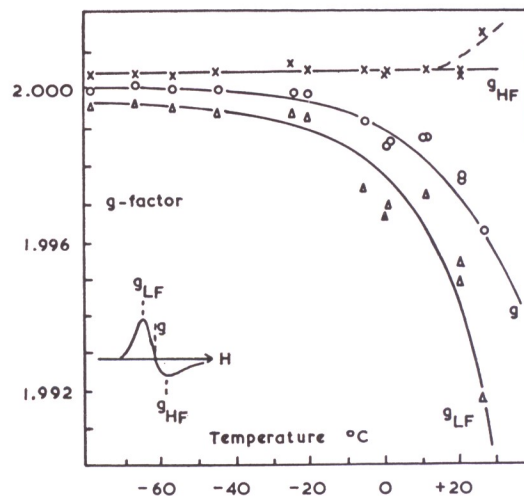


FIG. 2. Electron spin resonance parameters at 9400 Mc/sec for a 0.51*m* solution of Cs in liquid ammonia.

added cesium iodide on a 0.13*m* cesium solution is to remove the asymmetry and to increase the area under the absorption (corresponding to an unpairing of electron spin). A similar increase is observed in more dilute solutions showing only symmetrical absorption lines.

The characteristic asymmetry of the ESR arises from the delocalization of electrons over regions large or comparable to the microwave skin depth δ and the existence of such asymmetry may be taken as evidence³ of an accessible conduction band extending throughout the solution. The theory developed for electrons in metals predicts a lower limit of $A/B=2.7$ for samples having thicknesses considerably greater than δ , and an electron relaxation time long compared to the diffusion time. In fact A/B for 0.51*m* cesium solutions approaches 2.7 above 20° (Fig. 1), and also, in view of the large scatter in the determinations of A/B (compare Fig. 1), the values for solutions containing added salts show no significant increase above 2.7. For 0.51*m* cesium solutions having $A/B=2.7$ we can estimate a "true" g factor of 1.9995 (compare $g_{LF}=2.0004$). However the microwave skin depth [$\delta \propto 1/(\text{conductance})^{1/2}$] for ammonia solutions is much greater than for the pure metals, and at these concentrations is of the order of the sample thickness (1 mm). In the absence of any detailed theoretical treatment of line shapes in this "intermediate" case [Ref. 4, Sec. VII.b], any interpretation of line shapes must be speculative. Since we are observing a change in the distribution of unpaired electrons between solvent traps and the conduction band, the spectra at lower temperatures might consist of unresolved mixtures of symmetric and asymmetric absorptions. In support of this interpretation, Charru⁵ obtained two resolved signals from lithium solutions, one asymmetrically broad-

⁵ A. Charru, Compt. Rend. **247**, 195 (1958).

TABLE II. Electron spin resonance parameters (see Fig. 2) at 9400 Mc/sec for alkali-metal-ammonia solutions containing added alkali halides.

Sample ^a	Room temperature			-78°		
	-Δg ^b	-Δg _{LF} ^b	-Δg _{m(0)} ^c	-Δg ^b	-Δg _{LF} ^b	-Δg _{m(0)} ^c
64	20.0	16.1	15	7.7	7.1	8
63	24.1	19.3	12	7.2	6.9	5
34	61.9	56.9	60	50.0	46.4	50
47	39.1	20.3	5	10.4	7.4	4
53	165.2	147.0	107	123.9	103.0	102
50	126	34	48	43.5	39.9	42
49	145	-47	38	30.7	15.7	32
58	16.2	10.4	10	12.9	12.3	11
59	17.1	10.7	11	12.7	11.7	12
56	18.1	11.1	8	8.7	8.1	10
55	23.8	6.4	7	8.1	5.1	9
85	59.9	53.7	45	38.1	35.1	36
89	114.1	107.9	91	71.7	68.7	73
62	71.8	34.7	37	28.1	24.3	29
43	99.6	38.8	22	19.5	17.4	19

^a See Table I for compositions.^b Estimated maximum error ±4.0.^c Smoothed-out data from Ref. 2.

ened in the manner described above and favored by high concentration and temperature, and the other symmetrical. Since the lifetime of $M^+e^-_{\text{sol}}$ ion pairs is very short⁶ ($\sim 10^{-12}$ sec) it is unlikely that two lines would be observed if promotion to the conduction band occurred from this unit. In addition, although the lifetime of an unpaired spin with respect to spin pairing is long compared to its relaxation time ($\sim 3 \times 10^{-6}$ sec for lithium, sodium and potassium solutions) in the predominantly spin-paired region, the relaxation time drops rapidly with the onset of metallic character⁷ (Fig. 2). However, if promotion of electrons of the conduction band occurred preferentially from the spin-paired species (implying a lower trapping potential for the second electron) it is possible that separate lines from singly trapped and free electrons might be ob-

served within a relatively narrow concentration region despite the high mobility of the free electrons. It is interesting that the line shape appears to tend to the slow diffusion limit, in accord with the observed incompleteness of metallic character, and a tunneling process such as that described by Arnold and Patterson⁸ might be involved.

No attempt has been made to estimate conductances in the absence of quantitative estimates of the number of spin-paired and -unpaired free carriers. However, the temperature coefficient of the equivalent conductance should show a maximum in the region of the marked change in A/B . Such an effect is observed⁹ for solutions of sodium at 0.8*N* and -33°.

⁸ E. Arnold and A. Patterson, Jr., J. Chem. Phys. **41** 3089, 3098 (1964).

⁹ C. A. Kraus and W. W. Lucasse, J. Am. Chem. Soc. **44**, 1941 (1922).

⁶ D. E. O'Reilly, J. Chem. Phys. **41**, 3729 (1964).

⁷ V. L. Pollak, J. Chem. Phys. **34**, 864 (1961).