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Electron Spin Resonance Studies of Alkali Metal Trapping Sites in Solid Rare Gases

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Measurements of the hyperfine structure of alkali metals trapped in solid rare gases have been made. When the zero-field hyperfine splitting values obtained in the solid matrix are compared with the free atomic values, it is found that they fall into two groups. In one group the hyperfine values are within a few percent of the free atomic value. The other group has hyperfine values smaller than the free atomic value by 10 to 30%. It has been found that the latter trapping sites occur only when the sample is exposed to room temperture infrared radiation during deposition on the liquid helium cooled finger. The effects of annealing and concentration have also been studied. The annealing experiments show that once the shifted sites are formed they are very stable.

I. INTRODUCTION

THE hyperfine structure splitting of an atom in a $^2S_{1/2}$ state is proportional to the electronic spin density at the nucleus.[1] When an atom is trapped in a solid matrix, changes in spin density at the nucleus caused by atom-matrix interaction can be experimentally obtained from electron spin resonance hyperfine-splitting measurements. A simple example of such a system, hydrogen trapped in Ar, Kr, or Xe, has been studied experimentally by Foner *et al.*[2] and theoretically by Adrian.[3]

In contrast to the case of trapped hydrogen atoms, alkali metal atoms are trapped in a multiplicity of sites. Early experiments on the alkali metal rare-gas system gave somewhat different results. Jen *et al.*[4] found trapping sites with hyperfine splitting values within a few percent of the free atomic value. We also observed these sites, but also found that the strongest resonances had hyperfine values considerably smaller than the free atomic value.[5] We have found tha tthese differences were due to different conditions during sample deposition.[6]

In this paper the effect of various deposition conditions on the trapping sites will be described. The most surprising effect is that the presence of thermal radiation during sample deposition causes trapping sites with large decreases in hyperfine splitting to be formed.[6] Annealing experiments show that, once formed, these sites are very stable.

II. THEORY

The isotropic part of the Hamiltonian of an atom with $L=0$ in an external magnetic field H is given by

$$H=2\Delta W/(I+\tfrac{1}{2})\mathbf{I}\cdot\mathbf{J}+g_J\mu_0\mathbf{J}\cdot\mathbf{H}+g_I\mu_0\mathbf{I}\cdot\mathbf{H}\,, \qquad (1)$$

where ΔW is the zero-field hyperfine splitting, I is the nuclear spin and J is the electronic spin; for alkali atoms, $J=\frac{1}{2}$. In zero field, the levels $F=I+\frac{1}{2}$ and $F=I-\frac{1}{2}$ are separated by ΔW. In the presence of a field, the levels split; the ensuing energy levels for a state of given $m_F=m_J+m_I$ are given by the Breit-Rabi equation[7,8]

$$W(H,m_J,m_I)=-[\Delta W/2(2I+1)]+g_I\mu_0Hm_F \pm(\Delta W/2)\{1+[4m_Fx/(2I+1)]+x^2\}^{1/2}\,, \qquad (2)$$

where

$$x=(g_J-g_I)\mu_0H/(\Delta W)\,.$$

Conventionally, the sign of g_I is negative for alkali atoms and g_J is positive. The positive sign is used in Eq. (2) for the states where $F=I+\frac{1}{2}$ and the negative sign for the states where $F=I-\frac{1}{2}$. At high field, the microwave resonance transition will occur between states for which $\Delta m_I=0$, $\Delta m_J=\pm1$. The Breit-Rabi energy level diagram for a nucleus of spin $\frac{3}{2}$ is shown in Fig. 1, where the allowed transitions are indicated by arrows.

In a microwave resonance experiment, the microwave radiation at frequency ν will be absorbed at the $2I+1$ magnetic field values, H_i, which satisfy the equations

$$h\nu=W(H_i,m_J=\tfrac{1}{2},m_I)-W(H_i,m_J=-\tfrac{1}{2},m_I)\,, \qquad (3)$$

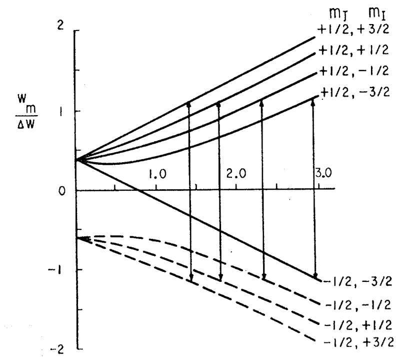

FIG. 1. Energy levels of the ground state of an atom with $S=\frac{1}{2}$, $I=\frac{3}{2}$, typical of most alkali metal atoms, as a function of magnetic field. The $\Delta m_I=0, \Delta m_J=1$ transitions are indicated by the arrows.

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or

$$h\nu=g_I\mu_0H_i+\frac{\Delta W}{2}\left[\left(x_i^2+\frac{2(2m_I+1)}{2I+1}x_i+1\right)^{1/2}+\left(x_i^2+\frac{2(2m_I-1)}{2I+1}x_i+1\right)^{1/2}\right].\quad(4)$$

One notes that Eq. (4) will have $2I+1$ real solutions for H_i only if $h\nu>\Delta W$.

In free space, the values of ΔW and g_J would be the same for each atom; in a matrix the free space values will be altered by interaction with the matrix atoms. Thus different trapping sites may have different values of ΔW and g_J; and more than one set of $2I+1$ lines can be obtained from an experiment with any given atom.

For the ΔW values and magnetic fields in these experiments it is necessary to use the exact Breit-Rabi equations since the high-field limit is not valid. In analyzing the experimental data, each of Eqs. (4) were solved explicitly for ΔW in terms of g, H_i, etc. With an IBM-7090 computer program, the value of g which minimized the rms deviation between the $2I+1$ corresponding values of ΔW was determined. As an aid for finding weak lines, the program was also used for predicting line position when two or more lines out of a set were known, or when g and ΔW were known.

III. EXPERIMENTAL

Figure 2 is a schematic diagram of the microwave spectrometer. A conventional matched magic tee with superheterodyne-detection forms the basis of the spectrometer. The outputs of the main klystron and local oscillator klystron are mixed and fed to a 30-Mc/sec discriminator. The discriminator output controls the local oscillator reflector voltage, maintaining a 30 Mc/sec frequency separation between the two klystrons. A conventional automatic frequency-control circuit employing frequency modulation of the main klystron and discrimination by the sample cavity is used to keep the main klystron tuned to the cavity frequency. Hence, only the absorption mode was observed. Conventional 400-cps field modulation and phase sensitive detection is used to display the resonance signal. The superheterodyne receiver enabled operation at power levels low enough to avoid saturation of the magnetic resonance. This power level was typically 50 dB below the 600 mW output of the klystron.

In order to vary the sample deposition conditions two different experimental arrangements were used. The original apparatus in which the sample was exposed to considerable thermal radiation during deposition is shown in Fig. 3. The microwave cavity and vacuum chamber remained at room temperature. The temperature immediately above the copper sample finger was about 15°K, as determined by a carbon-resistance thermometer.

The samples were prepared by mixing the alkali metal vapor with the inert gas and freezing the mixture on the sample finger. The alkali metal was placed in a stainless steel boat which was heated by passage of a current through it. At the boat temperatures used, the

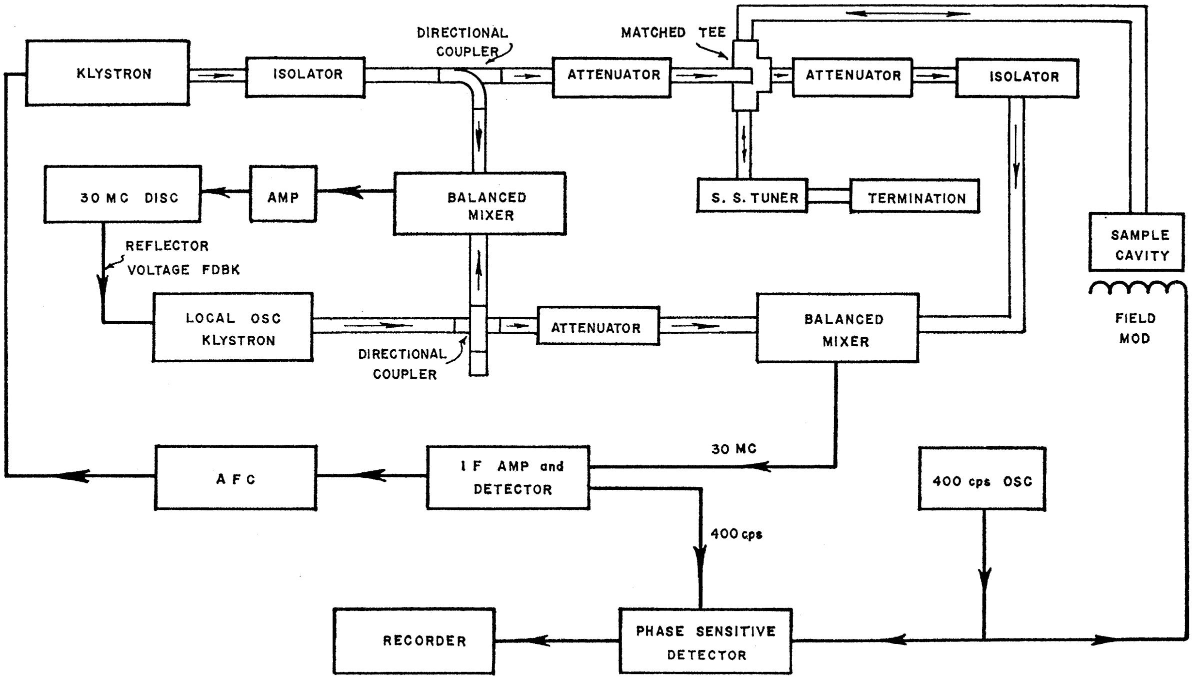

FIG. 2. Schematic diagram of the microwave superheterodyne spectrometer.

metal vapor pressure was about one μ. The inert gas flow rate was typically about 5 cc/sec. An upper limit to the alkali metal atom concentration obtained from an order of magnitude-kinetic theory calculation indicated that the samples contained at most about 10^{18} alkali-metal stoms per cc which corresponds to an inert gas-impurity ratio of about 10^4:1. Comparison of the alkali-metal signal-strength with a DPPH standard indicated the concentration was smaller by a factor of 10. This result is not surprising since it seems improbable that the alkali metal condensation as atoms is 100% efficient. A typical sample was deposited in about five minutes. The entire cavity and vacuum chamber were raised to place the sample within the microwave cavity. The above conditions will be referred to as apparatus I.

In the later experiments the apparatus was modified so the sample finger was inside the microwave cavity during deposition. In this case the heated boat was placed under the cavity. Provision was made to vary the cavity temperature between room temperature and 77°K. The finger temperature with the cavity at 77°K was about 5°K. It was possible to heat the sample finger to 50°K and then cool down to 5°K again with this arrangement, referred to below as apparatus II. With this apparatus it was possible to study the effect of thermal radiation on the sample and to perform annealing experiments. Because the alkali-metal vapor had to go through a small hole to enter the cavity, the deposition times were longer than with apparatus I, about 15 to 20 min. The argon flow rate was correspondingly reduced.

It was difficult to deposit a lithium sample which did not contain appreciable amounts of sodium and potassium since the higher vapor pressure of sodium and potassium produced a preferential evaporation of the latter impurities from the lithium metal. A sample deposited from lithium metal containing less than 0.01% sodium and potassium produced a larger signal from the impurities. By continued heating it was possible to boil off most of the sodium and potassium so that the lithium signal could be observed.

The most unexpected characteristic possessed by all of the alkali metal rare-gas samples was their color; all were colored blue—at least at certain concentrations. The colors of the samples actually varied from white (polycrystalline pure argon) through blue to a deep purplish black depending on the concentration. To the eye, there was no difference in colors between samples containing different alkali metals. It is possible that the blue color arises from impurity atoms other than those whose spin resonance is observed. These could be dimers or agglomerated groups. As judged by the color, the concentration was fairly uniform over the sample. Although the alkali metal source was not symmetrically placed with respect to the sample finger, the gas pressure was high enough during sample deposition so that diffusion produced a uniform sample. To obtain the desired concentration, the boat temperature was manually controlled while observing the sample. A light to medium blue color was used for most samples. The above concentration estimate of 10^{17} spins/cc applies to these samples.

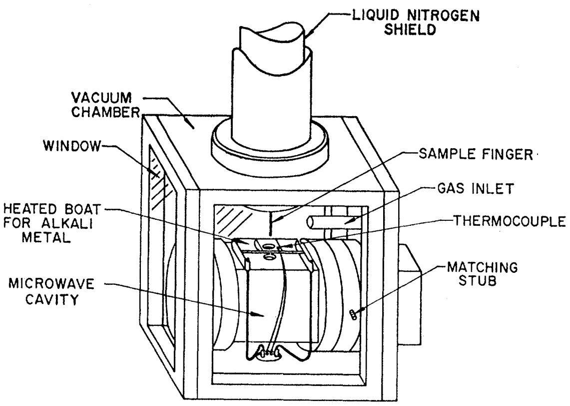

FIG. 3. Diagram of apparatus I. With this arrangement, the sample was exposed to room temperature thermal radiation during deposition. The vacuum chamber was raised to place the sample within the microwave cavity.

IV. RESULTS

A. General

Multiple trapping sites were observed for all samples in argon and krypton. Xenon has many isotopes with nuclear spin and, hence, the lines are broadened by hyperfine interaction with matrix nuclei. Krypton also has isotopes with nuclear spin, however, although the lines were broadened; lines due to multiple trapping sites were still resolvable. Argon has no nuclear spin and the lines are sharp, consequently most of the work was done with this matrix.

With the previously-mentioned estimate of 10^{17} spins/cc, a calculation of dipolar broadening[9] yields a linewidth of 0.03 G, however; the observed linewidth of potassium in argon is approximately 1 G. Unresolved but reproducible details of line structure, as well as the saturation behavior, indicate that the lines are inhomogeneously broadened. We believe that this broadening arises from a distribution of the hyperfine constant values characteristic of a given trapping site. This conjecture is supported by the fact that the lines are broader in the atoms with larger hyperfine interactions.

B. Results Obtained With Apparatus I

Most of the work was done with apparatus I in which the sample was exposed to visible and thermal radiation. Table I lists the results for the various alkali metals and matrices.

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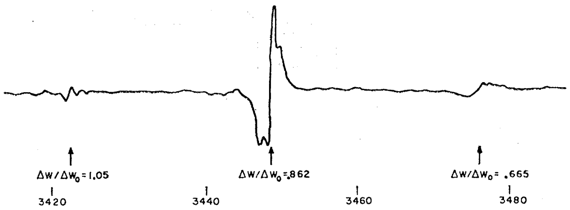

FIG. 4. Spectra of K in Ar in apparatus I. The low field $m_I=+\frac{3}{2}$ lines are shown. The magnetic field values are in Gauss.

Let us consider potassium in argon. It will be noted that the observed hyperfine quartets fall into two groups. In one group the ΔW values are within a few percent of the free atomic value ΔW_0 while the other group, called shifted lines, has ΔW values considerably smaller than the free atomic value. The group with ΔW near the free atomic value agrees with the observations of Jen *et al.*[2] Figure 4 shows the low field $m_I=+\frac{3}{2}$ lines of K in Ar. The lines of separate hyperfine quartets are the most separated for this transition. Note that the line with the large negative shift in ΔW is by far the strongest. This behavior is typical of all the alkali metals studied in apparatus I. The hyperfine constant shift ratio, $\Delta W/\Delta W_0$, for the 7% abundant isotope K^{41} agrees with the K^{39} values.

In Fig. 5 the $m_I=+\frac{3}{2}$ lines of Na in Ar are shown. This case differs from that of K in that there are two well-resolved sites with large negative hyperfine shifts.

As has been mentioned before, it was difficult to make a good lithium sample and, therefore, due to the poor signal-to-noise ratio, the only lines observed were the large amplitude negatively shifted lines.

Because of the larger linewidths with Rb in Ar, which result in a less favorable signal to noise, fewer trapping sites were observed than with Na and K. The strongest lines are again those with the largest negative ΔW shift. One notes (see Table I) that in progressing from Li to Rb in Ar the negatively shifted ΔW values tend toward the free atomic value.

No hyperfine octet $(I=\frac{7}{2})$ could be identified in the spectrum of Cs. This result may be because the ΔW value becomes larger than the 10 000-Mc/sec microwave quantum. This interpretation seems possible if the previously mentioned trend towards higher ΔW values and the 9191-Mc/sec free atomic splitting are considered. The broad lines observed in the Cs spectrum are probably due to transitions between those states which come closer together than ΔW as the magnetic field is increased from zero. However, it was not possible to obtain an accurate ΔW value for the Cs spectrum since the lines obtained were broad and weak.

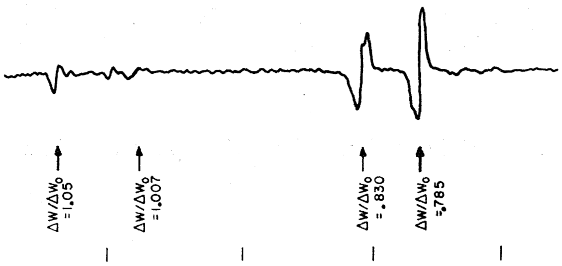

FIG. 5. The low-field lines of Na in Ar in apparatus I.

It can be seen from Table I that the deviation of the g values from the free atomic value is greater for those sites in which the ΔW deviation is largest. One also notes that the g-value shift for K becomes larger in going from Ar to Xe. This is because of the larger spin orbit coupling in the heavier atoms.

TABLE I. Zero-field hyperfine splitting ΔW and g values for the major trapping sites observed.

	ΔW(Mc/sec)	g	$\Delta W/\Delta W_0$[a]
Li^6 in Ar	153	1.9998	0.670
Li^7 in Ar	527	1.9992	0.656
Na^{23} in Ar	1857	2.0000	1.048
	1785	2.0005	1.007
	1757	2.0013	0.992
	1470	1.9992	0.830
	1391	1.9997	0.785
K^{39} in Ar	503	1.9993	1.09
	487	1.9998	1.05
	482	1.9998	1.04
	398	1.9984	0.862
	307	1.9977	0.665
K^{41} in Ar	268	1.9998	1.05
	219	1.9985	0.863
K in Kr	543±30	1.9870	1.18
	402±30	1.9920	0.87
K in Xe	450±30	1.980	0.97
Rb^{85} in Ar	3261	1.9981	1.07
	3216	1.9990	1.06
	2747	1.9974	0.905
Rb^{87} in Ar	6200	1.9980	0.905
Cs in Ar			>1?

[a] Free atom values, ΔW_0, from P. Kusch and V. W. Hughes, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1959), Vol. 37, Part 1, pp. 100 and 117.

	ΔW_0(Mc/sec)	I
Li^6	228.22	1
Li^7	803.54	3/2
Na^{23}	1771.75	3/2
K^{39}	461.75	3/2
K^{41}	254.02	3/2
Rb^{85}	3035.70	5/2
Rb^{87}	6834.1	3/2
Cs^{133}	9191.4	7/2

Experiments were also made in apparatus I to determine the effect of visible radiation on the sample. No effect was found.

C. Results Obtained With Apparatus II

Only runs with K in Ar were made using this apparatus since K was the most convenient metal to handle. Figure 6 shows the spectrum of a sample deposited within the microwave cavity when the cavity temperature was 77°K. In this case there is no sign of the lines with large negative shifts in the hyperfine constant. The spectra of Fig. 6 were made with the same sample after the cavity was warmed to room temperature. No effect

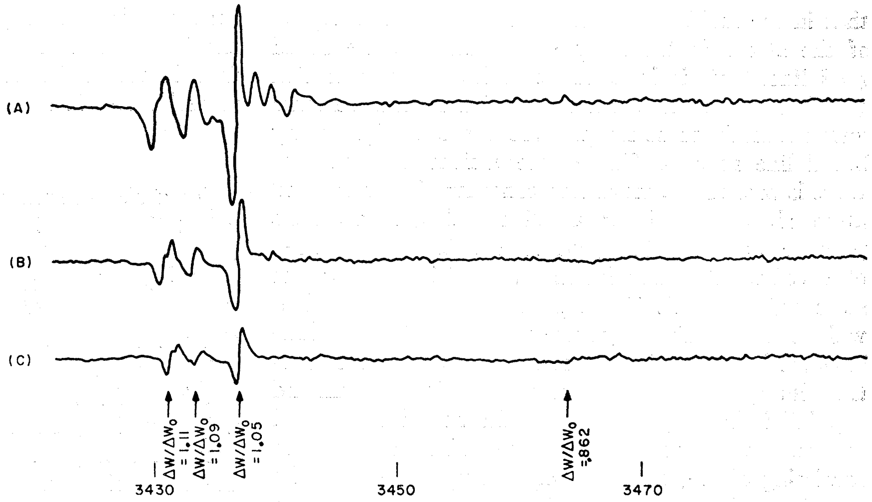

FIG. 6. Spectra of K in Ar in apparatus II. The sample was deposited with the surrounding microwave cavity at 77°K. (a) Fresh sample. (b) Annealed at 20°K. (c) Annealed at 40°K. After annealing the sample was returned to 5°K to record the spectra. Note the absence of the negatively shifted lines.

on the spectrum was seen indicating that infrared radiation has no effect on the sample once it is formed. It is interesting to note that after annealing the sample at about 40°K (the highest temperature possible without losing the sample due to sublimation) essentially three lines remain. This number corresponds to the expected number of sites in a face-centered cubic lattice,[2] however, this may be due to coincidence.

Figure 7 shows the spectra of a sample deposited when the cavity was at room temperature. These spectra show that this deposition condition produces the shifted lines. Note that the amplitude of the shifted lines relative to those near the free atom value is less than in Fig. 4. We believe this is because the sample in Fig. 4 was exposed to greater infrared radiation from the heated boat of apparatus I. Corresponding lines do not occur at the same field values in Figs. 4 and 7 because the microwave frequencies were different. Once the shifted sites are formed they are very stable, since annealing at temperatures sufficient to remove some of the lines near the free atomic hyperfine splitting does not affect the shifted lines.

Experiments in which the temperature of the sample finger during deposition was varied from 5 to 20°K, showed no effect on the spectra obtained.

D. Concentration Effects

Several runs in both apparatuses were made at higher concentrations. In general, the results were as one would expect. No effect of the concentration on the ratio of the shifted lines to those near the free atomic value was found.

Samples of K in Ar with estimated concentrations of up to 10^{19} spins/cc were made. These samples were pitch black. As the concentration increases, the linewidth of the individual hyperfine lines increases, reaching 3 to 4 G at the highest concentrations used. In the highly concentrated samples a broad line (≈ 20 G) appears in the center of the spectrum at approximately $g=2$. The amplitude of this line becomes larger than that of the hyperfine lines. Since the number of spins contributing to a line is proportional to the amplitude times width squared, these results indicate

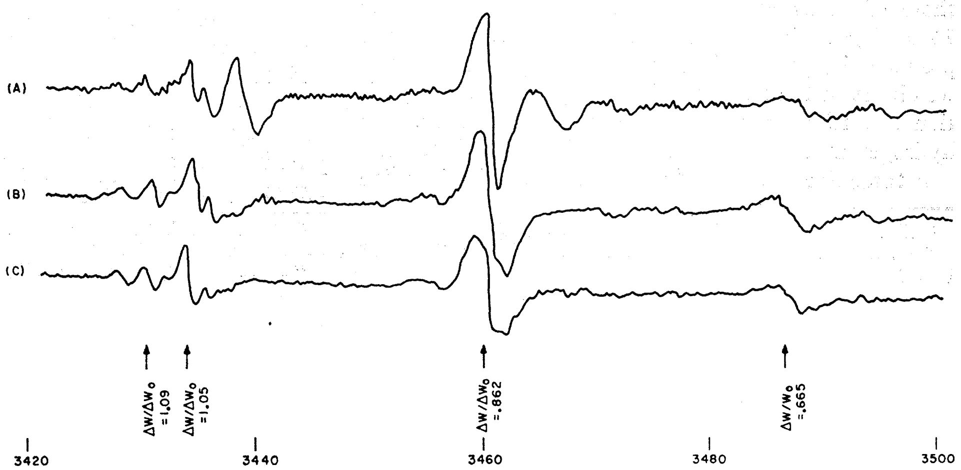

FIG. 7. Spectra of K in Ar in apparatus II. The sample was exposed to room-temperature thermal radiation from the microwave cavity during deposition. (a) Fresh sample. (b) Annealed at 20°K. (c) Annealed at 40°K. The sample was returned to 5°K to record the spectra.

that in the highly concentrated samples practically all of the atoms in the sample contribute to the broad $g\approx 2$ line. This is in contrast to lower concentration (blue) samples on which most of the measurements were made. In these samples there was no sign of any broad line at $g\approx 2$. These observations indicate that there is probably a maximum concentration of trapped atom sites and higher alkali metal concentrations produce agglomerated groups. No lines have been observed which can be identified as arising from triplet state pairs ($S=1$). These pairs should produce lines which fall approximately halfway between the hyperfine lines arising from single atoms.[10] We believe the spectrum interpreted as a pair spectrum by Weyhmann and Pipkin[11] is in fact the same as the negatively shifted spectrum that we have observed since a spectrum consisting of $2I+1$ lines of equal amplitude can arise only from single atom trapping sites. A spectrum due entirely to triplet pairs as suggested by Weyhmann and Pipkin would have an odd number of lines with the center line the most intense, which definitely disagrees with the observed spectra.

V. HYDROGEN IN ARGON

A complete report on hydrogen atoms as impurities in solid gas matrices has been published by Foner *et al.*[2] We describe our experiments here for completeness and to contrast with the alkali metal results. The experiments were made in apparatus I.

A mixture of hydrogen and argon was passed through a rf discharge and the products were condensed on the sample finger. The sample finger was far enough away from the discharge so that there was time for the excited argon atoms to decay, but not for the hydrogen atoms to recombine appreciably.

In two runs a single trapping site with a hyperfine splitting of 1413 Mc/sec was found. In one run this site and a 1436 Mc/sec trapping site was observed. No hydrogen sites were observed with a large decrease in the hyperfine constant. These results are the same as those of Foner *et al.*, except that they observed the 1436 Mc/sec site only when the hydrogen atoms were produced by photolysis. It is not clear why in one run we observed the two sites since supposedly the deposition conditions were the same in all three runs. The hydrogen atoms produce no coloration of the sample.

A three-line spectrum due to nitrogen and a four-line spectrum from methyl radical[12] were also observed in the hydrogen samples. The nitrogen probably came from impurities in the argon and the CH_3 from organic material used in the construction of the apparatus.

VI. CONCLUSIONS

Jen *et al.*[4] have made a calculation based on a previous calculation by Adrian[3] for hydrogen, which is in qualitative agreement with the experimental results on Li in Ar for the sites with ΔW near the free atomic value. They calculate $\Delta W/\Delta W_0$ for a Li-Ar pair by a perturbation method and then multiply the result by 12 nearest neighbors, corresponding to a substitutional site, to obtain a value to compare with experiment. The nearest neighbor distance is then adjusted to obtain agreement between theory and experiment. This procedure fixes the theoretical value of Δg which they then find is reasonably close to the experimental values.

It does not appear that this type of calculation can be extended to explain in a satisfactory manner the very large negative shifts of ΔW that we have observed. Jen *et al.*[4] find a maximum negative shift at a certain value of the nearest neighbor distance, but it is not large enough to fit our experimental results. However, the calculation involves the difference between the Van der Waals interaction, which produces a negative shift and the overlap plus repulsive interactions, which produce a positive shift, hence the error in the calculation could be very large. Furthermore, in an accurate computation of the spin density at the nucleus of an alkali metal atom it is necessary to include effects of the interaction between the valence electron and the inner shell *s* electrons with spin parallel to the valence electron.[13] This interaction causes a distortion of the inner *s* orbitals so that the spin density of the inner *s* electrons no longer cancels at the nucleus and an enhancement of the hyperfine interaction results.

Considering these shortcomings of the present theories, it appears that several aspects of the experimental results presented here lack a satisfactory explanation. Perhaps the most interesting questions are those concerning the nature of the trapping sites which have a large negative shift in the hyperfine constant and the unexpected large effect of thermal radiation during sample deposition. In addition, the occurrence of many discrete trapping sites with sharp lines is puzzling and a theory is needed to describe the local symmetry and stability of these multiple sites.

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[11] W. Weyhmann and F. M. Pipkin, Bull. Am. Phys. Soc. **8**, 23 (1963).

[12] C. K. Jen, S. N. Foner, E. L. Cochran, and V. A. Bowers, Phys. Rev. **112**, 1169 (1958).

[13] R. K. Nesbet, Phys. Rev. **118**, 681 (1960).