

PARAMAGNETIC RESONANCE OF FREE SILVER ATOMS TRAPPED IN NONPOLAR MEDIA AT 77°K

R. A. ZHITNIKOV, N. V. KOLESNIKOV, and V. I. KOSYAKOV

Leningrad Physico-technical Institute, Academy of Sciences, U.S.S.R.

Submitted to JETP editor May 9, 1962

J. Exptl. Theoret. Phys. (U.S.S.R.) 43, 1186-1196 (October, 1962)

Free silver atoms, trapped in various paraffins at the temperature of liquid nitrogen, were studied by EPR (electron paramagnetic resonance). The EPR spectra in all the investigated paraffins proved practically identical and closely similar to the spectrum of free silver atoms. The trapped atoms exhibit two different kinds of spectra, indicating two different kinds of trapping sites for silver atoms in the paraffins.

1. INTRODUCTION

THE free neutral atoms of the majority of elements exhibit electron paramagnetism in the ground state. The magnetic properties of such atoms (the gyromagnetic ratios of their electron shells, the interaction between the moments of these shells and the nucleus) have been extensively studied by atomic beam resonance techniques.^[1,2]

Very interesting systems can be obtained in those cases where it is possible to capture and stabilize these free neutral atoms in solids that do not react chemically with them, so that they remain neutral and practically free, restricted only in their motion and recombination. There are thus obtained very extraordinary paramagnetic substances, resembling an atomic gas or vapor the paramagnetic particles of which are stopped in their motion and imbedded in an inert diamagnetic medium. The density of the practically non-interacting particles of such a "gas" can be very great, corresponding in some cases to pressures of the order of an atmosphere or more. The interactions which hold the neutral atoms in the inert medium must be quite unusual in character. The medium in which the free atoms are trapped (the so-called matrix) can be either polar, i.e., consisting of polar molecules such as water, or ionic (e.g., alkali halide crystals), or, finally, non-polar, consisting of non-polar molecules held together by van der Waals forces (e.g., frozen inert gases, nitrogen, hydrogen, etc.).

Such systems open up the possibility of observing paramagnetic resonance in practically free atoms. On the other hand, the EPR method has special merits for studying these systems. One can investigate the degree of "freedom" (from

perturbations) of the captured atoms, the degree of immobility, the location of the atoms in the solid, the nature of the forces holding the neutral atoms in the solid, the interaction between these atoms and the surrounding molecules, ions, atoms, and atomic nuclei and the effect of these interactions on the electrons of the trapped paramagnetic atoms, etc. The trapping of free atoms in solids is doubly important for EPR work because such large values of the hyperfine interaction are encountered in ground-state atoms, compared to ions of the transition elements, free radicals, lattice defects, and other EPR objects of investigation.

The goal of the present investigation is to obtain free atoms trapped in various substances and to study them by EPR techniques. Up until now, resonance had been observed only in trapped atoms of hydrogen and nitrogen.^[3-7] Hydrogen atoms have been investigated in polar and ionic, as well as nonpolar matrices.^[3-6] Trapped nitrogen atoms have apparently been studied only in non-polar substances.^[3,6]

The capture of atoms in non-polar media is of great interest because the internal fields are weak, and the electrons of the trapped atoms would suffer the least perturbation. The atoms trapped in such substances would be most nearly free. The interaction of a paramagnetic atom with a trapping non-polar medium has been theoretically considered by Adrian.^[8]

In the experiments with hydrogen and nitrogen atoms trapped in non-polar matrices, free atoms were created either by irradiation or by means of a gaseous discharge, and gases frozen at helium temperatures ($\sim 4^\circ\text{K}$) served as the nonpolar matrices.^[3-7] Ingram asserted in his book^[7]

that liquid helium temperatures were necessary for the maintenance of free atoms in a molecular (non-polar) matrix, since at higher temperatures the free atoms would disappear as a consequence of diffusion and recombination.

The present work is devoted to obtaining and studying by EPR free atoms trapped in non-polar molecular substances at liquid nitrogen temperature (77°K). The investigation was carried out on silver, free atoms of which were obtained by vaporization of the metal. As non-polar, molecular matrices, normal paraffins having saturated bonds, linear chains, and the formula C_nH_{2n+2} , were chosen. This choice was dictated by the following properties of paraffins. Chemically, they are completely inert, particularly in relation to metals. Paraffins form molecular crystals with weak van der Waals forces, and the molecules are non-polar and diamagnetic. They are easily vaporized at relatively low temperatures in vacuum and then readily condensed on a cooled surface. The paraffins give a large number of completely analogous compounds with almost continuously varying bond energies between the particles of the molecular crystal, which is extremely valuable for the study of the effect of the matrix field on the properties of the trapped atoms.^[3,6] Paraffins that are liquid or solid at room temperature have significantly greater bond energies than the frozen gases used at helium temperatures. This should probably facilitate the stabilization of the free atoms and, hopefully, their maintenance in paraffins at liquid nitrogen temperature.

2. EXPERIMENTAL METHOD

A. The spectrometer. Frequency and magnetic field measurements. A 3 cm spectrometer utilizing high-frequency magnetic field modulation^[9] was employed in the work. Phase detection of the signal at the frequency of modulation of the steady magnetic field, equal to 975 kc, recording of the derivative of the absorption signal, and also automatic klystron frequency control on the cavity were employed. The cylindrical cavity of the transmission type, operating in the H_{011} mode, had central holes in the lids, 15 mm in diameter, for insertion of the nitrogen-cooled sample holders.

The electromagnet had poles 20 cm in diameter, a 5.4 cm gap, and was provided with coils for the low-frequency modulation for observing the EPR lines on the oscilloscope.

The spectrometer had a sensitivity of better than 10^{-11} mole of DPPH at room temperature with recorder presentation.

The steady magnetic field was determined with a standard IMI-2 proton resonance field meter, and a 526U heterodyne wavemeter. The field was measured with a precision of 10^{-4} . The probe of the proton meter was placed in the magnet gap right next to the cavity. Controlled experiments with DPPH determined the difference in the fields in the region of the probe and in the center of the resonator, where the sample was located. The measured field values were corrected for this difference.

The microwave frequency of the klystron generator was measured with a ShGVS heterodyne wavemeter with an accuracy of 5×10^{-5} .

B. Method of preparing samples. The samples were prepared directly in the spectrometer cavity in the following way. The silver, supported on a molybdenum coil, and the paraffin, placed in a glass oven, were vaporized in vacuum and then condensed together into the bottom of a nitrogen-cooled quartz dewar located in the center of the microwave cavity.

The apparatus for sample preparation is shown schematically in Fig. 1. Here 1 is the spectrometer cavity; 2, the bottom of the quartz dewar in which the sample is obtained; the dewar bottom is cooled by liquid nitrogen, 3, poured into this dewar; 4, the ring-shaped glass oven, open at the top, for vaporizing the paraffin; this is heated by a current passed through a winding provided with a thermocouple and has an opening in the middle to permit the passage of silver atoms volatilized from the coil 5 toward the sample 2; 5 is the electrically heated molybdenum coil used to vaporize the silver;

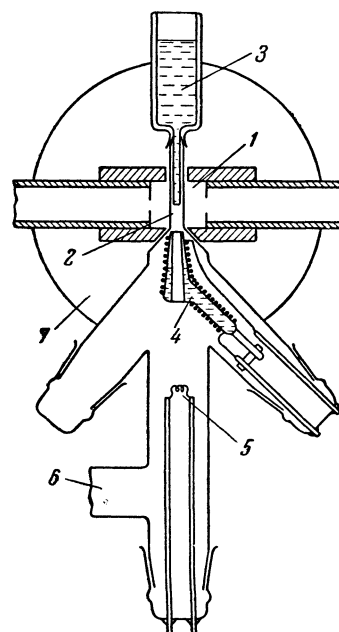


FIG. 1. Diagram of apparatus for obtaining samples.

6 is a tube connecting the apparatus to a vacuum pump; 7 is a pole-face of the magnet. Evacuation was carried out with an oil diffusion pump equipped with a nitrogen cold trap and having a pumping speed of 150 liter/sec. Before heat was applied to the vaporizers 4 and 5, the vacuum attained was usually of the order of 2×10^{-6} mm Hg. During heating, the pressure increased by about an order of magnitude; this did not interfere with the conduct of the experiment. The entire apparatus shown in Fig. 1, with the exception of the three large ground-glass joints and the vaporizers, was made of quartz.

3. THEORY AND CALCULATION OF THE PARAMAGNETIC RESONANCE SPECTRA OF ATOMS TRAPPED IN AN INERT MATRIX

A free atom placed in a magnetic field is characterized by the following Hamiltonian

$$\mathcal{H} = g_J \beta \mathbf{J} \mathbf{H} + g_I \beta \mathbf{I} \mathbf{H} + A \mathbf{J} \mathbf{I}, \quad (1)$$

where g_J is the Lande factor (gyromagnetic ratio for the electron shell), β is the Bohr magneton, $g_I = -\mu_I/\beta I$ is the gyromagnetic ratio for the atomic nucleus; μ_I is the nuclear magnetic moment, \mathbf{J} and \mathbf{I} are electronic and nuclear angular momentum operators, respectively, and A is the hyperfine interaction constant. The first and second terms of Eq. (1) represent respectively the interactions of the electronic and nuclear magnetic moments of the atom with the external magnetic field, and the third term describes the interaction between these moments. The first term of Eq. (1) is responsible for ordinary EPR, and the two others are responsible for its hyperfine structure.

An exact solution of the problem with Hamiltonian (1) for the case $J = 1/2$, to which the ground state $^2S_{1/2}$ of the silver atom also belongs, leads to the following Breit-Rabi formula for the Zeeman energy levels^[10]:

$$W_{I \pm 1/2} = -\frac{\Delta W}{2(2I+1)} + g_I \beta H m \pm \frac{\Delta W}{2} \left(1 + \frac{4m}{2I+1} x + x^2 \right)^{1/2}, \quad (2)$$

where $\Delta W = 1/2 (2I+1)A$ is the hyperfine splitting of the energy level of the ground state of the atom in zero magnetic field, m is the magnetic quantum number of the total moment of the atom $\mathbf{F} = \mathbf{J} + \mathbf{I}$, and $x = (g_J - g_I)\beta H/\Delta W$ is a dimensional parameter proportional to the magnetic field.

An atom trapped in an inert substance with which it does not react chemically will be characterized by a Hamiltonian containing the entire right hand member of Eq. (1), to which it is necessary to add terms describing the interaction between the

trapped atom and the host matrix. Even if we disregard the mathematical difficulties in the solution of such a complete Hamiltonian, we do not have at present detailed information about the immediate neighbors of atoms in a matrix and their interactions with these neighbors, information that is needed before such additional terms can be specified. It is possible, however, to characterize somewhat formally the atoms trapped in an inert matrix by the Hamiltonian for the free atom, Eq. (1), considering that the interaction with the matrix leads only to a change in the values of the quantities g_J and A . Then the deviation of these values from those for the free atom can serve as a sort of phenomenological characteristic of the effect of the matrix on the atom.^[3] Adrian has shown^[8] that a knowledge of these deviations allows, in certain cases, the determination of the sites occupied by the atoms in the matrix as well as the nature and magnitude of the strength of the interaction between the atoms and the matrix. Thus, from the EPR data and Eqs. (1) and (2) one finds these effective magnitudes g_J and A , and then compares them with the analogous values for free atoms. We shall follow this procedure below.

Silver, trapped atoms of which are the subject of this paper, has two isotopes, Ag^{107} and Ag^{109} , and the ground state of the atom is $^2S_{1/2}$. The nuclear spins of both isotopes $I = 1/2$, and the nuclear magnetic moments are negative. Hence, in the EPR spectrum of each isotope there will be observed two lines corresponding to the transitions

$$(F = 1, m = -1) \rightarrow (F = 0, m = 0),$$

$$(F = 1, m = 0) \rightarrow (F = 1, m = 1)$$

(see Fig. 2). Since in EPR experiments the frequency ν is kept constant and the magnetic field H varied, then for each isotope of silver one obtains from Eq. (2) the following expressions for the two transitions indicated above:

$$\begin{aligned} \nu &= -\Delta\nu \left\{ \frac{1}{2} (1 + x_1^2)^{1/2} + \frac{1}{2} (1 - x_1) - \frac{g_I \beta H_1}{h \Delta\nu} \right\}, \\ \nu &= -\Delta\nu \left\{ \frac{1}{2} (1 + x_2^2)^{1/2} - \frac{1}{2} (1 + x_2) - \frac{g_I \beta H_2}{h \Delta\nu} \right\}; \\ x_1 &= (g_J - g_I) \beta H_1 / h \Delta\nu, \quad x_2 = (g_J - g_I) \beta H_2 / h \Delta\nu, \quad (3) \end{aligned}$$

where H_1 and H_2 are the values for the magnetic field for the first and second transitions, $\Delta\nu = \Delta W/h$, and h is Planck's constant. Since the nuclear magnetic moment of both isotopes of silver are negative, the quantities A , ΔW , $\Delta\nu$, x_1 , and x_2 are likewise negative.

Having determined from the EPR experiments on trapped silver atoms the values of ν , H_1 , and H_2 for each isotopes, it is possible with the aid of

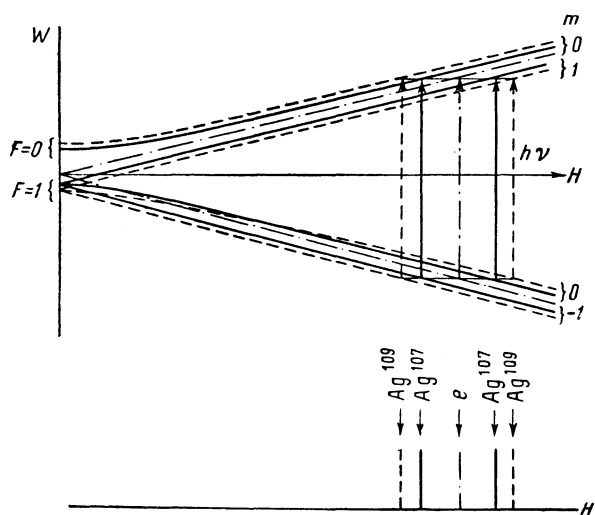


FIG. 2. Energy levels and EPR spectrum for the ground state of silver atoms (the difference in the values of ΔW for the silver isotopes is strongly exaggerated in this figure).

the system (3) to find the phenomenological parameters g_J and $\Delta\nu$ of these trapped atoms, which must then be compared with the corresponding magnitudes for free atoms. For silver atoms, for which the nuclear spins of the isotopes $I = 1/2$, the value of $\Delta W = A$, and $\Delta\nu = A/h$.

4. EXPERIMENTAL RESULTS

Both stable isotopes of silver occur in nature in practically the same proportion: Ag^{107} is 51.9%, and Ag^{109} is 48.1%. As has already been mentioned, both isotopes have spin $I = 1/2$. The nuclear gyromagnetic ratios are: $g_I(\text{Ag}^{107}) = 1.237 \times 10^{-4}$, $g_I(\text{Ag}^{109}) = 1.422 \times 10^{-4}$.^[1] The hfs splittings $\Delta\nu$ are proportional to the nuclear gyromagnetic ratios g_I and for the silver isotopes have closely similar values. For free silver atoms values for $\Delta\nu$ ^[1,2] are presented below in Table II.

Figure 2 shows the magnetic energy level

scheme for the ground state of silver atoms, constructed with the aid of Eq. (2). The levels for the isotope Ag^{107} are shown as continuous lines, those for Ag^{109} as dashed lines. For greater clarity, the difference in the splitting $\Delta\nu$ for the two isotopes is strongly exaggerated compared to its true value. For comparison, the magnetic levels of a free electron are shown as dot-dash lines. The observed EPR transitions are shown on the scheme and below this a representation of the EPR spectrum. The middle line corresponds to a free electron transition at $g = 2.0$. A spectrum of the type shown in Fig. 2 should be observed both in free and in trapped silver atoms.

In Fig. 3a is shown the experimental spectrum for atoms of silver trapped in technical grade paraffin (this and the following figures show derivative recordings). In this experiment ordinary technical petroleum paraffin was used without any special purification or treatment. This paraffin is usually considered to consist mostly of normal individual paraffins $\text{C}_n\text{H}_{2n+2}$, with values of n from 10 to 36 and averaging 23. The EPR spectrum seen in Fig. 3a is similar to that indicated in Fig. 2. In the middle of the spectrum in the vicinity of the free electron line one sees a signal having hfs at $g = 2.0$. This is a signal from the free radical created in the paraffin by the silver atoms. During the capture of free atoms of silver (as well as other metals) in technical or individual paraffin at liquid nitrogen temperature free radicals are always observed; these probably form as a result of a reaction between a portion of the free atoms and the paraffin molecules. When pure vapors of paraffins, without metal atoms, are condensed, the radicals are not observed. These radicals will not be considered here further. A special investigation will be devoted to them.

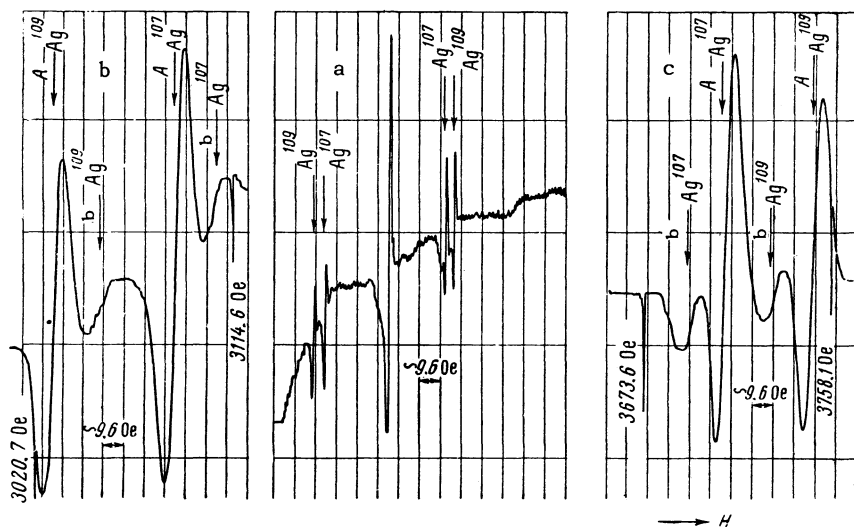


FIG. 3. EPR spectrum of silver atoms in technical paraffin ($\nu = 9600.0 \text{ Mc}$).

Table I

Atom	Matrix	Type of Spectrum	ν , Mc	H_1 , Oe	H_2 , Oe	$\delta H = H_2 - H_1$, Oe
Ag ¹⁰⁷	Technical paraffin	A	9600.0±0.5	3086.9±0.3	3710.3±0.3	623.4±0.6
Ag ¹⁰⁹	The same	A	9600.0±0.5	3028.5±0.3	3750.1±0.3	721.6±0.6
Ag ¹⁰⁷	» »	B	9600.0±0.5	3107.2±0.7	3694.6±0.6	587.4±1.3
Ag ¹⁰⁹	» »	B	9600.0±0.5	3051.2±1.2	3732.0±0.7	680.8±1.9
Ag ¹⁰⁷	C ₂₀ H ₄₂	A	9503.9±0.5	3052.1±0.3	3675.8±0.6	623.7±0.9
Ag ¹⁰⁹	C ₂₀ H ₄₂	A	9503.9±0.5	2993.8±0.3	3715.7±0.3	721.9±0.6
Ag ¹⁰⁷	C ₁₇ H ₃₆	A	9599.6±0.5	3087.6±0.3	3712.8±0.5	625.2±0.8
Ag ¹⁰⁹	C ₁₇ H ₃₆	A	9599.6±0.5	3028.7±0.5	3752.6±0.5	723.9±1.0

Table II

Atom	Matrix	Type of Spectrum	$\Delta\nu$, Mc	$\delta(\Delta\nu)/\Delta\nu$, %	g_J
Ag ¹⁰⁷	Free		1712.56±0.04		2.00224±0.00020
Ag ¹⁰⁹	»		1976.94±0.04		2.00224±0.00020
Ag ¹⁰⁷	Technical paraffin	A	1732.2±4.2	+1.14	2.00154±0.00055
Ag ¹⁰⁹	The same	A	1999.5±6.1	+1.14	2.00145±0.00054
Ag ¹⁰⁷	» »	B	1634.1±7.8	-4.58	2.0020±0.0010
Ag ¹⁰⁹	» »	B	1889.7±15.6	-4.42	2.0025±0.0015
Ag ¹⁰⁷	C ₂₀ H ₄₂	A	1732.5±6.2	+1.16	2.00161±0.00078
Ag ¹⁰⁹	C ₂₀ H ₄₂	A	1999.8±4.2	+1.15	2.00164±0.00055
Ag ¹⁰⁷	C ₁₇ H ₃₆	A	1736.2±5.5	+1.39	2.00043±0.00070
Ag ¹⁰⁹	C ₁₇ H ₃₆	A	2004.9±6.5	+1.41	2.00044±0.00083

Figures 3b and 3c show the low-field and high-field silver lines, respectively, recorded with slow sweep. These recordings appear as magnifications of portions of the spectrum in Fig. 3a. Alongside of the intense lines in Fig. 3b, c, can be seen weaker lines, two for each silver isotope. Thus, each isotope gives two spectra with different values of $\Delta\nu$ and g_J . This is evidence^[4,5] for two types of trapping sites for silver in paraffin differing in surroundings and matrix field. The more intense spectrum in Fig. 3 will be symbolized by the letter A and the weaker one by letter B. Figures 3b and 3c show proton resonance field markers on the recorded trace. Next to these markers are indicated the corresponding field values.

Table I presents the results of the measurements of the frequency ν , the magnetic fields for the transitions H_1 and H_2 , and the splitting $H_2 - H_1$. The rms errors are indicated.

In Table II are given the values of $\Delta\nu$ and g_J calculated from the data of Table I with the aid of Eq. (3) and also a comparison of these values with the analogous quantities for free atoms. Here $\delta(\Delta\nu) = \Delta\nu - \Delta\nu_{\text{free}}$.

The experiment on silver atoms in a matrix of technical paraffin was repeated several times. The results of a typical experiment are presented in Fig. 3 and in Tables I and II. The results of the other experiments agree with the data presented

in Table II within the limits of experimental error.

In order to determine the effect of the results of the presence in the technical paraffin of a large number of individual paraffins, it was decided to carry out experiments on matrices of a pure individual paraffin. The paraffin chosen was pure normal eicosane C₂₀H₄₂ having a melting point of 36.4°C.

The EPR spectrum of silver atoms trapped in eicosane is shown in Fig. 4a. This spectrum is very much like those shown in Figs. 2 and 3a. In the middle of Fig. 4a is seen a free radical signal the hfs of which differs from that in Fig. 3a. Figures 4b and 4c are slow-sweep recordings of the derivative signals from silver atoms in eicosane. Field markers appear in these traces. Data for silver atoms in eicosane are presented in Tables I and II. Fourteen runs were made on silver atoms in eicosane. The results presented in Fig. 4 and the tables are typical of the entire series. The results of the other experiments are completely similar and agree within the limits of error with the values presented in Table II.

The A spectrum is relatively easily obtained in eicosane; it is quite intense, and, as can be seen from Table II, it coincides completely with the analogous spectrum in technical paraffin, within the limits of error. The B spectrum is very much

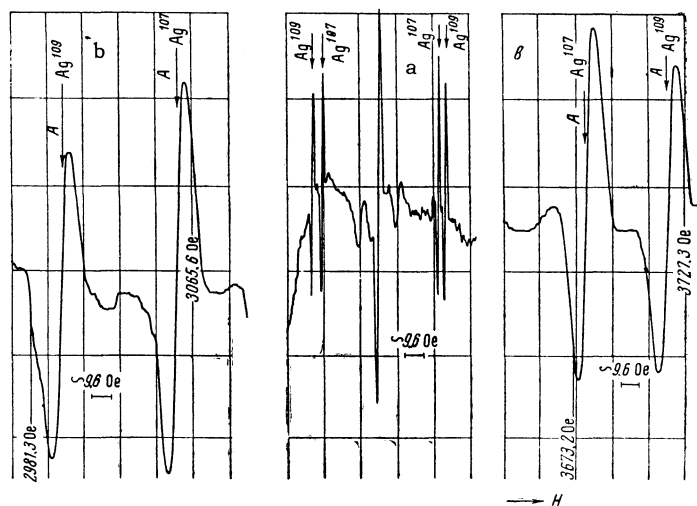


FIG. 4. EPR spectrum of silver atoms in eicosane, $C_{20}H_{42}$ ($\nu = 9515.0$ Mc).

less definite in eicosane than in the technical paraffin. This is probably explained by the fact that in eicosane this spectrum is significantly weaker. In not one of the fourteen trials with eicosane was it possible to record satisfactorily well the B spectrum and obtain its parameters reliably. However, this spectrum undoubtedly exists in eicosane, and its parameters are probably similar to those of the B spectrum in technical paraffin. A few lines of the B spectrum in eicosane, weak to be sure, are clearly seen in Figs. 4b and 4c.

More experiments were carried out on the single paraffin heptadecane $C_{17}H_{36}$, m.p. $20.5-22^{\circ}C$. These runs were also made in the apparatus shown in Fig. 1 according to the procedure described above; they were made very difficult because of the high volatility of heptadecane. The results of the single experiment with heptadecane that was sufficiently reliable in a quantitative sense are given in Tables I and II. The data shown are for the A spectrum, which within the limits of error agree with the parameters of the spectra of this type in the eicosane and the technical paraffin. An increase in the number of experiments on heptadecane would probably improve this agreement. The B spectrum was as difficult to observe in heptadecane as it was in eicosane. In our experiments we did not obtain sufficiently definite information about this spectrum in heptadecane. The free radical spectrum in heptadecane is essentially different from the ones obtained in eicosane and in technical paraffin.

In the experiments just described, the line width of the absorption varied markedly from measurement to measurement, even in the same run. These widths were determined as the separation between the maximum values of the derivative of the absorption line and in all experiments

had closely similar values, varying in the range 7–12 Oe.

Our experimental method did not permit a determination of the concentration of the trapped atoms. The total number of trapped atoms remaining free in the matrix, however, could be estimated from the intensity of the EPR signal. This number exceeded 10^{15} in the individual experiments.

During a discussion of the results presented above the possibility was suggested that the free silver atoms giving rise to the EPR spectrum were not trapped in the paraffin but were stabilized on the clean surface of the cooled quartz before it was covered by paraffin. This suspicion was strengthened by the practical coincidence of the spectra in the technical and in both individual paraffins. And although the estimates of the number of atoms responsible for the paramagnetic resonance showed that this number of atoms could not be distributed on the clean quartz surface, special controlled experiments were undertaken in order to check this assumption. In the apparatus used for the preceding experiments, a slow evaporation of silver alone, without paraffin, was carried out, first on the uncontaminated quartz cooled by liquid nitrogen and then on the same quartz surface but covered with a polyethylene film. Careful investigations showed that paramagnetic resonance of silver atoms was not observed in either case. Thus it was proved that silver atoms in a quantity sufficient to show resonance were not stabilized on either the cooled quartz or polyethylene surfaces. This was followed by an experiment involving the simultaneous deposition of silver and eicosane on a nitrogen-cooled polyethylene film covering the bottom of the quartz dewar. An EPR spectrum was obtained which co-

incided precisely with the spectra of silver in eicosane condensed on a quartz surface. These experiments proved conclusively that the resonances herein described are due to free atoms of silver trapped in paraffins.

No changes with time were observed in any of the investigated EPR spectra at nitrogen temperature. This is evidence for the immobility of silver atoms in the paraffin matrix at 77°K. After warming to room temperature the EPR spectrum completely and irreversibly disappears.

5. CONCLUSION

From the results presented in Table II it follows that in the experiments described above the quantities $\Delta\nu$ and g_J for trapped atoms differ very little from the analogous quantities for free atoms. This is evidence that silver atoms trapped in paraffin matrices can be considered to be free to a marked degree, and their electron orbitals can be regarded as weakly perturbed orbitals of free atoms.

It can also be seen from Fig. 2 that the ratio of the quantities $\Delta\nu$ for the two silver isotopes has for the trapped atoms the same value as for free atoms, in which case it equals the ratio of the g_J 's. This is evidently independent verification of the validity of the application of Eqs. (1), (2), and (3) for free atoms to the case of trapped atoms and the reasonableness of using the effective parameters $\Delta\nu$ and g_J derived from these equations.

As these investigations have shown, silver atoms trapped in paraffins exhibit two types of EPR spectra, symbolized by the letters A and B, which correspond to two different trapping sites with different surroundings in the matrix. For the A spectra the EPR parameters, and consequently the fields created by the immediate surroundings, were found to be identical within experimental error for matrices of individual paraffins with even and uneven numbers of carbon atoms ($n = 20$ and $n = 17$) and for a matrix composed of a mixture of individual paraffins (technical paraffin).

It follows from Adrian's theory of atoms in non-polar matrices^[8] that the surroundings for silver atoms of type A in the paraffins are such that the interaction caused by the Pauli principle is more important than the van der Waals forces. This conclusion is based on the positive shift in the value of $\Delta\nu$ corresponding to the A spectrum, i.e., the positive value of $\delta(\Delta\nu) = \Delta\nu - \Delta\nu_{\text{free}}$. In the case of the B spectra, which are character-

ized by a negative shift in the quantity $\Delta\nu$, the van der Waals forces predominate over the interaction associated with the Pauli principle. The very large negative shift in the B spectra compared to those observed for hydrogen in frozen gases^[3-5] attracts attention. It is possible that the absolute magnitude given for this shift in the B spectra is not completely accurate, since a careful separation of the incompletely resolved absorption lines in Figs. 3b and 3c was not made. It is probable, however, that the true value for the shift lies within the limits of experimental error.

In order to construct a theory of the interaction with the matrix of silver atoms trapped in paraffins, it is necessary to have reliable information both about the structure of the paraffin deposits obtained by condensation at nitrogen temperatures and about the trapping sites for the silver atoms and, consequently, the characteristics of their surroundings in these matrices. We do not as yet have such data. Some very preliminary information about the structure of the deposits was obtained by means of an x-ray analysis of a sample of eicosane taken from the quartz dewar after completion of the experiment with silver atoms. This analysis showed no apparent amorphous phase and indicated that the deposit had a polycrystalline structure. It is not clear, however, whether the deposit was polycrystalline from the very beginning or whether this structure appeared as a consequence of possible recrystallization of the paraffin as it warmed from the temperature of liquid nitrogen to room temperature, at which the analysis was performed.

As was mentioned above, the EPR line widths of silver atoms in paraffins were in the range 7–12 Oe. It is probable that dipole-dipole interactions do not give an important contribution to this width, since it did not change significantly under the conditions of very different concentrations occurring in the different runs. In order to find spin-lattice relaxation times it is necessary to make measurements at different temperatures, which we did not do, and in order to determine the role of anisotropy broadening it is important to have information about the structure of the matrix. All of this should be the object of further investigations.

At the present time work is continuing on the study of trapped atoms of silver and other elements in various matrices.

Note added in proof (September 13, 1962). Recently there has appeared a communication by the authors of^[3-5] about

the investigation of alkali metal atoms trapped in matrices of frozen inert gases at the temperature of liquid helium.

¹N. F. Ramsey, *Molecular Beams*, Oxford, Clarendon Press, 1955.

²P. Kusch and V. W. Hughes, *Handbuch der Physik* **37**, 100 (1959).

³Jen, Foner, Cochran, and Bowers, *Phys. Rev.* **112**, 1169 (1958).

⁴Cochran, Bowers, Foner, and Jen, *Phys. Rev. Letters* **2**, 43 (1959).

⁵Foner, Cochran, Bowers, and Jen, *J. Chem. Phys.* **32**, 963 (1960).

⁶Formation and Trapping of Free Radicals, Academic Press, 1960, p. 213.

⁷D. J. E. Ingram, *Free Radicals as Studied by Electron Spin Resonance*, London, Butterworths, p. 224.

⁸F. J. Adrian, *J. Chem. Phys.* **32**, 972 (1960).

⁹H. A. Buckmaster and H. E. D. Scovil, *Can. J. Phys.* **34**, 711 (1956); A. G. Semenov and N. N. Bubnov, *PTÉ* No. 1, 92 (1959).

¹⁰G. Breit and I. I. Rabi, *Phys. Rev.* **38**, 2082 (1931).

Translated by L. M. Matarrese
210