Matrix Perturbations of the ESR of Trapped H, N, P, and As Atoms at 4.2°K*

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Electron-spin-resonance spectra of N, P, As, and H atoms trapped in matrices formed from rare-gas elements at 4.2°K have been studied. The isotropic hyperfine coupling of N and P increases with the atomic number of the matrix element whereas that of As decreases. The van der Waals interaction theory devised by Adrian to explain the matrix effects on the nitrogen hyperfine splitting was generalized and applied with good success to the heavier group-V atoms. The results indicate that these group-V atoms occupy substitutional lattice sites, whereas the H atoms occupy octahedral sites. Recalculation of the matrix perturbations on nitrogen with more recent analytical self-consistent-field wave functions significantly improved agreement between theory and experiment. The isotropic g factor of N, P, and As was found to be less than the free-spin g and to decrease with increasing atomic number of the matrix elements. A weak fine structure observed for As atoms trapped in the Kr matrix is attributed to a small fraction of the atoms trapped in crystalline faults in the matrix.

I. INTRODUCTION

SEVERAL studies of electron spin resonance (ESR) of atoms trapped in frozen matrices have been reported over the last decade.[1-7] There has been, however, little systematic investigation of the perturbing effect of the surrounding matrix upon the magnetic properties of the impurity atom, namely, its isotropic hyperfine coupling A and its spectroscopic splitting factor g. The only studies of such matrix effects known to the authors are on the light atoms hydrogen,[8,9] nitrogen,[10] and the alkali atoms.[11] The present paper reports results on the heavier group-V atoms, phosphorus and arsenic, trapped in rare-gas matrices and also reports further results on nitrogen. The semi-quantitative van der Waals interaction theory, originally devised by Adrian[10] to explain the positive hyperfine splitting shifts for nitrogen, the lightest group-V element, is shown to be applicable to the heavier atoms. In particular, this theory, taken in conjunction with configuration interaction calculations of the hyperfine couplings, is capable of explaining such matrix-induced decreases in the hyperfine splitting as are observed for arsenic. Furthermore, a recalculation of Adrian's results for nitrogen with the more recently developed analytical SCF (self-consistent-field) nitrogen wave functions has resulted in significantly better agreement between theory and experiment for that element. The dependence of the spectroscopic splitting factor g of the group-V atoms on the trapping matrix is presented and explained qualitatively in terms of the theory. A fine structure for arsenic atoms trapped in krypton is reported and interpreted, and finally a study of the hydrogen atoms produced during the experiments is presented and the results compared with those of Foner, Cochran, Bowers, and Jen.[8]

II. EXPERIMENT

The atoms studied in these experiments were produced by the γ-irradiation of frozen solutions of the appropriate sample compound (2%) dispersed in a rare gas (98%). The sample compounds employed included the hydrides NH_3, PH_3, AsH_3, SbH_3, CH_4, SiH_4, GeH_4, SnH_4, and the fluoride PF_3. The rare gases argon, krypton, and xenon were employed as matrices. All irradiations (approximate dosage, 2×10^6 R) and ESR studies were carried out at 4.2°K. The microwave frequency was 24.0619 ± 0.0008 GHz. Other details of the experimental method have been reported elsewhere.[12]

III. ESR STUDY OF GROUP-V ATOMS

A. Theory

We briefly review the theory developed for nitrogen and then show that it can be generalized to include such atoms as arsenic. The nominal ground-state configuration of the group-V elements is $^4S_{3/2}$, the outermost or

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[1] C. K. Jen, S. N. Foner, E. L. Cochran, and V. A. Bowers, Phys. Rev. 112, 1169 (1958).
[2] H. N. Rexroad and W. Gordy, Phys. Rev. 125, 242 (1962).
[3] L. A. Wall, D. W. Brown, and R. E. Florin, J. Phys. Chem. 63, 1762 (1959).
[4] S. N. Foner, C. K. Jen, E. L. Cochran, and V. A. Bowers, J. Chem. Phys. 28, 351 (1958).
[5] L. A. Wall, D. W. Brown, and R. E. Florin, J. Chem. Phys. 30, 602 (1959).
[6] R. L. Morehouse, J. J. Christiansen, and W. Gordy, J. Chem. Phys. 45, 1747 (1966).
[7] F. J. Adrian, E. L. Cochran, and V. A. Bowers, Advan. Chem. Ser. 36, 50 (1962).
[8] S. N. Foner, E. L. Cochran, V. A. Bowers, and C. K. Jen, J. Chem. Phys. 32, 963 (1960).
[9] F. J. Adrian, J. Chem. Phys. 32, 972 (1960).
[10] F. J. Adrian, Phys. Rev. 127, 837 (1962).
[11] C. K. Jen, V. A. Bowers, E. L. Cochran, and S. N. Foner, Phys. Rev. 126, 1749 (1962).
[12] W. V. Bouldin, R. A. Patten, and W. Gordy, Phys. Rev. Letters 9, 98 (1962); W. V. Bouldin and W. Gordy, Phys. Rev. 135, A806 (1964).
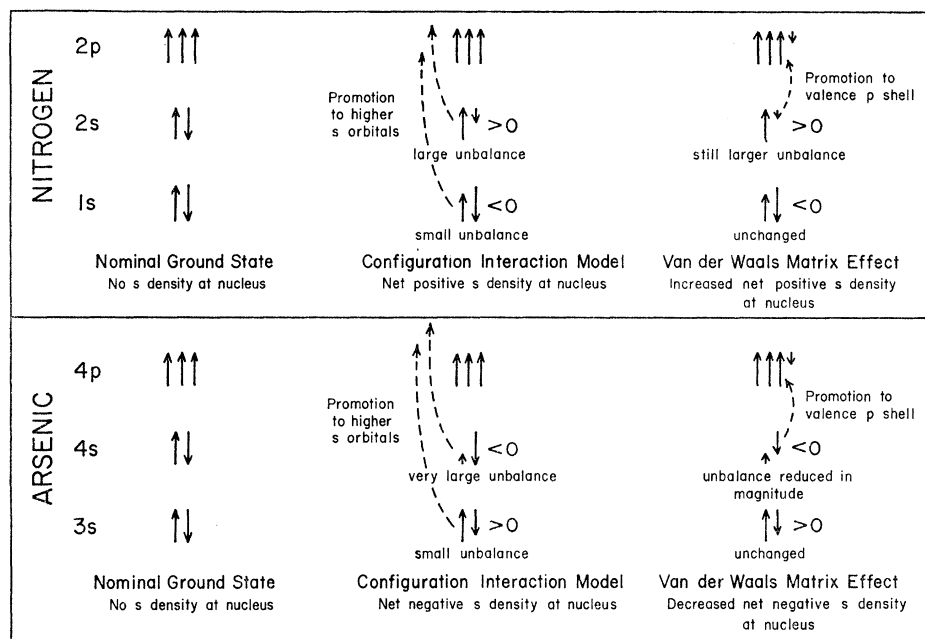
perturbation $\mathcal{K}'$ which were linear in $\mathcal{K}_{\text{hfs}}$. The resulting formula for the magnitude of the change in the hyperfine splitting constant for the general group-V atom X as caused by a single matrix particle is then

$$\Delta A_X = (-2e^2/R^6)[(E_X)^{-1} + (E_X + E_M)^{-1}]$$
$$\times E_M \alpha_M/(E_X + E_M) \langle ns \mid z \mid npz \rangle^2 A_{Xns}. \quad (1)$$

Here R is the separation of impurity atom and matrix atom; α_M is the polarizability of the matrix particle; F_X is the average excitation energy of the X atom and is taken to be the energy required to excite an ns electron into the np shell; E_M is the average excitation energy of the matrix particle and is taken to be the ionization energy of the rare-gas atom (with negative sign); A_{Xns} is the hyperfine coupling constant for an ns electron of atom X; and $\langle ns \mid z \mid npz \rangle$ is the matrix element of the operator z evaluated between the s and p_z valence orbitals of the impurity atom.

B. Results

1. Hyperfine Coupling Shifts

The isotropic hyperfine coupling constants for nitrogen, phosphorus, and arsenic atoms in rare-gas matrices which were determined in these experiments are tabulated in Table I and plotted in Fig. 2. The nitrogen data were obtained by use of the isotope ^{15}N, but for purposes of consistency with data in other matrices were converted into ^{14}N splittings. Data collected by other workers for nitrogen in argon[15] and for all three atoms in the free or vapor state[16–18] are also presented
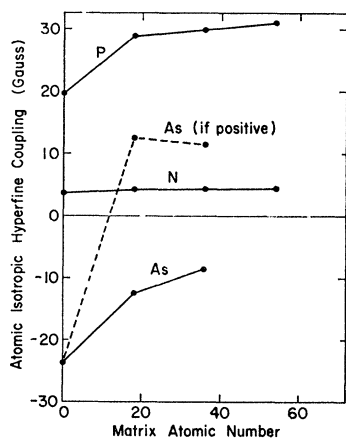
Fig. 2. Variation of the isotropic hyperfine coupling of nitrogen, phosphorus, and arsenic with the atomic number of the trapping matrix.

[15] E. L. Cochran, Phys. Rev. **127**, 837 (1962).
[16] W. W. Holloway, Jr., and R. Novick, Phys. Rev. Letters **1**, 367 (1958).
[17] H. G. Dehmelt, Phys. Rev. **99**, 527 (1955).
[18] J. M. Pendlebury and K. F. Smith, Proc. Phys. Soc. (London) **84**, 849 (1964).

TABLE I. Hyperfine coupling constants and g factors for nitrogen, phosphorus, and arsenic atoms in rare-gas matrices.

Impurity atom	Matrix	g	A (G)
^{14}N	"free"	2.0022[a]	3.73[a]
	Kr	2.0021	4.39
		±0.0006	±0.10
	Xe	2.0019	4.43
		±0.0006	±0.10
^{31}P	"free"	2.0019[b]	19.65[c]
		±0.0004	±0.003
	Ar	2.0012	28.75
		±0.0001	±0.10
	Kr	2.0001	29.76
		±0.0002	±0.60
	Xe		30.90
			±1.0
^{75}As	"free"	1.9965	−23.692[c]
		±0.0008	±0.0004
	Ar	1.9960	−12.52
		±0.0001	±0.16
	Kr	1.9951	−11.20
		±0.0001	±0.13
	Xe	1.9943	
		±0.0008	

[a] Reference 16.
[b] Reference 17.
[c] Reference 18.

for comparison purposes. As mentioned earlier, the free-atom coupling for arsenic is known to be negative. Since we determine only the magnitude of the splitting in our experiment, two possibilities are shown for the sign of the coupling in the rare-gas matrices. However, from the foregoing arguments, the original negative hyperfine coupling should monatomically increase (in an algebraic sense) with increasing matrix atomic weight, which effect will decrease the observed splitting for such an atom, and thus the lower curve is almost certainly the correct one. The $Z = 0$, or free-atom, splittings are taken from atomic beam measurements on the atoms in the vapor phase. These values have been arbitrarily assigned a matrix "atomic number" of zero. We now discuss the observed matrix induced shifts in the hyperfine coupling in light of the theory outlined earlier.

Equation (1) gives the shift for a single pair formed by an impurity atom and a matrix atom. Assuming the effect to be additive, one must multiply the right-hand side of the equation by 12, 6, and 4 to account for atoms trapped in substitutional, octahedral, and tetrahedral sites, respectively.

The formula may be employed in two ways. First, given the measured hyperfine shift, one can calculate the required distances between matrix atom and impurity atom for the different sites. By comparing these values with the experimentally known nearest-neighbor distances for these sites in the solid rare gases, one can decide which site is most likely occupied by the impurity atom. Adrian followed this method.

TABLE II. Comparison of the nearest-neighbor distance (R_{cal}) required to give the measured hyperfine shift (ΔA_{expt}) with the corresponding distance (R_{obs}) in the perfect rare-gas crystal, and calculation of the hyperfine shift (ΔA_{pred}) which is predicted for R_{obs}. [R_{cal} is calculated from Eq. (1) using ΔA_{expt}, and ΔA_{pred} is calculated from the same formula using R_{obs}.] The calculations are made for nitrogen, phosphorus, and arsenic atoms assumed to be trapped in substitutional, octahedral, and tetrahedral sites within the face-centered-cubic lattice.

Matrix	ΔA_{expt} (G)	Site	R_{cal} (a_0)	$R_{obs}{}^a$ (a_0)	ΔA_{pred} (G)	$\dfrac{(\Delta A_{pred}-\Delta A_{expt})^b}{\Delta A_{expt}}$ (%)	$R_{cal}{}^b$ (a_0)	$\Delta A_{pred}{}^b$ (G)	$\dfrac{(\Delta A_{pred}-\Delta A_{expt})^b}{\Delta A_{expt}}$ (%)
^{14}N									
A	0.47^c	Subst.	7.02	7.09	0.44	−6	7.84	0.86	83
		Oct.	6.25	5.01	1.78	278	6.98	3.40	624
		Tet.	5.84	4.34	2.79	494	6.53	5.45	1060
Kr	0.66	Subst.	7.68	7.59	0.71	7			
		Oct.	6.84	5.36	2.85	332			
		Tet.	6.39	4.65	4.43	571			
Xe	0.70	Subst.	8.19	8.15	0.72	3			
		Oct.	7.29	5.76	2.88	312			
		Tet.	6.82	4.99	4.56	571			
^{31}P									
A	9.1	Subst.	6.91	7.09	7.74	−15			
		Oct.	6.15	5.01	31.2	243			
		Tet.	5.75	4.34	49.1	440			
Kr	10.15	Subst.	7.17	7.59	7.21	−29			
		Oct.	6.39	5.36	29.1	187			
		Tet.	5.97	4.65	45.5	348			
Xe	11.25	Subst.	7.70	8.15	8.00	−29			
		Oct.	6.86	5.76	32.0	184			
		Tet.	6.41	4.99	50.3	347			
^{73}As									
A	11.16	Subst.	6.52	7.09	6.81	−39			
		Oct.	5.81	5.01	27.2	144			
		Tet.	5.43	4.34	42.7	283			
Kr	12.49	Subst.	6.83	7.59	6.62	−47			
		Oct.	6.09	5.36	26.8	115			
		Tet.	5.69	4.65	42.0	336			

^{a} Reference 19. ^{b} Reference 10. ^{c} Reference 15.

However, this method alone is inadequate for judgment on the accuracy of the theory for prediction of the coupling shift. In particular, taking the sixth root of hyperfine shifts which might differ by an order of magnitude will yield values for R which appear quite close. Thus it is also worthwhile to use Eq. (1) in the opposite direction and to calculate expected hyperfine shifts from the experimentally observed nearest-neighbor distances for R. We have followed both of the approaches in the present work; the results appear in Table II. In this table, R_{cal} is the distance between the impurity atom and the matrix atom required to produce the observed hyperfine shift ΔA_{expt} and ΔA_{pred} is the predicted hyperfine shift calculated from the experimentally known[19] distances R_{expt} in the perfect rare-gas crystals. For comparison purposes, the percentage error in the predicted hyperfine shift as compared to the measured shift is presented in column 7 of the table.

We repeated the matrix calculations for nitrogen in argon, using the earlier data available to Adrian, as a check on our computational methods. The results of both calculations appear in the top portion of Table II. It will be noted that our values agree much more closely with the experimental results than do Adrian's. This is interesting for several reasons. He himself commented that his results (i.e., predicted ΔA's) seemed high by a factor of 2 and the R_{cal}'s were thus high by (2)$^{1/6}$. Interestingly enough, our R's are almost exactly (2)$^{1/6}$ smaller than Adrian's. A comparison of the numerical values obtained for the various terms in Eq. (1) traces the discrepancy to the evaluation of the matrix element $\langle ns \mid z \mid np_z \rangle$, Adrian's being $0.779a_0 = 1.410(0.553a_0)$ or approximately $\sqrt{2}$ times our value for this term. The implications of this difference are significant. Adrian used numerically tabulated values[20] for his nitrogen wave functions in calculating this matrix element, whereas we employed the more recent

[19] E. R. Dobbs and G. O. Jones, Rept. Progr. Phys. **20**, 560 (1957).

[20] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A193**, 299 (1948).

analytical self-consistent-field wave functions of Roothaan and Kelly.[21] Apparently these latter wave functions allow much better calculations of quantities such as the matrix element required here, and one may thus conclude that the theory yields better results for nitrogen than was previously assumed. The good agreement between theory and experiment exists for nitrogen atoms trapped in krypton and xenon as well, and again the results favor the substitutional site overwhelmingly.

Before going any further, we should point out that, unfortunately, no single source of such wave functions could be found for carrying out the calculations for all three atoms. We used wave functions of similar type from other authors for our calculations for phosphorus[22] and arsenic.[23] Concerning these wave functions it should be noted that the final state $| np_z \rangle$ in the matrix element corresponds to the configuration sp^4, whereas the only $| np_z \rangle$ wave functions available for phosphorus and arsenic correspond to the configuration s^2p^3. However, the effect of this difference in configuration is probably negligible. This can be demonstrated directly for nitrogen since $| np_z \rangle$ nitrogen wave functions corresponding to both configurations are available, and values obtained for the matrix elements by use of the two wave functions are identical to three significant figures.

Turning now to the data for phosphorus and arsenic, one may draw several conclusions. First, for the assumptions made, quite good agreement between the results of theory and experiment is achieved for these heavier atoms. One may with confidence conclude that, as for nitrogen, the phosphorus atoms are trapped in substitutional sites within the lattice. Furthermore, the calculations also favor the substitutional site for arsenic in the rare-gas matrices. It can be seen from Table II that the absolute accuracy in prediction of the splitting shift falls off with increase in atomic number of the impurity atom. This dependency of accuracy on the atomic number of the impurity atom is probably caused by consideration of only the single excitation of the valence s electron to the valence p orbital $ns^2np^3 \rightarrow nsnp^4$ in the calculations. From Table II one sees that the substitutional sites, while giving the most accurate predictions of the splitting shift for the atoms of phosphorus and arsenic, at the same time give consistently low predictions for the splitting shift. If one includes the effect of the next most significant excitation, which an examination of the energy levels shows to be $ns^2np^3 \rightarrow ns^2np^2(n+1)s$, it can be seen that this excitation will also increase the predicted ΔA for both phosphorus and arsenic and thus bring theory still closer to experiment. Unfortunately, the wave functions needed for such calculations are not presently available.

Also, the theory can be used to supply a qualitative explanation of a heretofore puzzling result concerning the isotropic hyperfine coupling constant of phosphorus trapped in argon. Adrian, Cochran, and Bowers[7] photolyzed PH_3 and PD_3 in argon at 4.2°K with uv light. The resulting phosphorus doublet was rather broad, with a hyperfine splitting of 23.8 G. On warming the sample, however, at some temperature below 13°K, they observed the lines "sharpen markedly," and the separation between the lines increased to 28.8 G. These changes were irreversible. This latter hyperfine splitting is virtually identical to the 28.79 G we measured for phosphorus atoms produced by γ-irradiation of PH_3 in argon at 4.2°K. These lines (Fig. 2 of the preceding paper) are also much sharper than the 23.8-G doublet which is illustrated in the paper mentioned above, and thus the lines we observed resemble the warmed-up lines in this respect also. It seems very likely that the lines observed by Adrian et al. upon warmup are, in fact, caused by phosphorus atoms trapped in sites identical to those which have here been identified as substitutional sites. Since a smaller splitting for phosphorus implies a larger average distance between impurity atom and matrix atom, as seen from Eq. (1), the 23.8-G doublet can perhaps be explained if the phosphorus atoms initially observed by Adrian et al. are assumed to be trapped in large dislocation vacancies in which the average distance of the matrix particles from the phosphorus atoms is greater than that between the two adjacent substitutional sites. This would explain both the smaller hyperfine splitting and the greater linewidth caused by the anisotropies inherent in such a crystalline environment. When the sample is warmed, the largely disordered polycrystalline structure is annealed, and the phosphorus atoms move into substitutional sites as long-range order develops. The plausibility of the above explanation is given greater weight by the following consideration. Basic differences exist in the freezing process employed in the two experiments. Adrian et al. initially froze out the gas mixture from the vapor phase onto a surface cooled to 4.2°K, but we used a surface cooled to 77°K. Since, as Pimentel[24] has shown, solids formed from a gas by rapid condensation at a temperature well below half the melting point are probably extremely imperfect crystals at best, the sample frozen out at 4.2°K most likely had a large number of dislocations and vacancies into which the PH_3 molecules would more comfortably fit.

2. Matrix Effect on the g Factor of Group-V Atoms

The isotropic g factor of the group-V atoms in solid rare-gas matrices is tabulated in Table I and plotted in Fig. 3. The g values, which are always less than the

[21] C. C. J. Roothaan and P. S. Kelly, Phys. Rev. **131**, 1177 (1963).

[22] R. E. Watson and A. J. Freeman, Phys. Rev. **123**, 521 (1961).

[23] E. Clementi, J. Chem. Phys. **41**, 303 (1964).

[24] G. C. Pimentel, in *Formation and Trapping of Free Radicals*, edited by A. M. Bass and H. P. Broida (Academic Press Inc., New York, 1960), Chap. 4.
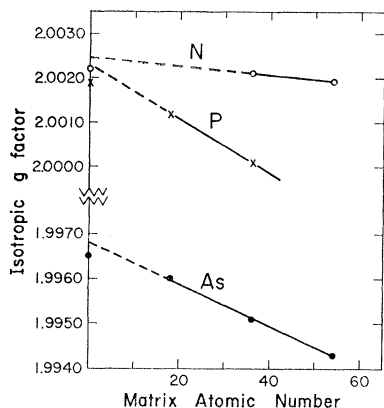
FIG. 3. Variation of the isotropic g factor of nitrogen, phosphorus, and arsenic with the atomic number of the tapping matrix.

free spin g_e, are seen to be further depressed by the matrix. The points plotted at $Z=0$ are those of the "free atom," i.e., measured in the vapor phase by atomic beam methods. Since the environment of the atoms in these experiments had a finite pressure, it may be looked at as possessing a small effective atomic weight. Thus, the points corresponding to the measurements of the free atom would probably be more accurately positioned if they were shifted a small amount to the right and were thus closer to the straight lines shown.

Recent measurements[25] of the g factor of nitrogen in argon and krypton, 2.0013 and 2.0012, respectively, agree qualitatively with the observations here. The observed dependence of g upon the matrix can be explained qualitatively in terms of the van der Waals interaction theory outlined earlier. The matrix induces excitations $s^2p^3 \rightarrow sp^4$, the lowest-lying state of the form sp^4 being ^4P. The orbital angular momentum thus introduced by the matrix interaction will lower the measured g factor. This effect will increase with the polarizability of the matrix; thus the g factor is expected to decrease with increasing atomic number of the matrix, as is observed.

IV. CRYSTALLINE FIELD SPLITTING OF THE ARSENIC RESONANCE

Most of the spectral interpretations presented here are based upon the assumption that the trapped radical is located in a spherically symmetric crystal site. In other words, each radical is assumed to occupy a substitutional or interstitial site in a face-centered-cubic crystal, and its nearest neighbors are all assumed to be crystallographically equivalent. There is a fair amount of experimental evidence to substantiate this assumption for most of the spectra from radicals trapped in

frozen gas matrices. Thus, Jen[26] and Foner, Cochran, Bowers, and Jen[8] conclude that samples deposited from the gas phase most likely consist of randomly oriented microcrystals, and one would expect most of the trapped radicals to be located in regions where there is a short-range crystal order as described above.

However, sites of lower symmetry certainly exist and can, under certain conditions, trap radicals. For example, Cole and McConnell[27] have observed satellites surrounding the main nitrogen triplet in a ^{14}N in N_2 system. They ascribed these satellites to nitrogen atoms trapped in an axially symmetric crystal site which resolves the three triply degenerate hyperfine lines into nine lines, only four of which are visible as satellites. We believe that a similar explanation holds for the small satellites which we have observed in an arsenic-in-krypton system (Fig. 4). These lines in the upper trace were obtained quite reproducibly in the several runs involving the dissociation of AsH_3 in krypton. Their separation, based on the three low-field lines, is found to be close to, though slightly larger than, the main arsenic quartet splitting. When this spectrum was first recorded, it was felt that this similarity in splitting might be fortuitous and that the satellites might belong to some $As-H_n$ species. To resolve this question, we
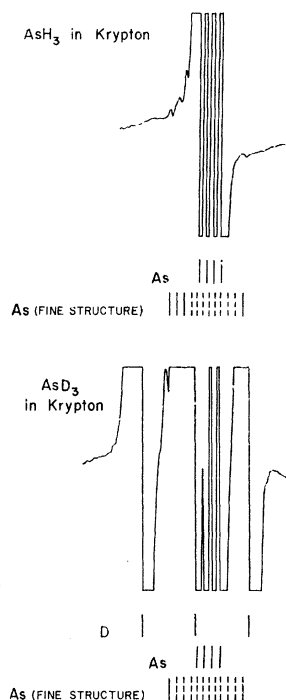
FIG. 4. Spectra from γ-irradiated AsH_3 and AsD_3 in krypton illustrating the crystalline-field-split satellites.

[25] P. H. H. Fischer, S. W. Charles, and C. A. McDowell, J. Chem. Phys. **46**, 2162 (1967).

[26] C. K. Jen, in *Formation and Trapping of Free Radicals*, edited by A. M. Bass and H. P. Broida (Academic Press Inc., New York, 1960), Chap. 7.

[27] T. Cole and H. M. McConnell, J. Chem. Phys. **29**, 451 (1959).

γ-irradiated AsD_3 in krypton, with the results appearing in the lower trace of Fig. 4. Only the lowest-field line is visible, the deuterium lines obscuring the others, but its position is identical to that of the corresponding line in the AsH_3-Kr spectra. This means that the satellites must be caused by arsenic atoms alone, since any As-H_n species would have had its spectrum altered drastically by the deuteration (the hyperfine splitting of D is less than a sixth that of H). While this lends strong weight to the explanation of the crystal-field splitting, there are still questions to be answered. For example, although it is easy to conceive of the existence of an axially symmetric crystalline field of sites within a matrix composed of N_2 molecules, how would such sites be found in a matrix such as Kr? Also, the satellites found by Cole and McConnell had the same g factor and hyperfine splitting as the main lines. Here, however, the pattern has a slightly higher g and A to be accounted for (Table III). All of these points, plus the intensity ratio of the main line to the satellite lines, may be explained if a small fraction of the arsenic atoms is assumed to be trapped in some statistically less likely site such as in the boundary between microcrystals or in crystal faults. Using x-ray diffraction techniques, Peiser[28] has shown that vapor-deposited argon at 4.2°K contains a fairly high concentration of dislocations. This includes edge dislocations, in which a plane of lattice points terminates inside the crystal. An atom trapped in such a dislocation will certainly experience an axially symmetric crystal field. The inequivalence of this site as compared with the main substitutional site (where most of the arsenic atoms have been shown to reside) can explain the shift in g factor. As is demonstrated in the section on the matrix effect, such a site would also be expected to cause the hyperfine splitting for arsenic to be slightly larger since the average distance between impurity atom and matrix atom would be larger, a condition which would result in a smaller decrease and hence a larger observed splitting than for atoms in substitutional sites. Finally, the observed intensity ratio is explained by the smaller probability that atoms would be trapped in such a site. This is in agreement with the nitrogen results, in which the satellites were much bigger relative to the main line than for arsenic. This follows from the fact that there should be more axially symmetric sites available within the N_2 matrix.
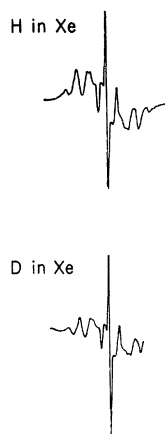

FIG. 5. Spectra of hydrogen and deuterium atoms trapped in xenon.

Assuming then that the satellites are part of the crystalline field splitting of the arsenic spectra, one may make the assignment as shown under the spectra in Fig. 4. For an axially symmetric crystalline field, the additional term $D[S_\lambda^2-\frac{1}{3}S(S+1)]$ must be added to the spin Hamiltonian. Here D is the zero-field splitting parameter, and S_λ is the component of the total spin angular momentum in the direction of the symmetry axis λ of the crystalline field. For an isotropic g factor, which arsenic has, the energy of the $S_z=\frac{1}{2}\leftrightarrow-\frac{1}{2}$ transition is unaffected by the crystalline field. However, the transition energies for $S_z=\frac{3}{2}\leftrightarrow\frac{1}{2}$ and $-\frac{1}{2}\leftrightarrow-\frac{3}{2}$ will be shifted by an amount proportional to $(3\cos^2\theta-1)$, where θ is the angle between the crystalline field axis and S_z, which is along the external field. Since the microcrystals are randomly oriented, the most probable orientation is $\theta=90°$, and it can be shown that the crystalline field term will shift the energy levels so that the principal absorption intensity of the two above-mentioned transitions will fall at $\pm D$ about the unsplit $S_z=\frac{1}{2}\leftrightarrow-\frac{1}{2}$ lines. The total spread of such a pattern, which was determined to be 84.2 G, will always equal $2D+3A'$, where A' is the hyperfine splitting of the satellites. Using the measured value $A'=11.7$ G, one obtains $D=24.6$ G. With these two parameters plus the pattern center, which was determined to be 9 G below that of the main quartet, a theoretical reconstruction of the lines of the crystalline field splitting is possible. This display, taken in conjunction with the observed width of the main lines indicates that the lines observed are the only lines which should be visible.

V. HYDROGEN ATOMS

For all hydrides investigated, resonances of hydrogen atoms were detected after the γ-irradiation. The features of the hydrogen lines observed in a given matrix were independent of the sample from which the hydrogen atoms originated.

Since the resulting doublets are separated by about

TABLE III. Arsenic fine structure in krypton.

A' (G)	D (G)	g
11.72	24.60	1.9971
±0.20	±1.0	±0.0003

[28] H. Peiser, in *Formation and Trapping of Free Radicals*, edited by A. M. Bass and H. P. Broida (Academic Press Inc., New York, 1960), Chap. 9.

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TABLE IV. Hyperfine coupling constants and g factors for H atoms in rare-gas matrices.

Matrix	A (MHz/sec)[a]	A (MHz/sec)[b]	A (G)[a]	g[a]	g[b]
A	1436.76	1436.24	512.97	2.00108	2.00161
	±0.98	±0.40	±0.35	±0.00011	±0.00008
Kr	1427.94	1427.06	510.37	1.998941	1.99967
	±1.50	±2.80	±0.54	±0.00014	±0.00031
Xe	1405.91	1405.57	502.23	1.99999	2.00057
	±0.53	±0.34	±0.19	±0.00008	±0.00008

[a] This work.   [b] Reference 8.

500 G, the intermediate-field case applies, and the Breit-Rabi formula must be employed for calculation of the isotropic hyperfine coupling constant and g factor from the measured magnetic field positions of the lines and the microwave frequency. These constants for hydrogen atoms in argon, krypton, and xenon appear in Table IV. Previous studies[8] of hydrogen atoms in such matrices employed methods of production of the atoms which differed from ours. Atoms produced in a gaseous discharge were mixed with the rare gas and the combination deposited at 4.2°K; or hydrogen compounds already trapped in frozen rare gases were photolyzed with ultraviolet radiation. The resulting lines were analyzed in terms of a matrix theory[9] similar to that described earlier for nitrogen, and the most probable trapping sites were determined. It is interesting to compare the present data with these earlier results. The deposition experiments produced single sets of lines assignable to hydrogen atoms trapped in substitutional sites. The photolysis experiments produced multiple spectra which always included the deposition doublets but which also had doublets ascribable to octahedral sites. The A and g values measured in the present experiments agree very well with these ascribed to octahedral sites by Foner et al.[8] Presumably the hydrogen atoms produced at the dissociation site, which is almost certainly substitutional in nature, diffuse away until they are trapped in nearby interstitial sites. That these sites are octahedral rather than tetrahedral is not surprising, since the tetrahedral sites are smaller.

No lines assignable to substitutional sites were observed in the present experiments. Presumably, almost no substitutional vacancies were formed during the freezing process, and any hydrogen atoms which failed to escape the substitutional sites where they were formed by dissociation would be lost by recombination.

The present measurements of the hydrogen satellites

in xenon (Fig. 5) serve to confirm the earlier workers' assignment of these lines to hyperfine interaction between the electron spin and the nearby magnetic xenon nuclei. The evidence is twofold. First, the splittings of the individual components of the complex pattern from the central strong line as determined by Foner et al. and the present authors are identical within the limits of experimental error. Since the two experiments were done at X band and K band, respectively, the splittings must be independent of the magnetic field and thus be true hyperfine lines and not lines caused by a second-order effect. Secondly, the patterns obtained from hydrogen and deuterium in xenon are identical, as is illustrated in Fig. 5, and this can be true only if the splittings are caused by overlap to common nuclei such as the xenon nuclei and do not depend on the nuclear moment of the impurity atom. The experiments done in xenon by the two groups also agree in that the main doublet splitting measured here indicates that the H atoms are trapped in octahedral trapping sites as already mentioned; the earlier workers detected the satellites only for atoms trapped in such sites.

A final point of interest in the discussion of hydrogen atoms is the nonderivative line shapes observed occasionally when hydrogen atoms were trapped in argon, as in Fig. 3 of the previous paper. Such a line shape has been ascribed[1] to an increase in the spin-relaxation time T_1 which changes the condition of resonance from one of slow passage to one intermediate passage. Such effects were not found here for the heavier, larger, more tightly bound krypton or xenon lattices. This is surprising, since consideration of the usual relaxation processes at this temperature would seem to predict an increase of T_1 with increase of atomic weight of the matrix, which is the opposite of what the observed spectra imply if the mechanism assumed by Jen et al. is indeed the cause of the change in line shape.