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Lifetime Measurements of the $4s^2S_{1/2}$ and $3d^2D$ States of Aluminum by the Phase-Shift Method

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Lifetimes of the upper states of two optical resonance transitions in aluminum have been measured using the phase-shift method. Data were taken over a large range of fluorescence intensities to allow for evaluation of the effects of scattered exciting light and radiation entrapment. The results obtained are: $\tau\ 4s^2S_{1/2} = 7.05 \pm 0.3$ nsec, $\tau\ 3d^2D = 13.7 \pm 0.4$ nsec.

Introduction

There have been a number of experimental and theoretical studies of transition probabilities in aluminum.[1] As is frequently the case, there is generally poor agreement among the various reported values. The most extensive works are those of Penkin and Shabanova,[2] who used anomolous dispersion (the hook method) to obtain f-values for nearly forty transitions, and Corliss and Bozman,[3] who have used emission intensities. Both of these methods suffer from the large uncertainties in the density of the species being studied when used to determine absolute f-values. The phase-shift method, which is one of the available density independent techniques,[4] has been used by Demtröder[5] to measure the lifetime of the $4s^2S_{1/2}$ state. The lifetime of the $^2D_{5/2}$ state has been measured by Budick[6] using the level-crossing technique, which is also density independent, and he has suggested that the configuration giving rise to this state is $3s3p^2$.

In the present work the phase-shift method has been used to measure the lifetimes of two states from which f-values have been calculated. These values are compared to the relative values of Penkin and Shabanova,[2] which should be accurate to within 15% and their absolute values are rescaled to be consistent with the observed lifetimes.

Apparatus and Procedure

For the work described in this paper the state being studied is optically excited with intensity modulated light. The shift in phase, $\Delta\phi$, between the exciting light and fluorescent light is measured and the lifetime, τ, determined from the relation $\tan\Delta\phi = \omega\tau$ where ω is the radial modulation frequency. The apparatus and procedures are in most respects the same as those used in previous work on other atoms and have been reported in detail.[7] Only changes necessary for the present work are discussed below.

The aluminum atomic beam was vaporized from an alumina crucible heated by a 0.05-mm tantalum-foil heating element. There was some difficulty obtaining a stable beam as the aluminum in the crucible had a tendency to "bump", thereby wetting the outside of the crucible and destroying the heating element. The addition of a small amount of graphite into the crucible apparently eliminated the formation of an aluminum oxide film on the aluminum surface in the crucible and resulted in a steady beam. The density of the beam was easily controlled by adjusting the heating power.

Resonance lamps of the type used in earlier work were not satisfactory. Several lamp designs were tried, the most satisfactory of which was a flow lamp inspired by lamps of Budick et al.[8] A diagram of the lamp is shown in Figure 1. In operation a discharge was started in the necked down portion of the lamp with the helium pressure at about 1 torr. An air cooled microwave cavity, similar to the type 5 cavity described by Broida et al,[9] powered by a 2450 MHz diathermy unit maintained the discharge. The molybdenum crucible containing anhydrous aluminum chloride[10] was then slowly warmed to the point where the chloride just vaporized and the discharge was taken over by the aluminum. At this point the performance of the lamp, as determined by fluorescence intensity from the beam, was quite insensitive to changes in helium pressure in the range from 0.1 to

10 torr and to microwave power. Increased heating of the aluminum chloride, however, resulted in a drop in fluorescence intensity. The lamp would operate stably for several hours. The life of the lamp could probably be lengthened considerably if an effort was made to eliminate water from the system. Water reacts with the aluminum chloride and forms aluminum hydroxide which effectively plugs the crucible openings.

With the lamp operating under normal conditions, the emitted $3d^2D$ - $3p^2P$ multiplet was examined under high resolution and these lines were found to be self-reversed. There was however sufficient light to excite fluorescence in the atomic beam over the density range necessary for the evaluation of the effects that scattered exciting light and radiation entrapment have on the measured lifetime. At high beam densities corresponding to severe entrapment up to 5% of the total exciting light could be absorbed.

The atomic energy levels of interest are shown in Figure 2. Selection of the wavelength of the exciting light was accomplished with filters. An interference filter centered at 3944Å was used for excitation of the ^2S state. A combination of a Corning 9-53 and a Schott UG-11 was used for excitation of the ^2D state. Placing a filter cell containing a $NiSO_4$-$CoSO_4$ solution in front of the sample photomultiplier produced no change in the measured lifetime of the $3d^2D$ state indicating that the $4s^2S$ state was not excited using this combination. This observation is also evidence against the presence of molecular species such as Al_2O, which are no doubt present in the beam, and which might interfere with atomic measurements. For both states fluorescence was detected with an Amperex 56UVP photomultiplier.

Analysis and Results

The lifetimes obtained are given in Table I. The errors indicated are the sums of estimated systematic error, based on the accuracy of measurement of the speed of light, and the error of fitting the measured data to theoretical curves[7] for the range of vapor density that is free of entrapment. For both states we could measure the lifetime over an entrapment-free range of at least 30 in the quantity $(1 + I_f/I_s)$, were I_f and I_s are the fluorescence and scattered-light fluxes, thus enabling us to evaluate the effects of scattered exciting light.

Demtröder measured the lifetime of the $4s\,^2S_{1/2}$ state by the phase-shift method;[5] he got a value of 6.43 ± 0.12 nsec as compared to our 7.05 ± 0.3 nsec. Scattered exciting light with a flux 10% that of the fluorescence light would lead to this shorter value, but Demtröder states that scatter was not strong enough to be detected. Our lack of agreement with his work therefore remains unexplained. Budick's previous measurement[6] of the $3d\,^2D_{5/2}$ state gave a value of 13.6 ± 1.4 nsec and is in good agreement with our 13.7 ± 0.4 nsec.

In calculations of absolute f-values from measured lifetimes, care must be taken to include all transitions depopulating the excited state. The following relations are applicable

$$f_{nm} = 1.499\,\lambda^2_{mn}\,A_{mn}\,g_m/g_n$$

$$\tau_m = 1/\sum_n A_{mn} \quad ,$$

where λ_{mn} is the wavelength in cm, g_m and g_n the statistical weights of the upper and lower states respectively, and A_{mn} is the transition probability in sec^{-1}. The f-values based on the lifetimes reported here are listed in column 6 of Table I. In these calculations it was assumed that $f_{3944} = f_{3961}$ and that $\tau^2D_{3/2} = \tau^2D_{5/2}$. These assumptions seem to be well justified by measured relative f-values,[2,3,11,12] by the lifetime measurement of Budick,[6] and by analogy to lifetime measurements on indium,[7] and are expected to be valid for Russell-Saunders coupling. The agreement between these calculated f-values and the relative values of Penkin and Shabanova[2] which are given in column 7 of Table I is good. The absolute values which they reported appear to be large by a factor of 1.3.

Acknowledgments

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References

1. B. M. Glennon and W. L. Wiese, Natl. Bur. Std. (U.S.) Misc. Publ. 278 (1966).
2. N. P. Penkin and L. N. Shabanova, Opt. Spectrosc. (U.S.S.R.) 18, 504 (1965).
3. C. H. Corliss and W. R. Bozman, Natl. Bur. Std. (U.S.) Monograph 53 (1962).
4. E. W. Foster, Rept. Progr. Phys. 27, 469 (1964).
5. W. Demtröder, Z. Physik. 166, 42 (1962).
6. Burton Budick, Colloq. Int. Centre Nat. Rech. Sci. 164, 185 (1966).
7. Paul T. Cunningham and John K. Link, J. Opt. Soc. Am. 57, 1000 (1967); John K. Link, J. Opt. Soc. Am. 56, 1195 (1966).
8. B. Budick, R. Novick, and A. Lurio, Appl. Opt. 4, 229 (1965).
9. F. C. Fehsenfeld, K. M. Evenson, and H. P. Broida, Rev. Sci. Instr. 36, 294 (1965).
10. Dr. Alan Gallagher suggested the use of anhydrous aluminum chloride in place of the metal because of its volatility.
11. E. I. Nikonova and V. K. Prokof'ev, Optika I Spektroskopiya 1, 290 (1956).
12. F. A. Korolev and Iu. K. Kvaratskheli, Opt. Spectrosc. (U.S.S.R.) 10, 200 (1961).

Table I

Tabulation of Results

Upper State	Lower State	Lifetime (nsec)	Transition $J_m - J_n$	λ in Å	f-value This work[a]	rel. f-value (Ref. 2)
$3d^2D$	$3p^2P$	13.7 ± 0.4	3/2 - 1/2	3082.2	0.173	1.49
			3/2 - 3/2	3092.8	0.017	0.155[b]
			5/2 - 3/2	3092.7	0.157	1.40[b]
$4s^2S$	$3p^2P$	7.05 ± 0.3	1/2 - 1/2	3944.0	0.111	1.00
			1/2 - 3/2	3961.5	0.111	1.00

a) See Text.

b) The reported sum 3/2,5/2 - 3/2 has been resolved assuming Russell-Saunders coupling.

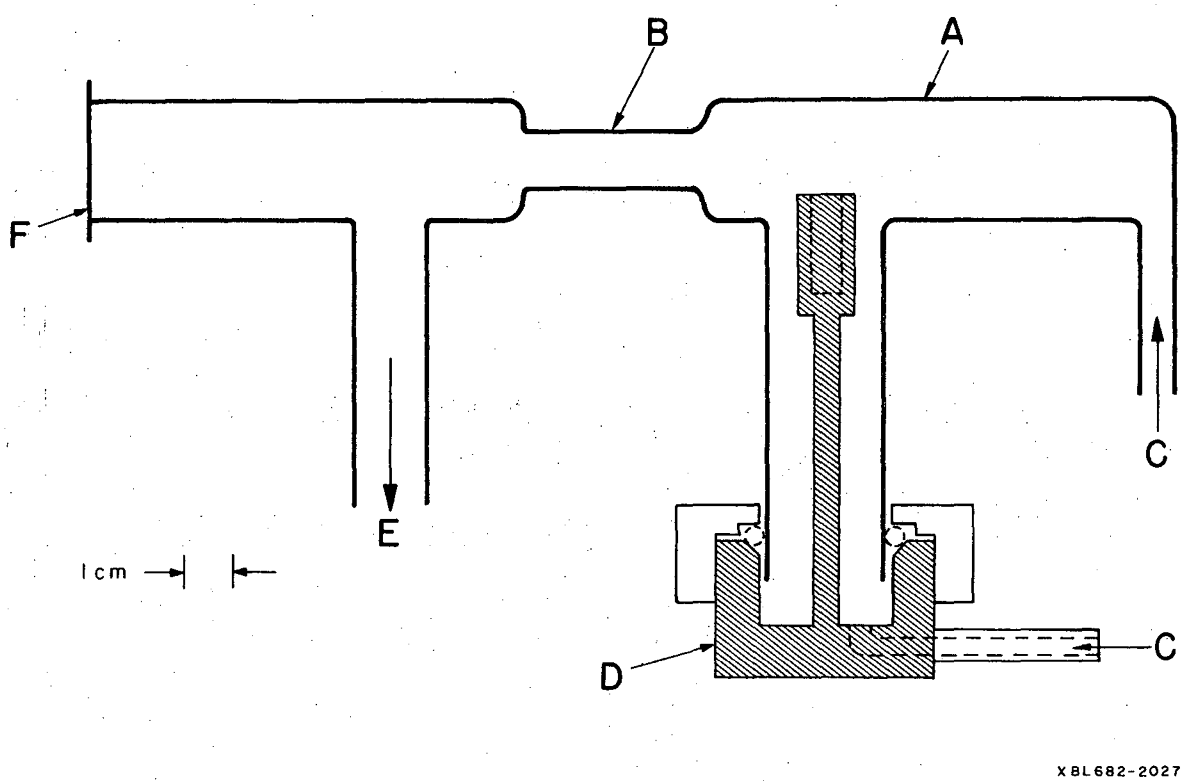

Figure 1. Diagram of the aluminum flow lamp drawn approximately to scale. A, Pyrex body of the lamp; B, necked down region of the lamp enclosed by microwave cavity; C, helium inlets; D, adjustable support for heating element and crucible; E, outlet to pump; F, quartz window.

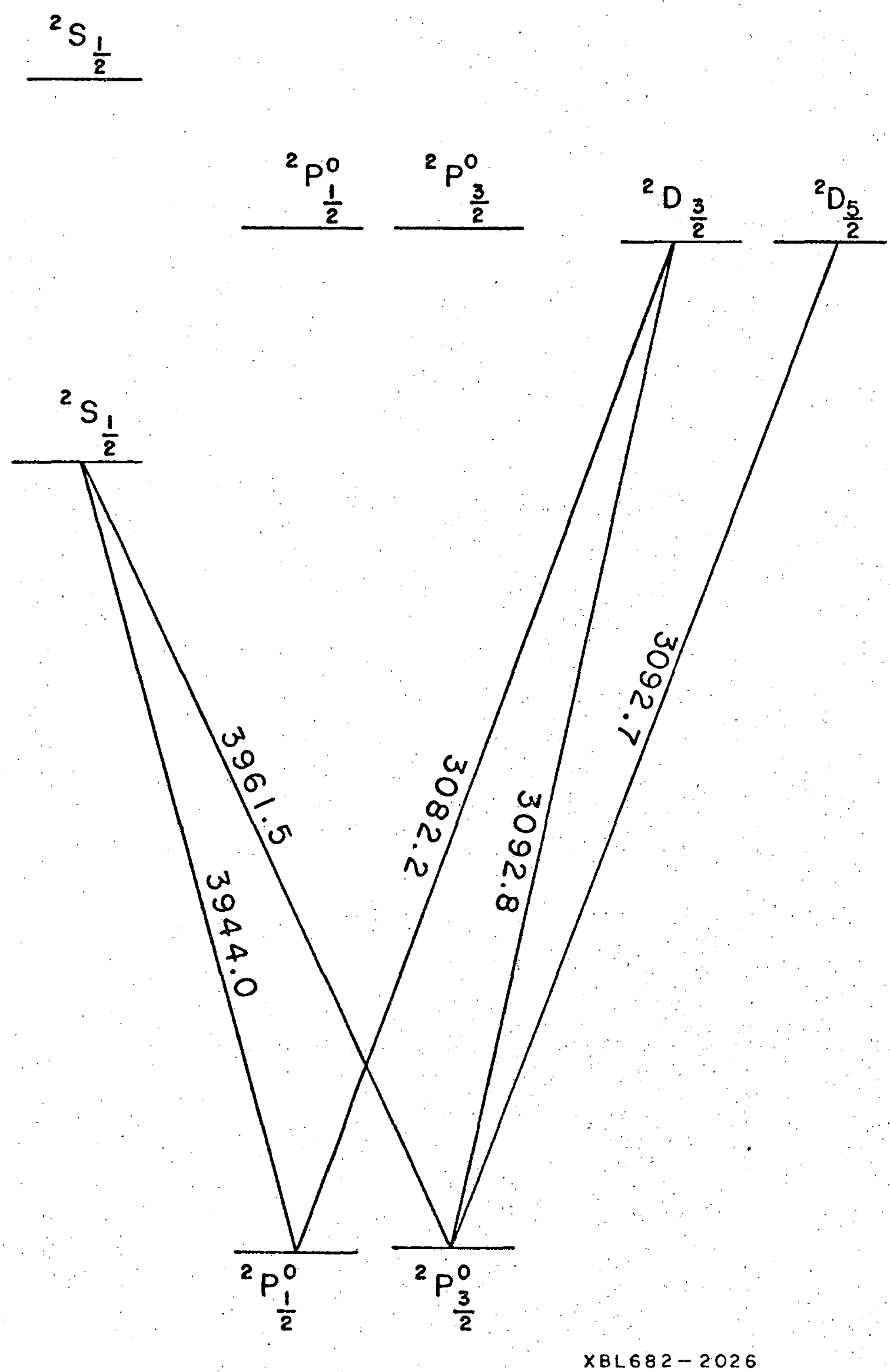

Figure 2. Atomic energy levels showing transitions studied with wavelengths indicated in Å. The level spacing is drawn to scale.