PHYSICAL REVIEW LETTERS

Volume 1

NOVEMBER 1, 1958

NUMBER 9

OPTICAL DETECTION OF NARROW Rb⁸⁷ HYPERFINE ABSORPTION LINES

P. L. Bender and E. C. Beaty National Bureau of Standards, Washington, D. C.

and

A. R. Chi United States Naval Research Laboratory, Washington, D. C. (Received October 8, 1958)

Within the last year optical detection of the $(M_F=0 \rightarrow M_F=0)$ ground state hyperfine transition has been reported for sodium vapor^{1,2} and for cesium vapor.^{3,4} The collisional narrowing technique suggested by Dicke⁵ was used to reduce the Doppler width. Results have now been obtained for Rb⁸⁷ vapor using a different optical pumping method. Absorption lines a factor 300 narrower than the normal Doppler width have been achieved.

The experimental arrangement is shown in Fig. 1. The sample consists of a Pyrex bulb containing Rb⁸⁷ vapor and a suitable buffer gas. Light from a rubidium spectral lamp is passed through a filter bulb containing Rb⁸⁵ vapor and then through the sample. The scattered light from the sample is monitored by a photomultiplier tube.

The strongest lines emitted by the rubidium lamp are the two resonance lines⁶ at 7800 and 7947A. These lines are absorbed by the rubidium vapor in the filter and in the sample and cause transitions to the $5 {}^{2}P_{3/2}$ and $5 {}^{2}P_{1/2}$ excited states. The hyperfine components of the Rb⁸⁵ lines are separated by only half as much as the Rb⁸⁷ hyperfine components and have slightly different mean wavelengths. When about 5 cm of argon is added to the filter bulb, the Rb⁸⁵ absorption lines are somewhat broadened. The lower energy hyperfine components of the Rb⁸⁷ lines from the lamp are then absorbed considerably more strongly in the filter than the higher energy ones. The light reaching the sample thus causes transitions mainly from the lower ground state hyperfine level to the excited states. Since the atoms return by spontaneous emission to both ground-state levels, they tend to accumulate in the higher level.⁷

Under the conditions described above where the intensities of the hyperfine components of the incoming light are not equal, the intensity of the light scattered by the sample depends on the populations of the two levels. It thus provides a means of monitoring the relative populations. When an oscillating magnetic field having the right frequency to cause the $(F=2, M_F=0) \rightarrow (F=1, M_F=0)$ hyperfine transition is applied to the sample, the population difference between the two hyperfine levels decreases and the intensity



FIG. 1. Apparatus for observing the Rb⁸⁷ hyperfine transition by an optical pumping method.

of the scattered light reaching the photomultiplier increases.

With the hyperfine filtering method described above measurements have been made of the resonance frequencies, line widths, and signal strengths for a number of sample bulbs containing various buffer gases. Most of the bulbs used were 500-ml Pyrex flasks which were thoroughly outgassed before filling. About 3 mg of Rb⁸⁷ was distilled into each bulb, and then the desired buffer gas was introduced and the bulb sealed off. The rubidium vapor pressure of about 2×10^{-7} mm at room temperature gave an absorption coefficient of about unity for the bulbs with fairly low buffer gas pressures. The inert gases and mixtures used were of spectroscopic grade, while the other gases came from sources believed to be of high purity. An accelerated aging test gave no indication of a frequency shift for a bulb held at 200°C for one week.

In Table I the observed pressure and temperature shifts measured near room temperature are given. The temperature shifts are the ob-

Table I. Changes in the hyperfine transition frequency for Rb^{87} absorption cells with pressure of the buffer gas and with temperature of the cell. The pressure coefficients were measured at constant temperature and the temperature coefficients at constant volume.

	· · · · · · · · · · · · · · · · · · ·	Temperature shift in
	Freq. shift in cps	cps per degree centi-
	per cm of buffer	grade per cm of
Buffer gas	gas pressure.	buffer gas pressure.
hydrogen	$+6600\pm130$	+10
deuterium	$+6700 \pm 150$	+ 10
helium	$+7200\pm140$	+10
neon	$+3920 \pm 80$	+ 2.6
nitrogen	$+5200\!\pm\!100$	+ 6
argon	-510 ± 10	- 3.0
krypton	-5800 ± 500	- 5
$methane^{a}$	-5000	- 6
n-pentane a	-28 000	- 7
neopentanea	-29 000	+ 2
n -heptane a	-42 00.0	+ 2
mixture I (11.7%Ne		
+ 88.3%A) mixture II	$+ 14 \pm 3$	- 2.4
(50%Ne		
+ 50%A)	$+ 1700 \pm 40$	- 0.2

 a The values for the hydrocarbons are somewhat uncertain because of possible reactions with stopcock grease in the vacuum system and pyrolysis in sealing off the samples.

served shifts in frequency for a given change in temperature of the whole bulb, and thus are not measured at constant pressure. It is clear that, as was observed⁴ for Cs¹³³, the pressure and temperature shifts are not simply related. However, the results given for the two mixtures demonstrate that it is possible to reduce greatly either the pressure or the temperature coefficient by choosing the proper composition. By using three gases together, such as neon, argon, and one of the hydrocarbons, it should be possible to reduce strongly both the pressure and temperature dependence. The accuracy of most of the pressure shifts given is limited almost entirely by uncertainty in the buffer gas pressures. The observed shifts are linear with pressure and extrapolate to the same zero-pressure frequency within the uncertainties in the measurements.

Line width and signal strength measurements were made with the light intensity and microwave power at levels which contributed little to the widths of the narrowest lines observed. The line width as a function of pressure gave a very broad minimum at several cm for most of the buffer gases used. For pressures above the minimum, the signal strength at room temperature went down quite rapidly, while the line width went up slowly. For neon and helium the line widths at 20 cm were about 25 and 40 cps, respectively.

The narrowest lines were obtained using neon and helium at pressures of several cm. The signal strength corresponded to a 5% change in the amount of light scattered from the Rb^{87} vapor. The line width was about 20 cycles, giving a Q of over 300 million.⁸ For argon the best lines were about 30 cps wide. Strong and narrow lines were also obtained for some of the hydrocarbons at pressures of several mm.

The frequency source used in the experiments described above was provided by Mr. W. Levitt of the Radio Techniques Branch, National Research Laboratory. For most of the measurements the applied frequency was sinusoidally swept at 4 cps between the points of maximum and minimum slope of the line, and the photomultiplier output displayed with a 30-cps bandwidth on an oscilloscope. Although the frequency could be set on the center of the hyperfine absorption line to 5 parts in 10^{11} , the over-all accuracy of the frequency measurements was not quite this high because of random minute-to-minute variations of 1 or 2 parts in 10^{10} in the frequency source.

For mixture I a fairly good extrapolation to zero pressure could be made. The accuracy was limited to about 1 part in 10^9 by a scatter of several cps in the points obtained with different sample bulbs. A set of 100-ml sample bulbs was also used in this extrapolation to eliminate the possibility of a size effect. The frequency obtained was 6 834 682 608 ± 7 cps with respect to the A.1 time scale introduced by Markowitz⁹ on which the Cs^{133} frequency is 9192 631 770 cps. This is in agreement with an extrapolated value of 6834682535 ± 70 cps on the same scale obtained by Carver by a power absorption method.¹⁰ However, since a preliminary extrapolation for Cs^{133} vapor made in the same way disagreed with atomic beam results by considerably more than the known uncertainties,⁴ there is still some doubt about the interpretation of the result.

We wish to express our thanks to Mr. W. Levitt and Mr. R. Stone of the Naval Research Laboratory Radio Techniques Branch for supplying the frequency source and synthesizer used in this work. Most of the sample bulbs used were filled by Mr. N. Williams of the National Bureau of Standards Atomic Physics Section. We have benefitted greatly from conversations with T. R. Carver, R. H. Dicke, A. L. Bloom, H. G. Dehmelt, C. O. Alley, M. Arditi, and W. E. Bell on optical pumping techniques.

- ¹M. Arditi and T. R. Carver, Phys. Rev. <u>109</u>, 1012 (1958).
- ²W. E. Bell and A. L. Bloom, Phys. Rev. <u>109</u>, 219 (1958).
- ³M. Arditi and T. R. Carver, Phys. Rev. <u>112</u>, 449 (1958); M. Arditi, Proceedings of the Twelfth Annual Frequency Control Symposium, Asbury Park, New Jersev, May 6, 7, 8, 1958 (unpublished).

⁴Beaty, Bender, and Chi, Phys. Rev. <u>112</u>, 450 (1958); Bender, Beaty, and Chi, Proceedings of the Twelfth Annual Frequency Control Symposium, Asbury Park, New Jersey, May 6, 7, 8, 1958 (unpublished).

⁵R. H. Dicke, Phys. Rev. 89, 472 (1953).

⁶D. A. Jackson, Proc. Roy. Soc. (London) <u>A139</u>, 673 (1933).

⁷The use of a Rb^{85} filter or Rb^{85} light source has also been suggested by T. R. Carver and C. O. Alley and by A. Kastler.

⁸Somewhat narrower lines have been obtained for the Rb⁸⁷ ground state Zeeman transitions in the earth's field: T. L. Skillman and P. L. Bender, J. Geophys. Research (to be published).

⁹Moscow Meetings, Commission 31, International Astronomical Union, August, 1958.

 10 T. R. Carver (to be published).

VALENCE BAND STRUCTURE OF SILICON

Lennart Huldt and Torsten Staflin Institute of Optical Research, Royal Institute of Technology, Stockholm, Sweden (Received October 3, 1958)

Cyclotron resonance experiments have indicated the existence of two kinds of holes with different effective masses in germanium, as well as in silicon.¹ Theoretical calculations by Herman² have given a picture of the band structure of these crystals, according to which the valence band is split into three sub-bands shown schematically in Fig. 1. The spin-orbit interaction causes a splitting between the levels $p_{3/2}$ (bands 1 and 2) and $p_{1/2}$ (band 3). The degeneracy of the $p_{3/2}$ level is cancelled for crystal momentum $k \neq 0$ which gives rise to the sub-bands 1 and 2 with different curvature, i.e., with the different effective masses observed in cyclotron resonance. The sub-band 3 has too low a population of holes at moderately high temperatures to be observed.

Full evidence for this theoretically predicted structure has been obtained for Ge from the infrared absorption spectra of *p*-type germanium,^{3,4} germanium with electrically injected holes,⁵ and photoelectrically excited intrinsic germanium.^{6,7} These spectra show distinct bands which can be unambiguously attributed to the three interband transitions 1-2, 2-3, and 1-3 with maxima at approximately 1000 cm⁻¹, 2100 cm⁻¹, and 3000 cm⁻¹ at room temperature. By examining the



FIG. 1. Valence energy band contours of silicon and germanium.