Determination of the vapor pressure of rubidium by optical absorption

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The vapor pressure of rubidium was determined in the neighborhood of 330 K from measurements of optical absorption of the resonance lines. A narrow-line source was used and a full analysis of the line profiles was done. Measurements of resonance-broadening depolarization give another check on the Rb vapor pressure in the 430-K range, assuming that theoretical cross section is correct. The results are very close to the analytic compromise previously suggested by Nesemeyanov.

Index Headings: Absorption: Rubidium; Source; Spectra.

Vapor pressures of atomic species are often essential for the interpretation of atomic-collisions data. This is particularly true for the alkali metals, whose use in optical pumping has led to many investigations of their collisional behavior.

The resonance-line absorption coefficient can in principle be used to measure the vapor density if the oscillator strength is known, but in practice systematic errors are hard to avoid. The basic complication in such measurements is that the apparent vapor absorption involves a convolution of source, absorption, and spectrometer profiles. Here we demonstrate the feasibility of dealing accurately with the problem by use of narrow lamp profiles and thorough convolution analysis. We will discuss the several measurements that have been made as well as the present approach. We reiterate Eqs. (1)-(3) of Ref. 1, which describe the convolutions that lead to the observed profiles,

\[ I_A(v) = \int f(v') \exp[-K_T(v')] g(v-v') \, dv', \]  

(1)

\[ I_0(v) = \int f(v') g(v-v') \, dv', \]  

(2)

\[ K_A(v) = \ln[I_0(v)/I_A(v)]. \]  

(3)

Here \( I_0(v) \) is the apparent lamp spectrum, \( I_A(v) \) is the apparent spectrum after traversing the absorption cell, \( K_A(v) \) is the apparent absorption coefficient, \( g(v-v') \) is the spectrometer instrument function, \( f(v') \) is the actual source spectrum, and \( K_T(v') = N L k_T(v') \) is the actual vapor absorption coefficient for a cell of length \( L \) at temperature \( T \) with density \( N \). Here \( k_T(v') \) may be a single line or a superposition of hfss and isotopic lines. If the vapor density is sufficiently low to avoid line broadening, the oscillator strength and any isotope shifts and hfss are known; then \( k_T(v') \) is exactly known.

If \( g(v-v') \) were much sharper than \( K_T(v') \), \( K_A(v') \) would approach \( K_T(v') \) and minor corrections could easily be made from knowledge of \( f(v') \) obtained by scanning the lamp spectrum. In practice, this has not been even approximately realized, because of inadequate signal-to-noise levels.

If a white-light source can be used, \( f(v') \) is a constant in Eq. (1) and the integrated absorption (effective width) can be used to obtain \( N \) accurately. This can immediately be seen by integrating Eq. (1) over \( v \) and reversing the order of integration. Such possibilities were analyzed in detail by Kostkowski and Bass, but measurements of this type have rarely been tried for visible resonance lines. Separating a very narrow band out of a visible continuum with negligible leakage is not simple; also, very low intensities and small fractional absorptions normally result.

Another approach is to attempt making \( f(v) \) proportional to \( k_T(v) \) for some \( T \) by utilizing fluorescence of an atomic vapor, then removing the resolving instrument \( [g(v-v') = \text{const}] \) to obtain a usable signal-to-noise ratio. This method has been used, but is quite complicated and subject to several potential sources of error. If the resonance line has resolved hyperfine or isotopic components, then the fluorescence will have component intensities far from \( k_T(v) \), whereas the subsequent vapor absorption is quite different for each of these components. Other causes of a fluorescent spectrum differing from \( k_T(v) \) include collisional broadening and shift, frequency-dependent radiative diffusion and escape, incomplete radiative redistribution on the wings of lines, wall scattering of the lamp profile, and self-trapping combined with quenching collisions or excitation-transfer collisions.

A very effective approach has been used by Ioli, Strumia, and Moretti on sodium. They replaced the scannable resolving instrument with a magnetically scanned lamp line. In terms of Eq. (1), \( f(v') \) becomes \( f(v-v') \) and \( g(v-v') \) is a constant. The analysis of Ref. 2 could then be used with \( f \leftrightarrow g \), and the integrated absorption can give an accurate value for \( N \).

In the case of multicomponent lines and nonlinear Zeeman effect at the useful fields, as in the Rb case studied here, this method would become considerably more complex.

Most measurements have utilized resonance lamps for the source spectrum, because these are intense and
easily filtered to pass only the desired line. For an ideal resonance lamp, \( f(v') \) would be proportional to \( k_T(v') \) for some source temperature \( T \). Real resonance lamps suffer from self-absorption (self-reversal) with a consequent flattening or dip in the core of the line. Self-reversal also causes the intensities of resolved components to depart from the statistical ratios given by \( k_T(v) \). Some measurements have used no resolving instruments at all, and are subject to major uncertainties due to the convolution with an unknown lamp profile. Several measurements have been made with optical resolution that partially resolves the source profile.\(^6\)

Major uncertainties were thereby avoided, but a very thorough analysis is still required to make accurate results possible.

The calculations of Hull and Bradley\(^4\) demonstrate many of the pitfalls inherent in this approach. One measurement on cesium\(^6\) attempted to overcome the problems inherent in the convolutions of Eqs. (1)–(3) when the instrumental width is \( \sim \frac{2}{3} \) the Doppler width, by broadening the lamp spectrum with a somewhat higher than usual pressure of inert gas. But it is apparent from the published spectrum that their source spectrum could still have contained considerable undetected self-reversal at the line centers. In addition, each of two observed absorption lines was an unresolved pair of partially overlapping lines. No general analysis of this situation is available, but it is clear that the equivalent width will depart from the isolated-line case, whereas a nonflat source spectrum adds additional complications. The absorption measurements by Jarrett and Franken on sodium\(^7\) are similarly beset by the problem of unresolved and partially overlapping components, as well as uncertainty regarding the source profile. The instrumental width was about \( \frac{1}{3} \) the Doppler width in this case.

The Rb absorption measurements by Gibbs and Hull\(^9\) utilized only slightly better instrumental resolution (about one-third the Doppler width) but their results are clearly the most accurate yet achieved with Fabry-Perot scanning. The key is in a very thorough analysis of the data. They demanded that the convolution of the instrument profile with the assumed source spectrum and with the absorbed source spectrum match the data. This is in essence the method utilized here, also for Rb. The necessity for repeating these measurements is primarily that the cell used by Gibbs and Hull was coated, for optical-pumping efficiency, and the reported vapor pressures are far below the expected equilibrium values. An additional improvement of the present measurements is due to an exceptionally narrow lamp spectrum, which has allowed much-more-accurate analysis of each separate component and better matching to the data.\(^9\) The source spectra in those Fabry-Perot measurements were badly self-reversed,\(^9\) whereas our results are extremely close to an ideal \( k_T(v) \).

In contrast to the above cases, this has allowed accurate experimental to theoretical comparisons of essentially isolated lines. The uncertainty in the present experiments, due to the convolutions of Eqs. (1)–(3), is correspondingly reduced to a few percent. Also, various peculiar features of the apparent absorption, which were pointed out by Hull and Bradley, are unambiguously seen in the present data.

In contradiction to Jarrett's observations,\(^8\) the present measurements indicate that an equilibrium Rb vapor pressure can be obtained in a Pyrex cell from 310–450 K. The indications are that this is true for Cs and Na in Pyrex as well,\(^8\) although care must be taken to saturate the wall pumping by operating the cell at high density for a reasonable period.

**EXPERIMENT**

A pressure-scanned Fabry-Perot interferometer was used to scan the resonance-lamp spectrum before and after transversing the absorption cell. The instrument functions of the Fabry-Perot was established by scanning narrow single-component Doppler-shaped Kr lines from the same lamp and utilizing primarily standard Voigt-profile analysis techniques.\(^11\) The instrumental width, 0.012 cm\(^{-1}\), was about 65% of the absorption Doppler width and 40% of the lamp Doppler width.

The Rb resonance-line spectrum was scanned and the isolated hfs-component line of \(^8\)Rb was selected for detailed analysis. The scans of this component of the 7800- and 7948-Å lines were then compared to the convolutions in Eqs. (1) and (2) using the known \( k_T(v) \) shapes and instrument function, and various assumed source profiles. These Rb source profiles were very close to the ideal Doppler shape of the Kr lines. A slight flattening of the peaks of the Rb lines, due to self-reversal, was reflected in a slightly higher apparent Doppler temperature for the Rb lines. Nearly ideal relative intensities of hyperfine components also indicated that only a trace of self-reversal was occurring in the source.

A minor gaussian smearing of \( g(v-v') \) to allow for flatness imperfections was tested and found to improve the fits slightly. The resultant change of \( k_1 \) or \( N \) was at most 2%. Owing in part to excellent signal-to-noise ratios, the \( N \) used in the calculations could not be adjusted more than a few percent without misfitting the data, even when \( f(v') \) or \( g(v-v') \) were altered somewhat. Particularly useful in this regard was the fact that the ratio \( I_a(v)/I_b(v) \) is insensitive to the exact \( f(v') \) and \( g(v-v') \) in the wings of the line.

**APPARATUS**

The optical system is sketched in Fig. 1; it consists of a lamp, absorption cell, and a pressure-scanned Fabry-Perot étalon system followed by a \( \frac{1}{2} \)-m monochromator and photomultiplier. The fraction of the étalon fringe system sampled was defined by the
The cell was placed 41.85° to the optic axis of the system. The Rb was an enriched sample containing 97% 86Rb; the absorption of this component was measured. The absorption cell consisted of a thin 5-cm-diam cylinder, with windows 2.134-0.04 mm apart and with a short side arm. The Pyrex cell was baked for several hours at -40.5°C. The 2.5-cm-diam étalon plates were coated with a medium to high dielectric coating of 91% reflectance. The spacer used was 1.506 cm. The étalon was scanned by filling the chamber with air through a needle valve.

The imperfection of the étalon plates were investigated by sampling the plate area with a 3-mm-diam pinhole and observing the relative shifts in the Kr line at 7601 Å. In use, the étalon was stopped down to a 1.5-mm-diam pinhole placed in the focal plane of the 1-m lens B. Light could be passed through or around the absorption cell by means of the system of fixed mirrors K and removable mirrors K' (Fig. 1). The relative beam attenuation in the two paths was measured with Kr lines from the lamp; the 20% difference was compensated by attenuation of the photomultiplier output to produce equal signals. The light source was a Varian optical-pumping lamp12 which was chosen for its stability, high luminosity, and, most important, for its narrow-line spectral profile. The absorption cell consisted of a thin 5-cm-diam cylinder, with windows 2.134-0.04 mm apart and with a short side arm. The Pyrex cell was baked for several hours at ~10⁻⁶ torr before Rb was distilled into it. The Rb was an enriched sample containing 97% 86Rb; the absorption of this component was measured.

The cell was placed 41.85° to the optic axis of the system and was mounted inside an oven (Fig. 1). This geometry, as well as the isotopic enrichment, was chosen to facilitate collisional depolarization measurements that were done concurrently. The temperature of the cell was monitored by four Chromel-Alumel thermocouples situated at the tip of the side arm, at both top and bottom rims of the cell and close to the center of the cell window. At ~340 K, at which the absorption data were taken, the temperature extremes varied ±0.5 K about the average value, which was used in the analysis. The total temperature uncertainty was typically ±0.8 K, including allowance for uncertainties of reference-junction temperature and thermocouple material. The Pyrex cell was operated at ~450 K for 10 days to saturate wall pumping of the Rb. No density dependence on the temperature history of the cell was seen.

The 2.5-cm-diam étalon plates were coated with multilayer dielectric coatings having 91% reflectance. The spacer used was 1.506 cm. The étalon was scanned by filling the chamber with air through a needle valve.

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The Rb resonance lines at 7800 and 7948 Å each consist of two groups of hyperfine components separated by an interval determined largely by the ground-state hyperfine splitting13 of 0.288 cm⁻¹ in 87Rb and 0.1015 cm⁻¹ in 85Rb. (See Fig. 2.) The excited-state hyperfine structure is approximately an order of magnitude smaller than that of the ground state14 and is obscured by the Doppler broadening of the D₁ line (7800 Å) and is just in evidence in the D₂ line (7948 Å). In the natural mixture, the ratio of the isotopes is 88Rb/85Rb = 2.57 but the intensity ratios of the components of the observed lamp profiles are usually distorted by effects of self-absorption. The spectral profile of the 7800-Å line obtained from the Varian lamp is shown in Fig. 2, together with details of the line structure. The profile is almost free from self-absorption.

The lines emitted by the Kr buffer gas proved to be useful in diagnosing the lamp conditions and étalon properties and also for accurate normalization of the transmittance of the two optical paths, through and around the cell. Analysis of five Kr lines between 7600 and 8300 Å in terms of Voigt profiles11 indicate 0.022 cm⁻¹ gaussian width of the lamp at λ = 7800 Å, corresponding to a discharge temperature of 480 K. Analysis of the Rb lines yielded a gaussian width of 0.028 cm⁻¹. Such increased gaussian width is a characteristic of profiles with a small amount of self-absorption, the lorentzian component being very little modified.15 This amount of broadening is consistent with the 5-10% disagreement between the theoretical and measured intensity ratios of the 85Rb hyperfine components. Lorentzian components of the Kr lines fall into two groups; the larger widths are associated with the presence of resonance broadening, which has

FIG. 1. Schematic diagram of the apparatus, not to scale: A, pressure scanned étalon; B, lens; C, monochromator; D, photomultiplier; E, aperture; F, oven assembly; G, copper shield; H, heaters; I, asbestos; J, cell; K, mirrors (mirrors K' are removable to allow optical paths through and around the cell); L, lamp.

1.5-mm-diam pinhole E placed in the focal plane of the 1-m lens B. Light could be passed through or around the absorption cell by means of the system of fixed mirrors K and removable mirrors K' (Fig. 1). The relative beam attenuation in the two paths was measured with Kr lines from the lamp; the 20% difference was compensated by attenuation of the photomultiplier output to produce equal signals. The light source was a Varian optical-pumping lamp12 which was chosen for its stability, high luminosity, and, most important, for its narrow-line spectral profile. The absorption cell consisted of a thin 5-cm-diam cylinder, with windows 2.134-0.04 mm apart and with a short side arm. The Pyrex cell was baked for several hours at ~10⁻⁶ torr before Rb was distilled into it. The Rb was an enriched sample containing 97% 86Rb; the absorption of this component was measured. The cell was placed 41.85° to the optic axis of the system and was mounted inside an oven (Fig. 1). This geometry, as well as the isotopic enrichment, was chosen to facilitate collisional depolarization measurements that were done concurrently. The temperature of the cell was monitored by four Chromel-Alumel thermocouples situated at the tip of the side arm, at both top and bottom rims of the cell and close to the center of the cell window. At ~340 K, at which the absorption data were taken, the temperature extremes varied ±0.5 K about the average value, which was used in the analysis. The total temperature uncertainty was typically ±0.8 K, including allowance for uncertainties of reference-junction temperature and thermocouple material. The Pyrex cell was operated at ~450 K for 10 days to saturate wall pumping of the Rb. No density dependence on the temperature history of the cell was seen.

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LAMP PROFILE AND INSTRUMENTAL FUNCTION

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FIG. 2. Experimental lamp profile of Rb(S²P₁→S⁵S₀) 7800-Å line. The excited-state hyperfine structure is not resolved and positions are indicated from the data of Refs. 8 and 10. A, Doppler half-width, 0.028 cm⁻¹; B, instrumental half-width, 0.012 cm⁻¹.
been studied by Vaughan. The Lorentz widths obtained are consistent with a pressure of 1.5–2.0 torr of Kr buffer gas and an instrumental contribution of 0.012±0.002 cm⁻¹ (effective finesse ~28). This agrees well with the 0.0116±0.0016-cm⁻¹ Lorentzian contribution obtained from the analysis of the Rb lines and with the upper limit of 32 for the optimum finesse, determined by the plate reflectance. We thus take the lamp profile $f(v)$ as a superposition of hyperfine components of gaussian shape and 0.028-cm⁻¹ half-widths.

**ABSORPTION PROFILE**

Over the range of densities investigated at about 330 K, the resonance broadening of the absorption-line profile was negligible; the absorption line shape was taken to be a purely gaussian profile with half-widths determined by the oven temperature, i.e., ~0.018 cm⁻¹.

Figure 3 shows a typical pair of Fabry–Perot scanned lamp and absorption profiles for the component of 7800 Å labeled a in Fig. 2. The baseline correction due to the overlap of $g(v-v')$ with other components is not identical for the two profiles. This correction is due to instrumental spreading of the adjacent components, so that the component b of $^{86}$Rb, which is strongly absorbed in the cell, gives different contributions to the right-hand sides of the two profiles. The component d, due to the minor isotope $^{87}$Rb, gives the same contribution to the left-hand side of the profiles. For each pair of traces, the lamp profile was analyzed to check the consistency of the source and instrument profiles discussed in the preceding section. The absorption profiles were then compared to line shapes calculated with Eq. (1) using the same instrument parameters. Figure 4 is an example of the calculated shapes for the data shown in Fig. 3. Table I summarizes the results. Most of the analysis was carried out on the line at 7800 Å because the larger excited-state hyperfine structure evident at 7949 Å complicated the analysis of that line. The density is determined from the line-center optical depth of the hyperfine component $F$ by

$$K = k_0 N L = \frac{2F+1}{2(2F+1)} \frac{2}{\Delta \nu_D} \left( \frac{\ln 2}{\pi} \right) \frac{\pi e^2}{m c} f N L. \quad (4)$$

Here $F$ is the resolved ground-state hyperfine component, $I$ is the nuclear spin, and the excited-state hyperfine has been neglected compared to the Doppler width. The absorption oscillator strengths of the resonances used to derive the number densities are $f(D_1) = 0.317\pm0.008$ and $f(D_2) = 0.673\pm0.015$, obtained by the present authors from Hanle-effect lifetime measurements. These oscillator strengths are each within 6% of several other theoretical and lifetime-experiment values.

Useful $K$ values for $^{86}$Rb (between 0.4 and 1.5) were obtained in the temperature range 325–340 K. In the region of 400 K, the absorption of the $^{86}$Rb components was essentially complete and data could be obtained on the absorption of the component c by $^{87}$Rb. Values of the total number density of Rb could not be derived accurately from these measurements because the ratio of concentrations of the isotopes $^{86}$Rb/$^{87}$Rb was not known with sufficient accuracy from independent data. The ratio of concentrations of the isotopes is determined by comparing these measurements of $^{86}$Rb density to the total-vapor-pressure curve in Fig. 4. We conclude that $^{86}$Rb/$^{87}$Rb = 32. A correction of 3% has been made in column 7 of Table I to allow for the contribution of $^{87}$Rb to the total density.
TABLE I. Optical-absorption results.

<table>
<thead>
<tr>
<th>Line (Å)</th>
<th>Temp (K)</th>
<th>Number density (×10¹¹ cm⁻³)</th>
<th>From component a (¹³Rb)</th>
<th>From component b (¹³Rb)</th>
<th>Average of ¹³Rb densities</th>
<th>Total density (1.03×¹³Rb density)</th>
<th>Analytic fit (Table II, Ref. 2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7800 7800</td>
<td>325.7±0.7</td>
<td>1.294</td>
<td>1.26</td>
<td>1.28</td>
<td>1.32±0%</td>
<td>1.29</td>
<td>1.29</td>
</tr>
<tr>
<td>7800 7947</td>
<td>327.0±0.7</td>
<td>1.378</td>
<td>1.406</td>
<td>1.392</td>
<td>1.43±0%</td>
<td>1.44</td>
<td>1.44</td>
</tr>
<tr>
<td>7800 7800</td>
<td>334.3±0.8</td>
<td>2.666</td>
<td>2.625</td>
<td>2.645</td>
<td>2.72±0%</td>
<td>2.72</td>
<td>2.72</td>
</tr>
<tr>
<td>7947 7800</td>
<td>333.8±0.8</td>
<td>2.33</td>
<td>2.29</td>
<td>2.31</td>
<td>2.36±0%</td>
<td>2.60</td>
<td>2.60</td>
</tr>
<tr>
<td>7800 7800</td>
<td>339.2±1.0</td>
<td>3.74</td>
<td>3.752</td>
<td>3.75</td>
<td>3.82±0%</td>
<td>4.04</td>
<td>4.04</td>
</tr>
<tr>
<td>7947 7800</td>
<td>339.2±1.0</td>
<td>3.91</td>
<td></td>
<td></td>
<td></td>
<td>4.02±0%</td>
<td>4.04</td>
</tr>
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</table>

The ±5% uncertainty given in Table I is obtained by mean-square addition of approximately 3% uncertainty in K, 3% uncertainty in f, and 2% uncertainty in L.

DISCUSSION

In Fig. 5, we plot our experimental results together with data reported in the literature. Our values are approximately 25% less than those of Killian in the same temperature region and about 60% greater than those of Scott.

The vapor pressure or density is usually reported in terms of

\[
\log_{10}(\rho) = -A/T - B \log_{10}T + C + DT, \quad (5a)
\]

\[
\log_{10}(N) = -A/T - (B+1) \log_{10}T + C + DT + 18.985, \quad (5b)
\]

where \( \rho \) is in torr and \( N \) is in cm⁻³. Ditchburn and Gilmour chose values of \( A, B, C \) (with \( D=0 \)) to fit the data of Killian in the 310-370-K region and of Hackspill in the 625-K region; their result is plotted in Fig. 4 and given in Table I. Nesemeyanov chose \( A, B, C, D \) values by a different weighting of the various data shown in Fig. 4, as well as some other thermodynamic data and a higher-temperature measurement, not shown. Probably by coincidence, the resulting expression (Table II) is an excellent fit to our data. (See Table I.) In the temperature region of our data, these two sets of constants in Table II yield values of density that differ by 25%. We do not quote other vapor pressures given in the literature because they are derived from the data shown.

Valuable support of these vapor pressures is obtained in the 430-K region from the measurements of resonance broadening of the Hanle-effect signals observed in the resonance fluorescence, if we assume that the theoretical cross section is correct. This is shown in Fig. 4, although the details of this determination are described elsewhere. This datum point is 20% above the curve of Ref. 22 and 10% above that of Ref. 21. The experimental uncertainty of that value is roughly ±5%, but it is not possible to estimate the uncertainty in the theoretical cross section. The temperature uncertainty is about ±2 K, equivalent to ±10% density.

Because our vapor pressures, determined by absorption, are 25% less than those of Killian, we should wonder whether we indeed attained the equilibrium

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**Table II. Values of the constants in Eq. (2).**

<table>
<thead>
<tr>
<th>Source</th>
<th>( A )</th>
<th>( B )</th>
<th>( C )</th>
<th>( D )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref. 1</td>
<td>4302</td>
<td>1.5</td>
<td>11.722</td>
<td>0</td>
</tr>
<tr>
<td>Ref. 2*</td>
<td>4529.6</td>
<td>2.991</td>
<td>15.8825</td>
<td>0.00059</td>
</tr>
</tbody>
</table>

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* some additional digits have been rounded off.
density. The walls of our Pyrex cell were not completely coated with Rb, and it is well known that Pyrex can react with, and thereby pump, Rb. Several considerations indicate, but do not prove, that the cell did attain an equilibrium density. First, the cell temperature was cycled several times between 293 and 473 K and density observations were taken hours to days after stabilizing the temperature. No indications of hysteresis, drifts or nonrepeatability were observed. Second, the cell was filled with about 10 mg of Rb, and micro-droplets of the metal were observed (with a microscope) scattered over all surface areas. Larger droplets were visible to the eye in some regions. Third, the temperature dependence of our density agrees with expectations based on the Killian data and other data. Finally, the density inferred from the resonance broadening (Ref. 14) was greater than the analytic curves, whereas the effectiveness of Pyrex as a Rb pump should increase at higher temperatures.

REFERENCES

*Staff Member, Laboratory Astrophysics Division, National Bureau of Standards.
†Present address: Department of Physics, University of Newcastle-upon-Tyne, U.K.
9See Figs. 19–21 of Ref. 3 for a comparison of the observed and calculated spectrums.
10Figures 19 and 20 of Ref. 3, Fig. 2 of Ref. 7, Figs. 2 and 3 of Ref. 6, Figs. 2 and 3 of Ref. 7. The large component-intensity anomaly is the indicator of serious self-reversal in the last two cases.
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19T. J. Killian, Phys. Rev. 27, 458 (1926).

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