

parallel to the rf field and the tetragonal axis is perpendicular to it. The external magnetic field is rotated in the plane parallel to the tetragonal axis, that is,  $H_0 \parallel z$  axis. Figure 2 shows the case when  $H_0 \perp z$  axis.

The line width varied sharply with the orientation. Except for the special orientations marked with arrows in Figs. 1 and 2, the line width was very wide, sometimes several hundred gauss. In these special orientations, the line width reached a minimum. The central  $\frac{1}{2} \rightarrow -\frac{1}{2}$  transition (see Fig. 1) was about 10 gauss at  $\theta = 0$ . We believe that the spectrum is connected with the ferroelectric state of  $\text{BaTiO}_3$ , in particular with its domain structure, and not with any paramagnetic impurity such as  $\text{Cr}^{3+}$  or  $\text{Fe}^{3+}$ .<sup>1</sup> The reasons are as follows:

(a) The spectrum is very intense, approximately  $10^{20}$  spins per gram of  $\text{BaTiO}_3$ , much too intense to be explained by impurities present in the crystals. The spectrum was found in all crystals although they were obtained from many different sources. The spectrum was observed in so-called "pure" crystals and in those to which Pb, Fe, or Mn had been added intentionally. Additional weak lines, caused by paramagnetic impurities like  $\text{Mn}^{2+}$ , were observed and will be reported separately.

(b) The intensity of the spectrum can be changed by varying the ratio of the magnitude of the  $a$  to  $c$  domain in the crystal. This was done by immersing the crystal in liquids of different dielectric constants as suggested by Fang *et al.*,<sup>2</sup> and applying a dc field. The temperature was slowly varied from  $-10^\circ\text{C}$  (orthorhombic phase) to room temperature (tetragonal phase).

If the crystal was transformed from a multi-domain structure to an almost pure  $a$  domain, the intensity of the lines decreased by at least a factor of 10. On the other hand, almost pure  $c$  domains gave intense lines.

(c) The spectrum vanishes below  $5^\circ\text{C}$ , that is, in the orthorhombic phase (showing a temperature hysteresis). It is of negligible intensity in the cubic phase. No new spectrum was observed either in the orthorhombic or cubic phases.

In addition, a few wide and very weak lines were observed at high and low fields at intermediate angles. Some polarization effects were also observed which seem to point to possible distortions of the rf field in the neighborhood of the crystal. A more complete report will be submitted at a later date.

We are grateful to Professor Pulvari, Dr. E.

Wainer (Horizons, Inc.) and Dr. Karan (I.B.M.) for furnishing some of the  $\text{BaTiO}_3$  crystals.

<sup>†</sup>Supported by the U. S. Air Force, Office of Scientific Research, Air Research and Development Command.

<sup>1</sup>Hornig, Jaynes, and Weaver [Phys. Rev. **96**, 1703 (1954)] have observed paramagnetic resonance spectrum in  $\text{BaTiO}_3$ . They explain the spectrum as caused by ferrous ion impurities present in the crystal field of  $\text{BaTiO}_3$ . Their observed spectrum can be attributed to the same origin as the spectrum observed by us, except that their lines were observed for a particular orientation of the tetragonal axis with respect to the field. Apart from the arguments against assigning the spectrum to an impurity which were advanced in this letter, calculations of the energy levels of the ferrous ion for all reasonable crystal fields yield  $g$  values which cannot be reconciled with the observed values of Hornig *et al.* Besides, the relaxation time of the  $\text{Fe}^{2+}$  is usually so short that it can be detected only at liquid helium temperatures.

<sup>2</sup>P. H. Fang, S. Marzullo, and W. S. Brower, Phys. Rev. **108**, 242 (1957).

#### POLARIZATION OF FREE POTASSIUM ATOMS BY EXCHANGE COLLISIONS WITH SODIUM ATOMS AND FREE ELECTRONS\*

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(Received June 9, 1958)

We wish to report an experiment in which free potassium atoms have been detectably polarized by exchange collisions with free polarized sodium atoms<sup>1</sup> and with free polarized electrons. The apparatus is very similar to that discussed by Dehmelt<sup>2</sup> for his electron polarization experiment in which free electrons were polarized by exchange collisions with an optically pumped (polarized) sodium vapor.

Our sample consists of a 6-cm diameter Pyrex bulb into which has been distilled a mixture of sodium and potassium metal,<sup>3</sup> together with 6 mm argon. There are two 0.03-in. tungsten wire electrodes oppositely located in the bulb, which are employed in creating momentary discharges in the sample. The bulb is normally held at  $170^\circ\text{C}$  at which temperature we estimate, from the optical data, that the density of Na atoms is  $\sim 5 \times 10^{10}/\text{cc}$  and the density of K atoms is  $\sim 2 \times 10^{10}/\text{cc}$ .

Na resonance radiation from an Osram spectroscopic lamp is sent through a Na-pass optical filter<sup>4</sup> followed by a circular polarizer. This light passes through the sample and is collected by a photcell, the signal from which is ampli-

fied and displayed on a CRO. The direction of light propagation coincides with that of a 9-gauss uniform magnetic field developed by 25 in. diameter Helmholtz coils. A 0.04-gauss peak-to-peak sinusoidal field modulation at 15 cycles/sec is supplied by coils coaxial with the main magnetic field. Radio-frequency magnetic fields are developed at the sample by means of 4 turns of wire wrapped around the bulb and excited by a General Radio Unit Oscillator.

The six Na transitions ( $F=2, \Delta m=1$ ), ( $F=1, \Delta m=1$ ) are well resolved. An example is shown in Fig. 1(b).

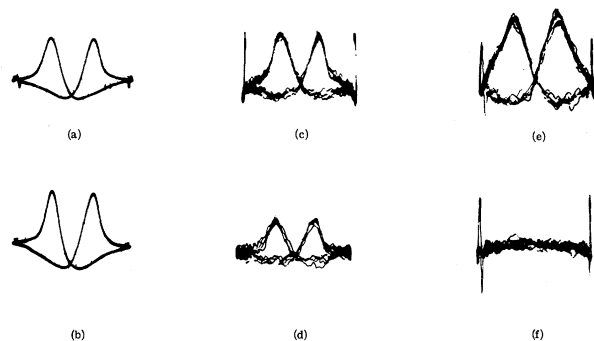


FIG. 1. CRO traces of the sodium, potassium, and free electron resonances. The homogeneous magnetic field is 8.9 gauss, and the modulation field is 0.04 gauss peak-to-peak at 15 cycles/sec. The Na transition ( $F=2; m=-1 \rightarrow m=-2$ ) occurs at 6.2 Mc, the K transition ( $F=2; m=-1 \rightarrow m=-2$ ) occurs at 6.4 Mc, and the free electron resonance occurs at 25 Mc. The discharge is at 30 cycles/sec and is seen as pips at the extreme ends of the traces.

- (a) Na resonance, discharge on. CRO gain = 1 (arbitrary units).  
 (b) Na resonance, discharge off. Gain = 1.  
 (c) K resonance, discharge on. Gain = 10.  
 (d) K resonance, discharge off. Gain = 10.  
 (e) Free electron resonance, discharge on. Gain = 10.  
 (f) No radio-frequency, discharge on. Gain = 10.

via the exchange process, so that a decrease in the Na light is observed. From a measured alkali relaxation time of  $\sim 10^{-2}$  sec and the data given above we compute that the cross section for Na-K exchange collisions is  $\sim 5 \times 10^{-14} \text{ cm}^2$ . This estimate is considered reliable to within a factor of three.

The calculation of Purcell and Field<sup>5</sup> for H-H exchange collisions was extended to the Na-K process, utilizing the parameters of the Na-K antisymmetric attraction given by Herzberg.<sup>6</sup> The result is  $\sim 7 \times 10^{-14} \text{ cm}^2$  and is considered reliable to within a factor of two.

Free electrons are introduced into the bulb by initiating 2-Mc/sec rf discharges of  $\sim 0.002$  sec duration, repetitive at 30 cycles per second, and phased so that the discharges occur at the extreme values of the 15-cycle/sec modulation field. (In the CRO displays of Fig. 1 the discharges occur at the extreme right and left hand sides of the trace.) The Na, K, and free electron resonances are shown in Figs. 1(a), 1(c), 1(e). The interpretation of the free electron resonance, following Dehmelt, is that the free electrons remaining after the discharge become polarized by exchange collisions with the optically pumped Na atoms.

When the discharge is turned on, the sodium resonance decreases by  $\sim 20\%$ , while the potassium resonance increases by  $\sim 40\%$  (see Fig. 1). We believe the decrease in sodium signal is due to two effects: (1) the discharge tends to "etch out" the sodium vapor, and (2) the free electrons exert a depolarizing effect on the sodium atoms. The potassium resonance increases, however, because the free electrons, polarized by the Na atoms, contribute constructively to the polarization of the potassium atoms via the electron-potassium exchange collisions. The potassium vapor is also etched out by the discharge, but the advantageous electron-potassium exchange effect is generally predominant. The alkali densities and hence the relative changes in the alkali resonances are temperature dependent.

The roles played by the Na and K atoms were reversed by running at higher temperatures ( $\sim 200^\circ\text{C}$ ) and using a potassium arc. The observations are similar to those described above and are in agreement with the computed Na-K exchange cross section.

From the data we estimate that the electron-potassium exchange cross section is  $< 3 \times 10^{-14} \text{ cm}^2$ , in agreement with Dehmelt's estimate for the electron-sodium cross section.<sup>2</sup> We have also obtained this value from unpublished data previously taken with an apparatus almost identical to Dehmelt's, but with potassium vapor only and a potassium arc.

These techniques may be useful in polarizing atomic and ionic species hitherto intractable to direct optical pumping. Experiments along this line are in progress.

The corresponding six potassium resonances occur at their proper frequencies with intensities approximately 1/10 that of the Na resonances. An example is shown in Fig. 1(d). The interpretation is that free K atoms have been

polarized by exchange collisions with the optically pumped Na atoms. The rf depolarization of the K atoms is "passed on" to the Na atoms

\* This work has been supported by the U. S. Atomic Energy Commission.

<sup>1</sup> While preparing this manuscript for publication we learned that R. Novick, University of Illinois, has been developing an atom-atom exchange polarization experiment in a sodium-rubidium system; see R. Novick and H. E. Peters, following Letter [Phys. Rev. Lett. 1, 56 (1958)]. We wish to express our gratitude to Professor Novick for several interesting telephone conversations in which ideas common to both of these experiments were discussed.

<sup>2</sup> H. G. Dehmelt, Phys. Rev. 109, 381 (1958).

<sup>3</sup> The Na metal used (Cenco) contains a trace of potassium impurity so that a pre-mixing of the two metals was not necessary.

<sup>4</sup> This filter consists of Corning CS3-69 and CS4-97 plates. It is used to absorb the small amount of potassium resonance radiation emitted by the Osram sodium lamp.

<sup>5</sup> E. M. Purcell and G. B. Field, *Astrophys. J.* 124, 542 (1956).

<sup>6</sup> G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, New York, 1955).

#### ORIENTATION OF RUBIDIUM ATOMS BY SPIN EXCHANGE WITH OPTICALLY PUMPED SODIUM ATOMS \* R. Novick and H. E. Peters

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Recently Dehmelt demonstrated that free electrons could be polarized by exchange collisions with optically oriented sodium atoms.<sup>1</sup> In this letter we report on an extension of this method to the orientation of atoms, in particular rubidium, by spin exchange with polarized sodium.<sup>2,3</sup> Rubidium was chosen for testing this method because the low-field Zeeman frequency of its most abundant isotope is well separated from that of sodium. Except for the absorption bulb, the experimental apparatus is essentially the same as that used by Dehmelt.<sup>1</sup> In our case the bulb consists of a 50 cm<sup>3</sup> spherical flask containing argon at a pressure of about 5 cm Hg and having metallic sodium deposited on its inner surface. The rubidium is contained in a small glass side arm that can be separately heated. The main bulb is maintained at a temperature of about 140°C while the side arm is kept cooler except when it is desired to transfer rubidium

into the absorption cell. The experiment is performed in a uniform magnetic field of about 0.46 gauss so that the sodium Zeeman resonance frequency is 320 kc/sec and the rubidium frequency is 213 kc/sec. The bulb is irradiated with circularly polarized sodium resonance light and its optical transmission monitored by a photodiode and oscilloscope. The optical transmission of the absorption cell for the circularly polarized sodium light provides a measure of the net polarization of the sodium atoms.<sup>1</sup> Low-frequency Zeeman modulation is used to facilitate observation of the Zeeman resonances. A very intense sodium Zeeman resonance signal is observed when a radio-frequency magnetic field of 320 kc/sec is applied to the absorption bulb. In addition, a resonance is observed at the rubidium Zeeman frequency (Fig. 1). The intensity

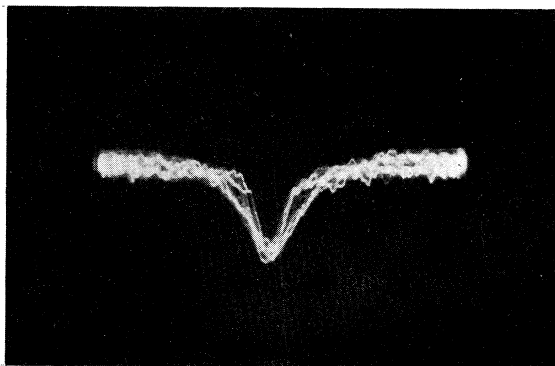


FIG. 1. Rubidium Zeeman resonance as observed by its effect on the optical transmission of a sodium resonance absorption cell.

of the rubidium resonance is about 5% of that of the sodium resonance. The shape of the rubidium resonance is quite distinct from that of the sodium and it only appears when a suitable quantity of rubidium has been distilled into the bulb. Tests with suitable optical filters have shown that the rubidium signal is not due to direct optical pumping of the rubidium by a rubidium impurity in the sodium arc. The rubidium resonances have been observed in two bulbs having slightly different construction. The effect has been observed using both a GE type NA-1 sodium arc and an Osram sodium spectral lamp. The sodium and rubidium resonances have been observed simultaneously by applying both 320- and 213- kc/sec signals to the radio-frequency coil surrounding the absorption cell. In this way it was found that the rubidium resonance disappears when the sodium resonance is saturated, indicating that the oriented sodium is essential