Hybrid Spin-Exchange Optical Pumping of ^{3}He

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We demonstrate spin-exchange optical pumping of ^{3}He using a "hybrid" K-Rb vapor mixture. The Rb atoms absorb light from a standard laser at 795 nm, then collisionally polarize the potassium atoms. Spin-exchange collisions of K and ^{3}He atoms then transfer the angular momentum to the ^{3}He with much greater efficiency than Rb-^{3}He. For a K-rich vapor, the efficiency of the hybrid spin-exchange collisions approaches 1/4, an order of magnitude greater than achieved by pure Rb pumping. We present the first measurements of actual photon efficiencies (polarized nuclei produced per absorbed photon), and show that a new parasitic absorption process limits the total efficiencies for both hybrid and pure Rb pumping.

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Hyperpolarized ^{3}He gas is used to address a wide variety of scientific and medical problems. These include magnetic resonance imaging [1], spin-polarized targets [2], neutron spin filters [3], and precision measurements [4]. Spin-exchange optical pumping (SEOP) [5,6] is widely used to produce hyperpolarized ^{3}He. The vast majority of SEOP experiments use high power diode laser arrays [7,8] to spin polarize a Rb vapor by optical pumping [9], with spin-exchange collisions between the Rb and ^{3}He atoms transferring the polarization via a weak hyperfine coupling between the Rb electron and the ^{3}He nucleus.

A convenient concept for evaluating SEOP is the efficiency with which light is converted into polarized nuclei. We consider two types of efficiencies that are measured in SEOP experiments. The "photon efficiency" η_γ is defined as the number of polarized nuclei produced per photon absorbed in the vapor. The "spin-exchange efficiency" $\eta_{\rm SE}$ is the ratio of the rate at which angular momentum is transferred to the ^{3}He nuclei to the rate at which it is lost by the alkali atoms through various collisional channels. Under ideal conditions, $\eta_\gamma = \eta_{\rm SE}$.

The Princeton group [10] recently showed that $\eta_{\rm SE}$ for Rb-^{3}He is limited to about 2% at common Rb operating temperatures ($\sim 180\,^\circ$C), so that ideally about 50 photons should be required to produce a single polarized ^{3}He nucleus. In contrast, only four photons per nucleus should be required for K-^{3}He. Experiments directly pumping K-^{3}He have not yet realized these improvements.

In this Letter, we demonstrate a hybrid approach to realizing the potential for K spin exchange, first proposed by Happer and co-workers [11]. We optically pump a K-Rb vapor mixture, lean in Rb, using a standard Rb laser. Spin-exchange collisions between the Rb and K atoms transfer the Rb polarization to the K atoms with little loss. If the K density greatly exceeds the Rb density, ^{3}He polarization is generated primarily by highly efficient collisions with K atoms and only slightly via lossy collisions with Rb atoms. We present measurements of both $\eta_{\rm SE}$ and η_γ for hybrid SEOP. For both types of efficiencies, we find order-of-magnitude SEOP improvements for KRb-^{3}He as compared to Rb-^{3}He. However, we find $\eta_\gamma \ll \eta_{\rm SE}$ for both pure and hybrid pumping. Our investigations show that small imperfections in the optical pumping process produce surprisingly large photon absorption.

Hybrid SEOP relies on rapid spin transfer from the Rb to the K atoms. The K-Rb spin-exchange cross section is extremely large, roughly 200 Å^2 [9]. At typical densities of 10^{14} cm^{-3} or more, the K-Rb spin-exchange rate exceeds 10^5/s, much greater than the typical 500/s alkali spin-relaxation rates in ^{3}He spin-exchange cells. Thus, the K and Rb atoms are in spin-temperature equilibrium [9,12] and have equal electron spin polarizations P_A. The ^{3}He polarization $P_{\rm He}$ is produced by collisions with both polarized K and polarized Rb, and is lost by the ^{3}He in other processes at a rate $\gamma_{\rm He}$:

$$\frac{dP_{\rm He}}{dt} = \gamma_{\rm SE}(P_A - P_{\rm He}) - \gamma_{\rm He}P_{\rm He}, \tag{1}$$

where the spin-exchange rate is $\gamma_{\rm SE} = k_{\rm K}[{\rm K}] + k_{\rm Rb}[{\rm Rb}]$, $k_{\rm K}$ and $k_{\rm Rb}$ are the spin-exchange rate coefficients, and the factors in brackets are the alkali densities.

The K atoms lose angular momentum by spin exchange to ^{3}He and also by spin relaxation in primarily K-K, K-Rb, and K-^{3}He collisions. (We estimate diffusion losses at the wall to be small.) The rapid K-Rb spin exchange thereby causes the effective Rb spin-relaxation rate to increase from its K-free value $\Gamma_{\rm Rb}$ to

$$\Gamma'_{\rm Rb} = \Gamma_{\rm Rb} + \mathcal{D}\Gamma_{\rm K} + q_{KR}[{\rm K}], \tag{2}$$

where $\mathcal{D} = [{\rm K}]/[{\rm Rb}]$ and the total K relaxation rate is $\Gamma_{\rm K}$. Under most conditions of interest, the K-Rb loss rate $q_{KR}[{\rm K}]$ will be small.

We begin our evaluation of hybrid pumping by considering the spin-exchange efficiency:

$$\eta_{SE} = \frac{\gamma_{SE}[^3\mathrm{He}]}{[\mathrm{Rb}]\Gamma'_{\mathrm{Rb}}} = \frac{(k_{\mathrm{Rb}} + \mathcal{D}k_{\mathrm{K}})[^3\mathrm{He}]}{(\Gamma_{\mathrm{Rb}} + \mathcal{D}\Gamma_{\mathrm{K}} + q_{KR}[\mathrm{K}])}. \quad (3)$$

For large $\mathcal{D}$, the K-Rb spin-exchange efficiency is equal to the K-^{3}He spin-exchange efficiency $k_{\mathrm{K}}[^3\mathrm{He}]/\Gamma_{\mathrm{K}}$.

Using the data of Baranga *et al.* [10] for both Rb and K spin-exchange efficiencies, and using measured K spin-exchange rate coefficients reported below, gives the curve shown in Fig. 1. Although modest density ratios $\mathcal{D} \sim 1$ already promise substantial improvements, $\mathcal{D} \gg 10$ will be necessary to achieve the full promise of hybrid spin exchange. Since the saturated vapor densities for pure metals obey $[\mathrm{Rb}]_0 \gg [\mathrm{K}]_0$ at a given temperature, it is necessary to sublimate from a metal mixture containing a small amount of Rb dissolved into mostly K metal. For a quantitative estimate, we assume that the vapor densities approximately obey Raoult's law, $[\mathrm{Rb}] \approx f_{\mathrm{Rb}}[\mathrm{Rb}]_0$, where f_{Rb} is the mole fraction of Rb in the metal and $[\mathrm{Rb}]_0$ is the saturated vapor density for pure Rb metal. Using saturated vapor curves, we estimate that $f_{\mathrm{Rb}} \approx 3\%$ gives a 10:1 vapor density ratio at 250 °C.

For first experiments, we did not attempt to accurately control the Rb mole fraction, but simply distilled a small amount of Rb and a much larger amount of K into a set of cells. We have studied four spherical hybrid cells, all made from GE180 glass. One of them was a sealed 22.5 cm^3 cell, made at the University of New Hampshire [13], that contained 3.3 amagat of ^{3}He. It has a room-temperature relaxation time of 92 h and a density ratio $\mathcal{D} = 1.5$. The other three cells were 187 cm^3, 7.9 amagat valved cells with 20, 65, and 55 h relaxation times and $\mathcal{D} = 2.5$, 34, and 500, respectively. The density ratios were measured using polarization-Faraday rotation of a tunable single-frequency diode laser tuned near the K and Rb resonances. Each cell had a nearly fraternal twin cell containing only Rb metal for relative comparisons.

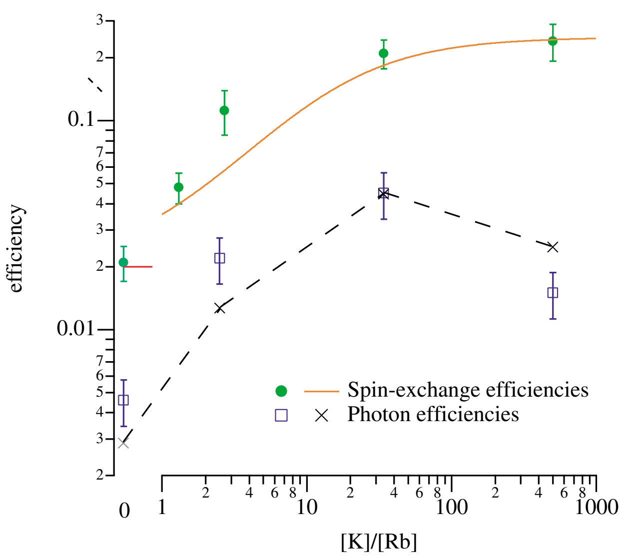

FIG. 1 (color online). K-Rb-^{3}He efficiencies, as a function of the K-Rb density ratio, at a temperature of 190 °C. The filled circles are spin-exchange efficiency results, with the associated solid line being the expected values from previous Rb and K efficiency measurements (Ref. [10]). The hollow squares are photon efficiency measurements for broad-band pumping, with the dashed line denoting the expected values corrected for imperfect optical pumping, using the results of Fig. 3.

Measurements were carried out at two locations. The sealed cells were studied at the University of Wisconsin using the apparatus described in Ref. [14]. A 12 W frequency-narrowed diode array was used for the optical pumping. The valved cells were studied at Amersham using a 60 W broad-band laser.

Our spin-exchange efficiency measurements, shown in Fig. 1, agree very well with the expectations from the Baranga *et al.* [10] experiments, and show the expected factor of 10 increase in spin-exchange efficiency for high density ratios. The measurements are based on rewriting Eq. (3) as

$$\eta_{SE} = \frac{[^3\mathrm{He}]P_{\mathrm{He}}^{\mathrm{eq}}/\tau_{\mathrm{up}}}{P_A[\mathrm{Rb}]\Gamma'_{\mathrm{Rb}}}, \quad (4)$$

where $P_{\mathrm{He}}^{\mathrm{eq}}$ is the equilibrium ^{3}He polarization attained via spin exchange, and τ_{up} the time constant for reaching equilibrium. All the quantities in Eq. (4) are measured as follows. We deduced τ_{up} from the polarization buildup, detected via free-induction decay NMR, $P_{\mathrm{He}}^{\mathrm{eq}}$ from the K EPR frequency shift [10], $P_A[\mathrm{Rb}]$ by Faraday rotation, and Γ'_{Rb} from the longest time constant τ_A of decay of the alkali polarization with time when the pumping light is extinguished. Note that $\Gamma'_{\mathrm{Rb}} = s/\tau_A$, where $s = 10.8 + 6\mathcal{D}$ is the slowing-down factor for hybrid relaxation in spin-temperature equilibrium.

The polarizations and spin-up times achieved using narrow-band pumping of the $\mathcal{D} = 1.5$ sealed cell are shown in Fig. 2. The best performance was achieved at a temperature of 244 °C, where the cell polarized to $P_{\mathrm{He}} = 0.73$ with $\tau_{\mathrm{up}} = 2.5$ h. This is twice as fast as the twin Rb cell, as expected for this density ratio. (Similar to our experience with Rb cells, the ^{3}He polarization does not achieve parity with the $> 95\%$ alkali polarization, even with extremely short spin-exchange times.)

During the course of these studies, we also determined the effective spin-exchange rate coefficient for K-^{3}He using several methods, as we recently did for Rb-^{3}He [14]. Our result, $k_{\mathrm{K}} = (6.1 \pm 0.4) \times 10^{-20}$ cm^3/s, is 10% less than the Rb-^{3}He value of $(6.8 \pm 0.2) \times 10^{-20}$ cm^3/s. This value is consistent with expectations based on the relative frequency shift enhancement factor [10] $\kappa_0(\mathrm{K}) = 0.96\kappa_0(\mathrm{Rb})$, a relation we have confirmed.

We now consider the photon efficiency of SEOP. It is the ratio of the ^{3}He polarization rate to the photon flux deposited in the volume V, at low P_{He}:

$$\eta_\gamma = \frac{[^3\mathrm{He}]VdP_{\mathrm{He}}/dt}{\Delta\phi} = \frac{[^3\mathrm{He}]VP_{\mathrm{He}}^{\mathrm{eq}}/\tau_{\mathrm{up}}}{\Delta\phi}. \quad (5)$$

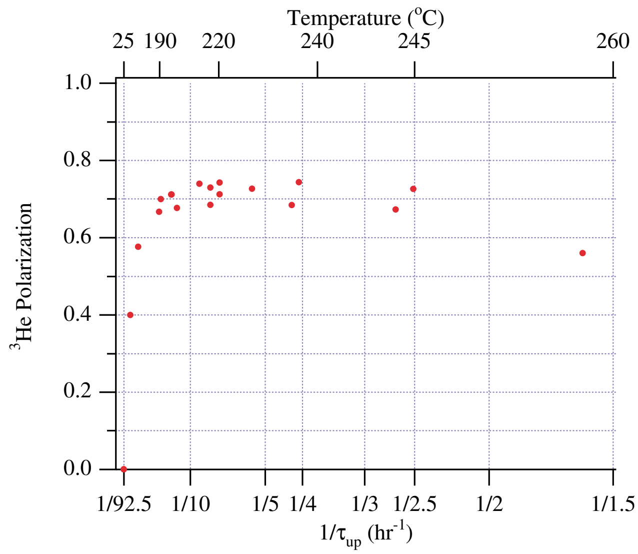

FIG. 2 (color online). Measured polarizations and spin-up times for a 25 cm^3, 3.3 amagat hybrid cell with $\mathcal{D} = 1.5$.

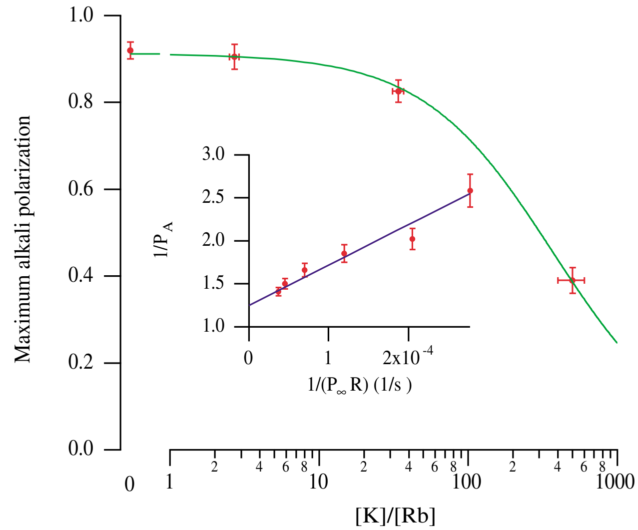

FIG. 3 (color online). Maximum attainable alkali polarization P_A(max) for the various eight amagat cells pumped by broad-band laser light. The solid line is the expectation assuming that the K atoms absorb the laser light at 0.27% of the Rb absorption rate, and that in the absence of K atoms the Rb polarization is limited to $P_\infty = 0.91$. Inset: Determination of P_A(max) from polarization measurements as a function of the initial slope of optical pumping transients.

Comparison with Eq. (4) shows that the photon and spin-exchange efficiencies are equal when the deposited photon flux is the ideal value

$$\Delta\phi_i = \Gamma'_{\mathrm{Rb}} P_A [\mathrm{Rb}] V. \tag{6}$$

If the deposited photon flux exceeds $\Delta\phi_i$, the photon efficiency will be smaller than the spin-exchange efficiency.

We present in Fig. 1 measured photon efficiencies, determined by measuring ^{3}He polarizations, spin-up time constants, and the absorbed photon fluxes following the right-hand side of Eq. (5). The data were taken using a 60 W broad-band diode laser using high pressure cells and are representative of current spin-exchange practice. The photon efficiencies for both pure Rb and hybrid cells are 5–20 times smaller than the spin-exchange efficiencies. Still, the efficiencies of the hybrid cells exceed that of pure Rb by as much as an order of magnitude.

A key experimental observation is that the alkali polarization, measured using EPR spectroscopy, saturates at a value less than 1, even for intense broad-band pumping. We measured the alkali polarization as a function of laser intensity, and extrapolated to infinite intensity. (This process is explained more fully below.) The results (Fig. 3) show that the maximum polarization decreases with increasing $\mathcal{D}$, reaching 38% for the $\mathcal{D} = 500$ cell.

We postulate two effects to explain these alkali polarization limits. The strong dependence of the maximum polarization on $\mathcal{D}$ is naturally explained by a small direct pumping rate (less than 1% that of Rb) for the K atoms. When $\mathcal{D}$ is large, the strong spin-exchange coupling of the two alkali species then results in increased Rb light absorption as well. The observation of less-than-perfect Rb polarization even under intense pumping conditions for pure Rb SEOP implies a light-induced relaxation phenomenon of some type, or an inherent lack of perfect dichroism for the Rb atoms. We now present a phenomenological model to account for these results.

We begin by reviewing the origin of Eq. (6). For ideal alkali $D1$ optical pumping, assuming that the pressure broadening and/or laser linewidth greatly exceeds the hyperfine splitting (a condition well satisfied here), the atoms absorb circularly polarized light at a rate per atom of $A = R(1 - P_A)$, where R is the optical pumping rate. The alkali atoms relax at a rate Γ_A, producing a polarization $P_A = R/(R + \Gamma_A)$, which then gives $A = \Gamma_A P_A$ from which Eq. (6) follows. A key assumption is that fully polarized atoms absorb no light. This may not hold in practice due to a variety of effects including (i) finite fine-structure splitting, (ii) fine-structure mixing by collisions and/or external fields, (iii) imperfect light polarization due to skew magnetic fields [15], and (iv) absorption by alkali dimers.

The general form of the absorption of circularly polarized light by a spin-1/2 atom is $A = R(1 - P_\infty P_A)$, with resulting spin polarization $P_A = P_\infty R/(R + \Gamma_A)$ whose maximum value is P_∞. Equation (6) then becomes

$$\Delta\phi = [\mathrm{Rb}] V \Gamma_A \frac{P_A}{P_\infty}\left[1 + \frac{R}{\Gamma_A}(1 - P_\infty^2)\right], \tag{7}$$

so the deposited flux exceeds the ideal case by the factor $\Upsilon = 1/P_\infty + R(1 - P_\infty^2)/(\Gamma_A P_\infty)$. For optically thick SEOP, it is common to have $R/\Gamma_A \sim 100$, so that for a modest $P_\infty = 0.95$ we find $\Upsilon = 11$. Thus, it is easy for the total efficiencies of spin exchange to be an order of magnitude smaller than the ideal value of Eq. (3).

Adding to these observations the possibility that the K atoms absorb light at a modest rate changes Eq. (7) in two ways. First, a similar K absorption term must be added, with absorption rate R_K. Since the 795 nm laser light is far from the K resonances, the dichroism of the K atoms should be quite small. For simplicity, we make the assumption that P_∞ for K is zero. (Allowing for a small nonzero value does not affect any conclusions.) Second, the absorption of light by the K atoms acts as an additional relaxation mechanism for the Rb atoms that provide polarization to the K atoms by spin exchange. When $\mathcal{D}$ is large, the Rb relaxation rate can be substantially increased, thereby increasing the Rb relaxation rate to $\Gamma'_{\rm Rb} + \mathcal{D}R_K$. The alkali polarization is therefore

$$P_A = P_\infty \frac{R}{R + \mathcal{D}R_K + \Gamma'_{\rm Rb}}, \tag{8}$$

so that the maximum attainable alkali polarization is $P_A(\max) = P_\infty R/(R + \mathcal{D}R_K)$. Plots of $1/P_A$ vs $1/(P_\infty R)$ should be a straight line with slope $\Gamma'_{\rm Rb}$ and intercept $1/P_A(\max)$. We experimentally determine $P_\infty R$ from the slope $S = dP_A/dt|_{P_A=0}$ of optical pumping transients that begin at $P_A = 0$; $P_\infty R = sS$. An example of such a plot is shown as an inset of Fig. 3. Within errors (typically 15%), we find excellent agreement between $\Gamma'_{\rm Rb}$ determined from such plots and the independent measurement $\Gamma'_{\rm Rb} = s/\tau_A$.

Values of $P_\infty = 0.91$ and $R_K/R = 0.0027$ account well for our experimental observations, as shown in Fig. 3. Taking into account these effects, the photon efficiency of hybrid pumping becomes $\eta_\gamma = \eta_{\rm SE}\eta_{\rm OP}$ where the optical pumping efficiency is

$$\eta_{\rm OP} = \frac{\Gamma'_{\rm Rb} P_\infty R}{(R + \mathcal{D}R_K)^2 + \Gamma'_{\rm Rb}(R + \mathcal{D}R_K) - P_\infty^2 R^2}. \tag{9}$$

Using the measured values for each of the quantities in this equation, we show the deduced photon efficiencies in Fig. 1 and see that they account for the low values of the directly measured photon efficiencies.

The physical explanations for $P_\infty < 1$ and $R_K \neq 0$ are not yet apparent. Using the narrow-band laser with the sealed Rb and KRb cells, we have obtained $> 98\%$ alkali polarization, so it seems clear that $P_\infty < 1$ likely depends on the spectral characteristics of the pumping laser. Such behavior is similar to recent observations at pressures below 1 amagat where some broad-band lasers are found to produce less ^{3}He polarization than others under conditions of intense pumping [3]. Fine-structure mixing via ^{3}He collisions might explain this distinction, and further studies are under way in our laboratories. The value of R_K we observe is only a factor of 3 larger than expected from a purely impact-broadened K-^{3}He line shape at 8 amagat. However, if pressure broadening is responsible for R_K, the measured ratio R_K/R should decrease with decreasing pressure, but we find in fact no pressure dependence of the attainable P_A for the $\mathcal{D} = 500$ cell.

These first studies of KRb hybrid spin-exchange optical pumping have confirmed the high spin-exchange efficiencies expected based on previous experiments on pure alkali vapors. Measurements of photon efficiencies derived from absolute polarimetry and photon absorption measurements also showed increased efficiency for hybrid pumping as compared to pure Rb pumping. Imperfect optical pumping of the atoms significantly reduces the spin-exchange efficiency from its maximum possible value for both the KRb and pure Rb cases.

The increased spin-exchange rates achievable with hybrid pumping should be beneficial not only for polarizing large quantities of helium in a short time as required for gas imaging or neutron spin filters, but also for polarizing in the presence of depolarizing effects, as in electron beam targets. We note that a NaRb hybrid should have virtually 100% efficiency [16], and might display much reduced Na pumping due to the much larger mismatch between the Na and Rb resonance wavelengths.

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