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Limits to the Polarization for Spin-Exchange Optical Pumping of ^{3}He

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Based on measurements of the temperature dependence of ^{3}He relaxation in a wide range of spin-exchange optical pumping cells, we report evidence for a previously unrecognized surface relaxation process. The relaxation rate was found to be linearly proportional to the alkali-metal density with a slope that exceeds the spin-exchange rate, which limits the polarization for current applications, including neutron spin filters, polarized targets, and polarized gas magnetic resonance imaging. We find that the magnitude of this excess relaxation can vary widely between cells, and that the variation is larger for cells of higher surface to volume ratio. We have observed ^{3}He polarization as high as 81%, but further improvements require understanding the origin of this relaxation.

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Spin-exchange optical pumping (SEOP) of ^{3}He [1] is an important method in several areas of physics, including neutron spin filters for neutron scattering and fundamental neutron physics [2], spin-polarized targets [3], and magnetic resonance imaging [4]. Despite decades of study, the fundamental processes that govern relaxation on the walls of the alkali-metal-coated, glass cells used for SEOP are not well understood and continue to reveal new features [5]. Nevertheless, it was generally expected that this wall relaxation would not increase strongly with temperature, as adsorption-based relaxation should decrease slowly with increasing temperature [6,7], and recent SEOP results with permeable glasses have revealed that dissolution-dominated relaxation is suppressed by the alkali-metal coating [8–10]. In addition, it has been possible to fabricate cells essentially free of wall relaxation [10,11], and it was expected that this suppression would continue to be operative at the typical temperatures employed for SEOP. Such cells would be of great utility for SEOP applications; indeed, ^{3}He polarization approaching 100% would already be possible. In this Letter we show evidence for a previously unrecognized surface relaxation process that is apparent only at SEOP temperatures. This "excess relaxation" has similar magnitude and dependence on alkali-metal density as the spin-exchange process itself, but its magnitude varies from cell to cell and the size of this variance is correlated with the surface to volume ratio of the cell. This effect limits the polarization to between 50% and 80%, depending on the magnitude of the excess relaxation. This conclusion was reached after an extensive study of a wide range of SEOP cells that was conducted at two different laboratories using different measurement techniques. From a fundamental point of view, it reveals a major new feature of wall relaxation for SEOP cells. From a practical point of view, it reveals the direction of future research needed for SEOP to reach its full potential. In neutron scattering, in which most instruments are oversubscribed, or for fundamental neutron physics or electron scattering, in which highly precise results must be obtained with either inherently weak sources or relatively thin targets, the decrease in running time that higher ^{3}He polarization would allow would have significant impact.

In SEOP spin angular momentum is first deposited into the valence electrons of an alkali-metal atom, usually Rb, through optical pumping. Through binary collisions with ^{3}He the spin-polarized electrons then transfer angular momentum to the nuclei of the ^{3}He. Until recently, it was expected that if the alkali-metal polarization were near unity and the relaxation time of the cell were much longer than the spin-exchange time constant, the ^{3}He polarization would also approach unity. However, we recently discovered that an "excess" relaxation that scales with the alkali-metal density limits the polarization [12,13]. Experimentally, the total ^{3}He relaxation rate, Γ_{He}, can be well represented by $\Gamma_{\mathrm{He}} = k_{\mathrm{se}}[\mathrm{Rb}](1 + X) + \Gamma_{\mathrm{r}}$, where k_{se} is the spin-exchange rate coefficient, $[\mathrm{Rb}]$ is the Rb density, Γ_{r} is the room temperature ^{3}He relaxation rate, and X is a phenomenological parameter that reflects that the slope of Γ_{He} vs $[\mathrm{Rb}]$ is observed to be greater than the spin-exchange rate [12]. This form for the relaxation implies that the ^{3}He polarization can be represented by

$$P_{\mathrm{He}} = P_{\mathrm{Rb}} \frac{k_{\mathrm{se}}[\mathrm{Rb}]}{k_{\mathrm{se}}[\mathrm{Rb}](1 + X) + \Gamma_{\mathrm{r}}}, \tag{1}$$

where P_{Rb} is the volume-averaged Rb polarization. For

$P_{\mathrm{Rb}} = 1$ and $\Gamma_{\mathrm{r}} = 0$, the predicted ^{3}He polarization limit $P_{\mathrm{He}} = 1/(1 + X)$ is independent of [Rb].

To further study this excess relaxation, we conducted measurements using optical pumping apparatus at the University of Wisconsin and the National Institute of Standards and Technology (NIST) that have been described earlier [12]. At Wisconsin, we have employed two methods to measure X. In the "hot relaxation method" we simply measure Γ_{He} as a function of [Rb], usually by measuring the variation in the time constant for optical pumping, τ_{p}, with [Rb], as $\tau_{\mathrm{p}} = 1/\Gamma_{\mathrm{He}}$. Since k_{se} is known to be $(6.8 \pm 0.1) \times 10^{-20}$ cm^3 s^{-1} from independent methods that make no assumptions about the nature of Γ_{He} [13,14], the value of X is determined from the slope of Γ_{He} vs [Rb]. [Rb] is determined from measurements of the Faraday rotation of a probe laser tuned near the $5s_{1/2} \rightarrow 5p_{3/2}$ Rb resonance [13]. Figure 1 shows the results of the hot relaxation method for four cells.

In the "polarization method," we determine X by measuring P_{He} as a function of [Rb]. X is determined from Eq. (1), where P_{Rb} is known to be unity, and all other quantities are measured or known. We estimate that the volume-averaged P_{Rb} in the experiments at Wisconsin is within 3% of unity by methods described earlier [13]. P_{He} was determined with a relative standard uncertainty of 3% from the shift of the Rb electron paramagnetic resonance transition [15]. For some cells we did not have P_{He} data for different Rb densities; hence for these cells we simply determined X from Eq. (1).

At NIST, measurements of [Rb] and P_{Rb} were not available. X was determined from the polarization method, with the assumption of $P_{\mathrm{Rb}} = 1$. k_{se}[Rb] was determined from measurements of P_{He} and τ_{p} using $P_{\mathrm{He}} = k_{\mathrm{se}}[\mathrm{Rb}]\tau_{\mathrm{p}}$. P_{He} was determined with a typical relative standard uncertainty of 4% from nuclear magnetic resonance measurements that were calibrated against neutron transmission [12]. Γ_{r} was typically small; hence measurements of P_{He} vs [Rb] were not required. The assumption of unity Rb polarization was based on observing a plateau in achievable ^{3}He polarization as the temperature (and thus [Rb]) was decreased and/or when the laser power was increased. In addition, we relied on experience with the laser power required to produce unity Rb polarization in a given cell volume. For the NIST data, we estimate that P_{Rb} is within 5% of unity.

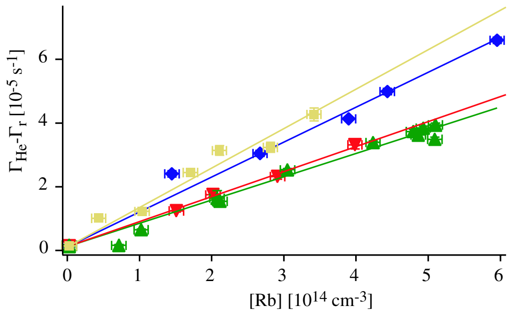

FIG. 1 (color online). Γ_{He}-Γ_{r} as a function of [Rb] for four cells: Oscar (green upward triangles), NHRb (red downward triangles), Felix (blue diamonds), and Bonnie (yellow squares). The Rb density increases from 5×10^{13} to 5×10^{14} cm^{-3} in the temperature range between 410 and 460 K.

Figure 2 shows the variation of X with S/V, and Tables I and II list information on the cells tested at Wisconsin and NIST, respectively. All cells were constructed and filled at NIST using procedures described elsewhere [10], except for the cells denoted by MITI, Amersham1.8 and Amersham 3.1, Michcell, NewHampRb, and Utah. Values of X from the polarization method were obtained at temperatures of 430 to 460 K.

The results in Fig. 2 indicate that X reaches ≈ 0.25 for S/V less than ≈ 1 cm^{-1}. At higher S/V, X tends to increase, but is more variable. Both sets of results show the same overall behavior with S/V. The hot relaxation and polarization methods are generally in good agreement, but

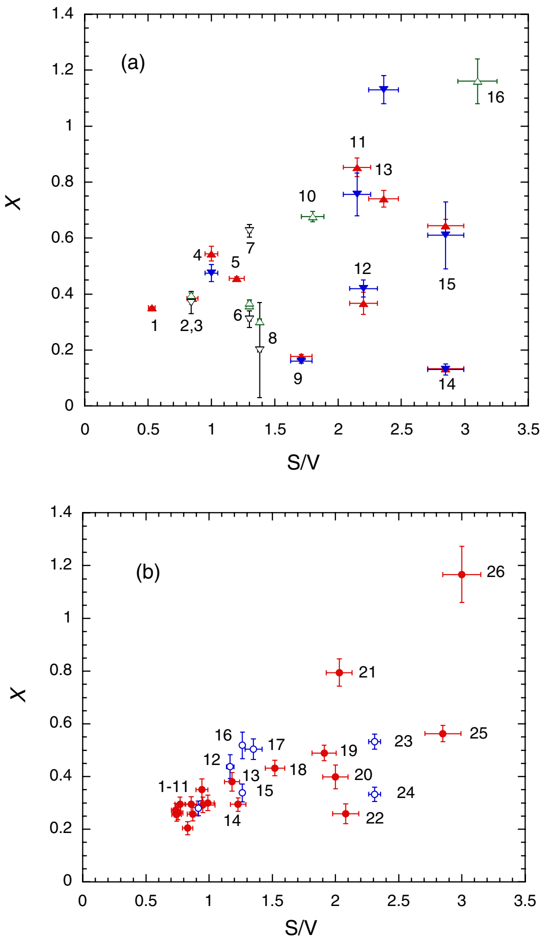

FIG. 2 (color online). The variation of X with S/V for cells tested at (a) Wisconsin and (b) NIST. For the Wisconsin data, upward pointing triangles show data obtained with the relaxation method, and downward pointing triangles show data obtained with the polarization method. For the NIST data, all measurements were performed by the polarization method, with the assumption of $P_{\mathrm{Rb}} = 1$. Closed symbols are used for blown cells and open symbols for flat-windowed cells. The cells are labeled by the numbers in (a) Table I and (b) Table II.

TABLE I. ^{3}He cells studied at Wisconsin. The cell name and construction, S/V (surface to volume ratio), X determined from relaxation rate measurements, X determined from the polarization method, the cell's room temperature relaxation time $T_1 = 1/\Gamma_r$ in hours, and the ^{3}He and N_2 gas pressures in bar are listed. The codes for blown cells following the cell name are bgs, bgc, bcs, bfc (GE180 sphere, GE180 cylinder, Corning 1720 sphere, fused silica cylinder, respectively); for flat-windowed cylindrical cells fcc, fcg, fgg (body and windows of Corning 1720 or GE180). The numbers in parentheses show the uncertainty in the last digit(s).

Cell	S/V	X (rate)	X (pol)	T_1	^{3}He	N_2
1. Sunshine (bgs)	0.53	0.35(1)		550	0.5	0.07
2. BamBam (fcc)	0.84	0.40(1)	0.37(4)	120	0.9	0.07
3. MITI (bgs)	0.85	0.39(1)		182	3.0	0.02
4. Barney (bgc)	1.0	0.54(3)	0.48(3)	380	1.1	0.07
5. Natasha (bfc)	1.20	0.46(1)		440	0.7	
6. *Betty* (fcg)	1.26	0.36(1)	0.31(3)	240	0.9	0.07
7. *Boris* (fcc)	1.26	0.37(1)	0.63(2)	70	0.9	0.07
8. Michcell (fcc)	1.38	0.30(1)	0.2(2)	8.1	0.7	
9. NHRb (bgs)	1.71	0.18(1)	0.16(1)	94	3.6	0.12
10. Amer1.8 (fgg)	1.8	0.68(2)		51	1.1	0.01
11. Bonnie (bgs)	2.15	0.85(3)	0.76(8)	110	3.4	0.07
12. *Snoopy* (bgc)	2.1	0.37(4)	0.38(4)	180	3.4	0.07
13. Ringo (bcs)	2.36	0.74(3)	1.13(5)	64	3.4	0.07
14. Oscar (bgc)	2.85	0.13(1)	0.13(2)	29	3.1	0.23
15. *Felix* (bgc)	2.9	0.64(2)	0.61(1)	143	2.8	0.13
16. Amer3.1 (fgg)	3.1	1.16(8)		44	1.1	0.01

TABLE II. ^{3}He cells studied at NIST. Column identification and other information is in the caption of Table I. The last column is the maximum ^{3}He polarization observed.

Cell name	S/V	X (pol)	T_1	^{3}He	N_2	P_{He}
1. Orvieto (bgc)	0.74	0.27(3)	80	1.1	0.07	0.71
2. Pebbles (bgc)	0.74	0.26(3)	350	0.9	0.07	0.76
3. Chardonnay (bgc)	0.75	0.26(2)	390	1.1	0.07	0.76
4. Dino (bgc)	0.77	0.30(3)	660	0.9	0.07	0.75
5. Chekhov (bgc)	0.83	0.20(2)	340	1.3	0.07	0.79
6. Chapel (bgc)	0.87	0.26(3)	330	1.3	0.07	0.76
7. Bullwinkle (bgc)	0.86	0.29(3)	560	1.3	0.07	0.72
8. Mars (fcg)	0.92	0.28(3)	150	0.9	0.07	0.72
9. Quasimoto (bgc)	0.94	0.28(3)	560	1.1	0.07	0.76
10. Margarita (bgs)	1.0	0.29(3)	820	0.9	0.07	0.76
11. Rand (bgc)	0.99	0.30(3)	650	1.2	0.07	0.72
12. Sulu (fgg)	1.17	0.44(5)	150	0.9	0.07	0.64
13. Uhura (bgc)	1.18	0.38(4)	180	1.2	0.07	0.64
14. Wilma (bgc)	1.23	0.29(3)	830	0.9	0.07	0.76
15. *Betty* (fcg)	1.26	0.34(3)	220	0.9	0.07	0.72
16. *Boris* (fcc)	1.26	0.52(5)	90	0.9	0.07	0.58
17. Algonquin (fgg)	1.35	0.50(4)	19	1.6	0.08	0.35
18. Marcy (bgc)	1.52	0.43(3)	360	2.2	0.08	0.68
19. Washington (bgc)	1.9	0.49(3)	540	0.9	0.07	0.65
20. Joe Cool (bgc)	2.0	0.40(4)	120	3.1	0.07	0.63
21. Red Baron (bgc)	2.0	0.80(5)	280	0.9	0.07	0.53
22. *Snoopy* (bgc)	2.1	0.26(4)	180	3.4	0.07	0.75
23. Cashew (fgg)	2.3	0.53(3)	370	1.9	0.13	0.65
24. Peanut (fgg)	2.3	0.33(3)	53	1.7	0.16	0.67
25. *Felix* (bgc)	2.9	0.56(3)	120	2.8	0.13	0.62
26. Otto (bgc)	3.0	1.2 (1)	420	0.9	0.07	0.45

there are two cells (denoted by Boris and Ringo) for which the difference is outside of the uncertainties. For four cells (denoted by Betty, Boris, Snoopy, and Felix and listed in italics in Tables I and II) measurements performed at both Wisconsin and NIST are in reasonable agreement. The overall trends of the data indicate a dependence on S/V but also that some other parameters affect X. However, we note that the wall relaxation contributions to the room temperature relaxation times listed in Tables I and II vary greatly from cell to cell and do not show a clear relationship to S/V. The correlation of X with S/V observed in Fig. 2 is actually more well defined. If we write the surface relaxation as $\alpha(S/V)$, where α is the relaxivity, then any variation in α will be amplified by the value of S/V. However, we note that, particularly for the NIST data, the cell construction and gas pressures are also more consistent at low S/V; whether this affects the consistency of X is a topic for further study.

We note that two early determinations of k_{se} were based on measurements of the variation of the relaxation rate with [Rb] in cells of high S/V, and disagreed with each other by a factor of 2 [16,17]. In retrospect, this disagreement may be related to the substantial cell-to-cell variation in excess relaxation. However, a perplexing question is the low value for the rate coefficient and the high polarizations reported in Ref. [16], both of which would imply cells with X close to zero.

Known contributions to Γ_r include dipole-dipole relaxation (given by $P/800\ \mathrm{h}^{-1}$, where P is the pressure in bar) [11], interactions with the wall of the SEOP cell, and magnetic field gradients [18]. As discussed above, alkali-metal coatings have a substantial effect on wall relaxation, but studies of the temperature dependence of metal-coated cells are quite limited [19]. We have not found any correlation between Γ_r and X.

While most of the cells tested were made from fully blown glass, a subset was made with flat windows that are optically sealed to either blown or commercial glass tubing [10]. Flat-windowed cells typically have larger values of Γ_r. The uncertainty in the S/V values listed is estimated to be 5% for blown cells and 1%–3% for flat-windowed cells, depending on construction. However, we do not have knowledge of the true, microscopic value of S/V, which certainly differs from the geometric value. Although we expect that the surface structure for polished windows is different from that of blown glass, the data for flat-windowed cells, shown as open symbols in Fig. 2, exhibit similar behavior with S/V as seen for blown cells.

Several of the cells tested at NIST contain alkali-metal mixtures for studies of hybrid optical pumping [20]. Orvieto, Chardonnay, and Quasimoto contain Rb and K, and Margarita contains Rb and Na. In the Rb/K cells, the total spin-exchange rate $\gamma_{se}^{Rb/K} = k_{se}^{Rb}[Rb] + k_{se}^{K}[K]$, where k_{se}^{Rb} and k_{se}^{K} are the spin-exchange rate constants for Rb and K, respectively. If we assume that the total relaxation rate is given by $\Gamma_{He} = \gamma_{se}^{Rb/K}(1 + X) + \Gamma_r$, then the limiting polarization is $1/(1 + X)$, as for pure Rb cells. With this assumption, the values of X listed in Table II are similar to those of pure Rb cells.

We have generally observed a linear dependence of the excess relaxation rate, although a different dependence cannot be excluded. It is possible that the excess relaxation phenomenon is not governed by [Rb], but instead might have an exponential dependence on temperature that mimics the rapid increase of [Rb] with temperature. For example, the relaxation could be explained by a dissolution-dominated form of relaxation with an activation energy of the order of 1 eV [8], perhaps associated with the alkali-metal film itself. Cell-to-cell variations could be related to differences in the form and/or purity of the film, but the relaxation would have to be uncorrelated with the permeability, composition, or surface structure of the substrate glass, as well as the room temperature relaxation rate.

Some of the excess relaxation observed could originate from anisotropic spin-exchange [21]. Whereas the isotropic magnetic-dipole hyperfine interaction arising from the contact term polarizes the ^{3}He nucleus in the same direction as the polarization direction of the alkali-metal atoms, the anisotropic interaction arising from the long range term polarizes the ^{3}He nucleus in the opposite direction. Prior calculations [21] indicate that this contribution should be small, but, if nonzero, the measured value for k_{se} using either the rate balance or the repolarization methods [13,14] would be $k_{se}^{m} = k_{se} - (k_{an}/2)$, where k_{an} is the anisotropic spin-exchange rate, and $3k_{an}/2k_{se}^{m}$ would be the measured value of X. Using the lowest values of X that we have observed, $X \approx 0.15$, we set an upper limit of $k_{an}/k_{se} \leq 0.10$. The highest ^{3}He polarization we have observed is 81%, which was obtained in the cell NHRb with $\tau_p = 8$ h. The last column in Table II reports the maximum ^{3}He polarizations observed at NIST, which were typically obtained with values of τ_p between 10 and 16 h.

In summary, we have found that the ^{3}He polarization in SEOP cells is limited by a temperature-dependent relaxation mechanism that is linearly proportional to alkali-metal density within the uncertainties of our measurements. This excess relaxation shows a correlation with S/V, but this ratio is not the only relevant parameter. These results indicate that a surface relaxation mechanism is present, but anisotropic spin-exchange could also be contributing. Future tests include studying a number of small cells, so as to amplify the effect and thus perhaps discover its origin, SEOP with different alkali metals to search for different limits from anisotropic spin exchange, determining whether the value of X in a given cell is constant even when the alkali-metal distillation is repeated, and studying the possible role of the N_2 and ^{3}He gas pressures.

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