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Paramagnetic relaxation of spin polarized ^{3}He at coated glass walls

Part II

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Abstract. In this second in a series of three papers on wall relaxation of ^{3}He-spins we discuss relaxation in metal-coated glass cells in terms of hyperfine coupling to paramagnetic conduction electrons at the Fermi surface. This scales with the square of the work function of the coating and thereby also with its He-adsorption energy. In this sense we investigate coatings with particularly low work function and adsorption energy, namely Cs and Cs-suboxides. Although we observe a suppression of relaxation rates by two orders of magnitude as compared to bare Pyrex and fused silica walls, their temperature dependence still shows the same Arrhenius dependence as observed for bare substrates, instead of a $T^{3/2}$ dependence expected for a metallic surface. From this finding we conclude that, on one hand, the surface coverage is not complete and, on the other hand, the relaxation at the alkali surface itself is extremely slow. This finding is supported, too, by a semi-empirical estimate based on measured relaxation rates at ordinary metal surfaces, rescaled then with the respective dependence on adsorption energy.

PACS. 33.25.+k Nuclear resonance and relaxation – 34.50.Dy Interactions of atoms and molecules with surfaces; photon and electron emission; neutralization of ions – 67.65.+z Spin-polarized hydrogen and helium

1 Introduction

In the course of attempts to suppress wall relaxation in storage cells for spin polarized ^{3}He many different materials have been checked in the past. The first breakthrough in this matter has been achieved by Fitzsimmons et al. [1] who cleared up the dynamics of ^{3}He-relaxation at glass walls and identified the impermeable aluminosilicate glasses as particularly suited. Latest developments in this domain have been reported in the preceding paper in this series [2] referred to as Part I. Later Timsit and Daniels [3] have checked a great number of common metals, semiconductors etc. They found typical surface relaxivities of $\rho = O(1\ \text{cm/h})$, distinctly faster than the limit of $\rho < 0.005$ cm/h reported for aluminosilicate glasses in Part I. Here ρ is connected to the observed wall relaxation rate $1/T_1$ and the surface to volume ratio A/V of the container through

$$1/T_1 = \rho A/V. \tag{1}$$

A decade ago Heil et al. [4] successfully increased T_1 relaxation times in glass vessels to quite interesting values well above 100 h by coating their inner surface with alkali metals, in particular Cs and Rb. Their original suggestion that alkali coating may lead to significant increase of relaxation times was based on the very low adsorption energy of ^{3}He of only $E_{ad} \approx 0.2$ meV on a Cs surface and $E_{ad} \approx 0.24$ meV on a Rb surface, respectively[1] [5,6]. Hence, according to the Frenkel law

$$\tau_s = \tau_{s,0} \exp(E_{ad}/kT) \tag{2}$$

the sticking time τ_s decreases at room temperature to its minimum value $\tau_{s,0}$ of order 10^{-13} s. Even more important arguments are given in Section 2 below.

Nowadays Cs- or Rb-coating of storage vessels for polarized ^{3}He is a well established technique and in use for accelerator targets and neutron spin filters [7–9]. Spin Exchange Optical Pumping (SEOP) with Rb-vapour [10] is profiting automatically from the Rb-film which covers the inner surface of the pumping cell. Wall relaxation rates

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[1] In reference [6] theoretical predictions are made for the adsorption energy E_{ad} of ^{3}He on metal surfaces, which in case of Cs give a somewhat lower value (≈0.13 meV) than observed experimentally [5]. Thus for Rb and other metal coatings we use the listed values multiplied by the factor 1.5.

of ≈1/(250 h) are routinely achieved nowadays in alkali coated glass cells. But recently a record relaxation time of 840 h has been observed in a Rb-coated glass cell [11] manufactured from GE 180 aluminosilicate glass [12]. Subtracting the already dominating ^{3}He-dipole-dipole relaxation rate in the gas phase, which amounts to 1/(950 h) at the partial pressure of 0.85 bar [13], a wall relaxation rate of only 1/(7000 h) remains (or less if other relaxation sources still contribute). In this paper we address:

1. theoretical considerations on ^{3}He relaxation at metal surfaces;
2. extension of ^{3}He relaxation study to Cs-suboxide coatings (Sect. 3);
3. study of temperature dependence of ^{3}He relaxation in coated glass cells (Sect. 4).

Item 2 has been motivated by the speculation on a positive impact of the still lower work function of Cs-suboxides with respect to the pure metal. By item 3 we wanted to check whether the observed relaxation rates in the coated vessels are dominated by the coating, indeed. For metal surfaces we expect a $T^{3/2}$ dependence of the relaxivity (Sect. 2), whereas a glass substrate would show some type of Arrhenius behaviour (see Part I). Moreover, we report on a brief checking of various other coatings, none of them yielding spectacular relaxation times.

2 On the mechanism of ^{3}He relaxation at metal surfaces

In metals and at metal surfaces the nuclear relaxation rate is given by Fermi's golden rule with the Fermi contact interaction entering in the transition matrix-element there [14,15]

$$\frac{1}{T_1} = \frac{64\pi^3}{9}\left(\frac{\mu_0}{4\pi}\right)^2 \gamma_e^2\gamma_{\mathrm{He}}^2\hbar^3 \left|\Psi_F(0)\right|^4 \rho(E_F)^2 kT. \qquad (3)$$

Here $\rho(E_F)$ is the spectral density of electronic states of the metal at the Fermi surface and $|\Psi_F(0)|^2$ is their respective local density at the site of the ^{3}He nucleus. According to theory the adsorption energy E_{ad} scales with $|\Psi_F(0)|^2$ [6] which results in a quadratic dependence of $1/T_1$ on E_{ad}. From this relation a particularly weak relaxation of ^{3}He on Cs surfaces is expected. Moreover, since E_{ad} is connected to the work function W of the metal, a small value of W leads to an extended exponential tail of the electronic density across the surface into vacuum [16] according to

$$\rho_e(z) \propto \exp\left(-2z\sqrt{2m_e W/\hbar^2}\right). \qquad (4)$$

It repels the closed electron shell of an approaching noble gas atom and hence leads to a shallow minimum of the van der Waals potential far away from the surface. This is found at $z = 0.5$ nm in case of Cs, e.g. [6,17]. Combining equations (8) and (9) from [2] and inserting equations (2) and (3) we finally derive the general expression for the relaxation rate $1/T_1$ in a metal coated cell as

Table 1. Workfunction of Cs depending on its stages of oxidation.

	W [eV]	References
pure Cs	2.0–2.1	[6,20–22]
$Cs_{11}O_3$	1.2	[22,23]
Cs_2O	1.0	[20,22]
CsO_2	2.2–2.5	[20,22]

$$\frac{1}{T_1} = \frac{A}{V}\frac{64\pi^3\hbar^3}{9\sqrt{2\pi m}}\left(\frac{\mu_0}{4\pi}\right)^2 \gamma_e^2\gamma_{\mathrm{He}}^2\rho\left(E_F\right)^2\left|\Psi_F\left(0\right)\right|^4 \times \left(kT\right)^{3/2}\tau_{s,0}\exp(E_{ad}/kT). \qquad (5)$$

We use equation (5) for a semi-empirical estimation of T_1 of ^{3}He on Cs or Rb surfaces by comparison with relaxation times which we have measured for some other metal surfaces obeying the same relaxation mechanism. In reference [4] we have reported a relaxation time of 6 h for a Mg surface and in reference [18] the same value was found for an Al surface. Both metals were evaporated as thick layers onto the inner surface of a glass vessel of a size similar to that as discussed above (see also Sect. 5). These metals adsorb ^{3}He with energy of 2.5 meV and 5 meV, respectively [6], as compared to 0.2 meV for Cs. Since we expect the relaxation rate to scale with the square of the adsorption energy, we extrapolate from the results of the Al surface a T_1 in the range of 5000 h for a Cs or Rb surface (assuming the same $\rho(E_F)$ but considering the change in adsorption time τ_s). This number falls well into the range of the observed record value of 7000 h [11]. Hence it may be that in this and only in this experiment the genuine relaxation of ^{3}He on Rb has shown up, unless the residual relaxation has been due to some other undiscovered source. In this context we have to see the two following investigations which we have pursued in the passed years.

3 Cs-suboxide coating

Our first attempt concerned a search for even better coatings speculating on particularly low work functions. It is known that Cs forms a number of suboxides and oxides, whose work function first decreases as function of oxygen content and finally rises again when the stage of the hyperoxide CsO_2 is approached (see Tab. 1). CsO_2 itself is paramagnetic as it contains O_2^--radical anions [19].

In the course of Cs oxidation first clusters $Cs_{11}O_3$ are formed within the Cs metal. In later stages the system runs through many phases and compounds [24]. If a free Cs surface is being exposed to an O_2 partial pressure of 10^{-6} mbar at room temperature, e.g., then it will take only 0.3 s to form a monolayer of $Cs_{11}O_3$ within the Cs film [20]. Such a tiny oxygen dose may occur by mistake in operation during the various manipulations in the course of refilling a Cs coated cell with polarized ^{3}He. Turning a stopcock is a potential risk, e.g. In fact, the T_1 history of

Table 2. Measured wall relaxation times on fused silica glass cells ($V = 350$ cm^3) with different Cs and Cs-suboxide coatings.

storage vessel	$T_{1,wall}$ [h]
Cell #111 coated with Cs	150 ± 4
Cell #111 coated with $CsO_{0.24}$	115 ± 1.5
Cell #111 coated with $CsO_{0.22}$	97 ± 1.2
Cell #111 coated with Cs_7O	570 ± 37
Cell #113 uncoated	7 ± 0.1
Cell #113 coated with Cs	30 ±0.8
Cell #113 coated with $CsO_{0.24}$	27 ± 0.4

some of our Cs coated accelerator target cells (made from Corning glass #7744) has shown an increase from about 100 h to 120 h in the course of several re-fillings [18]. In parallel, the appearance of the Cs surface changed from metallic-golden to white and grey. Moreover we have exposed Cs coatings for a short while to water vapour [23]. This initiated a partial hydrolysis which also leads to an increase of T_1. Hence, we may interpret these observations as a qualitative proof that some oxidation of a Cs coating assists to reduce the relaxation on alkali metal surface coatings.

In order to investigate this effect further, we have introduced macroscopic quantities of Cs suboxides of controlled composition through a brake seal and an appendix into fused silica cells. The suboxides wet the surface better than the pure Cs metal, such that a thick, visible film finally covered more than 50% of the surface. In case of pure metals, on the other hand, an evaporated Cs mirror segregates into droplets leaving large areas open which probably are still covered by very thin Cs layers of only a few monolayers. This should hold also for the suboxides. The results obtained with suboxide coated fused silica glass vessels ($V = 350$ cm^3) are presented in Table 2 [23].

The wall relaxation times vary between 27 h and 570 h (dipolar and gradient relaxation subtracted). These data do, however, not yet allow drawing a final picture of relaxation at Cs- and Cs-oxide surfaces: the apparent drop in cell #113 with respect to cell #111 seems to point to the presence of magnetized contaminants in the former[2]. In any case, the topmost value of 570 h, obtained (once) with a Cs_7O coating is remarkable and represents still the highest observed for a fused silica glass substrate.

4 Temperature dependence of ^{3}He relaxation on Cs coated fused silica and multi-component glass substrates

The second investigation in this context concerned the temperature dependence of ^{3}He relaxation rates in Cs coated vessels [23]. If it would be dominated by relaxation on the free Cs surface, then the rate should rise $\propto T^{3/2}$ according to equation (5) for $E_{ad}/kT \ll 1$. The temperature dependence of the relaxation rate was studied in cells manufactured from fused silica glass and from Corning 1720 glass. Figure 1 shows the results for a spherical fused silica cell of diameter $\Phi = 8.9$ cm ($V = 350$ cm^3) filled with polarized ^{3}He at $p = 1.6$ bar. The cell was investigated first bare, then Cs coated and finally coated with $Cs_{11}O_3$. In this example the Cs coating proved to yield the better relaxation suppression as compared to Cs-suboxide coating. But the latter result may well be superposed by some residual magnetized contamination.

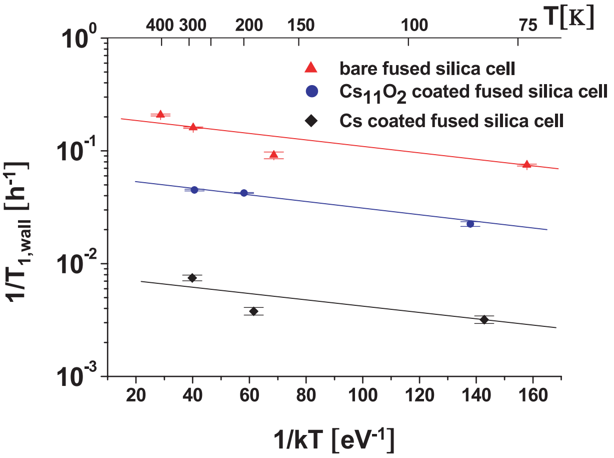

Fig. 1. Semi logarithmic plot of measured wall relaxation rate ($1/T_{1,wall}$) versus $1/kT$ for a bare fused silica cell (▲), the same cell coated with $Cs_{11}O_3$ (●), and coated with Cs (♦). A straight line fit to the data gives an activation energy of $E_{eff} = 0.007$ eV in all three cases. A temperature scale is given on top, in addition.

The striking feature, however, is that in all three cases an Arrhenius plot reveals a relaxation behaviour activated by the same effective activation energy of $E_{eff} \approx 0.007$ eV for bare and coated surfaces. This value is expected for diffusion-controlled relaxation in fused silica for temperatures >70 K (Eq. (17) of [2]). Besides the fact that alkali metal coating provides definitely reduced relaxation as compared to the bare fused silica surface, we conclude from its temperature dependence that the substrate still dominates the residual relaxation. The alkali coating is supposed to seal the fused silica surface, at least partially, and hence inhibit diffusion-controlled relaxation to a certain extent. Whether the residual penetration into the substrate stems from incomplete coverage or diffusion through the microscopically thin alkali coating cannot be decided by this experiment. We also cannot identify a separate relaxation mechanism on the surface of the coating through equation (5).

The temperature dependence of the relaxation rates in one bare and three Cs coated Corning 1720 glass cells is shown in Figure 2. For this aluminosilicate substrate an Arrhenius plot of the quantity $1/(T_1 T^{1/2})$ again reveals about the same slope for bare as well as for coated cells. The positive slope indicates adsorption-controlled

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[2] In this context we have to inform the reader that this particular line of research came to an end in our laboratory before we learned about the risk of magnetized contaminants (compare Part I [2] and Part III [25]).

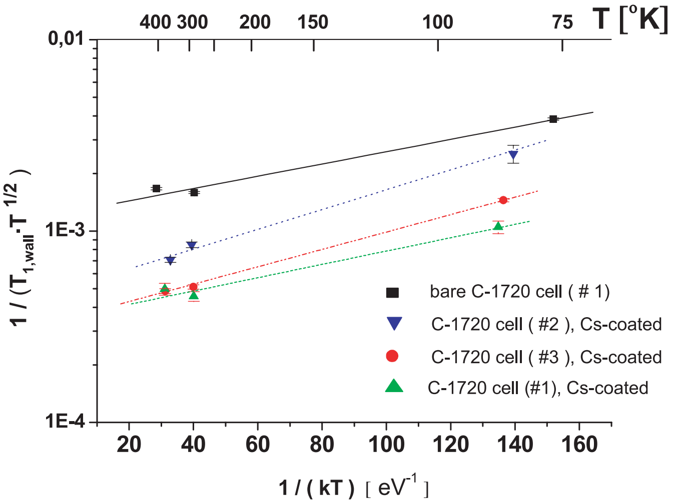

Fig. 2. Plot of $1/(T_{1,wall}T^{1/2})$ versus $1/kT$ for cells made from Corning 1720 glass (adsorption-controlled relaxation). Bare glass cell #1 (■). Cell #1 (▲), cell #2 (▼), and cell #3 (•) Cs-coated. A temperature scale is given on top.

surface relaxation according to equations (11) or (19) of [2]. The adsorption energy is found to vary in the range (3.5–5.4) meV which is a factor of 2 below the literature value of ^{3}He adsorption on glass surfaces but still a factor of ≈20 above that expected for a Cs surface. Moreover, since we expect a linear increase of $1/(T_1\,T^{1/2})$ with T for a complete Cs coverage in the temperature range considered (Eq. (5)), the plots in Figure 2 should even show a down slope. Obviously this does not show up[3].

Again, if coated, the influence of the glass substrate on the relaxation rate is reduced but still it is found to dominate. This behaviour can plausibly be explained by incomplete coverage of the surface up to a fraction x. If now $T_{1,Q}$ (typically 5 h) applies for a bare fused silica cell ($x = 0$) and $T_{1,\mathrm{Cs}}$ (let us assume 5000 h) for a pure Cs surface ($x = 1$), then one can deduce from a measured relaxation time T_1 in-between these limits (for example 150 h) an effective coverage of

$$x = \left(\frac{1/T_{1,Q} - 1/T_1}{1/T_{1,Q} - 1/T_{1,\mathrm{Cs}}}\right). \tag{6}$$

Inserting the numbers in brackets above yields an effective coverage of still 96.8%; much higher than the apparent visual impression. Nevertheless, relaxation and also its temperature dependence are still dominated by the little bare surface fraction. Furthermore we conclude that the observed (modest) improvement of T_1 on oxidizing or hydrolysing a Cs coating should not be ascribed primarily to a lowering of the work function of the respective surface. Rather we suggest that the coverage has improved somewhat by the well known lowering of the surface tension with respect to the glass.

5 Other coatings

In the course of 3 thesis works [18,23,27] we have briefly examined also a number of other coatings on various glass substrates and measured their ^{3}He relaxation times (in brackets): metals: Mg (6 h), Al (6 h), Zn (12 h), Se (5 h), Ag (5 h), Sb (7 h), Te (10 h), Au (20 h), Pb (26 h), Bi (50 h); salts: LiF (8 h), $\mathrm{MgF_2}$(8 h), CsF (25 h), CsCl (18 h); oxides: $\mathrm{Al_2O_3}$ (4 h); hard covalent coatings: diamond (3 h), titanium nitride (2 h). Most of the more volatile species have been evaporated in situ by a removable oven and ^{3}He relaxation has been measured without breaking the vacuum in between [18]. This might have insured the chemical purity of the surfaces but not so their tightness and microscopic flatness. Therefore, their effective surface might exceed the geometrical one by a large factor. Except for the heavy alkali metals and their oxides treated above, we have met only one more noteworthy result, namely the case of Bi [4,27], yielding a T_1 of 50 h on Supremax glass. We trace this back to the lack of paramagnetic conduction electrons at the Fermi surface of Bi, which drive the Korringa type relaxation (Eq. (3)).

6 Conclusions

We have collected some new material on suppression of ^{3}He relaxation in fused silica and glass vessels by wall coating with Cs and Cs-suboxides. Semi-empirical considerations on the basis of comparing work functions, adsorption energies, and local densities of states, lead us to expect extremely long relaxation times of many thousand hours as has been found actually for the case of a Rb coated aluminosilicate glass. For the much faster relaxing fused silica surface we have found a gain in relaxation time by a factor of 100 up to 570 h (in the best case) by coating with $\mathrm{Cs_7O}$. However, we do not find the temperature dependence of the relaxation rate of Cs coated fused silica and aluminosilicate glass to follow a $T^{3/2}$ law as derived for metals from the Korringa relation. Instead it still follows an Arrhenius law expected for the temperature dependence of relaxation at the respective substrate. This seems to point to incomplete alkali coverage of the glass surface.

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[3] In reference [26] the Cs–^{3}He spin-exchange rate coefficient k_{SE} was measured to be $k_{SE} = (13.6\pm1.3)\times10^{-20}$ cm^3/s. This results in a spin-exchange rate γ_{SE} of $\gamma_{SE} = k_{SE}[\mathrm{Cs}] \approx k_{SE} \times 1.2\times10^{13} = 1.6\times10^{-6}$/s at $T \approx 380$ K. Thus the saturation vapour contributes up to ≈0.006/h to the ^{3}He relaxation rate by spin exchange and raises the respective points in Figure 2 by about 0.0003 [$\mathrm{h^{-1}K^{-1/2}}$]. An effect of this size is not seen in the data. Hence we suppose the Cs vapour pressure not to have reached its full saturation value. The decisive slopes in Figures 1 and 2 are determined by the long arm between the points at lower temperatures, where the Cs vapour pressure is $<10^{-6}$ mbar and spin exchange is negligible.

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