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Super strong effect of surface impurities on the resistance and Hall effect of quench condensed Cs films*

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Abstract. Thin films of Cs, quench condensed onto a He cold quartz plate, possess electronic mean free paths which considerably exceed the film thicknesses. When theses films are covered *in situ* with sub monolayers of Au, Ag, In, Rh and Pb in the range between 0.01 and 1 monolayers the film resistance and the Hall constant increase dramatically. This corresponds to a scattering cross section of the surface impurities which is larger than 1 in units of $4\pi/k_F^2$. Various models are explored to explain these unusual behavior. None yields a satisfactory explanation for this extremely strong effect of surface impurities on the resistance and the Hall effect.

PACS. 71.20.Dg Alkali and alkaline earth metals – 72.10.Fk Scattering by point defects, dislocations, surfaces, and other imperfections (including Kondo effect) – 73.50.Yg Other thin film transport-related topics

1 Introduction

In this paper we report about some unusual properties of thin Cs films which have been covered with sub-monolayers of Au, Ag, In, Pb and Rh. The original experiment was performed to investigate whether Rh on the surface of Cs has a magnetic moment [1]. In that experiment we first condensed a thin Cs film with a thickness of 10.2 nm and a resistance of 13.79 Ω onto a He cold quartz plate. In the next step the Cs film was covered with 0.016 monolayers of Rh. During the evaporation the resistance of the Cs film increased from 13.79 Ω to 15.20 Ω. Such a large increase of 10% is very unusual. For Au, Ag and Mg substrates such a small fraction of a monolayer of a transition metal changes the resistance only by 10^{-4}. When we increased the Rh coverage to 0.1 monolayers the resistance increased further to 28.46 Ω. This behavior is so extraordinary that we decided to investigate the properties of Cs films.

The first quench condensed Cs films have been investigated by Appleyard *et al.* [2]. These authors condensed Cs onto a pyrex glass at temperatures down to 65 K. They observed electronic mean free paths of more than 1000 Å.

2 Experiment

The Cs films are evaporated from SAES-Getters Cs evaporation sources which uses Cs_2CrO_4 salt. The films are quenched condensed onto a substrate of He temperature in an ultra high vacuum of better than 10^{-11} torr. After condensation the films are annealed for several minutes at 40 K. We investigated a total of 9 films in which the Cs was condensed in several steps and afterwards covered with sub monolayers of Au, Ag, Rh, Pb and In. Figure 1a shows the conductance (per square) L_{xx} of a Cs film as a function of the Cs thickness. At a thickness of 645 Å the Cs is covered with Ag, beginning with about 1/100 of a monolayer and increasing the Ag coverage up to a monolayer. The resulting change in the conductance L_{xx} is shown in Figure 1b on an expanded scale. The conductance drops by about 20%, already showing a drop of 14% for 1/10 of a Ag monolayer. If one extrapalotes the resistance curve from small and large Ag thicknesses then the two lines intersect at about 0.05 atomic layers of Ag. We observed a similar characteristic coverage for other impurities and other Cs thicknesses (except for very small D_{Cs}). This suggests that the evaporated impurities remain essentially at the surface.

In the same experiment we measured the Hall constant of the film while the Cs was covered with Ag. The result is shown in Figure 2. At the same time when the resistance increases the Hall constant increases as well. We observed a similar behavior when the Cs was covered with Au, Rh, In and Pb. We investigated this phenomena for Cs thicknesses between 50 Å and 700 Å.

For smaller Cs thicknesses the change in the resistance and the Hall constant is more pronounced than for larger films. As an example we take a Cs film with the thickness of 53 Å and a resistance per square of 82 Ω. This film is covered with Pb. Figure 3 shows the resistance change

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* Dedicated to J. Zittartz on the occasion of his 60th birthday

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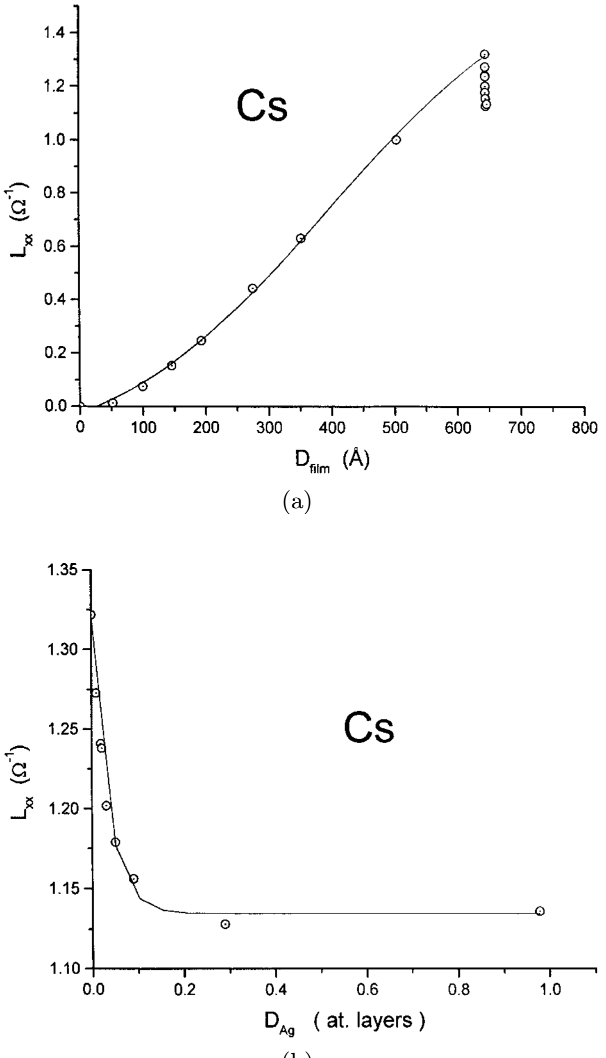

(a)

(b)

Fig. 1. (a) The conductance of a quench condensed Cs film as a function of the Cs thickness and the resistance change to a coverage with Ag. (b) The decrease of the conductance after a sub-monolayer coverage with Ag. The Ag thickness is given in atomic layers.

as a function of the Pb coverage which is given in atomic layers. The resistance increases by a factor of five. A similar change is observed for the Hall constant which increased roughly by a factor of two. In contrast to thick Cs films the increase in resistance does not saturate at small coverages.

The relative change of the conductance $\frac{\Delta L_{xx}}{L_{xx}}$ due to the coverage with different impurities is plotted in Figure 4 as a function of the Cs thickness for Cs films covered with different impurities. The impurity metals are labeled beside the experimental points. The relative change in the conductance clearly increases with decreasing Cs thickness. There is no pronounced difference between different impurities.

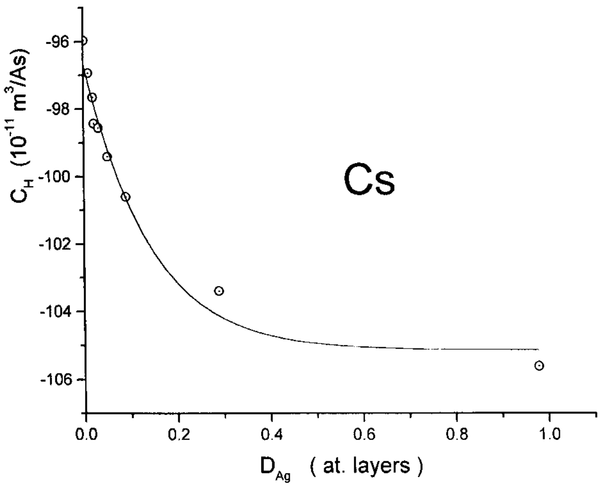

Fig. 2. The Hall constant of the same Cs film as in Figure 1 as a function of the Ag coverage.

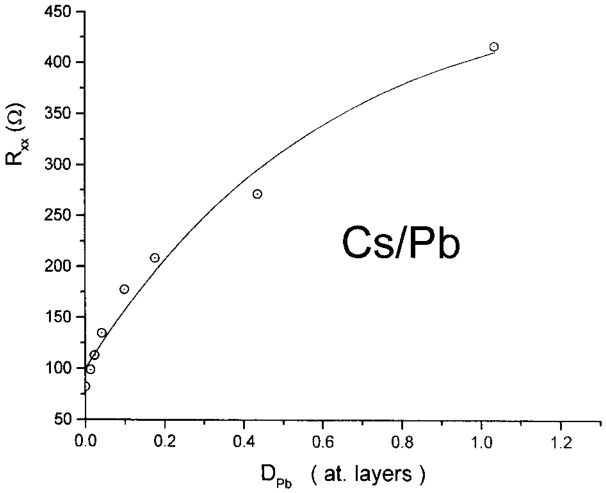

Fig. 3. The increase of resistance of a thin quench condensed Cs film of thickness of 53A due to a coverage of Pb.

In Figure 5 the relative change of the Hall constant $\frac{\Delta c_H}{c_H}$ is plotted for the same impurities. The change in the Hall constant is less reliable than the change in the conductance. Finally in Figure 6 the relative change of the Hall constant $\frac{\Delta c_H}{c_H}$ is plotted *versus* the relative change of the conductance $\frac{\Delta L_{xx}}{L_{xx}}$. Roughly the change in $\frac{\Delta c_H}{c_H}$ is equal to half the change in $\frac{\Delta L_{xx}}{L_{xx}}$.

3 Evaluation and discussion

Before we discuss the change in the resistance and the Hall constant we take a closer look at the Cs film.

3.1 Properties of the Cs film

A quench condensed Cs film with a thickness of 645 Å has a resistance of 0.76 Ω. This is a remarkably small

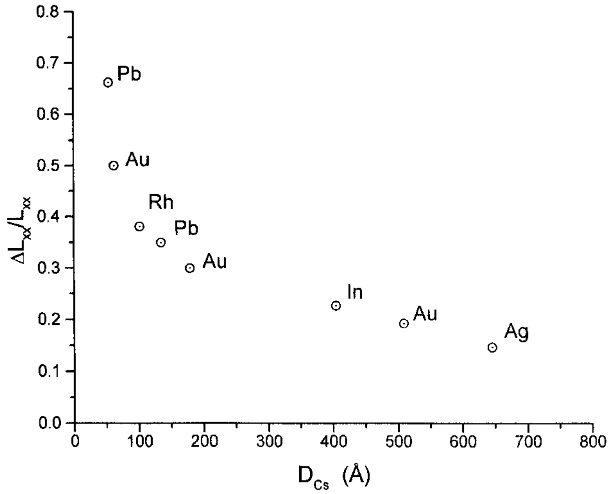

Fig. 4. The relative change of the conductance $\Delta L_{xx}/L_{xx}$ of Cs films of different thicknesses due to the coverage with different surface impurities. The symbols for the impurities are labeled beside the points.

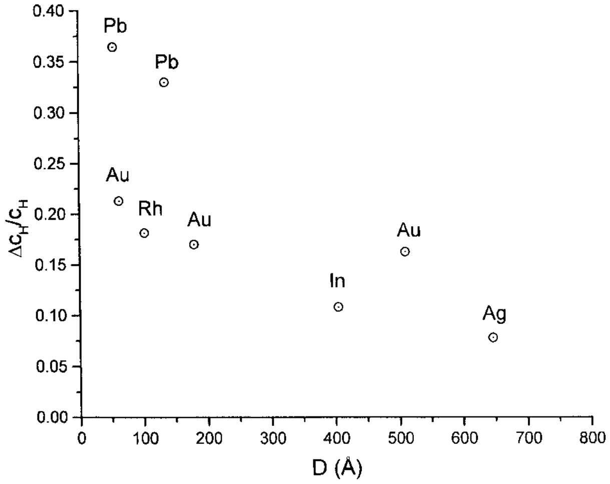

Fig. 5. The relative change of the conductance $\Delta c_H/c_H$ of Cs films of different thicknesses due to the coverage with different surface impurities. The symbols for the impurities are labeled beside the points.

resistance for a quench condensed film and shows that the Cs must have a relatively large (transport) mean free path (mfp). Since we evaporate the Cs in several steps we can calculate the effective mean free path l_{eff} as function of the Cs thickness. According to the free electron model the conductance L_{xx} is given by

$$L_{xx} = \frac{ne^2\tau}{m}D = \frac{e^2}{\hbar}\frac{l_{eff}D}{\Omega_{\mathrm{Cs}}k_F}$$

where D is the thickness of the film, τ is the relaxation time of the conduction electrons, Ω_{Cs} is the atomic volume of Cs, k_F is the Fermi wave number of Cs and l_{eff} is the effective mfp. In Figure 7 this l_{eff} is plotted as function of the Cs thickness. The figure shows two remarkable effects:

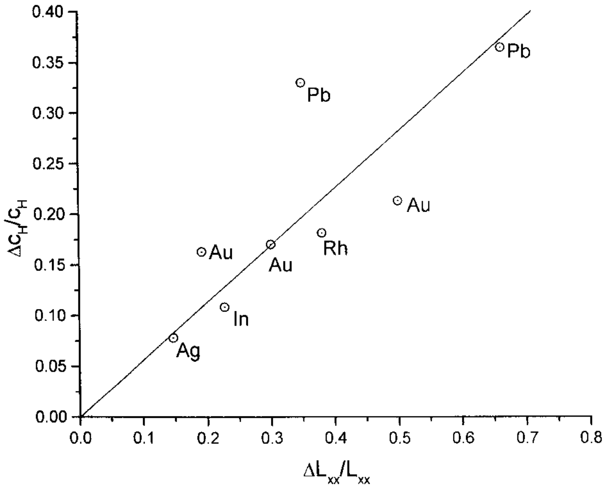

Fig. 6. The relative change of the Hall constant $\Delta c_H/c_H$ *versus* the relative change of the conductance $\Delta L_{xx}/L_{xx}$ for different surface impurities.

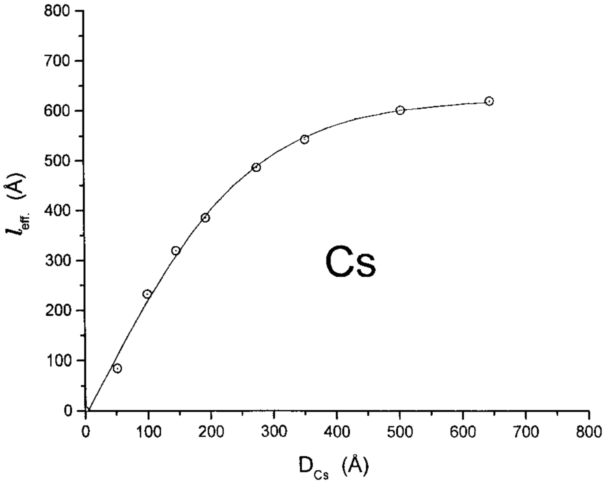

Fig. 7. The effective transport mean free path l_{eff} of a quench condensed Cs film as a function of the Cs film thickness.

(a) the mfp for the full film is remarkably large for a quench condensed film. Normally such films have a mfp of about 20 to 50 Å;

(b) the mean free path for smaller thicknesses exceeds twice the film thickness. This suggests that the surface of the Cs might be to a certain degree specular reflecting. This possibility is particularly interesting for the following reason. If the upper surface is specular reflecting then further deposition of Ag on Cs will progressively introduce a diffuse scattering at the surface and therefore increase the resistance. Therefore this might be a mechanism which could explain the strong increase of the Cs resistance with the Ag coverage.

A film of Cs with a constant bulk mfp l_0 and specular reflection at the surface should show a thickness independent effective mfp. The fact that the observed mfp is thickness dependent may have two reasons:

(a) the film structure improves for thicker films yielding a larger l_0;

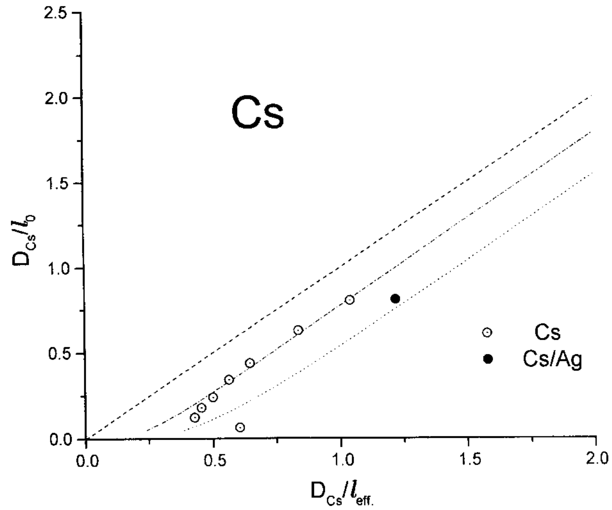

Fig. 8. A plot of $\frac{D}{l_0}$ *versus* $\frac{D}{l_{eff}}$ for a Cs film. The point labeled with "Cs" is obtained before the coverage with Ag and the point labeled "Ag" is obtained after the coverage with Ag. A constant l_0 is assumed. The dashed line is for specular reflection at both surfaces and the dotted curve for diffuse scattering at both surfaces. The dashed-dotted line is for one surface with specular reflection and the other with diffuse scattering.

(b) the bulk mfp l_0 is constant and the surface scattering is partially diffuse yielding a reduction in l_{eff}.

We will first try how far we can go with the assumption of a constant bulk mfp l_0. We consider two different cases:
(α) the fraction p of the conduction electrons is diffusively scattered at both surfaces;
(β) at the lower surface the fraction p of the conduction electrons is diffusively scattered while the upper surface has specular reflection.

α) According to Fuchs [3] the conductance of a film with diffusively scattering surfaces is

$$L_{xx} = \frac{e^2 S_F}{12\pi^3\hbar}\left(Dl_0 - p\frac{3}{8}T_x(\frac{D}{l_0})l_0^2\right) \qquad (1)$$

$S_F = 4\pi k_F^2$ is the area of the Fermi surface and $T_x(s)$ is given by

$$T_x(s) = 4\int_0^1 \left(\left(1-u^2\right)u\left(1-e^{-\frac{s}{u}}\right)\right)du \qquad (2)$$

with $s = \frac{D}{l_0}$.

β) If only the lower surface causes diffusive scattering then equation (1) must be slightly modified by replacing $T_x(s)$ by $\frac{1}{2}T_x(2s)$.

In Figure 8 we have plotted the theoretical dependence of $\frac{D}{l_0}$ *versus* $\frac{D}{l_{eff}}$. For perfect reflection one has a straight line with the slope 1 (dashed line). The dotted curve gives the theoretical result for full diffusive scattering ($p = 1$) at both surfaces and the dashed-dotted curve corresponds to complete diffusive scattering at one surface. Both curves are rather close to a straight line with a displacement of 0.45 and 0.22 respectively. To compare this theoretical behavior with our experimental results we take the experimental values for $\frac{D}{l_{eff}}$ from Figure 7. Since we do not know the bulk mpf l_0 we may first choose such a value for l_0 that the point $(\frac{D}{l_0}, \frac{D}{l_{eff}})$ lies on the dashed or full curve. We do this for the largest thickness. Since we assume a constant bulk mfp l_0, the $\frac{D}{l_0}$ values for the other thicknesses are determined from the choice of our first point. For a constant l_0 and p the resulting curve should be parallel to the theoretical curves. If this is not the case then we have to modify the choice of the first value for $\frac{D}{l_0}$. This scales the $\frac{D}{l_0}$ value for all other thicknesses. (In a log-log plot one just has to shift the curve vertically.) Our fitted experimental points lie on the dotted-dashed curve (for sufficient large Cs thickness). For this portion we obtain a bulk mfp of $l_0 = 730$ Å. The total fraction of diffusive scattering at the surface is $p = 0.5$. If we assume that one surface (the upper one) reflects specularly then the p-value of the other (lower) surface is 1. We can not determine the fraction of diffuse scattering at each surface. For smaller thicknesses the experimental curve deviates from the theoretical straight line. This is an indication that the bulk mfp l_0 for smaller thicknesses is reduced.

We consider this evaluation only as a semi-quantitative one since there are too many unknown facts involved (such as structure as a function of thickness and evaporation, structure of lower and upper surface, *etc.*). However, it gives us a reasonable model for the properties of the film.

3.2 Resistance and Hall constant change due to impurity coverage

The coverage of the Cs film by Ag, Au, Rh, In and Pb causes a strong increase of the resistance and the Hall constant. In the past we have performed numerous experiments in which a thin film of the metal A was covered with a second film of the metal B, the latter often in a thickness range down to 1/100 of a monolayer. In all these experiments we had no evidence that there was any diffusion of the metal B into the metal A. On the contrary, in many cases one could clearly distinguish the properties of surface impurities from those of bulk impurities and in all these cases it could be shown that the atoms of the second film stayed on the surface of the first one. Generally the change of resistance due to 1/100 monolayer of a second metal is 10^{-4} or less while in some of our Cs experiments we found a resistance increase of 10% or more.

Similarly the large increase of the Hall constant in the Cs experiments is rather unusual. When we add Ag or other surface impurity atoms the average concentration of conduction electrons is increased because the number of electrons per volume is much higher in these impurity metals than in Cs. However, experimentally we observe the opposite, $-c_H$ increases with the condensation of the impurities.

As we will see below it is rather difficult to explain these large changes in the resistance and the Hall constant. Therefore we will discuss several models some of which may appear rather unrealistic. But they will hopefully clarify the challenge presented by these experiments.

We consider the following three models:
(a) the impurities are homogeneously dissolved in the Cs;
(b) the impurities stick to the upper surface which originally was perfectly reflecting and introduce diffusive surface scattering;
(c) the impurities passivate a finite thickness d of the top layers of the film.

First, we want to discuss this phenomena for the Cs/Ag film in some detail.

3.2.1 Randomly dissolved Ag impurities inside the Cs film

The largest contribution of single impurities to the resistance of a film is generally obtained when the impurities are randomly dissolved in the film. We discuss this model first because it gives us a feeling for the magnitude of the required scattering strength.

The dimensionless scattering cross section σ' of bulk impurities is given by

$$\sigma' = \frac{\sigma k_F^2}{4\pi} = \sum_l l \sin^2(\delta_l - \delta_{l-1}) \tag{3}$$

where σ is the transport scattering cross section and δ_l are the Friedel phase shifts (see for example [4]). For Ag impurities in Cs one expects that only δ_0 differs noticeably from 0. This yields $\sigma' \simeq \sin^2\delta_0$. From our experimental data we find $\sigma = 1/(n_{\mathrm{Ag}} l_{\mathrm{Ag}})$, with $n_{\mathrm{Ag}} = \frac{d_{\mathrm{Ag}}}{d_{film}\Omega_{\mathrm{Ag}}}$ being the Ag concentration (Ω_{Ag} is the atomic volume of the Ag atoms). Here l_{Ag} is the mean free path which is caused by the Ag atoms alone, *i.e.*, $1/l_{\mathrm{Ag}} = 1/l_{\mathrm{Cs/Ag}} - 1/l_{\mathrm{Cs}}$. We calculate the mean free paths from the conductances using the free electron model for Cs. This yields a remarkable large scattering cross section with $\sigma' = 0.8$ for the first 1/100 monolayer of Ag dropping down to 0.5 at 1/10 of a monolayer of Ag. These values of σ' are about the maximal that one can expect for s-scattering with $\delta_0 = \pi/2$. For the other (surface) impurities Au, Rh, In, Pb we obtain similar values of σ' in the range between 1 and 2. The values of σ' fluctuate somewhat but do not show a clear dependence on the thickness of the Cs films.

This model of randomly distributed Ag impurities requires a very large scattering cross section of the impurities to explain the large change in resistance. Furthermore we consider this model as unrealistic for two reasons, (i) it required a diffusion of the Ag atoms at helium temperature over a distance of more than 600 Å and (ii) randomly distributed impurities might explain the increase in the resistance but they are unable to explain the increase in the Hall constant. Since the Fermi surface of Cs is not intersected by any Bragg plane, impurity scattering has only a very minor effect on the Hall constant [5]. Nevertheless this model throws some light on the scattering problem.

3.2.2 Diffusive surface scattering due to the Ag impurities

In this model we consider the Cs film as having perfect surfaces. The electrons are specularly reflected and have a bulk scattering rate τ_0 , *i.e.*, a bulk mean free path $l_0 = v_F\tau_0$ (v_F is the Fermi velocity). If one introduces diffusive scattering at the (upper) surface then electrons with different **k**-orientations will have different mean free paths. Electrons with their momentum perpendicular to the surface have a shorter relaxation time than those parallel to the surface. This increases, of course, the resistance of the film. Such a broadening of the relaxation time spectrum may also increase the Hall constant. This is suggested by a simple consideration. The longitudinal conductance (per square) of a thin film with length equal to width W is given by $L_{xx}=\frac{ne^2\langle\tau\rangle}{m}D = \frac{N}{W^2}\frac{e^2}{m}\langle\tau\rangle$ where N is the total number of electrons in the film and $\langle\tau\rangle$ represents the ensemble average over the relaxation times τ_0. Its transverse conductivity is given by $L_{xy} = \frac{N}{W^2}\frac{e^2}{m}\frac{eB}{m}\langle\tau^2\rangle$. This yields for the Hall resistance $R_{xy} = \frac{D}{ne^2}\frac{\langle\tau^2\rangle}{\langle\tau\rangle^2}B$. The Hall constant is enhanced by the ratio $\frac{\langle\tau^2\rangle}{\langle\tau\rangle^2} > 1$. Therefore the diffusive surface scattering appears to be a promising model to explain both the increase of the resistance and the Hall constant.

If we assume that the upper surface of the Cs film is perfectly reflecting before the Ag is deposited and that the Ag atoms at the surface have a scattering cross section σ then they will introduce the fraction p of diffuse surface scattering with $p = n_{\mathrm{Ag},2}\sigma$ where $n_{\mathrm{Ag},2}$ is the two dimensional concentration of Ag atoms on the Cs surface, *i.e.*, $n_{\mathrm{Ag},2} = \frac{d_{\mathrm{Ag}}}{\Omega_{\mathrm{Ag}}}$. The maximum increase of the resistance can be obtained from Figure 8 by moving from the point denoted by "Cs" to the right by the distance 0.22. This changes the ratio $\frac{D}{l_{eff}}$ from the value 1.04 to 1.26. This corresponds to a 21% increase of the resistance due to a transition from perfect specular reflection to total diffusive scattering. Our maximal experimental change in the resistance is 20%. Therefore the experimental change can be explained by diffusive surface scattering, but just barely.

This surface scattering requires a scattering cross section of the Ag atoms which is still larger than in the bulk case we discussed above. For a Ag coverage of 1/50 atomic layers the change in resistance is 0.05 Ω which is just 6.5% of the Cs resistance of 0.76 Ω. Since for $p = 1$ the resistance change is 20% the first 1/50 atomic layers of Ag introduce $p = 0.33$ diffusivity on the surface. The concentration $n_{\mathrm{Ag},2}$ of the Ag atoms on the surface is $n_{\mathrm{Ag},2} = \frac{0.05A}{17A^3} = 2.9 \times 10^{-3}A^{-2}$. This yields a $\sigma_{\mathrm{Ag},2} = 113A^2$ or for the dimensionless scattering cross section $\sigma'_{\mathrm{Ag},2} = 2.2$. This is a remarkably large scattering cross section for the Ag.

However, the main challenge is to explain the change in the Hall constant. In an earlier paper one of the authors [6] calculated the Hall constant for a thin film with diffusive surface scattering. The result can be transferred to the present problem. We find for the Hall conductivity of a film with one specularly and one diffusively scattering surface

$$L_{xy} = -\frac{e^2 S_F}{12\pi^3\hbar}\tau\omega l_0\left[D - \frac{3}{8}l_0 T_y(\frac{D}{l_0})\right] \tag{4}$$

where $T_y(s)$ is given by

$$T_y(s) = 1 - 4 \int_0^1 \left(1 - u^2\right) \left(e^{-2\frac{s}{u}} (u + s)\right) du. \qquad (5)$$

The evaluation of equations (4,5) indeed yields a considerable change in L_{xy} due to additional diffusive surface scattering. However, if one calculates the resulting Hall resistance then the changes in L_{xy} and L_{xx} cancel for the range of interest in this investigation. Down to a ratio of $s = 0.5$ the Hall constant changes by at most 2%. For the Cs film, covered with Ag, the ratio $\frac{D}{l_0}$ is about 0.7. Therefore we have to conclude that the surface scattering can barely explain the increase in the resistance and fails to explain the change in the Hall constant.

3.2.3 Passivated layers of Cs

An increase in the resistance and the Hall constant is obtained if one reduces the effective thickness of the Cs film. Let us assume for a moment that the surface impurities passivate some layers of the Cs so that the transport current flow essentially through the rest of the film. The thickness of the passivated layers may be d. Then the experimentally observed Hall constant is enhanced by the factor $\frac{D}{D-d}$. In this model the effective thickness $(D - d)$ is reduced by the same factor as the effective Hall constant is increased. This factor for the Cs film with a coverage of 1 atomic layer of Ag is 10% , which means that the passivated layer thickness is about 65 Å. For the calculation of the resistance increase due to a passivated layer one has to know how the latter influences the surface scattering. If we ignore this question for the moment then we can use the plot of the conductance *versus* Cs thickness to obtain the Cs thickness for which the conductance has the same value as after the coverage with the Ag. This yields $(D - d) = 550$ Å or $d = 90$ Å. The passivated layer thickness would be smaller if it introduces partial diffuse scattering which would account for part of the increase in the resistance. For the Cs films below 100 Å thick the passivated film thickness d is about 30 Å for the Hall constant and the resistance.

For a coverage of 0.05 Å of Ag the change in the Hall constant is 1.7%. This yields $d = 11$ Å. The Ag thickness of 0.05 Å contains $\frac{0.05}{\Omega_{\mathrm{Ag}}}$ Ag atoms per unit area while 11 Å of Cs contains $\frac{11}{\Omega_{\mathrm{Cs}}}$ Cs atoms. This means that one Ag atom passivates $\frac{11\Omega_{\mathrm{Ag}}}{0.05\Omega_{\mathrm{Cs}}} \approx 30$ Cs atoms. It is difficult to imagine a physical (or chemical) process which could achieve such a large effect on the Cs atoms. The only process which comes to our mind is the following: The Ag atoms penetrate into the Cs down to a depth of 60 Å. Along their path they destroy the crystalline order of the Cs film, leaving a highly disordered structure behind whose mean free path is much shorter than l_0. Therefore the current is essentially restricted to the rest of the Cs film with the effective thickness of $(D - d)$. Presently we do not believe in this interpretation and mention it only for completeness. At the present time we have no satisfactory explanation for the great increases in resistance and Hall constant.

4 Conclusions

Thin films of quench condensed Cs have been covered with various surface impurities. The Cs films possess a surprisingly large mean free path and the measurements suggest a partially specular reflecting surface. A very small coverage with different metals cause a dramatic increase in the resistance and the Hall effect of the films. We tried to interpret the experimental results within several models. These models were
a) homogeneously distributed impurities in the bulk of the film;
b) surface scattering due to the impurities;
c) passivation of a finite thickness of the film.

All these conventional models were either not able to explain all effects and/or it was not clear how their physical realization could be achieved. Therefore we might have to consider more unconventional explanations. The one most important property which distinguishes Cs from all other metals is its small electron density. The volume that a single electron occupies corresponds to a sphere with the radius of $r_s = 5.7a_0$ where a_0 is the Bohr radius. For such a large value of $\frac{r_s}{a_0}$ the Coulomb energy (including the exchange term) is of the same order of magnitude as the kinetic energy. Under these conditions the Coulomb energy can drastically change the electronic state [7]. For example in the Hartree-Fock approximation a ferromagnetic state has a lower energy than the paramagnetic free electron state. Furthermore Overhauser predicted the existence of spin-density waves [8,9] or charge density waves in alkali metals [10]. Such a state with spin-density or charge-density waves could be easily affected by surface impurities because these represent a δ-like electron density at the surface of the Cs film and alter the boundary conditions. At the present time this scenario is merely a hypothesis. We are considering possible experiments to test this idea.

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