Mystery of the Alkali Metals: Giant Moments of Fe and Co on and in Cs films

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Thin films of Cs are covered with $\frac{1}{100}$ of a monolayer of Fe or Co. Then the impurities are covered with several atomic layers of Cs. The magnetization of the films is measured by means of the anomalous Hall effect. The magnetization follows a Brillouin function with a magnetic moment of about 8 Bohr magnetons for Co on the surface and in the bulk of the Cs. For the Fe impurities, a magnetic moment of 7 Bohr magnetons is observed. These large moments suggest that the $3d$ impurities polarize the conduction electrons of the Cs similar to the giant moments in Pd.

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The alkali metals are described in the majority of solid state textbooks as the best example of a nearly free electron system. de Haas–van Alphen measurements [1,2] yield Fermi surfaces for the alkali metals that deviate very little from a perfect sphere, for example, for Na, by less than 0.1%. Measurements of the transport properties yield, however, a mixed picture. While some can be described within the free electron model [3], other cannot (see Overhauser's review paper [4]). Overhauser argues that the Coulomb interaction causes an instability in the electron system of the alkali metals which results in macroscopic charge-density waves, and he has collected a large body of experimental data which support his model.

Our group recently discovered a number of surprising properties of thin Cs films [5,6]. As an example, if a Cs film, 8.2 nm thick, is covered with 0.1 atomic layers of In, then the resistance increases by 58%, the Hall constant by 15%, the temperature dependence of the resistance by 12%, and the electron dephasing rate by 15%. The origin of this behavior is unknown. A detailed discussion of various attempts to explain this unusual behavior is given in [5].

In this paper we investigate the properties of magnetic impurities on the surface and in the bulk of Cs films. Our experimental method is the anomalous Hall effect (AHE). In metals or alloys with magnetic moments one observes, besides the normal Hall effect, also an "anomalous" component which results from the asymmetric scattering of the conduction electrons by the magnetic moments. This anomalous Hall resistance (AHR) is proportional to the magnetization of the magnetic atoms (see, for example, [7]). It has been used by one of the authors to investigate the magnetic moments of Fe on Pb films [8], to investigate the occurrence of dead Ni layers on the surface of polyvalent metals [9], and to observe the magnetization below the Curie temperature and the susceptibility above the Curie temperature in NiAu alloys [10], etc. [11]. For Fe impurities in Pd films giant moments of about $16\mu_B$ were observed [12]. Obviously, the AHE is a very powerful method in the investigation of magnetic properties, and we apply this method to investigate the moments of Fe and Co on the surface and in the interior of thin Cs films. For this purpose we prepare thin Cs films which are covered with $\frac{1}{100}$ of a monolayer of Fe or Co.

The Cs films are evaporated from SAES-Getters Cs evaporation sources. Prior to the evaporation of the Cs we condense a thin layer of MgF_2 onto a quartz substrate. The purpose of this insulating film is to have a fresh clean substrate onto which the Cs is then condensed. The quartz substrate is at He temperature and the ultrahigh vacuum is better than 10^{-11} torr. After the condensation the films are annealed for several minutes at 40 K. The magnetoresistance and the Hall resistance are measured in the field range between $-7 \le B \le +7$ T at several temperatures: 4.5, 6.5, 9.5, 14, and 20 K. Then the surface impurities of Fe or Co are condensed on top of the Cs film. As an example we discuss the investigation of a Cs film with Co impurities.

(i) A Cs film with a thickness of 7.3 nm and a resistance of 154 Ω is condensed and investigated.

(ii) The Cs film is covered with about 0.010 atomic layers of Co. The resistance increased to 181 Ω.

(iii) The Cs/Co "sandwich" is covered in two steps with a total of 1.5 and 4.9 nm of Cs.

After each condensation the sandwich is annealed to 35 K and the magnetoresistance and Hall resistance of the sandwich are measured.

The Hall resistance of pure Cs (and Cs with surface impurities) is slightly nonlinear in the magnetic field. This nonlinearity $\Delta R_{yx}/R_{yx}(7\ \mathrm{T})$ (the maximal deviation from linearity divided by R_{yx} at the maximum field of 7 T) is rather small, of the order of 7×10^{-4}, and does not interfere with our investigation.

When we superimpose the Cs film with 0.01 atomic layers of Co, the Hall resistance shows a clear deviation from linearity. At 4.5 K the nonlinearity is about 110×10^{-4}. This nonlinearity is caused by the anomalous Hall effect of the Co atoms and is a clear indication that the Co atoms are magnetic. We now divide the Hall resistance into a linear part, the normal Hall resistance, and a nonlinear anomalous Hall resistance which is proportional to the magnetization perpendicular to the film. We try

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to express the AHR by a Brillouin function $B_J(x)$ which describes the magnetization of noninteracting magnetic moments with the spin J and the Lande-factor g at the temperature T in a magnetic field B. The Brillouin function has the form

$$B_J(x) = \frac{2J+1}{2J}\coth\left(\frac{2J+1}{2J}\,x\right) - \frac{1}{2J}\coth\left(\frac{1}{2J}\,x\right), \qquad x = \frac{gJ\mu_B B}{k_B T}, \tag{1}$$

where k_B is the Boltzmann constant and μ_B is the Bohr magneton. We set $g = 2$ and adjust the total spin for the optimal fit of our experimental data. In Fig. 1 we show the anomalous Hall resistance of the Co atoms with reversed sign. (The anomalous Hall resistance of Co is negative.) The full curves are calculated with Brillouin function and have the form $A_0 B_J(x)$, using a spin of $J = 4.5$ and the amplitude of $A_0 = -0.038\ \Omega$. That means that all five theoretical curves are calculated with one (optimal) spin value, one fitted amplitude, and the experimental temperatures. The points in Fig. 1 are obtained from the experimental Hall resistance by subtracting for each temperature a linear Hall resistance (linear in the field B) which we define as the normal Hall resistance. Below we discuss an example where we can check the consistency of the extracted normal Hall resistance.

The points in Fig. 1 represent the magnetization of the Co atoms in arbitrary units. This large spin, $J = 4.5$, used to generate the theoretical curves, corresponds to a moment of the Co atoms of $\mu = gJ\mu_B = 9\mu_B$. This is a giant moment which is much larger than the moment of a Co atom which lies between $1\mu_B$ and $2\mu_B$.

We repeat the same evaluation for the CsCoCs sandwiches which represents a solid Cs(Co) solution since now the Co atoms are bulk impurities. In film No. 3 the Co is covered by only 3 atomic layers of Cs while in film No. 4 the Cs coverage is 10 atomic layers. The evaluation of film No. 3 yields a moment of $\mu = 8\mu_B$ and an amplitude of the AHR of $-0.037\ \Omega$ while film No. 4 can be best fitted with a moment of $(7-8)\mu_B$ and an amplitude of $-0.011\ \Omega$. The fits are of similar quality to Fig. 1.

The experiment with Fe on the surface and in the bulk of Cs yields similar results. Figure 2 shows the AHR of Fe on the surface of Cs with thickness of 4.94 nm and a resistance of 166 Ω. The Fe coverage is 0.01 atomic layers. This time we plot ΔR^{AHE} versus the ratio B/T. Then one obtains a universal curve. The full curve is a theoretical fit with $\mu = 7\mu_B$ and a saturation value of $-0.145\ \Omega$.

The AHR of Fe on Cs is negative. Normally Fe impurities have a positive AHR in the bulk of a host metal (bulk impurities). However, single Fe atoms on the surface of Pb [8] or Cu [13] show a negative AHR. The probable reason is that the large "crystal" field at the surface alters the internal occupation of the d states in the Fe atom. A theoretical investigation of this behavior has not yet been undertaken.

In this experiment we also test the dependence of the magnetic behavior on the Fe coverage (concentration) by adding another 0.01 atomic layer of Fe on the surface of Cs. The resulting magnetic moment hardly changed. We obtain a good fit with $\mu = 7.5\mu_B$. This result shows that the giant moment is not caused by clustering of Fe atoms, because the size of the clusters and the number of clusters would increase with a higher power of the concentration.

The saturation value of the AHR increases from $-0.145\ \Omega$ for the 0.01 atomic layers to -0.185 for the coverage of 0.02 atomic layers of Fe. The fact that the amplitude does not double probably has the following reason: The condensation of the first $\frac{1}{100}$ atomic layer of

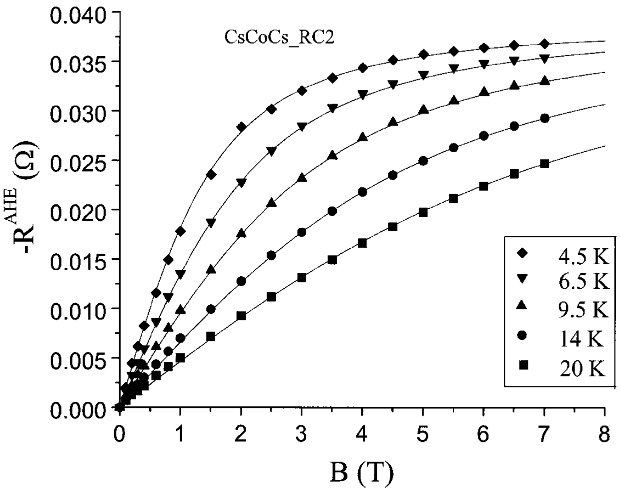

FIG. 1. The (negative) anomalous Hall resistance $-R^{\mathrm{AHE}}$ of Co impurities on the surface of a Cs film. The solid curves are fits using a Brillouin function [Eq. (1)] with spin $J = 4.5$ and an amplitude fitted only to the highest curve.

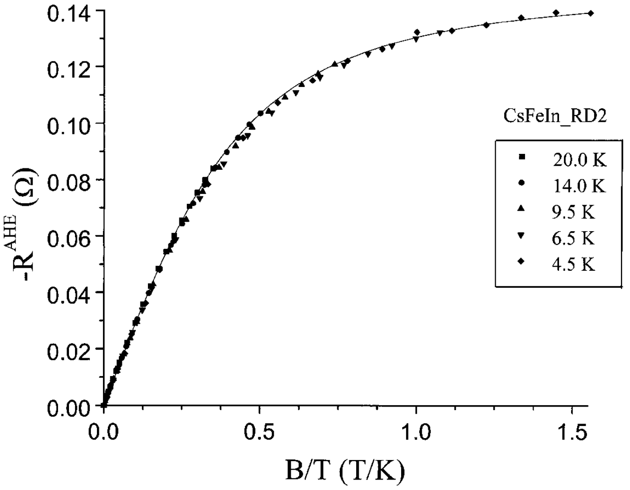

FIG. 2. The (negative) anomalous Hall resistance $-R^{\mathrm{AHE}}$ of Fe impurities on the surface of a Cs film as a function of B/T (universal plot).

Fe increases the resistance of the Cs film by 55 Ω and the second $\frac{1}{100}$ atomic layer by 48 Ω. This is the same behavior that we observed for other impurities such as Cu, Ag, Au, In, Pb, and Rh on the surface of Cs [5]. Its origin is still mysterious. This increase of the resistance reduces the mean free path of the conduction electrons in the Cs film, most likely close to the surface. The AHR of the Fe is proportional to the mean free path of the asymmetrically scattered electrons. So adding more Fe increases the number of (asymmetric Fe) scatterers but reduces their individual contribution to the AHR.

In the next step we cover the CsFe film with 2.4 nm of Cs. Now the Fe atoms are bulk impurities. The plot in Fig. 3 shows that they maintain their magnetic moment of $\mu = 7\mu_B$. Again we plot ΔR^{AHE} versus B/T and obtain a universal curve. This time the AHR is positive, which is the ordinary behavior of (bulk) Fe impurities. This change of sign in R^{AHE} gives us an important confirmation. Since the AHR has an opposite sign for surface and bulk Fe impurities we can easily distinguish between the two locations. The negative sign of R^{AHE} for the quench condensed Fe atoms gives a unique proof that the Fe atoms do stay at the surface and do not diffuse into the Cs (where the AHR would be positive).

In our fit and evaluation we split the total experimental Hall resistance into an anomalous Hall resistance and a normal Hall resistance. The anomalous Hall resistance is proportional to a Brillouin function, and the normal Hall resistance is linear in the magnetic field. We have seen in Figs. 1–3 that we can find a split where the anomalous part fits nicely a Brillouin function. It would be rather satisfying if we could find additional support that the remaining linear Hall resistance is, indeed, the normal Hall resistance. One might expect that the normal Hall resistance should be temperature independent. However, for Cs with its low Debye temperature, we find in films of 100 Ω still a change of 1% in the Hall constant between 4.5 and 20 K with a negative temperature coefficient. (The Hall constant is proportional to the linear part of the Hall resistance.) Since we cannot quantitatively describe this temperature dependence, it is not well suited for a consistency test.

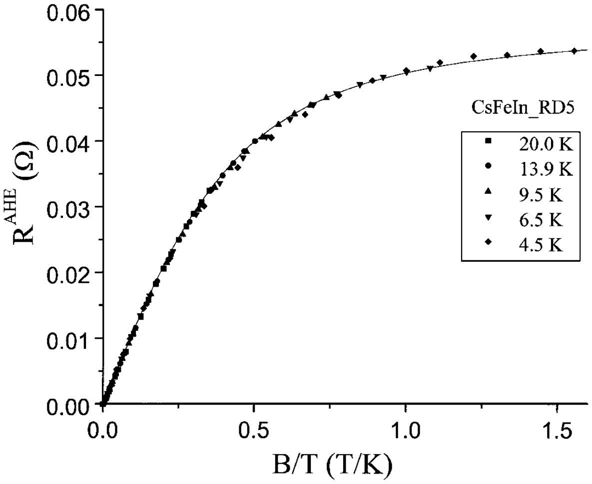

FIG. 3. The universal plot of the (positive) anomalous Hall resistance $+R^{\mathrm{AHE}}$ of Fe impurities in the bulk of a Cs film.

There is, however, one universal theoretical prediction about the Hall constant in disordered thin films. According to Altshuler *et al.* [14], the Hall constant shows a Coulomb anomaly as a function of temperature. If one plots $Y_H(T) = (1/R_0 L_{00})[C_H(T)/C_H(T_0)]$ (R_0 is the residual resistance per square and $L_{00} = e^2/2\pi^2\hbar$ is the universal conductance) as a function of $\ln(T)$, then one should obtain a straight line with the slope $-2(1 - F)$ where $F \ll 1$ is a screening factor. For films with sufficiently high resistance this logarithmic temperature dependence is dominant. To address this question we investigate a Cs film with a rather high resistance of 2443 Ω. For the pure Cs film with the above resistance we find a slope of (-1.5) for Coulomb anomaly of the Hall constants. When we cover this Cs film with about 0.01 atomic layer of Fe the plot of $Y_H(T)$ is no longer linear in $\ln(T)$, and, furthermore, it increases with temperature. However, when we fit the spin of the Fe atoms and subtract the resulting anomalous contribution of the Hall resistance, then the remaining normal Hall resistance yields a temperature dependence of $Y_H(T)$ which is reasonably linear in $\ln(T)$ and has a slope of (-1.75). This demonstrates the consistency of the evaluation.

The great question is why do we find giant moments for Co and Fe on the surface and in the bulk of Cs. There is a famous example for giant moments in solid state physics: The $3d$ impurities Mn, Fe, and Co possess moments of about $12\mu_B$ to $16\mu_B$ in a palladium host. In a much earlier work one of the authors [12] used AHR to confirm the giant moment of Fe in Pd, and showed that the AHR is well suited to detect a very small number of moments. The reason for the giant moments in Pd is the large Coulomb-exchange interaction in Pd which results in a large Stoner enhancement factor $1/(1 - NU)$ (N is the density of states at the Fermi surface and U is the exchange interaction). Palladium with its large Stoner factor is on the borderline to ferromagnetism (generally described as nearly ferromagnetic). It is well known that Cs, due to its small electron density, has the largest ratio of $r_s/a_0 = 6.5$ (r_s is the radius of a sphere which contains one electron and a_0 is Bohrs's radius). Wigner [15] showed that a Hartree-Fock calculation for Cs yields a ferromagnetic ground state. However, the correlation energy restores the paramagnetic state as the ground state. Our experiments show that the Coulomb interaction has profound consequences in Cs.

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