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Giant moments of Fe and Co on and in rubidium and potassium films

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Abstract. Thin quench-condensed films of Rb and K are covered with 1/100 of a mono-layer of Fe or Co. Then the impurities are covered with several atomic layers of the host. The magnetization of the films is measured by means of the anomalous Hall effect (AHE). The magnetization follows a Brillouin function with a magnetic moment of more than 10 Bohr magnetons for bulk Co and Fe impurities. These moments are much larger than the moments of the atomic configurations of Fe and Co and suggest enhanced magnetic moments of the impurities.

PACS. 75.20.Hr Local moment in compounds and alloys; Kondo effect, valence fluctuations, heavy fermions – 71.20.Dg Alkali and alkaline earth metals – 73.50.-h Electronic transport phenomena in thin films

The alkali metals are rather distinct from all other metals in the periodic system. For one thing they are very open metals, *i.e.* the volume of the alkali ions take only a small fraction of the total metal volume. Furthermore the Coulomb interaction plays an important role in the alkali metals. This has been studied in particular for Cs, which has the smallest electron concentration of any metallic element ($r_s = 6.6$). Already Wigner [1] showed that a Hartree-Fock calculation for Cs yields a ferro-magnetic ground state. Overhauser [2] discovered that a spin- and charge density state has even lower energy (in Hartree-Fock) and developed the charge-density wave model of the alkali metals.

Our group recently discovered a number of surprising properties of thin Cs films [3,4]. Of particular interest are transition metal impurities in the alkali metals. Their properties are difficult to investigate since the d-impurities do not dissolve in the alkali host. There are only a few methods to obtain alkali metals with magnetic impurities such as (i) ion-implantation, (ii) quenched condensation and (iii) nuclear reactions.

Riegel *et al.* [5] investigated the properties of Fe in the alkali hosts Cs, Rb, K and Li. These authors introduced the magnetic d-impurities by nuclear reactions or recoil from nuclear reactions into the alkali metals. For the investigation of the magnetic properties they used the experimental method of "time-differential perturbed angular γ-ray-distribution" in the temperature range from 20 K to 350 K. This method measures the hyperfine field at the Fe nucleus due to the susceptibility of the electrons in the Fe. They observed a Curie law for the temperature dependence of the local susceptibility, $\beta(T) - 1 = g_J\mu_B(J+1)B(0)/3k_BT$, where g_J is the Lande factor for the total spin J, μ_B=Bohr magneton, k_B=Boltzmann constant and $B(0)$ is the hyperfine field constant of the Fe atom. From the positive sign of $B(0)$ they concluded that the orbital angular momentum of the d-electrons contribute strongly to the Fe moment. They suggested a $3d^6$-configuration for the Fe atom dissolved in the alkali host (with exception of the Li host) and found a good agreement for $B(0)$ between a simple calculation and their experimental result.

Our group used the method of quenched condensation onto a substrate at helium temperature to obtain alkali films with d-impurities. The magnetization of the $3d$-impurities was measured by means of the anomalous Hall effect. At the present time this is the only experimental method to measure the magnetization as a function of both the temperature and the magnetic field. We observed giant magnetic moments for Fe and Co in thin Cs films [6] with a magnetic moment of the order of $7-8\ \mu_B$ (μ_B=Bohr magneton).

In comments on our results Gruyters and Riegel [7] and Mohn *et al.* [7] emphasized that the Fe and Co impurities in Cs possess their atomic electronic structure for the d-shell which are $3d^6$ for Fe and $3d^7$ for Co. The Fe has a total angular momentum of $J = 4$ and a Lande-factor $g = \frac{3}{2}$ while the Co has $J = \frac{9}{2}$ and $g = \frac{4}{3}$. In both cases the total magnetic moment should be $\mu = Jg\ \mu_B = 6\ \mu_B$. Both groups emphasized that there should be no polarization of the Cs host. Guo [8], stimulated by our experiments, performed "orbital-polarization corrected relativistic spin-density-functional" calculations for Fe and Co in the

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alkali hosts K, Rb and Cs. He obtained a similar electronic structure for the Fe and Co impurities and arrived at the conclusion that the host should not be polarized by the impurities. McHenry *et al.* in an earlier paper [9] obtained a different electronic structure for Fe impurities in alkali hosts (simulated by clusters). They found a $3d^7$ shell for the Fe impurities (which yields the same moment of 6 μ_B).

In this paper we investigate the properties of magnetic impurities on the surface and in the bulk of Rb and K 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 [10]).

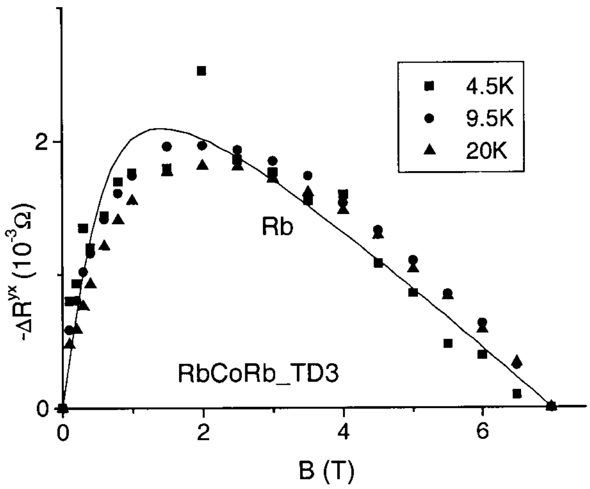

Fig. 1. The non-linear Hall resistance $\Delta R^{yx} = R^{yx}(B) - B\frac{R^{yx}(7\ \mathrm{T})}{7\mathrm{T}}$ of a pure Rb film for three different temperatures.

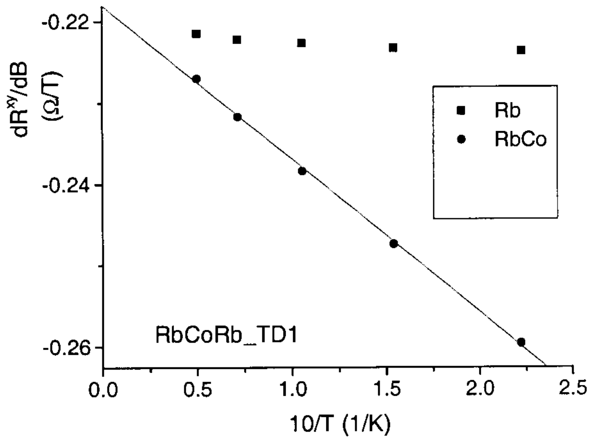

Fig. 2. The initial slope (at $B = 0$) of the Hall resistance $\frac{\mathrm{d}R^{yx}}{\mathrm{d}B}$ as a function of the reciprocal temperature 10/T for the pure Rb film (squares) and the Rb covered with 0.01 atomic layers of Co.

1 Experiment

The Rb and K films are evaporated from potassium and rubidium dispensers made by SAES-Getters. The quartz substrate is at He temperature and the ultra high vacuum is better than 10^{-11} torr. The magneto-resistance and the Hall resistance are measured in the field range between $-7\ \mathrm{T} \le B \le +7\ \mathrm{T}$ at several temperatures: 4.5 K, 6.5 K, 9.5 K, 14 K and 20 K. As an example we discuss the investigation of a Rb film with Co impurities: (i) A Rb film of 4.8 nm thickness is quench condensed and then annealed for several minutes at 40 K. After the annealing the resistance (per square) of the film is 78 Ω. (ii) The Rb film is covered with about 0.010 atomic layers of Co and annealed for several minutes at 35 K. The resistance increases to 96.5 Ω. (iii) The Rb/Co film is covered with 2.9 nm of Rb (about 6 atomic layers) and annealed for several minutes at 35 K. After each condensation the magneto-resistance and Hall resistance of the film (sandwich) are measured. Since the anomalous Hall resistance is a correction to the normal Hall resistance (which itself is a small resistance) it is necessary to use the largest measurement current possible. Since this current heats the film, one is at 4.5 K restricted to a relatively small current which makes the 4.5 K measurement less accurate than those at higher temperatures.

In our investigation we use a coverage of Fe and Co of 0.01 atomic layer. A smaller coverage reduces the accuracy of the evaluation because pure Rb (and K) films have a small but finite non-linearity in the Hall resistance R_{yx} as a function of the field B. This is shown in Figure 1 where $\Delta R^{yx} = R^{yx}(B) - B\frac{R^{yx}(7\ \mathrm{T})}{7\ \mathrm{T}}$ is plotted for three different temperatures. The relative non-linearity $\dfrac{\Delta R^{yx}}{R_{yx}(7\ \mathrm{T})}$ (the maximal deviation from linearity divided by R_{yx} at the maximum field of 7 T) is rather small, of the order of 1.3×10^{-3} for the discussed Rb film. The linear slope at $B = 0$ is, however, essentially temperature independent as Figure 2 shows.

When we superimpose the Rb film with 0.01 atomic layers of Co the Hall resistance shows a clear deviation from linearity. At 4.5 K the non-linearity is about 22×10^{-3}. This non-linearity is caused by the anomalous Hall effect of the Co atoms. The initial slope of the (full) Hall resistance at $B = 0$ shows, for the RbCo film (and the RbCoRb sandwich) a clear temperature dependence. In Figure 2 this initial slope of the RbCo film is plotted as a function of the inverse temperature (*versus* $10/T$). We observe a clear $1/T$-law. This Curie law is a clear indication that the Co atoms are magnetic. The extrapolation of $1/T$ towards zero yields the normal Hall slope. For a comparison Figure 2 shows also the absence of the (inverse) temperature dependence of the initial slope for the pure Rb film (squares).

As discussed in reference [6] we divide the Hall resistance into a linear part, the normal Hall resistance, and

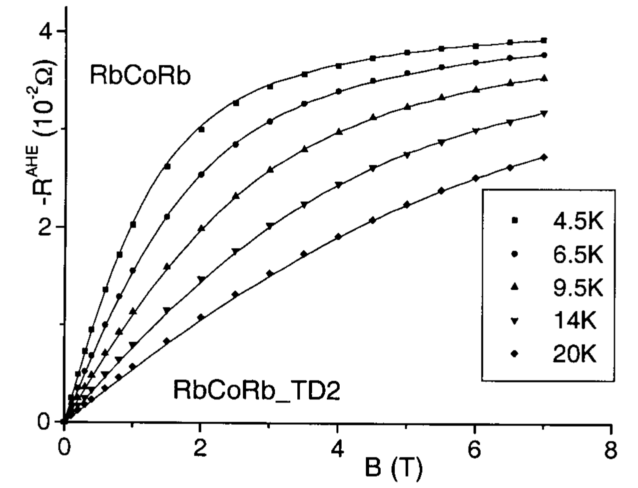

Fig. 3. The (negative) anomalous Hall resistance of bulk Co impurities in Rb. The solid curves are fits using a Brillouin-function. ($\mu = 10.5\ \mu_{\mathrm{B}}$).

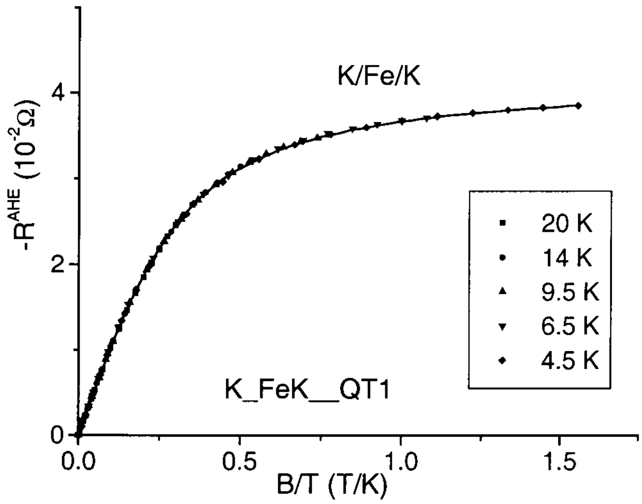

Fig. 4. A universal plot of the (negative) anomalous Hall resistance $-R^{\mathrm{AHE}}$ of bulk Fe impurities in K as a function of B/T. The solid curve is a Brillouin-function. ($\mu = 10.5\ \mu_{\mathrm{B}}$).

a non-linear anomalous Hall resistance which is proportional to the magnetization perpendicular to the film. The AHE has a negative sign. In Figure 3 the (negative) AHE resistance $-R^{\mathrm{AHE}}$ of the RbCoRb-sandwich is plotted as a function of the magnetic field for five temperatures, 4.5 K, 6.5 K, 9.5 K, 14.0 K and 20.0 K.

We try to express the AHR by a Brillouin function $B_J(x)$ which describes the magnetization of non-interacting magnetic moments with the total angular momentum J and the Lande-factor g at the temperature T in a magnetic field B (see Ref. [6]).

In our first attempt to evaluate the experimental curves we follow the suggestion by Riegel *et al.* [5] and use the value $g = \frac{4}{3}$ for the Lande factor of Co as given by the atomic model. However, a fit of the total angular momentum does not yield the value $J = \frac{9}{2}$, as expected for the atomic model. Instead we find the best fit for $J = 8$. This corresponds to a magnetic moment of $\mu = 10.7\ \mu_{\mathrm{B}}$. Obviously this result disagrees with the atomic model of a $3d^7$-state for Co, and one has to modify, at least, one of the values, either g or J. However, the fit of the magnetic moment of $\mu = gJ\ \mu_{\mathrm{B}} = 10.7\ \mu_{\mathrm{B}}$ is essentially independent of the choice g (as long as gJ is constant) because for such a large moment we are almost in the classical limit and the magnetization curve depends (almost) only on the total moment. The full curves in Figure 3 give the theoretical Brillouin functions for different temperatures with $g = \frac{4}{3}$, $J = 8$, *i.e.*, $\mu = 10.7\ \mu_{\mathrm{B}}$.

As another example, in Figure 4 we show the (negative) anomalous Hall resistance $-R^{\mathrm{AHE}}$ of bulk Fe impurities in K in a universal plot as a function of B/T. The solid curve is a Brillouin-function for $g = \frac{3}{2}$ and $J = 7$ yielding $\mu = 10.5\ \mu_{\mathrm{B}}$. In all our results for bulk Fe and Co impurities in the K and Rb host the experimental data can be well fitted with a magnetic moment of 10 μ_{B}–11 μ_{B}.

Table 1. The magnetic moments of Fe and Co impurities in the bulk and on the surface of the hosts Rb and K.

host	bulk imp.		surface imp.	
	Fe	Co	Fe	Co
Rb	10.0	10.7	7.8	9.3
K	10.5	11.3	7.8	9.3

For the $3d$-impurities at the surface of Rb and K the moments are smaller, in the range of 8–9 μ_{B}. The results are collected in Table 1.

Before we discuss the implication of our experimental results we address the question of diffusion and clustering at the surface and possible diffusion into the film. It is an interesting question what happens to the $3d$-impurities on the surface of an alkali metal when they are quench condensed. The alkali metals are open metals. In a simplified description one can picture them as alkali ions, floating in jellium. This distinguishes them well from other metals. Now we consider $3d$ impurities which are condensed onto the surface. While quench-condensed $3d$ impurities on top of other metals essentially stick and hardly diffuse on the surface or into the substrate, they can behave quite differently on top of an alkali metal. Do they glide on top of the jellium or do they dive into its outer layer? In particular we wish to know whether they might cluster on the surface.

First we investigate the question whether the $3d$-impurities diffuse into the alkali host metal when evaporated onto its surface. For this purpose we use Ni impurities in connection with the two hosts Na and Rb. Ni impurities on the surface and in the bulk of the host Na have no magnetic moment [11] while Ni impurities on the surface

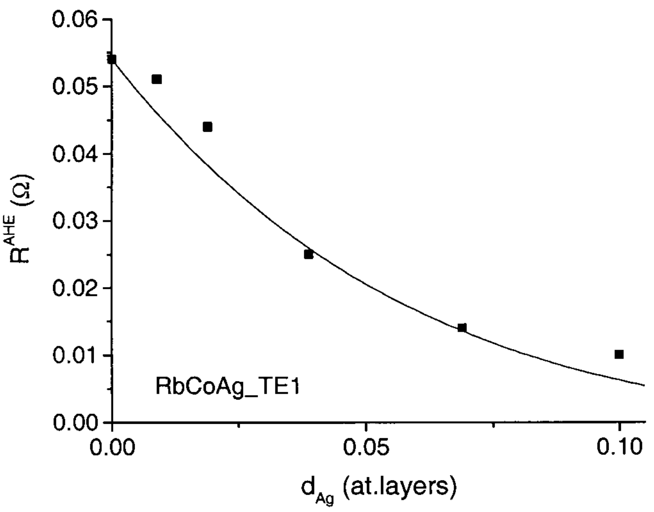

Fig. 5. The (negative) amplitude of the anomalous Hall effect of Co impurities on a Rb surface as a function of an additional coverage with Ag impurities.

and in the bulk of Rb have a moment of about 4 μ_B [12]. We prepare the following sandwich

- A film of Na with a total thickness of 5.3 nm is quench condensed.
- The Na surface is covered with 0.01 atomic layers of Ni. The Ni shows no magnetic moment.
- The Ni is covered with 2.4 nm of Rb. The Ni shows no magnetic moment.
- The Rb is covered with 0.01 atomic layers of Ni. The Ni impurities show a moment of 4.0 μ_B.
- The Ni impurities are covered with 1.4 nm of Na. The Ni shows no magnetic moment.

The Ni on top of Rb looses its moment when covered with Na. This shows that the Ni feels the presence of the Na and suggests that the Ni does not diffuse into the Rb film. (We started the experiment with NaNiRb because we did not know prior to the experiment whether Ni impurities sandwiched between Na and Rb possess a moment).

In the next experiment we investigate the question whether the impurities diffuse on the surface and cluster. For this purpose on top of 5.6 nm thick Rb film ($R = 56\ \Omega$) we deposit Co impurities with a coverage of 0.009 atomic layers. Then follows a sequence of Ag evaporations with total Ag coverages of 0.009, 0.019, 0.039, 0.069 and 0.1 atomic layers. Each time the Hall resistance is measured and the magnetic moment and the amplitude of the AHE is determined. It turns out that up to a Ag coverage of 0.039 the magnetic moment remains stable at 8 μ_B. The essential effect is that the amplitude decreases with increasing Ag coverage. In Figure 5 the (negative) amplitude of the AHE of the Co impurities is plotted as a function of the Ag coverage. The amplitude of the AHE decays with increasing Ag coverage.

We can model these experimental results surprisingly well by assuming that the position of the Co and Ag atoms is statistically distributed over the Rb surface and that a Co atom in contact with a Ag atom looses its giant moment. To discuss this scenario further we model the Rb surface as a (1,1,0) plane of a bcc lattice. The lattice parameter is $a = \sqrt[3]{2\Omega_a}$ where Ω_a is the volume per atom. The distance between (1,1,0) planes is $a/\sqrt{2}$ and the area per atom in the plane is $\Omega_a\sqrt{2}/a = \Omega_a^{2/3}\sqrt[6]{2}$. For Rb this yields an area per surface atom of 0.23 nm^2. There is one valley for each Rb atom in the surface which qualifies for the position of an impurity atom. At a coverage of 0.009 atomic layers the Co impurities occupy these valleys with a probability of about 4%, $p_{\mathrm{Co}} \approx 0.04$. The corresponding probability to find a Ag atoms in a valley is $p_{\mathrm{Ag}} = 3.5\, d_{\mathrm{Ag}}$ where d_{Ag} is the coverage with Ag in units of atomic layers. The chance for a Co atom "not" to be in contact with a Ag atom, *i.e.* "not" to have a Ag atom on its own or one of its four neighboring valleys, is $(1 - p_{\mathrm{Ag}})^5$. The full curve in Figure 5 represents the function $A_0\,(1 - p_{\mathrm{Ag}})^5$ which uses the amplitude A_0 at zero Ag coverage. There is a rather good agreement between the experimental amplitudes and the full curve which has no free parameter beyond A_0. Therefore the assumption of statistical distribution of the Co and Ag atoms is consistent with the experimental results. This suggests, that there is no diffusion and no clustering of the Co and the Ag impurities on the Rb surface. We do not consider these results an undisputable proof because the properties of magnetic impurities on the surface and in the bulk of the alkali metals are very complex. But the results are suggestive and worth being kept in mind.

2 Conclusions

Our experimental moments for bulk Fe and Co impurities in Rb and K are too large to be explained by the atomic moments, $3d^6$ for Fe and $3d^7$ for Co (according to Riegel *et al.*) or $3d^7$ for Fe and $3d^8$ for Co (according to McHenry *et al.*). Nor is there any other atomic 3d configuration that has a larger moment than 6 μ_B. In our previous paper on Cs with Fe and Co impurities we compared the (relatively) large moments of the $3d$ impurities with the enhanced moments of these impurities in Pd, a nearly ferromagnetic host. In two comments Gruyters and Riegel [7] and Mohn *et al.* [7] objected to this analogy. They argued that there is no enhancement of the susceptibility in Cs and therefore no polarization of the Cs host. In a recent calculation Okazaki and Teraoka [13] found that thin films of Cs are ferromagnetic in a certain thickness regime. This means, of course, that the polarizability (susceptibility) diverges in this regime. An enhanced polarizability in the non-ferromagnetic regime follows obviously from these results. Such an enhanced susceptibility would also enhance the magnetic moments of $3d$ impurities. Our experimental results suggest such an enhancement.

Abbreviations: AHE: anomalous Hall effect, AHR: anomalous Hall resistance.

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