Magnetic Behavior of Na Films with Fe, Co, and Ni Impurities

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Thin films of Na with Fe, Co, and Ni impurities are investigated. The magnetization of the impurities is measured by means of the anomalous Hall resistance. Fe and Co show a moment of about $6\mu_B$, while for Ni no moment is detected. Furthermore, the magnetic dephasing of the conduction electrons is measured by means of weak localization. The dephasing rate $1/\tau_\phi$ of the $3d$ impurities differ qualitatively. For Fe impurities, $1/\tau_\phi$ is so large that it cannot be measured. For Co, $1/\tau_\phi$ has a moderate value while Ni shows hardly a dephasing effect at all.

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The alkali metals are rather distinct from all other metals in the periodic system. For one, they are very open metals, i.e., the volume of the alkali ions takes only a small fraction of the total metal volume. Our group recently discovered a number of surprising properties in thin Cs films [1,2]. One particularly interesting aspect is the properties of $3d$ impurities in the alkali host. This question has been first studied by Riegel *et al.* [3]. They investigated the properties of Fe in the alkali hosts Cs, Rb, K, and Li (for further reference, see [4]). They 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 to 350 K. This yielded the enhancement of the hyperfine field $B(0)$ by an electronic magnetic moment at the $3d$ impurity. From the positive sign of $B(0)$, they concluded that the orbital angular momentum of the d electrons strongly contributed to the Fe moment. They suggest a $3d^6$ configuration for the Fe atom dissolved in the alkali hosts (with exception of the Li host) and find their experimental results and a simple calculation for $B(0)$ to agree. Our group [5] recently measured the magnetization of Fe and Co in Cs as a function of temperature and magnetic field. The magnetization follows a Brillouin function yielding a magnetic moment of about $(7-8)\mu_B$ for Fe and Co in Cs.

In this paper, we study the magnetic properties of the $3d$ impurities Fe, Co, and Ni in the alkali host Na. We find that the properties of these impurities in Na differ dramatically from each other. Kowallik *et al.* [6] studied the hyperfine field of the Ni impurities in Cs, Rb, K, Na, and Li. They observed an enhancement of the hyperfine field for the hosts Cs, Rb, and K which they interpreted as having a $3d^9$ configuration of Ni with a moment of $3\mu_B$. They could not unambiguously explain the results for Ni in Na. At low temperature, they observed a very weak enhancement factor of $\beta = 1.02$ (compared with values of about 2 for the other hosts).

In our experiment, the Na films are evaporated from Na dispensers from SAES-Getters onto a crystalline quartz substrate. The quartz plate is at He temperature and the ultrahigh vacuum is better than 10^{-11} torr. As an example, we discuss the investigation of a Na film with Co impurities.

(1) A Na film of 4.6 nm thickness is condensed and annealed to 35 K and investigated. The resistance per square is 94.7 Ω.

(2) The Na film is covered with 0.009 atomic layers of Co and annealed to 30 K. The resistance increases to 99.4 Ω.

(3) The Na/Co "sandwich" is covered with 1.4 nm of Na and annealed to 30 K. Now the resistance is 43.6 Ω.

Each time the magnetoresistance and Hall resistance of the sandwich are measured in the field range between $-7 \leq B \leq +7$ T at several temperatures: 4.5 (5), 6.5, 9.5, 14, and 20 K. In most of our investigations, we use a coverage of Fe, Co, and Ni of about $\frac{1}{100}$ atomic layers. This means that the average distance between two $3d$ atoms is about 10 times the diameter of the impurity. In some of our experiments, we need a large spin-orbit scattering in the sandwich. For these experiments, we first condense 0.1 atomic layers of Pb onto the quartz plate and then continue the evaporation procedure as described above.

If the impurities are magnetic, they align in the magnetic field. For free (noninteracting) moments, the z component of the magnetization follows a Brillouin function which depends on the total angular momentum J and the Lande-factor g. The magnetic impurities scatter the conduction electrons asymmetrically, yielding an anomalous Hall resistance (AHR). This AHR is proportional to the z component of the magnetization. In our evaluation, we separate the AHR from the normal Hall resistance and plot it as a function of the field for different temperatures. (For more details, see Ref. [5]). Such a plot is shown in Fig. 1 for Na with (bulk) Co impurities. The full curves represent the Brillouin function (for free moments) with $J = 4.2$ and $g = \frac{4}{3}$. The amplitude of the AHR as a fraction of the normal Hall resistance at 7 T is about 5% for the Co impurities and 25% for the Fe impurities. The latter represent an unusual large value. For the Ni impurities, the AHR was a factor of 50–100 smaller than for Fe and Co impurities, and we could not detect a magnetic moment.

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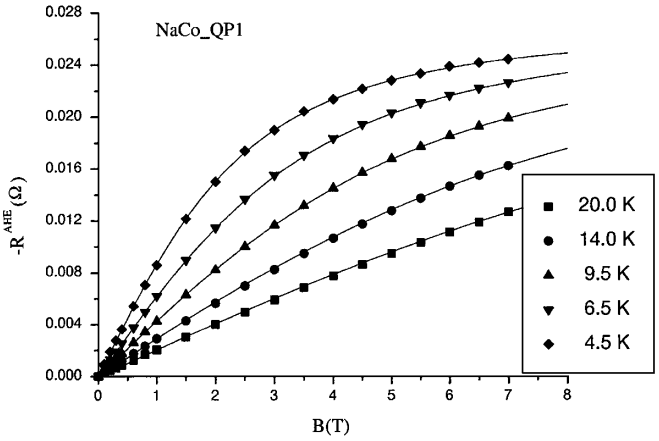

FIG. 1. The anomalous Hall resistance (proportional to the magnetization) of Co impurities in Na films.

We define the moment in units of μ_B as the product Jg. For Fe and Co on the surface of Na, we find a magnetic moment of $6\mu_B$. Inside the Na film the moments for Fe and Co are $5.5\mu_B$ (bulk impurities). The estimated error is about $0.5\mu_B$. These values are identical or close to the atomic values for the $3d^6$ configuration of Fe and the $3d^7$ configuration for Co ions. These configurations have been proposed by the Riegel *et al.* for Fe and Co impurities in the hosts Cs, Rb, and K. These authors suggest that the Hund's rules apply perfectly for the $3d$ impurities and assume that the d shell behaves almost as a full shell and has very little interaction (hybridization) with the conduction electrons.

McHenry *et al.* [7] investigated the properties of Fe impurities in Li, Na, K, and Rb by surrounding an Fe atom with up to 26 alkali atoms. They obtained for Fe in Na roughly a $3d^7$ configuration. Because of the electropositive Na host, they observe a promotion of about one s electron to the Fe d-electron shell. A similar electron transfer for Co and Ni impurities would yield a $3d^8$ for Co and $3d^9$ configuration for Ni in Na. The resulting theoretical moments for Fe and Co in Na are $6\mu_B$ for Fe and $5\mu_B$ for Co (if one includes the angular momentum). Both theoretical values are very close to our experimental results. A $3d^9$ Ni configuration should have a moment of $3\mu_B$. However, if there is a strong hybridization between the $3d$ states and the free electrons, then the $3d$ density of states $g_2\ (\varepsilon_F)$ of the Ni impurity is lowered and the product $Ug_d(\varepsilon_F)$ is less than 1, yielding a nonmagnetic impurity.

The alkali metal hosts with $3d$ impurities connect the field of solid state physics with that of atomic physics, showing a continuous transition from the host Cs (atomic configuration of the $3d$ impurity) to the host Li (impurity with d resonance). Our measurements confirm that, for the $3d$ impurity Ni in Na, we have already reached a sufficiently strong hybridization between the $3d$ shell and the conduction electrons to quench the magnetic moment.

The question of the interaction between the conduction electrons and $3d$ electrons is of particular interest. Therefore we investigate this interaction in more detail. For this purpose, we use the magnetoresistance of the films. The magnetoresistance can give much information about the interaction between the conduction electrons and the $3d$ shell: (i) For free magnetic moments, weak localization yields the additional dephasing of the conduction electrons due to the (s, d)-exchange interaction; (ii) the reduced spin disorder and spin-flip scattering in a magnetic field yield a negative magnetoresistance which depends on $(g\mu B)/(k_B T)$; (iii) for Kondo impurities, the magnetoresistance yields information about the Kondo temperature, i.e., the interaction between conduction electrons and the d shell.

For the pure Na films, we observe magnetoresistance curves which are well described by the theory of weak localization [8]. After deposition of 0.01 atomic layers of Ni and an additional five monolayers of Na, the magnetoresistance is measured again and evaluated. There is a slight broadening of the magnetoresistance curves. Such a broadening can be caused either by a dephasing or a very weak spin-orbit scattering. The two mechanisms can be distinguished if one goes to the large spin-orbit scattering limit. This is done in another experiment by first condensing 0.1 atomic layer of Pb onto the quartz plate (which introduces a large spin-orbit scattering). Then the same evaporation sequence is repeated. Both experiments yield a tiny increase of the dephasing due to the Ni which corresponds to a dephasing cross section of $\sigma'_\phi = (\sigma_\phi k_F^2)/4\pi \approx 0.004$.

The magnetoresistances of the NaCoNa system yield the following results. The pure Na film shows, as before, a perfect agreement with the theory. For the NaCo and NaCoNa (0.01 atomic layers of Co), we observe good agreement for fields below 2 T. The evaluation yields the dephasing rate of the pure Na, the Na with 0.01 atomic layers of Co on its surface, and the NaCoNa sandwich with bulk Co impurities. In Fig. 2 the dephasing rates are plotted. The Co essentially yields an additional temperature independent dephasing. The dephasing cross section for Co surface atoms is $\sigma'_\phi = 0.22$ and for bulk Co impurities $\sigma'_\phi = 0.15$. [For larger fields, we obtain a perfect fit by adding a quadratic term and a Lorentz curve with a width B_w to the weak localization part (see below).]

The magnetoresistance curves of the NaFeNa system are quite different. They consist of broad bell-shaped curves as shown in Fig. 3. From the shape of the curves, we were not quite sure to what extent the magnetoresistance was caused by weak localization. Therefore we performed an additional experiment in which we first condensed 0.1 atomic layer of Pb onto the quartz plate. Then a 2.63 nm thick Na film with high resistance of 226 Ω was condensed. A film with such a high resistance has a very small quadratic magnetoresistance. In the next step, an Fe film of 0.005 atomic layers was condensed on top of the Na yielding a resistance of 248 Ω. Finally, Na was condensed in two steps with a thickness of 0.6 and 1.64 nm on top the Fe, yielding a resistance of 156 and 78 Ω. The

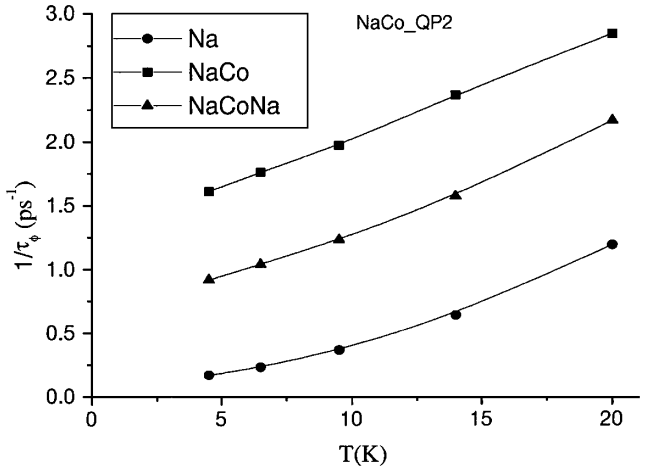

FIG. 2. The dephasing rate in a pure Na film, the same Na film covered with 0.01 atomic layers of Co, and after coverage of the NaCo film with five more layers of Na.

first Na film showed a strong positive magnetoresistance due to the strong spin-orbit scattering of the Pb. The positive magnetoresistance disappeared for the NaFe and the NaFeNa sandwich. In Fig. 3 the magnetoresistance of the NaFeNa sandwich with 78 Ω resistance is shown. In the presence of the large spin-orbit scattering, a very large dephasing is required to obtain a negative magnetoresistance. The dephasing cross section of the Fe impurities appears to be so large, $\sigma'_\phi > 0.7$, that a reliable determination is not possible. We set the dephasing essentially to infinite and fit the curves with simple Lorentz curves of the form $a_L[B_w^2/(B^2 + B_w^2) - 1]$ (see below). The resulting fits are drawn in Fig. 3. The coefficient a_2 of the quadratic expansion at small field a_2B^2 can be well determined from this fit. This coefficient follows a $T^{-4/3}$ law.

Free magnetic impurities are supposed to show a negative magnetoresistance because an increasing magnetic field freezes out spin-flip processes and reduces spin

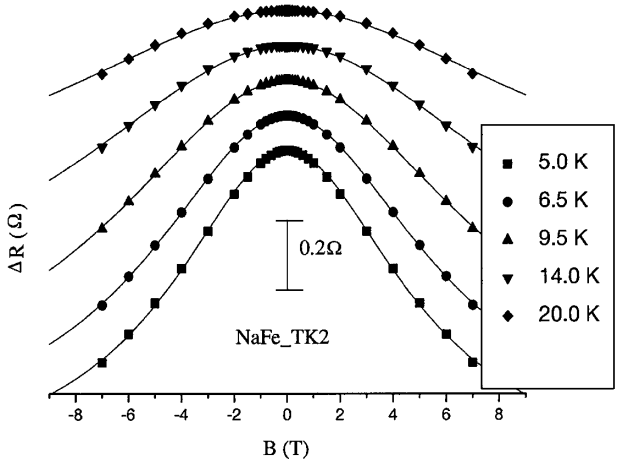

FIG. 3. The magnetoresistance of a NaFeNa film (0.005 atomic layers of Fe in between the Na layers) at different temperatures.

disorder. Yoshida [9] and Beal-Monod [10] calculated the magnetoresistance in the *sd*-interaction model. If the exchange interaction is much smaller than the potential scattering, then the magnetoresistance up to the second order in the exchange interaction is (according to Ref. [10])

$$f(B) = \frac{R(B) - R(0)}{|R(\infty) - R(0)|} = -\frac{1}{(4S^2 + S)}\left(\left\{4\langle S_z\rangle^2 + \langle S_z\rangle \times \left[\coth(\tfrac{1}{2}x) - \frac{\frac{1}{2}x}{\sinh^2(\frac{1}{2}x)}\right]\right\}\right),$$

where $x = (g\mu_B B)/(k_B T)$ and $\langle S_z\rangle$ is the thermal expectation value of S_z (or J_z), which is given by the Brillouin function (and is proportional to the magnetization). For $J = 4$ and $g = \frac{3}{2}$, this function can be well approximated by $[1 - 2.62^2/(2.62^2 + x^2)]$ (the deviation is less than 0.02). This is the reason why we include Lorentz curves to fit the experimental magnetoresistance curves.

The quadratic expansion of $f(B)$ for $S = 4$ and $g = \frac{3}{2}$ is

$$f(B) \approx \frac{1}{9}\,\frac{J(J+1)(2J+1)^2}{4J^2 + J}\,x^2 \approx \frac{0.1775}{T^2}\,B^2.$$

The quadratic coefficient should be proportional to T^{-2} while our experimental results yield a $T^{-4/3}$ law. It is, however, not clear that the *sd*-exchange model can be applied in this case and that the exchange interaction is much smaller than the potential scattering. A much more detailed investigation of the spin-induced magnetoresistance is required, experimentally as well as theoretically. At the present time, we derive only the important result that the dephasing rate due to Fe impurities is by a factor of 5 or more larger than that due to Co impurities.

The strong interaction of the Fe *d* states with the conduction electrons suggests a resonance at the Fermi energy. One interesting possibility is that the $3d^7$ state of the Fe's *d* shell lies at the Fermi energy and has a narrow energy width. This state has the same magnetic moment as the $3d^6$ configuration but a different degeneracy. The combination of the ($Fe^{++} + e$) and Fe^+ represent an interesting exotic magnetic Anderson model, in which an electron couples two states with the same magnetic moments. This should be a very tempting theoretical problem.

In conclusion, the 3*d* impurities Fe, Co, and Ni show in the Na host a remarkable variety of different behavior: (i) The Ni has essentially lost its magnetic moment. (ii) The Co impurity behaves as if it still has an atomic moment of $(5-6)\mu_B$. It causes a magnetic dephasing of weal localization which is moderate and temperature independent. (iii) The Fe impurity shows essentially the same temperature and field behavior of the magnetization as the Co. However, the amplitude of the AHR is by a factor 5 larger than for Co impurities and the magnetoresistance shows strong dephasing.

The two theoretical models for Fe and Co impurities in alkali hosts with the configurations Fe $\rightarrow 3d^6$, Co $\rightarrow 3d^7$ [3] and Fe $\rightarrow 3d^7$, Co $\rightarrow 3d^8$ [7] yield both magnetic moments of $(5-6)\mu_B$, and therefore our results are in agreement with both models. The absence of a moment in Ni shows that here the solid state hybridization has won over the atomic model.

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