Strongly Enhanced Magnetic Moments of Vanadium Impurities in Thin Films of Sodium and Potassium

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Thin quench-condensed films of Na and K are covered with 1/100 of a monolayer of V. 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. For V impurities on the surface of Na and K, a magnetic moment of 7 Bohr magnetons is observed. After coverage with the host, the V moment became $6.5\mu_B$ for the Na host. These results contradict the favored atomic model (predicting $\frac{3}{5}\mu_B$) and the resonance model. A polarization of the alkali host appears to be the only resolution.

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The properties of magnetic transition metal impurities in alkali metal hosts are a very fascinating field and represent one of the least investigated magnetic impurity systems. The alkali metals are the textbook example for "band-free" conduction electrons in a metal. They are often modeled as the so-called "jellium model." Transition metal impurities in the alkali hosts are excellent probes to investigate the jellium because they introduce a locally strong exchange repulsion between the d states of the impurities which couple to the conduction electrons. One of the central goals of this investigation is to answer the question of whether the magnetic impurities are capable of polarizing the electron gas.

Riegel *et al.* [1] investigated the properties of Fe in the alkali hosts Cs, Rb, K, and Li. These authors introduced magnetic d impurities by nuclear reactions or recoil from nuclear reactions into the alkali metals. For the investigation of the magnetic properties, they measured the hyperfine field $B(0)$ at the Fe nucleus in the temperature range from 20 to 350 K. These authors suggest a $3d^6$ configuration for the Fe atom dissolved in Cs, Rb, and K with a moment of $6\mu_B$. (We define the magnetic moment as $\mu/\mu_B = gJ$.)

Our group used the method of quenched condensation onto a substrate at helium temperature to obtain alkali films with d impurities. We investigated the magnetic moments of Fe and Co in thin Cs films [2] and, more recently, Fe and Co impurities in Rb and K [3]. 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.

In Comments on our earlier results, where we observed giant magnetic moments $(7-8)\mu_B$ for Fe and Co in Cs films, Gruyters and Riegel [4] and Mohn *et al.* [4] stated 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. In the following, we will call this the "atomic model" of $3d$ impurities in alkali hosts. Both groups emphasized that there should be no polarization of the Cs host. McHenry *et al.* obtained in an earlier paper [5] 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 $6\mu_B$). Guo [6], stimulated by our experiments, performed "orbital-polarization corrected relativistic spin-density-functional" calculations for Fe and Co in the alkali hosts K, Rb, and Cs. He obtained a similar electronic structure for the Fe and Co impurities, and he also arrived at the conclusion that the host should not be polarized by the impurities.

Obviously, the mainstream theoretical picture of magnetic impurities in alkali hosts is an atomic configuration, and it excludes a polarization of the conduction electrons by the impurities. This represents a beautiful challenge for the experimentalist. The persuasive observation of an enhanced moment in the alkali hosts would dramatically alter our picture of the "simplest and best understood" metal group, the alkali metals.

There is one $3d$ impurity, vanadium, which is uniquely suited for this purpose: (i) In the atomic model, vanadium should possess a very small moment of $\frac{3}{5}\mu_B$. (ii) Bulk V and clusters of V atoms are nonmagnetic (see below). (iii) Even in the d resonance (Friedel-Anderson) model V impurities can have only a maximum moment of $3\mu_B$ (for three d electrons occupying one d-spin subband).

Therefore an experimental observation of a V moment $0 < \mu/\mu_B < 1$ can be considered as a confirmation of the atomic model; a moment between $(2-3)\mu_B$ favors the resonance model. Larger observed moments are strong indicators for a host polarization. Vanadium is indeed a perfect impurity. We investigate in this paper its properties on the surface and in the bulk of Na and K films. Our experimental method is the anomalous Hall effect (AHE). The anomalous Hall resistance (AHR) is proportional to the magnetization of the magnetic atoms (see, for example, [7]).

Since transition metal impurities do not dissolve in the alkali hosts, one has to prepare the samples at low temperatures. We use the method of quenched condensation.

The Na and K films are evaporated from sodium and potassium dispensers made by SAES-Getters. The quartz substrate is at He temperature, and the ultrahigh vacuum is better than 10^{-11} torr. The magnetoresistance and the Hall resistance are measured in the field range between $-7\ \mathrm{T} \le B \le +7\ \mathrm{T}$ at several temperatures: 5, 6.5, 9.5, 14, and 20 K. As an example, we discuss the investigation of a Na film with V impurities: (i) A Na film of 10.5 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 20.5 Ω. (ii) The Na film is covered with about 0.010 atomic layers of V and annealed for several minutes at 35 K. The resistance increases to 21.7 Ω. (iii) A Na/V "sandwich" is created by covering with 1.6 nm of Na, followed by annealing for several minutes at 35 K.

After each condensation, the magnetoresistance and Hall resistance of the film are measured. The pure Na film shows (like all alkali films which we investigated thus far) a small deviation from linearity of the Hall resistance $\Delta R^{yx} = R^{yx}(B) - B\frac{R^{yx}(7\ \mathrm{T})}{7\ \mathrm{T}}$ with magnetic field. The relative deviation from linearity $\frac{|\Delta R_{yx}|}{R_{yx}(7\ \mathrm{T})}$ (the maximal deviation from linearity divided by R_{yx} at the maximum field of 7 T) is rather small, of the order of 4×10^{-4} for the Na film discussed. The initial slope dR^{yx}/dB at $B = 0$ of the Hall resistance is temperature independent within 10^{-3}. When this film is covered with 0.01 atomic layers of V, the nonlinearity of the Hall curves increases by roughly a factor of 50 at the lowest temperature. The initial slope dR^{yx}/dB depends linearly on the reciprocal temperature $1/T$. The results are qualitatively the same when the V impurities are covered with the second Na film. In Fig. 1, the initial slope dR^{yx}/dB of the K/V/K film is plotted as squares versus the inverse temperature $10/T$ (the full circles are discussed below). The extrapolation $1/T \to 0$ yields the (derivative of the) normal Hall resistance. The inverse temperature dependence of the initial slope (which is proportional to the susceptibility) is the typical behavior of a free magnetic moment. The magnitude of the AHR is remarkable; at 5 K the initial slope is of the order of 10% of the normal Hall resistance slope.

The anomalous Hall resistance curves show a strong curvature which suggests a relatively large moment for the V impurities (see Fig. 2). We tried to fit the AHR with a Brillouin function $B_J(x)$ which describes the magnetization of noninteracting magnetic moments with the total angular momentum J and the Landé factor g at the temperature T in a magnetic field B. However, if one tries to fit the AHR with a Brillouin function for free moments, one does not find a good fit. The initial slope of the AHR (after subtracting the normal Hall resistance) and the high field behavior cannot be described with the same magnetic impurity moment. In a second approach, we used the linear normal Hall resistance as an adjustable parameter. This yields a reasonable fit for the AHR curves. In Fig. 2, this (negative) anomalous Hall resistance, $-R^{\mathrm{AHE}}$, of the Na/V/Na sandwich is plotted as a function of the magnetic field for five temperatures. We first attempted to use the Landé factor $\frac{2}{5}$ of the atomic model. However, then the fit yields the value $J = 18$. This value is, of course, much larger than the predicted value of $J = \frac{3}{2}$ and not very meaningful. Therefore, we evaluate all the AHR curves for V impurities with the (default) value of $g = 2$. (An effect of the crystal field has been ruled out by Riegel *et al.* [1]). This yields a moment of $6.6\mu_B$ for V impurities in the Na host. The full curves in Fig. 2 give the theoretical Brillouin functions for different temperatures with $g = 2$ and $\mu = 6.6\mu_B$. For the V impurities on the surface of Na, we find the best fit for $\mu = 7\mu_B$.

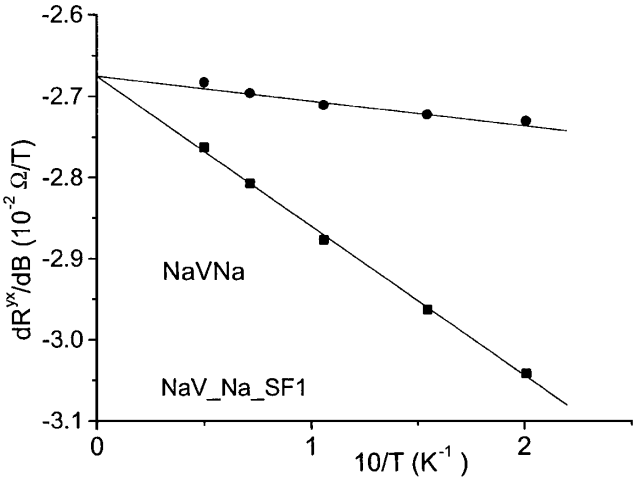

FIG. 1. The initial slope of the total Hall resistance as a function of $10/T$ (squares). The full circles give the same initial slope after subtracting the initial slope of the fitted Brillouin functions.

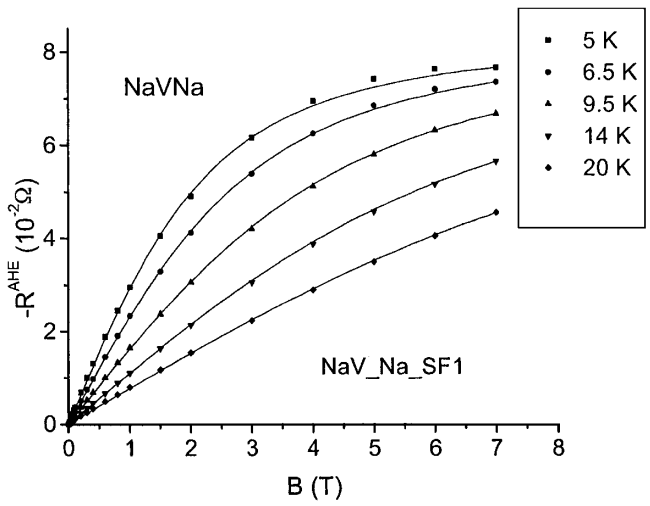

FIG. 2. The (negative) anomalous Hall resistance of bulk V impurities in Na. The solid curves are fits using a Brillouin function; $\mu = 6.6\mu_B$.

This evaluation and the resulting Brillouin function account for 90% of the initial slope of the AHR. This is shown in Fig. 1 by the circles. The circles represent the experimental initial slope of the Hall resistance minus the initial slope of the fitted Brillouin functions. The difference should be the temperature independent normal Hall resistance slope. One recognizes that there is a remaining 10% contribution, proportional to $1/T$, which is not accounted for by the fitted Brillouin function. The same behavior is observed for the V on the surface of Na and K. It is in striking contrast to our results for Fe and Co impurities in K and Rb [3], where the fitted AHR accounted for the whole temperature dependent initial slope.

In Fig. 3, we show the (negative) AHR ($-R^{\mathrm{AHE}}$) of V impurities on the surface of K. We use the same fitting procedure as for the Na/V system. The solid curves are Brillouin functions for $g = 2$ and $\mu = 7\mu_B$. The agreement between the experimental points and the solid curves is only reasonable. As for the NaV system, the fitted AHR accounts only for 90% of the temperature dependence of the initial slope of the AHR. In addition, the initial slope of the Hall resistance dR^{yx}/dB plotted versus $1/T$ shows deviations from linearity at 14 and 20 K.

When the V impurities are covered with K (bulk V impurities), the experimental results were rather surprising. In Fig. 4, we plot the deviation from linearity of the Hall resistance $\Delta R^{yx} = R^{yx}(B) - B\frac{R^{yx}(7\ \mathrm{T})}{7\ \mathrm{T}}$ as a function of the magnetic field. The relative deviation $|\Delta R^{yx}|/R^{yx}$ (7 T) of these curves lies between 0.9×10^{-3} at high temperatures and -1.9×10^{-3} at 5 K. The deviation for the 9.5, 14, and 20 K curves is roughly the same as for a pure K film. The results do not permit a clear separation of the normal and anomalous Hall resistance. We might have here the superposition of the background nonlinearity with an (very weak) AHE of magnetic origin. The structure in Fig. 4 is well reproducible in different experiments.

The strong reduction of the AHR could be interpreted as the disappearance of the magnetic moment on the V impurity. However, the measurement of weak localization still shows a large dephasing for bulk V impurities (loss of coherence of the electronic wave function with time). In Fig. 5, the total dephasing rate $r_\phi = 1/\tau_\phi$ is plotted for the K/V/K sandwich as a function of the temperature after each evaporation step. The bulk V impurities cause a strong (temperature dependent) dephasing.

One may suspect that the V atoms cluster at the surface of the alkali host and that the clusters have a much larger moment than the individual impurity. We have experimental evidence that the transition metal impurities do not diffuse or cluster on the surface of the alkali hosts [3]. Clustering would still not help explain the large observed magnetic moments. Bulk V is nonmagnetic, and we expect that clusters of V atoms do not possess large moments. Douglas *et al.* [8] investigated the magnetic moments of V clusters in vacuum in the range from 8 to 99 atoms. They observed $(0.000 \pm 0.008)\mu_B$ per V atom, i.e., no moment at all. We investigated in the past the dephasing effect of V impurities on the surface of Au films [9]. The experiment showed strongly reduced dephasing per atom with increasing V coverage, and we concluded that the magnetic moment of V clusters decreased strongly with cluster size (having a maximum for single V atoms). Even an indirect interaction between the V moment through the RKKY spin polarization of the conduction electrons should not enhance the V moments because of the random oscillation between ferro- and antiferromagnetic coupling.

In the past, we observed magnetic moments of $6\mu_B$ or more in the alkali hosts Cs, Rb, K, and Na with Fe or Co impurities on the surface and in the bulk. Ni impurities in Cs, Rb, and K have moments of about $4\mu_B$. On the other hand, we found no magnetic moments for Ni impurities in/on Na or for Pd impurities in/on K. Together with our results of V in/on Na and K, we observed a rather rich and distinct magnetic behavior. As we discussed in the introduction, a V moment of $6\mu_B$ cannot be explained

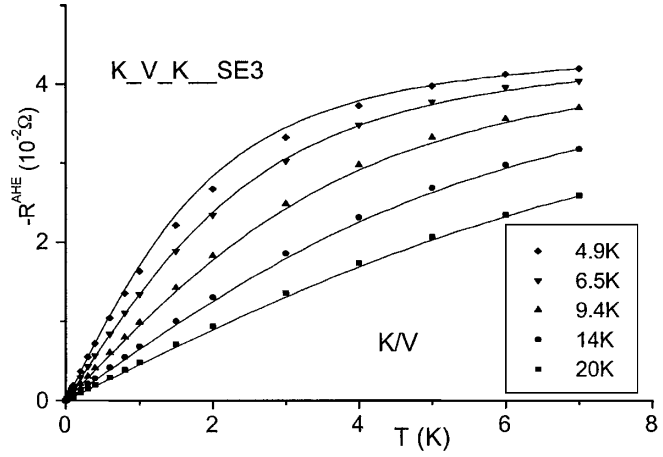

FIG. 3. The (negative) anomalous Hall resistance $-R^{\mathrm{AHE}}$ of V surface impurities on K as a function of B. The solid curves are fits using a Brillouin function; $\mu = 7\mu_B$.

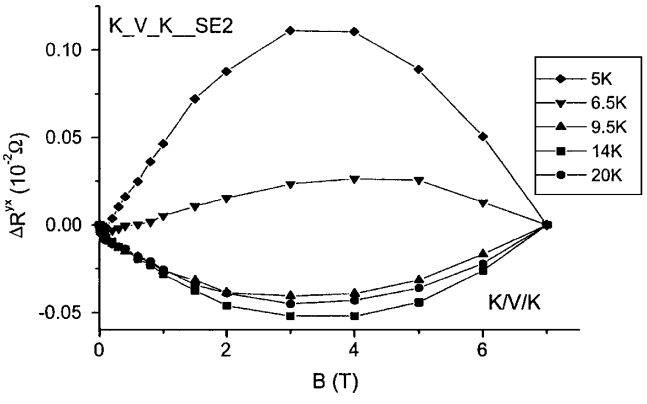

FIG. 4. The nonlinear part of the Hall resistance $\Delta R^{yx} = R^{yx}(B) - B\frac{R^{yx}(7\ \mathrm{T})}{7\ \mathrm{T}}$ for bulk V impurities in K. The full curves are a guide to the eye.

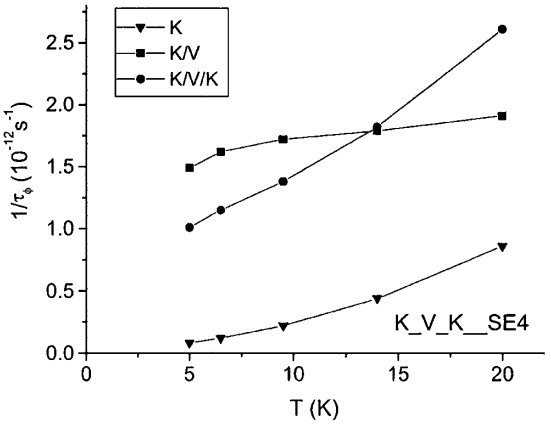

FIG. 5. The total dephasing rate in the sandwich K/V/K as a function of the temperature after each evaporation step.

within the atomic model or the *d*-resonance model. The size of the moment requires contributions from outside the impurity. We see no alternative but to conclude that the Na and K hosts are polarized by the V impurities and contribute to the large magnetic moment.

We expect that both the V impurity and the polarization cloud contribute to the AHR. In this model of magnetic impurity plus polarization cloud, the two reinforce and strengthen each other and the total moment. If one applies an external magnetic field, the size of the cloud can be slightly increased by the field if aligned parallel to the moment (and vice versa). This yields a slight deviation from a Brillouin function, i.e., a small deviation between the initial slope and the high field magnetization, and could be responsible for the 10% unaccounted initial slope in our experiment.

A polarization of the conduction electrons of the alkali host has a very serious implication for our understanding of the alkali metals. Its observation dramatically alters our modeling of the alkali metals. As pointed out in a number of theoretical numerical calculations (discussed in the introduction), the standard spin-density-functional theory does not yield such a polarization.

We suspect that the relaxation of the alkali atoms in the presence of the impurity may be responsible. In earlier experiments [10], we observed that impurities on the surface of Cs caused an anomalous large increase of the resistance. This suggests that the alkali atoms experience a rearrangement of their position over a relatively long range. The softness of the alkali lattice is well known (see, for example, [11]). Such a rearrangement modifies the local electron density and can severely alter the balance between Coulomb energy and kinetic energy. An extension of the theoretical investigation to a "soft" jellium model would be very desirable.

Since a polarization of the alkali host represents such a challenge for the theory, further experiments are in progress to explore this question. We are extending the investigation to impurities of Ti, Sc, and 4*d* atoms. Furthermore, the effect of boundary conditions on the size of the impurity moments is under investigation.

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