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# Host-dependent electronic structure of vanadium impurities in different alkali metals

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The magnetic moment of V impurities in different alkali hosts is measured by means of the anomalous Hall effect. The V moment on the surface and in the bulk of Cs is about $4\mu_B$ and considerably smaller than previously measured moments of V on the surface ($7\mu_B$) and in the bulk ($6.6\mu_B$) of Na. Furthermore the sign of the anomalous Hall resistance changes from negative for the Na host to positive for the Cs host. This indicates a change of the electronic structure of the impurity (plus host environment) when going from Na to Cs hosts.

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## I. INTRODUCTION

Our group recently investigated the magnetic properties of $3d$ impurities in different alkali hosts. Our experimental method is the anomalous Hall effect. The anomalous Hall resistance (AHR) is proportional to the magnetization of the magnetic atoms (see, for example, Ref. 1). We observed giant moments of more than $6\mu_B$ for Fe and Co in Cs, Rb, and K.[2,3] Fe and Co impurities in Na showed moments of $6.5\mu_B$ and $5.5\mu_B$.[4] Of particular interest are the properties of V impurities. For V on the surface and in the bulk of Na films we observed moments of $7\mu_B$ and $6.6\mu_B$.[5] On the surface of K the V moment was $7\mu_B$. For V in the bulk of K the AHR was so small that it did not permit us to determine the V moment in the K host.

In all the above systems of $3d$ impurities in the hosts Cs, Rb, K, and Na the AHR showed a negative sign. This is in remarkable contrast to other hosts such as the noble metals or polyvalent ($s$,$p$) hosts where the AHR is positive for a number of $3d$ impurities. The sign of the AHR contains information about the electronic structure of the impurity, such as the Friedel phase shifts.[6]

Recently we investigated the AHR of Ti impurities in these alkali hosts.[7] We observed much smaller moments of the order of $1\mu_B$ on the surface of K, Rb, and Cs. (In the bulk of K and Rb the Ti moment is still smaller; the AHR suggests moments of about $1/4\mu_B$). Another remarkable result was that the sign of the AHR was positive for the Ti impurities. Therefore the V impurities are in two respects on a borderline: (i) impurities to the right in the $3d$ series of the Periodic Table have negative AHR and to the left positive AHR, and (ii) the impurity moments to the right are large and to the left are small. This gave us additional motivation to investigate the properties of V impurities on the surface and in the bulk of Rb and Cs. In this paper we report the unexpected results of this investigation.

The Rb and Cs films are evaporated from rubidium and cesium dispensers made by SAES-Getters. The quartz substrate is at a liquid-He temperature, and the ultrahigh vacuum is better than $10^{-11}$ torr. The preparation of the film samples Rb/V/Rb and Cs/V/Cs is analogous to the preparation of previously investigated films (see, for example, Ref. 5). After each condensation step of the films their magnetoresistance and Hall resistance are measured in the field range between $-7T \leqslant B \leqslant +7T$ at several temperatures: 5, 6.5, 9.5, 14, and 20 K.

We discuss the experimental data for V impurities on the surface of a 78 Ω Rb film. The V coverage is 0.01 atomic layers. In Fig. 1 we plot the initial slope $dR^{yx}/dB$ of the AHR as a function of the inverse temperature $10/T$. The squares give the initial slope of the pure Rb film. This initial slope represents the normal Hall effect. It is temperature independent to a good approximation. The circles give the initial slope after the condensation of V onto the surface of Rb. In addition to the normal Hall resistance one has the anomalous contribution which is due to the asymmetric scattering of the conduction electrons by the magnetic impurities. The initial slope of the AHR is proportional to the susceptibility. The linear dependence of the total initial slope on the inverse temperature represents the magnetic behavior of free magnetic moments. The extrapolation towards infinite temperature ($10/T \rightarrow 0$) yields the slope of the normal Hall resistance. It turns out to be the same initial slope as that for the pure Rb film. With the normal Hall resistance known we can extract the AHR from the experimental Hall resistance by subtracting the normal Hall resistance. The result is shown in Fig. 2 for the V impurities on the surface of the Rb film. The AHR is plotted for five temperatures as a function of the

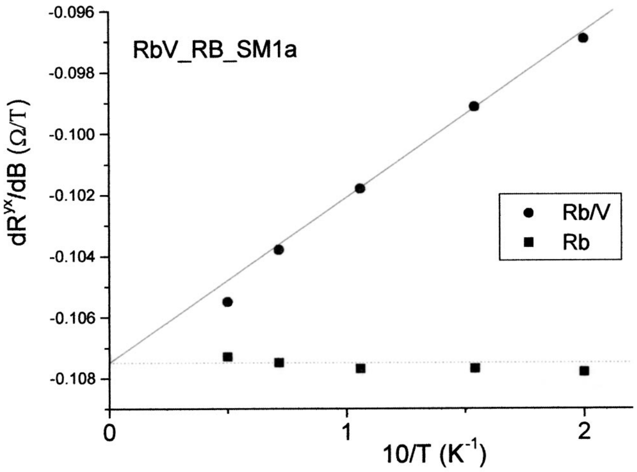

FIG. 1. The initial slope of the total Hall resistance as a function of $10/T$. The squares are for the pure Rb film and the circles for the Rb/V film.

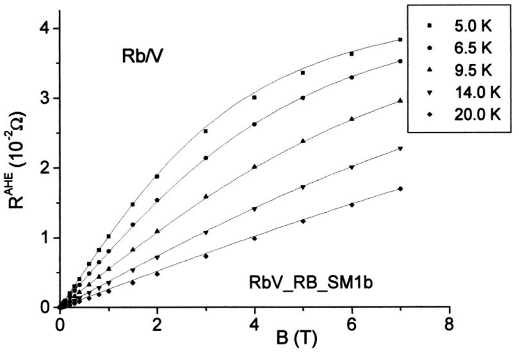

FIG. 2. The (positive) anomalous Hall resistance of V surface impurities in Rb. The curves are fits using a Brillouin function with $J=2$, $g=1.8$ (yielding $\mu=3.6\mu_B$).

magnetic field. The symbols represent experimental points. In the next step we fit our experimental results with the Brillouin function for free magnetic moments with the total angular momentum $J$ and the Lande factor $g$:

$$B_J(x)=\frac{2J+1}{2J}\coth\left(\frac{2J+1}{2J}x\right)-\frac{1}{2J}\coth\left(\frac{1}{2J}x\right),$$

$$x=\frac{gJ\mu_B B}{k_B T}. \tag{1.1}$$

In our previous paper on V impurities with the hosts Na and K we used first the Lande factor 2/5 of the atomic model. However, the fit then yields the value $J=18$. Since this value is not very meaningful we evaluate all the AHR curves for V impurities with the (default) value of $g=2$. To maintain consistency we first choose in this paper $g=2$. (An effect of the crystal field has been ruled out by Riegel, Barth, and Buermann[8]). Then we select the optimal half-integer value for $J$ (because only half-integer values are permitted for a free moment) and use this value of $J$ to optimize the Lande factor $g$. For the V impurities on the surface of Rb this procedure yields $J=2$, $g=1.8$. The curves in Fig. 2 represent the theoretical fits with the Brillouin function using these values. For the Rb/V/Rb sandwich we obtain the best fit with $J=3/2$ and $g=2$, yielding a moment of $3\mu_B$.

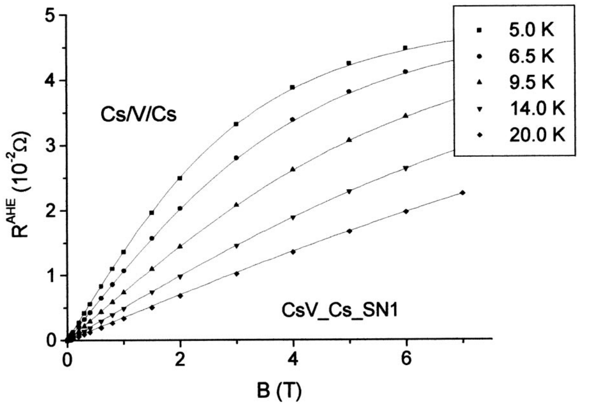

FIG. 3. The anomalous Hall resistance $R^{AHE}$ of V bulk impurities in Cs as a function of B. The solid curves are fits using a Brillouin function with $J=2$ and $g=2.1$ (yielding $\mu=4.2\mu_B$).

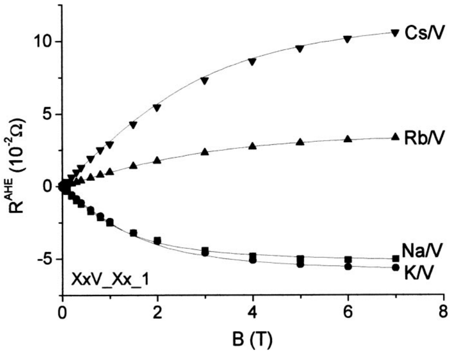

FIG. 4. The low-temperature anomalous Hall resistance of different alkali hosts with V impurities on the surface.

Similar results are obtained for the Cs/V and Cs/V/Cs films. For the V surface impurities we find the best fit for $J=2$ and $g=2.1$, yielding $\mu=4.2\mu_B$. In Fig. 3 we have plotted the experimental and theoretical fit for bulk V impurities in Cs (the Cs/V/Cs system). The symbols represent the experimental points for the anomalous Hall resistance $R^{AHE}$ of V surface impurities in Cs as a function of B. The solid curves are fits with the Brillouin function, using $J=2$ and $g=2.1$ (yielding $\mu=4.2\mu_B$), the same values as for V surface impurities.

For all four systems, Rb/V, Rb/V/Rb, Cs/V, and Cs/V/Cs, we obtain a positive AHR. The magnetic moments lie in the range between $3\mu_B$ and $4.2\mu_B$. These values are considerably smaller than those for the Na host.

An interesting feature is the fact that the AHR for V impurities on and in the alkali hosts changes sign along the series Na, K, Rb, and Cs. This is demonstrated in Figs. 4 and 5. In Fig. 4 we show the low-temperature AHR as a function of the magnetic field for the different alkali hosts with a coverage of 0.01 atomic layers of V on the surface of the host. One clearly recognizes that the Na and K hosts behave very similarly with a negative AHR. This is the sign of the AHR for the $3d$ impurities Fe, Co, and Ni on the surface and in the bulk of the different alkali hosts (with exception of the Na/Ni system where the Ni does not have a moment). For the Rb and Cs hosts the sign of the AHR has changed and is now positive.

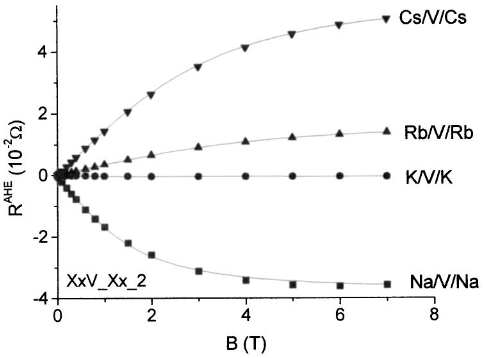

FIG. 5. The low-temperature anomalous Hall resistance of different alkali hosts with V impurities in the bulk.

TABLE I. The magnetic moment of V impurities on the surface and in the bulk of different alkali hosts.

| Host | Surface moment | Bulk moment |
|---|---|---|
| Na | 7 | 6.6 |
| K | 7 | |
| Rb | 3.6 | 3 |
| Cs | 4.2 | 4.2 |

Figure 5 shows the analogous series for the V impurities imbedded in the hosts. Qualitatively we observe the same behavior. However, there is the interesting difference that now the transition from negative to positive AHR occurs for the K host.

The size of the magnetic moment of V impurities shows also a clear change along the host series. The magnetic moments are shown in Table I. (The size of the V moment in K could not be determined because the AHR was much smaller than that in the other systems.)

## II. DISCUSSION

Riegel, Barth, and Buermann[8] suggested that the $3d$ shell of $3d$ impurities in alkali hosts behave similarly to the isolated atom. The $3d$ electrons barely hybridize with the conduction electrons and obey Hund's rules. If we assume that the V impurity possesses three electrons in the $3d$ shell then Hund's rules say (i) the $3d$ electrons align to form a maximum spin of $S=3/2$, (ii) for this spin choice the electrons choose the maximum orbital angular momentum, which yields $L=2+1+0=3$, and (iii) for the first subshell $L$ and $S$ align antiparallel and form a total angular momentum of $J=|L-S|$, which yields $J=3/2$ in our example. Together with a Lande factor $g=2/5$ this yields the very small moment of $\mu=3/5\mu_B$. If one assumes four $d$ electrons in the $3d$ shell then one obtains $L=S=2$ and therefore $J=0$ or no moment at all.

The observed large magnetic moments lie at roughly $7\mu_B$ on the Na side and $3\mu_B$–$4\mu_B$ on the Cs side. The large moment of V in Na is particularly surprising for several reasons:

(i) Na generally supports the formation of magnetic moments less than K, Rb, and Cs. This has been observed for the impurity Ni, which is magnetic in Cs, Rb, and K but nonmagnetic in Na.[9,4,10]

(ii) Our weak localization data show a strong dephasing of the conduction electrons by V impurities in Na. (The dephasing in weak localization due to magnetic impurities is discussed, for example, in Ref. 11. This behavior is actually quite similar to the dephasing effect of Fe impurities in Na. The strong dephasing points towards a strong hybridization of the conduction electrons with the magnetic impurity. Hybridization generally reduces the magnet moment of an impurity.

The V and Fe impurities in Na have rather similar behavior and moments. For Fe impurities a $3d^7$ configuration has been suggested,[10] with a total spin $S=3/2$ and a total orbital angular momentum of $L=3$. Both $S$ and $L$ align parallel and yield $J=9/2$ and therefore the large magnetic moment. V in the $3d^3$ configuration has the same $S$ and $L$ as Fe in the $3d^7$. However, the third Hund's rule predicts (at least for the atomic state) that the $S$ and $L$ align antiparallel in the V impurity ($n_d \leqslant 5$).

V impurities in Rb and Cs behave, on the other hand, quite differently from Fe impurities and have smaller moments. The change of the host should have two effects:

(i) The lower electron density in Cs should lower the energy for the $3d^{n-1}$ relative to the $3d^n$ configuration in V (where we assume $n=3$) or even reduce the number of $d$ electrons on the impurity.

(ii) The hybridization between the conduction electrons and the $3d$ impurity should decrease when going from Na to Cs. For the Na host multiple hopping of conduction electrons in and out of the $3d$ shell of the $3d$ impurity should be present, yielding a ground state for the impurity with a mixture of valences. (The Friedel-Anderson model is the extreme example because the impurity is in a mixture with $n_d=0,1,...,10$ $d$ electrons.) However, in the Cs host the V impurity should have a rather small hybridization with the conduction electrons and exist in a well-defined $3d^n$ state. But the moment of $4\mu_B$ is much larger than the $3/5\mu_B$ the atomic model predicts for $3d^3$, or the $4/3\mu_B$ for a $3d^2$ configuration (the $3d^4$ configuration has zero moment). A rather large enhancement through the host would be necessary to arrive at $4\mu_B$.

The sign change of the AHR for the V impurity when going from the Na to the Cs host is particularly interesting. It indicates that the electronic structure of the V impurity changes when going from Na to Cs, as discussed above. However, our understanding of the V structure is too incomplete and we cannot give even a qualitative explanation for the sign change.

All the numerical calculations of the magnetic moments of $3d$ impurities in alkali hosts assume that the Fermi surface of the alkali host does not touch any Bragg plane and has a spherical shape, i.e., they assume a "Bragg-free electron gas." They treat the $3d$ impurity in different modifications of the self-consistent local spin-density (functional) approximation.[12–14] However, there is an alternative model for the alkali metals given by Overhauser[15,16] who considered the presence of spin density or charge-density waves in alkali metals. According to Overhauser the charge-density waves win. In a private communication Overhauser suggested that at the $3d$ impurities the alkali host forms (spherical) spin-density waves which converge into a charge-density wave. If the spin-density waves exist only over a distance of $\lambda/4$ (where $\lambda$ is the wavelength of the spin wave) then the total spin of the host in the sphere of radius $\lambda/4$ enhances the impurity moment considerably. In the absence of any quantitative analysis we consider this an interesting idea. We believe that our experimental results present a considerable challenge to the traditional theory of magnetic impurities in alkali hosts.

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