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Electronic spin-spin coupling in rare earth doped semiconductor and semimetal clusters

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Abstract. Coupling between electronic spins in rare earth doped Te_N and Bi_N clusters is investigated by size selective Stern–Gerlach deflection experiments. The results are interpreted in terms of $\mathrm{Dy}^{3+}(\mathrm{Te}_N)^{3-}$ and $\mathrm{Dy}^{3+}(\mathrm{Bi}_N)^{3-}$ structures. This magnetochemical approach is consistent with a Zener type exchange spin coupling between valence electrons and the localized electrons in the impurity core.

PACS. 36.40.Cg Electronic and magnetic properties of clusters – 32.10.Dk Electric and magnetic moments, polarizability – 32.60.+i Zeeman and Stark effects

1 Introduction

The number of valence electrons plays an important role for the understanding of electronic properties of isolated semiconductor [1] and metal clusters [2]. Good examples are $\mathrm{Ga}_N\mathrm{As}_M$ clusters which show significantly higher polarizabilities and lower HOMO-LUMO-gaps for clusters with odd numbers of valence electrons than for clusters with even numbers of electrons [1, 3]. These effects can be related to the presence of an unpaired electron in clusters with odd numbers of electrons, which correspond to open shell quantum chemical systems [1, 3, 4]. We anticipate another interesting effect due to the presence of radical electrons in open shell clusters, when implanting rare earth metal impurities into semiconductor clusters. These metal atoms provide localized f electron systems with large electronic angular momenta $\mathbf{j}_\mathrm{I}$, for example $j_\mathrm{I} = 15/2$ for the Dy^{3+} ion ($4f^9$, ${}^6\mathrm{H}_{15/2}$), which exhibits a very large magnetic moment $\mu_\mathrm{I} = 10.6\mu_\mathrm{B}$ [5]. In these systems the question arises, whether the angular momentum vector $\mathbf{j}_\mathrm{I}$ of these localized electrons and the spin vector $\mathbf{s}_\mathrm{R}$ of the radical electron are coupled.

The impurity can be implanted into a semiconductor cluster according to the chemical reaction $\mathrm{Dy} + \mathrm{Te}_N \rightarrow \mathrm{DyTe}_N$, carried out in a buffer gas. The Te_N clusters provide an even number of electrons $6N$ for any given N, while each Dy atom adds three electrons to the s-p-electron system of the more electronegative Te_N clusters. This oxidation $\mathrm{Dy} \rightarrow \mathrm{Dy}^{3+} + 3\mathrm{e}^-$ is known very well for many Dy compounds with more electronegative elements [6]. In analogy to the Zintl concept for the bulk [7, 8], we propose a formal charge transfer $\mathrm{Dy} + \mathrm{Te}_N \rightarrow \mathrm{Dy}^{3+}(\mathrm{Te}_N)^{3-}$ in the cluster. Hence, the electronic structure of the polyanion Te_N^{3-} is dominated by one unpaired radical electron with the spin $\mathbf{s}_\mathrm{R} = 1/2$ located in an s-p molecular orbital (provided there is no molecular symmetry leading to higher multiplet states). As known from quantum theory, the spin $\mathbf{s}_\mathrm{R}$ of the $(\mathrm{Te}_N)^{3-}$ polyanion can couple to the spin of the $4f$ electrons of the Dy^{3+} ion via exchange interaction. In f systems the spin orbit coupling between the total spin $\mathbf{s}_\mathrm{I}$ and the total orbital angular momentum $\mathbf{l}_\mathrm{I}$ of the f-core is stronger than the coupling between $\mathbf{s}_\mathrm{I}$ and $\mathbf{s}_\mathrm{R}$ [9]. Hence, the interaction between the $4f$ spins and the spin of the radical electron is expressed most conveniently in terms of a $\mathbf{j}_\mathrm{I}\mathbf{s}_\mathrm{R}$ coupling scheme [9], where $\mathbf{j}_\mathrm{I} = \mathbf{s}_\mathrm{I} + \mathbf{l}_\mathrm{I}$ denotes the resulting total angular momentum of the f-core. In this model we assume either parallel alignment of the two vectors $\mathbf{j}_\mathrm{I}$ and $\mathbf{s}_\mathrm{R}$, leading to a total electronic angular momentum $J_\mathrm{e} = j_\mathrm{I} + s_\mathrm{R} = 15/2 + 1/2 = 17/2$ (ferromagnetic coupling) or antiparallel alignment resulting in $J_\mathrm{e} = j_\mathrm{I} - s_\mathrm{R} = 15/2 - 1/2 = 13/2$ (antiferromagnetic coupling).

Up to now, the exchange coupling between the spin of a radical s or p electron and the angular momentum of localized f core electrons has not been investigated in isolated inorganic clusters. However, in the atomic limit such an (ferromagnetic) exchange coupling has already been observed by optical spectroscopy of isolated rare earth ions in the gas phase, such as Nd^{2+} ($4f^46s$) [9], and of rare earth complexes [10]. Moreover, in solid state physics this coupling between conduction electrons and localized core electrons is known as the Zener s-d or s-f coupling model [11, 13], which describes the exchange interaction of magnetic impurities with the electron gas of a non magnetic metal. One of the consequences of this coupling model is that conduction electrons are scattered by the localized core electrons of the impurity. This gives rise to an unusual temperature dependence of the specific resistance which is known as the Kondo effect [11]. In addition to its significance for the understanding of the Kondo effect, the Zener model provides a suitable theor-

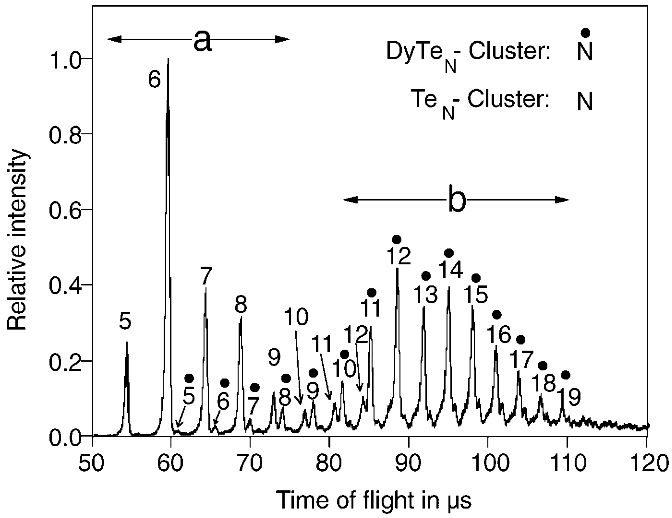

Fig. 1. Photoionization mass spectrum of DyTe$_N$ clusters ($h\nu = 7.9\,\text{eV}$). Bold numbers $\boldsymbol{N}$ with a point denote DyTe$_N$ clusters, while simple numbers N denote the pure Te$_N$ clusters. Small peaks to the right of large DyTe$_N$ clusters ($N = 13 - 19$) indicate Dy$_2$Te$_{N-1}$ cluster formation.

etical basis for the RKKY-magnetic ordering scheme [12] for magnetic impurities in non magnetic metals. In a first step the electron spin density of the electron gas is polarized by an impurity to form RKKY-oscillations in the spatial spin density distribution. In a second step the spin-polarized electron gas acts on the neighboring impurity electrons. This interaction can explain the magnetic ordering observed in the bulk [11,12]. Although the RKKY model was developed for bulk metal states, it can be transferred formally to molecular systems like clusters by replacing the Bloch functions (or, alternatively, the Wannier orbitals) [14] of the bulk metal by the molecular orbitals of the clusters [15]. Consequently, the valence electrons of the polyanions are polarized by magnetic impurity atoms like Dy. Then this polarized electrondensity distribution of the polyanion governs the coupling between the impurity atoms. This model provides expressions for the exchange interaction energies which depend on the specific forms of the molecular orbitals, i.e. the chemical bonding, in the clusters.

The effect of the discussed $\mathbf{j}_\mathrm{I}\mathbf{s}_\mathrm{R}$ coupling should become more obvious, if we replace the tellurium polyanions by bismuth polyanions. Bi and Te exhibit comparable electronegativities γ (Pauling scale) and radii $\mathbf{r}_\mathrm{s}$ (Bi: $\gamma = 2.02$, $r_\mathrm{s} = 1.53\,\text{Å}$; Te: $\gamma = 2.1$, $r_\mathrm{s} = 1.43\,\text{Å}$), but Bi has an odd number of valence electrons in contrast to Te. Therefore, the different numbers of valence electrons in the polyanions $(\mathrm{Bi}_N)^{3-}$ and $(\mathrm{Te}_N)^{3-}$ should be mainly responsible for any differing chemical behavior. As stated above, the $(\mathrm{Te}_N)^{3-}$ polyanion provides an odd number of electrons for any given N, while $(\mathrm{Bi}_N)^{3-}$ has an even number of electrons $5N + 3$ for odd N and an odd number of electrons $5N + 3$ for even N. This results in coupling schemes with $J_\mathrm{e} = j_\mathrm{I} + s_\mathrm{R}$ or $J_\mathrm{e} = j_\mathrm{I} - s_\mathrm{R}$ for aggregates with an even number N of Bi atoms, while we expect an unperturbed rare earth angular momentum $J_\mathrm{e} = j_\mathrm{I}$ for DyBi$_N$ clusters with an odd N, when the polyanion $(\mathrm{Bi}_N)^{3-}$ has no unpaired electrons.

Since it is experimentally very difficult to investigate directly the total electronic angular momentum $\mathbf{J_C}$ of the clusters, we have measured the average magnetization μ_z of the doped clusters in a strong magnetic field of $B = 1.6\,\text{T}$. We expect that the magnetization will depend monotonously on the total angular momentum J of the electronic system, i.e. we expect to find larger paramagnetic magnetizations for large J values and smaller magnetizations for small J values. Moreover, if this idea works, we might gain experimental information about the coupling between two or more magnetic impurities $\mathbf{J_{I1}}, \mathbf{J_{I2}}$,... giving rise to a total $\mathbf{J_C} = \mathbf{J_{I1}} + \mathbf{J_{I2}}$, ... in analogy to the coupling scheme for the bulk on the basis of the RKKY model, as discussed above.

2 Experimental

For the generation of mixed clusters we employ an apparatus which contains two independent laser vaporization cluster sources, using Helium as carrier gas. One source produces semiconductor clusters and the other a small amount of Dy atoms. The cluster-He mixture flows into a reaction chamber. There it is mixed with the Dy-He gas and the reaction of Dy with the semiconductor clusters takes place. The product clusters leave the reaction chamber through a cooled nozzle ($T_\mathrm{Nozzle} = 40\,\text{K}$) and are expanded together with the He to form a cluster beam. This beam is collimated and passes between the pole faces of a Stern–Gerlach magnet. There the clusters are magnetized in z direction, giving rise to a magnetic moment component μ_z (which will be called magnetization throughout the text). Since the field gradient points in z direction, there is a force F_z acting on the clusters [16–18]. This causes a small deflection of the cluster beam which can be measured behind the magnet by scanning the molecular beam with a collimated ionization laser beam ($h\nu = 7.9\,\text{eV}$) in combination with a time of flight mass spectrometer [1]. The apparatus is described essentially in [1]. The only difference is that we have installed an inhomogenous magnetic field instead of the electric field. Furthermore we have replaced the single laser vaporization source by the new source described above and in [19].

3 Results and discussion

Figure 1 gives an overview over a typical mass spectrum of doped clusters Dy$_M$Te$_N$ if the Dy source is switched off, one obtains simple Te$_N$ clusters with 5-10 atoms (size range a in Fig. 1). It is interesting to notice that the addition of Dy does not only achieve products by the reaction $\mathrm{Te}_N + \mathrm{Dy} \to \mathrm{DyTe}_N$, but that the majority of these DyTe$_N$ clusters seems to react immediately with other Te$_M$ clusters, forming larger doped species DyTe$_{N+M}$ with $N + M$ about $10 - 20$ (size range b in Fig. 1).

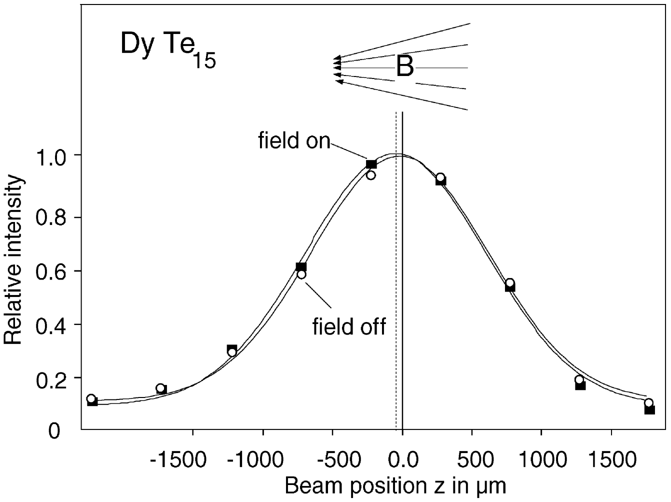

Fig. 2. Beam profiles of the $DyTe_{15}$ cluster with the magnetic field applied (full squares) and without magnetic field (open circles). The shift is about 50 μm. The line figure shows the B field in the Stern–Gerlach magnet schematically.

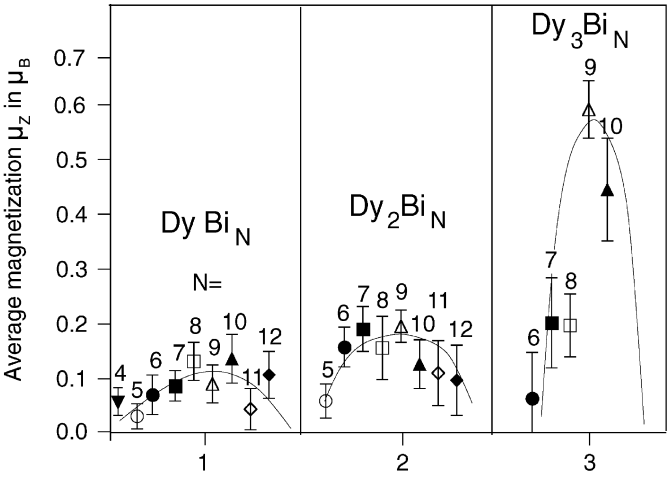

Fig. 3. Measured magnetization of Dy_MBi_N clusters with up to three magnetic impurities measured at $T_{\mathrm{nozzle}} = 40$ K and $B = 1.6$ T.

Figure 2 shows the typical change of the beam profile of a doped cluster when the field in the Stern–Gerlach magnet is switched on. Even for heavy particles containing only a single paramagnetic center small deflections can be resolved such as the shift of 50 μm for the $DyTe_{15}$ cluster. We find that the profiles measured with applied magnetic field are shifted (paramagnetically) to the side of the larger magnetic field. From these shifts we calculate the average magnetic moment μ_z for the investigated $DyTe_N$ and Dy_MBi_N species by taking into account the beam velocity and the apparatus constant, which was determined by calibration using Bi atoms [20].

Average μ_z values calculated from the measured profile shifts for Dy_MBi_N clusters are shown in Fig. 3. With increasing number of Bi atoms in the cluster, the average magnetization μ_z tends to pass a maximum at about $N = 9$ for all M values as indicated by the thin lines in Fig. 3. If we look at the values for clusters with single Dy atoms more closely, the general feature given by the thin line seems to be modulated by small oscillations. After enlarging the area for $N = 7...12$, we see that clusters with even N exhibit larger moments than those with odd N (Fig. 4a). This observation is in agreement with Zener-type-exchange coupling between the spins of the radical electrons and the spins of the Dy^{3+} cores as discussed in the introduction. In this case the exchange coupling must be ferromagnetic. Hence, the oscillation can be related to an additional radical electron spin in $Dy^{3+}(Bi_N)^{3-}$ clusters with even N, while no radical spin is present in $Dy^{3+}(Bi_N)^{3-}$ with odd N.

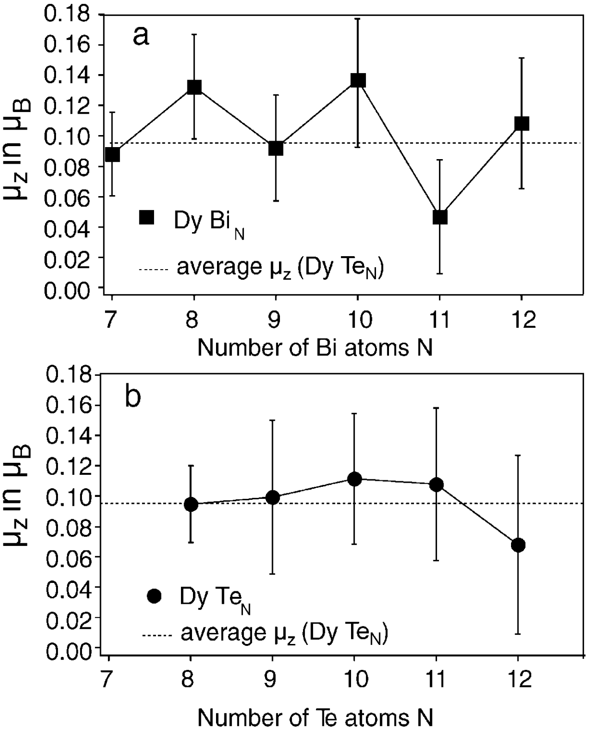

Fig. 4. Magnetization of $DyBi_N$-clusters (a) compared to the magnetization of $DyTe_N$ clusters (b) with the same number of ligand atoms. An explanation for the oscillations in (a) is given in the text.

To confirm this model we measured the average magnetization μ_z of $DyTe_N$ clusters, shown in Fig. 4b. In this case there is no odd even oscillation visible and the average μ_z value of the $DyTe_N$ clusters is very close to the average values measured for $DyBi_N$. This is in agreement with the fact that $(Te_N)^{3-}$ polyanions have an odd number of electrons independently of N, i.e. always one unpaired radical electron. We cannot decide, if this electron couples ferro- or antiferromagnetically to Dy^{3+}. However, in any case one cannot expect any variation of J with N nor an oscillation in $\mu_z(N)$.

The magnetic properties of the clusters with several magnetic centers seem to depend in a complicated way on the number of Bi atoms. This reflects the indirect coupling between magnetic centers via the molecular orbitals of the clusters, representing the complex bonding in this inorganic system.

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