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Magnetic properties of transition-metal nanoclusters on a biological substrate

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Abstract

We have investigated the magnetic properties of transition-metal clusters with a single grain size of about 1 nm. These metallic nanoclusters have been deposed on a biological substrate. This substrate is a purified self-assembling paracrystalline surface layer (S-layer) of the *Bacillus sphaericus* strain JG-A12, which exhibits square symmetry and is composed of identical protein monomers. First data of the magnetic susceptibility, taken in a SQUID magnetometer at $0<B<7\,\mathrm{T}$ and $1.8\,\mathrm{K}<T<400\,\mathrm{K}$, reveal unusual magnetic properties. The Stoner enhancement factor of the d conduction-electron susceptibility in the Pd and Pt nanoclusters is dramatically reduced compared to the one of the corresponding bulk transition metals. The weakened magnetism of the 5d electrons is considered to play a crucial role for the occurrence of superconductivity in microgranular Pt by adjusting the balance between electron–phonon interactions and competing magnetic interactions.

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Keywords: Metallic nanoclusters; Paracrystalline protein surface layer; Magnetism of transition-metal nanoclusters

Compared to their bulk counterparts, micro- and in particular nanogranular materials can reveal a diverse appearance of physical properties. In particular, their magnetic and superconducting behaviour can be drastically changed. We have produced and investigated metal clusters with a grain size of about 1 nm, which, in consequence, consist of about 100 atoms per grain only. In our project, we compare their magnetic and transport features to the properties of the same materials condensed in larger cluster and grain sizes on the microscopic, mesoscopic as well as bulk scale.

There are several procedures, such as condensation of metal vapour in inert gas, aerosol synthesis or chemical precipitation, for the production of metal particles with grain sizes in the micro- and nanometer scale. However, all of them result in a wider distribution of the grain size. Here, we describe magnetic properties of Pd nanoclusters regularly distributed on a purified protein surface layer (S-layer) of *Bacillus sphaericus* JG-A12. The nanoclusters were prepared by a two-step procedure as previously described [1]. The first step includes a complexation of Pd(II) by specific regions of the S-layer protein [2]. For this, the protein was dialyzed against H_2O and several milligrams of it were incubated in a solution of a Pd salt (Na_2PdCl_4). The solution has been prepared at least 24 h before use and stored in the dark. After several hours of incubation at room temperature, the samples were centrifuged (20 min at $10^5\,\mathrm{m\,s^{-2}}$) and the pellets were resuspended in H_2O. Residual salts were removed by dialysis of the metallized proteins against H_2O. In the second step, Pd(II) was reduced by the addition of H_2 or other reducing agents to

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produce Pd(0)-nanoparticles. The metallized protein samples were again centrifuged and finally dried in a vacuum oven (48 h at 80 °C).

The transition-metal nanoclusters were investigated using mass spectroscopy in order to determine the mass ratio of Pd and the protein. In the course of our investigation, we have produced mass ratios of Pd and the S-layer ranging from 5:1 to 1:3. We use typical sample masses of a few milligrams for all measurements described below. Extended X-ray absorption fine structure spectroscopy (EXAFS) performed at the ESRF (Grenoble, France) was used to measure the cluster size. The analysis of EXAFS data allows a determination of the coordination numbers (e.g., of Pd neighbours of Pd atoms in the first Pd–Pd coordination shell), for which we find five for the Pd nanoclusters instead of 12 for bulk Pd. This then results in a mean grain diameter of about 1.5 nm [3] for the Pd nanoclusters on the protein S-layer [1].

We have investigated the magnetic properties of nanoclusters of the transition metals, Pd and Pt, by means of SQUID magnetometry. We observe a clear reduction of the susceptibility compared to the one obtained from bulk Pd (see Fig. 1), which develops spin fluctuations and is nearly ferromagnetic. The maximum of the susceptibility of bulk Pd at $T = 80$ K is attributed to spin fluctuations, i.e., ferromagnetic correlations of the 4d magnetic moments on a small length and short time scale. While the Stoner enhancement ($\chi = S\chi_{\mathrm{Pauli}}$) is large and reaches a value of 10 in bulk Pd, the Stoner enhancement factor in the pure Pd nanoclusters almost vanishes to $S = 1$, i.e., the 4d electrons interact much less with each other in the nanograins. Our data do not support former observations of ferromagnetic contributions arising from oriented facets of the surface of nanograins with a larger diameter of about 10 nm as reported in Ref. [4]. Fig. 1 also demonstrates the strong dependence of the susceptibility of the Pd nanograins on the 3d impurity concentration.

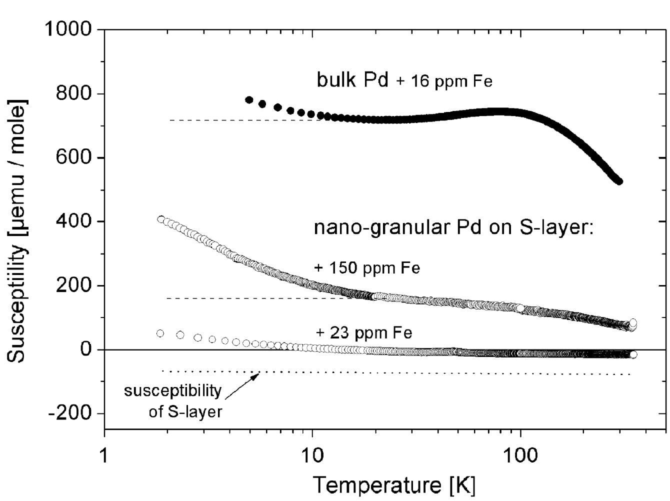

Fig. 1. Magnetic molar susceptibility of nanogranular Pd deposed on a protein S-layer (mass ratio 1:1) of two samples with different 3d impurity concentrations compared to bulk Pd. Dashed lines indicate low-temperature susceptibilities without the low-temperature increase resulting from the magnetization of the magnetic 3d impurities. In addition, the diamagnetic contribution per mole Pd of the protein S-layer is shown (dotted line).

The decrease of the magnetic d-band susceptibility agrees with the model of Fay and Appel [5], which considers the effect of spin–orbit scattering on the magnetic and superconducting properties of granular nearly ferromagnetic metals. In the case of micro- [6] and submicrogranular [7] Pt, the weakened magnetism of the 5d electrons has been found to play a crucial role for the earlier observed occurrence of superconductivity by adjusting the balance between electron–phonon interactions and competing magnetic interactions. As the superconducting transition temperature has been observed to increase with decreasing Pt grain size [7], we now focus our interest on the search of superconductivity in the transition-metal nanoclusters deposed on the biological template. For this, we are preparing to extend our investigations to the mK-temperature range.

Further to that, we have started to produce nanoclusters of superconducting elements such as Al, Sn, Ga and Pb on the S-layer protein sheets of *B. sphaericus* JG-A12. Recent improvements of our preparation method, in particular processing of highly pure chemical agents under anaerobic conditions in a nonmagnetic quartz-glass environment, made it possible to stabilize metallic Pb nanograins on the S-layer and to prevent them from agglomeration as well as from oxidation. The superconducting properties of these separated Pb clusters are under investigation. First data yield a superconducting critical field of the size of several T which is strongly enhanced compared to the corresponding critical magnetic field of 0.09 T of bulk Pb. Recently, Ovchinnikov and Kresin [8] have predicted the possibility of strengthening the superconducting properties in metallic nanoclusters. As a first experimental proof, Hagel et al. [9] have observed a clear increase of the superconducting critical parameters in a crystalline Ga_{84}-cluster compound.

The S-layer proteins have the capacity to bind selectively and reversibly high amounts of metals, making them interesting also for technological applications. Their usability for biosynthesis is not limited to elements only. Besides metal oxides, e.g., FeO, also binary magnetic compounds such as PtFe or CoNi and semiconducting nanoclusters, e.g., PbSe [10], can be produced.

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