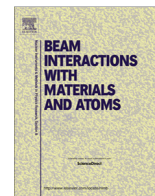




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# The potential of Rutherford Backscattering Spectrometry for composition analysis of colloidal nanocrystals

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## ABSTRACT

We investigate the potential of elastic scattering of energetic ions for compositional analysis of magnetic colloidal nanocrystals. Thin layers of nanocrystals deposited by spin coating on Si-wafers are investigated by two different set-ups for Rutherford Backscattering Spectrometry (RBS), employing different projectile ions (<sup>4</sup>He, <sup>12</sup>C) and primary energies (600 keV–8 MeV). The advantages and disadvantages of the different approaches are discussed in terms of obtainable mass resolution, necessary primary particle fluence and deposited energy. It is shown that different isotopes of transition metals can be resolved by employing 8 MeV <sup>12</sup>C<sup>3+</sup> primary ions.

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## 1. Introduction

Nanocrystals with complex composition and structure have emerged from a material class of fundamental interest to industrial relevance [1]. Postsynthetic modification of composition and structure of nanocrystals permits to tailor their electrical or magnetic properties in ways not practicable by direct synthesis (see e.g. [2,3]). Along such research lines a reliable composition analysis of the nanocrystalline material is demanded. An ideal analysis method for composition measurements should be able to operate with small amounts of sample material and permit unique identification of the constituents and determination of their respective concentrations. The analysis should be furthermore independent of the size and the size distribution as well as the organic coating or solvent in case of colloidal nanoparticles.

Elastic scattering techniques employing energetic ions with energies of several hundred keV per atomic mass unit can fulfil these requirements, since they yield information on the composition via scattering from the atomic nucleus, free from matrix effects, and for sample amounts of less than a microgram (see e.g. [4] for an overview).

Due to these properties, several recent studies explored and used the potential of elastic scattering – mainly the Medium-Energy Ion Scattering (MEIS) methodology – for analysis of colloidal nanocrystals [5–7]. As many of these studies demonstrate, enhanced scattering cross sections, and thus also lower sample

material amounts necessary for the analysis can be achieved e.g. by employing low primary energies of around 100 keV. This, however, demands drastically increased energy resolution to keep up analytical performance. This can be achieved e.g. by use of magnetic or electrostatic spectrometers [8,9].

We present an investigation of the composition of colloidal nanocrystals with different compositions by Rutherford Backscattering Spectrometry (RBS) employing different ion species at a number of different primary energies. In one approach, the primary ion energy is reduced for an increased scattering cross section and a high-resolution surface barrier detector is employed [10]. In the other approach heavier ions with at energies of several MeV are employed as projectiles to achieve superior mass resolution, necessary for characterisation of a system of magnetic nanocrystal heterostructures [11]. We give a detailed description of the experimental details, the evaluation and the achievable accuracy as well as how to avoid complications that may arise in such a kind of analysis.

## 2. Experiment

The ion scattering experiments in Linz were performed using the AN-700 van de Graaff accelerator at the Department of Atomic Physics and Surface Science of the JKU Linz. The accelerator is capable of creating monoenergetic beams of H, D atomic and molecular ions and He<sup>+</sup> ions with energies in the range 30–700 keV and primary beam currents up to several μA. In the present study 600 keV He<sup>+</sup> ions were used due to their favourable mass resolution. The samples were analysed in a HV-chamber with a base-pressure of 1·10<sup>−5</sup> Pa.

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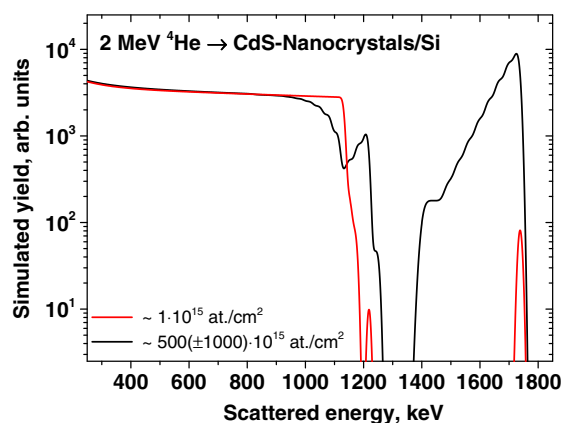
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Scattered ions were detected by two semiconductor surface barrier detectors. The first detector, situated in  $150.1^\circ$  in Cornell geometry features very high energy resolution (FWHM  $< 1.8$  keV). This is obtained by LN<sub>2</sub> cooling of the detector and of the input stage of the preamplifier, and by minimising the input capacitance of the set-up. Furthermore, the housing of the amplifying FET is optimised to keep it at optimum temperature ( $\sim 100$  K) and to avoid microphonic noise from mechanical vibrations [10]. The electronic noise of this detection system is found  $\sim 500$  eV from detection of soft X-rays. The main contribution that decreases energy resolution for ions is energy loss straggling in the dead layer of the detector which finally yields an energy resolution of 1.8 keV for protons and about 7 keV for He-ions. By use of this detector high-resolution depth profiling experiments of nm-films [12] and analysis of samples with high demands on mass resolution as identification of trace elements in organic samples [13] has been performed successfully. The second detector, situated in  $154.6^\circ$  in IBM geometry features a larger solid angle and thus higher count rate, but lower energy resolution.

The experiments in Uppsala were performed employing a 5 MV 15SDH-2 pelletron tandem-accelerator at the Ångström laboratory. By the use of different ion-sources beams of many different ion species with energies in the range of 2–50 MeV can be produced. In the present study 2 MeV  $^4\text{He}^+$  ions and 8 MeV  $^{12}\text{C}^{3+}$  ions were used. The scattering chamber with a base-pressure of  $< 1 \cdot 10^{-5}$  Pa holds two solid state detectors for RBS, in Cornell geometry, with the first situated fixed at  $170.0^\circ$  while the second can be positioned at almost arbitrary scattering angles.

Two different systems of nanocrystals were investigated. The first set (system I) were CdSe- and CdS-nanocrystals for which by cation-exchange Cd was exchanged via Hg to Mn. System II was formed from iron-oxide nanocrystals for which cation-exchange was employed to directly exchange Fe by Co [11].

The nanocrystalline samples were kept in high-purity chloroform solution after synthesis. In order to permit a unique identification of present elements by scattering kinematics thin films [14] of nanocrystals were prepared from the solutions. To obtain compositional information, a substrate with atomic number lower than the constituents is desirable. Deposition on a single crystalline Si-wafer was chosen, since it features a high-quality surface and permits identification of all constituting elements in system I and



**Fig. 1.** RBS spectra simulated by SIMNRA [15] for 2 MeV  $^4\text{He}^+$  ions scattered from thin films of CdS on a Si substrate. For a sub-monolayer film, without clustering of the crystals a sharp peak structure is expected (red line). The nanocrystals will tend to form clusters on the surface, which will lead to spectra as shown by the black curve. The exponentially decaying low energy tails of the spectra can complicate analysis, especially, when the interest is in species of similar mass. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

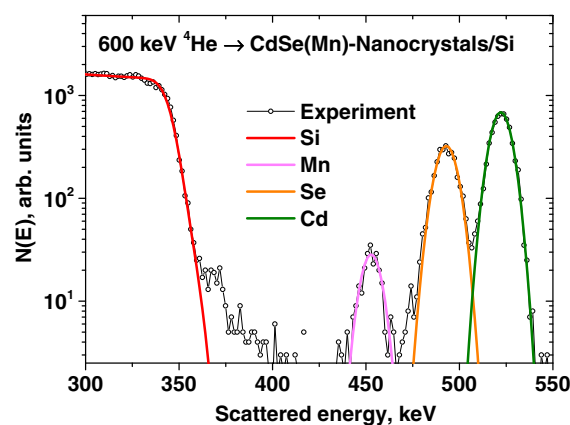
the metal components of system II, respectively. Deposition was done via spin coating at different rotation speeds. The aim was on achieving a thin homogenous layer of nanocrystals in order to perform quantitative analysis. Fig. 1 shows simulations for a typical RBS spectrum obtained for a high-quality thin film (red line), in comparison to a film featuring a broad thickness distribution (black line). For quantification of concentrations simulation of RBS-spectra was performed using the SIMNRA simulation package [15].

As can be readily deduced from the figure, a broad distribution of nanocrystals clearly hampers the analysis of the composition, especially for elements adjacent in the periodic table. Significant clustering can be expected in case of deposition of multilayers of nanocrystals. To compare, a monolayer of nanocrystals with typical diameters of about 5 nm corresponds to an areal density of  $\sim 25 \cdot 10^{15}$  atoms/cm<sup>2</sup>. Since significant clustering is expected for the equivalent of a monolayer, the aim is to achieve sub-monolayer coverage, which in turn, however, means a low but narrow signal, as can be seen from comparison to the substrate signal in Fig. 1.

### 3. Results and discussion

The analysis of samples for system I was performed mainly by the set-up in Linz and for several samples also in Uppsala. Experiments in Linz were performed using a 600 keV  $^4\text{He}^+$  primary ion beam. Reference experiments on the Si-wafers showed the absence of contaminations in the substrate. A typical spectrum resulting from an experiment using a spin coated thin film of crystals from system I is shown in Fig. 2. As can be seen, distinct peaks can be identified, each corresponding to scattering from a certain element in the sample. From fitting the primary ion current and the solid angle of the detector by the Si background spectrum the apparent thickness of the sample is found to be  $10 \cdot 10^{15}$  atoms/cm<sup>2</sup>, which corresponds to a coverage well below one monolayer. Some minor channelling effects in the Si can be observed in the shape of the spectrum, which indicates that the coverage might be even lower in consequence of the reduced Si yield. The Si-signal is also slightly affected by pile-up in the detection system which forms a tail towards higher energies.

The accuracy of the evaluation is affected in a significant way by only two contributions: the major contribution is due the experiments statistics. When giving the relative concentrations of the constituents, as in this case Mn, Se and Cd, the error is dominated by the element featuring lowest peak area, i.e. Mn with about 250 counts.



**Fig. 2.** Experimental RBS spectra for 600 keV  $^4\text{He}^+$  ions scattered from thin films of CdSe nanocrystals in which part of the Cd was exchanged via Hg to Mn (open symbols). The films are spin-coated on a Si substrate. The film exhibits good quality, the Si-signal is slightly affected by pile-up in the detection system. Also shown is a simulation by SIMNRA [15] to quantify the concentrations.

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