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AFM OF METALLIC NANO-PARTICLES AND NANO-STRUCTURES IN HEAVILY IRRADIATED NaCl

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AFM investigations are reported for heavily, electron irradiated NaCl crystals in ultra high vacuum (UHV) in the non-contact mode with an UHV AFM/STM Omicron system. To avoid chemical reactions between the radiolytic Na and oxygen and water, the irradiated samples were cleaved and prepared for the experiments in UHV. At the surface of freshly cleaved samples, we have observed sodium nano-precipitates with shapes, which depend on the irradiation dose and the volume fraction of the radiolytic Na. It appears that the nano-structures consist of (i) isolated nano-particles, (ii) more or less random aggregates of these particles, (iii) fractally shaped networks and (iv) "fabrics" consisting of bundles of Quasi-1D arrays forming polymeric networks of nano-particles. Almost independent of the concentration of the metallic Na in the samples the size of the individual nano-particles is in the range 1–3 nm. Our new AFM results are fully in line with our CESR and previous Raman scattering results.

Keywords: Radiation damage; Nano-structures; Atomic force microscopy

1 INTRODUCTION

Nanometer sized particles have received increased attention during the past few years, because they have intriguing properties, which are often quite different from their bulk counterparts. In our studies we produce nano-particles of metallic sodium in bulk NaCl by exposure of the samples to an intense beam of high-energy electrons (0.5 MeV) from an electron accelerator. In our facility we can irradiate more than 300 samples simultaneously. The production rate of Na particles depends on the irradiation temperature and shows a maximum at about 100 °C. During the irradiation run the irradiation temperature is kept constant within 1–2 °C. The samples are cylindrical with a diameter of 6 mm and a thickness of typically 0.5 mm. In the past many attempts have been made to observe the radiation induced nano-particles of Na in NaCl, unfortunately with very little success. This was probably due to the fact that AFM in the contact mode has been used. The Na-particles are relatively soft and as a result the metal is "smeared out" by the cantilever over the NaCl surface during

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the experiment. In the present experiment all investigated, irradiated samples were cleaved in UHV and always kept under these conditions, also during the AFM experiments to prevent chemical reactions between the radiolytic Na and oxygen and water. The AFM experiments were carried out with an atomic force microscope system produced by Omicron (Germany) operating in the non-contact mode. Si cantilevers NSC11 (Estonia, Mikromasch) with tip-radii of about 10 nm were used.

Below we have presented the first results of the successful AFM measurements of the sodium nano-particles and nanostructures embedded in crystalline matrix of heavily irradiated NaCl.

2 RESULTS AND DISCUSSION

Figure 1 shows nano-particles at a (100) surface of a natural rock salt sample. From the observed latent heat of melting of the Na-particles we have calculated that the Na-concentration is 0.66%, *i.e.* 0.66% of all original Na-ions in the sample were transformed into metal atoms. The nano-particles in this picture are more or less round and have an apparent size (along the x–y directions of the cleaved surface) of about 10 nm, which is determined almost completely by the size of the AFM tip due to the well-known convolution phenomenon. It can be seen in Figure 1 that the surface of the cleaved sample is quite flat. In the lower

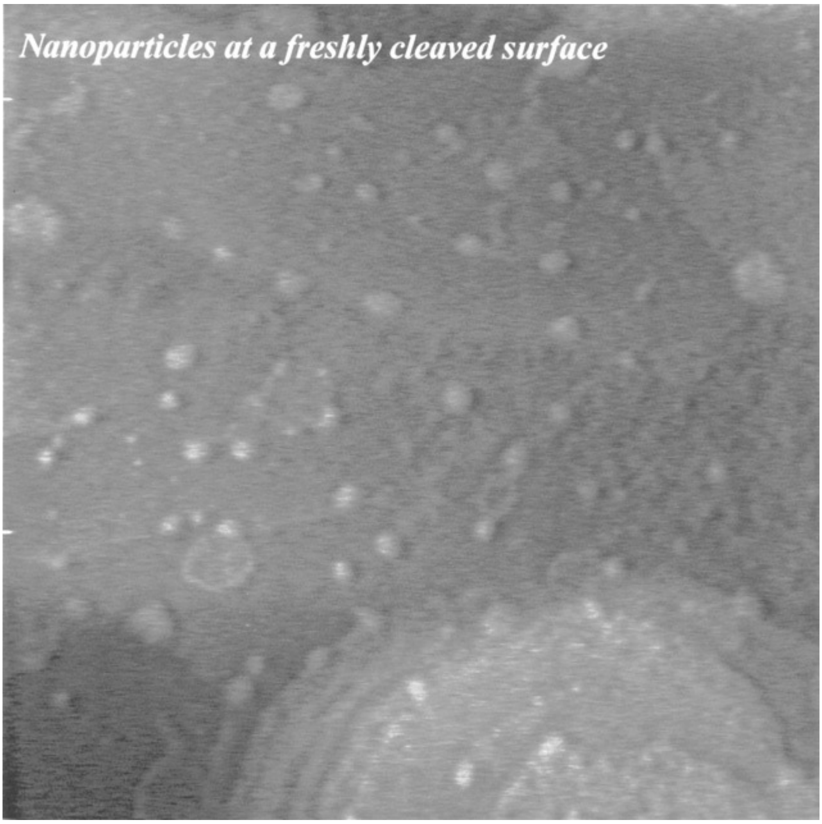

FIGURE 1 Isolated metallic nano-particles in NaCl with 0.66% Na. Size of the picture: $1600 \times 1600\,\text{nm}^2$. The nano-particles are visible as round protrusions at the cleavage plane.

part of Figure 1 we observe a number of crystal steps due to imperfect cleaving. More detailed information about the real size of the nano-particles can be obtained from the dimensions along the z-direction (*i.e.* the profile perpendicular to the cleaved surface), because here the errors caused by the tip geometry are much smaller. The sizes of the nano-particles along the z-direction were calculated from the heights of the protrusions. We estimate that the sizes of the nano-particles are between 1 and 3 nm, which means that the particles contain only a few dozen to a few hundred atoms.

When the damage percentage increases to values higher than 1% (*i.e.* more than 1% of the lattice Na^+ ions is transformed into metallic Na) the AFM pictures are different compared to the one shown in Figure 1. The pictures in Figure 2 (a,b,c) are taken from a sample with 1.52% Na. Here, we see that the particles cannot be considered as isolated objects anymore. They form complex conglomerates of nano-particles which cover the surface of a cleaved NaCl crystal. The shapes of the systems consisting of more or less connected nano-particles are highly irregular. The sizes of the individual nano-particles vary within a narrow range and the structures show features that resemble those of fractals. The details displayed in the enlarged picture in Figure 2b show that the structures are built up from very small nanoparticles. The z-profile of the AFM image, taken along the arrow shown in Figure 2b, has been presented in Figure 2c. From the heights of the protrusions one can see that in this more heavily damaged sample too the sizes of the nano-particles are in the range 1–3 nm. A very interesting point is that in this sample we can see that the nanoparticles are "lining up" to form Quasi-1D systems, which are observed in samples with high concentrations of Na. Apart from the nano-particles, which are connected, we observe in some regions of the cleaved surface isolated particles, which are very similar to those found in Figure 1 in terms of shape and average size.

The most intriguing results were obtained for the third sample, which revealed that the nano-particles form almost a fabric of bundles, consisting of linear arrays, in which the individual nano-particles can still be recognized (Fig. 3 a, b, c). This sample shows an extensive development of Quasi-1D structures consisting of nano-particles. The concentration of Na in this sample is 1.92%. From the enlarged picture of the region close to the central part of the image (Fig. 3b) individual nano-particles in the nanowires can be recognized. From the line profile shown in Figure 3c we have estimated the size of the individual nano-particles. It shows that the Quasi-1D structures in these materials are built up from nano-particles with sizes between 1 and 3 nm and it appears that Na nano-particles in heavily irradiated NaCl form new and intriguing "polymeric" networks of Na nano-particles parallel to the (100) cleavage planes. We assume that the donut shaped features are in fact bundles of linear formations with an orientation perpendicular to the cleavage plane.

Our AFM experiments have shown that Na-precipitates in heavily irradiated NaCl consist of strongly branched structures of nanometer sized particles, which are linked to one another or located at very close distances and in several cases form island shaped nano-wires of metallic Na. Our recent light scattering and magnetic resonance experiments strongly suggest that in nano-wires of metallic Na Quantum Confinement Effects are observable for both electron and phonon states. In two companion papers [1, 2] the results of Raman scattering, Conduction Electron Spin Resonance and SQUID are discussed. We have shown previously that in the early stages of the formation of radiation damage, when predominantly small and isolated precipitates of Na-metal exist, the samples show extensive quantum size effects [3]. When the concentration of metallic Na is less than 0.6%, the average size of the precipitates increases with the amount of Na-metal. For such samples the size of the Na particles has been determined from the temperature where the cross-over from Curie to Pauli paramagnetism occurs. From this particular Quantum Size Effect, which is associated with these isolated

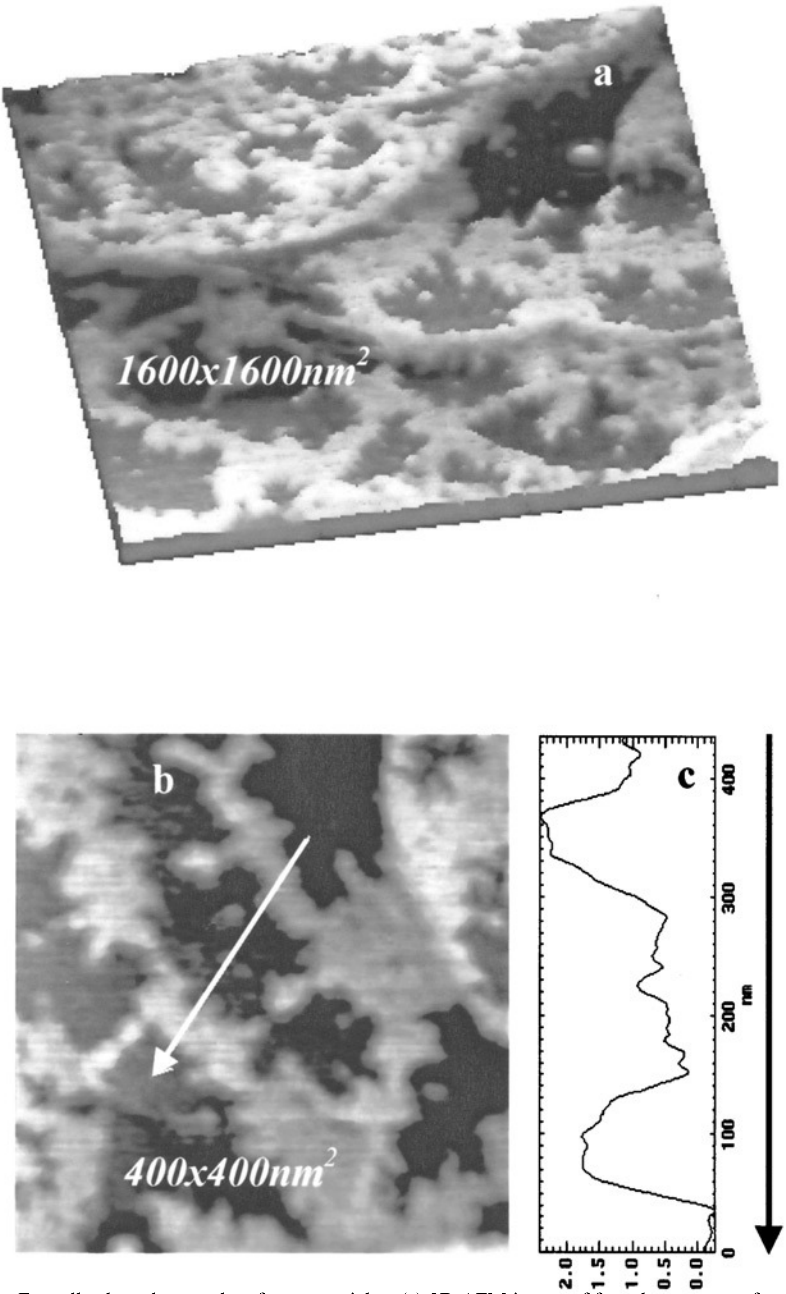

FIGURE 2 Fractally shaped networks of nano-particles; (a) 3D AFM image of fractal structures of nano-particles in NaCl with 1.52% metallic Na, (b) enlarged picture of strings of nano-particles, (c) the line plot of the image taken along the white arrow in Figure 2b.

nano-particles we have found that the diameters of the particles were a few nm [3], which is in good agreement with the AFM results presented here for nano-particles observed in moderately damaged samples (Fig. 1). In a companion paper [1] on low temperature CESR and SQUID experiments we propose that magnetic ordering with significant internal magnetism is present in our heavily irradiated samples. These observations indicate that ultimately

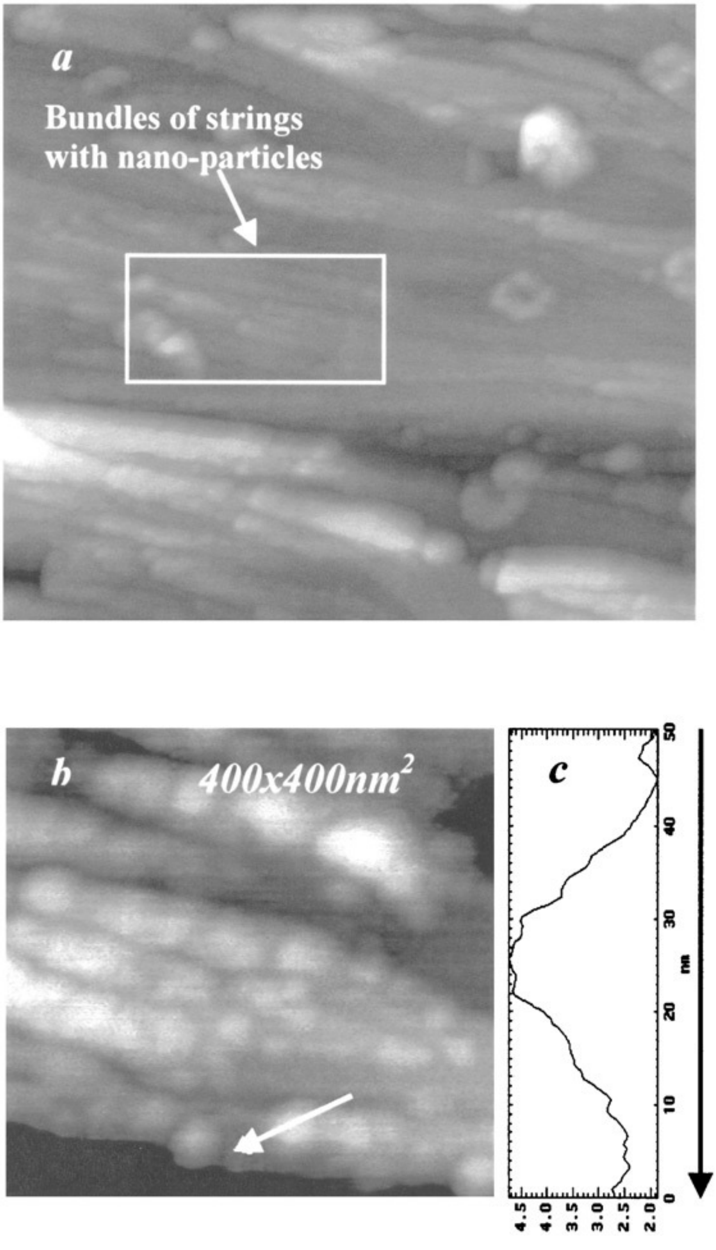

FIGURE 3 AFM of heavily irradiated NaCl with 1.92% Na; (a) quasi-1D bundles of nano-particles, (b) enlarged picture of the individual nano-wires, (c) line profile of the individual nano-particles.

mesoscopic defect structures are produced in our heavily damaged NaCl, revealing a metal-insulator transition similar to those found in conducting polymers. Considering the observation of several unusual Raman scattering peaks in a second companion paper [2] we can say that: (i) these observations support the idea of electron quantum confinement of excitations, which are quantized in wire like nano-particles of sodium with diameters of 2 nm and (ii) they also confirm our earlier proposal that metallic precipitates in heavily irradiated NaCl are not Euclidian objects, but complex systems with fractal geometry.

The results from the above-mentioned investigations are completely in line with the geometrical information of the nano-particles and nanostructures, obtained from the UHV AFM experiments reported in this paper. In the future we will continue our UHV AFM investigations on samples with different dopants and with different concentrations of radiolytic Na. In addition, UHV AFM and STM images at low and high temperatures on samples with very large amounts of radiolytic Na and extensive formation of Quasi-1D conducting nano-structures will be investigated.

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