Quantitative nanoscale characterisation by electron microscopy

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ABSTRACT: *The transmission electron microscope (TEM) is a choice instrument for the characterisation of materials and devices at the nanoscale. Apart from high spatial resolution, TEM offers a number of signals which can be exploited to obtain chemical and structural information concerning the specimen. Recent years have seen considerable advances in the use of electron microscopy and new techniques have been developed thanks to improved methodology, instrumentation and data acquisition systems. Here, we present a review of three such techniques particularly well suited for the study of nanoscale devices: strain mapping by high-resolution electron microscopy (HREM), elemental mapping by energy filtered microscopy (EFTEM), and measurements of magnetic and electric fields by electron holography.*

KEY WORDS: *transmission electron microscopy, electron holography, chemical mapping, strain*

1. Introduction

The study of nanomaterials is of fundamental interest because of what is known as the "size effect„. The phenomena governing physical properties of materials are characterised by length-scales, for example, the wavelength of light for optics, or the electron mean free path for conduction. A size effect is manifest when the physical dimensions of an object are smaller, or comparable, to these defining length scales. A simple example would be the scattering of light by particles which changes radically when their size is under a micron for visible light. It so happens that many of these characteristic length scales are in the nanometer range, thus explaining the interest in nanostructured materials or objects with nanometric dimensions. Totally new properties can be obtained by controlling object or grain size. It was shown recently that copper behaves completely differently mechanically when the grain size reaches nanometric dimensions (Champion *et al.*, 2003). In order to study these effects it is necessary to observe phenomena at the same length scale – hence the need for local characterisation techniques such as electron microscopy.

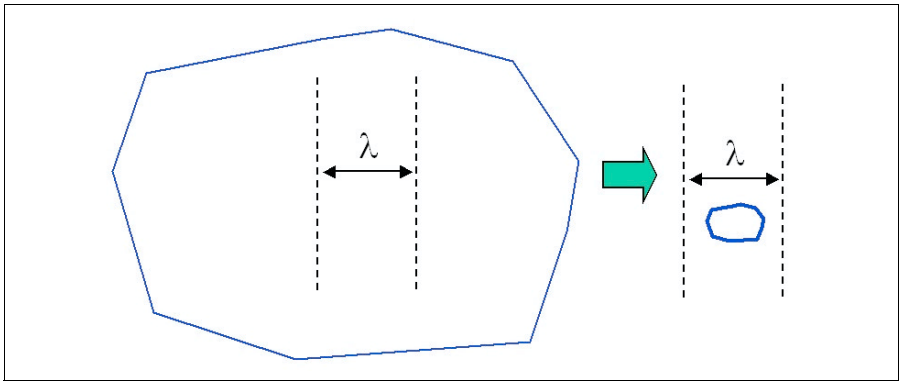

Figure 1. *Size effect in nanomaterials. Physical phenomena have associated characteristic length-scales, λ, which are usually much smaller than the object size (to the left). When object dimensions are smaller than λ (to the right) we can therefore expect new physics and a change in properties.*

The transmission electron microscope (TEM) is a choice instrument for the characterisation of materials and devices at the nanoscale. In addition to high intrinsic spatial resolution, TEM offers a number of signals which can be exploited to obtain chemical and structural information concerning the specimen. Recent years have seen considerable advances in the use of electron microscopy and new techniques have been developed thanks to improved methodology, instrumentation and data acquisition systems. Here we describe three such techniques for analysing strain, chemistry and magnetism at the near atomic scale.

2. Strain analysis by high-resolution electron microscopy

High-resolution electron microscopy (HREM) differs from conventional electron microscopy in that images are formed of the atomic lattice (see Figure 1). It is not our aim to explain how the images are formed; it is sufficient for the present purposes to know that the position of lattice fringes seen in the image are closely related to the atomic planes in the specimen. (For more ample details, see Spence 2003). It was realised early on that displacements could therefore be measured to very high accuracy from high-resolution images (Wood *et al.*, 1985). However, it was only with the development of image processing techniques and digital microscopy that maps of displacements and strains could be obtained.

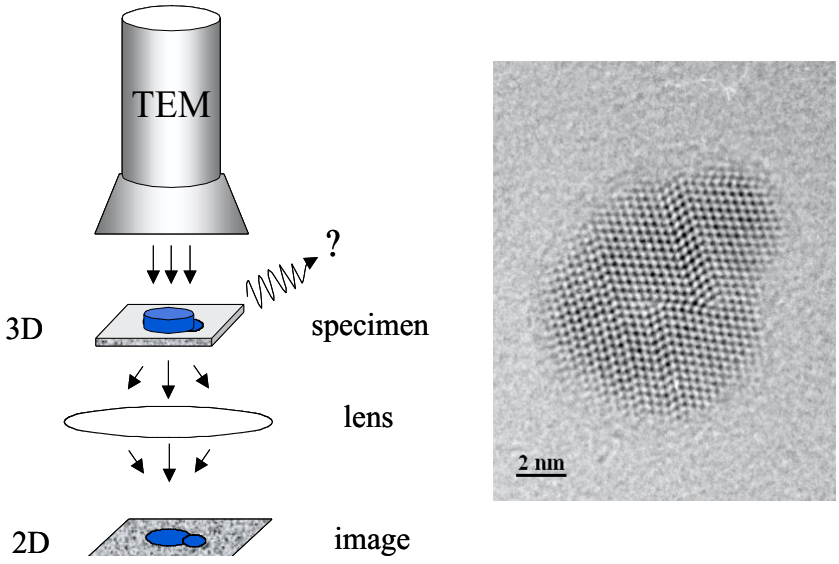

Figure 2. *General scheme for transmission electron microscopy. High-resolution image of a nanocrystal of CdS (Ricolleau et al., 1999).*

The positions of lattice fringes or image features are measured and compared with a perfectly regular lattice. This gives the displacement field. The local spacing of the lattice can then be obtained by subtracting neighbouring displacements, equivalent to taking the gradient of the displacement field. As displacements are defined with respect to a given reference, however, its choice is important. For example, the strain in elastic theory is defined with respect to the undeformed initial state and there is no way of knowing this from electron microscopy. The best that can be achieved is to use a region of crystal which is undistorted, far from defects and interfaces. A second point is that the local chemistry is not always known. If

the composition varies the lattice spacing will vary irrespectively of any strain present.

An additional problem is that high-resolution electron microscopy produces a view of specimens in projection. This will cause problems if the displacement field is not constant over the thickness of the foil i.e. in the presence of bending of the atomic columns. Similar problems occur when the crystal is not exactly oriented to a zone-axis with respect to the incident beam, in which case the atomic columns will be tilted in projection. In such cases, the position of lattice fringes depends on the thickness of the specimen. Therefore, if the thickness varies displacements will be seen in the image which are not due to any strain in the specimen.

The final point is that the displacement field measured is not necessarily representative of the bulk sample. This is because the specimen required for microscopy is extremely thin. As a result, there are two free surfaces which can relax the strains within the sample. The best solution is to carry out finite element modelling of strains, notably in thin films, coupled with image simulations.

2.1 Measuring displacements

The first image processing technique developed for mapping displacements involved localising the intensity maxima in an image, so-called "peak-finding„ and associating them with the atomic lattice (Bierwolf *et al.*, 1993). The aim was to associate variations in lattice spacings with changes in local chemistry, notably in compound semi-conductors (Jouneau *et al.*, 1994) and metal multilayers (Bayle *et al.*, 1994). An alternative, is the geometric phase technique which passes by filtering in Fourier space rather than carrying out the analysis in real-space (Hytch *et al.*, 1998). It is based on the fact that displacements in real-space become phase shifts in Fourier space. Therefore, by measuring the phase of lattice fringes in the image as a function of position, the displacement field can be mapped out. This technique was originally used in optical interferometry for accurately measuring very small displacements (Takeda *et al.*, 1982).

An example of the analysis comes from a study of the displacement field around an edge dislocation in silicon (Hytch *et al.*, 2003), see Figure 3. It was possible in this case to measure displacements to an accuracy of 0.03Å, which is more than a hundred times the resolution of the microscopy used, and to a spatial resolution of about 1 nm. The accuracy was determined by direct comparison with anisotropic elastic calculations. These were carried out at a certain distance from the dislocation core, firstly because elastic theory is a non-atomistic theory, and secondly because the lattice fringes no longer faithfully represent the atomic structure at the core due essentially to objective lens distortions. The local deformation was then determined from the derivative of the displacement field giving the results shown in Figure 3. Strains as little as 0.3% are correctly determined using the technique.

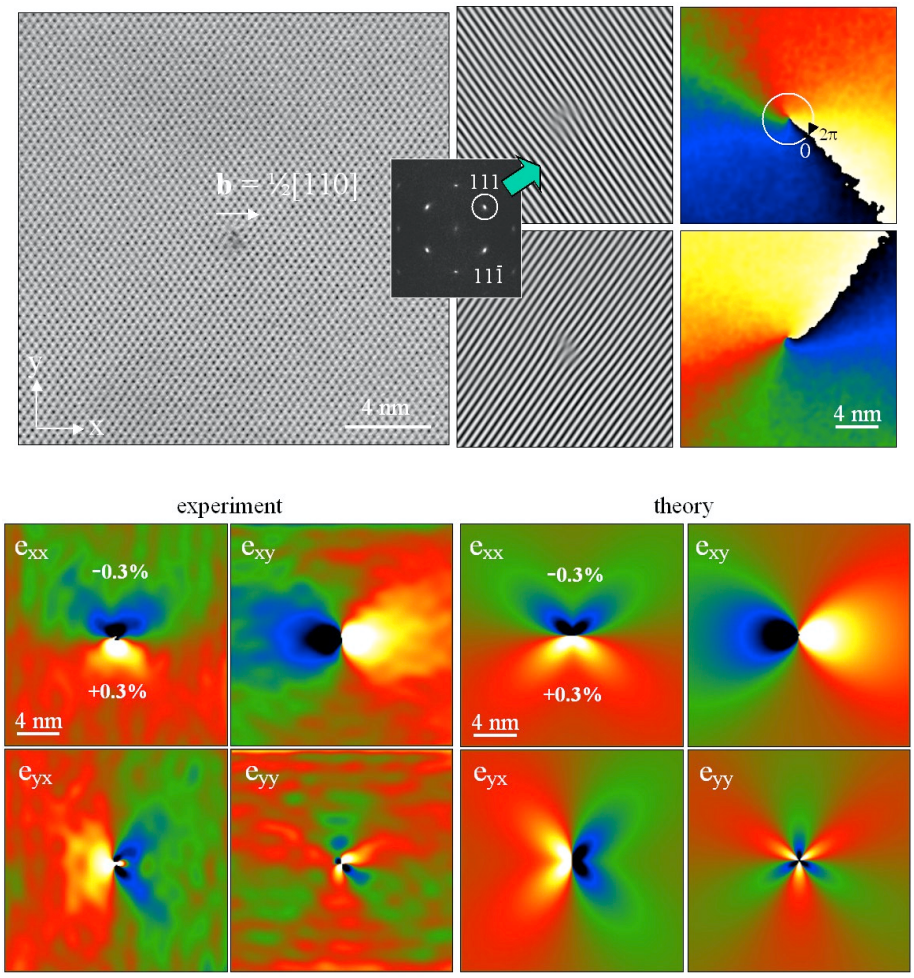

Figure 3. *Strain analysis by high-resolution electron microscopy. Image of a pure edge dislocation in silicon, seen end on, taken on a JEOL 200CX microscope. Geometric phase technique measures the phase of both sets of {111} lattice fringes (top right) proportional to the displacements. The local deformation of the matrix can then be calculated (bottom left) and compared with anisotropic elastic theory calculations (bottom right).*

1.3 Chemical mapping by energy-filtered electron microscopy

The fast electron is not only scattered elastically by the specimen but can also undergo inelastic scattering events. These can be the order of 0.1 eV for phonon scattering, 10-30 eV for plasmon scattering or over 100 eV for core losses where electrons in the sample are ejected from their atomic orbitals. A wealth of information can therefore be obtained by the study of the electron energy loss spectra (EELS). For example, each element in the periodic table has a characteristic set of "edges,, at particular energies corresponding to the ionisation thresholds, thus allowing their detection and quantification in a sample. Originally, spectra where obtained by irradiating a large area of the sample but with the development of field emission electron sources (FEG) sub-nanometre probes can now be obtained. By scanning the specimen, a spectrum can be obtained at each point and the elemental composition mapped out (Jeanguillaume and Colliex, 1989).

Recently, a new method of obtaining chemical maps has been development with the advent of imaging energy filters. The advantage of this technique is that conventional TEM microscopes can be so-equipped (EFTEM). The filter consists of a system of electro-magnetic lenses which generate the energy loss spectrum on the optic axis – electrons deflected proportionally to their energy loss (see Figure 4). A slit can then be positioned to select electrons having a particular range of energies, the originality now being that an image can be formed with these electrons – hence the term imaging filter. Two conceptions exist currently, either the filter is

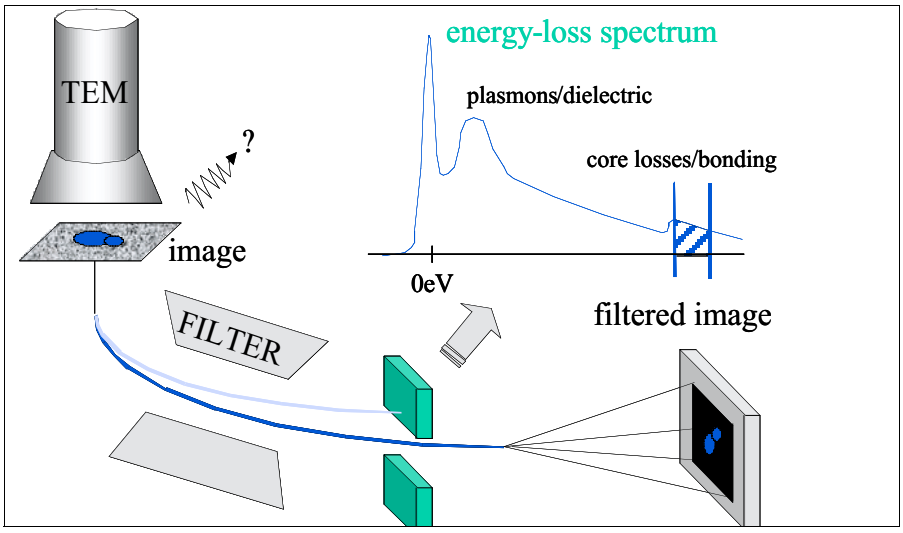

Figure 4. *Energy-filtered electron microscopy. Imaging filter (here represented post-column) disperses electrons according to energy loss. Electrons with certain energies can then be selected and imaged.*

integrated into the column (LEO Ω filter) or post-column (Gatan imaging filter or GIF). For more ample details see, for example, Reimer 1995. Images are acquired using a slow-scan CCD camera whose large dynamic range and linearity of response allows quantitative data to be obtained. Images can be obtained for different areas of the energy loss spectrum thus giving access to a wide range of analysis: purely elastic imaging, plasmon imaging or imaging at the different ionisation edges, for example.

Chemical mapping takes place in two steps: image acquisition and data processing. The first step is crucial and depends on number of experimental parameters. For example, the ultimate spatial resolution will depend on the width of the energy windows used to acquire the data and hence the signal-to-noise ratio. Large windows will improve contrast but reduce spatial resolution due to the chromatic aberration of the microscope (dependence of focus with electron energy). Data processing is equally important, as experimental contrast can also be due to variations in diffraction conditions or the sample thickness. Inadequate assessment of multiple scattering events or extrapolation of background noise can limit considerably the quality of results.

The usual experimental procedure is to acquire a series of images at different energy losses before and after the edge corresponding to the element of interest. The information obtained concerning the elemental concentrations can be qualitative or quantitative depending on the ensuing data analysis. A minimum of three images are necessary, two taken before the edge and one after. The first two allow an extrapolation of the background of energy losses which can be eliminated from the third to producing a map of the elemental composition as a position in the sample. Further analysis and processing can allow the removal of multiple scattering and thickness effects. Ideally, many more images can be taken but problems of specimen drift and irradiation damage can make this impractical.

In this way, maps of chemical composition which an accuracy of a few percent and nanometre spatial resolution can be produced. Figure 5 shows an example of the analysis of nanopowders of $Fe_{0.3}Ni_{0.7}$ produced by cryogenic evaporation-condensation (Champion & Bigot, 1996). The experimental procedure is similar to that described in Bayle-Guillemaud *et al.* (2001). The oxide layer covering particles can clearly be seen in the corresponding oxygen map. The halo effect is due to the view in projection, the signal is in fact the integrated oxygen content; oxygen is indeed detected across the whole of particle. The spatial resolution in this case can be estimated as 1 nm.

Energy filtered imaging has found many applications in materials science and in particular for interpreting the chemistry and composition of nanostructures. Examples can be found in nanoelectronics for the optimisation of process routes (analysing etching residues, diffusion barriers, or corrosion products), investigating quantum dots or more generally interdiffusion profiles across interfaces. The technique is not limited to elemental mapping. All parts of the spectrum can be

mapped out. This means that local dielectric behaviour can be investigated in the low loss part of the spectrum and even the fine detail of edge structures can be mapped at near nanometre level revealing valuable information about local bonding (Botton & Phaneuf, 1999).

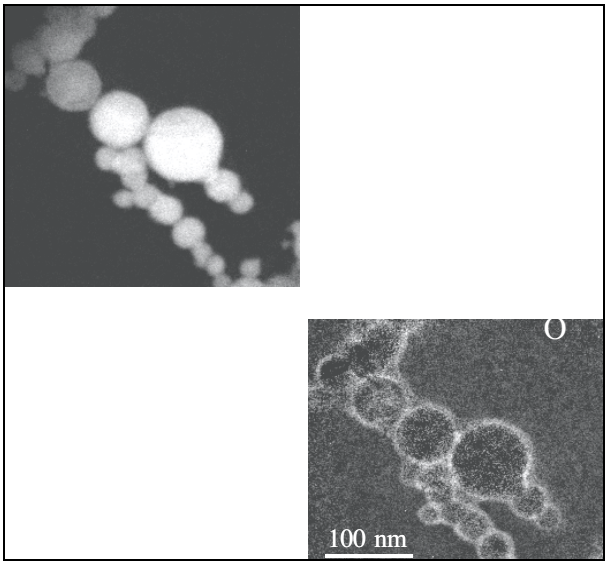

Figure 5. *Energy filtered microscopy of permalloy nanopowders . Conventional bright field image taken on a JEOL 3010 equipped with post-column imaging filter (GIF), along with maps for Fe, Ni and O using the 3-window technique.*

4. Mapping magnetic and electric field mapping

Off-axis electron holography in the transmission electron microscope can image magnetic fields at the nanometre scale. The high-energy electron beam is split in two coherent waves with the aid of a bi-prism, one passing through the specimen and the other through the vacuum (see Figure 6). Subsequent interference allows the amplitude and the phase shift of the high-energy electron to be recorded. The phase shift ϕ is sensitive to electric and in-plane magnetic fields in, and around, the sample. An important distinction with magnetic force microscopy (MFM) is that electron holography is fully quantitative giving the integrated field strength within particles and not restricted to stray surface fields.

Only specially equipped microscopes can, however, carry out holography experiments. Firstly, it is necessary to have a highly coherent electron source such

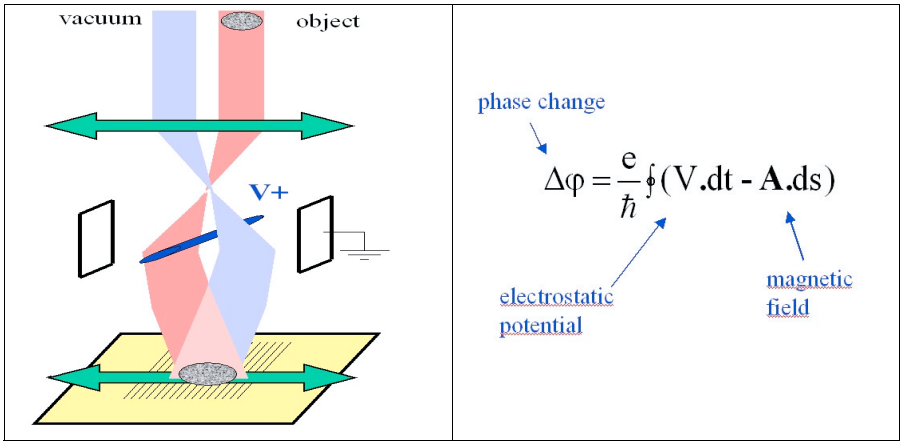

Figure 6. *Principle of electron holography. A bi-prism deviates the part of the highly coherent electron wave which passes through the vacuum with that having interacted with the specimen. The resulting set of interference fringes contains the information concerning the phase of the electron wave. This phase is directly related to the electric and magnetic fields within and around the sample.*

as a field emission gun (FEG) which combines excellent temporal coherence (ΔE~0.4eV) with high brightness. This explains why the original idea of Gabor (1948) has only been exploited relatively recently (1990s). Holography has also benefited from the development of slow-scan CCD cameras for quantitative image acquisition. Finally, the study of magnetic fields at high spatial resolution has required the development of special lens called Lorentz lenses. The reason is that the traditional objective lens subjects the specimen to intense magnetic fields, of the order of one Tesla, thus saturating the magnetic structure of the sample. In addition, the largest component is out of the plane, and hence undetectable by electron holography. The advantage of the Lorentz lens, whilst being less powerful, is that the specimen is in field-free conditions. Resolutions of a few nanometres are nevertheless possible.

A technical difficulty is that the phase depends on both the electric and magnetic fields in the sample. The phase will therefore depend strongly on the mean inner potential of the material, which is not necessarily of interest. Various schemes have been developed to remove this component, thus allowing the observation of magnetic fields (Dunin-Borkowski *et al.*, 1998) or electric fields within a device (Rau *et al.*, 1999). An example of the effect of the mean inner potential is shown in Figure 7. The phase of the holographic fringes is measured in exactly the same way as for the geometric phase technique presented earlier (holographic reconstruction was indeed the inspiration behind the method). In this case, the magnetic nanocrystal is magnetised out of the plane by the objective lens. The major component to the phase is therefore the mean inner potential of the material. The

phase is then simply proportional to the thickness of the sample viewed in projection. Iso-phase contours clearly show the spherical nature of the particle.

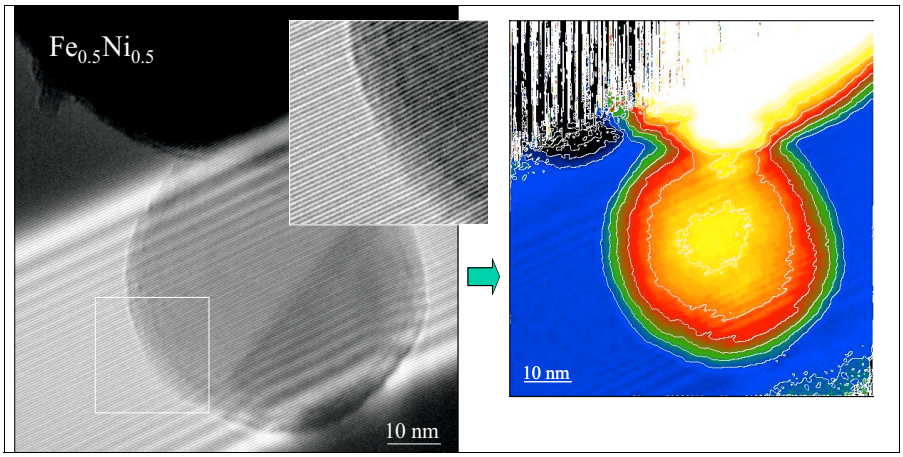

Figure 7. *Mean inner potential measurements by electron holography. The phase of the holographic fringes (see the displacement of the fringes) is proportional to the mean inner potential and thickness of the specimen. The widely spaced fringes are from Fresnel effects from the edges of the bi-prism wire and can be removed by taking reference holograms in the absence of a specimen.*

An example of the measurement of magnetic fields due to the same particles is shown in Figure 8. Here, the particles lying in a chain where magnetised in the plane of observation and the objective lens switched off. A Lorentz lens was used to obtain high magnification. The component due to the mean inner potential was removed as in Snoeck *et al.* (2003), leaving the phase change solely due to the in-plane magnetic field. The contours of the phase correspond to the magnetic field lines within and around the particles (see schematic diagram for 3-dimensional structure.) The remarkable feature is the vortex in the terminating particle. The particles are too small to create domain structures (domain walls normally ~150 nm wide), which is an example of the size effect in nanostructured materials.

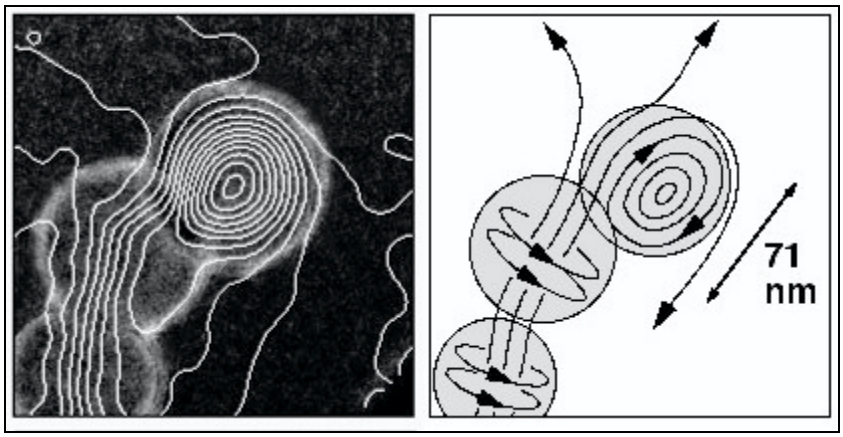

Figure 8. *Magnetic field measurements by electron holography of FeNi nanoparticles chains. Phase contours, corresponding to magnetic field lines, superposed on bright field image of particles. Schematic diagram shows 3-dimensional structure. Note the scale bar and vortex in terminating particle.*

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