WHAT DO WE REALLY KNOW ABOUT THE ATOMIC SCALE STRUCTURES OF NANOPHASE MATERIALS?*

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Abstract -- Robert W. Balluffi has spent a rich research lifetime critically investigating and elucidating the atomic scale defect structures of materials. Now, a new class of ultrafine-grained materials has been created in which such defects exercise a dominant role. The structures of these new nanophase materials, both metals and ceramics, have been investigated over the past several years by a wide range of experimental methods. These studies have included observations by x-ray and neutron scattering, transmission and scanning electron microscopy, Mössbauer, Raman, and positron annihilation spectroscopy, and most recently scanning tunneling and atomic force microscopy and nuclear magnetic resonance. While the experiments have yielded considerable useful information about the structures of nanophase materials on a variety of length scales, much about the local atomic arrangements in the grains and interfaces of these materials remains to be elucidated. The present status of our knowledge of these structures is reviewed and some future research needs and opportunities are considered.

JCPS Keywords: A. nanostructures, metals, oxides; B. defects, microstructure.

1. INTRODUCTION

The opportunity to create nanophase materials by means of a variety of methods has developed rapidly over the past decade or so. This development has resulted in a new class of materials that, in contrast to conventional solids, have an appreciable fraction of their atoms residing in defect environments. For example, a nanophase material with a readily achievable average grain size of 5 nm has about 50% of its atoms within the first two nearest neighbor planes of a grain boundary, in which significant atomic displacements from their normal lattice positions are exhibited. Since the properties of nanophase materials are so strongly related to their unique structures, it seems appropriate to now ask what we really know about the atomic scale structures of nanophase materials after almost a decade of research.

The structures of nanophase materials on a variety of length scales have an important bearing on their special chemical and physical properties [1, 2]. They are dominated by their ultrafine grain sizes and by the large number of interfaces associated with their small grains (see Fig. 1). However, other structural features such as pores (and larger flaws), grain boundary junctions, and other crystal lattice defects that can depend upon the manner in which these materials are synthesized and processed also play a significant role. It has become increasingly clear during the past several years that all of these structural aspects must be carefully considered in trying to fully understand the properties of nanophase materials.

The atom clusters that make up the grains of cluster-consolidated nanophase materials typically have rather narrow size distributions, whether they are created by the gas condensation method or by a variety of other physical or chemical methods. Most frequently, the clusters are found to be aggregated. The degree and nature of aggregation can vary from essentially none in the case of chemically capped clusters in solution to rather open fractal arrays in the gas condensation method to a large amount of hard agglomeration in chemical solution routes when insufficient special additives have been used. The difficulties encountered in consolidating the hard equiaxed agglomerates of fine powders with surface contamination that can result from conventional wet chemistry synthesis routes are mostly avoided in the gas condensation method for synthesizing nanophase materials from clusters. The sample densities resulting from gas-condensed cluster consolidation at room temperature have ranged up to about 97% of theoretical for nanophase metals and up to about 75-85% of theoretical for nanophase oxide ceramics. However, even the remaining porosity appears to be capable of being removed, if desired, by means of cluster consolidation at elevated temperatures and pressures without the occurrence of significant attendant grain growth.

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2. STRUCTURES OF NANOPHASE MATERIALS

2.1. *Grains*

Our present knowledge of the grain structures of nanophase materials, whether formed by cluster consolidation, intense mechanical deformation, or crystallization from amorphous precursors, has resulted primarily from direct observations using transmission electron microscopy (TEM) [4-8]. A typical high resolution image of a nanophase palladium sample formed by the consolidation of gas-condensed clusters is shown in Fig. 2. TEM has shown that the grains in cluster-consolidated nanophase compacts are essentially equiaxed, similar to the atom clusters from which they were formed, although departures from spherical structures are expected simply from the efficient packing of the clusters during consolidation. The grains also appear to retain the narrow (ca. ± 25 % FWHM) log-normal size distributions typical of the clusters formed in the gas-condensation method, since measurements of these distributions before or after cluster consolidation by dark-field electron microscopy yield similar results. The grain size distributions in deformation or crystallization produced nanostructructures tend to be somewhat broader than these, but similarly equiaxed.

The observations that the densities of nanophase materials consolidated from equiaxed clusters extend well beyond the theoretical limit (78%) for close packing of identical spheres indicate that an extrusion-like deformation of the clusters must occur during the consolidation process, filling (at least partially) the pores among the grains. A number of these observations indicate that cluster extrusion in forming nanophase grains may result from a combination of deformation and diffusion processes. Such processes are also evident from recent scanning tunneling microscopy (STM) and atomic force microscopy (AFM) observations [9] on nanophase palladium and silver. An example from the nanophase silver is shown in Fig. 3, where it can be seen that the cluster morphologies accommodate to one another to help fill the volume. Further evidence that local extrusion is important in the cluster-consolidation process has recently been obtained in molecular dynamics simulations [10]. Palladium clusters before and after consolidation at 10 kbar for 4 ps are shown in Fig. 4, again indicating that inter-cluster voids are at least partially filled via extrusion processes.

Observations by electron and x-ray scattering indicate, however, that no apparent preferred orientation or "texture" of the grains results from their uniaxial consolidation and that the grains in nanophase compacts are essentially randomly oriented with respect to one another. This is interesting with respect to the fact that deformation textures (such as those that result from uniaxial compression) in conventional grain size materials are the result of dislocation motion, which seems to be suppressed in nanophase materials. Indeed, only very few

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dislocations are observed within the grains in these ultrafine-grained materials, and these are normally in locked (i.e., sessile) configurations. The cluster consolidation process thus appears to resemble an Ashby-Verrall creep process [11] in which grains slide over one another accommodated by diffusionsal processes in the interfaces, but grain shape and orientation are retained while overall dimensional changes take place.

2.2. *Atomic defects and dislocations*

When an elemental precursor is evaporated in an inert gas atmosphere, as in the gas condensation method, the atom clusters formed and collected are the same material, only in a reconstituted form. In this case, the clusters and the subsequently consolidated nanophase material are expected to have only equilibrium concentrations of intrinsic atomic defects (e.g., vacancies or interstitials) present, since the mobility of these defects [12, 13] and the respective efficiencies of the surfaces and grain boundaries as sinks for them [14] are sufficiently high to maintain equilibrium during synthesis and processing. No experimental evidence to the contrary presently exists.

However, if clusters of a metal-oxide compound are to be made in order to synthesize a nanophase ceramic, the process is somewhat more complex and constitutional atomic defects can be present in significant concentrations. For example, in order to produce nanophase TiO_2 with a rutile structure, titanium metal clusters condensed in He are first collected and subsequently oxidized by the introduction of oxygen into the synthesis chamber [4]. A similar method has been used to produce α-Al_2O_3 [15] and Cr_2O_3 [16]. If the vapor pressure of a compound is sufficiently large, as in the cases of MgO and ZnO, it is possible to sublime the material directly from the oxide precursor in a He atmosphere containing a partial pressure of O_2 to attempt to maintain oxygen stoichiometry during cluster synthesis. Such a method has been used [15] to produce such nanophase oxides with average grain sizes down to about 5 nm. Frequently, however, oxygen stoichiometry is not maintained.

In the case of nanophase TiO_2 cited above, the oxygen deficiency is rather small and easily remedied as a result of the small grain sizes and short diffusion distances involved. Raman spectroscopy has been a useful tool in studying the oxidation state of nanophase titanium dioxide owing to the intense and well studied Raman bands in both the anatase and rutile forms of this oxide and the observation that these bands were broadened and shifted in nanophase samples [17]. The band broadening and shifting in both the anatase and rutile phases was confirmed [18] to be the result of an oxygen deficiency which could be subsequently removed by annealing these samples in air. A subsequent calibration of this deviation from stoichiometry [19] indicated that $TiO_{1.89}$ was the actual material produced by

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the gas condensation method used, as shown in Fig. 5, but that it could be readily oxidized to fully stoichiometric TiO_2 without sacrificing its small grain size (12 nm). Also, if intermediate deviations from stoichiometry were sought, in order to select particular material properties sensitive to the presence of oxygen vacancy defects, they could be readily achieved as well.

The presently available experimental evidence suggests that dislocations are seldom present in nanophase materials [6, 20, 21]. When dislocations are observed, it is primarily in either materials at the upper end of the grain size range [22] or in immobile or locked configurations [6, 7]. The reason for this substantial lack of dislocations is that image forces exist in finite atomic ensembles that tend to pull mobile dislocations out of the grains, especially when they are small, in analogy with the forces on a point electrical charge near a free surface of a conducting body. This paucity of mobile dislocations can have a significant effect upon the mechanical behavior of nanophase materials [23]. Since mobile dislocations are not initially available in sufficient numbers to effect plasticity in ultrafine-grained nanophase materials, new mobile dislocations must be created or other deformation mechanisms, such as grain boundary sliding, must come into play.

Dislocations can be created or can multiply from a variety of sources. A simple but representative example is the Frank-Read dislocation source in which a dislocation line, pinned between two pinning points that prevent its forward motion on a slip plane, can bow out between these pinning points to form a new dislocation, if the stress acting on the pinned dislocation is sufficient. The critical stress to operate such a Frank-Read source is inversely proportional to the distance between the pinning points and hence will also be limited by the grain size, which limits the maximum distance between such pinning points. This suggests that dislocation multiplication in nanophase metals will become increasingly difficult as the grain size decreases. The critical stress will eventually, at sufficiently small grain sizes, become larger than the yield stress in the conventional material and could even approach the theoretical yield strength of a perfect, dislocation-free single crystal.

2.3. Pores

Nanophase materials consolidated to date from clusters at room temperature have invariably posessed significant porosity ranging from about 25% to less than 5%, as measured by Archimedes densitometry, with a tendency for the larger values in ceramics and the smaller ones in metals. Porosity can also result from the deformation or crystallization synthesis of nanophase materials. Evidence for this porosity has been obtained by positron annihilation spectroscopy (PAS) [4, 24, 25], precise densitometry [26] and porosimetry [27, 28] measurements, and small angle neutron scattering (SANS) [28, 29].

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PAS is primarily sensitive to small pores, ranging from single vacant lattice sites to larger voids, but can probe these structures enclosed in the bulk of the material. Porosimetry measurements using the BET (Brunauer-Emmett-Teller) N_2 adsorption method, on the other hand, probe only pore structures open to the free surface of the sample, but can yield pore size distributions (although with some questions regarding their validity at nanometer pore sizes), which are unavailable from PAS. Densitometry using an Archimedes method integrates over all densities in the sample, including grains, pores (open or closed), and density decrements at defect sites as well. SANS is quite sensitive to pores in the 1-100 nm size range, but deconvolution of the scattering data can be difficult when a broad spectrum of scattering centers is present, as is often the case in nanophase materials. However, even in such a case, it was possible [29] to analyze SANS data from cluster-consolidated Pd in terms of a population of small (ca. 1 nm diameter) voids at grain boundary intersections and grain-sized voids.

A variety of such measurements to date have shown that the porosity in nanophase metals and ceramics is primarily smaller than or equal to the grain size of the material (although some larger porous flaws have been observed by scanning electron microscopy) and that the porosity is frequently associated with the grain boundary junctions (triple junctions) and, especially but not only in ceramics, it is interconnected and intersects with the specimen surfaces. Fortunately, consolidation at elevated temperatures should be able to uniformly remove this porosity without sacrificing the ultrafine grain sizes in these materials. Some evidence for this has already been obtained by means of sinter forging nanophase ceramics [30] and uniaxial pressing of nanophase metals at elevated temperatures [31].

It should be noted here that atomic diffusion in nanophase materials, which can have a significant bearing on their mechanical properties, such as creep and superplasticity, and other properties as well, has been found to be very rapid compared with conventional materials. Measurements of self- and solute-diffusion [32-36] in as-consolidated nanophase metals (Cu, Pd) and ceramics (TiO_2) indicate that atomic transport can be orders of magnitude faster in these materials than in coarser-grained polycrystalline samples. However, this very rapid diffusion appears to be intrinsically coupled with the porous nature of the interfaces in these materials, since the diffusion can be suppressed back to conventional values by sintering samples to full density, as shown by measurements of Hf diffusion in TiO_2 before and after densification by sintering [32]. Thus, in fully densified nanophase materials it is most likely that normal grain boundary diffusion [37], intensified by the large number density of available grain boundaries, will play a significant role in their mechanical behavior and in the ability to impurity dope these materials for a wide range of functional (e.g., optical, electronic, chemical) applications.

2.4. *Grain boundaries*

Owing to their ultrafine grain sizes, nanophase materials have a significant fraction of their atoms in grain boundary environments, where they occupy positions relaxed from their normal lattice sites. For conventional high-angle grain boundaries, these relaxations generally extend over about two atom planes on either side of the boundary, with the greatest relaxation existing in the first plane [38]. For an average grain diameter range between 5 and 10 nm, where much of the research on nanophase materials has focussed, grain boundary atom percentages range between about 15 and 50% (Fig. 1). Since such a large fraction of their atoms reside in grain boundaries, these interface structures can play a significant role in affecting the properties of nanophase materials.

A number of early investigations on nanocrystalline metals, including x-ray diffraction [39], Mössbauer spectroscopy [40], positron lifetime studies [24, 25], and extended x-ray absorption fine structure (EXAFS) measurements [41, 42], were interpreted in terms of grain boundary atomic structures that may be random, rather than possessing either the short-range or long-range order normally found in the grain boundaries of conventional coarser-grained polycrystalline materials. This randomness was variously associated [43] with either the local structure of individual boundaries (as seen by a local probe such as EXAFS or Mössbauer spectroscopy) or the structural coordination among boundaries (as might be seen by x-ray diffraction). However, direct observations by high resolution electron microscopy (HREM) [5, 6] have indicated that their structures are rather similar to those of conventional high-angle grain boundaries. An extensive review of these results has appeared elsewhere [44].

The direct imaging of grain boundaries with HREM can avoid the complications that may arise from porosity and other defects in the interpretation of data from less direct methods, such as x-ray scattering and Mössbauer spectroscopy, especially when the HREM observations are complemented by image simulations [45]. The only HREM study [5, 6] to date on a nanophase material that has included both experimental observations and complementary image simulations indicated no manifestations of grain boundary structures with random displacements of the type or extent suggested by earlier x-ray studies on nanophase Fe, Pd, and Cu [39, 41, 42]. As shown in Fig. 6, contrast features at the observed grain boundaries that might be associated with disorder did not appear wider than 0.4 nm, indicating that any significant structural disorder which may be present essentially extends no further than the planes immediately adjacent to the boundary plane. Such localized lattice relaxation features are typical of the conventional high-angle grain boundary structures found in coarse-grained metals. Indeed, the experimentally observed grain boundary images for nanophase Pd were far more similar to that simulated for a 'perfect' boundary (Fig. 7) than to those for model

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boundaries possessing the degree of disorder suggested by the early interpretations [43] of less direct methods. Additional HREM observations of grain boundaries in nanophase Cu [8] and Fe alloys [46] produced by surface wear and high-energy ball milling, respectively, appear to support this view. However, there are indications [47, 48] that metastable grain boundary configurations do exist in some cases that can be transformed by low temperature annealing to more stable states. Whether such behavior is associated with the intrinsic grain boundary structure itself or with extrinsic grain boundary dislocation configurations and/or strains remaining from synthesis or processing remains to be clarified.

Recently, nuclear magnetic resonance (NMR) studies of cluster-consolidated nanophase silver [49] have indicated that the grain boundaries in this material have an electronic structure that appears to be consistent with that expected for conventional high-angle boundaries. As shown in Fig. 8, it has been possible to approximately model the measured NMR spectrum from nanophase silver using a spin density decrement at the grain boundary of about 1% and an electronic width about twice that of the observed structural width. Since electronic healing distances for metals are about an interatomic spacing, such a picture seems quite natural.

The nanophase grain boundaries typically observed by HREM of cluster-assembled nanophase materials appear to take up rather low energy configurations exhibiting flat facets interspersed with steps, as that seen in Fig. 6. Weak grain boundary grooving seen within islands of grains by STM and AFM [9] appear to support such a view. Such low energy structures could only arise if sufficient local atomic motion occurred during the cluster consolidation process to allow the system to reach at least a local energy minimum. These observations suggest at least two conclusions [50]: first, that the atoms that constitute the grain boundary volume in nanophase materials have sufficient mobility during cluster consolidation to accommodate themselves into relatively low energy grain boundary configurations; and second, that the local driving forces for grain growth are relatively small, despite the large amount of energy stored in the many grain boundaries in these materials.

2.5. Stability

The narrow grain size distributions, essentially equiaxed grain morphologies, and low energy grain boundary structures in nanophase materials suggest that the inherent resistance to grain growth observed for cluster-assembled nanophase materials results primarily from a sort of frustration [51]. It appears that the narrow grain size distributions normally observed in these cluster-assembled materials coupled with their relatively flat and faceted grain boundary configurations place these nanophase structures in a local minimum in energy from which they are not easily extricated. Such frustration would also likely be increased by the multiplicity of

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grain boundary junctions in these materials. There are normally no really large grains to grow at the expense of small ones through an Otswald ripening process, and the grain boundaries, being essentially flat, have no local curvature to tell them in which direction to migrate. Their stability thus appears to be analogous to that of a variety of closed-cell foam structures with narrow cell size distributions, which are deeply metastable despite their large stored surface energy. Such a picture appears to have some theoretical support [52].

Exceptions to this frustrated grain growth behavior would be expected if considerably broader grain size distributions were accidentally present in a sample, which would allow a few larger grains to grow at the expense of smaller ones, or if significant grain boundary contamination were present, allowing enhanced stabilization of the small grain sizes to further elevated temperatures. Occasional observations of each of these types of behavior have been made. One could, of course, intentionally stabilize against grain growth by appropriate doping by insoluble elements or composite formation in the grain boundaries. For these cluster-assembled materials, such stabilization should be especially easy, since the grain boundaries are available as readily accessible cluster surfaces prior to consolidation. The ability to retain the ultrafine grain sizes of nanophase materials is important when one considers the fact that it is their small grain size and large number of grain boundaries that determine to a large extent their special properties.

2.6. Strains

Strains are a natural component of nanophase materials. Simply owing to the large number of grain boundaries, and the concomitant short distances between them, the intrinsic strains associated with such interfaces [38, 53] are always present in these nanostructured materials. Beyond these intrinsic strains, however, there may also be present extrinsic strains associated with the particular synthesis method. For example, intense plastic deformation synthesis of nanophase materials may lead to additional residual strains [54] that can be subsequently relieved via low temperature annealing, leaving only those intrinsic strains due to the presence of the high-angle grain boundaries. Evidence for the strains in nanophase materials is now becoming available. X-ray line broadening investigations of both cluster-consolidated [26] and ball-mill deformed metallic nanophase samples [55] have indicated residual strains of about 0.5-1%, which are consistent in magnitude with the strains expected from conventional high angle grain boundaries [38] in the grain size ranges investigated. Recently, NMR measurements [56] on cluster-consolidated nanophase copper have also yielded estimated strain values (ca. 0.7%) in this range. Clearly, much careful work remains to

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elucidate the nature and magnitudes of the strains in nanophase materials and their contributions to the properties of these new materials.

3. CONCLUSIONS

Even after almost a decade of research, we are really just beginning to understand the essential features of the structures of nanophase materials assembled from cluster building blocks created by a variety of methods or synthesized by other techniques. Much of the presently available information results from studies on nanophase materials made by the gas condensation method. These results have shown that clusters and resulting grains contain few if any mobile dislocations owing to image stresses acting on these finite atomic ensembles. However, sessile dislocations are observed along with frequent twin boundaries, presumably formed during the cluster synthesis. The mobile atomic defects in elemental nanophase solids are probably at equilibrium, but clusters of vacancies or voids may be present and deviations from stoichiometry in compounds are certainly rather common but easily controlled.

The grains formed by the consolidation of clusters are also essentially equiaxed and possess random crystallographic orientations, presumably a result of the grain boundary sliding mechanisms that are operative during consolidation. Yet the grains appear to be locally extruded, probably by diffusional mechanisms, in order to help fill in the open intergrain regions during consolidation. The interfaces formed during consolidation are similar in structure to those observed in coarse-grained polycrystals, but their detailed atomic structure needs to be further elucidated to see whether this similarity is exact or not. Owing to the high number density of grain boundaries, intrinsic strains are present in nanophase materials. The magnitude of these strains are consistent with the expectations from theoretical modeling studies, but better measurements are needed as are more realistic models. The nature and source of extrinsic strains from the various synthesis and processing routes for creating nanophase materials need to be more fully investigated.

Porosity exists on a variety of length scales from small vacancy clusters at the grain boundary junctions formed by consolidation to missing grains to larger porous flaws. However, by careful control of the synthesis and processing steps and consolidation under appropriate conditions, it appears that this porosity can be contolled to retain a desired degree of high surface area or removed without affecting the grain size of the nanophase material. Much work remains in all of these areas, however, if we are to fully understand the structures of nanophase materials and their cluster building blocks and how these structures relate to the properties of these new materials.

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Finally, nanophase materials, in addition to having a variety of unique grain-size dependent properties, should also be a valuable resource for studying the average properties of grain boundaries and interfaces in general. The high number density of these defects in nanophase materials enhance their influence on macroscopic properties, allowing their effects to be studied by a variety of experimental techniques. In order that the grain boundary properties can be accurately measured, however, specimen porosity will need to be removed via consolidation at elevated temperature and/or pressure so that its property contributions can be eliminated. Fortunately, this appears to be possible in cluster-consolidated nanophase materials without sacrificing their ultrafine grain sizes. By varying the grain size in a set of experiments, the contributions from interfaces and their junctions in nanophase materials could be effectively separated. In such a manner, a number of the type of critical experiments that have been the hallmark of Bob Balluffi's exceptional scientific career should result in the future. Our understanding of the atomic scale structures of nanophase materials and the properties of grain boundaries would thereby be permanently enriched.

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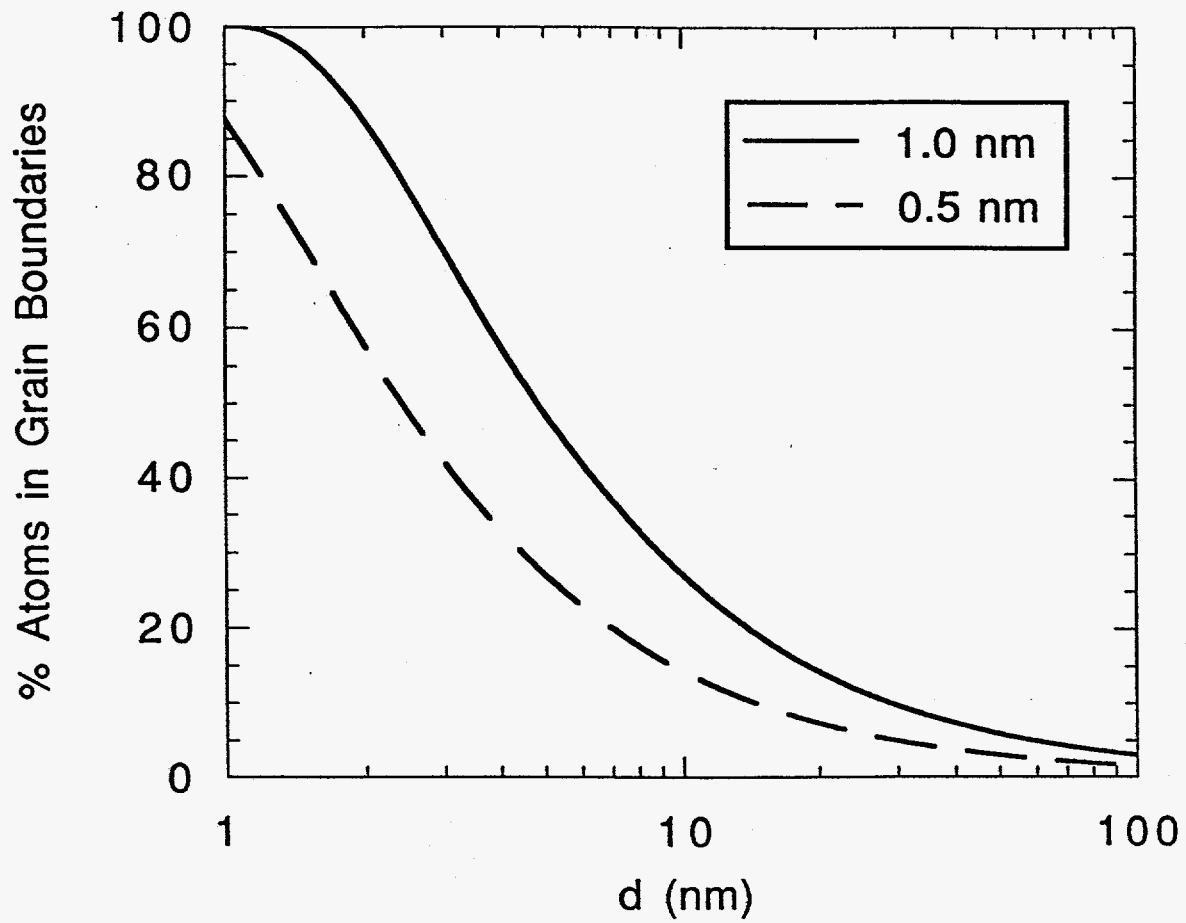
FIGURE CAPTIONS

Fig. 1. Percentage of atoms in grain boundaries (including grain boundary junctions) of a nanophase material as a function of grain diameter [3], assuming that the average grain boundary thickness ranges from 0.5 to 1.0 nm (ca. 2 to 4 atomic planes wide).
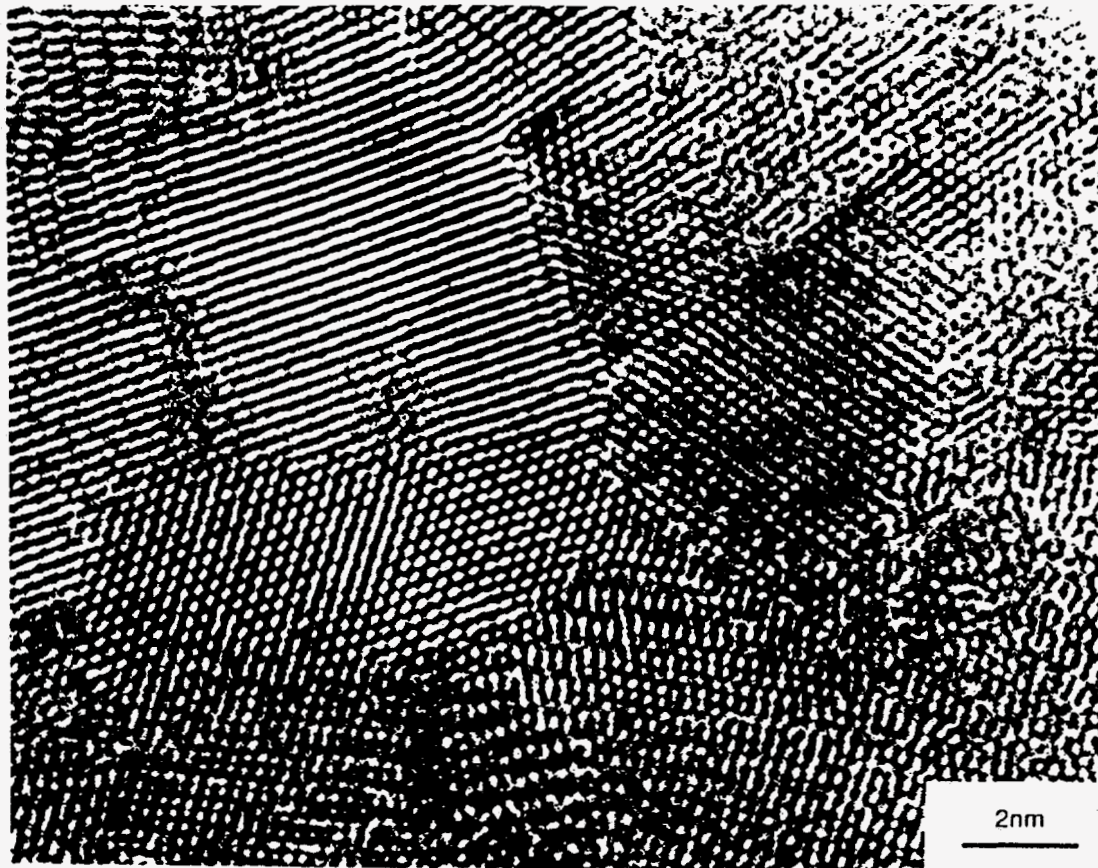
Fig. 2. High resolution transmission electron micrograph of a typical area in cluster consolidated nanophase palladium. From [6].

Fig. 3. Scanning tunneling micrograph of nanophase silver [9].

Fig. 4. Sections 0.4 nm thick through palladium clusters before (a) and after (b) consolidation for 4 ps under a uniaxial pressure of 10 kbar in the X direction. The consolidation simulation was carried out using molecular dynamics and an embedded atom potential for Pd. From [10].

Fig. 5. Variation with O/Ti ratio of the peak position of (a) the rutile "447 cm^{-1}" vibrational mode and (b) the anatase "143 cm^{-1}" vibrational mode, as well as (c) this anatase mode's full width at half maximum (FWHM). From [19].

Fig. 6. High resolution transmission electron micrograph of a grain boundary in nanophase palladium from an area as shown in Fig. 2. The magnification is indicated by the lattice fringe spacings of 0.225 nm for (111) planes. From [5, 6].

Fig. 7. Image simulation for a 'perfect' $\Sigma 5$ symmetric <001> tilt boundary with no atomic displacements in 7.6 nm thick palladium using microscope parameters and imaging conditions consistent with those used during HREM experimental observations [5, 6].

Fig. 8. Nuclear magnetic resonance (NMR) spectra from nanophase silver and a coarse-grained silver wire (a), relative variations in the spin density in the vicinity of a model grain boundary (b), and the NMR spectrum (c) simulated using the simple model of (b). From [49].

Fig. 1. Percentage of atoms in grain boundaries (including grain boundary junctions) of a nanophase material as a function of grain diameter [3], assuming that the average grain boundary thickness ranges from 0.5 to 1.0 nm (ca. 2 to 4 atomic planes wide).

Fig. 2. High resolution transmission electron micrograph of a typical area in cluster consolidated nanophase palladium. From [6].
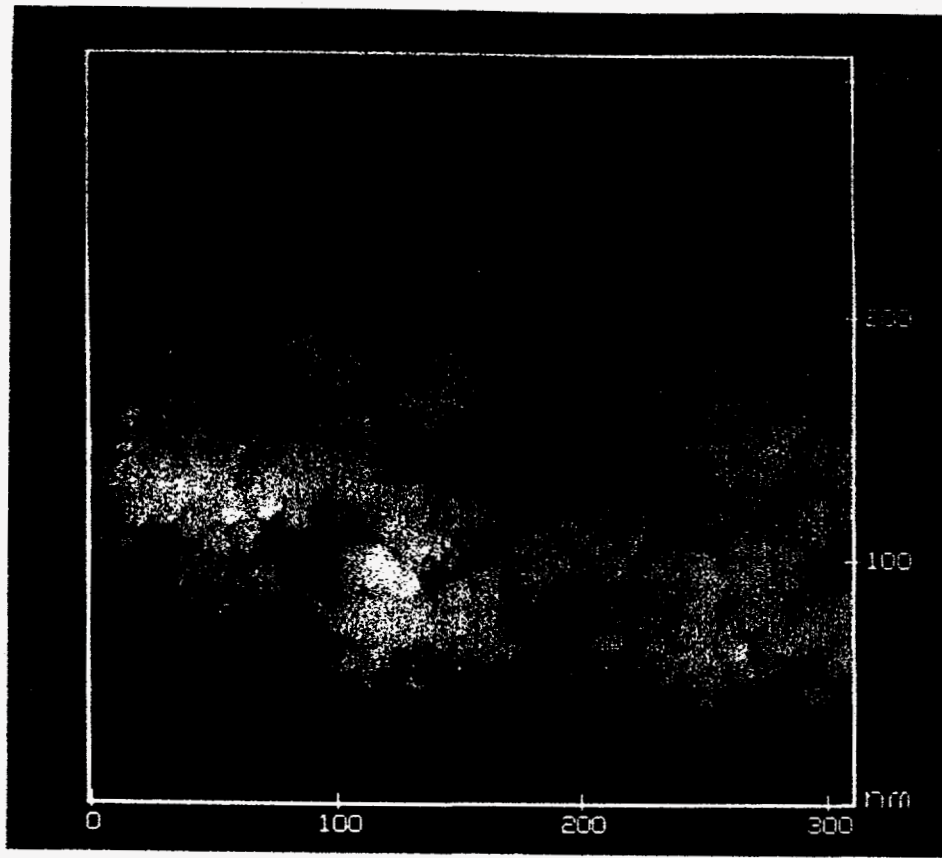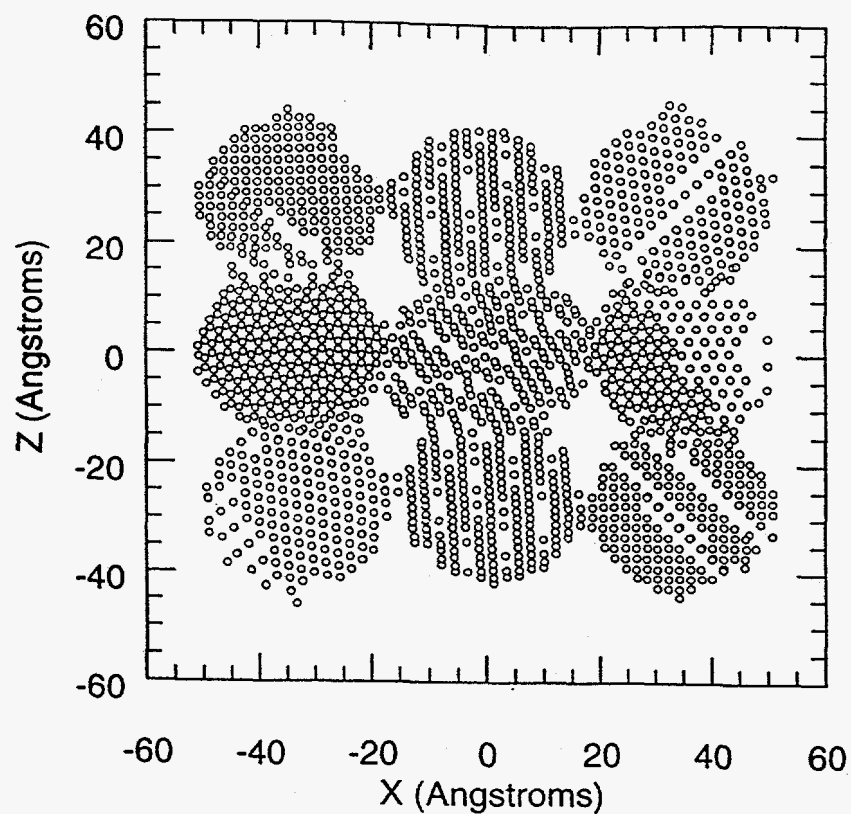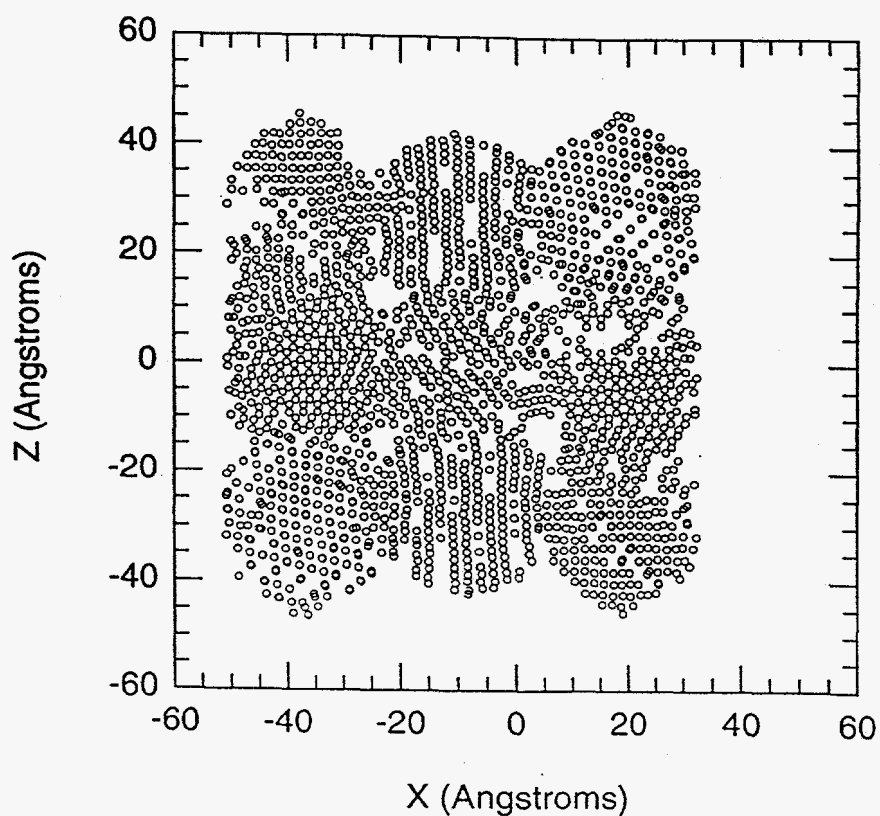
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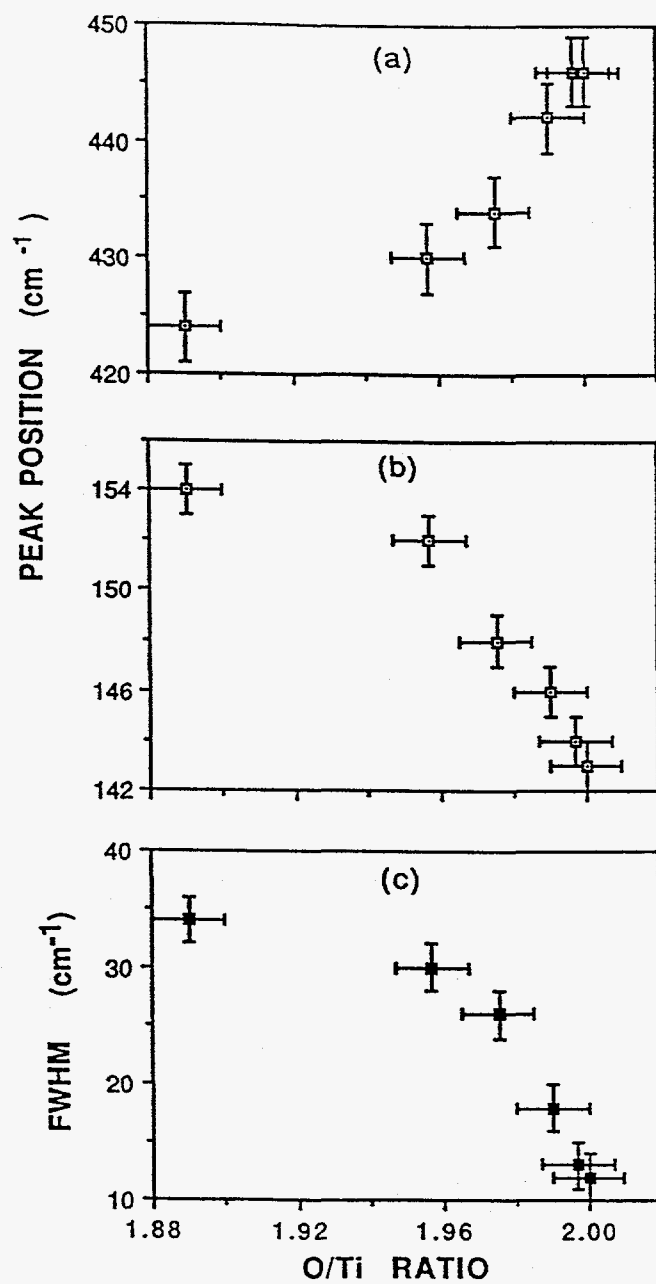
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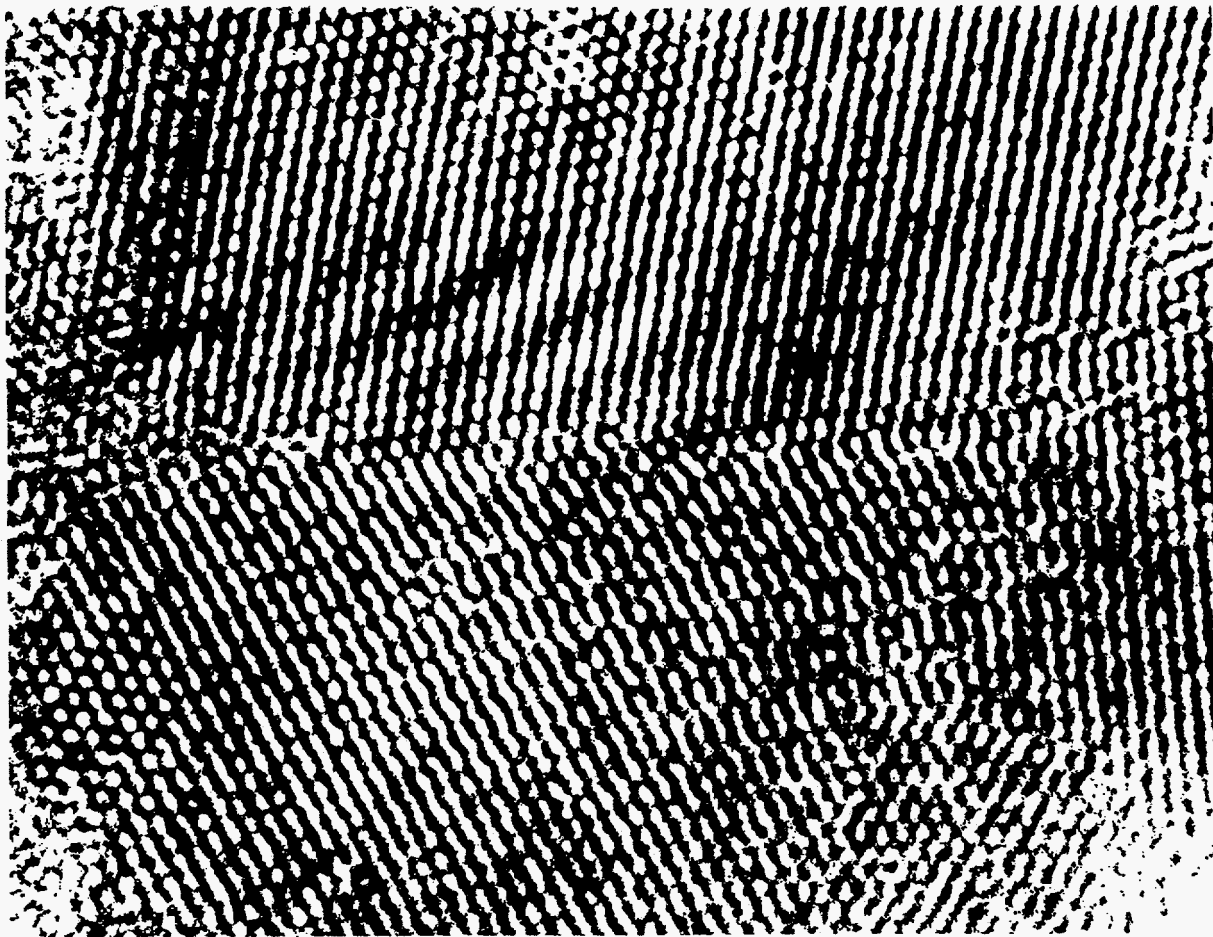
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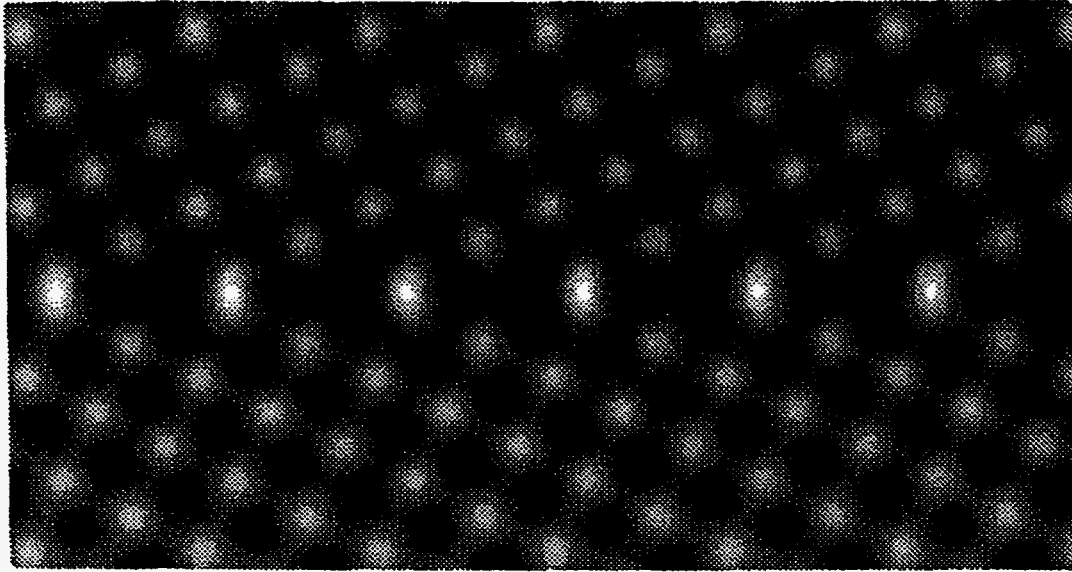
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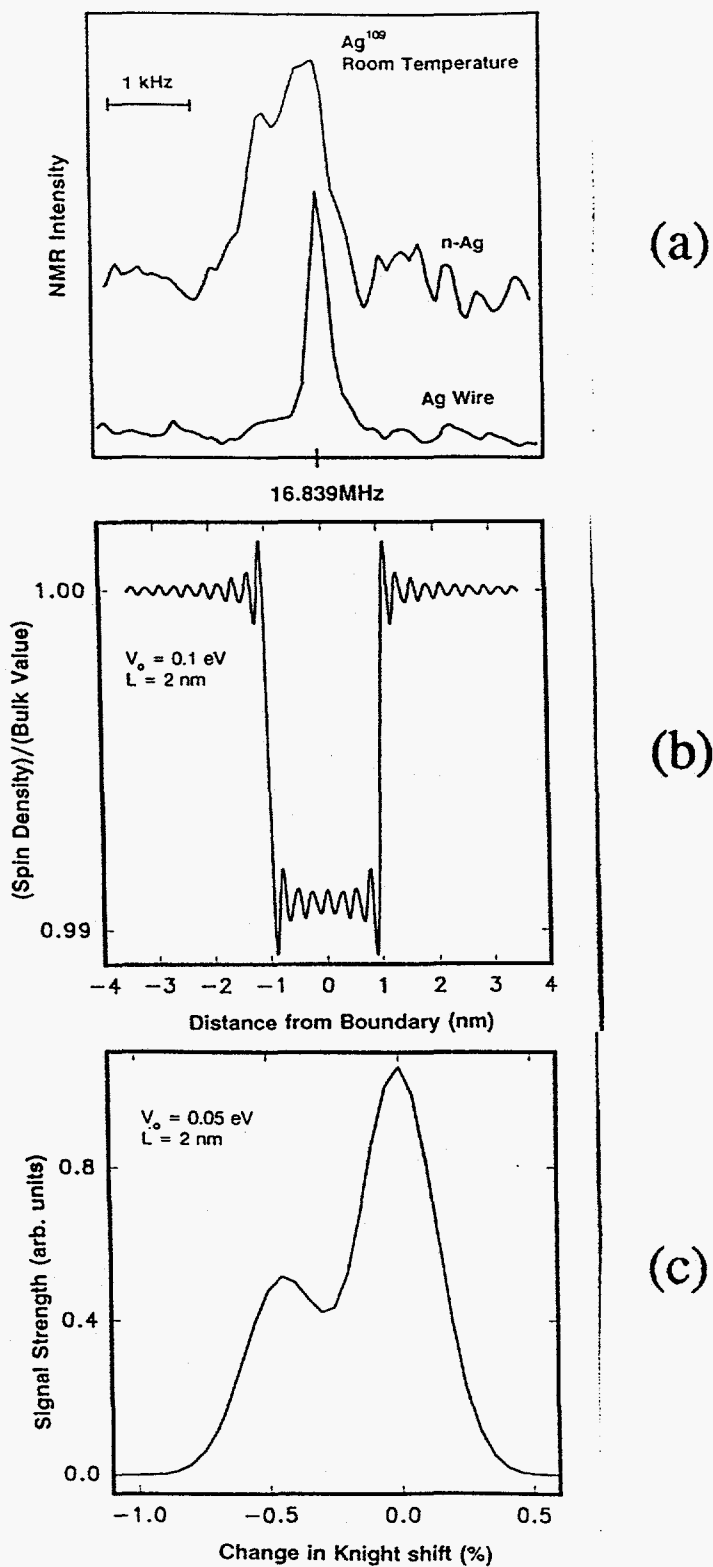
Fig. 8. Nuclear magnetic resonance (NMR) spectra from nanophase silver and a coarse-grained silver wire (a), relative variations in the spin density in the vicinity of a model grain boundary (b), and the NMR spectrum (c) simulated using the simple model of (b). From [49].