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Experimental and theoretical investigations on the compressibility of nanocrystalline nickel

S. REKHI, S. K. SAXENA
CeSMEC, Florida International University, Miami, Florida 33199, USA
E-mail: saxenas@fiu.edu.

R. AHUJA, B. JOHANSSON
Condensed Matter Physics, Physics Department, Uppsala University, Uppsala, Sweden

J. HU
Geophysical Laboratory and Center for High Pressure Research, Carnegie Institution of Washington, 5251 Broad Branch Road NW, Washington DC 20015, USA

We investigated nanocrystalline nickel experimentally (x-ray diffraction) and theoretically (cluster *ab initio* calculations). No phase transition was observed in nano-nickel. The volume, isothermal bulk modulus and its pressure derivative derived experimentally and theoretically are 43.56 (0.13) Å^3, 228(15) GPa, 4.02(0.51) and 44.00 Å^3, 217 GPa and 3.20, respectively. We found no appreciable change in the value of bulk modulus for nano-nickel as compared to the bulk-nickel. © *2001 Kluwer Academic Publishers*

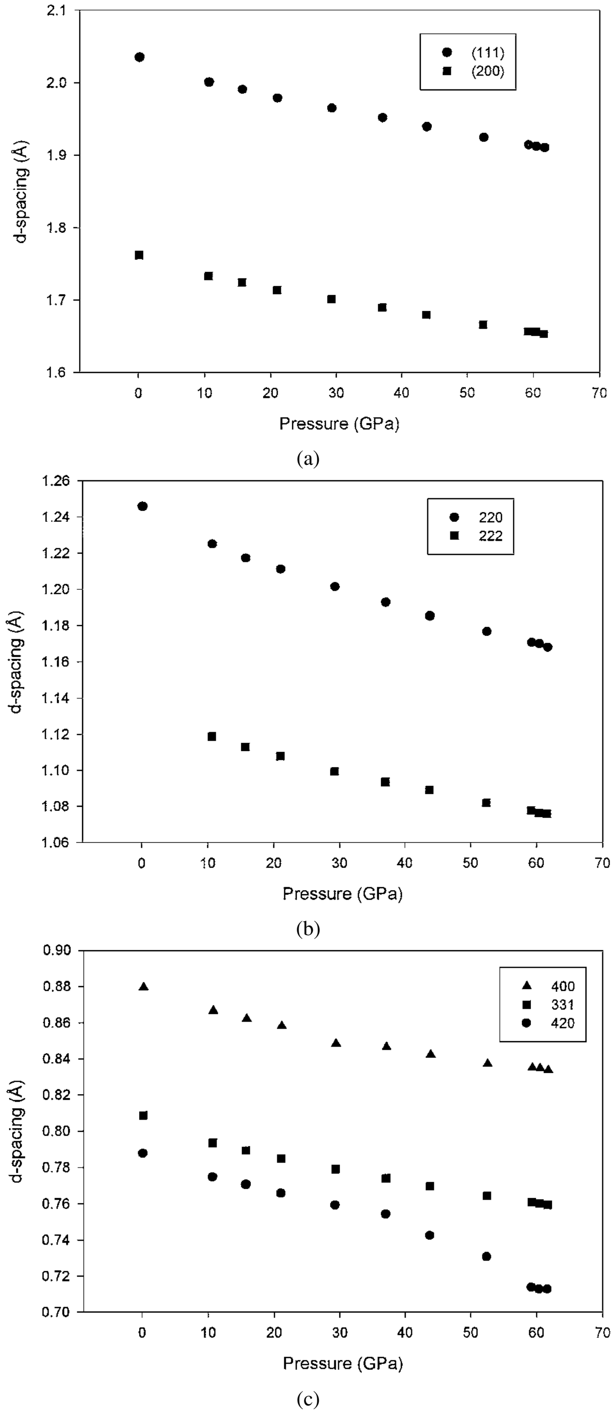
1. Introduction

Nickel is a transition metal and important from a technological point of view. Iron, Nickel and cobalt are transition ferromagnetic 3d metals belonging to eighth group and third period. Numerous investigations have been reported on the physical and electronic properties of materials with the change in particle size [1–4]. Therefore, we studied the properties of nickel or iron-nickel alloy at high pressure. Tolbert *et al.* [2] observed a large elevation in the phase transition pressure in materials with smaller particle size (nanometric) as compared to bulk material, which is in agreement with the predictions of homogenous deformation theories (HDT). According to the Hall-Petch effect, the hardness and yield stress of the material typically increases with decreasing grain size [5, 6]. On the contrary, a reverse Hall-Petch effect related to the softening of materials at very small grain size has also been reported [7, 8]. Schiotz *et al.* [9] reported computer simulation results of nanocrystalline copper and attributed this phenomenon due to a large fraction of atoms at grain boundaries thus resulting in 'sliding' of atomic planes. They also explained that this softening ultimately imposes a limit on the strength of nano-materials. Recent investigations report a conflicting view on the change in bulk modulus with particle size. Xiaogang *et al.* [10] studied the isothermal equation of state of nano and micro nickel powders up to 50 GPa. They found that the nano-nickel is more compressible than micro nickel. Chen *et al.* [11] studied the compressibility of nanocrystalline nickel as compared to the bulk nickel up to 55 GPa and reported that the bulk modulus does not vary with size for particles down to 20 nm. There are several experimental as well as theoretical studies on nanocrystalline nickel, which include magnetic [12–15], mechanical [16,17] and electrical [18] behaviour and data on diffusion coefficient [19], and vibration modes [20]. Many experimental reports deal with the study of the physical and microstructural properties using various techniques [21–24]. In the present work we report the effect of crystalline size on the compressibility of nickel both experimentally (x-ray diffractometry) and theoretically (cluster *ab initio* calculation).

2. Experiment and cluster *Ab initio* calculation

We conducted a synchrotron x-ray study on nano-sized Ni (Nanophase Technologies Corp., Burr Ridge, IL) with a mean particle size of 20 nm up to 61.5 GPa. The powder along with a small platinum grain was loaded into pressure chamber of a Mao-Bell type diamond anvil cell. The size of the gasket hole was around 100 μ in a 300 μ thick stainless steel gasket sandwiched between two anvils (300 μ diameter) of DAC. The gasket was pre-indented up to 80 μ. The platinum diffraction lines were used for pressure determination. The x-ray diffraction studies were carried out at the NSLS, Brookhaven National Laboratory using polychromatic synchrotron radiations (beamline X17C) The diffraction patterns were collected at $2\theta = 14.9873^\circ$ with a germanium solid state detector in the energy intervals between 5–80 KeV. Gold foil was used to perform angle calibration.

We briefly describe here the *ab initio* method to solve the Dirac equation (for the core electrons) or a (modified) Schrodinger equation (for the valence and semi-core electrons). We have used the generalized gradient approximation given by Perdew, Burke and Ernzerhof parameterization [25] for the exchange and correlation potential. The wave functions are expanded by means of linear muffin orbitals inside the non-overlapping muffin-tin spheres that surround each atomic site in the crystal. The muffin-tin radius was consistently chosen such that the muffin-tin occupied 66% of the total volume. We make use of a so-called double basis set since we allow the two tails with different kinetic energy for each muffin-tin orbital with a given l-quantum number. The calculations were done for one, fully hybridizing, energy panel in which we used values for the E_n's relating to the valence orbital: 4s, 4p and 3d, and 3p for the semi-core states. Within the muffin-tin spheres, the basis sets, charge density and potential were expanded in spherical harmonics with a cut-off l (max) = 8. Outside the muffin-tin spheres, in the interstitial region, the wave functions are Hankel and Neumann functions, which are represented by a Fourier series, using reciprocal lattice vectors. The same expansion is used to represent the charge density and the potential. This treatment of the wave function, charge density and the potential does not rely on any geometrical approximations and the described type of computational method is usually referred to as a full potential linear muffin-tin orbital method (FP-LMTO) [26]. In order to study nanocrystalline materials, we conducted cluster *ab initio* calculations. As it is time consuming to conduct cluster *ab inito* calculations for a large number of atoms in a cluster, we used 32 atoms cluster in the present study. Additionally, we observed that on replacing cluster size from 32 atoms to 64 the atoms do not change the electronic structure, which implies that the cluster size chosen in the present investigations can be well representative of the effect of size on the compressibility of nickel.



(a)

(b)

(c)

Figure 1 1a–c. The plot depicting the dependency of interplanar d-spacing as a function of pressure for a particular set of (hkl).

3. Results and discussion

The change in interatomic d-spacing as a function of pressure for sample is depicted in Fig. 1a–c. A continuous decrease in the values of the d-spacing (for a particular set of hkl value) has been observed with an increase in pressure.

We fit the experimental data (volume as a function of pressure) by using the second order Birch-Murnaghan EOS [27] having the following expression:

$$P = 1.5K_{300,0}\left[(V_{300,0}/V)^{7/3} - (V_{300,0}/V)^{5/3}\right] \times \left[1 - 0.75(4 - K'_{300,0})\{(V_{300,0}/V)^{2/3} - 1\}\right]$$

where $K_{300,0}$, $K'_{300,0}$, and $V_{300,0}$ are the bulk modulus, its pressure derivative and the volume of the unit cell at zero pressure and 300 K, respectively.

The experimental P-V data to this EOS was fitted using the Marquardt-Levenberg algorithm in commercial Sigma Plot for Windows (SPSS) program. Fig. 2

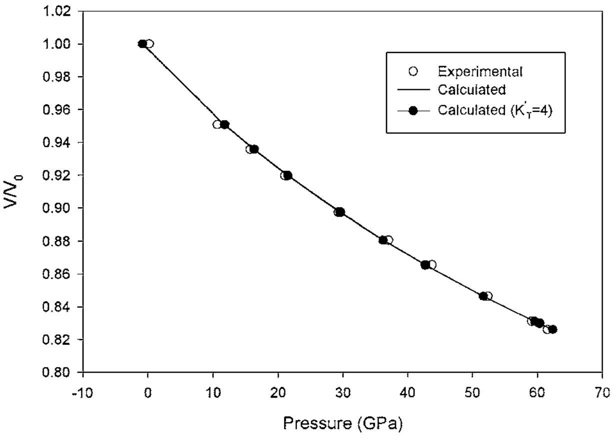


Figure 2 A plot depicting the fitting between the experimental (hollow circles) and calculated (solid line) values of pressure (up to 61.5 GPa) and volume. Using the second order Birch-Murnaghan equation of state has performed the fitting. The values of bulk modulus (K_T), its pressure derivative (K'_T) and unit cell volume (V_0) are 228(15) GPa, 4.02(0.51) and 43.56(0.13), respectively.

TABLE I Properties of nano and bulk nickel

Reference	Volume (V_0) Å^3	Bulk modulus K_T (GPa)	Pressure derivative of bulk modulus (K'_T)
Nano-nickel	43.56(0.13)	228(15)^a	4.02(0.51)
(Experimental)	43.55(0.09)	229(4)^a	4 (fixed)
Bulk nickel (*Ab initio*)	43.64	215	3.84
Nano-nickel (*Ab initio*)	44.00	217	3.2
Nano-nickel	43.756	217(14)^a	4 (fixed)
[11]		182(10)^b	4 (fixed)
Bulk-nickel	43.80(0.2)	181(7)^b	5.2(0.3)
[28]	43.77(0.1)	185(3)^b	5 (fixed)
Bulk-nickel	——	161(11)^b	7.55(1)
[29]	——	180^b	4 (fixed)

[a] non-hydrostatic compression.
[b] Quasi-hydrostatic compression.

shows the best-fit curve for the experimental data. We list the experimental and theoretical values of volume, isothermal bulk modulus (K_T) and pressure derivative of pressure derivative (K'_T) in Table I. There is no appreciable change (within the range of error) in the value of bulk modulus for bulk-nickel and nano-nickel. In contrary to the early report [14], we did not observe any increase in compressibility of nano-nickel. A possible reason for different values of bulk modulus obtained from our experimental and theoretical investigations can be attributed to the fact that the theoretical values were calculated at 0 K while the experimental data are at 300 K. We observe no phase transition up to 61.5 GPa.

4. Conclusions

We observed no phase transition in nanocrystalline nickel up to 61.5 GPa. The volume, isothermal bulk modulus and its pressure derivative are: 43.56 (0.13) Å^3, 228(15) GPa, 4.02(0.51): experimentally and 44.00 Å^3, 217 GPa and 3.20: theoretically, respectively. We report that there is no effect on the bulk modulus with the change in particle size, which may be contrary to Hall-Petch effect.

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