

# *In situ* X-ray diffraction study on the interatomic force of Ni nanowires

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## Abstract

We present an analysis of the interatomic force of Ni nanowires on the basis of the interatomic interaction potential energy curve, which is obtained from the results of *in situ* high temperature X-ray diffraction in the range of 25–800 °C. Compared with bulk Ni, Ni nanowires have larger interatomic force. Our research offers a simple method of studying the mechanical properties of the nanowires.

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**Keywords:** Ni nanowires; X-ray diffraction; Interatomic force; Interatomic interaction potential energy

## 1. Introduction

With the development of nanodevices, the study of unique physical and chemical properties of one-dimensional (1D) nanomaterials has become the focus of intensive research [1–5], and many interesting results have been obtained [6–8]. As one of the basic properties of materials, the mechanical properties of 1D nanomaterials are the important factors for designing functional nanodevices. However, up to now, these mechanical properties are rarely studied because the measurement is difficult. Recently, several methods have been developed to measure the mechanical properties of 1D nanomaterials. Wang et al. [9,10] have directly measured the elastic module of ZnO nanobelts and carbon nanotubes by the method of electric-field-induced resonant excitation in transmission electron microscopy. Li et al. [11,12] and Wu et al. [13] have studied the elastic module and the hardness of Au nanowires, Ag nanowires, and ZnS nanobelts with an atomic force microscope and a nanoindenter. Although these methods can measure the mechanical parameters of the nanowires, they are complicated and cannot give the crystalline direction along which these mechanical parameters are. As is well known, the interatomic force  $F$ , which is the origin of the mechanical properties, can

be calculated from the interaction potential energy  $U(r)$  as follows [14]:  $F = (\partial U(r))/\partial r$ , where  $r$  is the interatomic distance. In this paper, we have studied the interatomic force of Ni nanowires from the interatomic interaction potential energy curve, which can be obtained from the results of *in situ* high temperature X-ray diffraction (XRD).

It is well known that the interatomic interaction potential energy is related to the interatomic distance. Each value of the interatomic interaction potential energy corresponds to two different interatomic distances in definite range [14]. With the increase of the temperature, the interatomic interaction potential energy increases and the oscillation amplitude of the atoms also increases. However, the equilibrium position of atoms is always at the center point between two interatomic distances corresponding to the same interatomic interaction potential energy. The equilibrium position of the atoms can be obtained from the results of lattice thermal expansion on the basis of *in situ* high temperature XRD. So, we can draw the change trend of interatomic interaction potential energy curve of Ni nanowires and then deduce the interatomic force of Ni nanowires.

## 2. Experimental

As we know, the properties of the nanowires are dependent on the diameter of the nanowires [7]. In our experiments, in

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order to eliminate the effects of the diameter on the interatomic force, the nanowires with the same diameter need to be fabricated. The electrodeposition synthesis based on the porous anodic alumina membrane (PAAM) is a relatively simple and effective route to prepare the nanowires with uniform diameter. It is important that PAAM is chemically stable up to 1100 K and is suitable for measuring the thermal expansion at the high temperature [15]. The PAAM templates were prepared according to the two-step anodization method as reported [16,17]. The electrolyte for the preparation of Ni nanowires contains a mixture of 100 g/L  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ , 30 g/L  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , 40 g/L  $\text{H}_3\text{BO}_3$  solution, and the pH value of the solution was adjusted to 2.5 with 1 M  $\text{H}_2\text{SO}_4$ . In our experiments, Ni nanowire arrays were prepared with the potential of 3 V at the room temperature. The previous works indicated that the vacancies have effects on the lattice thermal expansion of the nanowires [18,19]. Therefore, in order to obtain the intrinsic result, the samples were annealed at 800 °C for 3 h in vacuum of  $10^{-3}$  Pa to remove the vacancies.

The morphologies and the growth orientation of Ni nanowires were characterized with transmission electron microscopy (TEM, JEOL-2010). For TEM observations, PAAM was completely dissolved with 1 M NaOH solution and then rinsed with absolute ethanol. The lattice thermal expansion of Ni nanowires was measured by *in situ* X-ray diffractometer (Philips X'Pert) with Cu  $K\alpha_1$  radiation ( $\lambda = 0.154056$  nm) in the  $\theta$ – $\theta$  geometry mode. The samples were placed on a Pt holder in the vacuum with  $5 \times 10^{-3}$  Pa and measured in the range of 25–800 °C. Before each measurement, the sample was heated to the defined temperature at the increasing rate of 10 °C/min and kept at that temperature for 8 min to stabilize the sample temperature. In our experiments, only the lattice thermal expansion along the axis of Ni nanowires was measured. For comparison, the lattice thermal expansion of high-purity bulk Ni (99.999%) annealed at 800 °C for 3 h was also measured with same procedure.

### 3. Results and discussion

The XRD pattern of Ni nanowires with the diameter of 45 nm embedded in PAAM is shown in Fig. 1(a). There is only one diffraction peak in the XRD pattern, which can be indexed to the (220) planes of face-centered cubic (FCC) Ni phase (JCPDS, No. 04-0850), indicating that Ni nanowires have a well-preferred growth orientation along the [110] direction. Fig. 1(b) shows the typical TEM image with the corresponding selected-area electron diffraction (SAED) pattern and high-resolution transmission electron microscopic (HRTEM) images, which further confirms the growth orientation of the nanowire.

The axial interplanar spacing can be calculated from the XRD patterns by Bragg equation:  $2d \sin \theta = \lambda$ , where  $d$ ,  $\theta$ , and  $\lambda$  are the interplanar spacing, diffraction angle corresponding to the peak position, and X-ray wavelength, respectively. In our experiments, the measured interplanar spacing corresponds to the (220) plane. Curve a in Fig. 2 shows the variation of the interplanar spacing of (220) plane with the temperature

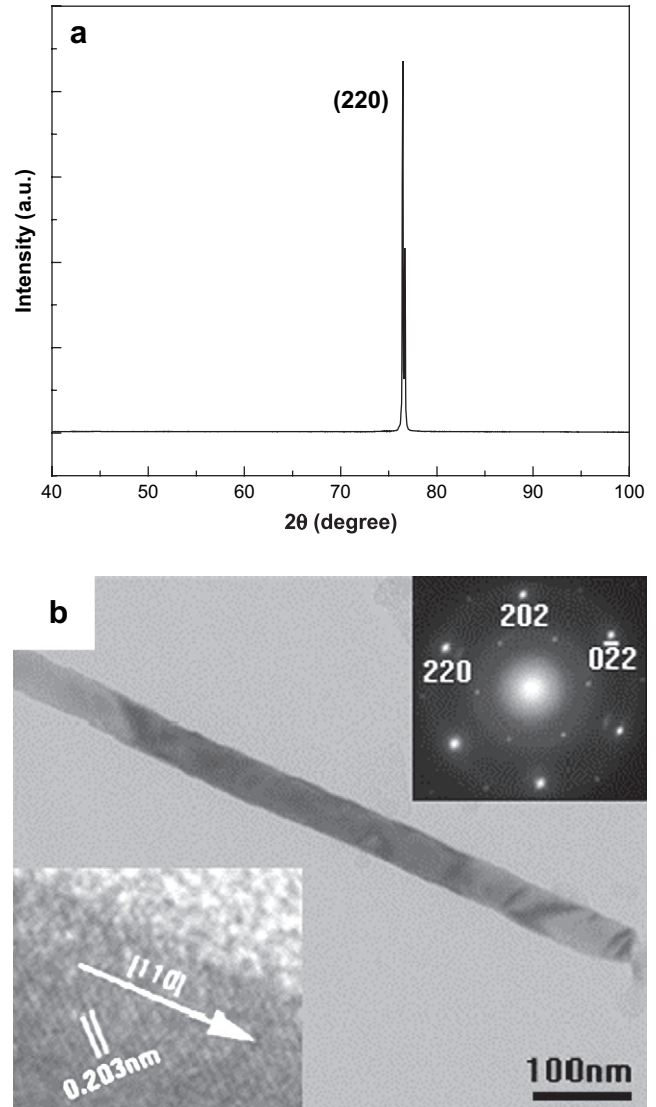


Fig. 1. (a) The XRD pattern of Ni nanowire array and (b) TEM images of Ni nanowires. The lower and upper insets in (b) are the corresponding HRTEM image and SAED pattern, respectively.

for Ni nanowires with the diameter of 45 nm and curve b shows the lattice thermal expansion of bulk Ni. Herein, the result has been amended by excluding the effect of the holder thermal expansion. From Fig. 2, it can be seen that the variational quantity of the interplanar spacing of (220) for Ni nanowires is much smaller than that for bulk Ni.

From the XRD results, the interatomic distance of Ni nanowires can be obtained, so the equilibrium position between atoms for Ni nanowires at different temperatures can be drawn. Here, in order to make the discussion clear we suppose that the interatomic interaction potential energy curve is the same when the interatomic distance is smaller than that corresponding to A point (see Fig. 3) for both the Ni nanowires and the bulk Ni, moreover, the minimum interatomic interaction energy is also the same. For the face-centered cubic structure, the lattice parameter  $a$  can be obtained from the interplanar spacing  $d$  of (220) plane as follows:  $a = 2\sqrt{2}d$ , and the interatomic distance

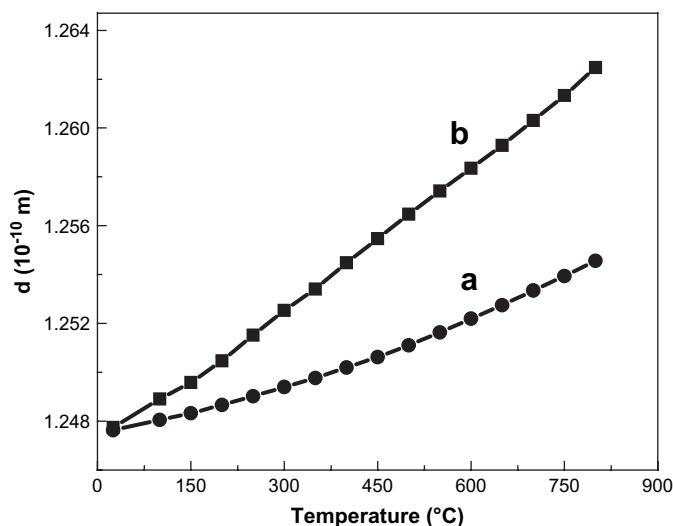


Fig. 2. The temperature dependences of the interplanar spacing  $d$  of the (220) plane for the annealed Ni nanowire arrays (curve a) and the annealed bulk Ni (curve b).

$r$  and the lattice parameter  $a$  have a relation as follows:  $r = (a/\sqrt{2}) = 2d$ . So, from the values of the interplanar spacing  $d$  of (220) plane shown in Fig. 2, the curve of the variation of the equilibrium position for Ni nanowires and that for the bulk Ni can be obtained. With the increase of the temperature, the value of the interatomic potential energy increases, and the interatomic distance also increases. Here we plot the curves of the interatomic potential energy versus the equilibrium position for Ni nanowires and the bulk Ni, respectively, in Fig. 3 (see curves 1 and 3 in Fig. 3).

According to the above description about the interatomic interaction potential energy, we know that two positions of atoms

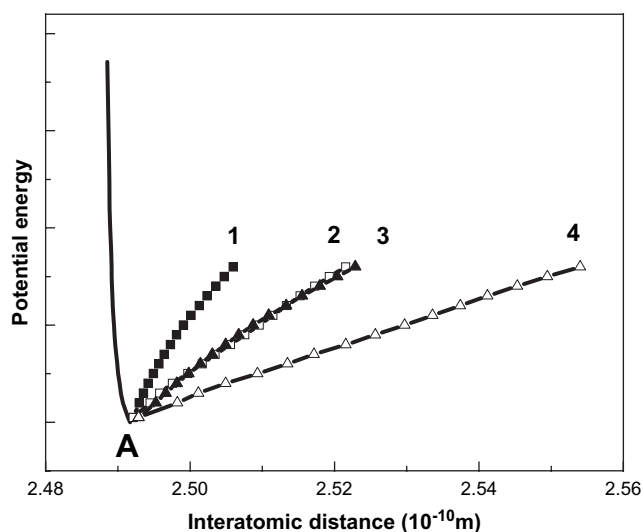


Fig. 3. The variation of the interatomic interaction potential energy with the interatomic distance. Curves 1 (solid square) and 3 (solid triangle) are the variation curves of the equilibrium position for Ni nanowire arrays with the diameter of 45 nm and the bulk Ni, respectively; curves 2 (hollow square) and 4 (hollow triangle) are the potential energy curves for Ni nanowire arrays with the diameter of 45 nm and the bulk Ni, respectively.

corresponding to the same interatomic interaction potential energy are symmetrical about the equilibrium position of atoms. So the interatomic interaction potential energy curves for Ni nanowires (curve 2) and the bulk Ni (curve 4) can be drawn as shown in Fig. 3. Comparing curve 2 with curve 4, it can be seen that the interaction potential energy curve of nanowires is much steeper than that of the bulk Ni. Based on this experimental result, we can know that the interaction force between atoms for Ni nanowires is larger than that for the bulk Ni. Because the interaction force is obtained from the lattice thermal expansion of (220) plane, the interaction force that we obtained here is along the [110] direction. Meanwhile, it implies that larger force is needed to stretch or deform Ni nanowires compared with the bulk Ni.

The strengthening of the interatomic force for Ni nanowires may be ascribed to their small size. With decreasing the material size, the effects of surface and interface become important. Sun et al. [20–23] considered that the surface bonds of the nanomaterials would contract because of the reduction of the coordination numbers of surface atoms. The contraction of surface bonds will result in the corresponding contraction of the atomic bonds in several layers closed to the surface. Meanwhile, the reduction of the coordination numbers of surface atoms induces the shrinking of atomic radius of the metal [24]. Rubio-Bollinger et al. [25] also considered that the bonds of low coordinated metal atoms are stronger than those of high coordinated metal atoms. In our case, Ni nanowires have a big surface-to-volume ratio, which indicates that atoms of several surface layers play an important role in the interatomic force. In Fig. 3, with the increase of interatomic distance, the interatomic interaction potential energy of Ni nanowires increases more rapidly than that of bulk Ni, which implies that the bonds of atoms for Ni nanowires are stronger than those for bulk Ni. So Ni nanowires have larger interatomic force compared with the bulk Ni. Wu et al. [13] obtained the same results in Au nanowires with an atomic force microscope and a nanoindenter. Therefore, the reduction of the coordination numbers of surface atoms for Ni nanowires makes the interatomic force to become stronger.

#### 4. Conclusion

In summary, the interatomic force of Ni nanowires with the diameter of 45 nm was investigated using *in situ* high temperature X-ray diffraction. The results indicate that the interatomic force of Ni nanowires is larger than that of the bulk Ni. The strengthening of the interatomic force for Ni nanowires might be due to their big surface-to-volume ratio. This method provides a simple way to study the mechanical properties of the nanowires. Furthermore, the crystalline direction along which the mechanical parameter is can be given. This method is expected to have more applications in nanoscale system.

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### Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version at doi:[10.1016/j.solidstatesciences.2007.12.022](https://doi.org/10.1016/j.solidstatesciences.2007.12.022).

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