MODULATED ORDERING Nb-H ALLOYS

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T. Kajitani, T. O. Brun and M. H. Mueller
Argonne National Laboratory*, Argonne, IL 60439

and

H. K. Birnbaum and B. J. Makenas
University of Illinois, Urbana, IL 61801

ABSTRACT

Ordering reactions in α' and β-NbH alloys have been investigated using elastic theory. The α'-β and β-λ phase transformations are driven by the elastic ineraction in the niobium lattice distorted by the protons on the t-site interstitials. The β phase is shown to have a three dimensional structure. The fundamental period of the long range modulation along the c-axis in the λ-phase, an incommensurated β phase, is approximately 5 lattice constants.

INTRODUCTION

In this paper, we present the results of self-consistent elastic free energy calculations for proton interstitials in a niobium lattice. The theory of elastic free energy has been discussed in detail by Villain,[1] Krivoglaz,[2] Khachaturyan[3] and Cook and deFontaine,[4] and the theoretical approach is outlined briefly in the following discussion. The elastic free energy is represented in a Fourier series.

$$F_{elastic} = 1/2 \sum_{k} F(k)\ T(-k)T(k) \qquad (1)$$

where $F_{elastic}$, F(k) and T(k) are the total elastic free energy, Fourier coefficient of the elastic free energy and the Fourier coefficient of the amplitude of the concentration waves, respectively. F(k) is composed of initial and relaxation energy terms.

$$F(k) = \phi_o(k) - R(k) \qquad (2)$$

The initial term, $\phi_o(k)$, is the elastic energy of an initial state in which the lattice distortion is limited to the vicinity of the interstitial. The relaxation term, R(k), is the elastic energy which is released, when the lattice is relaxed from this state. The term, R(k), can be written as

$$R(k) = \sum_{ij} \phi_{ij}(k) U_i(-k) U_j(k) \qquad (3)$$

where $\phi_{ij}(k)$ is the dynamical matrix, and $U_i(k)$ is a displacement field defined by

$$U_i(k) = - \sum_{j} \phi_{ij}^{-1}(k) P_i(k) T(k) \qquad (4)$$

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The term $P_i(k)$ is the Fourier transform of the Kanzaki force field[5] given by

$$P_i(r) = 1/2 \sum_{jr'} \phi_{ij}(r,r')\xi_i(r,r') \qquad (5)$$

where $\phi_{ij}(r,r')$ and $\xi_j(r,r')$ are the atomic force constants and the relative displacement between an atom located at r and an atom at r'.

RESULTS AND DISCUSSIONS

α'-β Transformation

In α' phase, protons are randomly distributed on the tetrahedral sites shown in Fig. 1. In the initial state, niobium atoms are locally expanded by the magnitude indicated in Fig. 1. The initial displacement of the niobium atoms at r can be written as

$$U_x^o(r) = \sum_k -4\, i[\varepsilon_1 \sin \pi k_x (\cos \tfrac{\pi}{2} k_y + \cos \tfrac{\pi}{2} K_z) + \varepsilon_2 \sin \tfrac{\pi}{2} k_x (\cos \pi k_y + \cos \pi k_z)] \times T(-k) \exp ikr \qquad (6)$$

where x,y and z denote the directions <100>, <010> and <001>, respectively. The term, $\phi_o(k)$, is calculated using the initial displacement field.

Figs. 2 and 3 show the elastic free energy, F(k), on (001) planes centered at (7/10 7/10 0)* and (1/2 1/2 1),respectively. The calculated free energy includes the contribution from the homogeneous expansion due to protons. Since the free energy surface has a minimum at (1/2 1/2 1) rather than (1/2 1/2 0), the calculation predicts that the concentration wave with the wave number (1/2 1/2 1) can be stabilized in bcc Nb at temperatures below a critical point. The difference of the free energy between (1/2 1/2 0) and (1/2 1/2 1) are due mainly to differences in the initial elastic energy $\phi_o(k)$.

β-λ Transformation

The elastic free energy for the β phase is calculated in a similar way. Fig. 4 shows the free energy surface on $(1\bar{1}0)$ plane centered at (1/2 1/2 1). The local distortion due to randomly distributed vacancies have been ignored. The elastic free energy minima are found in the vicinities of (1/2 1/2 0.78) and (1/2 1/2 1.22), in agreement with experiment.[6] The modulation is mainly caused by the stored strain energy along the c-axis which shows significant expansion by increasing the proton concentration.

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* All coordinates refer to reciprocal space of bcc.

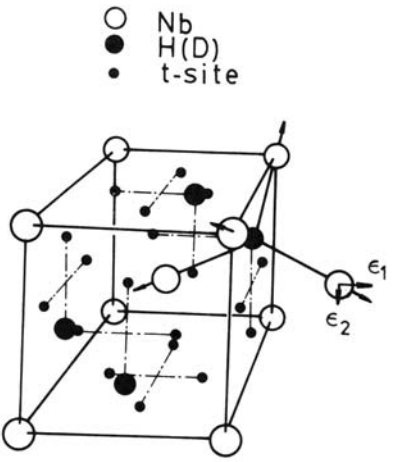

Fig. 1. bcc unit cell and t-site interstitials.

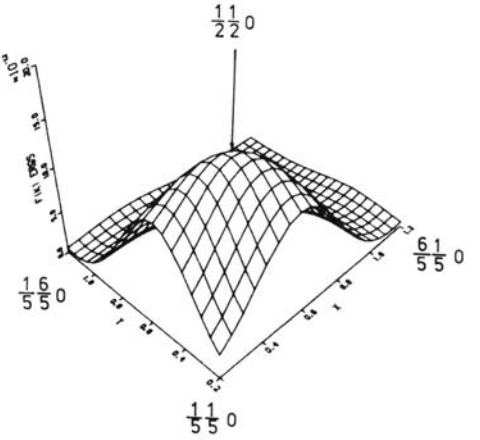

Fig. 2. F(k) on (001) plane centered at (7/10,7/10,0).

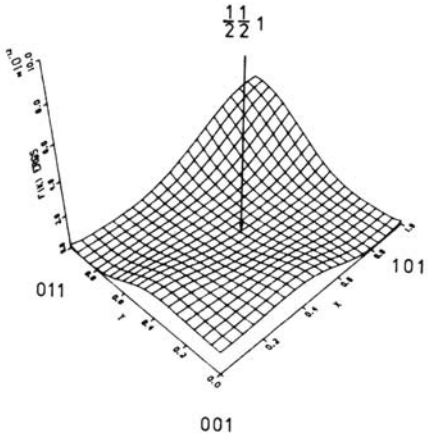

Fig. 3. F(k) on (001) plane centered at (1/2,1/2,1).

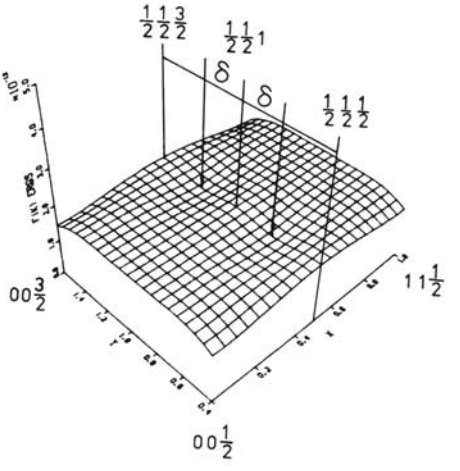

Fig. 4. F(k) on $(1\bar{1}0)$ plane centered at (1/2,1/2,1) in β phase.