



## APPLICATION OF THE EMBEDDED ATOM METHOD TO PHONONS IN TRANSITION METALS

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The lattice dynamical matrix has been derived from a new model of metallic cohesion, the Embedded Atom Method, based on approximations in density functional theory. The predictions of previously published empirical functions for Ni and Pd are compared to experimental phonon dispersions. The agreement shows that the Embedded Atom Method provides a reasonable description of transition metal lattice dynamics.

Interatomic pair potentials have long been used in the description of metallic bonding<sup>1</sup>. A formal derivation of the total energy of a solid in terms of N-body interactions can be achieved in many ways. The result usually involves an expansion which is terminated after one- and two-body terms<sup>2</sup>. The utility of pair interactions is limited by the breakdown in the two-body approximation, as often occurs at surfaces and defects. This breakdown also reflects itself in the lack of generality of a particular interatomic potential, e.g., potentials derived for solid metals often do not describe the liquid state very adequately.<sup>3</sup>

A new approach, called the Embedded Atom Method (EAM)<sup>4,5</sup>, provides a framework for a general picture of metallic bonding. The method, based on density functional theory<sup>6</sup> provides an approximate expression for the energy of an arbitrary arrangement of atoms in a metallic system. Because of its generality, it has been applied to surfaces<sup>5,7,8</sup>, defects<sup>5</sup>, liquids<sup>3</sup>, and fracture<sup>4</sup> with great success. Furthermore, its utility and simplicity is comparable to that of pair potentials. Effective, environment-dependent pair potentials can in fact be derived from the EAM<sup>3</sup>, but because of the inherent simplicity of the EAM this is unnecessary. In effect, the EAM sums up an

infinite series of N-body interactions into a simple expression for the total energy.

The purpose of this work is to apply the EAM to the calculation of phonon dispersion functions in transition metals. We will show that the EAM yields a simple expression for the dynamical matrix<sup>9</sup> of a crystal and gives quantitative agreement with experiment.

In the EAM<sup>5</sup>, the total energy of a homonuclear arrangement of atoms is given by:

$$E_{\text{tot}} = \sum_i F(\rho_{h,i}) + (1/2) \sum_{\substack{i,j \\ i \neq j}} \phi(R_{ij}) \quad (1)$$

where  $F(\rho)$  is the embedding energy,  $\phi(R)$  is a short-ranged core-core repulsion, and the sums are over lattice atoms. The embedding energy represents the interaction of an atom with the local electron gas provided by all the other atoms and thereby accounts for the cohesive energy of the solid. To make Eq. (1) of practical use, an approximation for the electron density  $\rho_h$  at atom  $i$  is provided by a linear superposition of atomic electron densities:

$$\rho_{h,i} = \sum_{j \neq i} \rho^a(R_{ij}) \quad (2)$$

where  $\rho^a(R)$  is the atomic electron density.

The dynamical matrix<sup>9</sup> for a crystalline metal can be obtained in a straightforward way from Eqs. (1) and (2). The result is:

$$D(\mathbf{q}) = \sum_j \chi_{0j}(1 - e^{i\mathbf{q}\cdot\mathbf{R}_{0j}}) + F(\rho_h)^{\prime\prime} f^*(\mathbf{q})f(\mathbf{q}) \quad (3)$$

where

$$\begin{aligned} \chi_{0j} = & (\phi(R_{0j})^{\prime\prime} + F(\rho_h)^{\prime} \rho^a(R_{0j})^{\prime\prime}) \mathbf{R}_{0j} \mathbf{R}_{0j} / (R_{0j})^2 \\ & + (\phi(R_{0j})^{\prime} + F(\rho_h)^{\prime} \rho^a(R_{0j})^{\prime}) (1 - \mathbf{R}_{0j} \mathbf{R}_{0j} / (R_{0j})^2) / R_{0j} \end{aligned} \quad (4)$$

and

$$f(\mathbf{q}) = \sum_{j \neq 0} \rho^a(R_{0j})^{\prime} (e^{i\mathbf{q}\cdot\mathbf{R}_{0j}}) \mathbf{R}_{0j} / R_{0j} \quad (5)$$

and primes denote derivatives with respect to the respective arguments. ( $f^*$  is the complex conjugate of  $f$ ). The subscript "0" in the preceding expressions denotes a reference atom. The density  $\rho_h$  is the host density defined by Eq. 2, which in a

crystalline solid is the same for all atoms. This result for the dynamical matrix leads to the usual relations between zone-center phonon dispersions (speeds of sound) and the elastic constants.<sup>9</sup>

The predictions of the EAM are tested in this communication by comparing them to experimental phonon dispersions for pure metals. The functions  $F(\rho)$  and  $\phi(R)$  have been determined semi-empirically for a variety of f.c.c. metals. In this work, the functions derived by Daw and Baskes for Pd and Ni<sup>5</sup> are used. These functions were determined by fitting to properties of the bulk metals: lattice constant, elastic constants, sublimation energy, vacancy formation energy, and difference in b.c.c. and f.c.c. phase energies.

The results for the phonon dispersion functions in Ni and Pd are presented in Figs. 1 and 2. The agreement with experiment is good.<sup>10,11</sup> Agreement is to be expected for small  $\mathbf{q}$ , of course, because the functions were determined by fitting to the elastic constants. However, agreement over the whole zone is evidence that the EAM provides a physically reasonable description of the vibrational excitations of a transition metal. The anomaly in the [011] direction in Pd<sup>12</sup> (visible in Fig. 2 in the  $T_1$  branch near  $\mathbf{q}=[0,1/4,1/4]2\pi/a$ ) is not predicted by the EAM because this involves details of the Fermi surface that the EAM neglects.

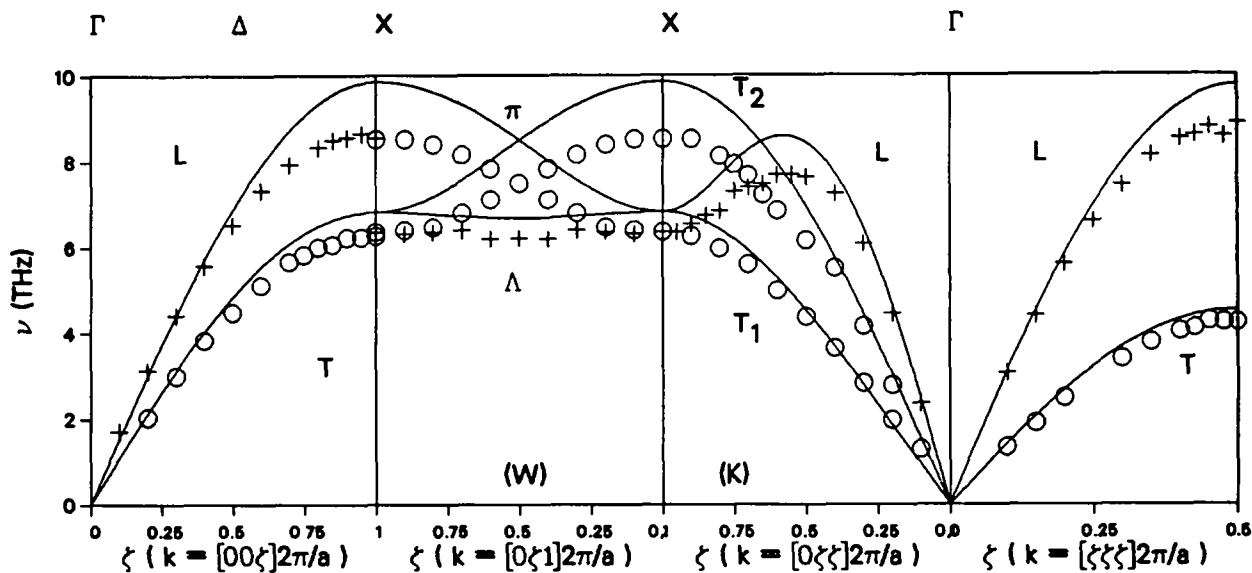


Figure 1. Phonon dispersion curves (solid lines) for Ni calculated by the EAM using the functions from Ref. 5. The experimental data (+'s and o's) are from Ref. 10. The labels follow the convention of Ref. 10.

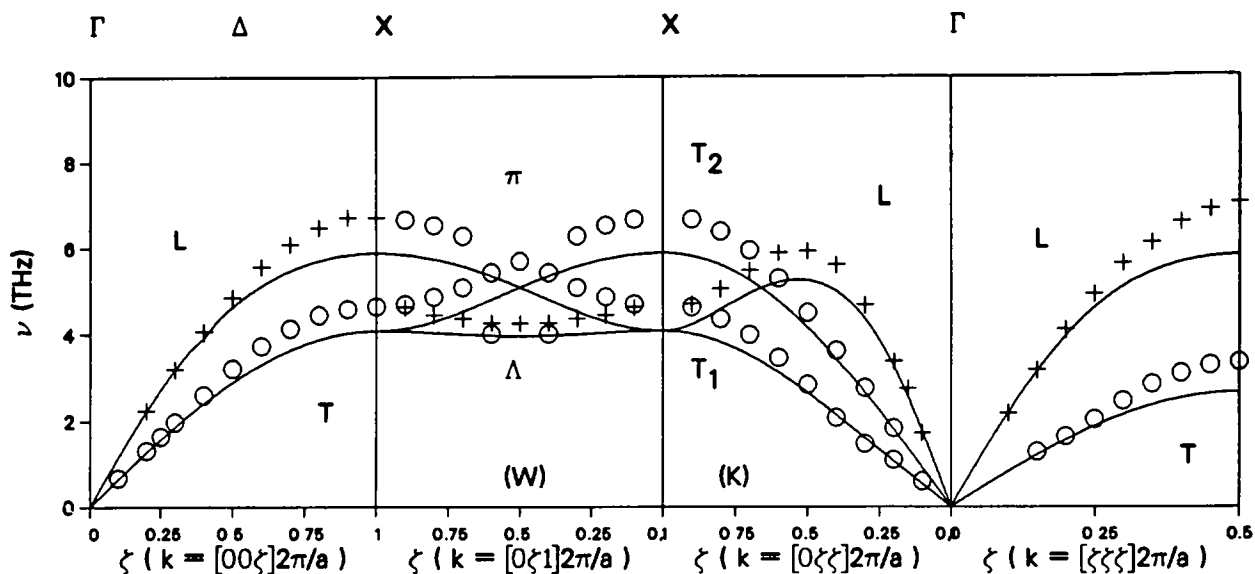


Figure 2. Phonon dispersion curves (solid lines) for Pd calculated by the EAM using the functions from Ref. 5. The experimental data (+'s and o's) are from Ref. 11. The labels follow the convention of Ref. 11.

Given the flexibility in the EAM, it is expected that one could improve the agreement between the calculated phonon dispersions and the observed ones. This could be done by parameterizing the functions in the EAM and fitting to the phonon curves, as is often done using models of force constants.<sup>10,11</sup> Considering that the current functions were fitted only to the zone-

center phonons, the agreement between the calculations and the observations is good.

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