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Lattice dynamics of magnesium using pseudopotential and *ab initio* Hartree-Fock approaches

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We have used first-principles pseudopotentials to calculate the phonon-dispersion curves and the elastic constants of magnesium. The predicted phonon spectra obtained from different interatomic potentials are in good agreement with the experimental measurements. The elastic constants computed from these atomic force constants are compared with Hartree-Fock values. [S0163-1829(96)03233-X]

I. INTRODUCTION

Materials of hexagonal close-packed structure (hcp) such as magnesium play a relevant role in nuclear industry. Mechanical, dynamical, and thermodynamical properties are strongly dependent on microstructure and also on processes involving defect interactions.¹ An ideal way to know some basic properties of these materials is obtained from calculation techniques basically determined by the knowledge of the interionic potential,² often through a pseudopotential (PSP) formulation very useful in the study of the properties of solids.³ We consider two models in our study: a Heine-Abarenkov PSP-type based on the phase-shift approach and the recent class of first-principles PSP's which have been enabled to do simple and accurate electronic calculations. In the formalism of Rasolt and Taylor,⁴ the PSP proposed by Dagens, Rasolt, and Taylor⁵ (first model) and those proposed by Hamann, Schlüter, and Chiang⁶ (second model) are known to have several practical advantages.

In the approach of Dagens, Rasolt, and Taylor,⁵ the displaced electronic density around an ion in an electron gas is calculated using a nonlinear self-consistent theory. Then a nonlocal PSP is selected in order to reproduce, as close as possible, this initial electronic density. In this way, the nonlinear effects are partly included in the PSP. The interionic potentials calculated using their PSP have been used with success to calculate phonon-dispersion curves.^{5,7}

An important property of first-principles PSP's is their transferability to various systems. The lack of this one is related to the difference between the exact density and the pseudodensity calculated from an equivalent PSP.³ The method of Hamann, Schlüter, and Chiang⁶ provides a class of numerical PSP's having an optimum transferability. Another important attribute of the PSP's is their ability to be fitted with a small set of analytical functions. Bachelet, Hamann, and Schlüter⁸ have obtained a complete analytical representation for all the elements of the periodic classification. Moreover, this method is known to correctly predict stable crystal structures.

Because phonon spectrum is the lattice characteristic which reflects the peculiarities of the interatomic interaction in crystals, this work presents an attempt of the application of two models of pseudopotential theory to explore lattice

dynamics of magnesium. In particular, we are interested in comparing the prediction of the phonon frequencies obtained from the Dagens, Rasolt, and Taylor (DRT) and Bachelet, Hamann, and Schlüter (BHS) approaches with the prediction made using the optimized model potential of the Shaw-Heine-Abarenkov (PSP) (Ref. 10) and experimental results.^{11,12} From atomic force constants computed through our PSP approaches we have determined the elastic constants at equilibrium volume. These values are compared with *ab initio* results obtained through Hartree-Fock calculations carried out from the CRYSTAL package.¹³

The paper is organized in the following way: some methodological and computational details are presented in Sec. II and Sec. III describes the results of lattice-dynamics calculations.

II. METHODOLOGICAL AND COMPUTATIONAL DETAILS

A. The interatomic potentials

The total energy of metals may be written as

$$E_T = E_0 + \frac{1}{2} \sum_{i,j} V_{\text{ion}}(R_{ij}) \quad (1)$$

within a pair interatomic potential approach. The electronic energy E_0 is independent of the distances R_{ij} between atom i and atom j . The pair interatomic potential $V_{\text{ion}}(R_{ij})$ between the two atoms i and j is calculated using two models of PSP and following the perturbative method proposed by Rasolt and Taylor.⁴ In this formalism, the pair potential $V_{\text{ion}}(r)$ takes the form of a screened Coulomb potential given by

$$V_{\text{ion}}(r) = \frac{(Ze)^2}{r} - \frac{(Ze)^2}{2\pi^2} \int_0^\infty \frac{F(q)}{q^2} \exp(-i\mathbf{q} \cdot \mathbf{r}) d\mathbf{q}, \quad (2)$$

where $F(q)$ is the energy wave-number characteristic dependent of the screening function of an interacting electron gas [$\Pi(q)$] and of the PSP $V_p(r)$. $\Pi(q)$ is deduced from the model of Geldart and Vosko¹⁴ and includes the exchange and correlation effects. The choice of the PSP is then an impor-

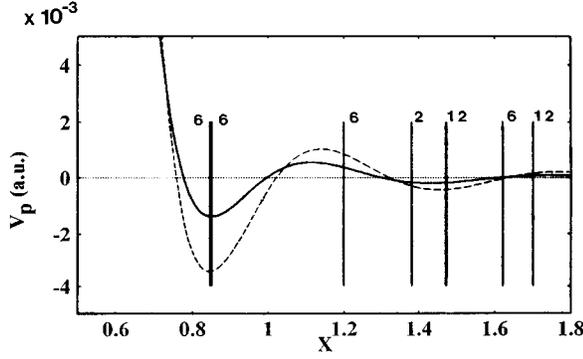


FIG. 1. Interatomic potential $V_p(r)$ for the DRT (full curve) and the BHS (dashed curve) as a function of the scaled variable x defined by $x=r/(a^2c)^{-1/3}$. Interatomic distances R_{ij} (up to eighth-nearest neighbors) are shown by vertical bars.

tant point. As previously described, the DRT (Ref. 5) and BHS (Ref. 8) approaches are adopted in our calculations.

The DRT pseudopotential is an energy-dependent nonlocal model potential similar to those introduced by Heine and Abarenkov¹⁵

$$V_p(r) = \sum_l \left[A_l \theta(R_l - r) - \frac{Ze^2}{r} \theta(r - R_l) P_l \right], \quad (3)$$

where $\theta(x)$ is the usual step function and P_l is the angular momentum projection operator. DRT suggested that the PSP parameters (A_l and R_l) should be adjusted so that the pseudocharge density calculated to first order in perturbation theory agrees precisely with a full nonlinear calculation of the same quantity outside of the ion core region. Hence by using these adjusted PSP's we take into account all multiple-scattering events at a single site.

The method proposed by Hamann, Schlüter, and Chiang⁶ is a great step forward and provides a simple means of extracting useful PSP's from *ab initio* atomic calculations. The method is transferable to a very good accuracy. A central point of their approach is that two important aspects of transferability are satisfied: firstly, these potentials are normalized, and secondly they are intrinsically soft core. This method was systematically used by Bachelet, Hamann, and Schlüter⁸ to obtain a nonsingular PSP. These norm-preserving PSP's (Ref. 8) have the following form:

$$V_p(r) = \sum_l V_l(r) P_l, \quad (4)$$

where the pseudopotential $V_l(r)$ is decomposed into a large-range local part [$V_{\text{core}}(r)$] and a short-range nonlocal part. The expressions for $V_l(r)$ are given in terms of few analytical functions.

We have applied the formulation previously given to the magnesium hcp metal to calculate the phonon frequencies of this compound. These calculations were performed using the optimized parameters given by Prakash and Joshy.¹⁶ Figure 1 shows the interatomic potentials obtained from the two approaches. One can see that the first- and second-neighbor interactions clearly dominate. The first- and second-neighbor distances are quite the same and fall near the principal minimum of each potential. At long distance, the DRT potential

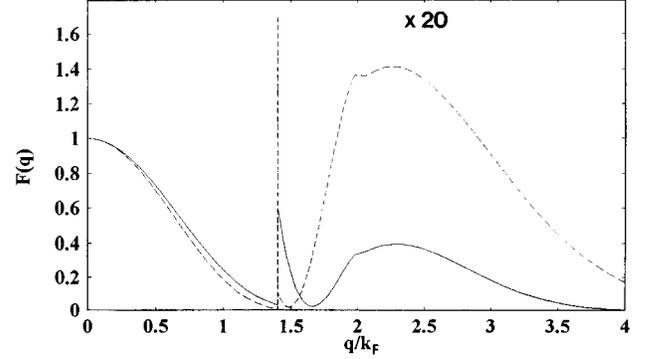


FIG. 2. Normalized energy-wave-number characteristics $F(q)$ for the DRT and the BHS pseudopotentials.

is smoother than the BHS one. This difference is due to the behavior of the normalized energy-wave-number characteristics. As shown in Fig. 2, the bump around $q=2.3k_F$ in $F(q)$ corresponding to BHS calculations is larger than the DRT one and the singular point at $q=2k_F$ is more clearly seen. This behavior was previously noted by Hasegawa *et al.*⁹ for their interatomic potential deduced from *ab initio* calculations.

B. Elastic constants and phonon frequencies

We have used the modified axially symmetric model (AS) in the quasi-harmonic approximation, defined by De Wames, Wolfram, and Lehman¹⁷ for the hexagonal metals. We then determine the dynamical matrix $D(\mathbf{k})$ for each vector \mathbf{k} in the first Brillouin zone and obtain phonon frequencies. The matrix elements of this perturbed central force model can be constructed from the atomic force-constant model (AFC) given by

$$\phi_{\mu\nu}^{ij} = \frac{\partial^2 V_p(R_{ij})}{\partial x_\mu \partial x_\nu} = \delta_{\mu\nu} A(R_{ij}) + \frac{x_\mu x_\nu}{R_{ij}^2} [B(R_{ij}) - A(R_{ij})], \quad (5)$$

where x_μ is the μ th Cartesian component of the i th atom. $A(r) = (1/r)[\partial V_p(r)/\partial r]$ and $B(r) = [\partial^2 V_p(r)/\partial r^2]$ are, respectively, a tangential AFC corresponding to bond bending and a radial AFC corresponding to bond stretching. These first and second derivatives of V_p are evaluated at near-neighbor distances (up to sixth-neighbors in our calculations).

The AFC may be related to the elastic constants by equating the elements of the dynamical matrix to those of the dynamical matrix of elastic theory in the limit of long wavelengths. Seven independent equations relating the AFC to the elastic constants were given by De Wames, Wolfram, and Lehman¹⁷ extending the model of Slutsky and Garland¹⁸ by inclusion of interactions with fourth- and fifth-nearest neighbors.

In this paper, we find it interesting to compare the above results to those obtained for the elastic constants from *ab initio* Hartree-Fock (HF) linear combination of atomic orbitals self-consistent field computer program CRYSTAL implemented by Dovesi *et al.*¹² The technique adopted for calculating the elastic constants using this code was already

TABLE I. Phonon frequencies (THz) at Γ , M , A , and K symmetry points computed using DRT and BHS pseudopotentials. Comparison with experiment (Refs. 11 and 12) and previous optimized model potential calculations (Ref. 10).

	Expt.	DRT	BHS	Ref. 10
Γ_5^+	3.70	3.92	3.66	3.78
Γ_3^+	7.30	7.64	8.54	8.10
M_4^+	3.70	3.77	3.57	3.73
M_3^+	4.15	4.24	4.67	4.26
M_3^-	5.45	5.67	6.01	5.66
M_4^-	6.12	6.33	7.20	6.52
M_2^+	6.58	6.97	7.77	7.28
M_2^-	6.88	7.15	7.96	7.63
A_1	2.94	2.76	2.52	2.78
A_3	5.20	5.58	6.24	5.73
K_1		5.38	6.12	
K_2		5.76	6.31	
K_3		6.22	7.00	
K_4		6.65	7.64	

described by Catti *et al.*¹⁹ The basis set used is a valence double ζ plus polarization one. The core electrons are treated by Durand and Barthelat's effective core potential.²⁰

III. RESULTS AND DISCUSSION

We have applied the formulation given in the previous section to investigate and compare the phonon frequencies predicted by the DRT and BHS approaches. To facilitate comparison of the various models we have listed in Table I, the predicted and observed phonon frequencies at Γ , M , A , and K symmetry points of the reciprocal lattice. The best calculated values deduced by Shaw and Pynn¹⁰ from an optimized nonlocal potential which includes exchange and correlation corrections are also given. The calculated phonon frequencies at the zone-boundaries points always are larger than the experimental phonon frequencies. For instance the calculated frequencies exceed the experimental values by a factor of 1.04, 1.13, and 1.07 in the DRT and BHS approaches and in the calculations of Shaw, respectively. The

worst deviation from experiment is 7% for DRT, 20% for BHS, and 11% for the previous calculations of Shaw *et al.* The maximum frequency is also greater in our calculations than the experimental value.¹¹

The elastic constants deduced from the DRT and the BHS atomic force constants by using the AS model¹⁷ are reported in Table II. Hartree-Fock values given for comparison, have been computed for the minimum energy structural parameters ($a=3.351$ Å and $c=5.173$ Å). The deviation of the lattice parameters a and c are, respectively, 4.0 and 0.8 % relatively to the experimental data given a unit-cell volume of 50.304 Å³. The HF binding energy (0.300 eV) is about 1.21 eV lower than the experimental value (1.51 eV). If the HF approximation used here gives usually quite reasonable elastic constants for ionic and semi ionic systems, little is known for its suitability to describe those of metallic systems. We can see a very good agreement between the two PSP's and experimental data. This agreement gives us some confidence on the validity of DRT and BHS formalisms for the prediction of elastic constants. Generally, the DRT evaluation is better than the BHS one where a significant discrepancy is observed for C_{33} (about 40%). The discrepancy of the behavior between the two PSP's can be attributed to the soft-core character of the *ab initio* BHS moderating in this case the success of the perturbative approach. In all cases, excepted for the ($C_{11}+C_{12}$) determination, the errors observed in HF calculations are larger than those obtained from pseudopotentials.

The average bulk modulus and its definition $B_T = (1/9)(2C_{11}+2C_{12}+4C_{13}+C_{33})$ are consistent with the elastic response to uniform dilatations implied in the case of an hcp crystal.²¹ Experimentally, the isothermal bulk modulus B_T for Mg is observed to be only weakly temperature dependent.²² Although the elastic constants calculated at the HF level of theory are too high for C_{11} and C_{33} and too small for C_{13} and C_{12} relative to the experimental data, the bulk modulus calculated at this level (35.2 GPa) is in perfect agreement with the value predicted from experiments [36.9 GPa (Ref. 1) and 35.4 (Ref. 23)]. Our computed ($T=0$ K) values of B_T very close in our DRT (39.3 GPa) and BHS (39.0 GPa) investigations are better than the values recently published by Magaña and Vasquez (44.5 GPa) (Ref. 24) and Althoff, Allen, and Wentzcovich (32.6 GPa).²⁵

We presented in this paper the results of a pseudopotential study of the elastic constants for Mg. The pseudopotential models based on the assumption of the mainly two-body

TABLE II. Elastic constants (in 10^{11} Nm⁻²) and bulk modulus B_T (GPa) calculated for magnesium using DRT and BHS pseudopotentials and RHF calculations. Comparison with experimental data (Refs. 11 and 12).

	Expt.	DRT	BHS	RHF
C_{11}	0.6347	0.7145	0.6738	0.8648
C_{33}	0.6645	0.7644	0.9558	0.9625
C_{44}	0.1863	0.1852	0.1801	
C_{13}	0.2170	0.1959	0.1833	0.1096
C_{12}	0.2594	0.2824	0.2336	0.0181
$C_{66}=0.5(C_{11}-C_{12})$	0.1878	0.1695	0.2383	0.3914
B_T	36.9	39.3	39.0	35.2

nature of the interatomic interactions have been used in the DRT and BHS approaches. These PSP's correctly reproduce the elastic constants, while the HF values are affected by larger errors. Investigation of the correlation contributions are now in progress to establish the limit of the HF approach in the elastic constants of metals.²⁶

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