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The interatomic interaction and the phonon dispersion relations of magnesium

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Abstract

In the present paper, the interatomic interaction between atoms in magnesium is calculated and the phonon dispersion relations for along the major symmetry directions, T, T', Σ , and Δ , in this metal are computed by use of a method different from the traditional ones. Instead of being fitted using the elastic constants or determined from the phonon frequencies at some special points in the first Brillouin zone, the force constants are directly calculated using the calculated potential, which is obtained from the cohesive energy by use of the Möbius theorem of number theory. This calculated interaction does not have any of the adjustable parameters that are present in the previous model potentials. The calculated phonon dispersions are compared with experiments and good agreement found.

1. Introduction

Up to now it has been hard to deal with large systems in condensed matter by use of first-principles methods. Therefore, the atomic force models are still useful for studying properties of these systems. In these models two problems are central. One of them is the interatomic interaction and the other is the validity of the description of this interaction. In the present work, we want to deduce the interatomic interaction in magnesium and test its correctness using the phonon dispersion relations of this metal.

The lattice of magnesium has hcp structure. It is well known that there are a lot of materials with this structure (shown in figure 1), but most of them do not have the ideal value of the ratio $c/a = \sqrt{8/3} \simeq 1.633$. However, magnesium has a ratio $c/a = 1.623$, which is very close to the ideal one, and has therefore attracted much interest. In fact, a lot of experimental measurements and theoretical analyses of the phonon dispersions in this metal have already appeared.

The phonon dispersions in magnesium have been measured by means of the inelastic scattering of neutrons [1, 2]. In particular, two experimental studies that went into more detail have been conducted: one by Squires [3] and the other by Pynn and Squires [4].

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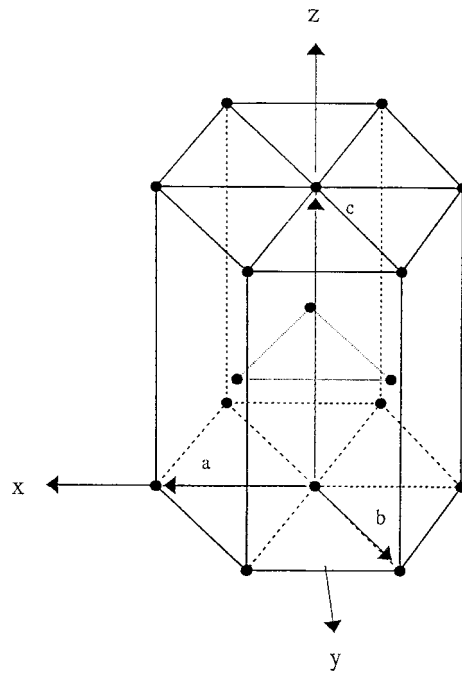


Figure 1. The hcp structure of a crystal. The primitive cell has $a = b$, with an included angle of 120° . The c -axis is normal to the plane of a and b , and $c = \sqrt{8/3}a$. There are two atoms in the cell. One is at the origin and the other at $\vec{r} = \frac{2}{3}\vec{a} + \frac{1}{3}\vec{b} + \frac{1}{2}\vec{c}$.

For the theoretical studies, there are two ways that can be followed. One way is that of using first-principles methods [5–14], from which good results have been achieved in recent years [15, 16]. But for our purposes, we are interested in the other way: that of using the force model methods. Many such models have been proposed, such as the tensor force model [17–19], the central-force model (S–G model) [20], the axially symmetrical model (AS model) [21], and so on [2, 22, 23]. In these models the interatomic interactions are unknown and are introduced as some force constants, which are deduced either from elastic constants or from the phonon frequencies at some special points in the first Brillouin zone, or from both. Meanwhile, if an interatomic potential is given, such as an empirical one, its validity can be tested using these models.

In the present paper, we calculate the interatomic potential in magnesium using the Möbius theorem of number theory [24] from the cohesive energy. In order to test the calculated interaction, the phonon dispersions along the T, T', Σ , and Δ directions in this metal were computed by use of a method proposed by the author and co-workers for calculating the phonon dispersions in fcc metals in 1993 [25]. By this method the atomic force constants and then the phonon dispersions can be directly calculated from the interatomic interaction obtained. We need neither to introduce any adjustable parameters nor to express the force constants in terms of the elastic constants or the phonon frequencies at some special points in the first Brillouin zone. In section 2, the cohesive energy per atom in magnesium is obtained by means of a first-principles calculation. Then a brief outline of the Möbius transform formula is introduced in section 3. The calculations of the force constants and the phonon dispersions are presented and compared with experiments in section 4. Finally, we draw our conclusions and discuss the results in section 5.

2. The cohesive energy of magnesium

Using the LAPW method [26–28], we calculated the cohesive energy $E(a)$ per atom for crystal magnesium, which has a hcp lattice with two atoms in the unit cell. In the calculation, 20 points in the irreducible Brillouin zone of the unit cell are employed. The potential is assumed to be of muffin-tin shape and spherically symmetric inside the muffin-tin sphere. Outside the sphere, no shape approximations for the potential are made for the interstitial region. In the result, eight points are calculated for the cohesive energy $E(a)$. Its argument a is the lattice constant and is taken as a variable. We found that the calculated cohesive energy $E(a)$ can be fitted by the Morse potential:

$$E(a) = E_0(e^{-2\alpha(a-a_0)} - 2e^{-\alpha(a-a_0)})/\text{atom} \quad (1)$$

with the parameters $E_0 = 1.5123$ eV, $\alpha = 1.2196 \text{ \AA}^{-1}$, and $a_0 = 3.1031 \text{ \AA}$. In this case, E_0 and a_0 are the cohesive energy and the lattice constant for the equilibrium configuration of the crystal respectively. The experimental values are $E_{0exp} = 1.51$ eV and $a_{0exp} = 3.21 \text{ \AA}$ [29]. The calculated values agree well with the experimental data.

3. The Möbius transform formula for hcp crystal and the interatomic interaction in magnesium

In 1992, Chen and Ren [30] proposed a method by which the pair potential between atoms could be obtained from the cohesive energy using the Möbius transform formula based on the Möbius theorem of number theory [24]. In their paper they gave the Möbius transform formulae for fcc and bcc structures. For hcp structure they only discussed a two-dimensional model. Recently, the author and a co-worker [31] gave a Möbius transform formula for the real three-dimensional hcp structure and by means of this formula the pair potential between atoms in magnesium was calculated from an empirical expression for the cohesive energy. Here we will give a brief outline of the derivation of this formula, as follows.

In the two-body interaction approximation, the cohesive energy per atom in a crystal can be expressed as

$$E(a) = \frac{1}{2} \sum_{|\vec{R}| \neq 0} \phi(|\vec{R}|) \quad (2)$$

where ϕ is the two-body interaction, i.e. the pair potential, between atoms and $|\vec{R}|$ the distance of an atom away from the one at the origin. For the hcp lattice $E(a)$ can be written as

$$E(a) = \sum_{i=1}^7 E_i \quad (3)$$

where

$$E_1 = 3 \sum_{n=1}^{\infty} \phi(na) \quad (4)$$

is the contribution to the cohesive energy from atoms which are located on the six symmetrical axes on the coordinate plane (see figure 1). In equation (4), a is the lattice constant, i.e. the distance of the first-nearest-neighbour atom away from the origin, and ϕ is the pair potential.

$$E_2 = \sum_{n=1}^{\infty} \phi\left(n\sqrt{\frac{8}{3}}a\right) \quad (5)$$

comes from the contribution of atoms located on the c -axis (see figure 1). In this equation, c is the distance between the origin and the nearest-neighbour atom on this axis.

$$E_3 = 3 \sum_{m,n=1}^{\infty} \phi(\sqrt{m^2 + n^2 + mna}) \quad (6)$$

is given by the atoms on the coordinate plane except those on the symmetrical axes.

$$E_4 = 6 \sum_{m,n,l=1}^{\infty} \phi\left(\sqrt{m^2 + n^2 + mn + \frac{8}{3}l^2a}\right) \quad (7)$$

is contributed by the atoms out of the coordinate plane and they are located at positions similar to those described in relation to E_3 .

$$E_5 = 6 \sum_{m,n=1}^{\infty} \phi\left(\sqrt{m^2 + \frac{8}{3}n^2a}\right) \quad (8)$$

arises from the atoms included in six symmetrical planes except the atoms on the axis.

$$E_6 = 3 \sum_{m,n,l=1}^{\infty} \phi\left(\sqrt{\left(m - \frac{2}{3}\right)^2 + \left(n - \frac{2}{3}\right)^2 + \frac{8}{3}\left(l - \frac{1}{2}\right)^2 + \left(m - \frac{2}{3}\right)\left(n - \frac{2}{3}\right)a}\right) \quad (9)$$

and

$$E_7 = 3 \sum_{m,n,l=1}^{\infty} \phi\left(\sqrt{\left(m - \frac{1}{3}\right)^2 + \left(n - \frac{1}{3}\right)^2 + \frac{8}{3}\left(l - \frac{1}{2}\right)^2 + \left(m - \frac{1}{3}\right)\left(n - \frac{1}{3}\right)a}\right) \quad (10)$$

are the contributions to the cohesive energy from the other atoms. It should be noted that the ratio $c/a = \sqrt{8/3}$ is used in these expressions, which means that these equations hold only for the ideal hcp structure. The cohesive energy $E(a)$ can be separated into two parts:

$$E(a) = E_0(a) + E'(a) \quad (11)$$

where

$$E_0(a) = 6 \sum_{n=1}^{\infty} \phi(na) + \sum_{n=1}^{\infty} \phi(\sqrt{8/3}na) + 3 \sum_{n=1}^{\infty} \phi(\sqrt{3}na) + \frac{1}{2} \sum_{n=1}^{\infty} \phi(\sqrt{8}na) \quad (12)$$

and

$$\begin{aligned} E' = & 3 \sum_{m \neq n=1}^{\infty} \phi(\sqrt{m^2 + n^2 + mna}) \\ & + 6 \sum_{m,n,l=1}^{\infty} \phi\left(\sqrt{m^2 + n^2 + mn + \frac{8}{3}l^2a}\right) + 6 \sum_{m,n=1}^{\infty} \phi\left(\sqrt{m^2 + \frac{8}{3}n^2a}\right) \\ & + 3 \sum_{m,n,l=1}^{\infty} \phi\left(\sqrt{\left(m - \frac{2}{3}\right)^2 + \left(n - \frac{2}{3}\right)^2 + \frac{8}{3}\left(l - \frac{1}{2}\right)^2 + \left(m - \frac{2}{3}\right)\left(n - \frac{2}{3}\right)a}\right) \\ & + 3 \sum_{m,n,l=1}^{\infty} \phi\left(\sqrt{\left(m - \frac{1}{3}\right)^2 + \left(n - \frac{1}{3}\right)^2 + \frac{8}{3}\left(l - \frac{1}{2}\right)^2 + \left(m - \frac{1}{3}\right)\left(n - \frac{1}{3}\right)a}\right) \\ & - 3 \sum_{n=1}^{\infty} \phi(3na) - \frac{1}{2} \sum_{n=1}^{\infty} \phi(\sqrt{8}na). \end{aligned} \quad (13)$$

Here, $E_0(a)$ contains E_1 , E_2 , the terms with $m = n$ in E_3 , the terms with $2l = 3m - 1$ for $m = n$ in E_6 , and the terms with $2l = 3m$ for $m = n$ in E_7 . The last term is an additional one,

which is used to match the Möbius transform formula. E' includes E_4, E_5 and the remainders in $E_3, E_6,$ and E_7 . Two and three primes on the sum mean that the sums do not cover the terms mentioned above, which have been included in E_0 . Two terms, one of which has been added to the first term in E_0 and the other of which appears in E_0 as the last one, must be subtracted from E' to ensure the correctness of $E(a)$. We define two operators T_0 and T_1 as follows:

$$E_0 = T_0\phi \tag{14}$$

and

$$E' = T_1\phi. \tag{15}$$

Then $E(a)$ can be given in terms of ϕ :

$$E = E_0 + E' = T_0\phi + T_1\phi = (T_0 + T_1)\phi = T_0(1 + T_0^{-1}T_1)\phi. \tag{16}$$

We can obtain the two-body interaction from the cohesive energy $E(a)$ by means of an inverse operation:

$$\phi = (1 + T_0^{-1}T_1)^{-1}T_0^{-1}E. \tag{17}$$

We have introduced a new operator N defined as [31]

$$N\phi(x) = \frac{1}{6} \sum_{m,l,u=1}^{\infty} (-1/6)^{m-1} (-1/2)^{u-1} \mu(l)\phi[(8/3)^{(m-1)/2}3^{(u-1)/2}lx] \tag{18}$$

where $\mu(l)$ is the Möbius function [24]

$$\mu(l) = \begin{cases} 1 & \text{if } l = 1 \\ (-1)^s & \text{if } l \text{ includes } s \text{ distinct primes} \\ 0 & \text{otherwise.} \end{cases} \tag{19}$$

Equation (18) is called the Möbius transform formula of the hcp lattice. We have proved [31] by means of the Möbius theorem of number theory [24] that (see appendix 1)

$$N = T_0^{-1}. \tag{20}$$

Therefore, we can substitute N for T_0^{-1} in equation (17):

$$\phi = (1 + NT_1)^{-1}NE. \tag{21}$$

Expanding equation (21) we obtain

$$\phi = (1 - NT_1 + NT_1NT_1 - \dots)NE. \tag{22}$$

Let

$$NE(a) = \sum_p W'_p E(s'_p a) \tag{23}$$

and

$$T_1E(a) = \sum_q W'_q E(s'_q a). \tag{24}$$

Here, $W'_p, s'_p, W'_q,$ and s'_q are some coefficients (see appendix 2). Therefore,

$$\begin{aligned} \phi &= \sum_{p_0} W'_{p_0} E(s'_{p_0} a) - \sum_{p_0, p_1, q_1} W'_{p_1} W'_{q_1} W'_{p_0} E(s'_{p_1} s'_{q_1} s'_{p_0} a) \\ &\quad + \sum_{p_0, p_1, q_1, p_2, q_2} W'_{p_2} W'_{q_2} W'_{p_1} W'_{q_1} W'_{p_0} E(s'_{p_2} s'_{q_2} s'_{p_1} s'_{q_1} s'_{p_0} a) - \dots \\ &= \sum_p W_p E(s_p a). \end{aligned} \tag{25}$$

We first calculated the coefficients W_p and S_p , which are suitable for all materials with the hcp lattice. Then the two-body interaction between atoms in magnesium was calculated by use of the cohesive energy calculated in section 2. The calculated two-body interaction is plotted in figure 2. We found that three terms in equation (22) are sufficient for the calculation. The high-order terms can be neglected.

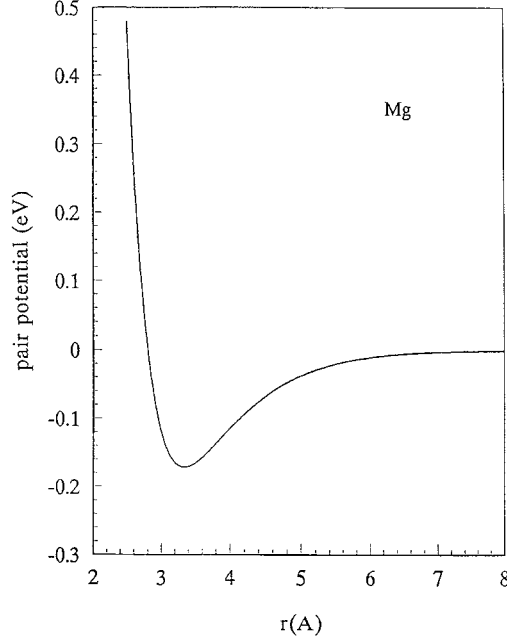


Figure 2. The two-body interaction, i.e. the pair potential, between atoms in magnesium.

4. The force constants and the phonon dispersions in magnesium

Using the calculated interatomic interaction, it is possible to express the total potential energy U of the crystal as a function of the positions of all of the atoms:

$$U = U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N). \quad (26)$$

Then the force constants

$$-\left(\frac{\partial^2 U}{\partial u_{m,n,\alpha} \partial u_{m',n',\alpha'}}\right)_0 u_{m,n,\alpha} u_{m',n',\alpha'} \quad (27)$$

can be calculated directly in terms of the calculated total energy U . In the above expression the subscript 0 denotes that the derivatives are evaluated at the equilibrium positions. $u_{m,n,\alpha}$ is the α -component of the displacement of the n th atom in the m th unit cell.

The vibration frequencies of phonons can be obtained by solving the secular equation

$$\left| D \begin{pmatrix} n & n' \\ \alpha & \alpha' \end{pmatrix} - M_n \omega^2 \delta_{nn'} \delta_{\alpha\alpha'} \right| = 0 \quad (28)$$

where ω is the angular frequency of the vibration, $\delta_{nn'}$ the Kronecker symbol, and

$$D \begin{pmatrix} n & n' \\ \alpha & \alpha' \end{pmatrix}$$

is an element of the dynamical matrix, which is defined as

$$D \begin{pmatrix} n & n' \\ \alpha & \alpha' \end{pmatrix} = - \sum_{m'} \left[\frac{\partial^2 U}{\partial u_{m,n,\alpha} \partial u_{m',n',\alpha'}} \right]_0 e^{i\vec{k} \cdot (\vec{r}_{mn} - \vec{r}_{m'n'})} \quad (29)$$

where \vec{k} is the propagation vector and \vec{r}_{mn} the position vector of the n th atom in the m th unit cell. Since n can take the values 1 and 2, equation (28) in fact represents a 6×6 determinant.

4.1. The force constants

In the tensor force (TF) model framework [17–19] we have calculated the force constants directly up to the third-nearest neighbours by use of equations (26) and (27). The calculated results are listed in table 1. These force constants are equivalent to those described in the previous work [22], but the symbols used are different. The relations between them are given below. The symbols used in the literature [22] appear in the left-hand sides of equations and ours in the right-hand sides. It should be noted that in our model the hcp structure is ideal, but in [22] it is not. Therefore, the definitions of the nearest neighbours are different.

Table 1. The force constants (in units of 10^4 dyn cm $^{-1}$).

Nearest neighbours	Force constants		
First	$\alpha_1 = 1.0599$	$\beta_1 = -0.0552$	$\gamma_1 = 0.2235$
	$\delta_1 = 0.7811$	$\lambda_1 = 0.0377$	$\sigma_1 = 0.6882$
	$\epsilon_1 = 0.3165$	$\alpha'_1 = 0.4828$	$\beta'_1 = 0.1609$
	$\gamma'_1 = 0.2628$	$\delta'_1 = 0.4552$	$\lambda'_1 = 0.5257$
Second	$\alpha_2 = 0.0155$	$\beta_2 = -0.0328$	$\gamma_2 = -0.0207$
	$\delta_2 = 0.0034$	$\lambda_2 = -0.0086$	$\alpha'_2 = -0.0241$
	$\beta'_2 = -0.0209$	$\gamma'_2 = -0.0171$	$\delta'_2 = -0.0296$
Third	$\alpha_3 = 0.0057$	$\beta_3 = -0.0387$	

For the first-nearest neighbours [22] (first to sixth atoms),

$$\alpha = \frac{1}{2}(\gamma_1 + \delta_1) \quad (30)$$

$$\beta = \frac{1}{2}(\delta_1 - \gamma_1) \quad (31)$$

$$\gamma = \delta_1 \quad (32)$$

$$\delta = 0. \quad (33)$$

For the second-nearest neighbours [22] (seventh to twelfth atoms; in our model they are the first-nearest neighbours),

$$\lambda = \frac{1}{2}(\gamma_1 + \lambda_1) \quad (34)$$

$$\sigma = \gamma'_1 \quad (35)$$

$$\mu = \frac{1}{2}(\lambda_1 - \gamma_1) \quad (36)$$

$$\nu = \sigma_1. \quad (37)$$

For the third-nearest neighbours [22] (in our model, they are the second-nearest neighbours),

$$\eta = \frac{1}{3}(\alpha_2 - \gamma_2) \quad (38)$$

$$\xi = \frac{1}{3}(\alpha_2 + 2\gamma_2) \quad (39)$$

$$\zeta = \lambda_2 \quad (40)$$

$$\chi = v'_2. \quad (41)$$

For the fourth-nearest neighbours [22] (in our model, they are the third-nearest neighbours),

$$\theta = \alpha_3 \quad (42)$$

$$\varphi = \beta_3. \quad (43)$$

4.2. The phonon dispersions

In terms of the calculated force constants, we calculated the dynamical matrix using equation (29) and then the phonon dispersions along the principal symmetry directions T, T', Σ , and Δ .

4.2.1. The phonon dispersions along the Δ direction. For this direction the determinant in equation (28) can be factorized into 2×2 and 4×4 determinants. We can solve the first one analytically. The solutions give two wave branches. One of them is the transverse branch, the frequencies of which are

$$M\omega^2 = 2 \left[(2\gamma_1 + \beta_1 + \alpha_2 + 2\gamma_2) + 2\alpha_3 \left(1 - \cos^2 \frac{1}{2}k_z c \right) \right] \pm 2(\beta_1 + 2\gamma_1 + \alpha_2 + 2\gamma_2) \cos \frac{1}{2}k_z c \quad (44)$$

for polarization direction \vec{x} and

$$M\omega^2 = 2 \left[(2\lambda_1 + \epsilon_1 + \beta_2 + 2\delta_2) + 2\alpha_3 \left(1 - \cos^2 \frac{1}{2}k_z c \right) \right] \pm 2(2\lambda_1 + \epsilon_1 + 2\delta_2 + \beta_2) \cos \frac{1}{2}k_z c \quad (45)$$

for polarization direction \vec{y} , respectively. The other is the longitudinal branch, the frequencies of which are

$$M\omega^2 = 6(\sigma_1 + \lambda_2) + 4\beta_3 \left(1 - \cos^2 \frac{1}{2}k_z c \right) \pm 6(\sigma_1 + \lambda_2) \cos \frac{1}{2}k_z c. \quad (46)$$

By means of equations (30)–(43) it can be easily proved that these results are in accord with the equations in table 3(b) in reference [22]. Finally, the phonon dispersions along this direction are plotted in figure 3.

4.2.2. The phonon dispersions along the Σ direction. Along this direction, equation (28) can also be factorized into 4×4 and 2×2 determinants and the second one can also be solved analytically. For polarization direction \vec{x} , the solutions are

$$M\omega^2 = A \pm \sqrt{D^2 + D'^2} \quad (47)$$

where

$$A = 2 \left[(\beta_1 + 4\gamma_1 + \alpha_2 + 2\gamma_2) - 2\gamma_1 \cos \frac{\sqrt{3}}{2}k_y a \right] \quad (48)$$

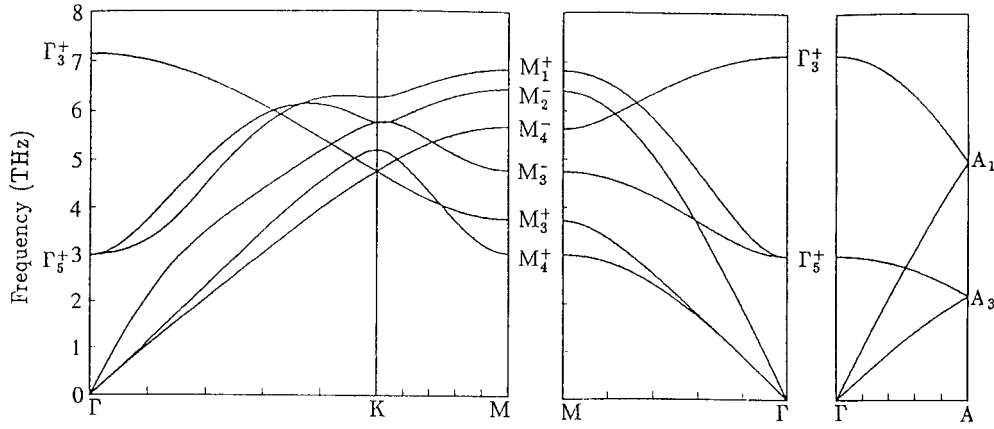


Figure 3. The calculated phonon dispersions in magnesium along the Σ , Δ , T, and T' directions.

$$D = -2 \left[2\gamma_1 \cos \frac{1}{2\sqrt{3}} k_y a + (\beta_1 + 2\gamma_2) \cos \frac{1}{\sqrt{3}} k_y a + \alpha_2 \cos \frac{2}{\sqrt{3}} k_y a \right] \quad (49)$$

$$D' = 2 \left[2\gamma_2 \sin \frac{1}{2\sqrt{3}} k_y a - (\beta_1 + 2\gamma_2) \sin \frac{1}{\sqrt{3}} k_y a + \alpha_2 \sin \frac{2}{\sqrt{3}} k_y a \right]. \quad (50)$$

For $k_y = 0$,

$$M\omega^2 = A \pm D = \begin{cases} 0 \\ 4(\beta_1 + 2\gamma_1 + \alpha_2 + 2\gamma_2). \end{cases} \quad (51)$$

The first solution corresponds to the transverse acoustic branch and the second one to the transverse optical branch. Considering the relations (30)–(43), it is found that

$$M\omega^2 = \begin{cases} 0 \\ 12(\lambda + \xi). \end{cases} \quad (52)$$

These are just the results from table 3(a) in the paper [22]. Similar results are obtained for the polarization direction \vec{z} of the transverse branch and the longitudinal branch. All of the results for the vibration modes along this direction are shown in figure 3, too.

4.2.3. The phonon dispersions along the T, T' directions. In these directions, equation (28) cannot be factorized and we are not able to solve the equation analytically. In order to solve this equation and obtain the eigenvalues, a standard computer program was used. The results are also shown in figure 3.

5. Discussion and conclusions

Unlike the empirical expressions for the interatomic interaction, the one calculated in the present work is based on a first-principles calculation and does not have any adjustable parameters. The validity of this calculated interaction is tested using calculations of the phonon dispersion relations. All of the calculated phonon dispersions along Δ , Σ , T, and T' directions are presented in figure 3 together, and compared with the inelastic neutron scattering data [2–4] shown in figure 4. From figure 3 and figure 4 we can see a good agreement between theory and

experiments. This might be the case because the spherically symmetric muffin-tin potential is a very good approximation for close-packed (fcc and ideal- c/a hcp) materials [28]. So, our calculated cohesive energy $E(a)$ is a good result. The inversion procedure in the present paper is strict mathematically. Therefore, the calculated pair potential for magnesium is close to the one found in practice. It should be noted that we omitted the many-body interaction in equation (2) in the inversion calculation. This is because the outer-electron configuration of magnesium is $s^2s^2p^6s^2$. So, the distribution of the electron cloud is spherical and the pair potential is dominant in the interatomic interaction. Both of the above statements are confirmed by the calculated results for the dispersions. Of course, there are still some discrepancies, especially for the transverse branches along the Δ direction. The maximum error is about 20%. This error might arise because, although the ratio c/a of magnesium is very close to the ideal value, there is a small difference between them. In our calculation we adopted the ideal value of $\sqrt{8/3}$ for the ratio c/a , which is somewhat larger than the experimental value. The larger value of c might reduce the shear modulus and therefore the transverse frequencies. Prakash and Joshi studied the effect of different values of the ratio c/a on the phonon frequencies in zinc, magnesium, and beryllium [12]. They found that the calculated phonon frequency decreased while the value of the ratio c/a increased. Their results coincide with the result given above.

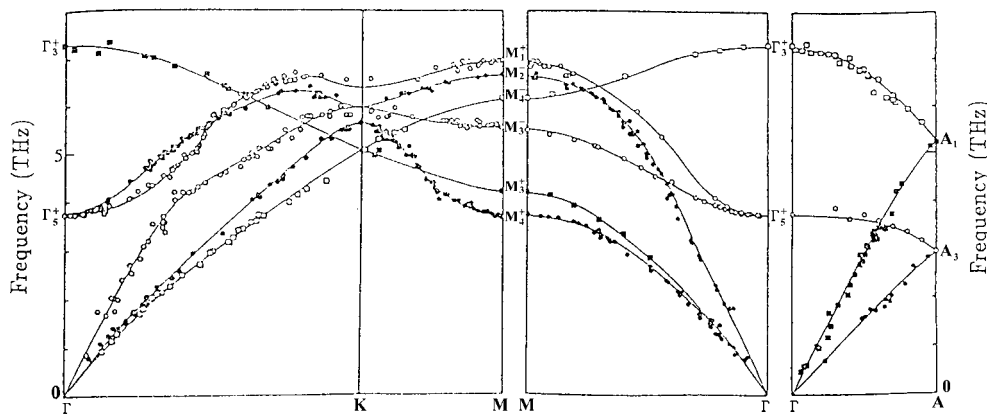


Figure 4. The experimental data for the phonon dispersions for magnesium along the Σ , Δ , T , and T' directions [2–4]. The solid lines represent an extrapolation between data points. (This figure is taken from Shaw and Pynn [10].)

The good agreement of the calculated phonon dispersion relations with the experiments shows that the calculated interatomic interaction is reliable and can be adopted for studying properties of large systems of magnesium. From the above, we know that the calculated interatomic interaction is, in fact, a pair potential. Generally speaking, the interatomic interactions cannot be simply described by a pair potential, and many-body interactions, for example the three-body interaction, have to be added in equation (2).

As mentioned in the introduction, a very interesting problem, which is encountered by scientists, is that of how to deal with various complex systems, such as a dislocation core, a plastic deformation region, and a fracture. In these systems there is no translation symmetry and it is hard to deal with them from first principles. Therefore, the value of the present work goes beyond the application to magnesium, as well as to the calculation of the phonon dispersions. In fact, we can use this method to calculate the interatomic interactions for all materials with hcp structure, even if their c/a ratios are not ideal. Then we can use the calculated interatomic interactions to deal with the complex systems of these materials instead

of using empirical interactions. This procedure gives an indirect method for studying the properties of the complex systems from first principles. Moreover, the calculated interactions can also be used in the molecular dynamics method and a relationship between the molecular dynamics method and first-principles method can be established.

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Appendix 1

Proof. According to equations (12), (14), and (18) in the main text, we have

$$\begin{aligned}
 NT_0\phi(x) &= NE_0 = N \sum_{n=1}^{\infty} \left[6\phi(nx) + \phi(\sqrt{8/3}nx) + 3\phi(\sqrt{3}nx) + \frac{1}{2}\phi(\sqrt{8}nx) \right] \\
 &= \sum_{m,u,l,n=1}^{\infty} (-1/6)^{m-1} (-1/2)^{u-1} \mu(l) \phi[(8/3)^{(m-1)/2} 3^{(u-1)/2} nlx] \\
 &\quad - \sum_{m,u,l,n=1}^{\infty} (-1/6)^m (-1/2)^{u-1} \mu(l) \phi[(8/3)^{m/2} 3^{(u-1)/2} nlx] \\
 &\quad - \sum_{m,u,l,n=1}^{\infty} (-1/6)^{m-1} (-1/2)^u \mu(l) \phi[(8/3)^{(m-1)/2} 3^{u/2} nlx] \\
 &\quad + \sum_{m,u,l,n=1}^{\infty} (-1/6)^m (-1/2)^u \mu(l) \phi[(8/3)^{m/2} 3^{u/2} nlx]. \tag{A1.1}
 \end{aligned}$$

Let $m' = m - 1$; equation (A1.1) becomes

$$\begin{aligned}
 NT_0\phi(x) &= \sum_{m'=0,u,l,n=1}^{\infty} (-1/6)^{m'} (-1/2)^{u-1} \mu(l) \phi[(8/3)^{m'/2} 3^{(u-1)/2} nlx] \\
 &\quad - \sum_{m,u,l,n=1}^{\infty} (-1/6)^m (-1/2)^{u-1} \mu(l) \phi[(8/3)^{m/2} 3^{(u-1)/2} nlx] \\
 &\quad - \sum_{m'=0,u,l,n=1}^{\infty} (-1/6)^{m'} (-1/2)^u \mu(l) \phi[(8/3)^{m'/2} 3^{u/2} nlx] \\
 &\quad + \sum_{m,u,l,n=1}^{\infty} (-1/6)^m (-1/2)^u \mu(l) \phi[(8/3)^{m/2} 3^{u/2} nlx]. \\
 &= \sum_{u,l,n=1}^{\infty} (-1/2)^{u-1} \mu(l) \phi(3^{(u-1)/2} nlx) - \sum_{u,l,n=1}^{\infty} (-1/2)^u \mu(l) \phi(3^{u/2} nlx). \tag{A1.2}
 \end{aligned}$$

Let $u' = u - 1$; equation (A1.2) changes into

$$\begin{aligned}
 NT_0\phi(x) &= \sum_{u'=0,l,n=1}^{\infty} (-1/2)^{u'} \mu(l) \phi(3^{u'/2} nlx) - \sum_{u,l,n=1}^{\infty} (-1/2)^u \mu(l) \phi(3^{u/2} nlx) \\
 &= \sum_{l,n=1}^{\infty} \mu(l) \phi(nlx). \tag{A1.3}
 \end{aligned}$$

In number theory, the Möbius theorem [24] states that if

$$F(x) = \sum_{n=1}^{\infty} f(nx) \quad (\text{A1.4})$$

then

$$f(x) = \sum_{l=1}^{\infty} \mu(l)F(lx) \quad (\text{A1.5})$$

where $F(x)$ and $f(x)$ are real functions and $\sum_{l,n=1}^{\infty} |f(nlx)|$ converges. $\mu(l)$ is called the Möbius function [24]. Using this theorem we can obtain

$$f(x) = \sum_{l=1}^{\infty} \mu(l)F(lx) = \sum_{l=1}^{\infty} \mu(l) \sum_{n=1}^{\infty} f(nlx) = \sum_{l,n=1}^{\infty} \mu(l)f(nlx). \quad (\text{A1.6})$$

Comparing equation (A1.3) with equation (A1.6) we find

$$NT_0\phi(x) = \phi(x) \quad (\text{A1.7})$$

and

$$N = T_0^{-1}. \quad (\text{A1.8})$$

Therefore, equation (20) in the text is proved.

Appendix 2

In this appendix we will show how to get the coefficients $W'_p, s'_p, W'_q, s'_q, W_p,$ and s_p in the text. According to the definition of the operator N in equation (18) we have

$$NE(a) = \frac{1}{6} \sum_{m,l,u=1}^{\infty} (-1/6)^{m-1} (-1/2)^{u-1} \mu(l) E[(8/3)^{(m-1)/2} 3^{(u-1)/2} la] \quad (\text{A2.1})$$

where a is the lattice constant. Expanding the summation and adding the same terms, we will get the coefficients W'_p and s'_p in equation (23). In the calculation it should be noted that the cohesive energy E decays rapidly as the argument increases. Therefore, we only need to consider a limited number of terms in the summation. By the same procedure we can obtain the coefficients W'_q, s'_q in equation (24) and W_p, s_p in equation (25).

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