

Three-Body Forces in the Lattice Dynamics of Beryllium

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We present a first-principles calculation of the lattice dynamics of Be. The dynamical matrix is set up by evaluating the total electron energy up to third order in the electron-ion pseudopotential. In this way we are able to describe the three-body forces, which are essential for reproducing the experimental data.

Recent experimental measurements¹ of phonon frequencies of Be have shown that a description of the lattice dynamics in terms of pairwise central forces between ions does not hold for this metal. This fact can be proved by looking at the experimental results at the point $K \equiv (2\pi/a)(0, \frac{2}{3}, 0)$ of the Brillouin zone. At this point a group-theoretical analysis gives the following expressions for the phonon frequencies with eigenvectors polarized in the basal plane in terms of the elements of the dynamical matrix:

$$\begin{aligned}\omega_{K_1}^2 &= D_{xx}(\vec{q}, 11) + \text{Im}D_{xy}(\vec{q}, 11) - 2 \text{Re}D_{xx}(\vec{q}, 12), \\ \omega_{K_3}^2 &= D_{xx}(\vec{q}, 11) + \text{Im}D_{xy}(\vec{q}, 11) + 2 \text{Re}D_{xx}(\vec{q}, 12), \\ \omega_{K_5}^2 &= D_{xx}(\vec{q}, 11) - \text{Im}D_{xy}(\vec{q}, 11).\end{aligned}\tag{1}$$

If only central two-body forces are assumed to exist in the crystal, $\text{Im}D_{xy}(\vec{q}, 11) = 0$, so that $\omega_{K_5}^2 = \frac{1}{2}(\omega_{K_1}^2 + \omega_{K_3}^2)$, i.e., the nondegenerate frequencies are equidistant from the degenerate one. For Be the experimental sequence of frequencies is $\omega_{K_1} > \omega_{K_3} > \omega_{K_5}$, showing the necessity of including many-ion forces to explain its lattice dynamics. Moreover, the distances between the experimental values indicate that the contribution of the unpaired forces is particularly strong. From this fact Roy *et al.*¹ conclude that simple pseudopotential theory, which consists in setting up the dynamical matrix by evaluating the total electron energy up to second order in the pseudopotential, is not adequate for this metal, since it describes the lattice dynamics through an interaction between the ions, which is a sum of two-body contributions.²

Previous theoretical calculations support this conclusion³⁻⁵: Both with Heine-Abarenkov⁶ and Shaw⁷ model potentials and with the orthogonalized-plane-wave form factors⁴ the agreement between theoretical results and experimental data is poor.

The aim of this Letter is to show that pseudopotential theory, when extended to include the third-order terms in the total electron energy, can account for the unpaired forces in the lattice dynamics of Be and leads to good agreement with experiment. For this purpose we write the dynamical matrix as

$$D_{\alpha\beta}(\vec{q}, ss') = \Phi_{\alpha\beta}(\vec{q}, ss') - \delta_{ss'} \sum_{s''} \Phi_{\alpha\beta}(0, ss''),\tag{2}$$

where $\Phi_{\alpha\beta}(\vec{q}, ss')$ is the sum of three contributions:

$$\Phi_{\alpha\beta}(\vec{q}, ss') = \Phi_{\alpha\beta}^{(C)}(\vec{q}, ss') + \Phi_{\alpha\beta}^{(2)}(\vec{q}, ss') + \Phi_{\alpha\beta}^{(3)}(\vec{q}, ss');\tag{3}$$

here $\Phi_{\alpha\beta}^{(C)}(\vec{q}, ss')$ arises from the direct Coulombic ion-ion interaction, $\Phi_{\alpha\beta}^{(2)}(\vec{q}, ss')$ comes from the indirect interaction between the ions as obtained by evaluating the total electron energy to second order, while $\Phi_{\alpha\beta}^{(3)}(\vec{q}, ss')$ is due to third-order contributions. The last two terms in Eq. (3) can be easily expressed in terms of a local electron-ion pseudopotential $v(\vec{q})$ by^{8,9}

$$\Phi_{\alpha\beta}^{(2)}(\vec{q}, ss') = \frac{\Omega}{M} \left[\sum_{\vec{G}} (\vec{q} + \vec{G})_{\alpha} (\vec{q} + \vec{G})_{\beta} \frac{v(\vec{q} + \vec{G})^2}{v(\vec{q})} \left(\frac{1}{\epsilon(\vec{q} + \vec{G})} - 1 \right) \exp(i\vec{G} \cdot \vec{R}_s) \exp(-i\vec{G} \cdot \vec{R}_{s'}) \right],\tag{4}$$

$$\begin{aligned}\Phi_{\alpha\beta}^{(3)}(\vec{q}, ss') &= \frac{\Omega}{M} \left(\sum_{\vec{G}} \sum_{\vec{G}' \neq \vec{G}} (\vec{q} + \vec{G})_{\alpha} (\vec{q} + \vec{G}')_{\beta} \frac{v(\vec{q} + \vec{G})v(\vec{q} + \vec{G}')v(\vec{G} - \vec{G}')}{\epsilon(\vec{q} + \vec{G})\epsilon(\vec{q} + \vec{G}')\epsilon(\vec{G} - \vec{G}')} \right. \\ &\quad \left. \times 6g(\vec{q} + \vec{G}, \vec{q} + \vec{G}', \vec{G} - \vec{G}') \{ 1 + \exp[-i(\vec{G} - \vec{G}') \cdot \vec{\tau}] \} \exp(i\vec{G} \cdot \vec{R}_s) \exp(-i\vec{G}' \cdot \vec{R}_{s'}) \right),\end{aligned}\tag{5}$$

where \vec{G} and \vec{G}' are reciprocal-lattice vectors, Ω is the cell volume, M is the mass of the ion, $v_C(\vec{q}) = (8\pi/q^2)[1 - f(\vec{q})]$ is the Coulomb potential modified by exchange and correlation corrections, $\epsilon(\vec{q})$ is the free-electron dielectric function including exchange and correlation corrections, and \vec{R}_s gives the position of the atom in the unit cell and may be equal to $(0, 0, 0)$ or $\vec{r} \equiv (\sqrt{3}a/6, \frac{1}{2}a, \frac{1}{2}c)$. The function $g(\vec{q} + \vec{G}, \vec{q} + \vec{G}', \vec{G} - \vec{G}')$ is the perturbation expansion coefficient and has been given explicitly by Lloyd and Sholl.¹⁰

Formulas (4) and (5) are given for a local pseudopotential. However, it is known that the pseudopotential of Be is rather nonlocal. A full nonlocal calculation of the third-order terms is not feasible at present, so that one is forced to evaluate $\Phi_{\alpha\beta}^{(3)}(\vec{q}, ss')$ with some local approximation. As shown in Ref. 9, a very accurate approximation is to use the local form factor $v(\vec{q})$, which reproduces the screening charge density of the valence electrons to first order in the nonlocal pseudopotential, i.e.,

$$v(\vec{q}) = \left[\int_{k \leq k_F} \frac{\langle \vec{k} + \vec{q} | v | \vec{k} \rangle}{k^2 - (\vec{k} + \vec{q})^2} d^3k \right] \left[\int_{k \leq k_F} \frac{1}{k^2 - (\vec{k} + \vec{q})^2} d^3k \right]^{-1}, \quad (6)$$

where the $\langle \vec{k} + \vec{q} | v | \vec{k} \rangle$ are matrix elements of the full nonlocal and energy-dependent pseudopotential, and k_F is the Fermi momentum.

An essential feature of this approximation is to give a rather smooth form factor, which oscillates considerably less than in the usual "on Fermi-sphere approximation" at large \vec{q} . Moreover, a second-order calculation of the phonon frequencies using $v(\vec{q})$ reproduces with great accuracy the results of the full nonlocal second-order calculation. As we have shown in great detail in Ref. 9, the use of $v(\vec{q})$ to evaluate the third-order contribution in simple metals allows one to overcome the difficulties which arise in going beyond second order with the usual local form factor. In this way we can account for the

nonlocality of the pseudopotential of Be.

To perform the calculation we used the Heine-Abarenkov model potential with the parameters A_i given by Animalu's tables.¹¹ The exchange and correlation corrections were taken according to Singwi *et al.*¹²

The results of the calculation along T and T' directions are displayed in Fig. 1 for branches with eigenvectors polarized in the basal plane and in Fig. 2 for the transverse perpendicular branches. In the same figures are also presented the results of second-order calculations.

The most relevant conclusion which can be drawn from a comparison between the two calculations is that the inclusion of three-body forc-

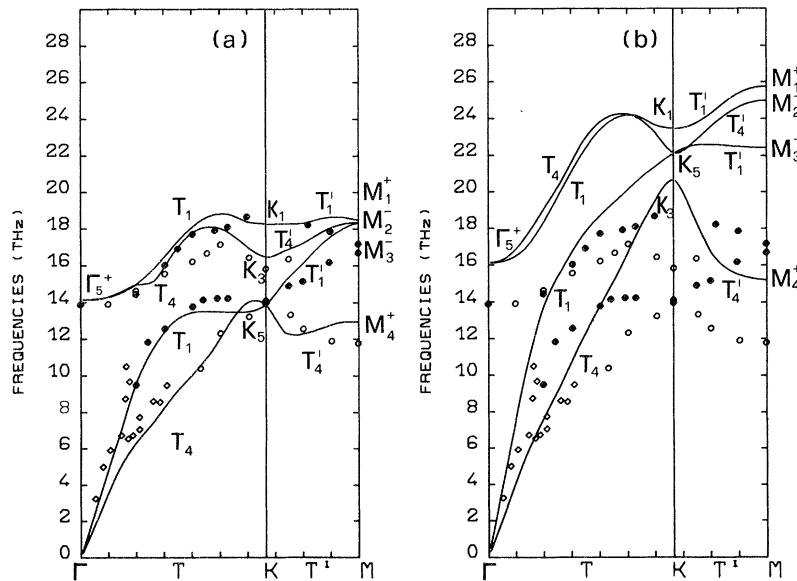


FIG. 1. Calculated phonon frequencies for Be along ΓKM for modes polarized in the basal plane: (a) third-order calculations; (b) second-order calculations. Experimental points are diamonds, Schmunk, Ref. 14; solid circles, T_1 frequencies from Roy *et al.*, Ref. 1; open circles, T_4 frequencies from Roy *et al.*, Ref. 1.

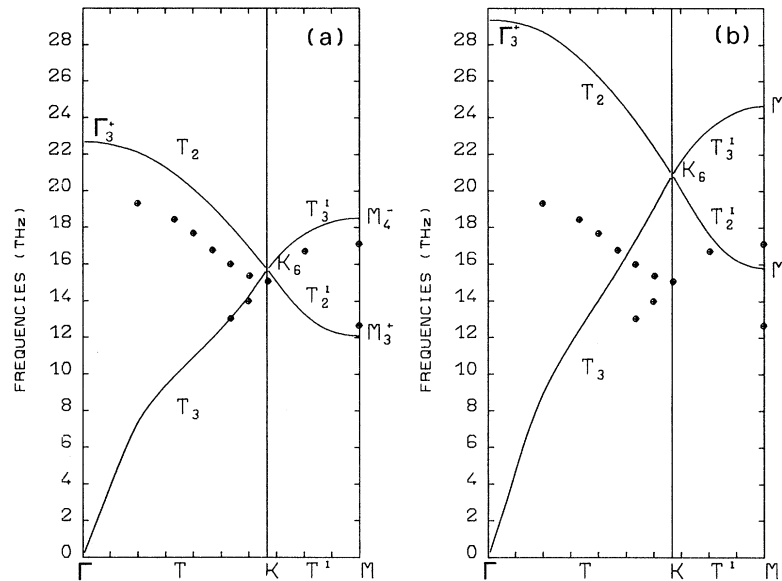


FIG. 2. Calculated phonon frequencies for Be along ΓKM for modes polarized perpendicular to the basal plane: (a) third-order calculations; (b) second-order calculations. Experimental points are from Roy *et al.*, Ref. 1.

es via third-order perturbation theory explains the essential features of the phonon spectrum of Be. It is seen both from Fig. 1 and from Fig. 2 that the theoretical values are considerably lowered with respect to the second-order theory, leading to a phonon spectrum which compares much more favorably with the experiments. In particular good agreement is obtained for the frequencies $\omega(\Gamma_3^+)$ and $\omega(\Gamma_5^+)$, for the transverse perpendicular branches T_2 and T_3 , where the third-order terms modify the second-order results by about 30%, as well as for T_1 and T_4 optical branches, whose crossing is shifted by the unpaired forces toward Γ , as indicated by the experimental data.

However, the most significant effect of the inclusion of the third-order contributions appears at the K point. Here the three-body forces lower considerably ω_{K_5} which falls below the nondegenerate frequency ω_{K_3} . In this way instead of having a degeneracy in K between the T_1 acoustic and the T_4 optical branches, we get, in agreement with experiment, the degeneracy between the T_1 and T_4 acoustic branches. As shown in Eq. (1) such a behavior of the frequencies at the K point is possible only if $\text{Im}D_{xy}(\vec{q}, 11) > 2|\text{Re}D_{xx}(\vec{q}, 12)|$ and so it is entirely due to third-order terms. In our calculation we obtain $\text{Im}D_{xy}(\vec{q}, 11) = 2167 \times 10^{24} (\text{rad/sec})^2$ and $\text{Re}D_{xx}(\vec{q}, 12) = D_{xx}^C(\vec{q}, 12) + D_{xx}^{(2)}(\vec{q}, 12) + D_{xx}^{(3)}(\vec{q}, 12) = (-7659 + 6442 + 590) \times 10^{24} (\text{rad/sec})^2$, where D_{xx}^C is the Cou-

lombic contribution and $D_{xx}^{(2)}$ and $D_{xx}^{(3)}$ are the electronic terms. It is seen that the effect of the inclusion of the third order in the evaluation of the total energy is twofold: It makes $\text{Im}D_{xy}(\vec{q}, 11)$ greater than zero and decreases the value of $\text{Re}D_{xx}(\vec{q}, 12)$.

It should be noted that this behavior is typical of beryllium. For other hexagonal metals, such as Mg and Zn, our preliminary calculations¹³ show that ω_{K_5} is considerably lowered by three-body forces and goes to a value rather close to ω_{K_3} , but there is not the large inversion between the two frequencies found in Be.

The importance of the third order in beryllium can be imputed to the strength of the electron-ion pseudopotential. Because of the absence of p states in the core there is no cancellation for the p part of the ionic potential, as can be seen from the high value of the parameter A_1 of the model potential¹¹ as well as from its strong energy dependence. For Mg, whose A_1 is lower and weakly energy dependent, the effects of third order are not so important.

In conclusion we want to emphasize that the pseudopotential theory, carried out to third order in the evaluation of the total electron energy, explains the lattice dynamics of Be. Moreover, theoretical results in good quantitative agreement with the experimental data can be obtained without the introduction of any adjustable parameter.

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ϵ Expansion in Semi-infinite Ising Systems

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The Wilson-Fisher ϵ expansion is used to calculate critical exponents in a semi-infinite Ising model to first order in ϵ . It is found that potentials renormalize just as in the bulk, and all surface information is contained in the wave-function renormalization. ν is $\frac{1}{2} + \frac{1}{12}\epsilon$ and η is 0, just as in infinite systems. η_{\perp} and η_{\parallel} are, respectively, $1 - \frac{1}{6}\epsilon$ and $2 - \frac{1}{3}\epsilon$ and the surface gap exponent Δ_1 is $\frac{1}{2} - \frac{1}{12}\epsilon$ if scaling is assumed.

The Wilson renormalization procedure has been highly successful in calculating critical exponents in bulk or infinite systems.¹⁻³ In this paper we will outline a calculation of critical exponents in a semi-infinite Ising system using the ϵ expansion.^{2,3} Particular emphasis will be placed on the calculation of the exponents η_{\parallel} and η_{\perp} introduced by Binder and Hohenberg⁴ and the gap exponent Δ_1 introduced by Fisher.⁵ The major purpose of this paper is to present results. Computational details will appear in a subsequent publication.

We start with the standard S^4 Hamiltonian

$$\mathcal{H} = \frac{1}{2}b^2 \sum_{\vec{x}} S^2(\vec{x}) - \frac{1}{2}K \sum_{\vec{x}} S(\vec{x})S(\vec{x} + \vec{\delta}) + u \sum_{\vec{x}} S^4(\vec{x}), \quad (1)$$

where $\vec{x} = (x_{\perp}, x_1, \dots, x_{d-1}) \equiv (x_{\perp}, \vec{x}_{\parallel})$ labels the sites on a semi-infinite cubic lattice and $\vec{\delta}$ is the nearest-neighbor position. \vec{x}_{\parallel} is the $(d-1)$ -dimensional vector parallel to the surface, and x_{\perp} the component of \vec{x} perpendicular to the surface. x_{\perp} takes on values $1, 2, 3, \dots$. All other components take on all positive and negative values. It is convenient to extend the sums in Eq. (1) to include the plane $x_{\perp}=0$ and to require that $S(0, \vec{x}_{\parallel})$ be zero. Then $S(\vec{x})$ can be expressed as a Fourier sine integral

$$S(\vec{x}) = \int_{-\pi}^{\pi} \frac{d^d \vec{p}}{(2\pi)^d} \sigma(\vec{p}) \exp(i\vec{p}_{\parallel} \cdot \vec{x}_{\parallel}) \sqrt{2} \sin p_{\perp} x_{\perp}, \quad (2)$$

where $\vec{p} = (p_{\perp}, \vec{p}_{\parallel})$. [The $\sqrt{2}$ appearing in Eq. (2) puts p_{\perp} and \vec{p}_{\parallel} on an equal footing in the Hamiltonian below.] Following Wilson, we introduce a modified Hamiltonian in which \vec{p} is restricted to a *unit cyl-*