

Phonon spectra of Zn and Cd using a model pseudopotential approach

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Abstract. Recently Animalu has developed a model potential approach to study the electronic properties of transition metals. We have applied the transition metal model potential (TMMP) of Animalu in the local approximation to derive the phonon dispersion curves of Zn and Cd along ΓA , ΓM and ΓKM symmetry directions. Our results differ widely from the experimental data. Further we have added the non-local contribution to the dynamical matrix following the scheme of Eschrig and Wonn and found the results comparable to the measured ones.

Keywords. Phonon spectra; pseudopotential calculations.

1. Introduction

In the family of hexagonal-close-packed metals, zinc and cadmium possess the highest axial ratio (c/a), being 1.856 and 1.886 respectively, while the ideal value of this ratio for the hcp structure is $\sqrt{8/3}$ (1.633). Both are divalent elements and belong to the same column of the periodic table. Further they possess similar electronic structure in the sense that in both the metals, the filled d-bands lie just below in close proximity to the Fermi energy. Hence they are grouped in a subclass of hcp solids. We have selected them to study their vibrational spectra. Although the phonon dispersion in Zn has been experimentally studied by a number of workers (Borgonovi *et al* 1963; Maliszewski *et al* 1965; Iyengar *et al* 1968; McDonald *et al* 1969 and Millington and Squires 1969), but the complete measurements have been recently made by Almqvist and Stedman (1971). Only recently Toussaint and Champier (1972) have measured the dispersion curves of cadmium by the method of diffuse scattering of x-rays. Probably due to the non-availability of phonon data earlier, the lattice dynamics of Cd has not been studied by professional theoreticians in the field. Brovman *et al* (1969), Gilat *et al* (1969), Prakash and Joshi (1970), Eschrig and Wonn (1970) and Bajpai (1973) have tried to explain the dispersion results of Zn using the pseudopotential approach in the simple metal approximation. In fact Zn and Cd are the members of d-band metals because of the hybridization of s, p, d bands in these solids. Panitz *et al* (1974) have performed for the first time the calculations of the dispersion relations in Zn by incorporating the effect of d-electrons. They have applied the generalized Harrison's first principle approach to derive the phonon dispersion curves. The results of calculation though reasonably good do not show any marked improvement over those which do not consider the influence of hybridization term.

Recently another fundamental approach has been developed by Animalu (1973) to study the electronic properties of d-band metals. He has extended the model potential approach of Heine-Abarenkov (HA) (1964, 1965) for transition metals and deduced the model parameters A_l from the spectroscopic data in the spirit of quantum defect method. To find the values of A_l parameters at the Fermi energy, A_l are determined at the observed term-values E_{nl} for the isolated ion which lie on a straight line and then an extrapolation is made to the Fermi energy E_F . If A_l versus Z^2 graph is drawn for group B elements, it shows a discontinuity at $Z = 2$ [figure 4 (b) Animalu 1973]. This is a new feature peculiar to transition metals which has provided a basis for the physical significance of the atomic core shift Δ [the new quantum defect introduced by Animalu by generalizing the quantum defect law as $E_{nl} = Z^2/(n - \delta_{nl})^2 + \Delta_{nl}$, δ_{nl} being the usual quantum defect] in the determination of the transition metal model potential (TMMP) parameters. The size of the core shift provides the distinction between the simple and transition metal model potential theories. To determine the A_l parameters for the elements with $Z > 2$, a parallel displacement of A_l vs Z^2 curve (obtained as for simple metals) is made so as to eliminate the discontinuity at $Z = 2$ and this is equivalent to using the same core shift for each of the 3d, 4d and 5d series of group B metals. Thus the parameters for Zn and Cd, considered as simple metals, are the same as the TMMP parameters. Therefore, Zn and Cd provide a basis for relating the TMMP and simple metal model potential parameters in the respective 3d and 4d series. From the calculational point of view, the TMMP approach differs from the usual simple metal one (Heine-Abarenkov 1964; Abarenkov-Heine 1965) in the approximation of the value of the model potential parameter C . In HA approximation C is put equal to A_2 while in TMMP method it is taken equal to A_l ($l \geq 3$). In the TMMP approximation C cannot be put equal to A_2 because A_2 being almost independent of the energy in the HA approximation, has now strong energy dependence and is related to the s-d hybridization in the transition metals. Further in the new scheme, it is assumed that $C = A_l$ ($l \geq 3$) = Z/R_M (Z = valency of the metal and R_M = model radius). This assumption is quite adequate because it reduces the magnitude of the form factor oscillations at short wavelengths. However, the parameters A_0 , A_1 , A_2 and R_M for Zn and Cd have the same values in both the approximations. In HA as well as in the TMMP approximations, Animalu (1973) has computed screened model potential form factor $V(q)$ of Zn for various values of the wave vector q and has displayed the results in a figure, showing the difference between the two only over the range $q/2k_F \gtrsim 1$. In Animalu's approach the resonance term is more important in the region $q \gtrsim 2k_F$, while Harrison (1969) found it to be important in low q region, $q < 2k_F$. Physically the former approach seems to be more satisfactory because if the resonance term is to transcend the tight-binding character of d-electrons, the Fourier transform of the associated potential should be appreciable at large q .

Animalu (1973) and Khanna *et al* (1974) have applied the TMMP in the local approximation to calculate the dispersion curves of a number of cubic d-band metals with a reasonable success. Therefore, we thought it interesting to compute the phonon spectra of hcp d-band metals using the local form of the TMMP. The TMMP and HA approximations predict the dispersion curves along the high symmetry directions for Zn and Cd without any marked difference. The results

for both metals are similar in nature but differs markedly from the experimental data. This indicates that this procedure of calculations has neglected some important contribution in the analysis.

More recently Senoy and Halder (1975) have developed a criterion for estimating the validity of the quasi-local approximation to the non-local model potential form factor. They have considered the Animalu-Heine parameters (1965) of the HA model potential and have shown that non-local contributions are important in Zn and Cd. Therefore, it seems essential that we should take into account the non-locality of the model potential in the calculations. We have considered the influence of the non-locality of the TMMP on the phonon spectra of Zn and Cd following the simple scheme of Eschrig and Wonn (1970). The calculations of the dispersion curves, so done, are very much improved, but still the results are not sufficiently satisfactory.

2. Theory, calculations and results

The phonon dispersion curves for a hcp metal are calculated by solving the secular equation

$$| D(\mathbf{q}) - M\omega^2 I | = 0 \quad (1)$$

where $D(\mathbf{q})$ is the dynamical matrix of the order (6×6) . M is the ionic mass, ω the circular frequencies, \mathbf{q} ($|\mathbf{q}| = 2\pi/\lambda$) the phonon wave vector and I the unit matrix.

The elements of the dynamical matrix are denoted by $D_{\alpha\beta}(\mathbf{q}, kk')$ ($\alpha, \beta = 1, 2, 3$ and $k, k' = 1, 2$) and are expressed as the sum of three parts:

$$D_{\alpha\beta}(\mathbf{q}, kk') = D_{\alpha\beta}^C(\mathbf{q}, kk') + D_{\alpha\beta}^E(\mathbf{q}, kk') + D_{\alpha\beta}^R(\mathbf{q}, kk') \quad (2)$$

where the superscripts C , E and R stand for Coulombic, electronic and repulsive contributions respectively.

Following Animalu (1973), we assume that the small core approximation is valid in Zn and Cd and therefore the repulsive contribution $D_{\alpha\beta}^R(\mathbf{q}, kk')$ is neglected in eq. (2). The electronic part of the dynamical matrix is evaluated by using the TMMP of Animalu (1973) with the dielectric function of Hubbard as modified by Sham (1965) and the electrostatic contribution is calculated with the help of Ewald's θ function transformation. The relevant expressions for the Coulombic elements $D_{\alpha\beta}^C(\mathbf{q}, kk')$ have been taken from the paper of Reissland and Osman (1975). The electronic elements of the dynamical matrix are evaluated by making use of the following expressions:

$$D_{\alpha\beta}^E(\mathbf{q}, kk') = \frac{2Z}{nM} \sum_{\mathbf{h}} (\mathbf{q} + \mathbf{h})_{\alpha} (\mathbf{q} + \mathbf{h})_{\beta} F(|\mathbf{q} + \mathbf{h}|) \exp(-i\mathbf{h} \cdot \mathbf{r}_{k\mathbf{v}}) \quad (3)$$

$$D_{\alpha\beta}^E(\mathbf{q}, kk) = \frac{2Z}{nM} \sum_{\mathbf{h}} [(\mathbf{q} + \mathbf{h})_{\alpha} (\mathbf{q} + \mathbf{h})_{\beta} F(|\mathbf{q} + \mathbf{h}|) - \mathbf{h}_{\alpha} \mathbf{h}_{\beta} F(|\mathbf{h}|) G(k)] \quad (4)$$

where n is the number of ions per unit cell, $G(k) = \sum_{k'} \cos(\mathbf{h} \cdot \mathbf{r}_{kk'})$ and \mathbf{h} are the reciprocal lattice vectors. The function $F(q)$ is the energy wave number characteristic given by

$$F(q) = -\frac{\Omega_0 q^2}{8\pi e^2} \frac{|V(q)|^2 \epsilon(q) - 1}{1 - f(q)} \quad (5)$$

where $V(q)$ is the form factor in local approximation and $f(q)$ is the term of Hubbard as modified by Sham (1965) to take account of exchange and correlation contributions.

The phonon frequencies $\nu (= \omega/2\pi)$ were then calculated for various values of q in [0001], [01 $\bar{1}$ 0] and [11 $\bar{2}$ 0] symmetry directions, by solving the secular equation (1) in the TMMP as well as in the HA approximations. The model parameters, used in the calculations are the same as given in the paper of Animalu (1973). Calculations show that the phonon dispersion curves for Zn and Cd in the two schemes are not much different and in figure 1, we have displayed the results for Zn along ΓA and ΓM directions only. The dashed and solid curves represent the calculations with HA and TMMP approximations respectively. Further, the computed curves for Zn and Cd, using the TMMP scheme, have been shown in

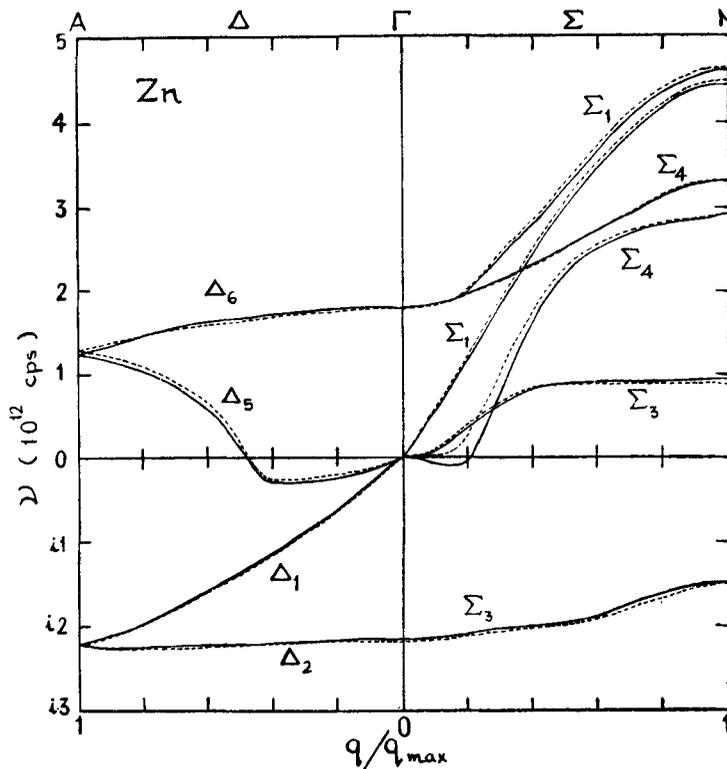


Figure 1. Phonon dispersion in Zn: Solid and dashed curves represent the calculations with the local approximation of HA model potential and TMMP respectively.

figures 2 and 3 by dashed lines with the experimental points of Almqvist and Stedman (1971), and Toussaint and Champier (1972) respectively. Figures show that though the dispersion curves for Zn and Cd are similar in nature yet they differ widely from the experimental data. Thus, in case of Zn and Cd, TMMP predicts bad and unstable results. In case of Zn, Eschrig and Wonn (1970) have also calculated the phonon dispersion curves in the HA approximation and obtained much improved results by considering the influence of the non-locality of the HA model potential. They have used a simple approximation for the non-locality for evaluating this influence. Seeing the simplicity of their scheme, we thought worthwhile to apply it with the TMMP parameters for Zn and Cd. In this scheme, the expression for the energy wave number characteristic is obtained to be

$$F_N(q) = F(q) \left[1 + a \frac{A_1(q)}{A_2(q)} + b \frac{A_3(q)}{A_2(q)} \right] \quad (6)$$

where a and b are the parameters and the expressions for $A_1(q)$, $A_2(q)$ and $A_3(q)$ are

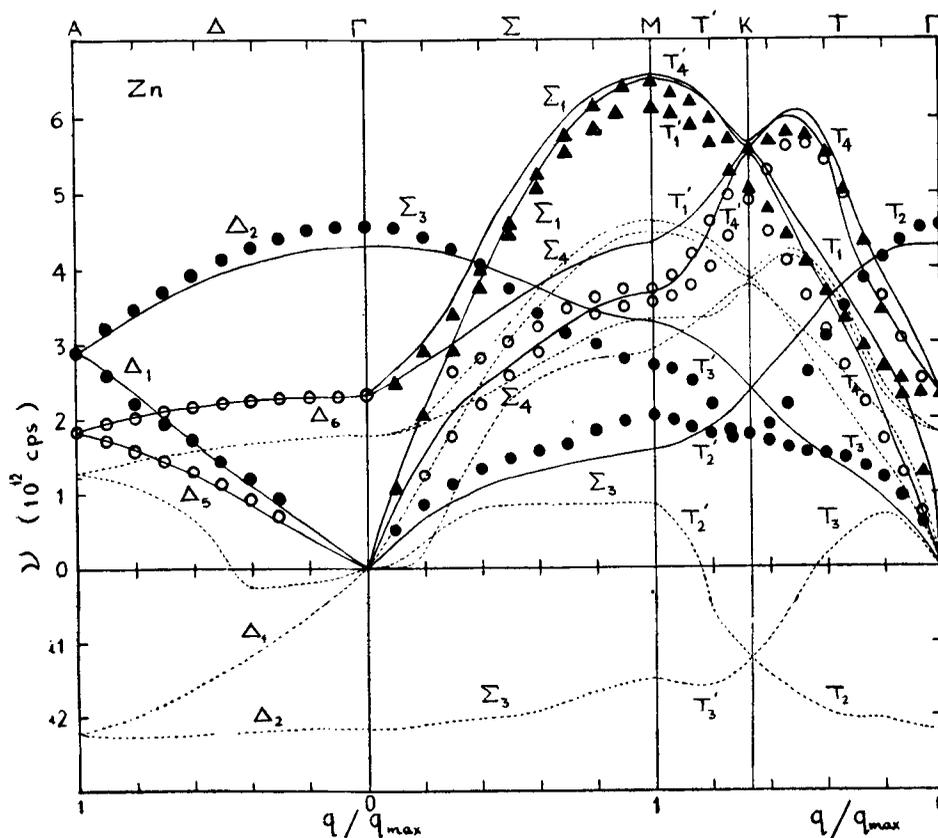


Figure 2. Phonon dispersion in Zn: dashed and solid curves represent the calculations with and without the non-local contribution in TMMP approximation; Δ , \bullet , \circ are the experimental points of Almqvist and Stedman (1971).

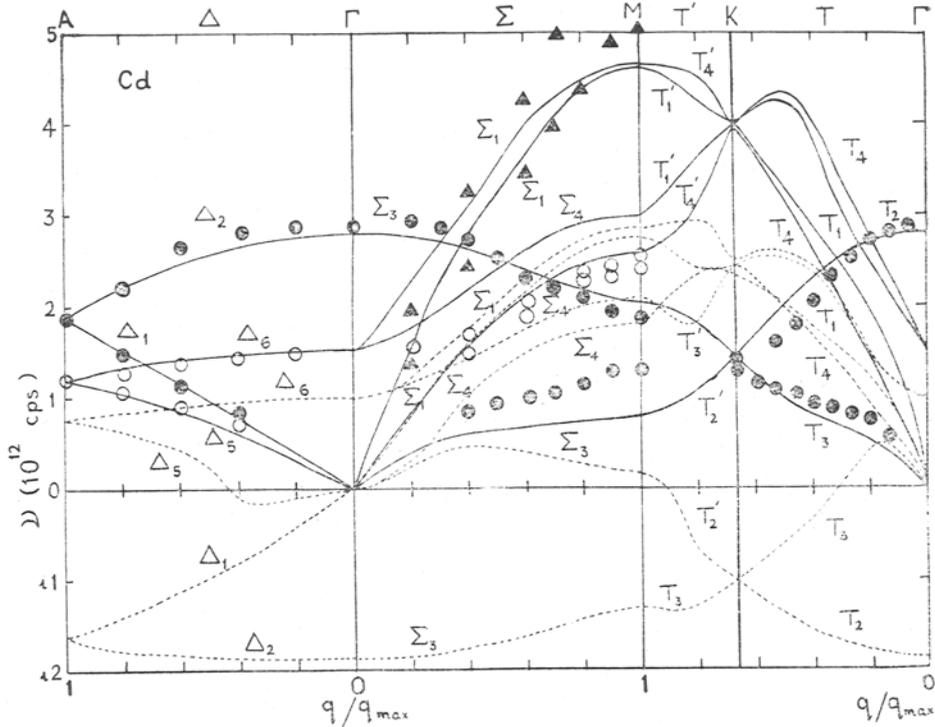


Figure 3. Phonon dispersion in Cd: Solid and dashed curves represent the calculations with and without non-local contribution in TMMP approximation; Δ , \bullet , \circ are the experimental points of Toussaint and Champier (1972).

$$A_1(q) = \frac{3Z}{2} \left[1 + \eta^2 - \frac{(1 - \eta^2)^2}{2\eta} \ln \left| \frac{1 + \eta}{1 - \eta} \right| \right] \quad (7)$$

$$A_2(q) = \frac{3Z}{2k_F^2} \left[1 + \frac{1 - \eta^2}{2\eta} \ln \left| \frac{1 + \eta}{1 - \eta} \right| \right] \quad (8)$$

and

$$A_3(q) = \theta(\eta - 1) 4k_F^2 \eta (1 - \eta) A_2(q) \quad (9)$$

where $\eta = q/2k_F$ and θ is the Heavieside function.

Now we replace $F(q)$ in expressions (3) and (4) by $F_N(q)$ and again calculate the phonon frequencies for the two metals along [0001], [01 $\bar{1}$ 0] and [11 $\bar{2}$ 0] symmetry directions. The phonon dispersion curves, so computed, are shown in figures 2 and 3 by solid lines for Zn and Cd along with the experimental points of Almqvist and Stedman (1971) and Toussaint and Champier (1972) respectively. It is to be remembered that the method of calculation of Eschrig and Wonn (1970) neglects the term $A_3(q)$, while the present investigation explores their full scheme. In actual calculations, the convergence for lattice sums in the Coulombic part of dynamical matrix was found for 525 reciprocal and 125 direct lattice vectors. To evaluate the band structure contributions, the expression for $F(q)$ (Animalu 1973 a) was multiplied by the damping factor $D(q) = \exp(-0.03(q/2k_F)^4)$ for obtaining the rapid convergence. A good convergence was obtained for 896

and 811 reciprocal lattice vectors for Zn and Cd respectively. The parameters a and b appearing in the expression of $F_N(q)$ were estimated by fitting them to both the phonon frequency of the A point. The values of the parameters so obtained are $a = -0.498$, $b = -0.996$ for Zn and $a = -0.812$, $b = -1.236$ for Cd.

3. Discussion

We note from figure 1 that the phonon dispersion curves, calculated by using the TMMP parameters, do not show any marked improvement over those considering Zn and Cd as simple metals. This conclusion is not different from that obtained by Panitz *et al* (1974) in case of Zn where they find that the phonon spectra with and without hybridization term are differing very slightly. Further Panitz *et al* comment that although hybridization may not be too significant for the phonon dispersion relations, it is nevertheless essential to take account of d-electrons. We also feel in consonance to Moriarty (1972) that though the hybridization may not significantly affect the calculation of the binding energy or phonon frequencies, yet it can make important contributions to the properties such as liquid metal resistivity and low temperature phase stability.

We see from figures 2 and 3 that the consideration of the influence of non-locality of the TMMP on the phonon spectra of Zn and Cd does not only improve the dispersion curves, but all the dispersion curves are found to be real and comparable to the experimental data. Thus we conclude that the dispersion results obtained by including the nonlocal contribution show good improvements over those with the local form of the TMMP. This also confirms the conclusions of Senoy and Halder (1975) about Zn and Cd.

Finally it is to be remarked that the transition metal model potential of Animalu (1973) seems to be a promising one and needs further investigations. In the present work, we have used the scalar dielectric function for electron gas which needs proper modifications when dealing with the problem of d-band metals. In fact, the d-electrons possess tight binding character and hence the consideration of the off diagonal terms in the dielectric matrix seems to be very important. Work is in progress in this direction. Gilat *et al* (1969) have obtained a good fit with the neutron data in hcp Mg by adjusting the effective mass (m^*) of the electrons and hence the present analysis requires further investigation regarding the effective mass of the electron in zinc and cadmium.

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