# Measurement of phonon dispersion curves in cadmium

A. A. Chernyshov, P. P. Parshin, A. Yu. Rumyantsev, I. P. Sadikov, and
M. N. Severov

(Submitted August 6, 1974)
Zh. Eksp. Teor. Fiz. **68**, 347–354 (January 1975)

Phonon dispersion curves in cadmium have been measured by the inelastic neutron scattering technique for the principal high-symmetry directions Δ, Σ, $T$, and $T'$. A single crystal grown from the $Cd^{110}$ isotope was employed. The measurements were made at room temperature and one of the low-lying branches ($T_3$) was also measured at $T = 90°K$ for an estimate of the influence of anharmonic effects. It was found that the Cd phonon spectrum in the ion plasma frequency scale is similar to the Zn spectrum and differs significantly from the Mg spectrum. A number of interesting details of the Cd spectrum are discussed. The experimental results are compared with calculations employing the Abarenkov–Heine local model potential with two fitting parameters. The calculation correctly represents the main features of the Cd spectrum, but with less accuracy than in the case of Mg.

## INTRODUCTION

The experimental study of the phonon spectra of hexagonal metals of the second group (Be, Mg, Zn, Cd) is of significant interest for the development of general representations of the metallic state. They belong to the group of transition metals, for which there already exists a systematic microscopic theory (see, for example, [1,2]). Comparison of the experimental data with such a theory makes it possible to obtain many important characteristics of the electron-electron and electron-ion interactions, which are necessary for the description of a broad class of phenomena in metals.

In contrast with the majority of nontransition metals, which crystallize in a cubic lattice, the considered elements possess the lower symmetry of the hexagonal structure with two atoms in the unit cell. In this connection, their phonon spectra have a very complicated form and, consequently, contain more information than is necessary for testing the theoretical representations. The anisotropy of their properties, which is especially clearly expressed in Zn and Cd, shows, according to existing representations, the large contribution of the conduction electrons to the binding energy of these metals, and the correct calculation of this contribution is one of the basic problems of the theory.

Among the metals considered, Cd is of greatest interest, inasmuch as it possesses a very complicated ion structure and is crystallized in a lattice with maximal anisotropy ($c/a = 1.89$, while for a perfect hexagonal close-packed (h.c.p.) structure $c/a = 1.63$). However, detailed investigations of the phonon spectrum of Cd have not been carried out to date because of the anomalously large absorption cross section of thermal neutrons. The only measurements of the dispersion relations in Cd, carried out recently with the help of x-ray diffraction scattering, [3] are insufficiently complete or exact because of the limited possibilities of the method used.

In the present work, results are given for measurements of the dispersion relations $\omega_s(q)$ for all high-symmetry directions, performed on a sample of the weakly absorbing isotope $Cd^{110}$.

## 1. SAMPLE AND CONDITIONS OF MEASUREMENT OF $\omega_s(q)$

The starting material for preparing the single crystal was the isotope $Cd^{110}$, bombarded in a reactor to eliminate the strongly absorbing impurity $Cd^{113}$. This isotope had been used earlier for measurement of the phonon state density in Cd. [4] The high cost of the isotope, the activity produced in the bombardment, and the low chemical purity of the material required the development of a special technology of purification and growing of the single crystal. [5] As a result, we obtained a single crystal of volume ~20 cm$^3$ and a mosaic structure ~45′, which had the shape of a cylinder of 18 mm diameter. The absorption cross section of the thermal neutrons in the sample did not exceed 2 barns.

Measurements of the dispersion relations were carried out on the three-axis crystal neutron spectrometer [6] installed on the IRT-M reactor, with a power of 6 MW. The spectrometer was assembled according to the classic scheme, with cantilever positions of the arms of the analyzer and detector. The accuracy of establishing the angular positions of all the elements of the spectrometer was no worse than 1′. The control of the spectrometer was fully automatic and was effected by a specified program, introduced by a punched tape. In these measurements, Cu(111) monochromators with a mosaic structure of 20′ were used at ~40′ divergence of the incident and scattered beams. All the measurements were made by the method of constant Q for several fixed values of the wavelength of the incident neutrons (from 1.3 to 1.85 Å). The conditions of the measurement were chosen with account of the effect of the geometric focusing. [7]

The phonon frequency was found from the position of the midpoint at half-height of the reflection, and the error due to the statistical accuracy of the measurements was estimated, similar to [8], from the formula

$$\Delta\omega \approx \Delta\omega_{1/2}\frac{N_{max}^{1/2}}{N_{max}-N_b}\frac{1}{n^{1/2}},$$

where $\Delta\omega$ is the error in the frequency determination, $\Delta\omega_{1/2}$ the half-width of the reflection, $N_{max}$ the number of counts at the maximum, $N_b$ the background count, and n the number of points on the total width of the peak. For the branches $T_3$ and $\Sigma_3$, where the measurements were made with the greatest accuracy, and the reflections had a symmetric shape, the phonon parameters were determined by a least-squares fit to a Gaussian curve.

The measurements were performed for the directions Δ, Σ, T and T′ (see Fig. 1a) at room temperature (T = 295 ± 3° K). The conditions for observation of the different branches of the spectrum were selected by starting from the behavior of the dynamic structure factor, calculated for Zn[9,10], and shown in Fig. 1b for branches polarized in the basal plane. The measured dispersion curves are shown in Fig. 2. The values of the frequencies obtained in measurements along one direction in the reciprocal lattice are shown by identical symbols. The values of the statistical errors are also shown. The maximum statistical error due generally to insufficient perfection of the sample can be judged from the difference in the frequencies at the point $M_4$, measured for different orientations of the sample.

## 2. DISCUSSION OF THE RESULTS

The phonon spectrum obtained can be compared with the values of certain end-point frequencies estimated from measurements on the density of states in Cd[4], and with x-ray data.[3] Most of the characteristic frequencies of the spectrum obtained in[3,4] do not differ from the results of the given measurements by more than 10%. The frequencies of the longitudinal modes at the point M, where the error in the x-ray method is a maximum are an exception, and the end-point frequency was evidently extracted from the function g(ω) with insufficient accuracy.

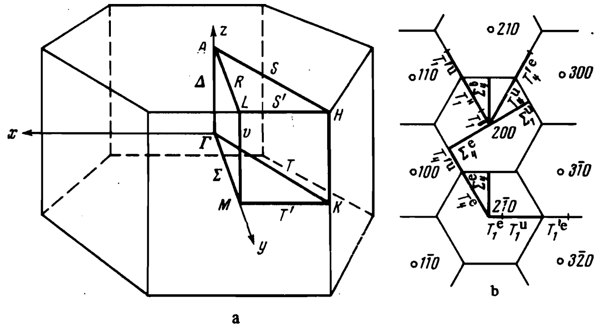

FIG. 1. a) Designations of the symmetric points and directions in the first Brillouin zone for the h.c.p. lattice; b) directions along which the various branches of the spectrum, polarized in the basis plane, were measured. The indices "u" and "l" denote the upper and lower branches of the same symmetry.

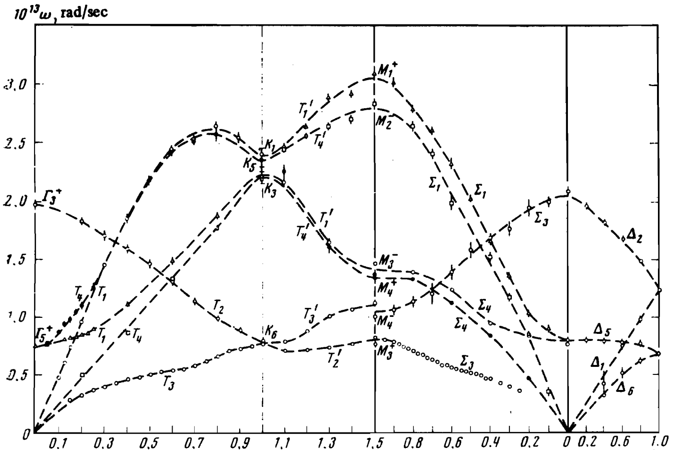

FIG. 2. Cd phonon spectrum at T = 295 ± 3°K. Lines are arbitrarily drawn through the experimental points for the sake of visualization.

It is of interest to compare the phonon spectrum of Cd with detailed studies of the spectra of Mg[11] and Zn[12], inasmuch as the magnesium has a h.c.p. structure with almost ideal ratio of the axes, (c/a = 1.623), and zinc evidently is the structural homolog of Cd. It is convenient to make such a comparison in the scale of the ion plasma frequency

$$\omega_0^2=4\pi Z^2e^2/M\Omega_0.$$

In this way, the trivial dependence of the frequency on the mass of the atom is eliminated and the difference in the volumes of the elementary lattice $\Omega_0$ is taken approximately into account.

The table gives the values of $\omega/\omega_0$ for the most characteristic points of the spectrum, at the center and on the boundary of the Brillouin zone. As was demonstrated earlier on the basis of measurements of the density of states,[4] the spectrum of Cd turns out to be very close to Zn in the selected scale, and differs significantly from Mg. The strong anisotropy of the lattices of Cd and Zn appears in the phonon spectrum (in comparison with the isotropic Mg) in that the frequencies of the longitudinal oscillations in the basis plane increase significantly (see the points $M_1^+$ and $M_2^-$), while the oscillations polarized along the c axis turn out to be anomalously weak (the points $K_6$, $M_3^+$, $M_4^-$). The presence of low-lying branches with weak dispersion ($T_3$, $\Sigma_3$) is the most characteristic mark of the phonon spectrum of Cd and Zn, having an important effect on the thermodynamic properties of these metals.

Some curious features also appear in the Cd phonon spectrum, as also in Zn, connected with the behavior of ω(q) in the directions T and T′. Thus, for $q/q_{max} = 0.175$, almost complete degeneracy occurs (within the limits of experimental accuracy) of the two branches of the oscillations having the same symmetry as $T_1$. In order to understand under what conditions this takes place, we write out the explicit form for ω(q), which is obtained as a result of partial diagonalization of the matrix for this direction:[13]

$$\begin{gathered}\omega^2={}^1/_2\{(A+B)\pm[(A-B)^2+4C^2]^{1/2}\},\\ A=D_{11}{}^{xx}\pm D_{12}{}^{xx};\quad B=D_{11}{}^{yy}\mp D_{12}{}^{yy};\\ C=\operatorname{Im}D_{12}{}^{xy}\mp\operatorname{Im}D_{11}{}^{xy}.\end{gathered}\tag{1}$$

In the expressions for A, B, and C, the upper signs refer to the branches $T_1$, and the lower, to the branches $T_4$; the different signs in front of the root give the upper or lower branch of identical symmetry. It is then seen that, for complete degeneracy of the branches $T_1$, simultaneous satisfaction of two conditions is necessary:

$$D_{11}{}^{xx}+D_{12}{}^{xx}=D_{11}{}^{yy}-D_{12}{}^{yy},\qquad \operatorname{Im}D_{12}{}^{xy}=\operatorname{Im}D_{11}{}^{xy}.$$

Therefore, the observed case of degeneracy indicates either a definite correlation in the change of the different elements of the dynamic matrix, or is an extraordinarily rare coincidence. It should be noted that on going through the degeneracy point, a symmetric renormalization of the polarization vectors takes place, such that, by measuring ω(q) in the chosen direction, we automatically transform from $T_1^l$ to $T_1^u$ (or conversely). This transition takes place without significant change in the scattering intensity, which creates the illusion of two smooth and overlapping branches similar to the branches $\Sigma_1$ and $\Sigma_4$.

Comparison of phonon frequencies at the symmetric points of the Brillouin zone for Mg, Zn and Cd, expressed in units of the ion plasma frequency

| | $\omega_0$, $\frac{\text{rad}}{\text{sec}} \cdot 10^{-13}$ | $\omega/\omega_0$ | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $\Gamma_3+$ | $\Gamma_5+$ | $K_6$ | $K_3$ | $K_5$ | $K_1$ | $M_3+$ | $M_4-$ | $M_4+$ | $M_3-$ | $M_2-$ | $M_1+$ |
| Mg | 11.166 | 0.408 | 0.208 | 0.281 | 0.316 | 0.332 | 0.366 | 0.233 | 0.346 | 0.205 | 0.309 | 0.377 | 0.394 |
| Zn | 8.376 | 0.343 | 0.172 | 0.134 | 0.367 | 0.378 | 0.416 | 0.151 | 0.202 | 0.264 | 0.279 | 0.458 | 0.483 |
| Cd | 5.362 | 0.377 | 0.144 | 0.144 | 0.410 | 0.438 | 0.447 | 0.147 | 0.201 | 0.254 | 0.263 | 0.537 | 0.576 |
| | | ±0.009 | 4 | 4 | 10 | 20 | 20 | 6 | 7 | 4 | 7 | 9 | 13 |

Another interesting point of the spectrum of h.c.p. metals is the point K. As was first noted in[13], the character of the splitting of the branches $T_1$ and $T_4$ at this point is determined by the value of the matrix element Im $D_{11}^{xy}$, which differs from zero only in a noncentral type of interatomic interaction. Using the expression (1) and additional conditions that follow from the symmetry of the point K ($D_{11}^{yy} = D_{11}^{xx}$ and $D_{12}^{xx} = -D_{12}^{xy} = -\text{Im } D_{12}^{xy}$), we can analyze the relation between the values of $\omega_2$ for the branches $T_1$ and $T_4$ at this point. For Im $D_{11}^{yy} = 0$, the double-degeneracy point $K_5$ should be located midway between the points $K_1$ and $K_3$, and for Im $D_{11}^{xy} \neq 0$, this symmetry will be destroyed.

The existing experimental data indicate that the second case is realized in all the hexagonal metals studied, and that the interaction in them has a noncentral character. This circumstance turns out to be very important for the description of the phonon spectrum within the framework of the pseudopotential theory. It means that, in the expansion of the energy of the electron-ion interaction in powers of the pseudopotential, it is not possible to limit oneself to terms of second order only.[2] This situation was recently considered specially for Be.[14,15] The problem of the value of the non-pair interaction in Mg, Zn and Cd evidently requires more detailed and accurate measurements of the dispersion curves in the region of the point K. In our measurements on Cd, the resolution was not sufficiently high to separate all these branches accurately, and therefore the values of the frequencies at the point K were obtained with large errors.

Cadmium, along with zinc, is a convenient object for the study of the anomalies in the dispersion curves that are connected with the appearance of singularities in the electron-ion interaction (Kohn type anomalies). One can expect a considerable effect of these singularities on the oscillations that are polarized parallel to the c axis, inasmuch as the principal contribution from the conduction electrons to the energy of these oscillations is made by the strongest sites of the reciprocal lattice (00.*l*). On the measured dispersion curves $\Sigma_3$ and $T_3$, significant nonmonotonicities actually appear, which are more clearly observed in the dependence of the phonon group velocity $d\omega/dq$ on the wave vector. However, as was noted in[12] for Zn, the character of the anomalies cannot be described within the framework of the simplest approximations—a spherical Fermi surface and simple bipolar singularities. In this connection, the problem of the nature of the observed oscillations in the dispersion curves is of great interest and requires a more detailed study both from the experimental and the theoretical point of view.

Inasmuch as Cd has a rather low Debye temperature (~170°), it follows that the measurements of $\omega(q)$ at room temperature should be significantly affected by the effects of anharmonism of the oscillations. For the determination of their value, one of the low-frequency branches ($T_3$) was also measured at a temperature of 90 ± 3°K. Attention is called to the significant frequency shift and its important dependence on the momentum (see Fig. 3). In the temperature measurements, a significant narrowing of the single-phonon reflections also occurs, which allows us to estimate the temperature-dependent part of the width $\Delta\omega_T$ due to phonon-phonon interaction. At 300°K, it turns out to be appreciable: $\Delta\omega_T/\omega = 20-25\%$.

Evidently, the most valuable physical information can be obtained from a comparison of the measured $\omega_s(q)$ with the results of calculations based on the modern theory of nontransition metals. Figure 4 shows such a comparison with the calculations (see [17]) based on one of the most universal variants of the theory, which allows us, for example, to describe the phonon spectrum of Mg with high accuracy.[18] In the employed scheme of calculation, terms up to third order inclusively were taken into account in expansion of the energy of the electron-ion interaction in powers of the pseudopotential. This corresponds to allowance for unpaired ion-ion interaction of the covalent type, which can be extremely important in an anisotropic structure. As the potential of electron-ion interaction, we used the local model potential of Abarenkov-Heine, the parameters of which were varied to obtain the best agreement, averaged over the spectrum, with the experiment. The given spectrum corresponds to the values of the parameters $q_0 = 1.6\ K_F$ and $r_0 = 0.8$ Å. It is seen that the calculation correctly reproduces the basic features of the phonon spectrum of Cd; however, it is done with significantly less accuracy than was done in the case of Mg.

As noted in[17], the discrepancies from experiment exist also in the value of the elastic modulus and in the ratio of the axes c/a. Evidently, to improve the agreement with experiment in the case of Cd, it is necessary to introduce a nonlocal form of the pseudopotential, which would take into account the electron-spectrum singular-

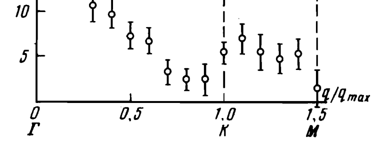

FIG. 3. Relative shift in the phonon frequencies for a temperature change from 295 to 90°K. The point at q = 0 was obtained from measurements of the elasticity modulus. [16]

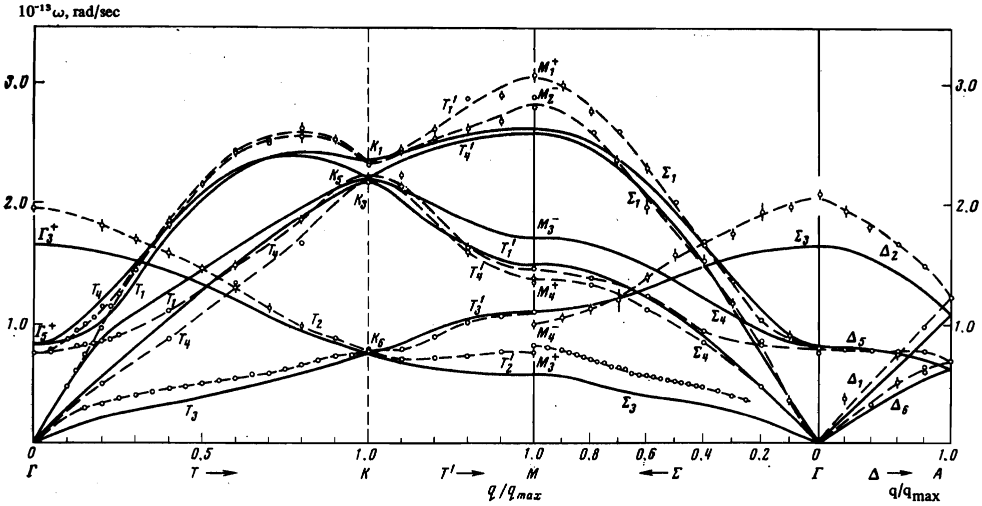

FIG. 4. Cd phonon spectrum. The dashed lines are experimental, the continuous lines were calculated.

ity connected with the proximity of the filled d-band to the bottom of the conduction band.

## CONCLUSION

The measurements of the dispersion curves give a sufficiently full representation of the phonon spectrum of Cd as a whole. Along with this, it is of interest to investigate in more detail certain features of this spectrum: the character of the splitting of the branches at the point K, the dispersion-curve anomalies due to the singularities of the electron-ion interaction, and so on. Experiments in this direction will be continued. Further theoretical studies of the properties of Cd are also necessary, together with analysis of the whole series of hexagonal metals of group II with the aim of clarifying the role of the nonlocality of the pseudopotential in these metals, the reasons for the significant anisotropy of their structures, and other questions of basic interest for the theory of nontransition metals.

In conclusion, the authors wish to emphasize the great and fruitful effect exerted on this research by E. G. Brovman, who did much for the development of the theory of nontransition metals. We express our gratitude to V. V. Pushkarev for useful discussions and calculations of the phonon spectrum, to N. A. Chernoplekov and M. G. Zemlyanov for constant interest and support of the research, and to V. V. Golovnev and É. L. Bokhenkov for help in the measurements.

---

[1] W. Harrison, Pseudopotentials in the Theory of Metals (Russian translation, Mir Press, 1968).

[2] E. G. Brovman and Yu. M. Kagan, Usp. Fiz. Nauk **112**, 369 (1974) [Sov. Phys.-Uspekhi **17**, 125 (1974)].

[3] G. Toussaint and G. Champier, Phys. Stat. Sol. (B) **54**, 165 (1972).

[4] I. P. Eremeev, A. A. Chernyshov and I. P. Sadikov, ZhETF Pis. Red. **18**, 302 (1973) [JETP Lett. **18**, 177 (1973)].

[5] M. N. Severov, I. P. Sadikov and A. A. Chernyshov, in: Problems of Atomic Science and Technology, series of Certain Problems of Solid State Physics, Appendix to issue No. 1 [in Russian], I. V. Kurchatov Institute of Atomic Energy, 1974, p. 65.

[6] A. E. Golovin, G. I. Zakokhin, M. G. Zemyanov, N. I. Karpov, Yu. M. Krasnikov, V. P. Moryakov, I. V. Naumov, P. P. Parshin, A. Yu. Rumyantsev, V. A. Somenkov and N. A. Chernoplekov, Preprint, Institute of Atomic Energy, No. 2445, 1974.

[7] G. E. Peckham, D. H. Saunderson and R. J. Sharp, Brit. J. Appl. Phys. **18**, 473 (1967).

[8] R. Stedman and J. Weymouth, Brit. J. Appl. Phys. **D2**, 903 (1969).

[9] G. Borgonovi, G. Caglioti and J. J. Antal, Phys. Rev. **132**, 683 (1973).

[10] D. L. McDonald, M. M. Elcombe, and A. W. Pryor, J. Phys. C. (Solid State Phys.) **2**, 1857 (1969).

[11] R. Pynn and G. L. Squires, Proc. Roy. Soc. (London) **A326**, 347 (1972).

[12] L. Almqvist and R. Stedman, J. Phys. F. Metal Phys. **1**, 785 (1971).

[13] E. G. Brovman, Yu. Kagan, and A. Cholas, Neutron Inelast. Scattering **1**, IAEA, Vienna, 1968, p. 165.

[14] A. P. Roy, B. A. Dasannacharya, C. L. Thaper and P. K. Iyengar, Phys. Rev. Lett. **30**, 906 (1973).

[15] C. M. Bertoni, V. Bortolani, C. Calandra and F. Nizzoli, Phys. Rev. Lett. **31**, 1466 (1973).

[16] G. W. Garland and J. Silvermen, Phys. Rev. **119**, 1218 (1960).

[17] E. G. Brovman and V. V. Pushkarev, ZhETF Pis. Red. 1974 (in press).

[18] E. G. Brovman, Yu. Kagan and A. Kholas, Zh. Eksp. Teor. Fiz. **61**, 737 (1971) [Sov. Phys.-JETP **34**, 394 (1972)].

Translated by R. T. Beyer
40