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Dispersion Relations for Hexagonal Close-Packed Crystal Lattices*

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The dispersion relations for waves propagating in the [0001] and [01$\bar{1}$0] directions were calculated, using a Born–von Kármán model of the hexagonal close-packed crystal lattice. The interactions between nearest neighbors in the plane were considered to be central forces, while the interactions between nearest and next-nearest neighbors out of the plane were considered to be noncentral forces, i.e., the interactions involved both central and angular forces. The atomic force constants were evaluated (1) from the elastic constants by the method of long waves, (2) from a least-squares analysis of the eigenvalues of the secular equation for elastic waves propagating in certain symmetric crystallographic directions at critical points in the Brillouin zone, i.e., from a least-squares analysis of the dispersion relations, and (3) from a least-squares analysis of the elastic constants and the dispersion relations. The correlation between theoretical and experimental dispersion relations from the noncentral-force model is good for magnesium and zinc and is limited for beryllium. If the atomic force constants have been calculated by a least-squares analysis of certain points in the dispersion relations with or without the elastic constants, these atomic force constants greatly enhance the agreement between theory and experiment. As a result of this work it seems that better agreement between theory and experiment is obtained if angular forces are included in a model of the hcp crystal lattice rather than simply extending the sphere of interaction to more and more neighbors.

INTRODUCTION

THERMAL neutrons, because their wavelength is of the order of magnitude of interatomic distances in crystals and because their energy is of the same order as the energy of lattice vibrations, provide a direct means of studying the lattice dynamics of crystals. The interaction of thermal neutrons with lattice vibrations takes place through the emission or absorption of sound quanta or phonons. The process by which a neutron and the lattice exchange energy, i.e., when the final energy of the neutron is different from its initial energy, is referred to as inelastic scattering. The scattered neutron waves from one nucleus may interfere with the scattered waves from other nuclei. This interference part of the scattering is called "coherent" scattering.

Inelastic, coherent, one-phonon neutron scattering experiments yield the dispersion law for lattice vibrations

$$\omega=\omega_j(\mathbf{q}), \tag{1}$$

which relates the frequency ω to the wave vector $\mathbf{q}$ and the polarization index j of a plane wave vibration of the lattice. Measurements of neutrons scattered along symmetry axes in reciprocal space by single crystals can yield directly the dispersion curves for elastic waves (both longitudinal and transverse polarizations) propagating along the primary crystallographic directions. Fitting the theoretical dispersion curves to the experimental ones by a least-squares analysis leads to numerical values for the atomic force constants. As a check on the internal consistency of the experimental data, the atomic force constants which are determined solely from the experimental dispersion data can be used to calculate the macroscopic elastic constants which can be compared with values obtained by other methods.

The dispersion relations of beryllium,[1,2] magnesium,[3–8] and zinc[9,10] have been studied, using Born–von Kármán models of the hexagonal close-packed (hcp) crystal lattice when the interactions have been extended to different numbers of neighbors. The models used can be conveniently cataloged according to the type of interactions: tensor-force models,[11,12] central-force

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models with or without the contribution from the electron gas,[13–17] and noncentral-force models.[18–20]

The purpose of this investigation was to study the hcp crystal lattice by means of a Born–von Kármán model, using noncentral forces with the added restriction of limiting the number of interactions so that the atomic force constants could be evaluated from the elastic constants. The study was accomplished by examining the frequency spectra,[21] lattice specific heats,[21] and dispersion relations of three hcp lattices with different axial (c/a) ratios: beryllium (1.568), magnesium (1.624), and zinc (1.855).

The lattice model of this investigation uses a combination of central and angular forces. The central-force term is assumed to act along the line joining two atoms, and is a bond-stretching term. The angular force, a bond-bending term, assumes that a change in angle corresponds to a change in the potential energy. If V is the potential energy and $\delta\varphi$ is change in angle, one obtains

$$V=\tfrac{1}{2}\gamma(\delta\varphi)^2, \qquad (2)$$

where γ is a Hooke's-law force constant.

The change in angle is formed for each side of the angle, and the corresponding change in potential is then calculated. When this has been done for all sides of all angles, the potential energy is found by summing the individual contributions. The selection of the angles whose changes contribute to the potential energy is extremely important. Two types of angles were used in this investigation. One type of angle was between nearest neighbors out of the plane on the same side of the basal plane, while the other type of angle was between next-nearest neighbors out of the plane on the same side of the basal plane. By choosing the angles in this manner, the matrix of the resulting secular equation contains the correct symmetry for the hcp crystal lattice and is Hermetian.

LATTICE DYNAMICS

A thorough description of the lattice, the types of interactions in the model and the resulting equations of motion have been previously published.[21] The model assumes five force constants. A central-force interaction exists between the central atom and its neighbors in the plane while a noncentral-force interaction (both central and angular forces) exists between the central atom and its nearest and next-nearest neighbors out of the plane. The atomic force constants have been evaluated in three ways: (1) The five atomic force constants have been related to the five elastic constants in the limit of long wavelengths. (2) The eigenvalues of the reduced matrix become linear combinations of the atomic force constants at critical points in the Brillouin zone of hcp crystal lattice when a wave is propagated through the lattice in certain symmetry directions. In our case, eight such eigenvalues were related to the five atomic force constants. (3) Finally, the atomic force constants were determined by a least-squares analysis of the five equations from the elastic constants and the eight equations from the dispersion relations.

The thirteen equations used to evaluate the atomic force constants as well as the values of the atomic force constants have been previously published.[21]

DISPERSION RELATIONS

The inelastic scattering of slow neutrons by the normal modes of vibration of the hcp crystal lattice has been used as a means of comparing the proposed noncentral-force model to experimental observations. The dependence of the frequency on the wave vector (the dispersion relation) has been examined for waves propagating in the crystallographic directions, [0001] and [01$\bar{1}$0] with both longitudinal and transverse polarization. The transverse polarization for the [01$\bar{1}$0] direction is perpendicular to the basal plane. The force constants used in calculating the dispersion relations have been determined by three different methods. In order to avoid a large degree of repetitiveness, a symbolic

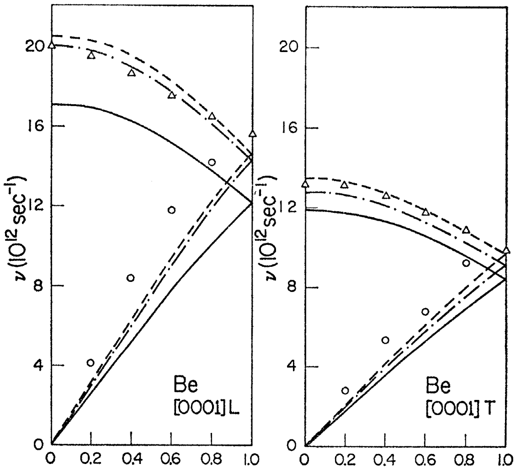

FIG. 1. The dispersion relation for longitudinal and transverse waves propagating in the [0001] direction for beryllium calculated from the noncentral-force model. The experimental points are from Ref. 2. The dispersion relations were calculated using atomic force constants obtained from the elastic constants (solid curve), from the neutron-scattering data (dashed curve) and from the elastic constants and neutron-scattering data (dot-dash curve).

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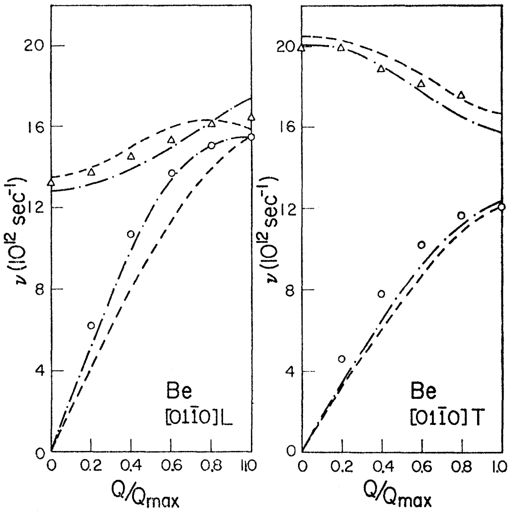

FIG. 2. The dispersion relation for longitudinal and transverse waves propagating in the [01$\bar{1}$0] direction for beryllium calculated from the noncentral-force model. The experimental points are from Ref. 2. The dispersion relations were calculated using atomic force constants obtained from neutron-scattering data (dashed curve) and from the elastic constants and neutron-scattering data (dot-dash curve).

abbreviation will be used. Method 1 will designate force constants evaluated from elastic constants directly, while method 2 will indicate that a least-squares analysis of the eigenvalues of the dispersion relations at certain critical points was used to calculate the atomic force constants and finally, method 3 will denote that the force constants were calculated from a least-squares analysis which included the elastic constants as well as the eigenvalues of the dispersion relations.

The dispersion relations for beryllium are shown in Figs. 1 and 2, for magnesium in Figs. 3 and 4, and for zinc in Figs. 5 and 6. These dispersion relations are compared to the experimental dispersion relations for Be measured by Schmunk,[2] for Mg measured by Iyengar *et al.*[6] and for Zn measured by Borgonovi *et al.*[10]

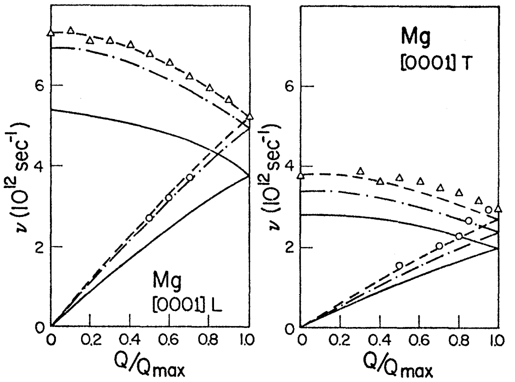

FIG. 3. The dispersion relation for longitudinal and transverse waves propagating in the [0001] direction for magnesium calculated from the noncentral-force model. The experimental points are from Ref. 6. The dispersion relations were calculated using atomic force constants obtained from the elastic constants (solid curve), from neutron-scattering data (dashed curve) and from the elastic constants and neutron-scattering data (dot-dash curve).

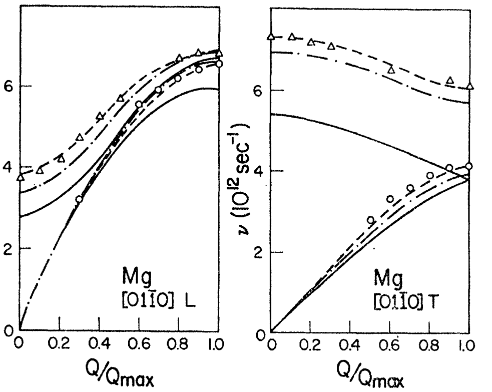

FIG. 4. The dispersion relation for longitudinal and transverse waves propagating in the [01$\bar{1}$0] direction for magnesium calculated from the noncentral-force model. The experimental points are from Ref. 6. The dispersion relations were calculated using atomic force constants obtained from the elastic constants (solid curve), from neutron-scattering data (dashed curve) and from the elastic constants and neutron-scattering data (dot-dash curve).

For a wave travelling in the [0001] direction of beryllium with longitudinal polarization, the best agreement between the model and experiment is obtained for the optical branch when the force constants are calculated by method 2. The agreement between the model and experiment for the acoustical branch is unsatisfactory and surprising. The dispersion relations for a transverse wave propagating in the [0001] direction imply from the optical branch that the force constants should be evaluated by method 2. The acoustical branch again lacks agreement and as in the case of the longitudinal vibrations has an incorrect slope.

The best fit for the optical branch of the dispersion relation for a wave travelling in the [01$\bar{1}$0] direction

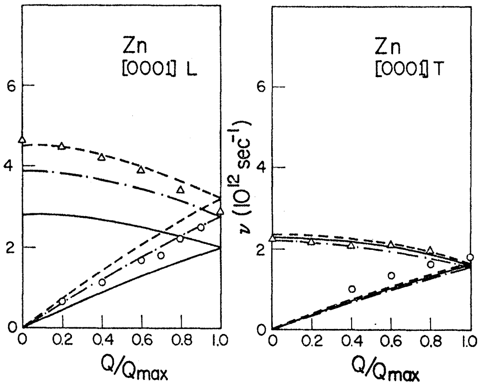

FIG. 5. The dispersion relation for longitudinal and transverse waves propagating in the [0001] direction for zinc calculated from the noncentral-force model. The experimental points are from Ref. 10. The dispersion relations were calculated using atomic force constants obtained from the elastic constants (solid curve), from neutron-scattering data (dashed curve) and from the elastic constants and neutron-scattering data (dot-dash curve).

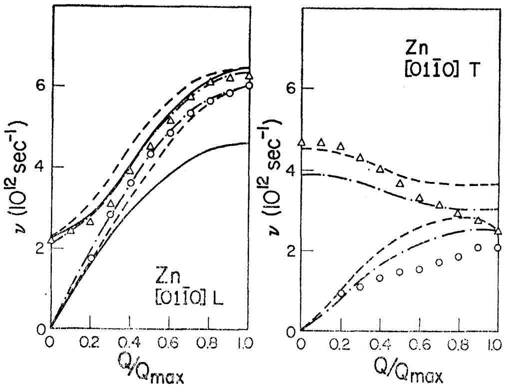

FIG. 6. The dispersion relation for longitudinal and transverse waves propagating in the [01$\bar{1}$0] direction for zinc calculated from the noncentral-force model. The experimental points are from Ref. 10. The dispersion relations were calculated using atomic force constants obtained from the elastic constants (solid curve), from neutron-scattering data (dashed curve) and from the elastic constants and neutron-scattering data (dot-dash curve).

with longitudinal polarization occurs when the force constants are evaluated by method 2 while the acoustical branch gives the best agreement if the force constants are evaluated by method 3. For transverse polarization of a wave propagating in the [01$\bar{1}$0] direction, the optical branch gives good agreement if the force constants are calculated by method 3 for values of the ratio of Q to $Q_{\max}$ up to 0.7 while for higher values of this ratio the agreement is best when method 2 is used to calculate the force constants. The acoustical branch of the transverse wave travelling in the [01$\bar{1}$0] shows little correlation and again exhibits an incorrect slope.

In magnesium very good agreement is found for a longitudinal wave travelling in the [0001] direction in both the optical and acoustical branches if the force constants are computed by method 2. The best agreement between the model and experimental observations for a transverse wave propagating in the [0001] direction for both the acoustical and optical branches also occurs if the atomic force constants are computed by method 2. This same agreement carried over to waves, both longitudinal and transverse, travelling in the [01$\bar{1}$0] direction if the force constants are evaluated by method 2.

For zinc the agreement of the theoretical and experimental dispersion relation for a longitudinal wave propagating in the [0001] direction is good for both the optical and acoustical branch. The optical branch indicates that the force constants should be calculated by method 2 while the acoustical branch implies that the atomic force constants should be evaluated by method 3. If a transverse wave is propagated in the [0001] direction all three methods give good agreement for the optical branch but the acoustical branch has an incorrect slope and poor agreement.

The dispersion relations for a longitudinal wave travelling in the [01$\bar{1}$0] direction calculated from the proposed noncentral-force model gives good agreement for both the optical and acoustical branches of the atomic force constants as evaluated by method 3. The correlation between theory and experiment for a transverse (perpendicular to the basal plane) wave propagating in the [01$\bar{1}$0] direction is poor for both the optical and acoustical branches.

The comparison between theoretical and experimental dispersion relations is good for magnesium and zinc and fair for beryllium. The comparison depends on the method of evaluating the atomic force constants. For consistently good agreement the atomic force constants must be evaluated from the dispersion relations. The poor agreement found when the atomic force constants are evaluated from the elastic constants indicates that the elastic constants should be modified, perhaps, by a contribution from the electron gas.

CONCLUSIONS

The dynamical properties of the hcp lattice have been studied using a Born–von Kármán model of the crystal lattice. A combination of central and angular forces has been employed between various sets of neighbors.

The atomic force constants have been calculated by three different models. The independence of the thermodynamical values, i.e., the lattice specific heats, on the details of the frequency spectra has been previously demonstrated[21] by calculating the Debye and Einstein characteristic temperature from the three different frequency spectra.

The theoretical dispersion relations as calculated from this model give good agreement to the data of various experimenters for magnesium and zinc and limited agreement for beryllium. The manner in which the atomic force constants are evaluated contribute greatly to the correlation between theory and experiment. If a least-squares analysis of the dispersion relations with or without the elastic constants is used to evaluate the atomic force constants, then the theoretical dispersion relations are in accord with experimental dispersion relations. When only the elastic constants are used to evaluate the atomic force constants, the theoretical values of the dispersion relations do not agree nearly as well with the experimental dispersion relations.

The number of atomic force constants which can be adjusted for each material in order to evaluate the dispersion relations from a particular model is of interest in comparing the "goodness" of fit between theory and experiment. This model uses only five atomic force constants. The model of Gupta and Dayal[17] requires six atomic force constants; the fourth-neighbor tensor-force model of Iyengar *et al.*[6] needs eleven atomic force constants while the modified axially symmetric model of DeWames *et al.*[19] demands thirteen atomic force constants. Obviously the greater the number of adjustable parameters the better the "goodness" of the fit should be.

From this model the agreement between theory and experiment for beryllium exhibits the greatest disparity. Schmunk[2] has compared his data to the theoretical calculations of Gupta and Dayal,[17] Iyengar *et al.*,[6] and DeWames *et al.*[19] concluding that the last model gives the best agreement with the data but that further improvements are desired. This best agreement when compared to the results of this model, on the same scale, is only slightly better but utilizes thirteen adjustable parameters compared to only five in this model.

For magnesium and zinc the goodness of fit between theory and experiment is just as good if not better for this model when compared to the models of Iyengar *et al.*,[6] DeWames *et al.*,[19] Collins,[3] Squires,[8] and Borgonovi *et al.*[10] All of the other models utilize many more atomic force constants than the five used with this model.

A modification of the elastic constants by a consideration of the contribution of the electron gas on them could lead to dispersion relations, where the atomic force constants have been evaluated by these new elastic constants, that correlate well to experimental observations. One such modification, proposed by Gupta and Dayal,[17] has been criticized[2,22,23] because of its assumption that the electron gas term is shear free, a position which is untenable for the hcp divalent metals. The modification has also been criticized because it violates symmetry requirements.[24] A slight innovation of this model making it compatible to the hcp metals might lead to new elastic constants that imply theoretical dispersion relations in good agreement with experimental dispersion relations.

The questions of the number of neighbors needed to truly represent the lattice and of the types of interactions between atoms is not fully resolved although the results of this investigation indicate that it is better at the outset to include angular forces in the model of the hcp crystal lattice rather than simply extending the sphere of interaction to include more and more neighbors.

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Optical Properties of Tellurium in the Fundamental Absorption Region*

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An analysis has been made of the optical absorption edge and reflectivity spectrum of single-crystal tellurium. Transmission measurements, using polarized light, were made between 10 and 300°K covering a range of absorption coefficient from 0.4 cm^{-1} to 5×10^3 cm^{-1}. Below 100°K a sign reversal of the temperature coefficient of the absorption edge was observed for both directions of polarization. The low-absorption region for $\mathbf{E}\parallel c$ showed behavior indicative of indirect transitions, while the absorption edge for $\mathbf{E}\perp c$ varied exponentially with photon energy for over two decades. These features, together with the observation of an exciton at 0.336 eV for $\mathbf{E}\perp c$, are similar in nature to those previously reported for trigonal selenium. Optical constants, such as the real and imaginary parts of the dielectric constant, have been calculated over a wide range of wavelengths at 10°K, as well as at 300°K, by applying the Kramers-Kronig relation to the reflectivity spectrum.

I. INTRODUCTION

The present paper is concerned with the experimental investigation of the optical properties of Te single crystals in the fundamental absorption region. Optical constants such as the real and imaginary parts of the dielectric constant have been calculated over a wide range of wavelengths, at 10°K as well as at 300°K, by applying the Kramers-Kronig relation to the reflectivity spectrum. The temperature and polarization dependences of the absorption edge have been studied between 300 and 10°K in order to elucidate the nature of the transitions involved at the band edge. In extending previous optical data on Te, which facilitate comparison with theoretical attempts to determine its precise energy band configuration, our investigations have shown several interesting features. These include

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