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Energy Bands in Diamond

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Calculations of the valence and conduction bands of a covalent crystal by the augmented-plane-wave (APW) method are carried out in the case of diamond for 256 points in the first Brillouin zone. The bands show an unexpected gap between the first conduction bands and those that lie immediately above them. The calculated position in the Brillouin zone of the conduction-band minimum agrees with that determined experimentally by Warren, Wenzel, and Yarnell by the inelastic scattering of neutrons. It proved necessary to use the average potential between the APW spheres as a disposable parameter in order to obtain a satisfactory energy gap for the bands.

I. INTRODUCTION

CARBON in the diamond form has been investigated from both an experimental[1] and a theoretical[2] standpoint. Numerous energy-band calculations[3] have been made on the diamond crystal. In this paper, the augmented-plane-wave (APW) method is applied to this covalent crystal in order to obtain the band structure. The APW method is described by Slater[4] and Wood[5] and many calculations of the energy bands of metals and other close-packed structures have been made using the method.

The assumed crystal potential and the average potential between the APW spheres provide the principal sources of differences in nonrelativistic energy bands calculated with the APW method. Scop[6] proposed that the average potential between the spheres be used as a disposable parameter in order to fit the band gap determined by experiment. In the present work, Scop's suggestion is adopted and results are calculated for diamond at 20 points in the first Brillouin zone. A brief description of the calculation is contained in the following section, including a discussion of the crystal potential which was used. The results of the calculation are discussed in Sec. III, comparisons with earlier results are made in Sec. IV, and the validity of the APW method for covalent crystals is discussed in Sec. V.

II. DESCRIPTION OF THE CALCULATION

The present nonrelativistic energy-band calculations were carried out using the IBM programs developed by Wood and Nielson.[7] It is convenient to adopt the irreducible representations of the diamond space group given by Slater.[8] A summary of the relevant parameters of the APW calculation is given in Table I. The crystal potential, given in Table II, has been approximated by means of a computer program developed by Mattheiss,[9] who obtains crystal potentials as a superposition of atomic potentials in which contributions of the Coulomb and exchange terms are treated separately. Energy-band calculations were run for four different crystal potentials[10] for the first six bands along the symmetry directions from Γ to X and from Γ to L in order to determine a suitable value for the average

TABLE I. A summary of the values of the basic parameters used in the calculation.

Lattice constant	6.7406 a.u.
APW sphere radius	1.4594 a.u.
Potential at sphere radius	−2.7356 Ry
Average potential between spheres	−1.3928 Ry

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[8] J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill Book Company, Inc., New York, 1963, 1965), Vols. 1 and 2; J. C. Slater, Rev. Mod. Phys. **37**, 68 (1965); J. C. Slater, Massachusetts Institute of Technology, Solid-State and Molecular Theory Group Quarterly Progress Reports No. 46–49 (unpublished); E. R. Keown, *ibid.* No. 51 (unpublished); L. F. Mattheiss, *ibid.* No. 51 (unpublished).

[9] L. F. Mattheiss, Phys. Rev. **133**, A1399 (1964); **134**, A970 (1964); **139**, A1893 (1965).

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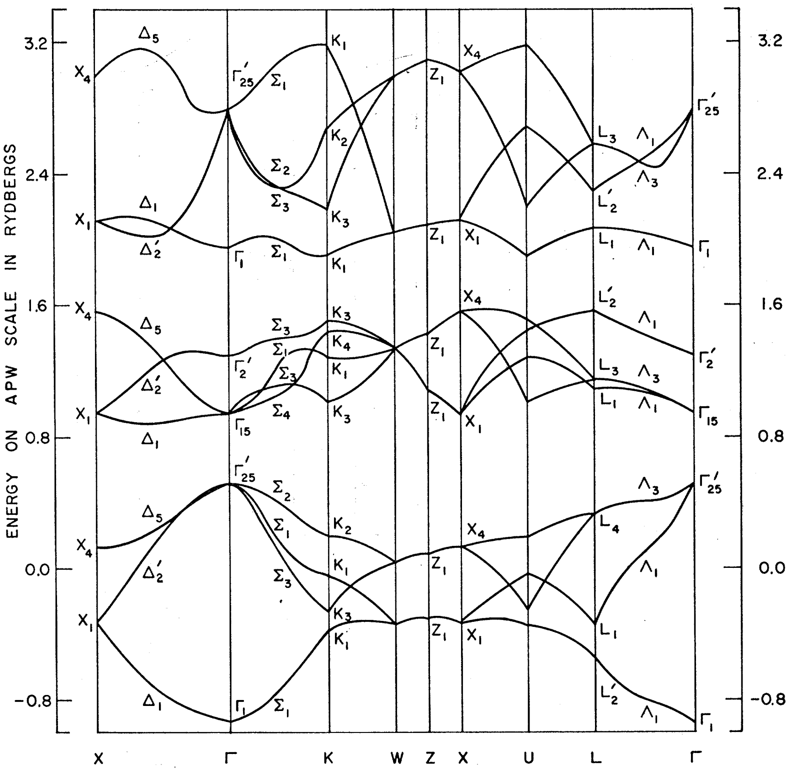

FIG. 1. Energy bands along the principal symmetry directions for diamond. The energy is measured in rydbergs on the APW scale, i.e., with the zero of potential energy taken to lie in the region between the APW spheres. Bands without symmetry labels were drawn using the compatibility relations. Symmetry labels are not given for *W* and *U* since they were analyzed with less than their full symmetry. The coordinates of the **k** vectors are given in Table III.

potential between the APW spheres. The final selection of the average potential was made on this basis. Since the original calculation, Wood[11] has given an explanation of the large discontinuity of the potential at the APW sphere radius.

The basic atomic potential was obtained from Hartree-Fock-Slater atomic charge densities provided by the computer program of Herman and Skillman[12] with the carbon atom taken to be in the configuration $(1s)^2(2s)(2p)^3$, generally accepted as the most appropriate for calculations of the properties of diamond.

The calculations were carried out for the 20 symmetry points of the first Brillouin zone which are listed along with their weights in Table III. By symmetry, these points give a mesh of 256 points in the first zone. The existing APW program is not equipped to treat symmetrized augmented plane waves with complex coefficients. This required that some points on the zone boundary be computed with less than their full sym-

TABLE II. A tabulation of the potential used in the present calculations for carbon. The radial distance is tabulated in terms of r/r_0 (where r_0 is 0.00243611 a.u.) and $V(r)$ is given in rydbergs. The APW sphere radius $R_s=1.4594$ a.u.; the constant value of the potential between the APW spheres equals -1.3928 Ry.

r/r_0	$-V(r)$	r/r_0	$-V(r)$	r/r_0	$-V(r)$	r/r_0	$-V(r)$	r/r_0	$-V(r)$
1	4911.16	24	188.87	72	52.89	172	16.40	380	5.08
2	2448.08	26	173.05	76	49.43	180	15.34	396	4.78
3	1626.98	28	159.49	80	46.34	188	14.39	412	4.51
4	1216.37	30	147.74	84	43.55	196	13.53	428	4.26
5	969.96	32	137.47	88	41.04	204	12.75	444	4.04
6	805.66	34	128.42	92	38.75	212	12.04	460	3.84
7	688.27	36	120.38	96	36.67	220	11.39	476	3.66
8	600.22	38	113.19	100	34.76	228	10.80	492	3.49
9	531.71	40	106.73	104	33.01	236	10.26	508	3.35
10	476.90	42	100.90	108	31.39	244	9.77	524	3.21
11	432.04	44	95.60	112	29.90	252	9.31	540	3.09
12	394.65	46	90.77	116	28.53	260	8.89	556	2.98
13	363.01	48	86.35	120	27.24	268	8.50	572	2.88
14	335.88	50	82.30	124	26.05	276	8.14	588	2.79
15	312.36	52	78.56	128	24.94	284	7.80	604	2.71
16	291.79	54	75.10	132	23.90	292	7.49	620	2.64
17	273.63	56	71.90	136	22.93	300	7.19	636	2.57
18	257.48	58	68.93	140	22.02	316	6.66	652	2.52
19	243.04	60	66.16	148	20.36	332	6.20	668	2.47
20	230.04	64	61.16	156	18.89	348	5.78	684	2.43
22	207.58	68	56.77	164	17.57	364	5.41	700	2.40

TABLE III. A listing of the principal symmetry points in the first Brillouin zone, according to the notation of Bouckaert, Smoluchowski, and Wigner, at which the calculations were made together with their corresponding weight factors. Some points of low symmetry have been given numerical designations.

Name	$4(a/\pi)k$	Weight	Name	$4(a/\pi)k$	Weight
Γ	000	1	11	640	24
Δ	200	6	*W*	840	6
Δ	400	6	*K*	660	4
Δ	600	6	Λ	222	8
X	800	3	15	422	24
Σ	220	12	16	622	24
7	420	24	*U*	822	8
8	620	24	18	442	24
Z	820	12	*Q*	642	24
Σ	440	12	*L*	444	4

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[11] J. H. Wood, Massachusetts Institute of Technology, Solid-State and Molecular Theory Group, Quarterly Progress Report No. 59, 1966 (unpublished).

[12] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963).

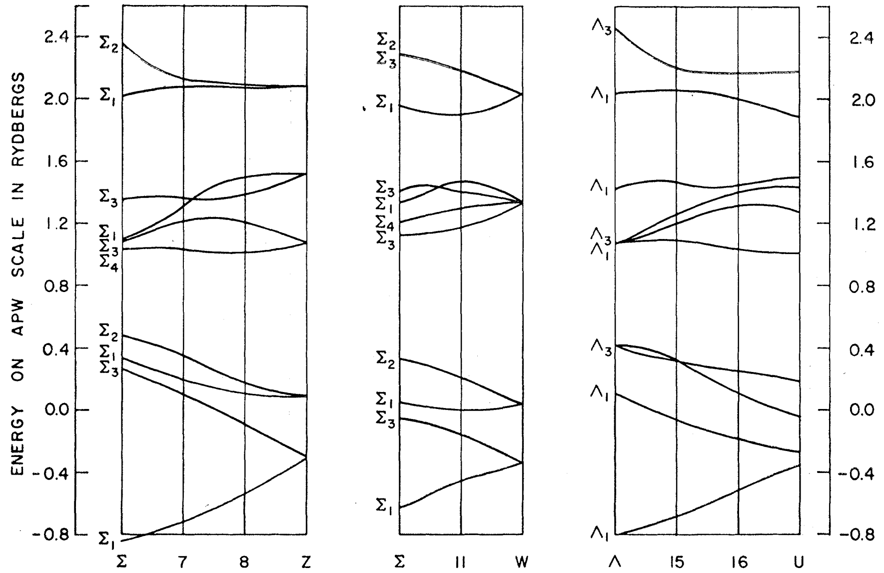

FIG. 2. Energy bands along the minor symmetry directions for diamond. The coordinates of the **k** vectors are given in Table III. The two Σ points, reading from left to right, are $(\pi/4a)(2\ 2\ 0)$ and $(\pi/4a)(4\ 4\ 0)$.

metry. The points *X* and *Z* are calculated with lower symmetry corresponding, in the case of *X*, to an interior point on the axis of symmetry through *X*, and in that of *Z*, to the symmetry plane through *Z*. The point *U* theoretically should have the same energy eigenvalues as the point *K*. Eigenvalues are calculated at *U* with less than normal symmetry.

III. RESULTS

The energy bands along the principal symmetry directions are presented in Fig. 1 and those along the minor directions in Fig. 2. A density-of-states histogram and a smoothed density-of-states curve are given in Fig. 3. These results are based on a rather small sample in **k** space so that their accuracy is limited. For the results presented in Fig. 1, the computed engenvalues at *U* were replaced by those computed at *K*. The results, not modified in this way, are presented in Fig. 2. The eigenvalues at *W* were calculated using the group of the symmetry plane through *W*. For these reasons, the eigenvalues at both *W* and *U* are shown in Figs. 1 and 2 without symmetry labels. Other bands in Figs. 1 and 2 which do not bear symmetry labels were sketched in without the benefit of intermediate calculations. Results at high-symmetry points are collected in Table IV.

TABLE IV. A list of the energy eigenvalues of diamond in electron volts at a number of selected **k** vectors[a] in the first Brillouin zone. Each zero of energy is with respect to the lowest point at Γ_1 in each valence band.

k	Present calculations	Kleinman[b]	Stocker[c]	Bassani[d]	Cohan[e]
Γ_1	0.0	0.0	0.0	0.0	0.0
Γ_{25}'	19.6	21.9	14.7	23.2	25.2
Γ_{15}	25.4	28.0		28.7	34.7
L_2'	5.2	5.6	6.7	5.5	8.8
L_1	8.0	11.7	8.1	8.4	10.9
L_3'	17.2	17.2	14.2	17.8	24.5
L_3	28.2	30.9		28.0	36.7
L_1	27.5	30.9		31.2	35.4
X_1	8.1	10.5	9.4	9.1	12.2
X_4	14.4	15.2	12.0	14.7	21.8
X_1	25.5	29.0		27.8	36.1

[a] The state L_3' is denoted by L_4 in the notation of Slater.
[b] Reference 13.
[c] Reference 14.
[d] Reference 16.
[e] Reference 15.

IV. COMPARISONS WITH EARLIER CALCULATIONS

Earlier calculations with which we shall compare our results are the calculation of Kleinman and Phillips[13] by their version of the orthogonal-plane-wave (OPW) method, the calculation of Stocker[14] by means of linear combinations of bond orbitals, the calculation of Cohan, Pugh, and Tredgold[15] by means of equivalent "bond orbitals," and the calculation of Bassani and Yoshimine[16] by the OPW method. Since the methods employed by Kleinman and Phillips, Bassani and Yoshimine, and the present author are more elaborate than those of the other two calculations, we refer to these three as "the detailed calculations."

The width of the valence band is found to be 14.7 eV by Stocker. The other three results are roughly the same; when averaged together with our value the mean is 22.5 eV. The experimental width of the valence band is found by Chalkin[17] to be 10 eV from measurements of x-ray absorption and emission.

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[13] L. Kleinman and J. C. Phillips, Phys. Rev. **116**, 880 (1959); **125**, 819 (1962).

[14] D. Stocker, Proc. Roy. Soc. (London) **A270**, 397 (1962).

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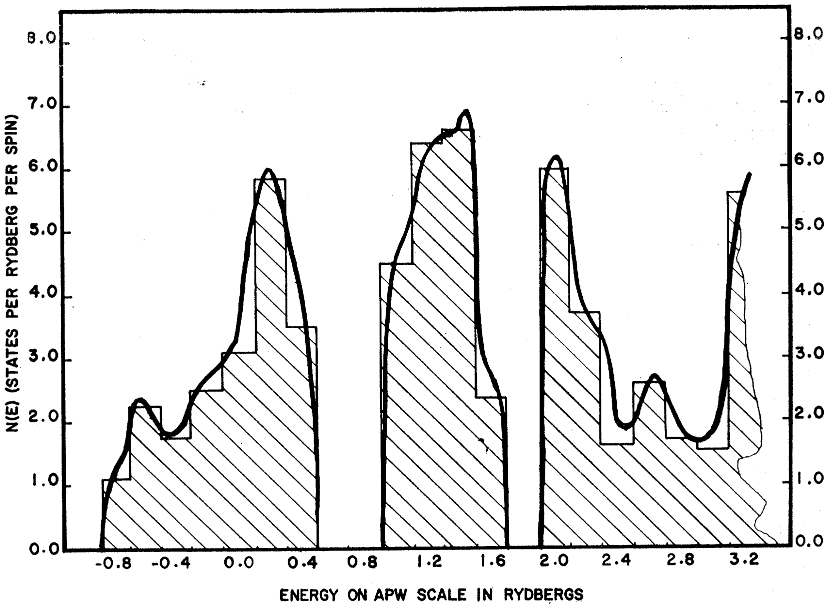

FIG. 3. Density-of-states histogram and curve for the valence and lower conduction bands of diamond. These were prepared from data at 256 points in the first Brillouin zone with a sample size of $\Delta E = 0.2$ Ry.

In diamond, the direct gap at the center of the Brillouin zone occurs between the highest state Γ_{25}' in the valence band and the lowest state Γ_{15} in the conduction band. Cohan and his collaborators find a direct band gap of 9.5 eV here. Stocker does not give a value. The remaining papers obtain similar values for this direct gap, with Bassani and Yoshimine finding the smallest value of 5.5 eV and Kleinman and Phillips finding the largest value of 6.1 eV. The present calculation is based on a value of 5.8 eV for the direct gap at Γ determined by varying the average potential between the APW spheres. The most recent of a number of experimental papers on the absorption edge in diamond appears to be that of Clark, Dean, and Harris[18] who find a value of 5.47 eV for the indirect and 7.02 eV for the direct gap in diamond.

The computed values of the eigenvalues at major symmetry points given in Table IV are compared with corresponding values obtained in the other calculations in this table. In each instance, the eigenvalues are measured with respect to the energy of a Γ_1 state which is the lowest occurring in the valence band. Except for those of the present work, all eigenvalues were estimated from graphs in each of the respective articles.

The over-all nature and appearance of the bands are similar for all five calculations. In each case, the maximum of the valence bands occurs at a triply degenerate Γ_{25}' state while the minimum in the conduction bands occurs along [100] well out towards the zone edge. The width, shape, and curvature of the bands found in the five calculations compare satisfactorily.

There is quantitative agreement in the eigenvalues of the various states at Γ, X, and L. The average of the minimums in the conduction band at Γ_{15} is 29.2 eV, with the present work having the lowest value of 25.4 eV and the calculation of Cohan *et al.* having the highest value of 34.7 eV. The average, omitting the value of Cohan, is 27.4 eV. There is good agreement at the first L_2', the lowest point in the valence band at L, the three detailed calculations obtaining values of 5.2, 5.6, and 5.5 eV while the average of the five is 6.4 eV. The present work, Stocker, and Bassani find values of 8.0, 8.1, and 8.4 eV, respectively, for the values of the lowest L_1 state, while Kleinman and Cohan find values of 11.7 and 10.9 eV, respectively, here. The highest point in the valence band at L is an L_3' state, labeled L_4 in the notation of Slater, where Stocker finds a value of 14.2 eV and Cohan a value of 24.5 eV. On the other hand, the APW, the modified OPW, and the OPW methods give consistent values of 17.2, 17.2, and 17.8 eV, respectively. The bottom of the conduction band at L occurs at 28.2, 30.9, and 28.0 eV for the three detailed calculations in the above order. There is disagreement between the APW and the OPW results about the relative positions of L_1 and L_3 at the bottom of the conduction band at L. The agreement at X is less satisfactory than that at L. The APW bands seem to turn down more at X than do the OPW bands. Actually, the APW calculation was made with partial symmetry at X so that convergence here is not as good as at other symmetry points.

The lowest eigenvalue computed in the conduction band falls at $(\pi/2a)(3\ 0\ 0)$ in the present calculation. Unfortunately, no comparisons were made with nearby points during the calculation to make certain that it is actually a minimum. However, this particular location of the minimum, as computed, coincides with its location obtained by Yarnell, Warren, and Wenzel[19] by

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[18] C. D. Clark, P. J. Dean, and P. V. Harris, Proc. Roy. Soc. (London) **A277**, 312 (1964).

[19] J. L. Yarnell, J. L. Warren, and R. G. Wenzel, Phys. Rev. Letters **13**, 13 (1964); also private communication.

inelastic scattering of neutrons and agrees with both experimental and theoretical results that the minimum in the conduction band is along the [100] axis. Comparisons can be made with a minimum 7/9 of the way to the zone face along the [100] axis in the case of silicon and a minimum along the [111] axis for germanium as given by a number of experiments.[20] The magnitudes of the direct transitions at L are 11.0, 13.7, and 10.2 eV for the APW, the modified OPW, and the OPW methods, respectively. Reflectivity measurements of Phillip and Taft[21] identify the magnitude of the direct transition at L as about 9 eV. The magnitudes of the direct transitions at X are found to be 11.1, 13.8, and 13.1 eV for the three methods, as compared with an experimental value of 12.5 eV quoted by Phillip and Taft.

Although Fig. 3 is based on too few points from which to estimate the density of states accurately, the gross features found in the valence band are similar to those of the experimental density-of-states curve determined by Chalkin from x-ray scattering experiments. On the other hand, the two curves do not agree in detail. The theoretical curve has a sharp edge at higher energies and a trailing edge at lower energies while the experimental curve has the oppositve features. The computed density-of-states curve has five distinct peaks, denoted by P_1 through P_5, reading from left to right.

Recent optical data on diamond,[21,22] although not in total agreement, indicate peaks, M_1 through M_5, in a number of the optical parameters at 7.4, 12.6, 16.0, 20.0, and 24.0 eV. These peaks are identified with the appearance of interband transitions from Γ_{25}' to Γ_{15}, X_4 to X_1, L_3' to L_1 and with less certainty from L_3' to L_3 and L_3' to L_2'. Detailed arguments have been given by J. C. Phillips for these assignments and his conclusions have been reported by Walker and Osantowski.[22] Although these transitions are in agreement with our APW calculation, we have also looked for relations between the peaks in the optical data and those observed in the computed density-of-states curve. With so many peaks, one will find some correlations. The peak in the optical properties at 16.0 eV corresponds closely to the energy difference between P_2 and P_3 in the density-of-states curve and those at 24.0 eV to the difference between P_2 and P_4. The other peaks of the optical data show no particular relations to the peaks in the density-of-states curve.

V. DISCUSSION

The real problem that is involved in applying the APW method to a covalent crystal is the validity and accuracy of introducing a "muffin-tin" potential approximation in these materials. This is closely related to what Herman[23] has classified as three fundamental problems in band theory: (a) How critically do calculated energy bands depend on the form of the assumed potentials? (b) How much error is introduced by taking the same potential for each state? (c) If a self-consistent energy-band solution could actually be obtained on the basis of a particular approximation, how closely would the results agree with experiment?

In the case of diamond, the band structure is stable for calculations performed by different methods with different potentials. Furthermore, there is agreement between the theoretical and the experimental results.

Nevertheless, there is evidence that the "muffin-tin" potential may be unsatisfactory in the case of covalent crystals. Wiff[24] has made a number of APW calculations on germanium, another covalent crystal, with 14 different crystal potentials without obtaining a satisfactory band picture along the principal symmetry directions. The present success with diamond depends upon our use of the suggestion of Scop[6] to use the average potential $V(0)$ between the spheres as a disposable parameter in order to obtain a satisfactory band gap. In the case of diamond, the general shapes of the energy bands maintain themselves under large variations in $V(0)$, although there is some flattening of the conduction bands for large values.[10]

Germanium presents the difficulty that the critical energy eigenvalues of the states Γ_2', Γ_{25}', and Γ_{15}, are highly dependent upon the choice of the average potential between the spheres. For a wide collection of trial crystal potentials, there is a limited range of values of $V(0)$ for which these states have eigenvalues in the proper order, namely, Γ_{25}', Γ_2', and Γ_{15}. The variations in the energy eigenvalues at these points resulting from changes in $V(0)$ have been studied in some detail by Wiff.[24] These variations are remarkably like those reported by Bassani and Yoshimine of the same eigenvalues resulting from changes of the value of the core shift $V^S(0)$. As a matter of fact, it is clear that the use of the core shift $V^S(0)$ as a disposable parameter in OPW calculations is quite analogous to the use of the average potential $V(0)$ between the APW spheres as a disposable parameter in APW calculations. For values of $V(0)$ which have the states at Γ in the proper order, germanium fails to have an indirect band gap by several tenths of a rydberg.

Calculations are presently underway on boron nitride in order to determine whether or not the APW method is satisfactory in the case of a zinc-blende–type crystal of a nature analogous to that of diamond. Since boron

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[20] C. S. Smith, Phys. Rev. **92**, 42 (1954); R. N. Dexter, B. Lax, A. F. Kip, and G. Dresselhaus, *ibid.* **96**, 222 (1954); G. L. Pearson and C. Herring, Physica **20**, 975 (1954); R. N. Dexter, H. J. Zeiger, and B. Lax, Phys. Rev. **104**, 637 (1956).

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[22] W. C. Walker and J. Osantowski, Phys. Rev. **134**, A153 (1964).

[23] F. Herman, Rev. Mod. Phys. **30**, 102 (1958).

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nitride has an even wider band gap than diamond, we are hopeful that the APW method will prove applicable.

ACKNOWLEDGMENTS

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Optical Modes of Vibration in an Ionic Crystal Slab Including Retardation. II. Radiative Region*

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The optical modes of an ionic crystal slab are examined in the radiative region starting from Maxwell's equations including retardation. Since any excitation of the crystal in this region will radiate its energy, it is argued that the modes which characterize the system are virtual modes, which have oscillatory fields outside the slab and correspond to energy transport out of the slab. The determining equations for the virtual modes are obtained and are solved for LiF considering both S and P polarizations and a wide range of slab thicknesses. Characteristics of the modes of particular importance in determining the optical properties of a slab are emphasized. The effect of lattice anharmonicities on the properties of the virtual modes is discussed.

I. INTRODUCTION

In this paper we continue our study of the optical modes of vibration of an ionic crystal slab. Working in the long-wavelength region[1] and the harmonic approximation, the optical modes were obtained initially neglecting the effects of retardation of the Coulomb interactions.[2] We then generalized these results by including retardation in a treatment of the nonradiative region.[3] The present work extends the fully retarded solution of I into the radiative region.

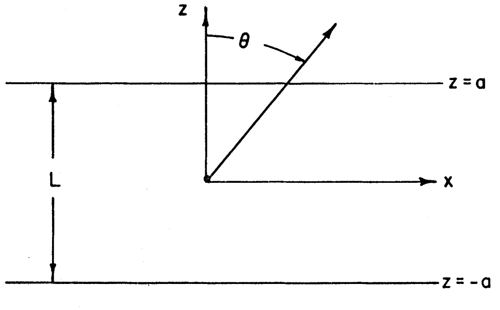

FIG. 1. A diagram giving the orientation of the slab, the thickness parameters, and the definition of θ.

The crystal we continue to examine, oriented as indicated in Fig. 1, is taken to have the NaCl structure. With reference to Fig. 2, the nonradiative region examined in I lies to the right of the line $\omega=k_xc$, where ω is the angular frequency, k_x the wave vector of the fields in the x direction, and c the velocity of light. The present study is thus concerned with the region to the left of the line $\omega=k_xc$.

When retardation of the Coulomb interactions is included, there is a strong coupling between the transverse optical phonons and the photon field.[4] The resultant mixed excitation is called a polariton.[5,6] It was shown in I that polaritons occur in regions L_1 and L_1' of Fig. 2. In terms of the quantities

$$\alpha_0=[k_x^2-(\omega^2/c^2)]^{1/2}, \tag{1.1}$$

and

$$\beta=[\epsilon(\omega^2/c^2)-k_x^2]^{1/2}, \tag{1.2}$$

it was found that the fields decayed exponentially outside the crystal as $\exp(-\alpha_0|z|)$ (hence, the description of the region as nonradiative) and that the equations giving the polariton dispersion relations for P polarization were

$$\epsilon=\frac{i\beta}{\alpha_0}\left(\frac{e^{-i\beta a}\mp e^{i\beta a}}{e^{-i\beta a}\pm e^{i\beta a}}\right), \tag{1.3}$$

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[1] The wavelengths of the excitations are long compared with the interionic spacing.

[2] R. Fuchs and K. L. Kliewer, Phys. Rev. **140**, A2076 (1965).

[3] K. L. Kliewer and R. Fuchs, Phys. Rev. **144**, 495 (1966), to be referred to subsequently as I.

[4] Longitudinal optical phonons are unaffected by retardation effects. Thus the discussion of these vibrational modes for a slab given in Ref. 2 is valid in the present case and no more will be said of them.

[5] U. Fano, Phys. Rev. **103**, 1202 (1956).

[6] J. J. Hopfield, Phys. Rev. **112**, 1555 (1958).