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Polarized Light Transmission of $BaTiO_3$ Single Crystals

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Optical transmission and reflection measurements were made on poled $BaTiO_3$ single crystals in the tetragonal phase (crystal class C_{4v}) with light polarized parallel and perpendicular to the c axis. The absorption coefficients, $\mu_{\|}$ and $\mu_{\perp}$ are presented as functions of the incident photon energy at room temperature. At the absorption edge, $\mu_{\perp} > \mu_{\|}$. A theoretical basis for this selection rule, which has been derived from first principles, is presented. The theory represents a generalization of earlier work on wurtzite crystals and extends the applicability of the wurtzite selection rule to all solids in the crystal classes, C_{nv} and C_n, where $n = 3$, 4, or 6. Limitations of the theory are discussed. The dichroic effect in $BaTiO_3$ has also been studied experimentally at elevated temperatures, in the vicinity of the Curie point. It is concluded that the extrema of the valence and conduction bands of $BaTiO_3$ probably lie at (or very close to) the origin of the Brillouin zone.

I. INTRODUCTION AND THEORY

IN this paper we describe an experimental study of the anisotropic behavior of the fundamental optical absorption process in barium titanate and propose a theoretical interpretation of the results obtained. Recently, substantial experimental and theoretical effort has gone into similar studies of crystals having the wurtzite symmetry. Since, in the point of view adopted here, the barium titanate and wurtzite structures are not unrelated, we shall begin by reviewing briefly the present status concerning wurtzite. Recent experimental work includes that of Dutton[1] and Gross and Razabirin[2] on CdS, Piper, Marple, and Johnson[3] and Keller and Pettit[4] on ZnS, and Thomas[5] on ZnO. For each of these materials one finds that at the absorption edge, light polarized perpendicular to the c axis is much more strongly absorbed than light polarized parallel to the c axis. Hopfield[6] has given a theoretical treatment of Thomas' results in terms of an exciton model. Wheeler[7] has subsequently treated the CdS data using the exciton picture. Paralleling Hopfield's work Birman[8] and Casella[9] independently proposed an explanation of the CdS and ZnS data by invoking direct interband transitions. The theoretical work demonstrates that the selection rule follows whether one assumes an exciton model or one of direct interband transitions. To our knowledge, neither model correctly predicts the frequency dependences of the absorption coefficients of these materials.

Further discussion in this paper will be limited to the interband approach. Both Birman[8] and Casella[9] have pointed out that the selection rule depends critically on the fact that the component of the one-electron momentum, $\mathbf{p}$, parallel to the c axis transforms according to the identity representation of the group $G^{\mathbf{k}}$ of the wave vector, $\mathbf{k}$, at $\mathbf{k}=0$. That is, p_z is invariant under the point-group operations in the group, C_{6v}, where the z axis has been chosen coincident with the c axis of the crystal.[10] Birman has based his conclusions about the selection rule upon explicit assumptions regarding the detailed symmetries of the conduction and valence bands of ZnS, whereas Casella has noted that, at the absorption edge, the selection rule follows independently of the symmetries of the bands, provided only that they be different. The latter viewpoint, coupled with the invariance of p_z under the operations in $G^{\mathbf{k}}$ at $\mathbf{k}=0$ for any crystal possessing a unique unidirectional axis, led us to the conjecture that the selection rule should apply to all solids belonging to the crystal classes C_{nv} where $n=3$, 4, or 6, provided their band extrema lie at $\mathbf{k}=0$.[11]

Since barium titanate belongs to the crystal class C_{4v} at room temperature,[12] it was selected as a prototype to test this assumption, both theoretically and experimentally. The conjecture was verified theoretically for barium titanate for both the single and double groups of $\mathbf{k}$ at $\mathbf{k}=0$ by precisely the same method outlined in reference 9, with the aid of character

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[1] D. Dutton, Phys. Rev. **112**, 785 (1958); and J. Phys. Chem. Solids **6**, 101 (1958).

[2] E. F. Gross and B. S. Razbirin, J. Tech. Phys. U.S.S.R. **27**, 2173 (1957) [translation: Soviet Phys. (Tech. Phys.) **2**, 2014 (1957)].

[3] Piper, Marple, and Johnson, Phys. Rev. **110**, 323 (1958); also Piper, Johnson, and Marple, J. Phys. Chem. Solids **8**, 457 (1959).

[4] S. P. Keller and G. D. Pettit, Phys. Rev. **115**, 526 (1959).

[5] D. G. Thomas, Bull. Am. Phys. Soc. **4**, 154 (1959).

[6] J. J. Hopfield, Bull. Am. Phys. Soc. **4**, 154 (1959).

[7] R. G. Wheeler, Phys. Rev. Letters **2**, 463 (1959).

[8] J. L. Birman, Phys. Rev. Letters **2**, 157 (1959) and Phys. Rev. **114**, 1490 (1959). We wish to thank Dr. Birman for a preprint of his work.

[9] R. C. Casella, Phys. Rev. **114**, 1514 (1959).

[10] This point was overlooked in an earlier work of Dresselhaus. [G. Dresselhaus, Phys. Rev. **105**, 135 (1957).]

[11] Although a crystal in the class C_{2v} also has a unique unidirectional axis, there are two reasons why one might expect the general selection rule not to be valid for C_{2v}. Firstly, unlike the classes we have considered above, C_{2v} is characterized by two inequivalent axes, a and b, perpendicular to the polar c axis. Thus, one might expect the absorption to depend upon whether the light is polarized along the a, b, or c axis. Secondly, the double group of C_{2v} has only one extra irreducible representation. [See, for example, Table XLV of reference 13.] Hence, in the limit of strong spin-orbit interaction, the assumption that the initial and final states have different symmetries is incorrect. In the limit of vanishing spin-orbit interaction, a more detailed analysis shows that one cannot predict the polarization selection rules for crystals in C_{2v} without additional knowledge of the specific symmetries of the conduction and valence bands of each crystal.

[12] W. Känzig, *Solid State Physics* edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 4., p. 1.

tables which are given in a review article by Koster.[13] Since the procedure has already been given, details will not be presented here. The analysis leads to the following result. Treating *k*, the magnitude of the wave vector, as an expansion parameter in a perturbation calculation, one finds that if the first nonvanishing matrix element describing the optical transitions is of order k^n for light polarized perpendicular to the *c* axis, then the first nonvanishing matrix element for light polarized along the *c* axis is of order k^{n+1}. As will be shown in Sec. III, the theory is qualitatively in agreement with the experimental results. That is, at the absorption edge $\mu_\perp > \mu_{\parallel}$ where μ is the absorption coefficient. However, the effect is considerably less pronounced in $BaTiO_3$ than in the wurtzite materials. Further discussion of this point will be given in Sec. IV, which also contains a discussion of the conditions under which the general selection rule applies.

An experimental difficulty occurs because of the lack of a unique *c* axis in a macroscopic barium titanate crystal, resulting from its well-known domain structure.[12] To a considerable extent it is overcome by poling the crystal electrically prior to making the optical measurements. Crystal treatment is discussed further in Sec. II, which is devoted to experimentation.

In order to determine the absorption coefficient as a function of incident photon energy and polarization, transmission as well as reflection measurements were made. The results are presented in Sec. III.

II. EXPERIMENTATION

The apparatus is the same as that described earlier.[4] Light from a high-pressure, dc-operated, Xe lamp was focussed into a Perkin Elmer (PE) 112 monochromator. During transmission measurements the resultant monochromatic light from the PE 112 was passed through the sample crystal into a PE 98 monochromator. Both monochromators were scanned simultaneously with their wavelength settings coincident. The transmitted light was detected and recorded. For reflection measurements the monochromatic light was deflected perpendicular to the plane of the optical path by means of a standard reflectance attachment. The light reflected from the crystal was focussed into the PE 98, which was scanned simultaneously with the PE 112, and subsequently detected and recorded.

Polarized light was obtained with polaroid films from which the cellulose coatings had been removed by dissolving them in acetone in order to increase their transmission in the uv. The polaroid film was placed between the exit slit of the PE 112 monochromator and the sample crystal where it could be rotated to give the desired direction of polarization. Since, in the spectral region of interest, the absorption coefficient is strongly dependent on wavelength, the measurements were taken with the polaroid axis first parallel and then perpendicular to the *c* axis of the crystal, at *fixed* wavelength. This procedure was repeated at closely spaced wavelength intervals. Each transmission and reflection run was corrected for the background light by repeating the measurement with the polaroid in place and the crystal out of the beam. Thus, polarizing effects of the optical instrumentation were cancelled. The efficiency of the polaroids is greater than 98% in the region of interest, i.e., between 360 mμ and 590 mμ. No correction was made for the imperfectness of the polaroids. The detector was an RCA 1P21 photomultiplier tube. Most of the measurements were made at room temperature.

At elevated temperatures the transmission data were obtained by mounting the sample on a brass holder which was inserted in a tubular wire-wound furnace in such a manner that light from the PE 112 could be focussed onto the sample within the furnace. After traversing the sample the light was focussed into the second monochromator. The temperature was recorded by a thermocouple placed in contact with the brass holder.

The $BaTiO_3$ samples were cut from single-crystal plates and electroded on opposite edges. Each electroded crystal was then heated above the Curie point and a

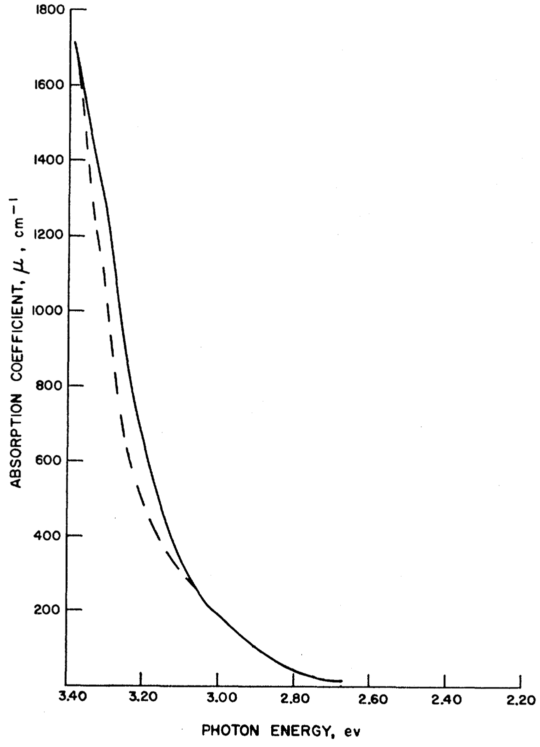

FIG. 1. The absorption coefficient, μ, of $BaTiO_3$ as a function of photon energy. The solid curve represents $\mu_\perp$, the absorption coefficient for light polarized perpendicular to the *c* axis, and the dashed curve represents $\mu_{\parallel}$. The data were obtained at room temperature.

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[13] G. F. Koster, *Solid State Physics* edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 5, p. 173.

field was applied. Next, with the field maintained, the crystal was cooled slowly to room temperature and the field removed. The resultant crystals were "*a*" plates with the tetragonal axis in the plane of the crystals parallel to the direction of the applied field. Measurements were made on four crystals, of which the thinnest was 0.009 cm in thickness. Two of the four were polished. The poled crystals were supplied to us by S. Triebwasser of this laboratory.

III. EXPERIMENTAL RESULTS

The results obtained with the four samples were essentially the same. We shall present data obtained from the thinnest crystal, which was one of the two that were polished. In treating our data we have used the well-known approximate expressions,

$$I_T = I_0(1-R)^2 e^{-\mu t}, \tag{1}$$

$$R = I_R/I_0, \tag{2}$$

where I_0, I_T, and I_R are the intensities of the incident, transmitted, and reflected light, respectively, μ is the absorption coefficient, and t the crystal thickness. Equations (1) and (2) are valid provided one can neglect interference effects due to multiple reflections, i.e., provided $\exp(-\mu t) \ll 1$. As will be seen, for an incident photon energy equal to 3.21 ev, corresponding to the peak in the dichroism, $\mu \sim 600$ cm^{-1}. Thus, even for our thinnest crystal (0.009 cm), this condition is well satisfied in the wavelength region of interest.

By means of the procedure outlined in Sec. II, I_T, I_R, and I_0 were measured directly as functions of incident photon energy, $h\nu$, for both positions of the polaroid. These quantities and the measured thickness were inserted in Eqs. (1) and (2) and values for the coefficients $\mu_\perp$, $\mu_\parallel$, $R_\perp$, and $R_\parallel$ were obtained. The quantities, $\mu_\perp$ and $\mu_\parallel$ are plotted as functions of $h\nu$ in Fig. 1. The coefficient, $\mu_\perp$ assumes values ranging from approximately 2.0 cm^{-1} for $h\nu$ equal to 2.56 ev to about 1700 cm^{-1} at 3.39 ev. At the photon energies quoted $R_\perp$ equals 0.17 and 0.16, respectively, and the ratio $(I_T/I_0)_\perp$ ranges from 0.67 to less than 4×10^{-8}. The magnitude of $R_\perp$ does not vary appreciably with $h\nu$ and exhibits a minimum value, 0.12, for $h\nu$ equal to 2.88 ev. The quantities $\mu_\parallel$, $R_\parallel$, and $(I_T/I_0)_\parallel$ exhibit similar qualitative behavior. Figure 2 depicts the ratio, $100(\Delta\mu/\mu_{\text{Av}})$ as a function of $h\nu$, where $\Delta\mu$ equals $(\mu_\perp - \mu_\parallel)$ and μ_{Av} is the average value of the μ's. We note that at room temperature there is a maximum relative difference between the absorption coefficients at 3.21 ev.

In the wavelength region studied, the difference between the intensities of the reflected beams for light polarized parallel and perpendicular to the *c* axis was considerably smaller than the difference between the intensities of the transmitted beams. Hence, the dichroism exhibited in the transmission measurements is due mainly to differences in the absorption coefficients. A relative measure of the contributions of the two effects can be obtained from the following expression, which is derived from Eq. (1):

$$\mu_\perp - \mu_\parallel = \frac{1}{t}\left\{2\ln\left[\frac{1-R_\perp}{1-R_\parallel}\right] + \ln\left[\frac{(I_T/I_0)_\parallel}{(I_T/I_0)_\perp}\right]\right\}. \tag{3}$$

At the peak in the dichroism the magnitude of the first term in the brackets is less than 1% of the second term.

Since the magnitude of R obtained from Eq. (2) does not vary appreciably with wavelength, it is reasonable to compare it with a value given by the relation

$$R = (n-1)^2/(n+1)^2, \tag{4}$$

where n is the index of refraction at a wavelength where the crystal is nonabsorbing. Inserting a published value,[14,15] 2.4 for n in Eq. (4) we obtained the result $R = 0.17$. The results compare favorably.

As is the case for the wurtzite materials, the frequency dependences of the absorption coefficients do not follow the integral or half-integral power laws predicted by theory for the various models. Between the values of 30 cm^{-1} and 1000 cm^{-1} the dependences are approximately exponential.

We have also investigated the dichroic effect at elevated temperatures. The dichroic peak, which is located at 3.21 ev at room temperature, shifted to 3.17 ev at 112°C. The shift in the position of the peak was accompanied by a decrease in its height. As a further check on our instrumentation we verified that the dichroism disappears above the Curie point, where

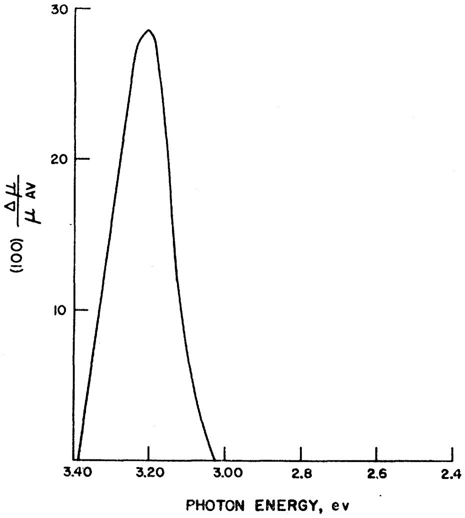

FIG. 2. The percentage difference in the absorption coefficients, $(100)(\mu_\perp - \mu_\parallel)/\mu_{\text{Av}}$, *versus* photon energy. The measurements were made at room temperature.

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[14] W. J. Merz, Phys. Rev. **76**, 1221 (1949).

[15] Recently the birefringence of BaTiO$_3$ has been studied extensively by Meyerhofer [D. Meyerhofer, Phys. Rev. **112**, 413 (1958)].

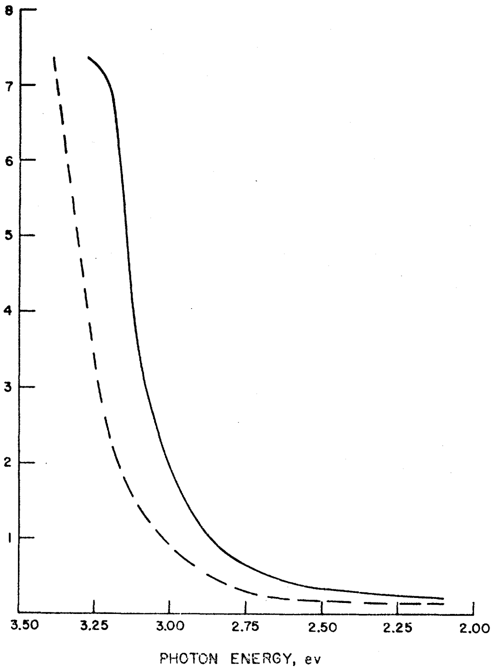

FIG. 3. The optical density, $A=\log(I_0/I_T)$ *versus* photon energy at two temperatures. The solid and dashed curves represent data obtained at 135°C and room temperature, respectively. The measurements were made with unpolarized light.

$BaTiO_3$ is known to exist in the cubic phase. The measurement was actually made at 135°C, well above the Curie temperature.

Finally, we have measured the optical density, A, equal to $\log(I_0/I_T)$, at room temperature and at 135°C, using unpolarized light. The results are compared in Fig. 3. The room temperature data agree with those of Iatsenko.[16] It is seen that the absorption edge shifts toward longer wavelengths with increasing temperature. The magnitude of the shift between the two temperatures is 0.14 ev. The result is in agreement with the findings of Horie, Kawabe, and Sawada.[17]

IV. DISCUSSION

As shown in Sec. III, the experimental results agree qualitatively with the theoretical prediction. Quantitatively, however, there exists a major distinction between the agreement recorded here and that discussed in Sec. I for materials having the wurtzite symmetry. For the wurtzite crystals $\mu_\perp$ generally exceeds $\mu_\parallel$ by an order of magnitude at the absorption edge, whereas for $BaTiO_3$, $(\Delta\mu/\mu)$ is only about 29% at the peak in the dichroism (Fig. 2). Since the theory[9,10] deals with transition probabilities, proportional to the squares of matrix elements which either vanish or do not in a given order of a perturbation expansion in the wave vector, an order of magnitude effect is more readily understood in the terms of the theory than one expressed in terms of relatively small percentages. There are two reasons which might explain the smallness of the observed dichroic effect in $BaTiO_3$ as compared with the wurtzite structures, even though the assumptions of the theory may be strictly fulfilled. We shall consider these first and subsequently discuss the assumptions and their effect in limiting the generality of the theory.

Firstly, we did not ascertain whether or not we had achieved complete alignment of the crystal domains (Sec. II). The samples appeared uniform when viewed through crossed polaroids. However, this does not rule out the existence of small regions in which the c axis is aligned parallel to the crystal faces but normal to the direction in which the crystal was poled. Secondly, when $BaTiO_3$ is in the tetragonal phase, the deviation of the unit cell from cubic is rather small.[18] In fact, as is well known, the polarity of the crystal can be reversed readily upon application of moderate electric fields. In contrast, the wurtzite crystals do not exhibit ferroelectricity. If the atomic displacements are sufficiently small, one can regard the polarity of the lattice as a perturbation upon the electronic wave functions[19] which transform according to the group O_h in zeroth order rather than according to C_{4v}. From this point of view, the crystal field which introduces the critical symmetry property (see Sec. I) enters only as a first-order correction and the smallness of the dichroic effect is understandable. The reasoning can perhaps be stated better in terms of an example. Suppose, for definiteness, that the valence band wave functions at $\mathbf{k}=0$ are primarily composed of p-type atomic orbitals in the tight-binding approximation. Then, in the cubic phase there is a threefold degeneracy at $\mathbf{k}=0$, if we disregard the spin degeneracy for simplicity. The wave functions transform like the linear polynomials, x, y, z. In the tetragonal phase a singly degenerate band corresponding to, say, the z function is split off from a doubly degenerate band corresponding to the x and y functions. Our assumption is that the smallness of the atomic displacements involved in the transition from the cubic to the tetragonal phase implies that the energy separation between the z and x, y bands is small. Thus, as the wave vector departs from the origin of the Brillouin zone, the z and x, y functions undergo considerable mixing via the $\mathbf{k}\cdot\mathbf{p}$ perturbation in a way that has been discussed in references 9 and 10. As a result of this mixing the optical transition probabilities for the two polarizations approach each other at relatively small values of k.

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[16] A. F. Iatsenko, J. Tech. Phys. U.S.S.R. **27**, 2422 (1957) [translation: Soviet Phys. (Tech. Phys.) **2**, 2257 (1957)].

[17] Horie, Kawabe, and Sawada, J. Phys. Soc. (Japan) **9**, 823 (1954).

[18] See reference 12, pp. 162–164.

[19] This viewpoint has also been adopted, in a somewhat different context, by Triebwasser [S. Triebwasser, J. Phys. Chem. Solids **3**, 53 (1957)].

The following remarks concerning the assumptions of the theory generally apply to all solids in the crystal classes[20] C_{3v}, C_{4v}, and C_{6v}. Our derivation of the selection rule is based on the following assumptions: (1) The relevant energy-band extrema lie at $\mathbf{k}=0$; (2) the electronic transitions are direct from the valence band to the conduction band; (3) the wave functions of the electrons at the two band extrema belong to different irreducible representations of the group of $\mathbf{k}$, $G^{\mathbf{k}}$. Of these, the first is certainly the most severe in limiting the applicability of the theory. The cubic semiconductors, Ge and Si are obvious examples suggesting the possibility of exceptions to this assumption among the crystals we are considering. The possibility of violating the third assumption is believed unlikely, but cannot be disregarded. There exist three types of optical transitions which are excluded by assumptions (1) and (2), but for which, nevertheless, the selection rule is believed to be valid. The first, and most trivial, is one where the band extrema do not lie precisely at $\mathbf{k}=0$ but are displaced slightly due to a small spin-orbit interaction. This case has been discussed with respect to the wurtzite systems in reference 9. The second concerns Dumke's[21] mechanism for indirect vertical transitions at $\mathbf{k}=0$, which he applied to InSb. In the event that the first assumption is grossly incorrect the symmetry analysis may be applied to the theory of indirect transitions due to Hall, Bardeen, and Blatt.[22] The conditions under which the selection rule may still apply have been discussed in references 8 and 9. Birman[8] has noted that, in the case of wurtzite, the rule ought to be valid even if the extrema are displaced from the origin by a considerable amount along the k_z axis. We believe his comment also applies to the general systems we have considered. Thus, the applicability of the rule to indirect transitions involving multiple valleys centered on the k_z axis constitutes the third relaxation of our initial assumptions.

V. CONCLUSIONS

From our experimental results we tentatively conclude that the selection rule applies to $BaTiO_3$. We believe the smallness of the atomic displacements involved in the transition from the cubic to the tetragonal phase explains why the dichroic effect is less pronounced than it is in the wurtzite materials. Assuming our interpretation, we may infer that probably the transition is direct and that the conduction and valence band extrema lie at (or very close to) $\mathbf{k}=0$, although other possibilities clearly exist. Moreover, there may be several closely spaced sub-bands in the neighborhood of one or both of the band edges.

We have shown theoretically that the selection rule applies to a considerable number of anisotropic crystals. In addition to the crystal classes we have considered above, the rule also applies to the relatively low-symmetry crystals associated with the cyclic point groups, C_3, C_4, and C_6.[23] Moreover, it has been derived independently of the symmetry types of the valence and conduction bands and applies to a variety of models. Thus, it provides an additional tool for investigating the band structures of these solids and allows interpretation of optical data in cases such as $BaTiO_3$ where the order of levels has not been ascertained by energy-band calculations.

ACKNOWLEDGMENTS

The generalization of the wurtzite selection rule occurred to one of us as a result of discussions with R. Landauer. We are also grateful to G. D. Pettit for assistance with the measurements and to S. Triebwasser and G. Cheroff for helpful discussions.

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[20] The applicability of the selection rule to crystals in the class C_{3v} was also verified theoretically within the limitations discussed in this section.

[21] W. P. Dumke, Phys. Rev. **108**, 1419 (1957).

[22] Hall, Bardeen, and Blatt, Phys. Rev. **95**, 559 (1954).

[23] The derivation is essentially the same as for the groups C_{nv}. As is the case for C_{3v}, the effects of time-reversal symmetry are nontrivial for the cyclic groups. These have been taken into account where necessary. The limitations discussed in Sec. IV also apply here. We are grateful to Professor H. Juretschke for bringing these additional systems to our attention.