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Optically Active Phonon Processes in CdS and ZnS*

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Transmission spectra of thin (10 to 30 μ) CdS single-crystal samples have been recorded in the hitherto uninvestigated region of 250 to 400 cm^{-1}. A number of new absorption maxima are located which necessitated a new phonon assignment with considerably lower values of the acoustic modes. Some 30 absorption peaks are attributed to multiphonon combinations of the following Brillouin zone-edge frequencies: LO$=295$ cm^{-1}, TO$_1=261$ cm^{-1}, TO$_2=238$ cm^{-1}, LA$=149$ cm^{-1}, TA$_1=79$ cm^{-1}, and TA$_2=70$ cm^{-1}. The transmission spectrum of hexagonal ZnS is obtained for the first time in the region 300 to 750 cm^{-1}. Again some 27 absorption maxima are assigned to multiphonon combinations of LO$=346$ cm^{-1}, TO$_1=318$ cm^{-1}, TO$_2=297$ cm^{-1}, LA$=181$ cm^{-1}, TA$_1=92$ cm^{-1}, and TA$_2=73$ cm^{-1}. The phonon assignment for the optical lattice absorption in cubic ZnS due to Deutsch is shown to be inconsistent with the requirements of the Brout sum rule and other regularities expected for the zincblende-type semiconductors. Two new assignments (LO$=339$ cm^{-1}, TO$=298$ cm^{-1}, LA$=155$ cm^{-1}, and TA$=93$ cm^{-1}, and LO$=339$ cm^{-1}, TO$=298$ cm^{-1}, LA$=190$ cm^{-1}, and TA$=115$ cm^{-1}) only slightly different from each other are proposed. The characteristic phonon frequencies are discussed in terms of structure and effective ionic charge.

1. INTRODUCTION

INFRARED lattice absorption arising from multiphonon combinations has been observed in many group III–V compounds and group IV elements.[1,2] The combination bands are a continuous absorption. However, peaks in absorption occur because of singularities in the phonon frequency distribution. These singularities arise from critical points in the Brillouin zone where the frequency wave vector (**k**) curves have zero slope. Such critical points are believed to occur at or near the zone boundary. Usually the critical point characterizes a phonon branch and the combination bands may be classified into summations or differences of the longitudinal optical (LO), transverse optical (TO), longitudinal acoustic (LA) and transverse acoustic (TA) phonons at the zone edge. The interaction of an infrared photon with the lattice vibrations are governed only by the conservation of energy and wave vector. Turner and Reese[1] have assigned some forty components in the lattice absorption of AlSb in this manner.

Only a limited amout of experimental evidence of these effects has been obtained for group II–VI compounds. Mitra[3] has recently explained the infrared absorption observed in ZnSe by Aven *et al.*[4] in terms of phonon combinations, and it appears that the conditions are similar to those governing the behavior of III-V compounds. In the case of CdS, Collins[5] using the reflection technique located the zone-center optical transverse mode at 241 cm^{-1}. Subsequently, Balkanski and Besson[6] reported seven absorption maxima between 400 and 600 cm^{-1} which were assigned to various binary combinations using four assumed characteristic frequencies. Spitzer[7] has recently shown that the same two-phonon bands can also be explained by another set of four-phonon frequencies; one of which is different from those used by Balkanski and Besson. Deutsch[8] has reported a few additional bands, resolved under polarized radiation, in the same region. He proposed two different sets of assignments which almost fully explained his own observations but failed to explain some of the bands reported by Balkanski and Besson. Mitra[9] observed further absorption bands in the region 600–1400 cm^{-1} and used a five-frequency assignment for a comprehensive explanation. They were composed of the four frequencies of Balkanski and Besson and the alternative frequency of Spitzer.

All transmission measurements on CdS to date have been confined to frequencies greater than 400 cm^{-1}, despite the observation of Collins that the zone-center transverse optical-mode phonon has a value of 241 cm^{-1}. Thus, it was felt that a transmission study in the region below 400 cm^{-1} could provide additional important information, particularly regarding the low-frequency characteristic phonons. These were considerably larger than in the case of ZnSe[3] and the III–V compounds.[1] Furthermore, if the proposed frequencies are designated LO, TO, LA, and TA phonons, there is a lack of consistency with various correlations described by Keyes,[10] Mitra,[3] and Mitra and Marshall,[11] including the Brout sum rule.[12] It was also anticipated that by using very thin crystals, structure in the broad absorption bands would be resolved and be of considerable assistance in obtaining a reliable assignment.

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[2] J. R. Hardy and S. D. Smith, Phil. Mag. **6**, 1163 (1961).

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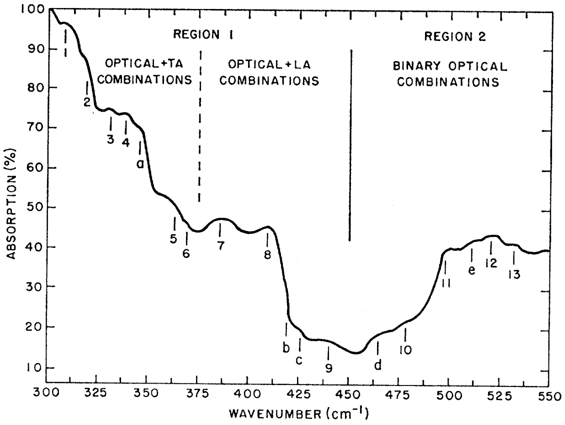

FIG. 1. Transmission spectrum of CdS in the region 300 to 550 cm^{-1}.

In the case of ZnS, Deutsch[13] has studied absorption in the cubic modification, over the frequency range 410–830 cm^{-1}. His assignment fails to explain the strong absorption at 431 cm^{-1}. Furthermore, the characteristic frequencies used (particularly the low-frequency value), as in the case of CdS, do not conform with the correlations mentioned earlier. Thus a new assignment for cubic ZnS, with lower values for the acoustic branches, seemed necessary.

Lattice absorption in hexagonal ZnS is reported here for the first time. Thin crystals have been used in order to cover the optical-acoustical phonon combination region and to resolve the structure involved in the anticipated removal of degeneracy of the zone-boundary TO mode and possibly the TA mode as well.

2. EXPERIMENTAL

Platelet crystals of CdS and ZnS, grown from the vapor phase by nucleation on a quartz seed as described by Fochs and Lunn,[14] were used in this investigation. This growth technique yields thin crystals ($\sim$10 μ) of high optical quality and low impurity content, but relatively small surface areas ($<$0.5 cm^2).

Absorption data was obtained for both compounds over the region 300–800 cm^{-1} using a Perkin Elmer double-beam spectrometer (model 521) with grating optics.

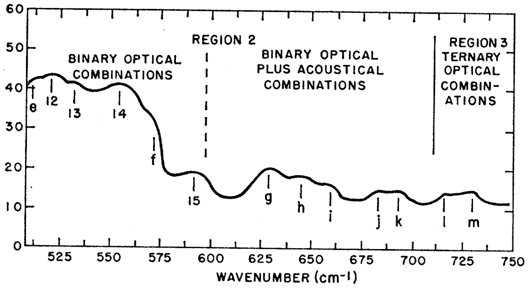

FIG. 2. Transmission spectrum of CdS in the region 525 to 750 cm^{-1}.

3. ANALYSIS OF SPECTRA

a. CdS

The absorption spectrum is shown in Figs. 1 and 2, and the positions of the bands observed listed in Table I. The absorption spectrum may be conveniently divided into three regions: (1) the group of strong bands below 450 cm^{-1}, (2) bands of medium absorption between 450 and 710 cm^{-1}, and (3) the weak bands above 700 cm^{-1}. Since the zone-center transverse optical-phonon frequency as determined by Collins is at 241 cm^{-1}, these three regions may be considered as arising from one, two, and three optical-phonon processes. First, considering the second region the six prominent bands [Nos. 10, 11, 12, 13 (Fig. 1) and Nos. 14 and 15 (Fig. 2)] are assigned to various binary combinations of the three zone-boundary optical phonons, LO = 295 cm^{-1}, TO$_1$ = 261 cm^{-1}, and TO$_2$ = 238 cm^{-1}. It may be commented here that the first two char-

TABLE I. Assignment of the absorption maxima observed in CdS in terms of phonon combinations of frequencies (cm^{-1}):

$$\mathrm{LO}=295 \quad \begin{matrix}\mathrm{TO}_1=261\\ \mathrm{TO}_2=238\end{matrix} \qquad \mathrm{LO}=149 \quad \begin{matrix}\mathrm{TA}_1=79\\ \mathrm{TA}_2=70\end{matrix}$$

Band No.	Present study (300°K) cm^{-1}	Balkanski and Besson (77°K) cm^{-1}	Deutsch (77°K) cm^{-1}	Assignment	Calcd. cm^{-1}	Calcd.–Obsd.
1	308			$\mathrm{TO_2+TA_2}$	308	0
2	318			$\mathrm{TO_2+TA_1}$	317	−1
3	331			$\mathrm{TO_1+TA_2}$	331	0
4	340			$\mathrm{TO_1+TA_1}$	340	0
a	347			$\mathrm{TO_1+TO_2-LA}$	350	+3
5	365			$\mathrm{LO+TA_2}$	365	0
6	374			$\mathrm{LO+TA_1}$	374	0
7	387			$\mathrm{TO_2+LA}$	387	0
		403				
8	410			$\mathrm{TO_1+LA}$	410	0
b	421			$\mathrm{TO_1+TO_2-TA_1}$	420	−1
c	428		432	$\mathrm{TO_1+TO_2-TA_2}$	429	+1
9	442		443	$\mathrm{LO+LA}$	444	+2
d	467			$\mathrm{TO_2+LA+TA_2}$	466	−1
10	478			$\mathrm{2TO_2}$	476	−2
11	498	500	502	$\mathrm{TO_1+TO_2}$	499	−1
e	511			$\mathrm{2LO-TA_1}$	511	0
12	522	524	526	$\mathrm{2TO_1}$	522	0
13	533	540		$\mathrm{LO+TO_2}$	533	0
14	555	562	562	$\mathrm{LO+TO_1}$	556	+1
f	571	579	576	$\mathrm{TO_1+TO_2+TA_2}$	569	−2
15	590	599	598	$\mathrm{2LO}$	590	0
g	628			$\mathrm{LO+TO_1+TA_2}$	626	−2
h	647			$\mathrm{TO_1+TO_2+LA}$	648	+1
i	660			$\mathrm{2LO+TA_2}$	660	0
j	684			$\mathrm{LO+TO_2+LA}$	682	−2
k	695			$\mathrm{LO+TO_1+2TA_2}$	696	+1
l	715			$\mathrm{3TO_2}$	714	−1
m	730			$\mathrm{2LO+2TA_2}$	730	0
	795a			$\mathrm{LO+TO_1+TO_2}$	794	−1
	1045 (broad and weak)[a]			$\mathrm{LO+2TO_1+TO_2}$	1055	+10
	1345 (broad and weak)[a]			$\mathrm{2LO+2TO_1+TO_2}$	1350	+5

[a] Reported earlier (Ref. 9).

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[13] T. Deutsch, in *Proceedings of the International Conference on Semiconductors, Exeter, 1962* (The Institute of Physics and Physical Society, London, 1962), p. 505.

[14] P. D. Fochs and B. Lunn, J. Appl. Phys. 34, 1762 (1963).

acteristic phonons have been considered by all the previous investigators, Balkanski and Besson, Deutsch, Spitzer, and Mitra. Since the zone-center value of the transverse phonon is 241 cm^{-1}, it seems reasonable that the zone-boundary phonons should split into 261 and 238 cm^{-1} in the hexagonal wurtzite structure.

Balkanski and Besson have studied the temperature dependence of the prominent bands in the two-optical-phonon region. In Table II, we have made a comparison, based on our assignment, between the calculated and observed values of the absorption coefficient at 80 and 293°K. It may be shown[15] that the net power absorbed in a two-phonon summation band $\nu_n+\nu_k$ is proportional to

$$\alpha_c=1+F_n+F_k\,, \tag{1}$$

where

$$F_n=[\exp(hc\nu_n/kt)-1]^{-1}\,, \tag{2}$$

and ν_n = wave number of the nth phonon. Thus the terms f_c and f_0 listed in Table II are

$$f_c=\alpha_c(80°\mathrm{K})/\alpha_c(293°\mathrm{K})\,, \tag{3}$$

and

$$f_0=\alpha_0(80°\mathrm{K})/\alpha_0(293°\mathrm{K})\,, \tag{4}$$

where α_0 is the observed absorption coefficient at the peak absorption after correction for background. The excellent agreement shown in Table II between the calculated and the observed temperature dependencies, although perhaps a bit fortuitous, is a further confirmation of the essential correctness of the assignment of the optical modes.

Table II. Comparison of the observed and predicted temperature dependence of the optical phonon combinations in CdS.

Peak position cm^{-1}	Assignment	Observed[a] f_0	Calculated f_c
498	TO_1+TO_2	0.56	0.556
522	$2TO_1$	0.57	0.574
533	$LO+TO_2$	0.60	0.578
555	$LO+TO_1$	0.64	0.598
590	2LO	0.63	0.624

[a] Determined from Balkanski and Besson's data (Ref. 6).

Having obtained the optical-mode frequencies, the acoustical-mode frequencies at the zone boundary are obtained from the prominent bands in region (1). A perusal of region (1) reveals that one may further subdivide it into two groups: one above and one below 375 cm^{-1}. The three bands at 387, 410, and 442 cm^{-1} (numbers 7, 8, and 9, respectively, in Fig. 1) seem an obvious choice for the bands arising from combinations of the three optical modes with the longitudinal acoustical mode at the zone boundary. Each one of them yields a value close to 149 cm^{-1} for LA. Below 375 cm^{-1} there are six prominent bands (Nos. 1 to 6 in Fig. 1). They occur as three pairs, each with an average splitting of 9 cm^{-1}. This splitting is attributed to two transverse acoustical phonons, which, like the transverse optical phonons, seem to be in order for the wurtzite structure. The two zone-boundary acoustical phonons assigned in this manner are TA_1 = 79 cm^{-1} and TA_2 = 70 cm^{-1}. The complete assignment for all the observed absorption maxima is presented in Table I.

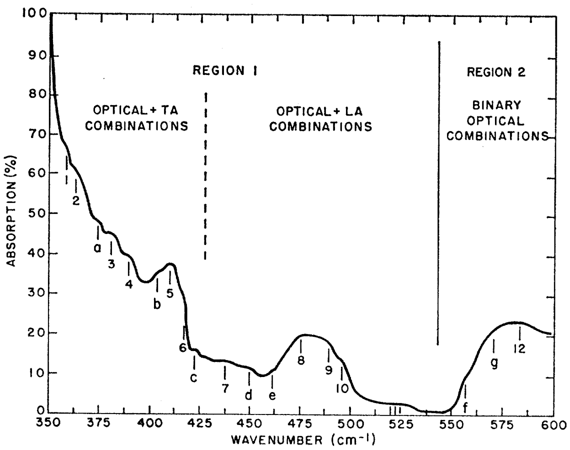

Fig. 3. Infrared absorption in wurtzite ZnS (350 cm^{-1} to 600 cm^{-1}).

b. Wurtzite ZnS

The absorption spectrum of wurtzite ZnS is shown in Figs. 3 and 4 and the band positions are listed in Table III. In this case, the absorption regions are not as clearly defined as in CdS, but similar broad classifications can be made: region 1—below 545 cm^{-1}, can further be divided into regions above and below 430 cm^{-1}; region 2—between 545 and 700 cm^{-1}, and region 3—above 700 cm^{-1}.

The absorption in region 2 is again thought to arise primarily from the binary combination of optical phonons with assumed characteristic phonon frequencies, LO = 346 cm^{-1}, TO_1 = 318 cm^{-1}, and TO_2 = 297 cm^{-1}. In region 1 two areas are distinctive, comprising

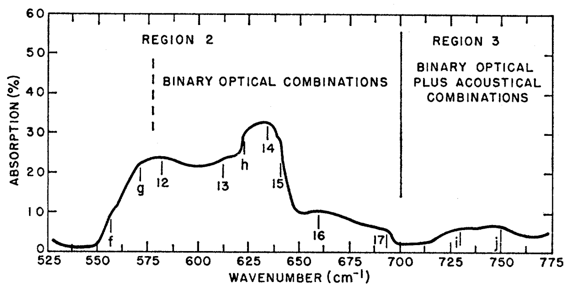

Fig. 4. Infrared absorption in wurtzite ZnS (525 cm^{-1} to 775 cm^{-1}).

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[15] W. Cochran, S. J. Fray, J. A. Johnson, J. E. Quarrington, and N. Williams, J. Appl. Phys. 32, 2102 (1961).

TABLE III. Assignment of the lattice absorption in hexagonal ZnS in terms of the phonon frequencies (cm^{-1}):

$TO_1=318$ $TA_1=92$
$LO=346$ $LA=181$
$TO_2=297$ $TA_2=73$

Band No.	Peak position at 300°K cm^{-1}	Assignment	Calcd. cm^{-1}	Calcd.–Obsd.
1	358	TO_2+TA_2	360	+2
2	362	2LA	362	0
a	374	$2LO-TO_1$	374	0
3	381	TO_2+TA_1	383	+2
4	390	TO_1+TA_2	391	+1
b	404	$TO_1+LA-TA_1$	406	−2
5	409[a]	TO_1+TA_1	409	0
6	419	$LO+TA_2$	419	0
c	423	$TO+LA-TA_2$	425	+2
7	437	$LO+TA_1$	437	0
d	450	$TO_1+TA_1+TA_2$	452	+2
e	463	TO_1+2TA_2	464	+1
8	475[a]	TO_2+LA	474	−1
9	487	$TO_1+TA_1+TA_2$	483	−4
10	498	TO_1+LA	500	+2
11	526	LO+LA	528	+2
f	555	$LO+TO_2-TA_1$	551	−4
g	571	$TO_1+LA+TA_2$	572	+1
12	583[a]	$2TO_2$	584	+1
13	612	TO_1+TO_2	610	−2
h	622	$LO+LA+TA_1$	620	−2
14	634[a]	$2TO_1$	636	+2
15	640[a]	$LO+TO_2$	638	−2
16	658	$LO+TO_1$	658	0
17	694	2LO	692	−2
i	730	$LO+TO_2+TA_1$	730	0
j	750	$2LO+TA_1$	750	0

[a] Relatively intense bands.

the absorption maxima arising from the combination of the optical phonons with the zone boundary TA (between 370 and 450 cm^{-1}) and with the zone boundary LA (between 435 and 525 cm^{-1}) phonons. Six components are observed in the optical-plus-TA region, and again it has been necessary to assume that the TA modes are nondegenerate. Characteristic phonon frequencies of $TA_1=92$ cm^{-1} and $TA_2=73$ cm^{-1} predict the observed structure in the absorption spectrum with good accuracy. From the optical-plus-LA combination bands (8, 10, 11, Fig. 3), a value of $LA=181$ cm^{-1} has been obtained. This also explains the relatively intense absorption band observed at 362 cm^{-1} as a 2LA combination.

c. Zincblende ZnS

The lattice infrared spectrum of cubic ZnS single crystals was investigated by Deutsch.[13] The reflectivity was measured between 15 and 34 μ. The reststrahlen band with a reflectivity maximum at 30.8 μ was located. A Kramers-Kronig dispersion analysis of the reststrahlen band gave a value of 312 cm^{-1} for the zone-center transverse optical phonon (ν_t). The transmission spectrum of cubic ZnS was measured between 1 and 24 μ by Deutsch. The transmission is essentially constant up to 14 μ. Ten absorption maxima were observed at longer wavelengths between 430 and 820 cm^{-1}. These bands were attributed to optically active two- and three-phonon processes. Using characteristic zone-boundary phonon frequencies of $A=379$ cm^{-1}, $B=297$ cm^{-1}, $C=263$ cm^{-1}, and $D=228$ cm^{-1}, Deutsch could explain seven out of the ten observed bands.

Since a diatomic cubic crystal usually has two optical and two acoustic branches, the higher two phonons must be from optical and lower two from acoustic branches. In a predominantly ionic crystal like ZnS, one would expect that the LO modes should have a higher frequency than the TO modes throughout the Brillouin zone. One may thus identify the four characteristic phonon frequencies, A, B, C, and D assigned by Deutsch as zone boundary LO, TO, LA, and TA, respectively. However, a comparison[3] with the phonon frequencies of the other zincblende-type crystals reveals that the acoustical phonon frequencies as assigned by Deutsch are unusually large. Furthermore, since the zone-center longitudinal optical phonon frequency (ν_l) is 377 cm^{-1} as calculated from the Lyddane-Sachs-Teller formula,[16] a value of 379 cm^{-1} for the zone boundary LO seems improbable. The Brout sum at the zone center amounts to 1.200×10^{28} sec^{-2} as compared with a value of 1.754×10^{28} sec^{-2} near the zone edge. This large difference (45%) is quite unexpected for a predominantly ionic cubic crystal such as ZnS, and may be attributed to high values of LA and TA phonons as assigned by Deutsch. The discrepancy is even larger if one uses the ν_t given by Mitsuishi, Yoshinaga, and Fuyita.[17]

A fresh assignment of the zone-boundary characteristic phonon frequencies of cubic ZnS with lower values of the acoustic modes has therefore been attempted.

TABLE IV. Assignment of the multiphonon absorption bands in cubic ZnS.

	Deutsch		Present study			
Observed[a] cm^{-1}	Assignment[f]	Calc. (cm^{-1})	Assignment 1[g]	Calc. (cm^{-1})	Assignment 2[h]	Calc. (cm^{-1})
431[b] 415[c]	···	···	LO+TA	432	TO+TA	413
455	$2D$	456	TO+LA	453	LO+TA	454
491[b]	$C+D$	491	LO+LA	494	TO+LA	488
526	$2C$, $B+D$	526	LO+2TA	525	LO+LA	529
593[b]	$2B$	594	2TO	596	2TO	596
605[d]	···	···	TO+2LA	608	LO+LA+TA	603
642[b]	$A+C$	642	LO+TO	637	LO+TO	637
677[b]	$A+B$	677	2LO	678	2LO	678
733[e]	···	···	LO+TO+TA	731	LO+2LA	719
823	$2B+D$	822	LO+TO+2TA	824	LO+TO+LA	827

[a] Data from Deutsch (Ref. 13).
[b] Relatively stronger bands.
[c] Although Deutsch lists a value of 431 cm^{-1}, this band appears to be beyond the range of his observation. A lower value seems probable both from the extrapolation of his spectrum and from a comparison of his spectrum with that of the hexagonal modification reported in this paper.
[d] Not listed by Deutsch but is apparent from his spectra.
[e] Broad and very weak.
[f] $A=379$ cm^{-1}, $B=297$ cm^{-1}, $C=263$ cm^{-1}, and $D=228$ cm^{-1}.
[g] $LO=339$ cm^{-1}, $TO=298$ cm^{-1}, $LA=155$ cm^{-1}, and $TA=93$ cm^{-1}.
[h] $LO=339$ cm^{-1}, $TO=298$ cm^{-1}, $LA=190$ cm^{-1}, and $TA=115$ cm^{-1}.

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[16] R. H. Lyddane, R. G. Sachs, and E. Teller, Phys. Rev. **59**, 673 (1941).

[17] A. Mitshuishi, H. Yoshinaga, and S. Fuyita, J. Phys. Soc. Japan **13**, 1235 (1958).

TABLE V. Comparison of the observed and predicted temperature dependence of the two-phonon combinations in cubic ZnS.

Peak position cm^{-1}	Assignment	Observed[a] $\frac{\alpha(77°\mathrm{K})}{\alpha(300°\mathrm{K})}$	Observed[a] $\frac{\alpha(420°\mathrm{K})}{\alpha(300°\mathrm{K})}$	Calculated $\frac{\alpha(77°\mathrm{K})}{\alpha(300°\mathrm{K})}$	Calculated $\frac{\alpha(420°\mathrm{K})}{\alpha(300°\mathrm{K})}$
491	LO+LA[b]	0.50	...	0.490	1.34
	TO+LA[c]	0.50	...	0.518	1.34
593	2TO	0.69	1.25	0.616	1.31
642	LO+TO	0.79	1.14	0.643	1.29
677	2LO	0.80	1.12	0.671	1.28

[a] Determined from Deutsch's spectra (Ref. 13).
[b] Assignment 1.
[c] Assignment 2.

With assumed values of LO = 339 cm^{-1}, TO = 298 cm^{-1}, LA = 155 cm^{-1}, and TA = 93 cm^{-1}, all the observed absorption maxima could be satisfactorily explained. However, the LA-phonon frequency seems to be a bit low when compared with the corresponding phonon frequency of the hexagonal ZnS. An alternative assignment with the same LO and TO but LA = 190 cm^{-1} and TA = 115 cm^{-1} seems also possible although the numerical agreement with the observed band positions is a trifle worsened in this case. The assignments are shown in Table IV.

Deutsch's data are used for the comparison of observed and calculated temperature dependences. Table V shows the calculated and observed temperature factors for the relatively prominent bands. There are usually two contributions to the background absorption; the first due to free charge carriers and the second to the tail of the resonance absorption at ν_t. The former is expected to decrease with the energy of the absorbed photon. Since the background absorption in the high-frequency side of the lattice bands of ZnS is very low and independent of temperature, the contribution of free carrier absorption to the background may be completely neglected. This is to be expected for a crystal of large band gap. The essentially temperature-independent contribution from ν_t to the background absorption is obtained from the extinction coefficient calculated from the reststrahlen spectrum (the temperature-dependent portion chiefly arises from the multiphonon processes). For the bands where data is available, the absorption coefficient is rather temperature insensitive. Thus the agreement between the observed and the calculated values may be regarded as only fair. The two assignments proposed here only differ in the case of the band at 491 cm^{-1}. Temperature dependence alone can not therefore decide between the two assignments. A fresh high-resolution transmission study of the cubic sample seems desirable.

4. DISCUSSION

As noted earlier, the multiple structure observed in the lattice infrared spectra of the zincblende-type crystals can usually be accounted for in terms of four characteristic phonon energies belonging to the four branches: TA, LA, TO, and LO at the Brillouin zone boundary. In certain cases, notably diamond[2] and GaAs,[15] it has been deemed necessary to assume the breakdown of the degeneracy of the transverse modes in order to satisfactorily account for all the observed optically active multiphonon combinations. Since the Brillouin zone-boundary value of a branch may differ in different $\mathbf{k}$ space directions, it is only natural to assume such a splitting of the transverse modes in the case of the wurtzite structure. For satisfactory assignments of the numerous lattice absorption maxima in hexagonal CdS and ZnS we have indeed taken recourse to two TA and two TO phonons.

The transverse frequency is smaller than the longitudinal one for all values of the propagation vector for the acoustical branches, except at the zone center where both are zero. Therefore there is no difficulty in identifying the lowest characteristic phonon frequencies with definite TA and LA modes. However, the identification of the optical-branch phonons to definite transverse and longitudinal modes is not so clear cut, and some confusion has resulted in the past.

Keyes[10] has noted some correlation between the zone-boundary optical-phonon energies of the zincblende-type crystals and the effective ionic charge q^*, derived from the Szigeti relation.[18] For a purely covalent crystal ($q^* = 0$) such as diamond or Ge, the transverse and longitudinal optical branches are degenerate at the zone center whereas TO > LO at the zone boundary. Although $\nu_l > \nu_t$ at $\mathbf{k} = 0$ (Lyddane–Sachs–Teller formula[16]) for weakly ionic crystals like InSb ($q^* = 0.42$), TO is still greater than LO at the zone boundary. In the case of a crystal of intermediate ionicity ($q^* \simeq 0.7$), Keyes predicted that LO = TO at $\mathbf{k}_{\max}$, which indeed is the case with ZnSe as shown by Mitra.[3] However, strongly ionic crystals ($q^* > 0.7$) such as the alkali halides[19] are expected to have LO greater than TO for all values of $\mathbf{k}$.

The effective ionic charge on CdS and ZnS is 1.00 and 0.854, respectively. The highest characteristic phonon frequency for these materials may therefore be termed the zone boundary LO. The next two characteristic frequencies of the hexagonal CdS and ZnS, and the next single characteristic frequency of the cubic ZnS may now be identified with the TO modes. For predominantly ionic crystals, the transverse optical branches as a rule undergo only limited dispersion. The zone boundary values of $\mathrm{TO}_1 = 261$ cm^{-1} and $\mathrm{TO}_2 = 238$ cm^{-1} for CdS, $\mathrm{TO}_1 = 318$ cm^{-1} and $\mathrm{TO}_2 = 297$ cm^{-1} for the wurtzite ZnS and TO = 298 cm^{-1} for the zincblende ZnS are not too different from their zone-center values, 241 cm^{-1} and 312 cm^{-1}, respectively, for CdS and ZnS. The zone boundary LO, TO, LA, and TA phonon fre-

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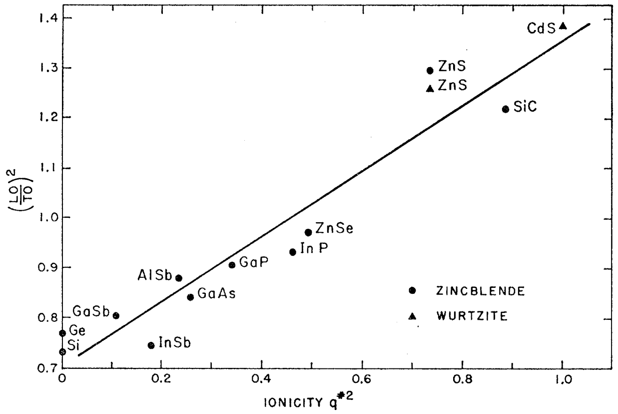

FIG. 5. Correlation of the ratio of the optical frequencies of the zincblende- and wurtzite-type semiconductors with the effective ionic charge.

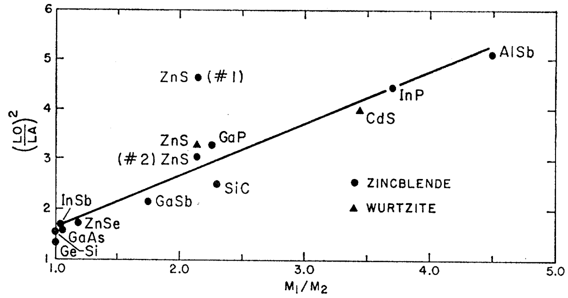

FIG. 6. The effect of mass difference on the separation between the optical and the acoustical branches.

quencies for a number of IV-IV, III-V and II-VI compounds along with their effective ionic charge are listed in Table VI. Keyes noted that $(LO/TO)^2$ is a linear function of q^{*2} for crystals of diamond and zincblende-type structures. Such a plot is shown in Fig. 5. The crystals of wurtzite structure also seem to follow the general pattern if one uses the mean of the two TO values.

The Brout sum rule[20] for lattice vibrations,

$$\sum_i \omega_i^2(\mathbf{k}) = \text{constant}, \qquad (5)$$

where $\omega_i(\mathbf{k})$ is the circular frequency in the ith branch when the wave vector is $\mathbf{k}$, was believed to be strictly valid for diatomic ionic crystals of cubic symmetry, whose constituent atoms interact only by Coulomb forces between all ions and the repulsive interaction is between nearest neighbors alone. However, relation (5) seems to hold reasonably well for a number of zincblende[1,3]-type crystals. Rosenstock[21] has recently demonstrated that Eq. (5) with little or no modification can also be applied to more general force models and to nonionic crystals.

TABLE VI. Zone-boundary phonon frequencies and effective ionic charge of some IV-IV, III-V, and II-VI semiconductors.[a]

Compound	LO cm^{-1}	TO cm^{-1}	LA cm^{-1}	TA cm^{-1}	q^*
C[b]	1161	1275	991	750	0
Si	413	482	333	139	0
Ge[c]	247	280	215	65	0
SiC	851	770	540	363	0.94
GaSb	193	215	134	49	0.33
InSb	155	179	118	43	0.42
GaAs	234	258	188	70	0.51
AlSb	297	316	132	65	0.53
GaP	361	378	197	115	0.58
InP	318	329	150	62	0.68
ZnSe	212	208	162	87	0.71
ZnS(cubic)[d]	339	298	155	93	0.85
	339	298	190	115	
ZnS(hexagonal)[e]	346	318; 297	181	92; 73	
CdS(hexagonal)[f]	295	261; 238	149	79; 70	1.00

[a] Data from Ref. 3 if not otherwise stated.
[b] Reference 2.
[c] B. N. Brockhouse and P. K. Iyengar, Phys. Rev. **111**, 747 (1958).
[d] This study (assignment 1).
[e] This study (assignment 2).
[f] This study.

In Table VII the zone-edge Brout sums $(\nu_l^2+2\nu_t^2)$ for CdS and ZnS are compared with their zone-boundary values $(LO^2+2TO^2+LA^2+2TA^2)$. The agreement is fair. Such a comparison may therefore be regarded as a check on the upper bounds of the zone-boundary phonon frequencies of diatomic crystals.

Other than the numerical agreement between the observed and calculated positions of infrared absorption peaks involving the acoustical modes, there are but few checks on the soundness of the LA and TA assignments. In analogy with the diatomic linear chain, Keyes has shown that one may expect a linear relationship between $(LO/LA)^2$ and σ, the ratio of the larger to the smaller ionic masses for the zincblende-type crystals. Such a plot is shown in Fig. 6, in which the wurtzite crystals are included as well. The LA assignment of hexagonal CdS and ZnS seems reasonable. For the cubic ZnS assignment, No. 2 seems to be more probable. If such is the case, the difference between the hexagonal and cubic ZnS characteristic phonon frequencies is not very

TABLE VII. Comparison of the zone-center and zone-edge Brout sums for some 2–6 compounds.

Compound	Structure	Brout sum at $\mathbf{k}\approx 0$ in 10^{27} sec^{-2}	Brout sum at $\mathbf{k}_{\max}$ in 10^{27} sec^{-2}
CdS	Wurtzite	7.73	8.70
ZnS	Zincblende	12.00	11.84[a]
			12.60[b]
ZnS	Wurtzite	...	12.61
ZnSe	Zincblende	5.35	6.13

[a] Assignment 1.
[b] Assignment 2.

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large, which is to be expected from the essential similarity in the gross features of the spectra of these two modifications. Such a similarity was also noted between cubic and hexagonal modifications of SiC by Spitzer, Kleinman, and Walsh.[22]

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Theory of Electron Backscattering*

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An exact integral equation is derived for the backscattering coefficient as a function of energy and angle. The equation has an approximate symmetry which allows one to determine the conditions under which backscattering will be independent of the energy of the incident electrons. The validity of some approximations is discussed, and a possible method for obtaining numerical solutions is proposed. It is found that small and large-angle individual scatterings are of about equal importance. For those electrons that have lost very little energy, the equation can be solved exactly, and some interesting results are obtained.

1. INTRODUCTION

When a beam of electrons is directed against a thick solid target, many of the electrons stop in the target but some are scattered back out. These are the backscattered electrons.[1] Over the past few years a considerable amount of experimental information has been collected [2–6] and from an empirical point of view there now exists a fairly complete picture of the phenomenon. On the other hand, attempts at a theoretical interpretation of the data[7–10] have been based on rather severe approximations and have met with only limited success. The purpose of this paper is to present a reformulation of the problem which circumvents many, but by no means all of the difficulties which one encounters in trying to treat backscattering through the usual methods of multiple-scattering theory.

Mathematically, the problem can be formulated as follows. Given a uniform, monoenergetic flux of electrons incident on a semi-infinite block of scattering material, what is the energy and angular distribution of electrons that are scattered back out? In order to solve this problem using standard multiple-scattering theory, one must find the distribution function for the electrons at each point within the block. A more economical method would be to obtain an equation for the distribution of backscattered electrons alone, thereby freeing ourselves from the unnecessary task of finding the distribution within the block. In the following section we will derive an integral equation for the backscattering coefficient as a function of energy and angle. An application of this equation to the energy dependence of the backscattering coefficient is given in Sec. 3. Section 4 contains a critical analysis of some

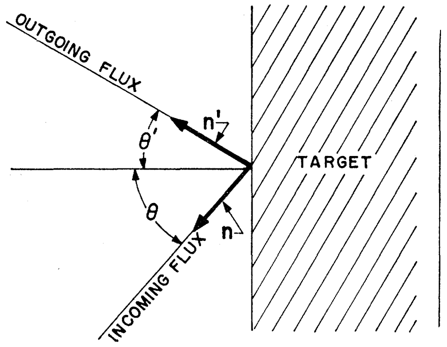

FIG. 1. Kinematics.

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[1] Secondary electrons are also emitted. Experimentally, it is usually assumed that an electron emerging from the target with an energy of more than 50 eV has been backscattered.

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