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Raman Effect in Zinc Oxide

T. C. Damen, S. P. S. Porto, and B. Tell
Bell Telephone Laboratories, Murray Hill, New Jersey

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The Raman effect in zinc oxide has been measured using the continuous helium-neon and ionized argon lasers as sources. The frequency and symmetry character of the fundamental modes have been determined. The results are: two E_2 vibrations at 101 and 437 cm^{-1}; one transverse A_1 at 381 cm^{-1} and one transverse E_1 at 407 cm^{-1}; one longitudinal A_1 at 574 cm^{-1} and one longitudinal E_1 at 583 cm^{-1}.

INTRODUCTION

The optical-phonon spectra of solids have been studied mainly by neutron-diffraction, Raman-effect, infrared-absorption, and reflectivity techniques. The role of the Raman effect as a tool for these determinations of optical-phonon spectra, particularly of semiconductors, has been limited because of the difficulties associated with crystal size and the relatively low flux density associated with the classical Raman light sources. This has often led to the inability to obtain good angular-dependence and polarization measurements, so that much of the information that would allow unequivocal identification of symmetry character of these vibrations is lost.

The laser—in particular, the visible continuous gas laser—is able to overcome these disadvantages associated with the Raman observations in solids. The advantages of the laser are high-power density, monochromaticity, parallelism, and linear polarization.

In the case of liquids or gases, where there is random orientation of the molecules, one has to average the Raman process over all molecular orientations with respect to the incident electric field. This averaging process smears out many of the properties of the polarizability tensor associated with the molecules of the liquid or gas.

In the case of a single crystal, where this averaging process is not needed, the polarization measurement of a certain Raman line will be a direct indication of which of the components of the polarizability tensor change during the vibration. The angular dependence will allow us to study the influence of the conservation of momentum of the phonon on the frequency and selection rules of the Raman effect.

For ZnO, the phonon spectrum has been studied by both Raman and infrared techniques. Infrared-absorption data have been mostly connected with multiphonon processes, with phonons having wave vectors in the vicinity of the Brillouin zone edge.[1] Those multiphonon spectra are, in our opinion, not well resolved and difficult to interpret. The infrared-reflection data yield the infrared active transverse optical phonons near the zone center.[2] Finally, preliminary Raman measurements reported[3] on ZnO lack polarization data, and therefore cannot unambiguously designate symmetry. In view of the present interest in the wurtzite piezoelectric semiconductors, it was felt that a verification of the selection rules would be of value.

However, our interpretation is in almost complete disagreement with the work of Mitra and Bryant,[3] and there also appears to be some discrepancy with respect to the reflection work of Collins and Kleinman.[2]

EXPERIMENTAL

The experimental setup is similar to the one used for Raman effect of liquids.[4] It consists of a gas-laser source focused into the crystal, an oriented crystal sample, a light-collector lens, a polarizer, a spectrometer, a photomultiplier, and a lock-in amplification and recording system.

The exciting wavelengths used were 6328 Å from an He-Ne laser and 4880 or 5145 Å from a continuous A$^+$ laser with average powers of around 50 mW. (No significant shift in phonon frequencies was observed for different laser frequencies.) The laser light was chopped at 400 cps and scattered light observed at 90° from incidence, after a single pass of the laser light through the crystal; this technique yields less direct scattering and eases interpretation of results in terms of the crystal symmetry. The spectrometer used is a "tandem" grating spectrometer[5] consisting of two identical f:6.8 grating spectrometers driven by the same shaft. In this spectrometer stray light and grating ghosts are strongly suppressed and the background light at 15 cm^{-1} from the laser frequency is down by 10^8. The slit widths used were of the order of 8 cm^{-1}.

Final data was taken on two ZnO crystals. One of the crystals was cut so that the z or optical axis was parallel to a sample edge (designated the z-cut crystal), and the other was cut so that the z direction was parallel to a sample face and at 45° to the sample edges (designated 45° crystal). Both crystals were approximately cubic with the z-cut crystal having a linear dimension of about 6 mm and the 45° crystal about 3 mm. All data were

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[1] S. S. Mitra and R. Marshall, in *Proceedings of the International Conference on the Physics of Semiconductors, Paris, 1964* (Academic Press Inc., New York, 1965), p. 1085.

[2] R. J. Collins and D. A. Kleinman, J. Phys. Chem. Solids **11**, 109 (1959).

[3] S. S. Mitra and J. I. Bryant, Bull. Am. Phys. Soc. **10**, 333 (1965).

[4] R. C. C. Leite and S. P. S. Porto, J. Opt. Soc. Am. **54**, 981 (1964).

[5] D. Landon and S. P. S. Porto, Appl. Opt. **4**, 762 (1965).

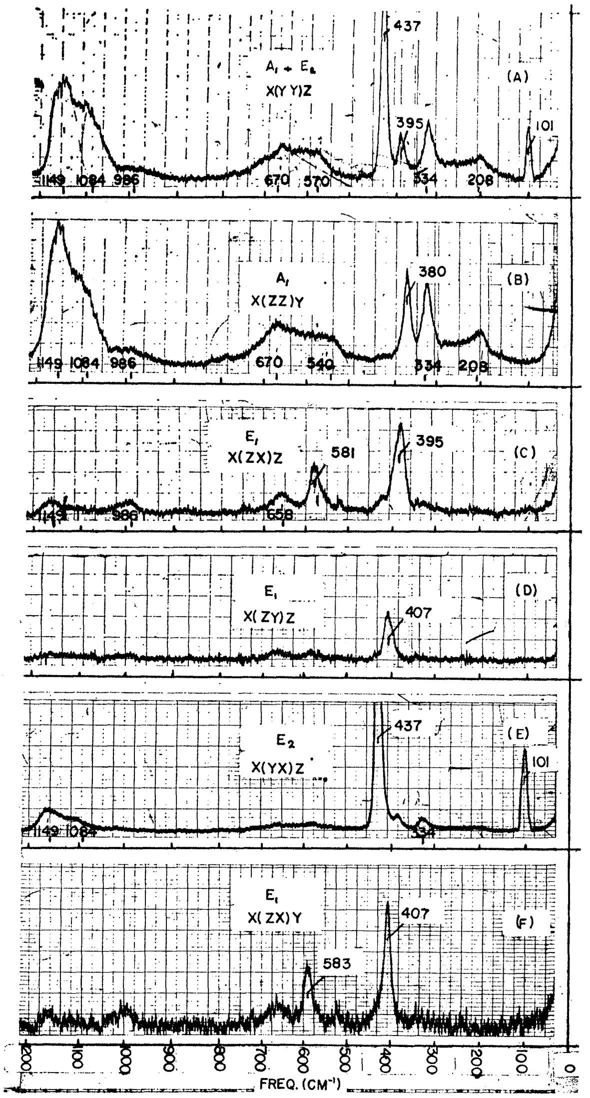

FIG. 1. Right-angle Raman scattering in ZnO for various polarization and propagation directions sufficient to define the vibrations at room temperature with 4880-Å excitation.

taken with the incident and scattered light at right angles.

In the notation we will follow in this paper a spectrum is described by four symbols, two inside a parenthesis and two outside, for example $x(yz)y$. The symbols inside are, left to right, the polarization of the incident and of the scattered light, while the ones to the left andright of the parenthesis are the propagation directions of the incident and of the scattered light, respectively.

The 45°-cut crystal was used in order to study the infrared- and Raman-active longitudinal optical phonon. With this orientation, the phonon could be forced to propagate approximately along either the z or x axis by reversing the incident propagation vector.

DISCUSSION

ZnO has wurtzite symmetry with C_{6V} or 6 mm symmetry. There are 4 atoms per unit cell leading to 12 phonon branches, 9 optical and 3 acoustic. Group theory predicts, near the center of the Brillouin zone, that there is an A_1 branch, a doubly degenerate E_1 branch, two doubly degenerate E_2 branches, and two B branches.[6] The A_1 and E_1 branches are both Raman- and infrared-active, the E_2 branches are Raman-active only, while the B branches are inactive. Group theory, however, does not take into account the macroscopic electric field associated with the infrared-active longitudinal optical mode,[7] and the interpretation of the A_1 and E_1 branches must be modified.[6,8] This is discussed below.

The scattering intensity of a Stokes-Raman transition, if a harmonic-oscillator approximation is assumed, can be written

$$I=C\nu_s^4[(n_p+1)/\nu_p](e_\rho^i\alpha_{\rho\sigma}'e_\sigma^s)^2,$$

where C is a constant, ν_s is the Stokes-shifted Raman frequency, ν_p is the vibrational frequency of the oscillator, n_p is the occupation number of the initial vibrational state, e_ρ^i is the ρth component of the unit polarization vector of the incident light, e_σ^s is the σth component of the scattered light, and $\alpha_{\rho\sigma}'$ is the change of the polarizability tensor component $\alpha_{\rho\sigma}$ during the vibration having normal coordinate q_a:

$$\alpha_{\rho\sigma}'(q_a)=(\partial\alpha_{\rho\sigma}/\partial q_a).$$

For each normal mode, only certain polarizability components change during the vibration: For the C_{6V} point group these tensors are given by[6]

$$\alpha'(A_1(z))=\begin{bmatrix}\alpha_{11}' & & 0\\ & \alpha_{11}' & \\ 0 & & \alpha_{33}'\end{bmatrix},$$

$$\alpha'(E_1(-x))=\begin{bmatrix}0 & 0 & -\alpha_{13}'\\ 0 & 0 & 0\\ -\alpha_{13}' & 0 & 0\end{bmatrix},$$

$$\alpha'(E_1(y))=\begin{bmatrix}0 & 0 & 0\\ 0 & 0 & \alpha_{13}'\\ 0 & \alpha_{13}' & 0\end{bmatrix},$$

$$\alpha'(E_2)=\begin{bmatrix}0 & \alpha_{12}' & 0\\ \alpha_{12}' & 0 & 0\\ 0 & 0 & 0\end{bmatrix},\quad \alpha'(E_2)=\begin{bmatrix}\alpha_{12}' & & 0\\ 0 & -\alpha_{12}' & 0\\ 0 & 0 & 0\end{bmatrix}.$$

For the infrared- and Raman-active A_1 and E_1 modes the coordinate in parenthesis designates the direction of phonon polarization. That is, an A_1 phonon is polarized parallel to the z axis, while the E_1 phonons are polarized in the xy plane.

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[6] R. Loudon, Advan. Phys. 13, 423 (1964).

[7] See, for example, M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1956), p. 82 ff.

[8] H. Poulet, Ann. Phys. (Paris) 10, 908 (1955).

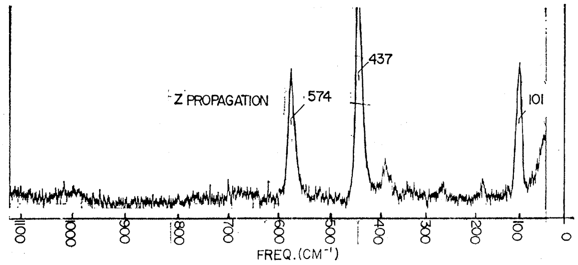

FIG. 2. Right-angle Raman scattering for phonon propagation along z, which shows the longitudinal optic phonon at room temperature and 4880-Å excitation.

As is well known by the Lyddane-Sachs-Teller relation,[7] electrostatic forces in polar cubic crystals lift the degeneracy of the infrared-active optical phonons into two transverse and one longitudinal branches. A generalization of the Lyddane-Sachs-Teller relationship to uniaxial crystals, leads to the twofold degeneracy of the E_1 phonons being lifted except for phonon propagation along the z axis.[6,8] For phonon propagation in the xy plane, there will be an A_1 transverse, an E_1 transverse, and an E_1 longitudinal. The E_1 degeneracy is lifted and the phonons will have frequencies related by the Lyddane-Sachs-Teller relationship. Furthermore, because of the anisotropy of the force constants, the A_1 transverse phonon designated $\nu_t^{\parallel}$ will in general have a different frequency from an E_1 transverse phonon designated $\nu_t^{\perp}$. $\nu_t^{\perp}$ can be thought of as the transverse ordinary phonon since its polarization will always be chosen normal to both its propagation direction and the z axis. The other two extraordinary phonons could in arbitrary directions be mixtures of transverse and longitudinal. However, in the limit that electrostatic forces are much greater than anisotropy forces, the frequencies of the extraordinary waves will be sufficiently separated that the mixing of transverse and longitudinal waves will be small.[9] In other words

$$|\nu_t^{\parallel}-\nu_t^{\perp}| < |\nu_l^{\parallel}-\nu_t^{\parallel}| \quad \text{and} \quad |\nu_l^{\perp}-\nu_t^{\perp}|,$$

where $\nu_l^{\parallel}$ and $\nu_l^{\perp}$ are the frequencies of a longitudinal wave polarized parallel and perpendicular to the z axis.

In this limit,[6]

$$\nu_t^2 = (\nu_t^{\parallel})^2 \sin^2\theta + (\nu_t^{\perp})^2 \cos^2\theta,$$

for the "quasitransverse" phonon and

$$\nu_l^2 = (\nu_l^{\parallel})^2 \cos^2\theta + (\nu_l^{\perp})^2 \sin^2\theta$$

for the "quasi-longitudinal" phonon, where θ is the angle between the phonon propagation vector and the z axis, and $\nu_l^{\parallel}$ and $\nu_l^{\perp}$ are expected to obey a modified Lyddane-Sachs-Teller relationship:

$$\nu_l^{\parallel} = \nu_t^{\parallel}(\epsilon_0^{\parallel}/\epsilon_\infty^{\parallel})^{1/2} \quad \text{and} \quad \nu_l^{\perp} = \nu_t^{\perp}(\epsilon_0^{\perp}/\epsilon_\infty^{\perp})^{1/2},$$

where ϵ_0 is the static dielectric constant and ϵ_∞ is the high-frequency dielectric constant.

Furthermore, the change in the polarizability for a transverse component need not be equal to that for a longitudinal component. This difference arises from the nature of the electron-phonon coupling. For transverse waves, there is only deformation-potential coupling, while for longitudinal waves there is also electrostatic coupling. Since both contributions are of the same order of magnitude and can be additive or subtractive,[10] the polarizability change and the resulting Raman intensities due to the longitudinal and transverse phonons can be considerably different.

Figure 1(A–F) shows for the z-cut crystal the spectra for 90° Raman scattering at room temperature, when the polarization of the incident and scattered light are monitored and the exciting wavelength is 4880 Å. Each spectrum is designated by its incident and scattered polarization and propagation directions and by the normal mode expected to be active under these conditions. The "fundamentals" are designated by arrows and their frequencies in wave numbers (cm⁻¹) are given directly alongside. In the figure are also shown the frequencies for other prominent peaks. We estimate that the fundamental frequencies are reliable to ±3 cm⁻¹.

In addition to magnitude and symmetry considerations, we have eliminated lines as "fundamentals" by virtue of their temperature dependence. For example, a

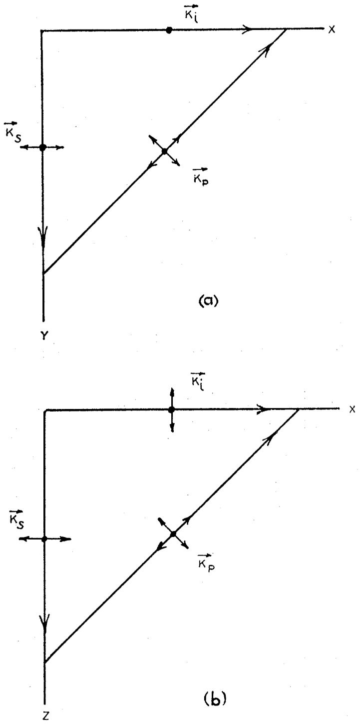

FIG. 3. Vector diagram (a) for the cases $x(zz)y$ and $x(zx)y$, and (b) for $x(zy)z$, $x(zx)z$, and $x(yy)z$ and $x(yx)z$. The single arrows indicate propagation direction, and double-headed arrows indicate polarization direction. The dot indicates polarization normal to the interaction plane.

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[9] The reflection data of Collins and Kleinman (Ref. 2) led us to believe that this limit (electrostatic effects much larger than anisotropy effects) would be well satisfied. Their results are two transverse optical modes both at 414 cm⁻¹ and a longitudinal optical mode at 591 cm⁻¹ with no measurable anisotropy. We find that this limit is still satisfied, but there is a definite and striking anisotropy.

[10] R. Loudon, Proc. Roy. Soc. (London) **A275**, 218 (1963).

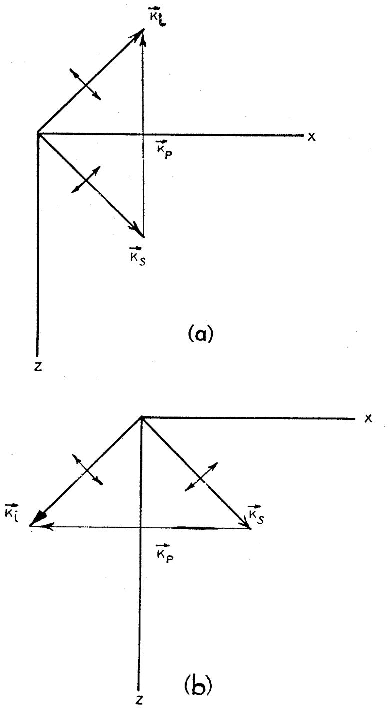

FIG. 4. Vector diagram illustrating phonon traveling (a) along z, and (b) along x, by reversing propagation direction of incident light. The light propagates and is polarized in the xz plane.

preliminary study of the temperature dependence has led us to eliminate the line at 334 cm^{-1} [Figs. 1(A) and 1(B)] from being a fundamental. A fundamental Stokes line has temperature dependence $n+1$ where $n=1/(ehv/kT-1)$ is the thermal occupation number for a phonon of energy $h\nu$. This would lead, for the 334-cm^{-1} line, to an intensity decrease of around 25% from room temperature to liquid-nitrogen temperature. The observed decrease was at least a factor of 5, i.e., a factor of 20 too large.

We now give the detailed interpretation, based on Poulet[8] and Loudon,[6] of Figs. 1 and 2 by the use of the vector diagrams given in Fig. 3. In Fig. 3(a), the incident light is propagating in the x direction and polarized along z, and the scattered light along y and analyzed along z or x. The phonon must conserve energy and momentum given by $\nu_p=\nu_i-\nu_s$ and $\mathbf{k}_p=\mathbf{k}_i-\mathbf{k}_s$. The first case ($z$ polarization) is designated as $x(zz)y$ [Fig. 1(B)] and has A_1 character. Since the phonon propagates in the xy plane and is polarized along z, it is pure transverse and is the A_1 transverse phonon $\nu_t^{\|}$ at 380 cm^{-1}. The second case (scattered light with x polarization) has E_1 character and is shown in Fig. 1(F). For this $x(zx)y$ arrangement, phonons will be excited having polarization along the x and y axis. These are decomposed into vibrations parallel and perpendicular (in the xy plane) to the phonon-propagation direction, and give rise to the E_1 transverse phonon $\nu_t^{\perp}$ and the E_1 longitudinal phonon $\nu_l^{\perp}$ with $\nu_t^{\perp}=407$ cm^{-1} and $\nu_l^{\perp}=583$ cm^{-1}.

Similarly, in Fig. 3(b) for the incident and scattered light in the xz plane the $x(zy)z$ arrangement [Fig. 1(D)] gives the E_1 transverse phonon $\nu_t^{\perp}$. In Fig. 1(A), $x(yy)z$, and Fig. 1(C), $x(zx)z$, the phonons have "quasi-transverse" and "quasilongitudinal" components and mixed character for which the A_1 character is observed in 1(A) and the E_1 in 1(C). The transverse-phonon frequency is given, for $\theta\approx 45°$, by

$$\nu_t^2=\tfrac{1}{2}[(\nu_t^{\|})^2+(\nu_t^{\perp})^2],$$

so that $\nu_t=395$ cm^{-1} for $\nu_t^{\|}=380$ cm^{-1} and $\nu_t^{\perp}=407$ cm^{-1}. Only the E_1 character of the "quasi-longitudinal" phonon at 581 cm^{-1} can be seen, and because of its weak intensity and poor line shape, no conclusive frequency shift can be determined from the E_1 longitudinal phonon $\nu_l^{\perp}$.

However, as seen in Fig. 4, the 45°-cut crystal permits right-angle Raman scattering while requiring the phonon to propagate along either the x or the z axis by simply reversing the propagation direction of the incident light. This was done specifically to observe the A_1 longitudinal phonon, since in none of the above cases was it possible for the longitudinal phonon to be polarized along the z axis. Since the incoming and scattered light propagate and are polarized in the xz plane, the E_1 longitudinal should be observed for phonon propagation along the x axis and the A_1 longitudinal along the z axis. Because of the relatively weak E_1 component and the smaller crystal size as compared to the z-cut crystal, the E_1 longitudinal phonon was not observed here. The A_1 longitudinal is, however, well resolved with frequency $\nu_l^{\|}=574$ cm^{-1} and is seen in Fig. 2. [This is probably due to the α_{33}' component, since the α_{11}' was shown to be small in Fig. 1(A).] There is thus a definite anisotropy of the longitudinal phonon, although it is smaller than we would have expected from the modified Lyddane-Sachs-Teller relationship.

Lastly, with regard to the E_2 vibrations, two lines are found at 101 and 437 cm^{-1} which unambiguously have E_2 character as can be seen in Figs. 1 and 2. That is, they appear with large intensities in $x(yy)z$, [Fig. 1(A)] and $x(yx)z$, [Fig. 1(E)] directions and are missing in all (zz) and (xz) directions. There is no measurable frequency shift in these lines.

Our interpretation can be compared to the results of Mitra and Bryant.[3] They find a transverse E_1 at 438 cm^{-1}, a transverse A_1 at 420 cm^{-1}, two E_2 vibrations at 180 and 383 cm^{-1}, and two phonons of unspecified symmetry at 538 and 588 cm^{-1}.

TABLE I. Frequency and symmetry of the fundamental optical modes in ZnO.

Symmetry character	Frequency (cm^{-1})
E_2	101
E_2	437
E_1 (transverse)	407
A_1 (transverse)	380
E_1 (longitudinal)	583
A_1 (longitudinal)	574

TABLE II. Frequencies of various well-resolved multiphonon processes.

208 cm^{-1}
334 cm^{-1}
Broad, from 540–670 cm^{-1}
986 cm^{-1}
Broad, starts at 1050 cm^{-1}, peaks at 1084 and 1149 cm^{-1}.

In Table I are listed the frequencies and symmetries of the fundamental optical phonons in ZnO.

In Table II are listed the most prominent multiphonon processes. These processes presumably occur for phonon wave vectors considerably removed from the center of the Brillouin zone, and we have not seriously attempted an interpretation. Such an interpretation would require a knowledge of critical points and selection rules for various points in the zone, and may soon become available.[11]

CONCLUSIONS

We have made a careful polarization study of the 90° scattering for the fundamental Raman-active phonons in ZnO. We have found two E_2 phonons, and one transverse E_1 phonon and one transverse A_1 phonon with a definite anisotropy shift. The "quasitransverse" phonon of "impure" symmetry has the expected frequency. The A_1 and E_1 longitudinal phonons have also been found, and an anisotropy, although small, has been determined. We cannot, however, say anything conclusive concerning the "quasilongitudinal" phonon. There are also several prominent peaks which are attributed to multiphonon processes.

ACKNOWLEDGMENTS

The paper has greatly benefited from a critical reading by D. A. Kleinman. We are also indebted to him for, hopefully, clarifying our notation. We wish to thank R. J. Martin for sample preparation.

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[11] M. Nusimovici and J. L. Birman, Bull. Am. Phys. Soc. **10**, 616 (1965).