Defect Structure of Crystalline Quartz. I. Radiation-Induced Optical Absorption*

George W. Arnold

Sandia Laboratory, Albuquerque, New Mexico

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Low-temperature bombardment (77°K) of synthetic crystalline quartz with fast electrons induces optical absorption (C band) near 220 mμ. For 40°C neutron irradiations the absorption maximum is near 210 mμ. The absorption has an orientation dependence when produced by electron irradiation. This dependence is exhibited by a shift in the position of maximum absorption from 220 mμ for samples cut perpendicular to the c axis (Z cut) to 217 mμ for samples cut parallel to the c axis (Y cut). The absorption in the Z-cut samples is about twice that of the Y-cut samples for equal integrated flux. In neutron-irradiated material no such dependence is noted. The defect giving rise to the C-band absorption anneals near 225°C. The electron or hole occupying the defect, however, is relased below room temperature, removing the optical absorption. After heating to temperatures below 225°C, the original absorption obtained after electron irradiation at 77°K can be regained by a brief re-irradiation at 77°K (0.01 of the original integrated flux). A similar electron exposure at low temperature augments the absorption induced by fast neutrons at 40°C and introduces a strong absorption at 230 mμ which was not previously discernible. The magnitude of the C-band absorption in electron-irradiated material is strongly dependent on the crystal growth rate, increasing by a factor of about 17 for a growth rate increase of 4.5. The increase for the band produced by neutron bombardment [5×10^{17} nvt (fast)] is only about 25%. The comparison of electron irradiation and x-ray bombardments, and noncorrelation of absorption with impurity content, indicate that the defect responsible for the C-band absorption is produced by direct Coulomb encounters with lattice constituents.

I. INTRODUCTION

OPTICAL absorption bands can be induced in crystalline quartz by ionizing or displacing radiation.[1] In order to identify basic lattice defects and determine their displacement thresholds, bands which are specific to displacing radiation are of the greatest interest. A particular band in crystalline quartz, whose maximum has been variously reported[2] as lying in the wavelength range of 207 to 230 mμ, has thus been the subject of much study because it is induced to a significant degree only by fast electrons and neutrons. There exist, however, very definite points of disagreement between various investigators both as to the conditions necessary for the production of the band and models for its interpretation.

The band under discussion was called the C band by workers at Reading University[3-6] who made the first thorough studies of the optical effects brought about in crystalline quartz by radiation. The work of this group, with respect to the generation of a C band, may be summarized as follows: (1) X rays can produce a C band in some natural and synthetic crystalline quartz, but the intensity usually saturates at absorption-coefficient values below 5 cm^{-1}; (2) Irradiation with fast neutrons induces a C band whose intensity varied from about 5 to 100 cm^{-1} for integrated fluxes of 10^{17} to 10^{19} neutrons per cm^2 with no evidence of saturation in this range; (3) γ rays produce a C band, but the variation of intensity with absorbed dose was not studied; (4) Bleaching results suggested that the C-band absorption was due to an electron trapped at an O^{-2} vacancy. The x and γ irradiations were made at room temperature. Neutron irradiations were performed at about 50°C.

Quite different results and interpretations were later reported by investigators at Oak Ridge National Laboratory.[7-11] Their findings are: (1) A distinct C band appears in crystalline quartz when irradiated with fast neutrons only for fluxes greater than 10^{20} neutrons/cm^2; (2) Neutron fluxes of the order of 10^{17} neutrons/cm^2 produce only a structureless absorption in the C-band region; (3) the C-band absorption, it is suggested, is caused by a partial valence bond localized at a silicon or oxygen atom. They suggest that such broken valence bonds are stable only after the regular crystalline structure has been destroyed by extensive irradiation. The γ-ray irradiations were made at room temperature. The neutron-irradiation temperatures were not given.

Arnold and Compton[1] found that a distinct C band ($\alpha \approx 6$ cm^{-1}, $\Phi = 1.63\times10^{17}$ 2-MeV electrons/cm^2) was produced in crystalline synthetic quartz by fast electron bombardment at 77°K but not when irradiated at room temperature. They also found that 50-kV x irradiation ($\sim10^7$ rads) at 77°K did not induce a C band. Their findings suggested that the apparent differences

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[1] Discussions of these bands can be found in the following references: G. W. Arnold, J. Phys. Chem. Solids **13**, 306 (1960); G. W. Arnold and W. D. Compton, Phys. Rev. **116**, 802 (1959).

[2] Specific references are cited by Arnold, Ref. 1.

[3] Ditchburn, Mitchell, Paige, Custers, Dyer and Clark, *Report of Bristol Conference on Defects in Crystalline Solids, July 1954* (The Physical Society, London, 1955), p. 92.

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[5] E. W. J. Mitchell and E. G. S. Paige, Phil. Mag. **1**, 1085 (1956).

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[7] R. A. Weeks, J. Appl. Phys. **27**, 1376 (1956).

[8] C. M. Nelson and J. H. Crawford, Jr., J. Phys. Chem. Solids **296** (1960).

[9] C. M. Nelson and R. A. Weeks, J. Am. Ceram. Soc. **43**, 396 (1960).

[10] R. A. Weeks and C. M. Nelson, J. Am. Ceram. Soc. **43**, 399 (1960).

[11] R. A. Weeks, Phys. Rev. **130**, 570 (1963).

in the neutron-irradiation results might be related to differences in the irradiation temperatures.

Recently, Jones and Brown[12] have shown that the mechanical properties of synthetic crystalline quartz are influenced by the crystal growth rate. They demonstrated that a 50 °K internal friction peak, associated by Bommel, Mason and Warner[13] with the motion of nonbridging oxygen atoms, increased by 2 orders of magnitude when the growth rate increased by a factor of 4. This increase in the density of structural defects with growth rate suggests that the production of defects by displacing radiation might also be affected and it could be responsible for diverse results by different investigators using different samples.

In order to resolve the discrepancies in the past work and attempt to determine the nature and origin of the C band, the following were investigated: (1) the production of the C band in synthetic crystalline quartz by fast electron and neutron bombardment, (2) the temperature dependence of C-band defect production, (3) the role of crystallographic orientation, and (4) the effect of crystal growth rate.

II. EXPERIMENTAL PROCEDURE

All electron irradiations were made with 2.0-MeV electrons. The quartz samples were mounted on the cold finger of a stainless steel Dewar. A 4-aperture rotatable head surrounded the sample area. Two sapphire windows on opposite apertures permitted optical measurements. One of the other ports carried an aluminum cup insert with a 0.003-in. window. The extended 0.003-in. window of the accelerator closely mates into this cup. This arrangement allows for close positioning ($\sim\frac{1}{4}$ in.) of the sample behind the resulting 0.006-in. aluminum scatterer, which separates the Van de Graaff vacuum and the cryostat vacuum. The separate vacua permit rapid removal of the cryostat from the accelerator, yet beam broadening due to scattering is minimized so that the electron-beam heating can be re-restricted to the sample, resulting in lower irradiation temperatures for a given flux. A small electromagnetic scan was applied to the beam in order to provide uniform irradiation over the sample area. The aperture opposite the accelerator window accommodated a Faraday cup for monitoring beam currents. The entire assembly, without a sample, was calibrated such that a measurement of total accelerator beam current could be converted into electron flux in electrons/cm² min. Most irradiations were made at liquid-nitrogen temperatures. Optical measurements were made, without intervening warmup, in a Cary 14 R spectrophotometer in which the absorption can be continuously recorded from 186 mμ to 2.6 μ.

Neutron irradiations were made in the Sandia

Engineering Reactor Facility (SERF), with the samples in a borel-lined aluminum can through which water was continually circulated. The temperature was maintained at about 40°C.

Most of the work reported here was performed on synthetic quartz grown by Sawyer Research Products, Inc. The quartz was grown by hydro-thermal techniques on Y-bar[14] seeds. All samples used in the present investigation were taken from the Z-growth sections in which the impurity pickup is least during growth. They were cut both parallel and perpendicular to the Z axis and were polished to 0.635-mm thickness. Average total growth rates varied from 0.45 to 1.91 mm/day in the Z direction.

III. RESULTS

The optical absorption, induced by 2-MeV electron bombardment at 77°K and by a comparable irradiation at room temperature, is shown in Fig. 1 for samples cut parallel to the Z axis (Y cut) from a crystal grown at 1.91 mm/day. At the lower temperature a prominent peak (C band) at 217 mμ and a smaller one near 200 mμ are developed. At room temperature, for the same electron flux, only the 200-mμ absorption is evident. This absorption is at the same wavelength as that found by Nelson and Weeks[9] for γ-irradiated quartz and by Nelson and Crawford[8] for neutron-irradiated material; the former irradiation temperature was room temperature and the latter was not specified. A band at 230 mμ found by these investigators is not discernible. No data are shown for wavelengths greater than 360 mμ because of negligible absorption.

Differences in absorption due to crystallographic orientation are shown in Fig. 2. The position of maximum C-band absorption for the Z-cut sample is located at 220 mμ while that of the Y-cut (cut parallel to the Z axis) sample is at 217 mμ. The subsidiary band is located at about 200 mμ for both orientations.
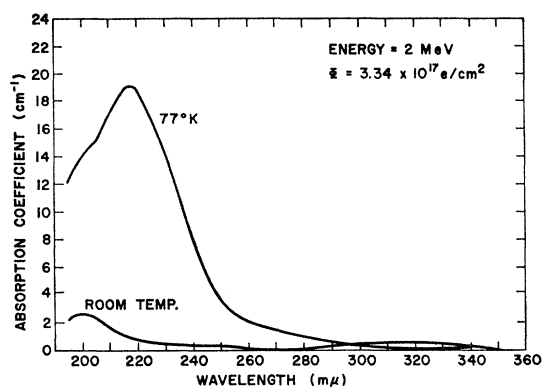

FIG. 1. Absorption coefficient versus wavelength. The upper curve is for electron irradiation and measurement at 77°K; the lower curve is for irradiation and measurement at room temperatures.

[12] C. K. Jones and C. S. Brown, Proc. Phys. Soc. (London) 79, 930 (1962).

[13] Bommel, Mason, and Warner, Phys. Rev. 99, 1894 (1955).

[14] U. S. patent application Serial No. 459,052 of 29 October 1954.
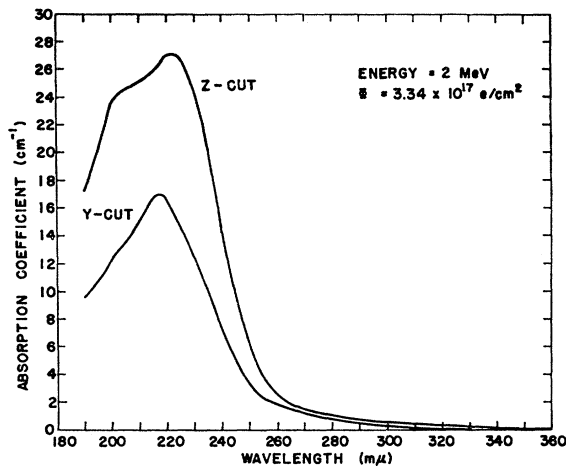
FIG. 2. Absorption coefficient versus wavelength. Electron irradiation and measurement at 77 °K of samples cut perpendicular (Z cut) and parallel (Y cut) to the c axis.

The magnitude of the C-band absorption for the Z-cut sample is roughly twice that for the Y-cut material.

It is evident from Fig. 1 that since the subsidiary absorption at 200 mμ is independent of the C-band absorption, the absorptions are caused by separate defects. Further evidence of the different nature of the defects is given in Fig. 3. After electron irradiations at 77°K and measurement at that temperature, optical-bleaching experiments were performed using a narrow band-pass filter whose maximum transmission was located at 215 mμ. The C band was selectively bleached by this treatment; the diminution of the absorption at 200 mμ was due to the overlap of the transmission band of the filter with the 200 mμ absorption band which also is bleachable. The bleaching of the C band was not accompanied by any discernible changes in absorption at other wavelengths where measuremens were possible.

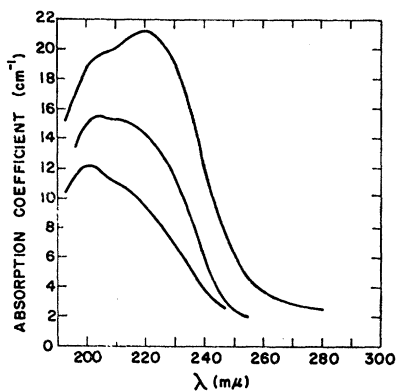The importance of low-temperature electron irradiation and subsequent measurements without warmup

FIG. 3. Absorption coefficient versus wavelength for 77°K electron-irradiated (2-MeV, $\Phi=2.81\times10^{17}$ electron/cm²) Z-cut sample. Upper curve is measurement made at 77°K after irradiation. Lower two curves are measurements made at 77°K in course of optical bleaching with 215-mμ narrow-band pass filter.

has been noted above. Warming to room temperature, after irradiation, results in an absorption curve (Fig. 1), identical to that produced at room temperature, i.e., the pronounced C band disappears, leaving a small band at 200 mμ. This does not, however, mean that the defect has annealed as can be demonstrated by again bringing the sample to 77°K and subjecting it to a short electron irradiation (∼0.01 of the original dose). This irradiation serves only to subject the sample to an intense ionization field. If optical measurements are then made, without warmup, it is found that the original absorption intensity has been regained. The process of warming the low temperature bombarded sample to successively higher temperatures, cooling to 77°K, and subjecting it to a burst of ionization indicates that the annealing of the defect occurs at about 225°C. After heating at this temperature or above, the original radiation induced absorption can only be obtained by repeating the original irradiation conditions.
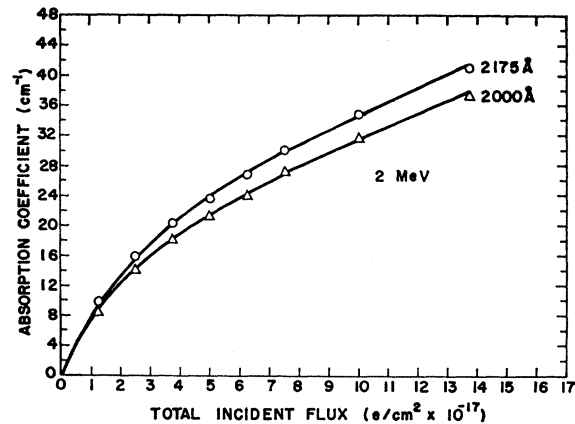

FIG. 4. Absorption coefficient for Y-cut sample versus total incident 2-MeV electron flux at 217.5 and 200 mμ. Irradiation and measurement at 77 °K.

The growth of the bands with 2-MeV electron irradiation at 77°K is shown in Fig. 4. In this case the sample was oriented parallel to the Z-axis so the absorption was monitored at 217.5 mμ and 200 mμ. The curves are characterized by a rather rapid initial growth followed by a nearly linear increase with increasing flux. This behavior is similar to that noted in other dielectric materials and is presumed to arise from two separate processes, i.e., the filling of traps which are inherent in the material and the nonsaturable process of defect production by the displacement process.

The preceding data were obtained on material grown at a rate of 1.91 mm/day. Similar features are obtained on quartz grown at slower growth rates. There is, however, a marked difference in the number of defects produced by a 2-MeV irradiation at constant integrated flux for quartz grown at various rates. This is shown in Fig. 5 where the relative absorbance, for the C-band absorption in Z-cut material, is plotted against average

total growth rate for constant integrated fluxes of 1.54×10^{18} 2-MeV electrons/cm^2. The increase in absorbance for these irradiation conditions is about a factor of 17 for an increase in growth rate by a factor of 4.25.

Samples from the various crystals were neutron irradiated for a time-integrated flux of 5×10^{17} nvt (>0.1 MeV), with the temperature maintained near 40°C. Absorption measurements at 77°K for the 1.91 mm/day Z-cut sample are shown in Fig. 6, curve 1. A single absorption peak is obtained at about 210 mμ with a subsidiary maximum evidenced by a shoulder near 220 mμ. Measurements made on both orientations, i.e., parallel and perpendicular to the c axis, gave no evidence of differences in peak positions or their magnitudes.

The results on electron-irradiated material, with respect to temperature effects, led to a closer inquiry on neutron-irradiated quartz. The results are shown in
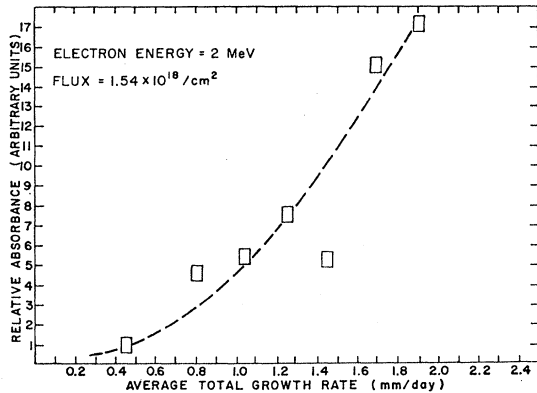

FIG. 5. Relative absorbance versus average total growth rate for Z-cut samples irradiated and measured at 77°K for the same 2-MeV electron flux.

Fig. 6, curve 2. It is seen there that after a short 2-MeV electron exposure at 77°K of a neutron-irradiated sample, large changes have taken place. Not only has the C-band absorption increased by a factor of 1.55, but a band near 230 mμ is now observed of approximately the same intensity. By warming to room temperature, the 230-mμ band is caused to disappear as shown in curve 3. The increase in C-band absorption is not decreased appreciably by defect annealing until the samples are warmed above 190°C. This series of experiments was also performed on the slowest growth rate neutron-irradiated material. The changes in absorption features were the same as in Fig. 6, with the magnitudes of the absorptions being proportionally less by the ratio indicated in Fig. 7 which shows the effect of growth rate on the induced absorption in neutron-irradiated material. The absorption measurements of Fig. 7 were made at 77°K without electron-beam ionization. The increase in absorption is only about 25% between the slowest and fastest growth rates.
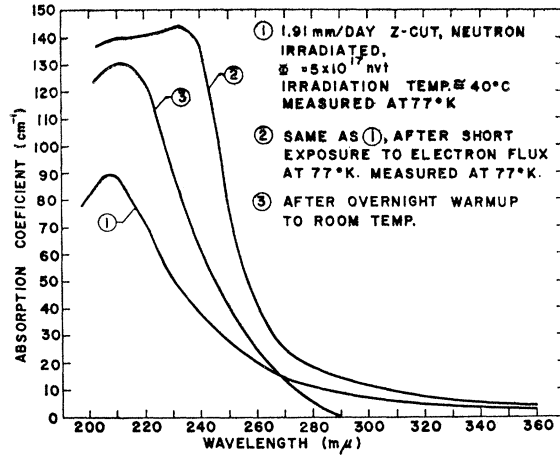

FIG. 6. Absorption coefficient versus wavelength for neutron-irradiated Z-cut sample. Irradiations at 40°C.

It is interesting to note that quite appreciable C-band absorption ($\alpha = 90$ cm^{-1}) was obtained for neutron-flux values of 5×10^{17} nvt. This contradicts the conclusion reached by Nelson and Crawford, i.e., that neutron fluxes that completely disorder the quartz lattice (>10^{20} nvt) are necessary in order to produce a band in this wavelength region.

Although the preceding data indicate that the defects leading to C-band absorption are generated by displacements, it is of interest to investigate the effects of a purely ionizing source. Figure 8 shows the absorption resulting after an extensive x-ray irradiation at 77°K. A small, but distinct, absorption maximum is observed at 230 mμ. No absorption maxima are noted at 200 mμ or 220 mμ. The absorbed dose in this irradiation is about two orders of magnitude less than in the electron irradiation of Fig. 1. The 230 mμ band was not observed in Fig. 1 because of overlap of the C band.
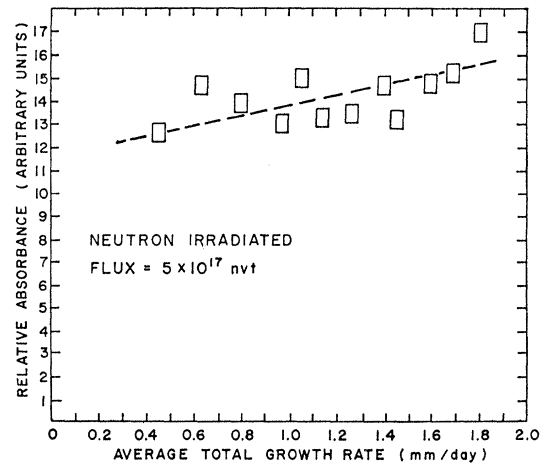

FIG. 7. Relative absorbance versus average total growth rate for Z-cut samples irradiated at 40°C for the same neutron flux. Measurements made at 77°K.
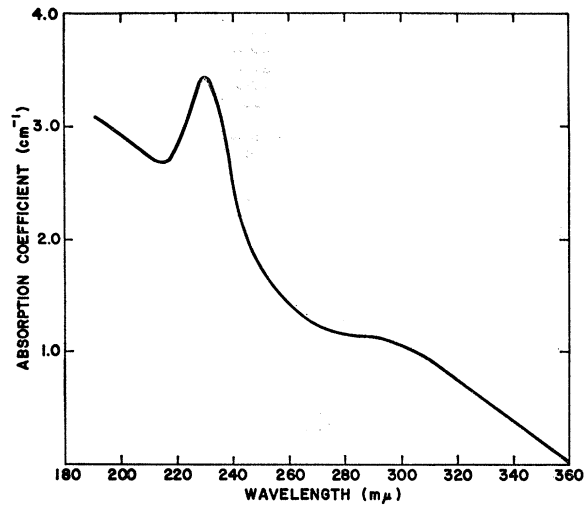
Fig. 8. Absorption coefficient versus wavelength for x-irradiated Z-cut sample (growth rate=1.91 mm/day). Total x-ray time (100-kV peak, 12 mA, W target) was 115.5 h. Irradiation and measurement at 77°K.

The Al- and Na-impurity concentrations of representative samples at each growth rate were obtained by neutron activation. Some of these data are shown in Table I along with the radiation induced C-band ab-

TABLE I. Typical aluminum- and sodium-impurity concentration and absorption coefficients for various growth rates (2 MeV, $\Phi=6.68\times10^{17}$ electrons/cm^2).

Growth rate (mm/day)	Al (ppm)	Na (ppm)	α (cm^{-1})
1.91	490±150	6.1±0.3	34
0.97	820±150	11.9±0.6	10.9
0.80	380±170	16.0±0.7	9.5
0.63	N.D.<200	10.5±0.5	4.0
0.45	1300±160	8.8±0.5	2.0

sorption coefficient. It is evident that there is no correlation between the concentration of these impurities and the absorption coefficients.

IV. DISCUSSION

The present results show that C-band absorption can be induced in synthetic crystalline quartz by fast electrons and by fast neutrons at moderate integrated fluxes. This observation is in agreement with the findings of the Reading group but not with those of investigators at Oak Ridge. The major point of disagreement concerns the absorption induced under neutron bombardment. The data presented in this paper have shown that a 40°C neutron irradiation at a flux level of 5×10^{17} nvt produces appreciable C-band absorption ($\alpha \approx 90$ cm^{-1}) but that this absorption is not indicative of the total number of defects which are responsible for C-band absorption. This is made clear in Fig. 6 which shows that additional C-band absorption is produced by placing the

sample in an intense ionization field at 77 °K. In addition, this treatment revealed the presence of defects which give rise to equally intense absorption at 230 mμ.

Since, for neutron irradiations, crystal growth rate does not greatly affect the production yield of C-band defects, as seen in Fig. 7, it is suggested that temperature effects are the most important factors leading to the lack of experimental agreement among investigators. The Reading neutron irradiations were made near 50°C while those reported in this paper were made near 40°C. The temperature of the Oak Ridge irradiation was not stated and there exists the possibility that the Oak Ridge irradiation temperature was sufficiently high to cause annealing of the defects formed by the irradiations which lead to C-band absorption.

That the defect giving rise to C-band absorption is indeed a displacement defect is substantiated by the following: (1) The annealing data indicate that the effect of fast electron irradiation is to produce a defect which anneals near 225°C, although the electron or hole which occupies the defect is released below room temperature; (2) Soft x rays which produce photoelectrons with energies far below reasonable threshold values are not effective in producing absorption in the C-band region at low temperatures; and (3) the impurity content of the various materials used does not correlate with the magnitude of the absorption.

The electron- and neutron-irradiation data, for various growth rates, indicate that the influence of growth rate is much more pronounced in the case of fast-electron irradiation. Since even large variations in threshold energy would not significantly influence defect production by fast neutrons but would influence it for the case of electrons, the growth-rate dependence might be the result of a variation of displacement threshold energy with growth rate. This question will be the subject of a further study.

In electron-irradiated material there is an orientation dependence of the wavelength of maximum absorption, as well as a difference in defect yield for equal time-integrated flux. The larger yield for Z- over Y-cut material holds true for all growth rates and is probably related to the orientation of the open channels which lie parallel to the Z-axis in the quartz structure. For material cut perpendicular to the Z-axis, dislodged atoms, whose momenta would be, for the most part, along the open channel directions, would produce larger interstitial-vacancy separation distances than would atoms which move perpendicularly to such channels. The differences in interstitial-vacancy separations for the two orientations could also result in the observed shift in the position of maximum absorption. The anisotropy found for different crystallographic orientations in the electron-irradiated material does not exist for the neutron irradiations. The absence of anisotropy exhibited after neutron irradiation could result from the creation of defect regions in which crystalline order does not exist. Such defect regions

could also account for the shift in position of the C-band maximum. The subsidiary maximum (curve 1, Fig. 6) at 220 mμ indicates that some C-band absorption due to point defects is also present.

The two additional bands observed in this work, i.e., a subsidiary maximum at 200 mμ and the 230 mμ band noted after extensive x-ray irradiation and after neutron irradiation, have been examined in detail by the Oak Ridge investigators[7,9,10] by electron spin-resonance and optical-absorption measurements. In a recent paper by Weeks,[11] specific models were suggested for these two

defects. The 200-mμ absorption was ascribed to an oxygen divacancy with a trapped electron. The 230-mμ absorption was suggested to be due to an Si-O divacancy with an electron trapped in the defect Si from which the oxygen ion is missing. The results of the present paper do not add to nor do they contradict these models.

ACKNOWLEDGMENT

Selection Rules for Second-Order Infrared and Raman Processes in the Rocksalt Structure and Interpretation of the Raman Spectra of NaCl, KBr, and NaI

E. BURSTEIN*

Physics Department and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania

AND

F. A. JOHNSON AND R. LOUDON

Royal Radar Establishment, Malvern, Worchester, England

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Group-theoretical selection rules are given for two-phonon infrared absorption and Raman scattering processes in crystals having the rocksalt structure. In common with the diamond structure, two-phonon overtones are infrared inactive. The selection rules for second-order infrared absorption processes in the rocksalt structure are much less favorable than those in the diamond and zinc-blende structures. The selection rules for second-order Raman scattering processes are less restrictive and there are many more Raman-active phonon pairs than infrared-active pairs. With the help of the selection rules, the second-order Raman spectra of NaCl, KBr, and NaI are interpreted in terms of phonon pairs at specific symmetry points in the Brillouin zone, using the theoretical phonon dispersion curves calculated by Hardy and Karo for NaCl and the experimental phonon dispersion curves determined by Woods, Brockhouse, Cowley, and Cochran by neutron spectroscopy for KBr and NaI.

1. INTRODUCTION

THE infrared lattice absorption spectrum of a crystal is due to processes where a photon is absorbed and one or more phonons are emitted into the lattice. In the case of semiconductors with either diamond or zinc-blende structures, the absorption spectrum shows a large amount of detailed structure, arising from two-phonon processes. This structure has been successfully interpreted in terms of a few characteristic phonon energies corresponding to peaks in the combined density-of-states curves.[1] In the case of the alkali halides, however, the infrared lattice absorption bands due to two-phonon emission are relatively few in number and, consequently, precise interpretation is difficult. There are two reasons for this. Firstly, the width of the restrahlen (reflection) band is very much

greater in alkali halides than in zinc-blende semiconductors (there is no restrahlen band in diamond-type semiconductors) and masks a number of the expected two-phonon lattice bands. Secondly, as will be shown in Sec. 2, the selection rules for dipole processes in the rocksalt-structure alkali halides are much less favorable than those in the diamond and zinc-blende semiconductors.

The second-order Raman spectrum, which is due to the inelastic scattering of a photon by two phonons, also exhibits structure arising from structure in the combined density-of-states curve.[2] In the case of rocksalt-structure alkali halides the second-order Raman spectra show a wealth of detailed structure. This is primarily due, as will be shown in Sec. 2, to very favorable selection rules for the second-order Raman process. The main purpose of this paper is to show that the peaks in the Raman

[1] F. A. Johnson, *Progress in Semiconductors 9* (Heywood and Company Ltd., London, to be published).

[2] F. A. Johnson and R. Loudon, Proc. Roy. Soc. (London) A281, 274 (1964).