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Infrared Absorption of Oxygen in Silicon

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Three infrared absorption bands have been correlated with the oxygen concentration of silicon. Spectra taken between 4.2°K and 297°K show an unusual temperature-dependent fine structure in the most intense band at 1106 cm^{-1}. Isotopic shifts of two bands have been observed at low temperatures in samples enriched with O^{18}. These results can be explained by a model in which interstitial oxygen is bonded to two adjacent silicon atoms in a nonlinear Si-O-Si unit. Observations on samples with different history indicate a direct but complicated dependence of some growth-dependent variables on oxygen concentration.

INTRODUCTION

CERTAIN properties of silicon crystals are strongly dependent on growth variables.[1] Trap densities,[2] sensitivity to various heat treatments,[3] and even elastic[4] and mechanical[5] properties vary with the method of crystal preparation. Although these variations have not been correlated with any known impurities or structural defects, it has recently been demonstrated that oxygen contamination varies considerably with growth conditions[6,7] and that crystals pulled[8] from the melt may contain 10^{18} or more oxygen atoms/cm^3. No simple correlation between oxygen concentration and growth-dependent variables exists, but the evidence indicates that oxygen plays an important role in these phenomena.

Kaiser, Keck, and Lange[6] have related the intensity of the 1106 cm^{-1} infrared absorption band of silicon with oxygen concentration determined by vacuum-fusion analysis. Lederhandler[9] has observed intensity variations in another weaker band at 515 cm^{-1}. We show here that these absorptions are indeed Si-O vibrations from observation of isotopic shifts on substitution of O^{18} for O^{16}. Infrared spectra of various samples over a wide range of temperature and frequency give information about the configuration of oxygen in silicon. The observed absorptions lead to a model in which the oxygen is widely separated with each oxygen atom bonded to two adjacent silicon atoms in dispersed nonlinear Si-O-Si units. The fine structure in the 1106 cm^{-1} band at low temperatures appears to be associated with minor rearrangement of the oxygen atom in the silicon lattice as the temperature is lowered.

EXPERIMENTAL

Transmission measurements were taken with a Perkin-Elmer double-pass spectrometer using NaCl, CsBr, and CsI optics. Samples were mounted in a three-walled cryostat placed at a focal point in the exit beam. Liquid nitrogen and helium were used as refrigerants. The whole optical system was flushed with dry nitrogen to eliminate atmospheric absorptions. Absorption coefficients were calculated from observed percent transmission correcting for multiple internal reflections. Temperatures were measured with a helium gas thermometer with an accuracy of better than 2°K at fixed points and 5°K at intermediate temperatures. Errors in the absorption coefficients are due primarily to the sharpness of the observed bands. The maximum error which occurs in regions of strong absorption is approximately 10%. Spectral slit widths are indicated in each figure.

Some samples were prepared by pulling[8] from fused-quartz crucibles with or without rotation of the seed, with oxygen introduced "naturally" by reduction of the crucible during growth. Others, prepared by the floating-zone process,[10] were sometimes intentionally contaminated with oxygen by reduction of water vapor during growth.[11] In these experiments the water was enriched with about 12% O^{18} to permit observation of isotopic shifts. Several samples were measured after heat treatments at 450°C and 1000°C.[12] The low-temperature treatment introduces donors while the 1000°C treatment "stabilizes" the sample in the sense that it inhibits formation of donors on further heating at 450°C if the 1000°C treatment has been given for a

Table I. Sample histories.

Sample No.	1	2	3	4	5
History	Pulled, nonrotated	Floating zone 12%, O^{18}, 1% O^{17}	Floating zone	Pulled, rotated	1000°C treatment

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[1] N. B. Hannay, in *Progress in Semiconductors* (Heywood and Company, London, 1956).

[2] Hannay, Haynes, and Shulman, Phys. Rev. **96**, 833(A) (1955).

[3] Fuller, Ditzenberger, Hannay, and Buehler, Phys. Rev. **96**, 833(A) (1955).

[4] D. F. Gibbons (private communication).

[5] Pearson, Read, and Feldman, Bull. Am. Phys. Soc. Ser. II, **1**, 295 (1956).

[6] Kaiser, Keck, and Lange, Phys. Rev. **101**, 1264 (1956).

[7] H. J. Hrostowski and R. H. Kaiser, Bull. Am. Phys. Soc. Ser. II, **1**, 295 (1956).

[8] G. K. Teal and J. B. Little, Phys. Rev. **78**, 647 (1950).

[9] S. Lederhandler (private communication).

[10] P. H. Keck and W. Van Horn, Phys. Rev. **91**, 512 (1953).

[11] H. C. Theuerer, Trans. Am. Inst. Mining Met. Engrs. **206**, 1316 (1956).

[12] Fuller, Ditzenberger, Hannay, and Buehler, Acta Metallurgica **3**, 1 (1955).

sufficient length of time. In all cases the original sample resistivity was high enough so that no appreciable absorption by free charge carriers was observed in the spectral region studied. Sample histories are shown in Table I.

OXYGEN ABSORPTIONS

In the region between 200 and 5000 cm^{-1} we observed three absorptions whose intensities depended on oxygen concentration. The most intense band at 1106 cm^{-1} was previously studied[6] at 300°K and 90°K. Figures 1(a), (b), and (c) show the variation of the shape of this band with temperature in a crystal pulled without rotation, sample 1. The observed frequencies are given in Table II. Identical behavior except for magnitude of absorption coefficient, α, was observed prior to heat treatment in all samples with detectable absorption due to oxygen at 1106 cm^{-1}. This band, which is quite broad at room temperature, shifts toward higher frequency on cooling while $\alpha_{\max}$, the maximum absorption coefficient, increases. These effects continue down to approximately 120°K where a separate peak is resolved at 1135.5 cm^{-1}. At 48°K three distinct peaks are observed. The lowest frequency peak is difficult to resolve and appears as a shoulder in most spectra. Once a given peak is resolved its frequency is unchanged by further cooling. The value of $\alpha_{\max}$ of 1135.5 cm^{-1} continually increases with decreasing temperature while $\alpha_{\max}$ of 1127.9 cm^{-1} decreases after having attained a maximum value near 45°K. The temperature dependence of 1121 cm^{-1} is apparently similar to that of 1127.9 cm^{-1}. Approximate relative intensities,

$$(\alpha_{\max}-\alpha_{\text{background}})\times\text{half-width},$$

of the 1135.5 cm^{-1} and 1127.9 cm^{-1} peaks are plotted as a function of absolute temperature in Fig. 2 using data obtained from three samples with different oxygen concentrations. Although the uncertainty is large because the absorptions in this region overlap considerably, all samples investigated fit these curves within experimental error.

TABLE II. Oxygen absorption frequencies (cm^{-1}).

	297°K	50°K	Relative intensity at 4.2°K
O^{16}	...	1205	0.5
	1106±2[a]	1135.5±0.3 1127.9±0.3 1121 ±1.0	10
	514.6±3.0[b]	517.3±2.5[b]	1
O^{18}	...	~1180 (calculated)	...
	...	1084.6±0.2 1077.0±0.2	1.4
	...	506.4±2.5[b]	~0.14

[a] This uncertainty arises from the breadth of the band.

[b] The apparent center of this band shifts slightly with oxygen concentration because of the influence of the neighboring strong lattice vibration.

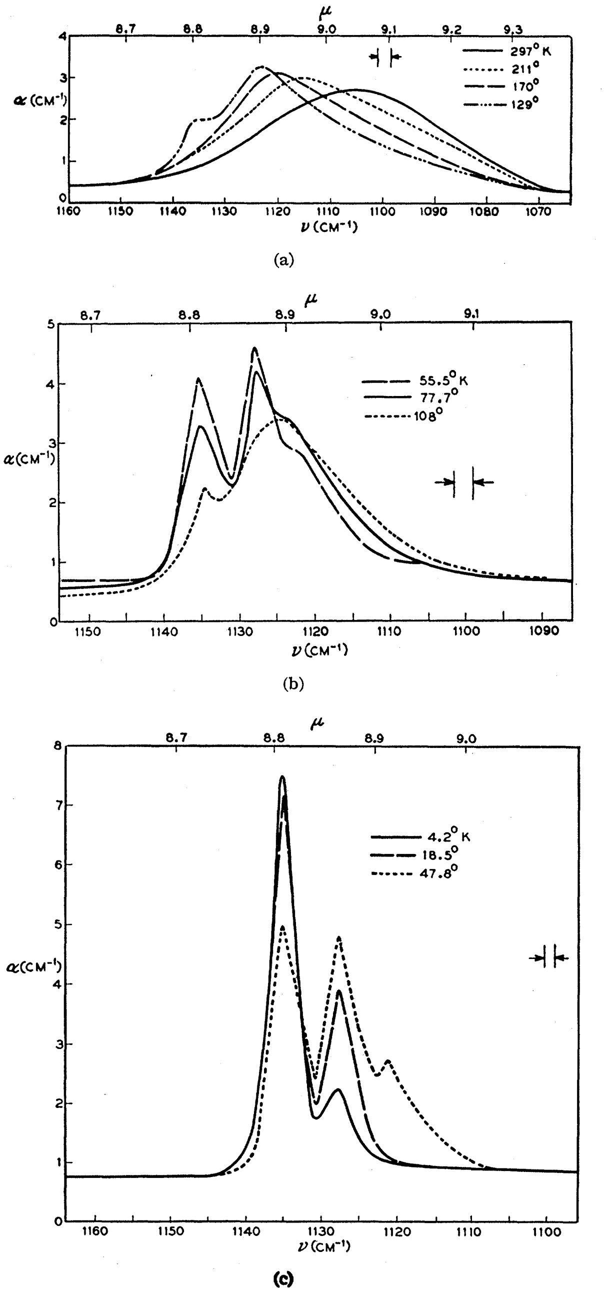

FIG. 1. Variation of the absorption coefficient of the 1106 cm^{-1} band with temperature for a nonrotated, pulled crystal. Spectral slit widths are as shown.

Figure 3 shows absorption at several temperatures of sample 2, which has 12% of the O^{16} replaced by O^{18}. About 50 cm^{-1} toward lower frequency from the O^{16} fine structure we observe similar absorptions with the intensities expected from the abundance of O^{18}. These results prove that the 1106 cm^{-1} band and the fine structure result directly from oxygen in the silicon

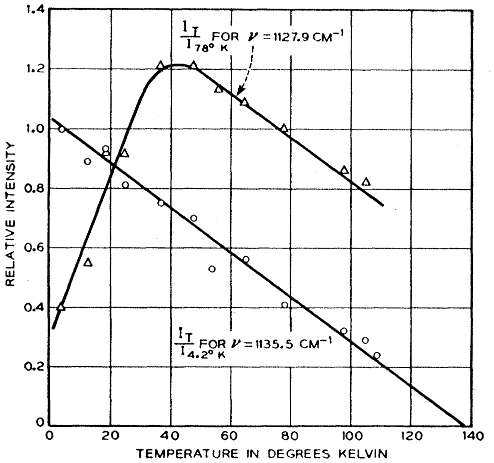

FIG. 2. Relative intensities of the 1135.5 cm^{-1} and 1127.9 cm^{-1} absorptions as a function of temperature.

lattice. The magnitude of the isotopic shift indicates that a Si-O vibration is associated with these bands although the temperature variations of the intensities of the resolved peaks are unusual. In thicker samples a small peak is observed at 1109 cm^{-1} at 4.2°K. This is the corresponding absorption due to O^{17} which amounts to about one percent of the total oxygen concentration.

Figure 4 shows the temperature dependence of the 515 cm^{-1} band for sample 2. There is little change on cooling below 80°K and no fine structure is observed. In addition there is no appreciable shifting of $\alpha_{\max}$ toward higher frequency at lower temperatures. The low-frequency peak which appears on cooling is the O^{18} absorption which verifies that this is also a Si-O vibration. This peak is absent in samples not enriched with O^{18}.

Another band which varies with oxygen concentration occurs at 2305 cm^{-1}. This is less intense than the 515 cm^{-1} band and has been observed only at low temperatures. There is a shoulder on the high-frequency side which shows a different behavior on cooling.[13] Otherwise no fine structure or frequency shift was observed. This band is so weak that no isotopic shift was detectable with our samples. The behavior of this absorption for a pulled rotated crystal at low temperatures is shown in Fig. 5.

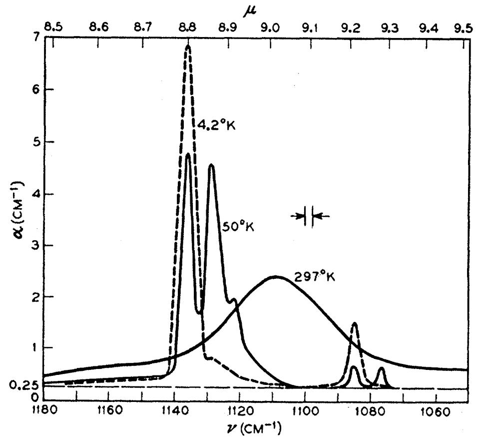

FIG. 3. The absorption coefficient of the 1106 cm^{-1} band at several temperatures for a floating-zone crystal containing oxygen enriched with 12% O^{18} and 1% O^{17}.

Within experimental error the total intensities of the 1106 cm^{-1} and 515 cm^{-1} oxygen bands are temperature independent. The 1205 cm^{-1} band intensity increases with decreasing temperature. The rate of increase seems greater than that of the 1135.5 cm^{-1} peak. The 1106 cm^{-1} band is about an order of magnitude more intense than the others and exhibits a much larger frequency shift on cooling. Relative intensities at all bands are listed in Table II.

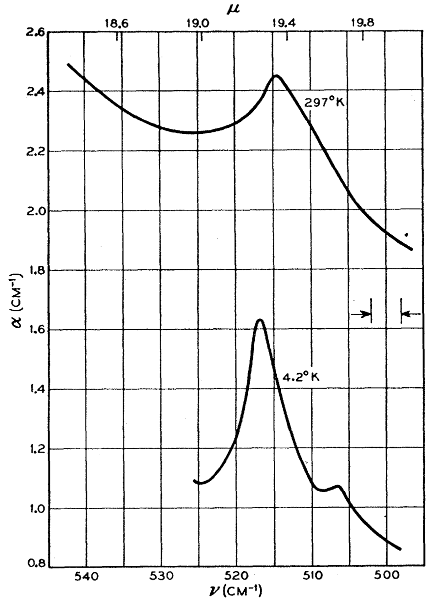

FIG. 4. The absorption coefficient of the 515 cm^{-1} band for a floating-zone crystal containing oxygen enriched with 12% O^{18} at 297°K and 4.2°K.

CONFIGURATION OF OXYGEN IN SILICON

A strong absorption in the 1100 cm^{-1} region occurs in quartz[14] and organic siloxanes.[15,16] Observation of the 1106 cm^{-1} band in silicon containing oxygen led Kaiser, Keck, and Lange[6] to suggest a model, shown in Fig. 6, in which the silicon-oxygen configuration is similar to

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[13] Several other extremely weak bands have been observed at higher frequencies. Since their intensity behavior on cooling is very similar to that of lattice vibrations these are probably combination frequencies of the Si lattice vibrations.

[14] I. Simon and H. O. McMahon, J. Chem. Phys. **21**, 23 (1953).

[15] N. Wright and M. J. Hunter, J. Am. Chem. Soc. **69**, 803 (1947).

[16] R. E. Richards and H. W. Thompson, J. Chem. Soc. **1949**, 124.

that of the above compounds. A bond between adjacent silicon atoms is broken providing two electrons for the formation of two Si-O bonds bridging the broken Si-Si bond. If interaction with the silicon lattice is neglected, this configuration can be treated as a hypothetical nonlinear Si_2O molecule. The validity of this model can be determined from (1) the number of Si-O absorptions, (2) the intensity ratios of corresponding isotopic frequencies, and (3) the calculated force constants and isotopic shifts.

(1) Although any configuration of oxygen in the silicon lattice will result in three vibrational degrees of freedom, an isolated linear Si_2O or a doubly bonded $Si=O$ group would have two degenerate vibrations. If the potential of the lattice has a lower symmetry than these groups, the degeneracy would be removed. However, the expected splittings of these frequencies would be small since the forces between nonbonded atoms are extremely weak compared to those between covalently bonded atoms. In addition a $Si=O$ stretching frequency should occur at a frequency considerably higher than 1100 cm^{-1}. If the oxygen were bonded to some other electrically inactive impurity atom, X, the O–X stretching vibration would also be infrared active.[17] The observation of three widely separated absorptions is in agreement with the expected behavior of nonlinear Si_2O.

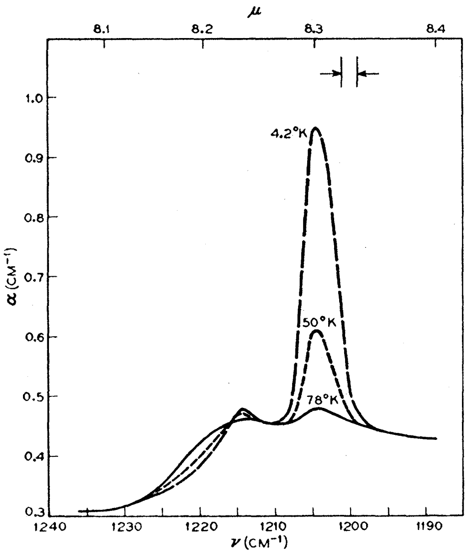

FIG. 5. The absorption coefficient of the 1205 cm^{-1} band at low temperatures for a pulled, rotated crystal.

(2) If the effect of the silicon lattice is neglected, information about the smallest structural unit containing all the SiO bonds is obtained directly from the relative intensities of the O^{16} absorptions and the strongest corresponding absorptions of the O^{18}. Sample 2 contains approximately 87% O^{16}, 1% O^{17} and 12% O^{18}. For nonlinear Si_2O the value expected for the intensity ratio of an O^{16} absorption to an O^{18} absorption is 7.2. With two oxygen atoms bonded to a single silicon atom this ratio becomes 3.6 and decreases further for a silicon atom bonded to three or four oxygen atoms. The experimental values (10/1.4, 1.0/~0.14) are very close to 7.2 (see Table II). This result supports the assumption that there is only one oxygen atom in the isolated silicon-oxygen unit.

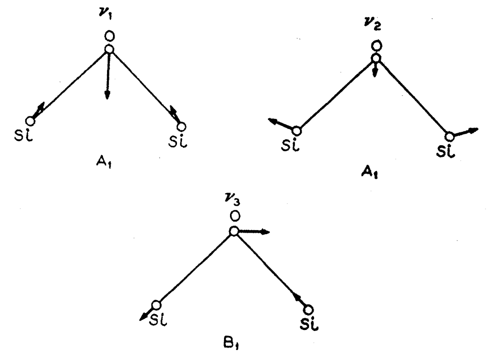

FIG. 6. Schematic normal vibrations of Si_2O.

(3) Figure 6 shows schematically the expected form of the normal vibrations and their symmetry types for a hypothetical Si_2O molecule. All three vibrations are infrared active. With the previously unobserved 1205 cm^{-1} band we have sufficient information to calculate[18] the bond stretching (k_1) and bending[19] (k_2) force constants, the Si_2O angle (2α), and the isotopic shifts.

In order to identify the observed bands with the vibrations shown in Fig. 6, we note the following. It seems certain that only one vibration occurs in the region of 1106 cm^{-1} band. This is indicated by the intensity variation of the fine structure on cooling. If all three absorptions in this region were vibrations of a particular oxygen configuration, the temperature dependence of the intensities would be quite similar, in contradiction to the results shown in Fig. 2. Furthermore, identical isotopic shifts of two accidentally degenerate stretching frequencies, ν_1 and ν_3, would require an impossibly small value of 2α and would be easily resolved for Si_2O^{18} for any reasonable value of 2α.

From the observed isotopic shift we then assign the 1106 cm^{-1} band as ν_3, the antisymmetric stretching motion. It then follows that ν_1 is 1205 cm^{-1} and ν_2 is 515 cm^{-1}. Values of k_1, k_2, and 2α calculated at 4.2°K and room temperature are listed in Table III. For these calculations ν_1 was taken to be 1205 cm^{-1} at room temperature (where it is not observed) and ν_3 to be 1135.5 cm^{-1} at 4.2°K. Both k_1 and 2α increase on cooling while k_2 remains essentially constant.

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[17] Spectra of samples prepared by the reduction of D_2O were identical with those prepared by reduction of H_2O.

[18] G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945). The nomenclature used here is essentially that of Herzberg.

[19] Here $k_2=k_\delta/l^2$, where k_δ is the true bending constant and l the Si-O distance.

TABLE III. Force constants and isotopic shifts for Si_2O.

T(°K)	k_1(10^5 dynes/cm)	k_2(10^5 dynes/cm)	2α	ν_3/ν_3^i Calc[a]	ν_3/ν_3^i Obs[b]	$\nu_1\nu_2/\nu_1^i\nu_2^i$ Calc
297	7.21	1.61	91°40′	⋯	⋯	⋯
4.2	7.37	1.61	94°30′	1.042	1.047	1.047

[a] Calculated assuming $2\alpha = 110°$.
[b] Taking $\nu_3(O^{16}) = 1135.5$ cm^{-1}, and $\nu_3(O^{18}) = 1084.6$ cm^{-1}.

In this treatment, the force constants are calculated from the experimentally observed frequencies neglecting the presence of the lattice which actually restrains the SiO vibrations. The extra restraints are absorbed in our calculated force constants making them larger than the true force constants associated with the Si-O bond stretching and angle bending. Qualitative calculations, which depend strongly on the value assumed for the Si-Si bond-stretching force constant, indicate that the calculated k_1 may be 20% higher than the actual Si-O stretching force constant. Thus the true k_1 is in reasonable agreement with the value of 5.0×10^5 dynes/cm estimated from an analysis of the spectra of organic siloxanes.[15] A similar argument leads to a lower value for k_2. The value of 2α is as good as can be expected from such a calculation.[18] However the isotopic shift of ν_3 indicates that 2α is approximately 110°. Observed and calculated isotopic shifts, assuming $2\alpha = 110°$, are also given in Table III. The agreement between ν_3(Si-O^{16}) and ν_3^i(SiO^{18}) is as good as that obtained for many gaseous triatomic molecules.[18] Although v_1^i was not detected, this band should be observed near 1180 cm^{-1} in samples with high concentrations of O^{18}. These results are entirely consistent with the proposed model.

Similar calculations for oxygen bonded to a completely rigid lattice also show a separation of ν_1 and ν_3 for physically realizable values of α. However, the force constants obtained are roughly twice those given above and all frequencies have the same isotopic shift with

$$\nu_n/\nu_n^i = (18/16)^{\frac{1}{2}} = 1.061.$$

The results indicate that the experimental data are approximated much more closely by the isolated Si_2O model. The Si_2O model neglects interactions between Si-O vibrations and lattice vibrations of the same symmetry type. Although the magnitude of this effect is unknown, it should be remembered that to a first approximation the Si motions are not infrared active.

FINE STRUCTURE OF THE 1106 cm^{-1} BAND

The isotopic shift indicates that there is one Si-O vibration associated with this band. Identical separations of 7.6 ± 0.5 cm^{-1} or 9×10^{-4} ev are obtained for the two major peaks in both isotopic species. Yet the observed splitting at low temperatures cannot be interpreted as the resolution of different Si-O stretching vibrations of a particular oxygen configuration. If this were the case the intensities of the individual peaks would have similar temperature dependence. The intensity variations with temperature are not consistent with those expected for electronic or rotational energy levels associated with this vibration. Any rotational mechanism would produce a more symmetrical structure. The electronic centers would certainly be ionized at room temperature yet no charge carriers have been directly correlated with oxygen in silicon. Other considerations eliminate higher anharmonic vibrations or oxygen-oxygen interactions as possible explanations. It is also unlikely that there are several widely different oxygen configurations of comparable concentrations since the 515 cm^{-1} band does not vary much with temperature.

The normal coordinate analyses at 297°K and 4.2°K indicate, however, that the oxygen configuration is somewhat temperature-dependent as evidenced by the increases in 2α and k_1 on cooling. These changes correspond to an increased separation of the two unbonded silicon atoms or an over-all expansion of the lattice in the neighborhood of the oxygen atoms at low temperature. Since expansion in the direction of the bridged silicon atoms is accompanied by some contraction in the perpendicular direction through the oxygen atom, the total effect is not large. Measurements of the linear coefficient of thermal expansion of silicon containing oxygen by Gibbons[4] verify this expansion of the silicon lattice on cooling. After first contracting on cooling below 300°K the lattice expands again below 125°K, the temperature at which the fine structure becomes observable. The amount of expansion varies with oxygen concentration in a complicated fashion[4] suggesting that other factors are involved. This conclusion is substantiated by the fact that the observed expansion is considerably larger than that which can be accounted for by oxygen alone. These considerations indicate a possible explanation for the fine structure based on minor rearrangements of the oxygen atom.

Although oxygen is interstitial in the sense that it does not occupy a lattice site, it is not at the center of an interstice and theoretically can occupy slightly different positions of varying energy. There are repulsive forces between the oxygen atom and neighboring nonbonded silicon atoms in addition to strong repulsion between the closely spaced nonbonded silicon atoms bonded to the oxygen. These are opposed by the barrier for torsional oscillation of oxygen about the unbounded silicon atoms, strain in the nontetrahedral bonds of these atoms and the general contraction of the lattice on cooling. During growth oxygen atoms are randomly trapped in the silicon lattice. At room temperature thermal agitation permits the oxygen atoms to occupy a number of slightly different configurations of varying energy. On cooling the above interactions force the oxygen into equilibrium configurations dependent on the temperature of the lattice. At 4.2°K most of the oxygen atoms are frozen into the equilibrium position for this temperature.

This mechanism requires only very minor shifts in the positions of the oxygen atoms. Only partial rotations about the bridged Si-Si bond are required. Furthermore it explains the lack of observed fine structure in ν_1 and ν_2. The maximum separation expected for the ν_2 structure is 0.8 cm^{-1} which cannot be resolved with our equipment. The frequency of ν_1 increases with increasing k_1 but decreases with increasing α. Frequency changes produced by this rearrangement are of almost equal magnitude but of opposite sign and thus the position of ν_1 remains constant. The intensities of the separate peaks in ν_3 indicate the relative population of the different equilibrium sites. The intensity increase of ν_1 on cooling is more difficult to explain. The ν_1 motion is greatly restricted by the repulsion of the nonbonded Si atoms, whose separation is not much greater than the normal Si-Si band distance,[20] as indicated by the high value of k_2. The ν_1 band is not detectable at high temperature, either because it is greatly broadened or because the rearrangement on heating reduces the change in dipole moment associated with this motion.

VARIATION OF THE 1106 cm^{-1} BAND WITH METHOD OF GROWTH AND HEAT TREATMENT OF CRYSTAL

Figure 7 shows the absorption of two pulled crystals. The seed was rotated in one case during growth, sample 4, and not rotated in the other, sample 1. Also included is the absorption of sample 3, prepared by the floating-zone technique, which behaves like a typical lattice vibration and decreases on cooling.[6] Rotated and nonrotated samples exhibit the behavior attributed to oxygen on cooling. This figure also shows how the absorption is affected in the rotated sample, 4, after heating for some time at 1000°C. Heating at 450°C for periods of several hours has little effect on the absorption due to oxygen and merely increases the background free charge-carrier absorption due to donor introduction.[21] Table IV gives the relative intensities for these samples. These are typical results which vary slightly with the speed of rotation during growth, crystal diameter, or other variables. Some rotated crystals have shown an α_{max} of about 6 at room temperature. Similar behavior is observed for the 1205 cm^{-1} and 515 cm^{-1} bands.

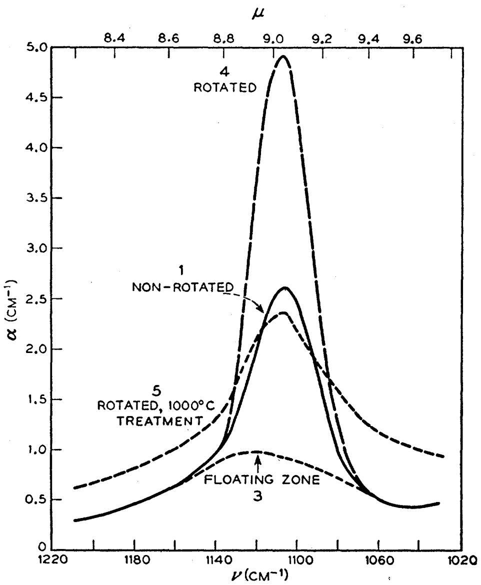

FIG. 7. Room-temperature absorption of various samples in the 1100 cm^{-1} region.

TABLE IV. Relative intensities of 1106 cm^{-1} band for different crystals.

Sample	α_{max} (cm^{-1})	Relative intensity
Floating zone	1.0	1.0
Nonrotated	2.6	2.2
Rotated	4.9	3.7
Rotated (1000°C treatment)	2.4	1.8[a]

[a] Calculated neglecting increased "background" absorption.

Oxygen contamination is high in rotated crystals, low in nonrotated crystals and not detectable in floating-zone crystals. Prolonged heating at 1000°C greatly reduces oxygen absorption in this region indicating that the oxygen has rearranged in a manner which decreases its infrared activity. Kaiser[22] has recently shown that the decrease in absorption is accompanied by the formation of clusters, presumably of SiO_2, dispersed throughout the lattice. The low-temperature spectra of rotated samples heated at 1000°C for as much as 100 hours show the fine structure attributed to dissolved oxygen superimposed on a broad, less intense absorption band of the clusters.[22] These results and the observed intensities of different isotopic species indicate that the three bands discussed here are vibrations of dissolved, widely separated oxygen atoms rather than quartz clusters.

Storage trap densities are roughly $10^{13}/cm^3$ in pulled rotated crystals, $10^{11}/cm^3$ in nonrotated crystals and much less in crystals prepared by the floating-zone technique.[2] This trend parallels the oxygen concentration in similar samples. Heating at 1000°C decreases trap densities by several orders of magnitude in rotated crystals, indicating that if the traps are associated with the presence of oxygen, it is dissolved oxygen atoms rather than SiO_2 clusters that are responsible. The relation between trap density and oxygen contamination is further indicated by the fact that reduction of H_2O vapor during growth of a floating-zone crystal introduces oxygen and also increases the trap density.[23] However trap density is not simply related to oxygen concentration. Although dissolved oxygen appears

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[20] This was pointed out to us by S. Geller.

[21] H. J. Hrostowski (unpublished). There is some indication that heating for long periods (about 100 hours) at 450°C reduces absorption in this region.

[22] W. Kaiser (private communication).

[23] Hannay, Haynes, and Shulman (unpublished).

necessary for the creation of traps, their exact nature is still unknown.

ACKNOWLEDGMENTS

We are indebted to many of our colleagues for assistance in the course of this work. We are particularly grateful to H. Bridgers for furnishing many of the samples and to R. G. Shulman, H. Reiss, M. Lax, and N. B. Hanney for numerous helpful discussions. We also wish to thank W. Kaiser and S. Lederhandler for profitable discussions of their results prior to publication.

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Elastic Constants of Magnesium from 4.2°K to 300°K*

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The adiabatic elastic constants of magnesium single crystals have been measured by an ultrasonic pulse technique. The values at 298°K are in good agreement with the recent values of Long and Smith. The values extrapolated to 0°K are $c_{11}=0.635$, $c_{33}=0.664$, $c_{44}=0.1842$, $c_{12}=0.259$, $c_{13}=0.217$ in units of 10^{12} dynes/cm^2. A Debye characteristic temperature, θ, of 388±3°K has been calculated at 0°K by averaging the inverse cube of the longitudinal and transverse elastic wave velocities over all directions of propagation. Atomic force constants for a central-force model with an electron gas term are also obtained.

I. INTRODUCTION AND METHOD

THE adiabatic elastic constants of single crystals of the metallic elements at 0°K are of interest in the application of the Born-von Kármán theory of lattice dynamics to metals.[1,2] It has been proposed by de Launay[1] that the deviations from the Cauchy relations which are observed experimentally may arise from an electron gas contribution to the elasticity. If this is the case, a central-force model for the lattice forces may be valid for some metals. For such a central-force lattice model, it is possible to compute the interatomic force constants for a reasonable number of neighbor interactions directly from the elastic constants. Moreover, the low-temperature elastic constants provide an experimental test of the validity of any force model.

Magnesium has a hexagonal close-packed structure with an axial ratio (c/a) of 1.623, closely approximating the ratio of 1.633 for ideal closest packing. A crystal with hexagonal symmetry has five independent elastic constants, c_{11}, c_{33}, c_{44}, c_{66} (or c_{12}), and c_{13}, which can be obtained from the velocity of longitudinal and transverse waves propagating in directions parallel, perpendicular, and at 45° to the c axis. The relations between the elastic constants and acoustical wave velocities (U) have been derived previously[2] and are given below.

1. Propagation parallel to the c axis:

$$\rho U_l^2=c_{33},$$

$$\rho U_t^2=c_{44} \text{ (any polarization).}$$

2. Propagation perpendicular to the c axis:

$$\rho U_l^2=c_{11},$$

$$\rho U_t^2=c_{44} \text{ (polarized parallel to the } c \text{ axis),}$$

$$\rho U_t'^2=c_{66}=\tfrac{1}{2}(c_{11}-c_{12}) \text{ (polarized perpendicular to the } c \text{ axis).}$$

3. Propagation at 45° to the c axis:

$$\rho U_t^2=\tfrac{1}{2}(c_{66}+c_{44}) \text{ (polarized perpendicular to the } c \text{ axis),}$$

$$\rho U^2=\tfrac{1}{4}\{c_{11}+c_{33}+2c_{44}\pm[(c_{11}-c_{33})^2+4(c_{13}+c_{44})^2]^{\frac{1}{2}}\}$$

(U_{ql} is given by the plus sign; U_{qt}, by the minus sign).

The subscripts l and t refer to the longitudinal or transverse character of the wave, and ρ is the density. In the direction at 45° to the c axis, it is possible to propagate only one pure wave (the transverse wave polarized perpendicular to the c axis); the two waves of mixed character obtained in that direction are referred to as quasi-longitudinal (*ql*) and quasi-transverse (*qt*). For magnesium the coupling between these waves is weak, and it is possible to excite only the quasi-longitudinal or only the quasi-transverse waves separately.

In this work the velocity of the pure transverse wave in the direction at 45° to the c axis was measured as a check only at 77.6°K and 298°K. The velocities of the other seven waves enumerated above were measured as a function of temperature from 4.2°K to 300°K and

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[2] L. J. Slutsky and C. W. Garland, J. Chem. Phys. **26**, 787 (1957).