

Defects in Irradiated Silicon. II. Infrared Absorption of the Si-A Center

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The Si-A center is a major, radiation-damage defect produced in "pulled" silicon by room temperature irradiation. In this paper (II), we present the infrared measurements which, in conjunction with the spin resonance measurements of the preceding paper (I), establish the identity of the Si-A center. A new infrared absorption band is observed at $12\ \mu$ in electron-irradiated silicon. This band is shown to be a vibrational band of impurity oxygen in the lattice. Macroscopic and microscopic correlations between the $12\text{-}\mu$ band and the spin resonance of the Si-A center are presented. The macroscopic correlations are of production rate, recovery, etc. The microscopic correlations derive from the absorption of polarized infrared radiation by samples of various crystallographic orientations, subjected to a uniaxial, compressive stress. Partial alignment of the defects is induced by the stress and is detected

as a dichroism in the $12\text{-}\mu$ band. This alignment is compared to the corresponding alignment studies in the spin resonance measurements in Paper I. It is shown that the kinetics and magnitude of the response to the stress are the same for the defects observed in both types of measurements. This shows that the $12\text{-}\mu$ band arises from the Si-A center and established the configuration of the oxygen in the defect. These results, together with the results of Paper I, allow us to conclude that the Si-A center is a lattice vacancy with an oxygen atom bridging two of the four broken bonds associated with the vacancy. The remaining two bonds can trap an electron, giving rise to the spin resonance spectrum of the defect. The identification of the Si-A center indicates that the vacancy is mobile in a room temperature irradiation.

I. INTRODUCTION

IN this paper we consider some infrared absorption experiments which are correlative to the spin resonance experiments discussed in the preceding paper.¹

There have been many infrared absorption bands observed in irradiated silicon. The work in this area has been summarized recently in a paper by Fan and Ramdas.² In some cases there have been tentative assignments of energy levels, and other macroscopically measured properties, to certain infrared absorption bands. However, none of these bands has been clearly identified with a microscopic defect configuration. In this paper we discuss a new absorption band at approximately $12\ \mu$, which appears upon electron irradiation of oxygen-containing silicon. This band is sharper and weaker than those bands previously observed, but is adequately intense. We will present evidence which shows that this band is an oxygen vibrational band and that it arises from the same defect which gives rise to the Si-A center spin resonance.³ In addition, we will conclude that the position of the oxygen in the previously proposed model for the A center is correct. This evidence is of two types. First, there are a variety of macroscopic comparisons between the $12\text{-}\mu$ band and the A center resonance (e.g., production rate, annealing, etc.). Second, there are the infrared measurements on samples subject to a uniaxial stress. These measurements agree with the predictions based on the model for the A center and on the results of the spin resonance on samples subjected to a uniaxial stress. They represent a correlation between the $12\text{-}\mu$ band and the spin resonance results, on a microscopic level, and are the most cogent arguments for establishing the model for the A center.

II. EXPERIMENTAL

The only experimental matters we will discuss in this paper are those unique to the infrared experiments. For such matters as sample material, irradiation procedure, etc., see the preceding paper.

Several types of infrared spectrometers were used: two Perkin-Elmer prism spectrometers [a model 112 (4000 to 350 cm^{-1}) and a model 21 (700 to 300 cm^{-1})] and a Beckman (IR7) grating spectrometer (3000 to 650 cm^{-1}). The spectral slit width of these instruments differ. The smallest spectral slit width we used was $\sim 1\text{ cm}^{-1}$ in the Beckman. The data were reduced to values of absorption coefficient by using the formula which includes multiple reflections, given by Fan and Becker.⁴ When accurate values of intensity were required, care was taken that the spectral slit width of the spectrometer was small compared to the natural width of the absorption line.⁵ Then the product of the maximum absorption coefficient and the half-width at half maximum was used as the measure of the intensity of the absorption band.⁵

The device shown in Fig. 1 was used to apply a uniaxial stress to samples during infrared measurements. It is essentially a "C" clamp with a movable member on top. By tightening the screw at the open end, a force can be applied through the leveling pedestals to the silicon sample. The strain gauge allows the force to be applied in a calibrated and reproducible way. The calibration of this strain gauge, and the temperature dependence of the calibration, was obtained by comparison with a strain gauge mounted on a dummy sample, which had been calibrated on an Instron machine. As is shown in Fig. 1, the infrared aperture

¹ G. D. Watkins and J. W. Corbett, *Phys. Rev.* **121**, 1001 (1961).

² H. Y. Fan and A. K. Ramdas, *J. Appl. Phys.* **30**, 1127 (1959).

³ In the remainder of this paper (except for the summary) we will refer to this center as the A center.

⁴ H. Y. Fan and M. Becker, *Semiconductor Materials* (Butterworths Scientific Publications, Ltd., London, 1951).

⁵ See *Chemical Applications of Spectroscopy*, edited by W. West (Interscience Publishers, Inc., New York, 1956), p. 271 ff; D. A. Ramsay, *J. Am. Chem. Soc.* **74**, 72 (1952).

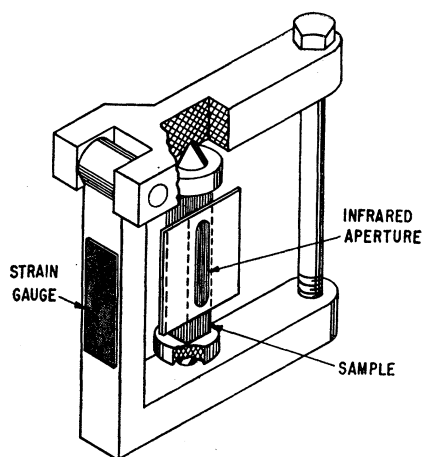


FIG. 1. Device for applying a uniaxial stress to samples during infrared measurements.

is smaller than the sample size. The whole device shown in Fig. 1 could be placed inside a cryostat so that infrared measurements could be made as a function of stress applied at low temperatures. In this case sample temperatures were monitored by a thermocouple mounted on the side of the sample, but shielded from the infrared beam.

Some of the infrared absorption measurements were made with an Eastman Kodak Far Infrared filter, series 230, placed before the sample. This filter absorbs the radiation of wavelength less than 3μ . No differences in the $12\text{-}\mu$ band were observed in measurements with and without this filter. The filter was used to reduce the amount of the sample heating by radiation from the source.

When polarized infrared measurements were required, an analyzer was used which had a polarization efficiency of approximately 85%, as estimated by measurements of transmission through two crossed analyzers. Of course, the combination of cryostat, polarizer, and beam filter resulted in considerable light loss. As a result, adequate signal-to-noise for the intensity measurements was achieved by using a long integration time and slow scan. All the intensity data presented represent an average of several spectrometer runs.

III. INFRARED ABSORPTION IN UNIRRADIATED SILICON

Before discussing the observations on irradiated silicon, it is helpful if we discuss the infrared absorption before irradiation. There are three types of absorption which concern us: free-carrier absorption, lattice bands, and impurity vibrational bands. In our samples the free-carrier absorption is small and readily assessable. Upon irradiation it disappears because of carrier removal. It will not enter further into our considerations.

The lattice band absorption⁶ is appreciable, but, in the spectral region of our interest, appears to be unaffected by irradiation.

The impurity vibrational bands that will concern us are associated with oxygen. Several bands have been previously observed and ascribed to isolated oxygen atoms in the silicon lattice.⁷ We will discuss primarily the most intense band, the one at approximately 1136 cm^{-1} (and its isotopic shift upon the substitution of O^{18} for O^{16}). It is conventional to refer to this band as the $9\text{-}\mu$ band.

The configuration of oxygen in the silicon lattice which has been suggested⁷ to account for these bands is shown in Fig. 2(a). The oxygen does not occupy a substitutional site, but, rather, interrupts a normal Si-Si valence bond, forming a nonlinear Si-O-Si molecule imbedded in the Si lattice. We will refer to the oxygen in this molecule as interstitial. The various bands are then attributed to the normal vibrational modes of this nonlinear molecule. Specifically, the $9\text{-}\mu$ band is identified with the antisymmetric stretching vibration (ν_3).^{7,8}

In this configuration the Si-Si axis of the molecule is an axis of rotation of the Si-O-Si molecule, there being six equivalent positions for the oxygen. There is a mode of oscillation corresponding to this degree of freedom. The $9\text{-}\mu$ band has a fine structure which causes the band shape and position to vary substantially with temperature.⁷ This fine structure has been interpreted as arising from the coupling of the ν_3 vibration and this "rotational" mode of oscillation.⁹

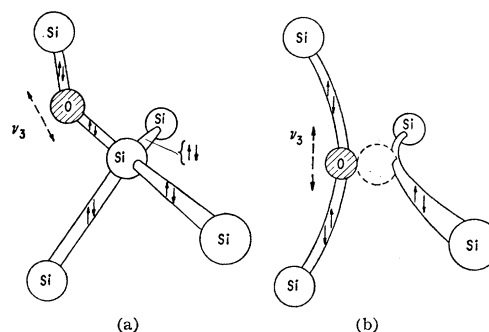


FIG. 2. Configuration of the nonlinear Si-O-Si molecule for (a) the case in which the oxygen is in the "interstitial" site which is associated with the $9\text{-}\mu$ band, and (b) the case in which the oxygen is in the "substitutional" site which is associated with the $12\text{-}\mu$ band and the A center. The ν_3 dipole moment direction is indicated.

⁶ For a discussion of these bands, see R. J. Collins and H. Y. Fan, *Phys. Rev.* **93**, 674 (1954); M. Lax and E. Burstein, *ibid.* **97**, 39 (1955); and F. A. Johnson, *Proc. Phys. Soc. (London)* **73**, 265 (1959).

⁷ H. J. Hrostowski and R. H. Kaiser, *Phys. Rev.* **107**, 966 (1957); *J. Phys. Chem. Solids* **9**, 214 (1959).

⁸ G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1945), p. 168 ff.

⁹ H. J. Hrostowski and B. J. Alder, *J. Chem. Phys.* **33**, 980 (1960).

IV. INFRARED ABSORPTION IN IRRADIATED SILICON

A. 12- μ Band

We are now ready to consider what happens upon irradiation. We have observed the growth of a new infrared absorption band as a result of electron irradiation of silicon.^{10,11} The temperature dependence of this band is shown in Fig. 3. As can be seen, the band narrows and shifts to high frequency with decreasing temperature. We will refer to the band as the 12- μ band. The relative intensity variation with temperature shown in Fig. 3 cannot be considered quantitative since the band narrows to appreciably less than our spectrometer spectral slit width, making quantitative measurements unfeasible. The band as it appears in a double-beam spectrometer run at room temperature is shown in Fig. 4. Here the normal lattice band absorptions are retained in the figure. In Fig. 5 we show the same type of data for two successive irradiations of a sample of silicon kindly supplied us by Dr. H. J. Hrostowski. This sample was doped with oxygen enriched to approximately 12% O¹⁸. We see from the figure that not only do we get the usual 12- μ band (828 cm⁻¹), but we also get a band at approximately 791 cm⁻¹, corresponding to the isotopic substitution of O¹⁸ for O¹⁶. This clearly established that the 12- μ band is a vibrational band involving oxygen.

It will be recalled that for interstitial oxygen [see Fig. 2(a)] the most intense band, the 9- μ band, is identified with the antisymmetric stretching vibration (ν_3). We therefore suggest that the 12- μ band is the

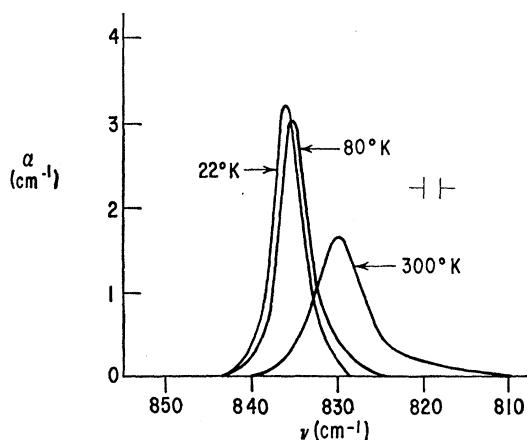


FIG. 3. The temperature dependence of the 12- μ band. As mentioned in the text, with decreasing temperature the band narrows to less than our spectral slit width (shown) so that the absorption coefficients and apparent half-widths must be considered instrumental.

¹⁰ J. W. Corbett, G. D. Watkins, and R. M. Chrenko, Bull. Am. Phys. Soc. 5, 25 (1960).

¹¹ Some other bands were observed upon irradiation but only in one silicon boule. See also A. K. Ramdas and H. Y. Fan, Bull. Am. Phys. Soc. 5, 197 (1960).

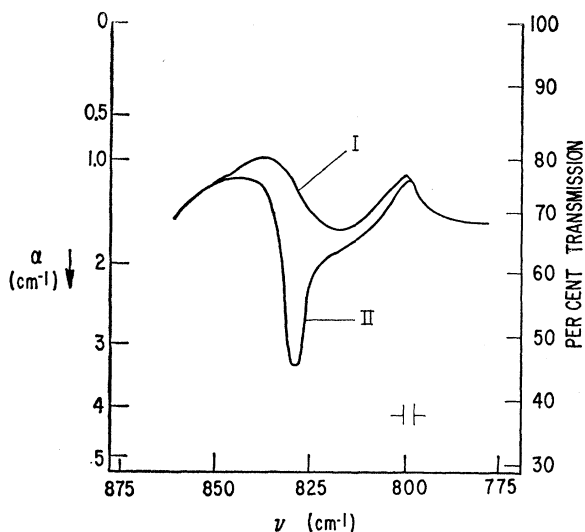


FIG. 4. Infrared transmission (double beam) of oxygen-doped silicon measured before (I) and after an irradiation of 1.7×10^{19} elec/cm² (II). The band at 830 cm⁻¹ ($\sim 12\mu$) appears superimposed on the normal lattice bands. The transmission scale is corrected for the reflection losses at the surface of the sample. The spectral slit width is shown.

corresponding vibration¹² for the oxygen configuration in the model of the *A* center discussed in the preceding paper and shown in Fig. 2(b). We will refer to the oxygen in this nonlinear Si-O-Si molecule as substitutional. In this configuration, the oxygen bridges the valence bonds of two of the nearest neighbor silicons of a silicon vacancy site. As discussed in the preceding

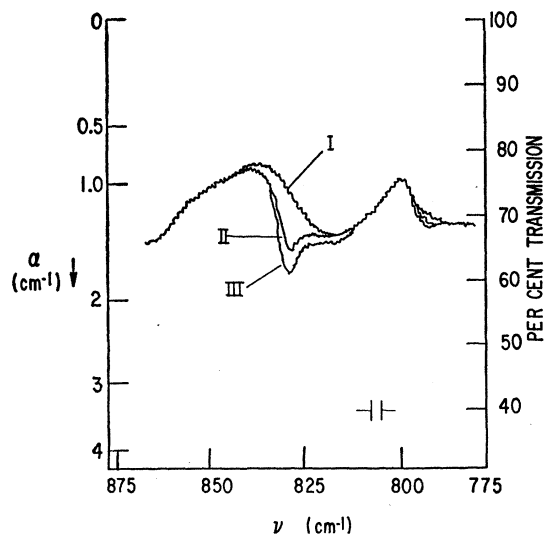


FIG. 5. Infrared transmission (double beam) of a silicon sample doped with oxygen containing 12% O¹⁸, before irradiation (I), after a total flux of 2.6×10^{18} elec/cm² (II), and after a total flux of 5.8×10^{18} elec/cm² (III). The transmission scale is corrected for reflection losses. The spectral slit width is shown.

¹² The assignment of the 12- μ band to this particular vibration receives support from the polarized light absorption measurements described in Sec. IV(B-2).

paper¹ the remaining two valence bonds neighboring the vacancy site form a molecular bond. In this state [as shown in Fig. 2(b)] the defect is electrically neutral. The molecular bond can trap an additional electron and give rise to the spin resonance of the *A* center. In all the infrared measurements in this paper the defect is observed in the neutral state.

In the valence force treatment⁸ of the vibrational modes of the Si-O-Si molecule, the frequency ν_3 is given by

$$(2\pi\nu_3)^2 = [1 + (2M_{\text{Si}}/M_{\text{O}}) \sin^2\alpha] k_1/M_{\text{Si}}, \quad (1)$$

where M_{O} is the mass of the oxygen atom, M_{Si} the effective mass of the silicon atom, k_1 the restoring force constant for changes in the equilibrium Si-O bond distance, and 2α the interior angle between the two Si-O valence bonds. In the isotope shift it is assumed that the only parameter change is the change in M_{O} corresponding to the substitution of O^{18} for O^{16} . Since for the 12- μ band the ratio of the observed frequencies in the isotope shift $\nu_3(16)/\nu_3(18) = 1.047$ is the same as the ratio observed for the 9- μ band,⁷ Eq. (1) implies that the quantity $[1 + (M_{\text{Si}}/M_{\text{O}}) \sin^2\alpha]$ is the same for the 12- μ band as for the 9- μ band. Since we do not expect the effective mass of the silicons to change much, this implies that the angle between the bonds is not much different in the two configurations.

From Eq. (1) and the change in frequency from that for the 9- μ band to that for the 12- μ band, we can conclude that the restoring force constant k_1 for the 12- μ band is approximately one-half that for the 9- μ band. This we interpret as the result of the increased Si-O bond distance for the 12- μ configuration [Fig. 2(b)] over that for the 9- μ configuration [Fig. 2(a)].

It is interesting to inquire as to why the 12- μ band does not exhibit fine structure as does the 9- μ band. As has been mentioned in Sec. III, an interpretation of the 9- μ band fine structure has been given by Hrostowski and Alder⁹ in terms of a coupling between the ν_3 vibration and the "rotational" mode of oscillation around the axis joining the two silicon atoms of the Si-O-Si molecule. We notice that for the 12- μ configuration [Fig. 2(b)], this axis is not an axis of rotation in that there is not the multiplicity of equivalent sites for the oxygen that exists in the 9- μ configuration. There is still a mode of oscillation corresponding to this degree of freedom but it is not a rotational mode. This suggests that the absence of fine structure for the 12- μ band may be the result of the difference in the character of this mode for the two defect configurations.

We made a cursory search in the range 4000 to 350 cm^{-1} and found no additional bands we could associate with oxygen. We attribute this to the fact that in analogy with the additional bands found for interstitial oxygen, the other vibrational modes of the substitutional Si-O-Si molecule should be much weaker than the ν_3 .

B. Identification as the *A* Center

We are now ready to consider if the defect which gives rise to the 12- μ band is the same defect seen in the spin resonance of the *A* center. We will conclude that it is. The arguments fall into two categories. First, there are macroscopic correlations between the infrared and spin resonance experiments. Second, there are microscopic correlations between the experiments.

1. Macroscopic Correlations

Of the macroscopic correlations, we will consider first the production of the 12- μ band as a function of sample material and total irradiation flux. As is observed for the *A* center in spin resonance, the production rate varies grossly with total interstitial oxygen content (as estimated from the intensity of the 9- μ band). That is, in floating zone silicon (oxygen concentration equal to approximately $10^{16}/\text{cm}^3$), the production rate is below detectability; in pulled silicon (oxygen concentration equal to approximately $10^{18}/\text{cm}^3$), the production rate can be quite high.

In detail, however, the production rate curve can vary significantly from boule to boule in a way that does not appear to be correlated simply with oxygen content alone. Even so, a detailed correlation between the production rate of the spin resonance of the *A* center and the production rate of the 12- μ band is found to exist. Consider, for example, the two production curves shown in Fig. 6. These are for samples from two different pulled crystal boules, the 410 boule containing approximately twice as much oxygen as the 404 boule. For doses above approximately 10^{18} elec/ cm^2 the 12- μ

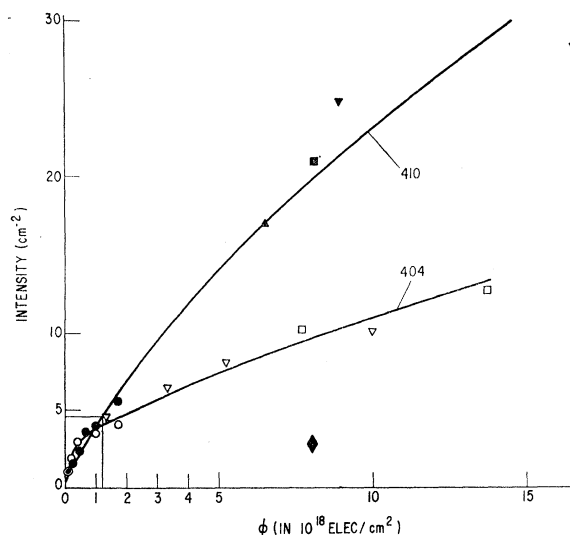


FIG. 6. Intensity of 12- μ band vs total flux of irradiating electrons for samples from two boules; No. 410, solid points and No. 404, open points. The solid diamond refers to the irradiation of a No. 410 sample heat-treated to "precipitate" the oxygen in solution in the silicon.

intensity is greater in the 410 than in the 404, correlating with their relative oxygen contents. However, at lower doses, the 404 curve actually crosses over the 410 curve, giving a higher initial 12- μ production rate in this lower oxygen content material. It is this low-dose production rate that must be compared to the spin resonance *A*-center rate, which is taken in the dose range less than 10^{17} elec/cm² (see preceding paper¹). The *A*-center spin resonance production rate η measured in the identical 404 sample was $\eta = 0.14$ cm⁻¹ (i.e., defect/cm³ per 1.5-Mev electrons/cm²); for the 410 sample, the result was $\eta = 0.07$ cm⁻¹. The absolute values of these production rates may be in error by a factor of ~ 1.5 – 2 ,¹³ but the ratio of 2, being insensitive to some of the instrumental errors, should be somewhat more accurate. The accuracy of the infrared measurements in this low-flux region is poor, the bands at approximately 10^{17} elec/cm² being just above the noise. However, it is clear that the initial production rate in the 404 boule is the greater (see Fig. 6) in agreement with the spin resonance result, and a ratio of 2 between the two boules is not inconsistent with the experimental data.

In addition to the relative production rate correlations, it is possible to make a rough comparison of the *absolute* production rates. To obtain an estimate of the defect concentration corresponding to a certain intensity of the 12- μ band, we use the correlation established by Hrostowski and Kaiser⁷ between the intensity of the 9- μ band and the oxygen content as measured by vacuum fusion analysis. Estimating the 12- μ defect concentration in this way in essence assumes the same oscillator strength for the 12- μ band as for the 9- μ band. This assumption is weak, but is the best that can be done at this point. The value estimated in this way for the 404 defect production rate from the initial slope of Fig. 6 is $\eta \sim 0.15$ cm⁻¹. This agreement must be considered fortuitous in view of the possible errors in both the spin resonance and 12- μ estimates, but it certainly demonstrates that the rate data are consistent.

It is the high-dose region of Fig. 6 that correlates most closely with the oxygen content. Also shown in Fig. 6 is the 12- μ intensity at $8 \cdot 10^{18}$ elec/cm² in a 410 sample which had been given a heat treatment (100 hr at 1000°C) prior to irradiation. The 9- μ band intensity had been reduced by a factor of 7.5 as a result of this treatment, in close agreement with the subsequently produced 12- μ intensity. This would tend to confirm that the 12- μ band results when a vacancy is trapped by an interstitial oxygen atom in that the total number of such defects that can be produced is proportional to the initial interstitial oxygen content.

The variation of the initial production rates suggests a competition with other traps for the vacancy. It is known that oxygen exists in unirradiated silicon in a

variety of agglomerate configurations¹⁴ as well as in the isolated form. It is possible that oxygen in these configurations can also trap vacancies causing the variation, for instance, between the 404 and 410 samples of Fig. 6. The equilibrated concentration of the competing agglomerates should increase as a relatively high power of the oxygen concentration,¹⁴ explaining the decreased *A*-center production rate in the higher oxygen content material (410). On the other hand, reducing the isolated oxygen content by heat treatment should reduce the *A*-center production rate because the higher aggregates are being formed in the process. This is borne out in the heat-treated 410 sample of Fig. 6 in that the *A*-center production rate was measured by spin resonance to be reduced a factor of 2.5 (see previous paper¹).

The association of a vacancy with an oxygen to form the *A* center removes the oxygen from its normal configuration. Therefore, we would expect to observe a decrease of the 9- μ band upon irradiation. We have performed such measurements and find, at best, a qualitative correlation. There is a change upon irradiation which saturates upon increasing irradiation. However, depending upon the temperature at which measurements were made, we found different results. We attribute these difficulties to the problems in assessing the lattice bands under the 9- μ band, and to possible changes in the agglomerate oxygen bands under the 9- μ band.

Next in the way of macroscopic measurements we consider the behavior of the 12- μ band upon annealing. In Fig. 7 are shown the isochronal recovery of the 12- μ band and of the *A*-center spin resonance. Again we see the correlation between the two measurements. Also shown in Fig. 7 is the recovery of the lifetime in irradiated silicon as measured by Bemski and Augustyniak.¹⁵

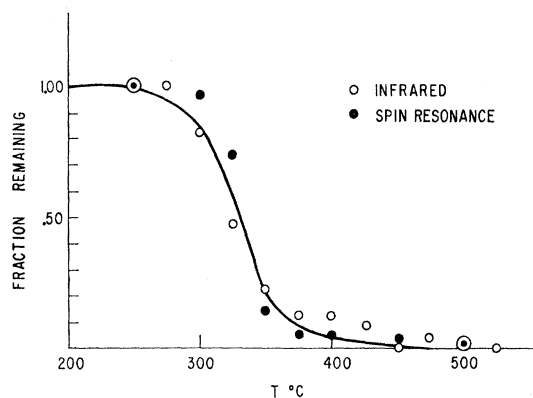


Fig. 7. Recovery of the 12- μ band (open circles) and the *A*-center spin resonance (closed circles) during a (15 min) isochronal anneal. The solid line is calculated from the recovery of lifetime data of Bemski and Augustyniak (see footnote 15) using their activation energy of 1.3 ev.

¹⁴ W. Kaiser, H. L. Frisch, and H. Reiss, Phys. Rev. **112**, 1546 (1958).

¹⁵ G. Bemski and W. M. Augustyniak, Phys. Rev. **108**, 645 (1957).

¹³ G. D. Watkins, J. W. Corbett, and R. M. Walker, J. Appl. Phys. **30**, 1198 (1959).

It has been thought that the recombination did not¹⁶ proceed through the *A*-center level at ($E_c - 0.17$ eV), but more recent work has been interpreted¹⁷ as showing that it does. The agreement of our data with the lifetime recovery suggests the latter interpretation but is not decisive on this question.

More information concerning the end product of the recovery is available in the infrared measurements.¹⁸ These data are again consistent with the detailed identification of the *A* center, but a more extended discussion must be deferred to a subsequent publication.

2. Microscopic Correlations

Thus far we have discussed macroscopic correlations between the 12- μ band and the *A*-center resonance. These have all been accounted for by the model for the *A* center. However, we have not as yet considered a comparison of microscopic information obtained in the infrared with the detailed predictions of the spin resonance. This type of information can be obtained by studying the absorption of polarized infrared radiation by a sample subjected to a uniaxial stress. As discussed in the preceding paper,¹ as the result of a uniaxial stress applied to the crystal, all the defect orientations are no longer equally probable. If the stress is applied at a temperature at which the defects can reorient, the resultant population of the various sites will reflect the influence of the stress. This means that the Si-O-Si molecules will be preferentially oriented along certain directions. Hence the dipole moment for the ν_3 vibration, which is parallel to the Si-Si axis in the Si-O-Si molecule, will also manifest this alignment. Consequently, the absorption of polarized infrared radiation will no longer be independent of the orientation of the plane of polarization with respect to the crystal axes. Rather, we will find an induced dichroism for polarized radiation as a result of the uniaxial stress. Using this technique we can compare the results of uniaxial stress experiments performed in the infrared to those performed with the spin resonance.

In the first type of experiment, the rate at which the induced dichroism decays upon releasing the stress is measured. We have done this type of experiment both isothermally and in a tempering experiment. The isothermal experiments are conceptually the simplest. A stress is applied to the crystal to induce a dichroism and then the sample temperature is lowered to the isothermal temperature. The spectrometer is set to the frequency of maximum absorption. Upon releasing the stress the decay of the additional intensity is continuously recorded. From this record the relaxation time can be measured. The isothermal experiment, of

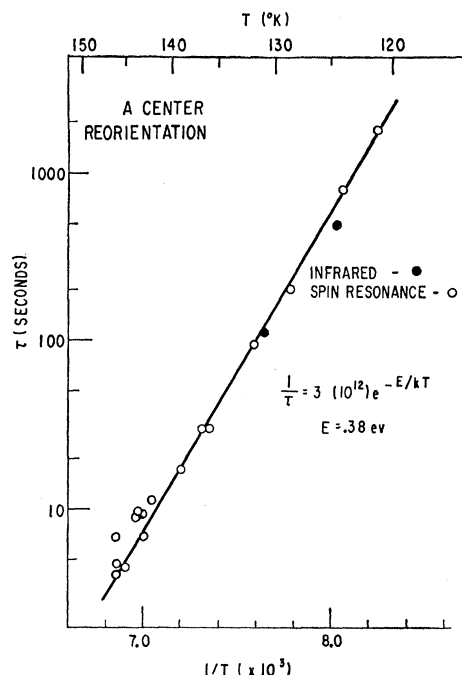


FIG. 8. Isothermal relaxation time (τ) vs temperature for measurements in the infrared (closed circles) and spin resonance (open circle).

course, requires care in maintaining the temperature control in the cryostat. Results for relaxation times in the isothermal infrared measurements are shown in Fig. 8, superimposed on the spin resonance isothermal data from the preceding paper.

In the tempering experiment the stress is applied to induce the dichroism and then the temperature is lowered to the point at which the defects cannot reorient. Then the stress is removed. The induced dichroism remains "frozen in." Now the sample is allowed to warm slowly. The spectrometer scans through the absorption band periodically during the warming. The results of such an experiment are shown in Fig. 9. The

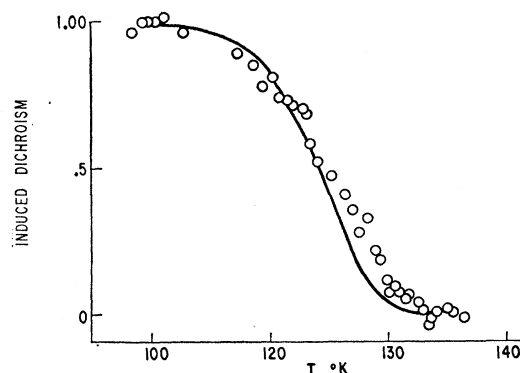


FIG. 9. The fractional recovery of the stress-induced dichroism during a tempering experiment. The circles indicate experimental values. The solid line was calculated from the spin resonance data.

¹⁶ G. K. Wertheim, Phys. Rev. **105**, 1730 (1957); **110**, 1272 (1958); **111**, 1500 (1958).

¹⁷ G. N. Galkin, N. S. Rytova, and V. S. Vavilov Fiz. Tverd. Tela, **2**, 2025 (1960).

¹⁸ G. D. Watkins, J. W. Corbett, and R. S. McDonald, Bull. Am. Phys. Soc. **5**, 26 (1960).

warming rate in this experiment was quite constant over the temperature range considered. This simplifies the comparison to the spin resonance data. The mathematical description of a constant warming-rate tempering curve has been given by Primak.¹⁹ Using the recovery parameters from the preceding paper and the warming rate of $6.9 \times 10^{-3} \text{ K/sec}$ we arrived at the solid curve in Fig. 9 for the corresponding recovery of spin resonance.

As can be seen from Figs. 8 and 9, the defect reorientation which takes place in the infrared is the same reorientation that takes place in the spin resonance. We therefore conclude that the $12\text{-}\mu$ band arises from the same defect as does the A -center resonance.

In the second type of experiment, we compare the amount of defect alignment produced in the infrared experiments to the amount expected from the spin resonance experiments. In these experiments a stress is applied along a specific crystallographic axis and the infrared absorption measured parallel and perpendicular to the stress axis. The type of results obtained can be seen in Fig. 10. Here we see a double-beam spectrometer recording of the $12\text{-}\mu$ absorption at room temperature before stress, and after stress with the E vector of the analyzer parallel and perpendicular to the stressed axis. The actual data in the numerical comparison are given as the ratio R of absorption coefficient for the stressed sample to that of the unstressed sample, for a given analyzer orientation. These data are sensitive to changes in the experimental conditions (e.g., sample position) upon applying the stress and hence are more difficult to obtain than data comparing parallel and perpendicular polarizer orientations (the dichroic ratio) for a given sample configuration. However, this procedure preserves more information and is a more critical test.

The data obtained in these experiments are presented in Table I. These data were taken at 310°K . We also took data at 155°K . Lowering the temperature, of course, increases the Boltzmann factor which describes the defect alignment and, consequently, the ratios were larger. However, obtaining quantitative data at 155°K was not feasible because the absorption band was too sharp for the spectrometer spectral slit width. Moreover, the apparent linewidth changed upon stressing. While this is quite interesting, our apparatus was unable to cope with these problems. Therefore, we present only the room temperature data where these effects do not introduce errors.

Also shown in Table I are predictions based on the spin resonance data¹ of the ratio to be observed in the infrared. These predictions were arrived at by using the formulas for the populations of the various nonequivalent sites given in the preceding paper,¹ correcting the Boltzmann factors for the fact that the infrared experiments were performed at 301°K and a stress S higher than the spin resonance measurements. (The spin reso-

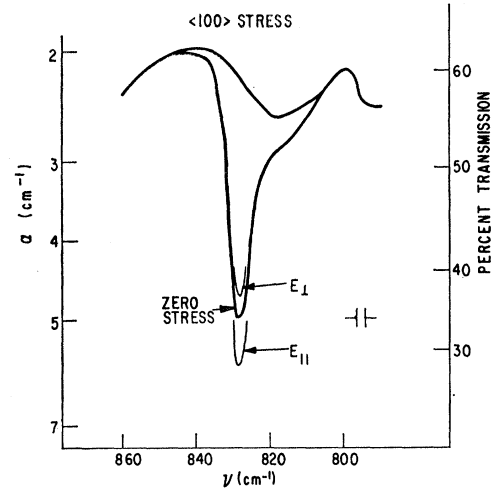


FIG. 10. Infrared transmission (double beam) for the case of a $\langle 100 \rangle$ uniaxial stress experiment. The data shown are for 0 stress and for 26 800 psi stress, with the polarizer E vector \perp and \parallel to the stress axis. The lattice bands are also shown and the transmission scale is corrected for reflection losses.

nance measurements were performed at 120°K and $S = 12\,500$ psi.) Once the various populations were obtained the predicted ratios were readily obtained by resolving the components of the dipole moment for each site along the analyzer directions (E_\perp and E_\parallel) and correcting for the polarization analyzer's efficiency. We see there is rather good agreement. Since the axis of the dipole moment of the ν_3 vibration is perpendicular to that of the other major modes of vibration of the Si-O-Si molecule, this agreement supports the assignment of the $12\text{-}\mu$ band to the ν_3 vibration.

The data in Table I show that the Si-O-Si molecule alignment by the stress field is as predicted by the spin resonance. (An interpretation of this response in terms of the model of the center and how it reacts to the local

TABLE I. Results of measurements of the ratio R of the $12\text{-}\mu$ absorption coefficient at stress S to that at 0 stress for experiments performed on crystals of different orientations. The column marked "polarization" refers to the orientation of the E vector of the polarizer with respect to the stress axis.

Stress axis	Viewing axis	S (psi)	Polarization	Spin res. prediction	Infrared experiment
$\langle 100 \rangle$	$\langle 100 \rangle$	26 800	\parallel	1.23	1.24
			\perp	0.92	0.92
	$\langle 100 \rangle$	25 900	\parallel	1.11	1.06
			\perp	1.08	1.03
$\langle 110 \rangle$	$\langle 110 \rangle$	26 400	\parallel	1.07	1.06
	$\langle 110 \rangle$		\perp	0.85	0.80
$\langle 111 \rangle$	$\langle 110 \rangle$	19 300	\parallel	1.00	0.98
			\perp	1.00	1.00

¹⁹ W. Primak, Phys. Rev. **100**, 1677 (1955).

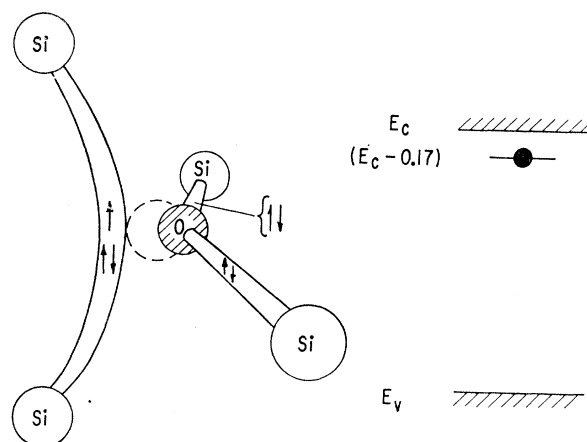


FIG. 11. Model of the *A* center showing the unpaired electron which gives rise to the spin resonance, in the Si-Si molecular bond. The associated electrical level is at $(E_c - 0.17$ ev).

strain field is presented in the preceding paper.¹) These data we consider sufficient to establish that the oxygen is properly placed in the model of the *A* center.

V. SUMMARY

In these papers we have discussed the detailed properties of the Si-*A*-center spin resonance and the 12- μ infrared band. On the basis of both macroscopic and microscopic correlations, it is concluded that these are properties of the same defect. It is, moreover, concluded

that the previously proposed model for the Si-*A* center correctly described this defect.

The Si-*A* center is then a vacancy associated with an oxygen atom as shown in Fig. 11. The oxygen bridges two of the dangling bonds of the vacancy and the remaining two bonds form a molecular bond. This molecular bond can, provided the Fermi level is high enough, trap an extra electron in an antibonding orbital. This state we have previously¹⁸ shown to be the $(E_c - 0.17$ ev) level of Wertheim¹⁶ and Hill.²⁰

We have previously¹³ drawn conclusions concerning the mobility of the lattice vacancy. These conclusions were contingent on the identification of the Si-*A* center and another center (Si-*E*) as containing a vacancy. In this paper we have seen that the Si-*A* center does have a vacancy as previously proposed. In a subsequent paper²¹ we will show that the Si-*E* center also incorporates a vacancy. The identification of these centers being established, we can conclude that *the silicon lattice vacancy is mobile under the conditions of the irradiation experiment.*

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²⁰ D. E. Hill, Phys. Rev. **114**, 1414 (1959).

²¹ G. D. Watkins and J. W. Corbett (to be published).

Solution of the Functional Differential Equation for the Statistical Equilibrium of a Crystal*

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The *s*-particle distribution functions ($s=1, 2, \dots$) of classical equilibrium statistical mechanics are determined for a crystal, as power series in the temperature. They are obtained by solving Bogolyubov's functional differential equation. From the distribution functions, the thermodynamic functions of a crystal are computed as power series in the temperature. The leading terms in these series are the usual classical results which are customarily derived by assuming that the potential energy is a quadratic function of the particle displacements. The further terms, which depend upon the nonquadratic or anharmonic terms in the potential, provide corrections to the usual results, which become more important as the temperature increases. If only a few terms in the series are used, the results will be valid at temperatures low compared to some characteristic temperature of the crystal, e.g., the melting temperature. Since they are based on classical mechanics, the results are valid only at temperatures high compared to the Debye temperature.

The series expansions of the distribution functions and thermodynamic functions may be viewed as the low-temperature analogs of the virial expansions, which are low-density expansions. As in the case of the virial expansions, all the terms are determined explicitly in analytic form, but their actual evaluation is difficult.

1. INTRODUCTION

THE properties of a classical mechanical system in thermal equilibrium are expressible as multiple integrals involving the canonical distribution function

of statistical mechanics.¹ If the system consists of a large number of interacting particles, the evaluation of

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¹ This is so provided that the energy is the only measurable integral of motion of the system. See, for example, R. M. Lewis, Arch. Ratl. Mech. Anal. **5**, 355-381 (1960).

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