

New Oxygen Infrared Bands in Annealed Irradiated Silicon

J. W. CORBETT, G. D. WATKINS, AND R. S. McDONALD
General Electric Research Laboratory, Schenectady, New York
 (Received 6 April 1964)

Infrared and electron-spin-resonance measurements on the recovery of silicon irradiated with 1.5-MeV electrons are presented. In the infrared measurements the disappearance of the previously reported 829-cm⁻¹ (12 μ) oxygen vibration band is followed, and the appearance and subsequent disappearance of a succession of new infrared bands are observed. The major new bands are at 887, 904, 968, and 1000 cm⁻¹, although others are also found. Tentative defect models are proposed to account for these recovery features.

I. INTRODUCTION

OXYGEN as normally dissolved in silicon gives rise to a number of infrared (ir) absorption bands. In silicon, three have been assigned to isolated oxygen—the dominant band¹ at 9 μ , or 1106 cm⁻¹, and lesser bands² at 1205 and 515 cm⁻¹. The configuration of the isolated oxygen in silicon has been quite well established³ to be that shown in Fig. 1(a). It is referred to as “interstitial” oxygen. Oxygen can also be present in these materials in other forms than as isolated interstitial oxygen. The heat-treatment of oxygen-doped silicon gives rise to complicated electrical and optical effects. The explanation that has been given⁴ for these effects is that a succession of oxygen aggregates are formed, one of which, a four-oxygen complex, is a donor and can be detected electrically⁵ and optically.⁶ Two small ir bands, 9.5 and 9.75 μ , have been reported⁷ as appearing upon annealing and presumably correspond to specific agglomerates. Finally, there is a broad ir band in the vicinity of 9 μ which appears as a result of prolonged annealing.

We have previously shown⁸ that in high-energy-electron irradiated silicon, a lattice vacancy can be trapped at an oxygen atom resulting in the configuration shown in Fig. 1(b). This configuration gives rise to an ir band at 12 μ , or 829 cm⁻¹, and to an electron-spin-resonance spectrum⁹ termed the Si-A center resonance. Oxygen in this configuration is called “substitutional” oxygen or the vacancy-oxygen pair.

In the present paper,¹⁰ we report a number of ir bands that are observed upon heat treatment of irradiated oxygen-doped silicon, i.e., heat-treatment bands apparently associated with substitutional oxygen.

II. EXPERIMENTAL

The samples were $\sim 0.1 \times 0.1 \times 0.75$ in. in size. They were *n*-type (phosphorus $\sim 10^{16}$ /cm³), grown in an argon atmosphere and were rotated while pulling from the melt, the melt being contained in a quartz crucible. The samples were irradiated equally on both sides at room temperature by 1.5-MeV electrons from a resonance transformer accelerator. The current density on the samples was about 3 μ A/cm², and the maximum temperature rise of the sample was about 25°C.

All spectra were measured with the samples at room temperature using a Beckman IR-7 grating spectrophotometer (4000–650 cm⁻¹). The spectral slitwidth was about 2 cm⁻¹. Samples were placed at the focus of a standard Beckman beam condenser. The data were reduced to absorption coefficients using the formula of Fan and Becker¹¹ which includes multiple reflections.

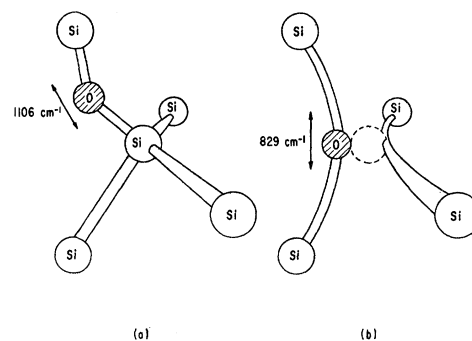


FIG. 1. (a) Configuration of interstitial oxygen. (b) Configuration of substitutional oxygen with the dashed circle indicating the position of the vacancy. In both (a) and (b) the axis of the ir transition moment is indicated.

¹ W. Kaiser, P. H. Keck, and C. F. Lange, *Phys. Rev.* **101**, 1264 (1956).

² H. J. Hrostowski and R. H. Kaiser, *Phys. Rev.* **107**, 966 (1957).

³ See J. W. Corbett, G. D. Watkins, and R. S. McDonald, *Phys. Chem. Solids* (to be published) and references contained therein.

⁴ W. Kaiser, H. L. Frisch, and H. Reiss, *Phys. Rev.* **112**, 1546 (1958).

⁵ C. S. Fuller, J. A. Ditzgenberger, N. B. Hannay, and E. Buehler, *Acta Met.* **3**, 97 (1955).

⁶ H. J. Hrostowski and R. H. Kaiser, *Phys. Rev. Letters* **1**, 199 (1958).

⁷ W. Kaiser, H. J. Hrostowski, and C. D. Thurmond, *Bull. Am. Phys. Soc.* **5**, 61 (1960).

⁸ G. D. Watkins and J. W. Corbett, *Phys. Rev.* **121**, 1001 (1961); J. W. Corbett, G. D. Watkins, R. M. Chrenko, and R. S. McDonald, *ibid.* **121**, 1015 (1961).

⁹ G. D. Watkins, J. W. Corbett, and R. M. Walker, *J. Appl. Phys.* **30**, 1198 (1959); G. Bemski, *ibid.*, 1195 (1959); G. Bemski, G. Feher, and E. Gere, *Bull. Am. Phys. Soc.* **3**, 135 (1958).

¹⁰ A preliminary account of these results was given in G. D. Watkins, J. W. Corbett, and R. S. McDonald, *Bull. Am. Phys. Soc.* **5**, 26 (1960).

¹¹ H. Y. Fan and M. Becker, in *Semiconductor Materials*, edited by H. K. Reisch (Butterworths Scientific Publications, Ltd., London, 1951), p. 132.

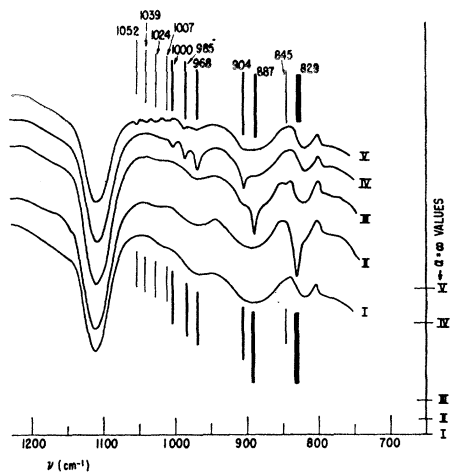


FIG. 2. IR absorption spectra observed on the 410-CC sample, I—before irradiation, II—after 1.7×10^{19} electrons/cm², III—after 1458 min annealing at 305°C, IV—after 409 min additional annealing at 485°C, and V—after a total of 3535-min annealing at 485°C. The various IR bands are denoted by vertical lines.

All data presented represent an average of several spectrometer runs.

The annealing was performed in air, and the temperatures are accurate to $\pm 5^\circ\text{C}$.

III. EXPERIMENTAL RESULTS

Figure 2 summarizes the changes in the IR transmission spectrum observed in a typical sample after irradiation and at several stages in the subsequent annealing. Curve I shows the spectrum before irradiation, the strong band at 1106 cm^{-1} ($9\ \mu$) being due to

the isolated interstitial oxygen [Fig. (1a)]. Curve II shows the spectrum after irradiation to a total flux of $1.7 (10^{19})$ electrons/cm². The single strong band at 829 cm^{-1} ($12\ \mu$) is due to isolated substitutional oxygen⁸ [Fig. 1(b)] produced by the irradiation. Curves III–V show the spectrum at subsequent stages in the annealing. We note that the bands disappear, new ones emerge, then disappear, etc., as the annealing proceeds, and that a number of discrete bands can be identified throughout this sequence.

The general features of the annealing are demonstrated in Fig. 3. In this figure we have plotted the intensities of the dominant bands determined in an isochronal anneal up to 600°C. This sample (410 XY) had had a total dose of $8 (10^{18})$ electrons/cm² prior to the annealing. We note that the disappearance of the 829-cm^{-1} band is accompanied by the emergence of a single new band at 887 cm^{-1} (ignoring the weak band at 845 cm^{-1} , see Fig. 2) and that this "conversion" takes place over a rather wide temperature range ($250\text{--}450^\circ\text{C}$). Above 450°C , a second stage in the annealing sets in which the 887-cm^{-1} band decays and four new bands appear. The weaker bands shown in Fig. 2 are also emerging at $\sim 600^\circ\text{C}$, but are too weak to measure accurately.

The disappearance of the 829-cm^{-1} band and the corresponding growth of the 887-cm^{-1} band have been studied in somewhat more detail by an isothermal anneal at 305°C . These results are shown in Fig. 4. This sample (410 CC) had a total dose of $1.7 (10^{19})$ electrons/cm² prior to annealing. For comparison, we have also plotted the isochronal anneal data of Fig. 3, which has been converted to an equivalent isothermal anneal¹²

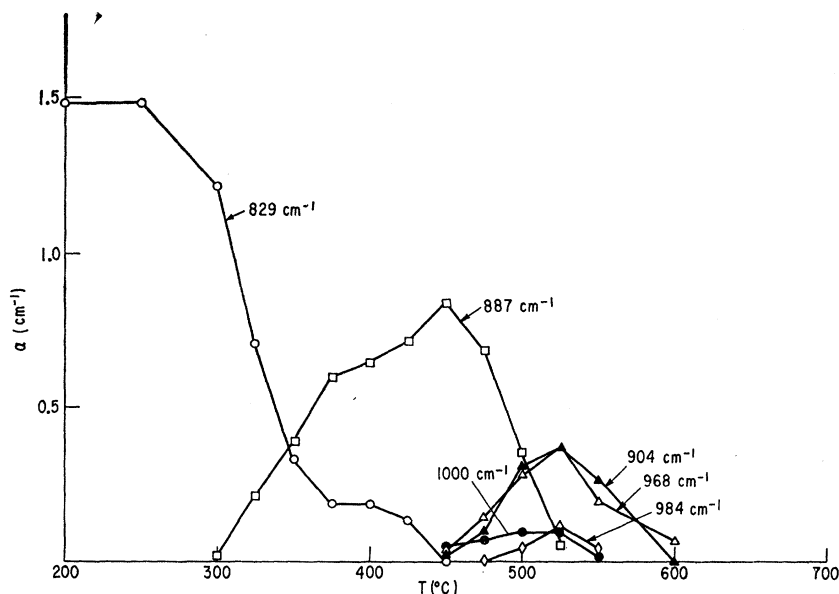


FIG. 3. Absorption coefficients (α) of the various IR bands (as designated) observed in an isochronal (15-min) anneal of the 410 XY sample which had an irradiation of 8×10^{18} electrons/cm² prior to the annealing.

¹² For a discussion of this technique, see C. J. Meechan and J. A. Brinkman, Phys. Rev. **103**, 1193 (1956).

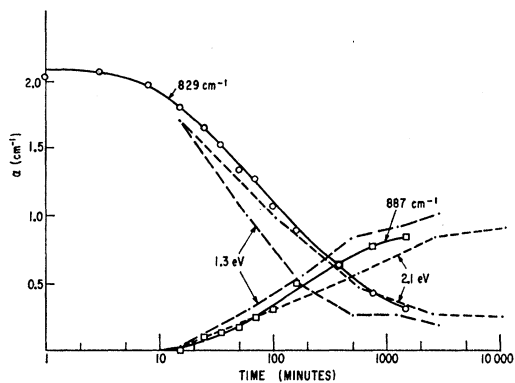


FIG. 4. Absorption coefficients (α) of the 829- and 887- cm^{-1} ir bands observed during the isothermal (305°C) annealing of sample 410 CC, which had an irradiation of 1.7×10^{19} electrons/ cm^2 prior to the annealing. The dashed lines indicate the isochronal data (Fig. 3) converted to an equivalent isothermal using activation energies of 1.3 and of 2.1 eV.

using two different assumed activation energies as indicated. In order to facilitate the comparison, the absorption coefficients for the 410 XY isochronal data have been scaled up by 44% throughout to normalize the data to the same absorption coefficient for the 829- cm^{-1} band. This normalization appears valid in that, within accuracy, the same fractional conversion to the 887 cm^{-1} band occurs in both samples. This comparison will be discussed in the next section.

The second stage of annealing was also studied by a subsequent isothermal anneal at 485°C on the same sample. These results are given in Fig. 5. The reduced accuracy in the intensity measurements of these new bands does not warrant a detailed comparison to the isochronal data.

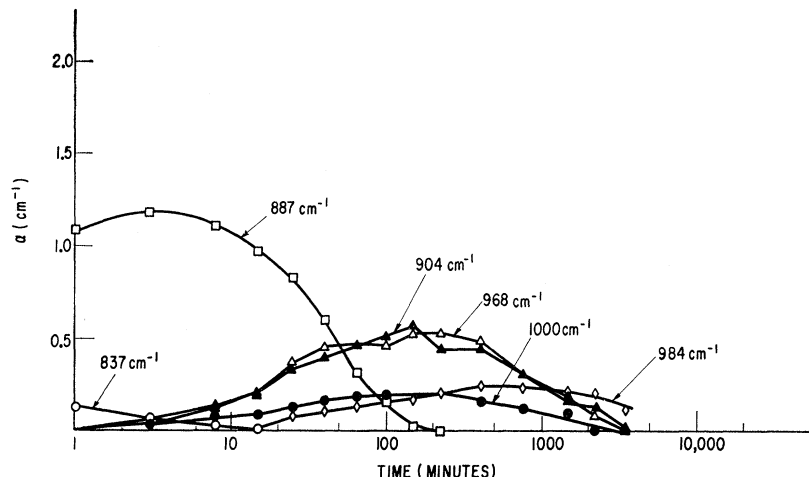


FIG. 5. Absorption coefficients (α) of the ir bands observed during the 485°C isothermal anneal subsequent to the anneal shown in Fig. 4.

Further information concerning the disappearance of the substitutional oxygen (giving rise to the 829- cm^{-1} band) can be obtained from the recovery monitored by electron-paramagnetic-resonance (EPR) studies. We have previously shown⁸ that the 829- cm^{-1} band and the EPR Si-A center anneal together. This result is shown in Fig. 6, where we also show the recovery observed by Bemski and Augustyniak¹³ in lifetime measurements for similar oxygen-containing materials. Bemski and Augustyniak obtained an activation energy for recovery of 1.3 eV and we have used this value in converting their isothermal data at 350°C to an equivalent isochronal curve. In their studies, it is not clear whether the defect being studied is the substitutional oxygen or not,¹⁴ but the similarity to the ir and EPR results in Fig. 6 suggests that it is. Additional evidence in this regard comes from studies in low-oxygen-content material. In Fig. 6, we also compare the equivalent isochronal results of Bemski and Augustyniak for a floating-zone silicon with EPR studies that we have recently performed on the Si-A center in Merck vacuum floating-zone silicon. In both we note that the annealing proceeds faster and without the long "tails" to high temperature which are characteristic of the high-oxygen-content material. This would appear to support the view that the defect that is limiting the lifetime in their studies is the substitutional oxygen.¹⁵⁻¹⁷

The close correlation observed in Fig. 6 between the ir, EPR, and lifetime studies in high-oxygen content materials exists even though the dose levels for the respective measurements span a factor of 1000. This suggests that the same annealing processes are operative in the various studies and that the corresponding kinetics are independent of defect concentration.

¹³ G. Bemski and W. M. Augustyniak, Phys. Rev. **108**, 645 (1957).

¹⁴ See J. A. Baicker, Phys. Rev. **129**, 1174 (1963), and references contained therein.

¹⁵ The divacancy is also observed (Ref. 16) to anneal with an activation energy of ~ 1.3 eV. However, in vacuum floating-zone silicon the divacancy recovery proceeds slower than in high-oxygen-content silicon (Ref. 17). This would appear to rule out the divacancy as the defect responsible for the lifetime degradation in the Bemski and Augustyniak experiments.

¹⁶ G. D. Watkins and J. W. Corbett, Discussions Faraday Soc. No. 31, 86 (1961).

¹⁷ G. D. Watkins and J. W. Corbett (to be published).

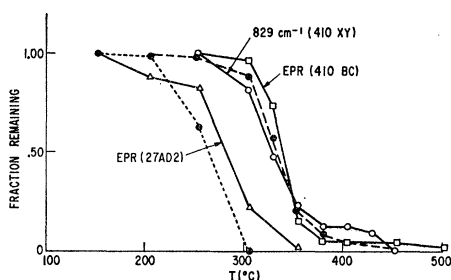


FIG. 6. Comparison of the fractional recovery observed in pulled crystals in an isochronal anneal for the 829-cm⁻¹ ir band (sample 410 XY with an irradiation of 8×10^{18} electrons/cm²), EPR (sample 410 BC— 6.3×10^{16} electrons/cm²) and lifetime measurements (in the dashed line) of Bemski and Augustyniak ($\sim 10^{15}$ electrons/cm²). The results observed in floating-zone crystals are also compared: EPR (sample 27AD2— 3.5×10^{16} electrons/cm²), and lifetime measurements of Bemski and Augustyniak (dotted line).

IV. DISCUSSION

As can be seen in Figs. 3 and 4, some of the intensity in the 829-cm⁻¹ band disappears before the 887 cm⁻¹ appears. This suggests that more than one process is occurring during the annealing and complicates the analysis. This is also borne out in the comparison of the isothermal to the isochronal data (Fig. 4). The decay of the 829-cm⁻¹ band suggests an activation energy ~ 2.1 eV, while the growth of the 887-cm⁻¹ band suggests a lower energy (~ 1.7 eV).¹⁸ We conclude that we cannot unravel the energetics and kinetics of the recovery process from our present data.

As a result, it is not possible to come to definite conclusions as to the microscopic processes involved in the various annealing stages. However, the simplicity of the results, the succession of a limited number of sharp, well-resolved, discrete bands, is sufficiently suggestive to warrant speculation as to the processes. Therefore, in this section, we will present tentative models for the successive annealing stages which we feel are reasonable ones and ones which can logically account for the experimental observations. They are not presented as "proven," however. It is hoped that they may serve as guides to future experiments which can test their validity.

A logical model for the conversion of the substitutional oxygen to the new defect giving rise to the 887-cm⁻¹ band is that the substitutional oxygen diffuses as an entity until it encounters and is trapped by another isolated interstitial oxygen atom. The new defect would then involve two oxygen atoms in the vacancy as shown in Fig. 7(a). Because of the equivalence of the two oxygen atoms, and the orthogonality of their respective vibrations, only one band would result in this frequency range. Such a model would give

¹⁸ The accuracy of such determinations is not great, and the 887-cm⁻¹ growth may well be 1.3 eV, corresponding to that found by Bemski and Augustyniak. The 829-cm⁻¹ decay, however, appears to have a sizeable component that definitely has a larger activation energy.

first-order kinetics for annealing of the 829-cm⁻¹ band, independent of the defect concentration. The high-conversion efficiency would result from the fact that isolated interstitial oxygen is still the dominant defect in the lattice.

Such diffusion can be considered as vacancy-enhanced diffusion of the oxygen atom due to the attraction to the vacancy. Inspection of the silicon lattice suggests that this motion requires partial dissociation of the vacancy-oxygen pair in much the same way required for vacancy-enhanced diffusion of a substitutional impurity.¹⁹ It seems likely that complete dissociation is taking place as well, since in low-oxygen-content material, this dissociation would dominate, explaining the faster anneal in that material. Dissociation in high-oxygen-content material is not so important because the vacancy will be continually retrapped by other oxygen atoms and the limiting process can remain that of bringing two atoms together to form the defect of Fig. 7(a).

In its travels, the vacancy may also encounter other kinds of defects accounting for the additional loss of the 829-cm⁻¹ band not accounted for in the 887-cm⁻¹ band. A logical possibility is annihilation at a trapped interstitial silicon site. Conversely, the interstitials may be released from traps and diffuse to the vacancies.²⁰ Analysis of the initial decay of the 829-cm⁻¹ band in Fig. 4 indicates a second-order component, consistent with either of the possibilities.

The next stage of the recovery, where the 887 cm⁻¹ disappears, could be the result of adding additional oxygen to the O₂-vacancy pair. We note from Curves IV and V of Fig. 2, that the intensity of the 9- μ isolated

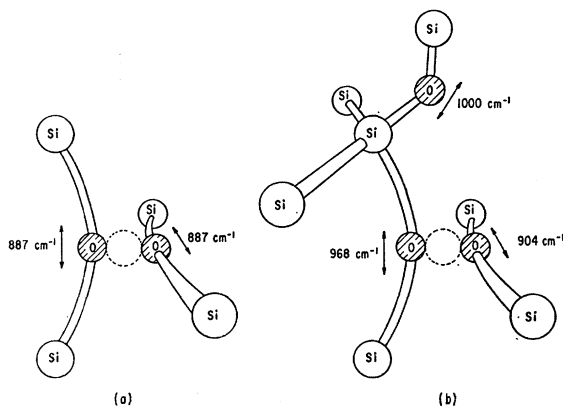


FIG. 7. Tentative models for (a) the 887-cm⁻¹ ir band and (b) the 904-, 968-, and 1000-cm⁻¹ bands. The transition-moment axes are indicated. The dashed circles indicate the position of the lattice vacancy.

¹⁹ Such an example is the phosphorus-vacancy pair discussed by G. D. Watkins and J. W. Corbett, Phys. Rev. **134**, A1359 (1964).

²⁰ The activation energy ~ 2 eV perhaps favors this second possibility. If the process were limited by vacancy diffusion, we would expect the same activation energy observed by Bemski and Augustyniak, ~ 1.3 eV.

oxygen band is decreasing during this stage, consistent with this interpretation. We expect the oxygen atoms in the vacancy [Fig. 7(a)] to pull the silicon neighbors inward. This leaves the immediate neighborhood in tension and presents a favorable environment for trapping additional interstitial oxygen atoms. The addition of just one oxygen to the O_2 -vacancy complex renders the three oxygen atoms inequivalent, as shown in Fig. 7(b). In Fig. 5, we note that three bands (at 904, 968, and 1000 cm^{-1}) appear to grow and disappear together as if possibly associated with such a defect. We note further from Fig. 2 that the defect configurations at each successive annealing stage are characterized by bands which generally increase in vibrational frequency, approaching that of the original interstitial oxygen. This would suggest a correlation between the low restoring forces, hence low vibrational frequencies for the oxygen in the roomy substitutional environment and a general tendency to become progressively more crowded. Using this as a guide, we very tentatively identify the individual oxygen atoms in Fig. 7(b) with these three bands as shown in the figure. This is, of course, highly speculative.

One possible mechanism for the formation of the O_3 -vacancy complex is the diffusion of interstitial oxygen to the O_2 -vacancy complex. However, from previous measurements,³ we estimate the jump rate of interstitial oxygen to be only ~ 2 per min at 485°C, or ~ 100 jumps during the decay of the 887- cm^{-1} band. Since there are $\sim 10^{18}$ oxygen atoms/ cm^3 , this would require either a very large effective capture cross section or a considerable departure from homogeneous distribution of the oxygen. An alternative possibility is the diffusion of the O_2 -vacancy pair to pick up the interstitial oxygen.

V. CONCLUSIONS

The models that we have presented here have interpreted the various annealing stages as the initial steps

in the nucleation and growth of oxygen agglomerates in the vicinity of a lattice vacancy. The nucleus of this process is the substitutional oxygen produced by the irradiation.

These models are to be considered only as tentative ones. Another model, for instance, that cannot be ruled out is that the vacancy dissociates from the single oxygen and is subsequently captured by oxygen atoms in other configurations which give rise to the necessary ir bands. The concentration of such oxygens would have to be $\sim 10^{17}/\text{cm}^3$ to account for the observed intensities, but could not be much higher or we would have observed them upon the initial irradiation. In this regard, Fan and Ramdas²¹ have found that several ir bands (between 9 and 12 μ) are produced directly in their samples by neutron and electron irradiations. Since their bands are presumably oxygen vibrational bands, their results suggest that oxygen in other configurations can be present in sufficient quantities to satisfy this model. They^{21,22} also reported the modification or disappearance of several of their bands upon annealing at temperatures $\lesssim 250^\circ\text{C}$. None of the bands reported by Fan and Ramdas appear to correspond to the annealing bands reported in the present paper.

ACKNOWLEDGMENTS

The authors are grateful to Dr. R. O. Carlson who kindly supplied the samples used in these experiments. The authors gratefully acknowledge the general assistance of W. C. Colliton in the conduct of the experiments, and thank R. M. Chrenko for his interest and assistance in the infrared experiments.

²¹ H. Y. Fan and A. K. Ramdas, in *Proceedings of the International Conference on Semiconductor Physics, Prague, 1960* (Publishing House of the Czechoslovak Academy of Sciences, Prague, Czechoslovakia, and Academic Press, Inc., New York, 1961), p. 309.

²² A. K. Ramdas and H. Y. Fan, *J. Phys. Soc. Japan* **18**, Suppl. II, 33 (1963).