Comparison of Thermal Behavior of Vacuum-Crushed, Air-Crushed, and Mechanically Polished Silicon Surfaces by Electron Paramagnetic Resonance

D. HANEMAN, M. F. CHUNG, AND A. TALONI
School of Physics, University of New South Wales, Sydney, Australia
(Received 30 November 1967)

Surfaces of Si produced by crushing in vacuum, in air, and by mechanical polishing have been studied by monitoring the EPR signal at $g=2.0055$, arising from such specimens. Effects of heat treatment in vacuum to 400°C are similar for both samples crushed in air and samples that have been fine-polished, but annealing behavior differs markedly for samples crushed in high vacuum (10^{-9} Torr). The polished samples have a surface stress which drops rapidly with annealing from the initial value of 16 000 dyn cm^{-1} at room temperature to 2000 dyn cm^{-1} after 125°C, and thereafter slowly to below 400 dyn cm^{-1} after 400°C. Detailed comparisons of effects of heat on line intensity, shape, and width indicate that the surfaces produced by mechanical polishing and by crushing in air are essentially similar. Surface stresses do not appear to have a significant effect on the resonance signal. The principal effect of the various treatments, as monitored by EPR, is to produce extra surface area, in the form of cleavage surfaces on fissures and fragments, contaminated by atmosphere in the case of specimens processed in air.

I. INTRODUCTION

SILICON samples show electron paramagnetic resonance after subjection to mechanical polishing or crushing.[1–5] Recent studies on aligned single crystals cleaved in high vacuum[6] show that the resonance is due to unpaired bonds on the surface, the resonance being increased by exposure to oxygen. This suggests that the resonance from mechanically polished samples might also be due to the extra surfaces produced (and contaminated) during abrasion. Taper sections[7] of polished or abraded surfaces have indeed revealed myriads of fissures, all contributing surface, extending to some depth below the surface. This damaged region must be removed, e.g., by etching, in order to remove the extra surface.

Further evidence on the origin of the resonance on abraded specimens can be obtained by comparing the detailed properties of the signal as a function of annealing with the signal from samples produced in other ways, such as crushing in air and in high vacuum. Such tests are reported here and show a close correspondence between abraded specimens and air-crushed powders, which differ significantly from vacuum-crushed powders. These phenomena are entirely consistent with the hypothesis that the production of extra surface area is the principal effect of the various treatments.

II. POWDERS CRUSHED IN ULTRAHIGH VACUUM

Samples were prepared in the all glass sealed-off system shown in Fig. 1. A few silicon lumps were tested to be free of detectable resonance centers and then crushed by inverting the system and mildly jerking the glass slug up and down. The base pressure of $\sim 10^{-9}$ Torr increased into the 10^{-8} Torr range during this procedure, probably due to abrasion desorption from the glass walls, but quickly (few seconds) recovered. Minimal surface contamination ($\ll 0.1\%$) on the 50–100 cm^2 of powder area produced in the approximate 1-liter volume system would have occurred, as discussed previously.[4]

Isochronal annealing (30 min) was carried out by immersing the quartz-tube portion of the system, with the powder in it, into a narrow diameter, preheated coil furnace. Measurements were made after cooling to room temperature. Reproducibility of signal height due to removal and replacement of the sample in the cavity was better than 95%. The quartz tube, together with the uncrushed Si crystals, was thoroughly outgassed before seal-off from the system, at 800–900°C for more than 12 h, reaching a pressure of less than 10^{-8} Torr during outgassing. The pressure in the sample tube of approximately 1-liter volume might increase to order 10^{-7} Torr during annealing at the highest temperatures around 800°C, but at lower temperatures the gas content was still insufficient to cause appreciable surface coverage.

The polished specimens and some powders were measured in a cylindrical cavity in a Japan Electron Optics Laboratory Co. (J.E.O.L.) X-band electron-spin-resonance spectrometer with 12-in. magnet and 1×10^{11} spins/G sensitivity. Some of the powders were measured in a cylindrical cavity in a Varian X-band spectrometer with 9-in. magnet and 2×10^{11} spins/G sensitivity. In some cases the polished specimens' resonance signal was improved by use of a J.E.O.L. spectrum accumulator on the spectrometer output.

A marked decrease in the signal height after annealing to temperatures higher than 400°C had been previously reported[4] and correlated with a change in clean surface

[1] R. C. Fletcher, W. A. Yager, G. L. Pearson, A. N. Holden, W. T. Read, and F. R. Merritt, Phys. Rev. **94**, 1392 (1954).
[2] G. Feher, Phys. Rev. **114**, 1219 (1959).
[3] G. K. Walters and T. L. Estle, J. Appl. Phys. **32**, 1854 (1961).
[4] M. F. Chung and D. Haneman, J. Appl. Phys. **37**, 1879 (1966).
[5] P. Chan and A. Steineman, Surface Sci. **5**, 267 (1966).
[6] D. Haneman *et al.*, preceding paper, Phys. Rev. **170**, 705 (1968).
[7] E. N. Pugh and L. E. Samuels, J. Electrochem. Soc. **109**, 409 (1962); **108**, 1043 (1961).

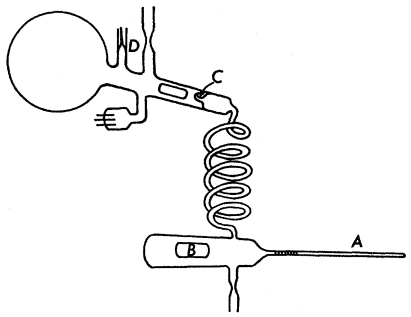

FIG. 1. Sealed-off vacuum system. A—quartz tube containing powder specimens, B—glass hammer, C—gas inlet break seal, D—air inlet break seal.

structure from the cleaved to the annealed configuration.[8] However, details of behavior below 400°C are of special interest in this paper. The behavior of signal height with annealing temperature, in vacuum, in H_2 and in O_2 is shown in Fig. 2 and the behavior of signal width in Fig. 3. The measured signals are those at room temperature after annealing. Changes both in height and width occur with small changes in annealing temperature. Since the number of spins is proportional to the signal height and to the square of signal width, the number of spins remains approximately constant after heating to about 200°C, decreases a little after heating to 400°C, and then drops more rapidly, particularly after heating between 500 and 600°C. The changes in signal in this latter region correspond to the cleaved-to-annealed surface transformation.[8] The changes at the low (<200°C) temperatures are, however, surprising.

If the powders are exposed to 10^{-2} Torr of H_2 or O_2, the signal height is increased.[4] The variation with annealing temperature is also affected as shown in Figs. 2 and 3. This again emphasizes the effect of gases on the observed resonance. Changes in sample resistivity due to heat treatment were checked by applying the same cycles to small bulk specimens cut from the same single crystal and checking the resistivity with a four-point probe method. The initial p-type resistivity of 300 Ω cm changed to 315 Ω cm after high vacuum bakeout at 300°C. An initial resistivity of 297 Ω cm changed to 270 Ω cm after 30-min anneal at 445°C. These effects are negligible.

III. POWDERS CRUSHED IN AIR AND MECHANICALLY POLISHED SAMPLES

To minimize side effects, the polishing treatments were carried out with least gross disturbance. Specimens of size 5×2 mm were produced from a lapped (111) plate and the faces chemically etched so as to remove a layer many times the thickness conceivably damaged by previous mechanical treatment (e.g., 0.5 mm removed by acid after grinding and polishing). The surfaces were then polished with $\frac{1}{4}$-μ diamond paste on a

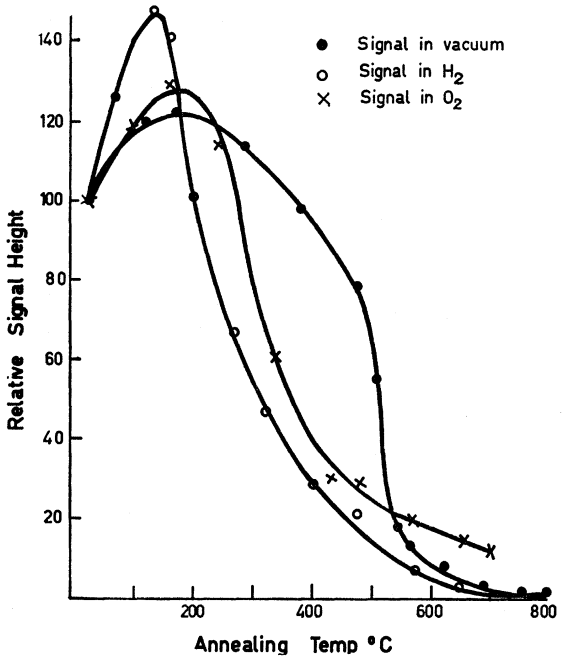

FIG. 2. EPR signal height (arbitrary units) versus temperature of anneal (30 min) for Si crushed in high vacuum. All resonance measurements are at room temperature after annealing. The pressures of gas were 0.01 Torr in a sealed system. The signal behaves rather similarly when annealed in H_2 and O_2; however, the reduction of signal intensity appears at a lower temperature and proceeds faster when annealed in H_2 or O_2 than in vacuum.

Buehler No. 40–7058 felt pad. Final thicknesses were of order 100–200 μ. A number of such specimens were required in the sample tube to obtain a signal of sufficient strength for proper measurement. With careful cleaning and handling, no resonances from the polishing media were detectable.

Samples were placed in a quartz tube sealed to a Pyrex glass vacuum system. The quartz tube protruded below the oven base so that during bakeout the samples

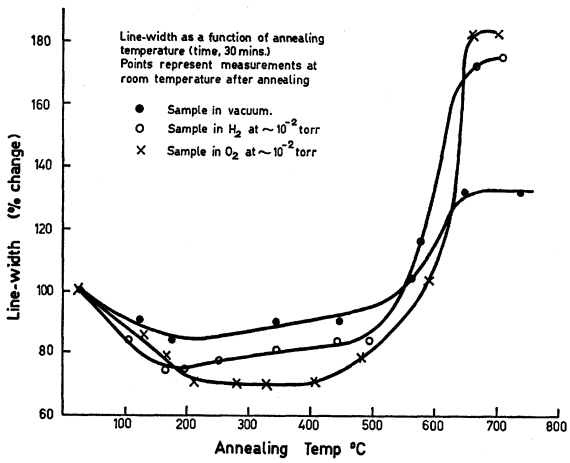

FIG. 3. Linewidth (arbitrary units) versus temperature of anneal (30 min). Same conditions and samples as in Fig. 2.

[8] J. J. Lander, G. W. Gobeli, and J. Morrison, J. Appl. Phys. 34, 2298 (1963).

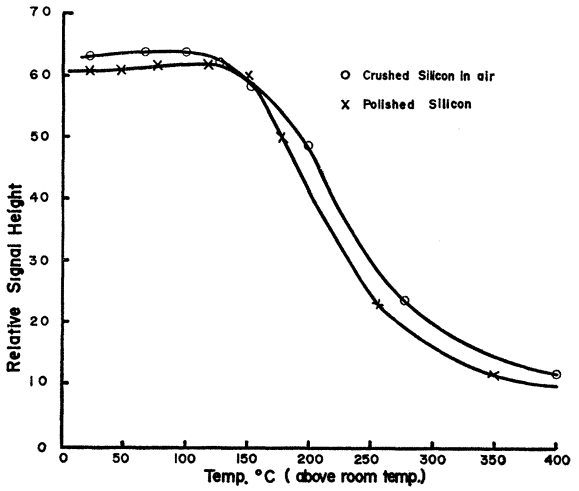

FIG. 4. EPR signal height (arbitrary units) versus temperature of anneal (30 min). Zero refers to room temperature.

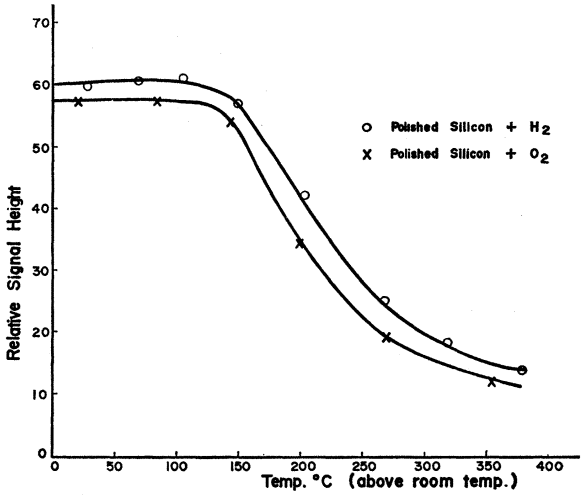

FIG. 5. EPR signal height (arbitrary units) versus temperature of anneal (30 min) in a sealed volume of 0.1 Torr H_2 or O_2. Zero refers to room temperature.

stayed at room temperature. Seal off was performed at about 5×10^{-8} Torr.

For EPR measurements, after annealing up to 200°C, the evacuated sample tube remained undisturbed in the cylindrical cavity. For higher-temperature annealing, the tube was as before lowered into a vertical, small internal diameter coil furnace and subsequently carefully replaced in the cavity without altering orientations of the specimens. Dummy runs indicated that this procedure permitted reproducibility of better than 95%.

During heating, only about an inch of the preoutgassed quartz tube became hot. Although these samples had already been exposed to air, these precautions were taken to minimize possible effects arising from outgassing products during annealing, still having some effect on the surfaces. A further check on this was made by repeating the experiments on samples in a sealed gas atmosphere of 0.1 Torr (gas let in after high vacuum obtained), H_2 in one case and O_2 in another.

The results are shown in Fig. 4 for vacuum sealed polished samples and for crushed samples, and in Fig. 5 for polished samples sealed in H_2 and in O_2. The changes in the line shape and linewidth are shown in Figs. 6 and 7. Two major features stand out. First, the behavior of the air-crushed specimens and of the mechanically polished specimens is almost identical. Second, this behavior is markedly different from that of vacuum-crushed specimens (Figs. 2 and 3). In addition, the presence of an ambient (0.1 Torr) of H_2 or O_2 during annealing has little effect on the behavior (Fig. 5).

The almost identical annealing behavior of the air-crushed and mechanically polished samples suggests strongly that the centers produced by crushing silicon in air are the same as those produced by mechanical polishing. One aspect of these processes that could be significant is the introduction of stress, which is known to affect spin resonance centers[9] and which would be expected to be sensitive to annealing.

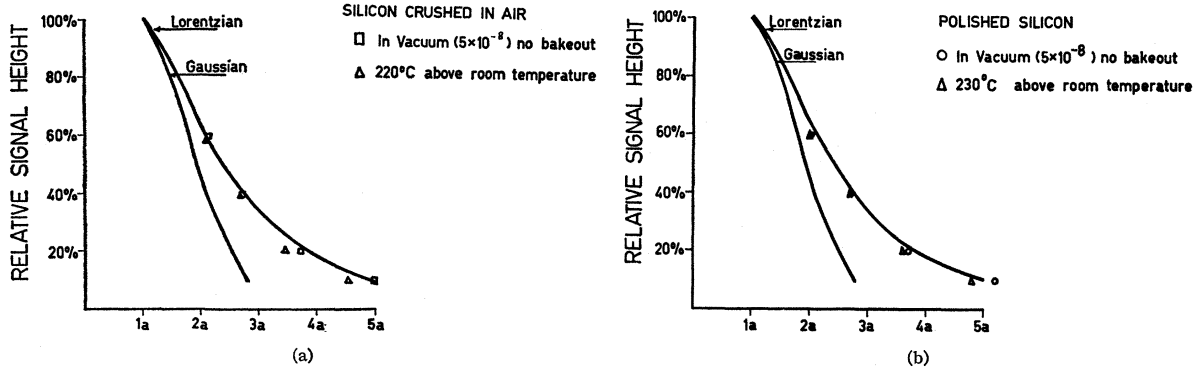

FIG. 6. Line shape of signal at room temperature and after annealing in high vacuum (30 min).

[9] D. K. Wilson and G. Feher, Phys. Rev. 124, 1068 (1961).

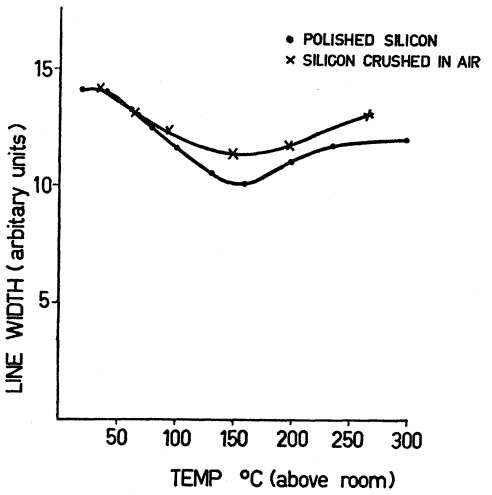

FIG. 7. Linewidth of signal (peak to peak of differentiated absorption curve) as function of annealing temperature (30 min). Points refer to measurements at room temperature after annealing.

IV. SURFACE-STRESS MEASUREMENT

The role of stress was investigated by measuring it in the mechanically polished specimens. Full details of the method appear elsewhere.[10] In brief, specimens were prepared of thickness in the range 10–20 μ, with the bottom side chemically etched and stress free, resting on an outgassed molybdenum block in a high-vacuum but unbaked system. The top surface, containing the ($\frac{1}{4}$-μ diamond) polishing damage, was viewed by laser interferometry, the reference surface being outside the system. With specimens so thin, the difference in stress between the opposite polished and etched faces was sufficient to cause an observable curvature of the whole specimen, the polished side being convex. From the curvature, the stress can be calculated.

Specimens were heated by a focused projection lamp for 30 min at a given temperature and the curvature was subsequently measured after return to room temperature. The results are shown in Fig. 8. The stress, originally 16 000 dyn cm^{-1}, falls rapidly and irreversibly with heat treatment to 150°C and is below detection limit (400 dyn cm^{-1}) after annealing at 400°C. The signal height remained fairly constant after annealiug to 125°C (Fig. 4). The width however did reduce to a minimum at approximately 150°C and then recovered somewhat. The signal width therefore shows some correlation in behavior with the surface stress in the region from room temperature to about 150°C. However, the subsequent recovery of the width after annealing in the region above about 150°C, whereas the surface stress becomes still smaller, makes one suspect that the above correlation is at least to some extent fortuitous. We therefore interpret the behavior as indicating that the surface stress which is concentrated at fissures, does not have a pronounced effect on the EPR signal.

[10] A. Taloni and D. Haneman, Surface Sci. 8, 323 (1967).

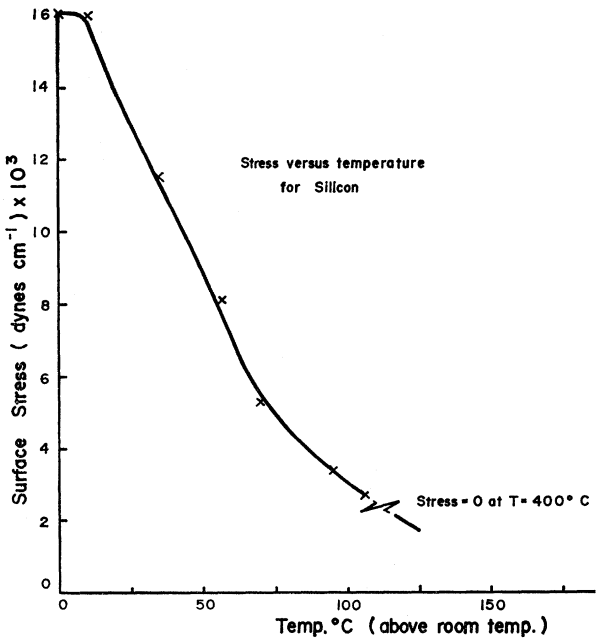

FIG. 8. Surface stress for silicon polished with $\frac{1}{4}$-μ diamond paste, annealed in high vacuum (30 min at each temperature) and examined at room temperature. Zero refers to room temperature.

V. DISCUSSION

The above results have shown that the resonances observed from mechanically polished samples and from air-crushed powders are the same and have the same behavior after annealing up to 400°C. From this we conclude that the resonance centers are the same in both cases. We then compare the annealing behavior of the resonances from air-crushed and from vacuum-crushed powders. Presumably, the mechanical forces are much the same in both cases, the only essential difference being that the powders crushed in air consist of freshly cleaved fragments which are then quickly contaminated by the atmosphere, whereas the vacuum-crushed fragments retain their clean surfaces. A detailed study by one of us[6] has shown that the EPR signal from vacuum-crushed Si powder is essentially the same as that from aligned vacuum cleaved faces. The signal was found to be due to unpaired but partially overlapping surface electrons (forming a narrow energy range conduction band). On exposure to oxygen the signal was increased, due to the mutual overlap of the surface wave functions being reduced.

From this, one concludes that the resonance from Si powders crushed in air is due to the contaminated surfaces of the fragments. Upon annealing, the contaminant layers interact more strongly with the surface, so that the signal is affected differently by heat treatment than in the case of uncontaminated surfaces (c.f. Figs. 2 and 3 with Figs. 4 and 7). We do not have sufficient knowledge to explain these differences in

detail, but the principal point at this stage is to observe the presence of such differences.

Then, since the mechanically polished samples gave the same resonance behavior as the air-crushed powders, one concludes that the signal arising from polished samples is also due to the production of extra surface. This occurs in the numerous fissures (observable by taper sectioning) that are formed. The depth of the fissures increases with increasing coarseness of the polishing treatment, so that thicker layers must be etched away to remove the signal, as qualitatively observed.

Thus the above results show that the occurrence of an EPR signal on Si subjected to mechanical polishing or crushing is intimately related to the area of the new surface that is produced during these treatments. Both processes involve the creation of fresh cleavage surfaces, on which unpaired but partially overlapping electrons contribute to a resonance, interaction with the atmosphere serving to alter the magnitude and annealing behavior of the signal, but not to destroy it.

ACKNOWLEDGMENTS

This work was supported by a grant from the Australian Research Grants Committee. The authors express gratitude also to Japan Electron Optics Laboratory Company for the loan of resonance and computing equipment. One of us (D.H.) thanks the National Science Foundation for award of a Senior Foreign Scientist Fellowship during which some of the work was completed, and Brown University for hospitality and for provision of facilities.

PHYSICAL REVIEW VOLUME 170, NUMBER 3 15 JUNE 1968

Knight Shift in Lead Telluride via Relativistic Augmented-Plane-Wave Functions*

PAUL T. BAILEY†

Materials Theory Group, Department of Electrical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts

(Received 23 June 1967; revised manuscript received 5 February 1968)

The augmented-plane-wave method, including relativistic corrections, is used to calculate the Knight shift for Pb^{207} in p-type PbTe. The s character is determined to be 0.59, and the hyperfine parameter to be 1.2 cm^{-1}. The spin paramagnetic susceptibility, including allowance for g-factor anisotropy, is found to be 5.8×10^{-8}-cgs units at 300°K, for a hole concentration of 1.5×10^{18} cm^{-3}. Under these conditions, the measured Knight shift is 2.34×10^{-3}. The calculated Knight shift is 2.0×10^{-3}.

INTRODUCTION

As part of a theoretical study of the lead salts[1–4] by the augmented-plane-wave (APW) method, a calculation has been made of parameters which determine the Knight shift for Pb^{207} in p-type PbTe. The calculation includes the effect of relativistic corrections. The parameters involved are the s character, the hyperfine parameter, and the paramagnetic susceptibility. The Knight shift so obtained may be compared with the measured value[5–7]; experimental data for susceptibility are also available.[8]

From the previous relativistic APW work on PbTe we obtain data regarding the band structure,[1] the g-factors, and effective masses.[4] The energy gap is direct and occurs at L, the zone edge in the [111] direction; the next valence and conduction band extrema both occur along [110]. In the case of PbTe for which Knight shift data are available, only the holes at L contribute.

In the following, the major contribution to the Knight shift in PbTe is discussed, and the s character, the hyperfine parameter, and the paramagnetic susceptibility are evaluated. The experimental and theoretical results are compared. The details of the present determination are available in report form[9] so the approximations made and the results obtained are given here in summary. A complete account of the data and terms employed in the relativistic APW calculations for PbTe is given in Refs. 1 and 4.

KNIGHT SHIFT

The principal contribution to the Knight shift for Pb in p-type PbTe arises from the contact interaction; other contributions have been considered and found to

* Based on part of a dissertation for the degree of Doctor of Science in Physics at MIT. This research was supported in part by the U. S. Office of Naval Research.

† Present address: Monsanto Company, St. Louis, Mo.

[1] J. B. Conklin, Jr., L. E. Johnson, and G. W. Pratt, Jr., Phys. Rev. **137**, A1282 (1965).
[2] G. W. Pratt, Jr., and L. G. Ferreira, in *Physics of Semiconductors*, edited by M. Hulin (Academic Press Inc., New York, 1964).
[3] L. G. Ferreira, Phys. Rev. **137**, A1601 (1965).
[4] S. Rabii, Phys. Rev. **167**, 801 (1968).
[5] I. Weinberg, Bull. Am. Phys. Soc. **7**, 396 (1962).
[6] I. Weinberg and J. Callaway, Nuovo Cimento **24**, 190 (1962).
[7] I. Weinberg, J. Chem. Phys. **39**, 492 (1963).
[8] M. Matyas, Czech. J. Phys. **8**, 301 (1958).