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Lattice parameter study of silicon uniformly doped with boron and phosphorus

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Powder and single-crystal X-ray techniques have been employed to obtain precise lattice parameters of silicon uniformly doped with boron or phosphorus. Good agreement is found between the two methods. Previous accurate determination of the Cu$K\alpha_1$ effective wavelength has yielded $\lambda = 1.540621 \pm 0.000006$ Å. Particular care has been devoted to the chemical and electrical characterization of the alloys, whose maximum dopant concentrations were 8×10^{19} atoms cm^{-3} for P and 4.4×10^{20} atoms cm^{-3} for B.

A linear dependence of lattice parameter on concentration has been found for P in the whole examined range, while for B a deviation from the linear trend starts at about 2.25×10^{20} atoms cm^{-3}. Tetrahedral radii are found to be 1.176 Å for pure Si, 1.07 Å and 0.91 Å respectively for dissolved substitutional P and B. Values of the linear lattice contraction coefficient, volume size factor, Vegard's law factor and elastic strain energy in both alloys are reported and discussed. The deviation from linear trend in boron-doped alloys is analysed and it is shown that the phenomenon is insensitive to heat-treatments and does not depend on the degree of ionization of boron atoms.

1. Introduction

We have carried out accurate determinations of the lattice parameters of primary solid solutions of boron and phosphorus in silicon. Besides its basic interest, this research is intended to provide reliable data for a study on the solubility and diffusivity of these elements. Further interest arises in connection with a deeper insight in the problem of electrically inactive phosphorus [1] and the determination of the stresses connected with concentration profiles of the dopants.

Previous work, among which that of Horn [2] offers particular evidence, has shown that in dilute solutions these solutes occupy substitutional positions in the silicon lattice. On the other hand, considerable scatter exists in the lattice parameter data reported in the literature: the improvements in silicon technology and the different experimental conditions seem responsible for these discrepancies. The pioneering work of Pearson and Bardeen [3] was carried out on polycrystalline specimens. Cohen [4] and McQuhae and Brown [5] examined specimens whose surface had been doped by diffusion, whereas Horn [2], followed by Dubrovskii [6] and Kishino [7] examined single crystals uniformly doped with boron, limiting their studies to dilute solutions.

An accurate definition of the impurity content, solute concentration and homogeneity seems necessary to improve the reliability of the results.

2. Experimental

2.1. Sample characterization and chemical analysis

Our specimens consisted of single crystal silicon slices, about 300 μm thick, uniformly doped with boron or phosphorus. The most heavily doped samples were prepared by Montedison S.p.A., starting from zone-refined silicon.

Maximum concentrations were 8×10^{19} atoms cm^{-3} of phosphorus and 4.4×10^{20} atoms cm^{-3} of boron; the composition richest in boron was polycrystalline. These values should be compared with the maximum solubilities: a

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value of about 6×10^{20} atoms cm^{-3} is reported for boron [8]; for phosphorus the old estimate is about 1.2×10^{21} atoms cm^{-3} [8], and more recent values range between 2.5×10^{20} and 5×10^{20} atoms cm^{-3} [9, 10].

Determinations of the dopant content were carried out by analytical techniques: neutron activation analysis for phosphorus, and a colorimetric method for boron [11]. Activation by high-energy ions has been used* to analyse carbon, nitrogen and oxygen in selected specimens. The C and N contents turn out to be approximately the same in the different types of specimens, namely about 4×10^{17} atoms cm^{-3} for carbon and about 1.5×10^{17} atoms cm^{-3} for nitrogen. Oxygen concentration was found to range between 6×10^{15} and 1×10^{18} atoms cm^{-3}: the latter value has been observed only in a doped alloy produced by the CZ technique. The presence of other impurities has been checked by γ spectrometry: the data are not reported because the concentrations proved generally to be below the sensitivity of the technique and, in any case, extremely low.

The absence of precipitates in the heavily doped alloys has been checked both by X-ray topography and TEM after ion-beam thinning. We have verified that lattice spacing was unaffected by heat-treatments by comparing, for heavily doped specimens, two extreme situations: cooling the slice slowly in the furnace, or quenching it in a helium stream, after annealing 3 h *in vacuo* at 1100°C.

2.2. Electrical measurements

Accurate four-point probe conductivity measurements and the Irvin data [12] have been used to determine the concentration of electrically active dopant and to confirm, by comparison with the chemical composition, the absence of precipitates. Further, to analyse the lattice parameter results obtained with specimens heavily doped with boron, conductivity and Hall effect measurements were performed employing the van der Pauw method [13]. The ohmic contacts were placed at the border of the slices and consisted of small dots of aluminium evaporated under vacuum through a mask and sintered at 525°C. The electrical leads consisted of aluminium wires ultrasonically welded to the contacts.

Conductivity determinations were carried out in the temperature range -80 to $+20$°C by keeping the samples in a thermostat and using a digital voltmeter of 0.1 μV sensitivity. Hall effect determinations were performed at room temperature.

2.3. X-ray techniques

Two different techniques were employed and compared: the classical Debye-Scherrer method [14] and the Bond's method of symmetric equivalent reflections from single crystals [15].

For the powder method the slices were milled in an agate mortar, as several tests proved this to be non-contaminating; powders were subsequently passed through a 380-mesh screen, leaving grains of maximum diameter about 35 μm. A Lindemann glass capillary 0.5 mm in diameter was filled and examined in a 114.6 mm Philips camera. To record the spectra we used Ilford Industrial G film, mounted in the Straumanis asymmetric position, with an exposure time of 4 h, Cu$K\alpha$ radiation and a tube working at 50 kV and 30 mA. The diffractograms were measured by a Wooster Mk. III optical microdensitometer, giving a precision of 25 μm on the film and the data were corrected to account both for the variation in length of the film due to photographic processing [16] and for sample absorption [17].

The corrected angular values were worked out by two procedures: (a) graphical extrapolation [18, 19]; (b) least squares analytical calculations [20]. The values so obtained coincided not only within the accuracy of our experimental determinations (about 35 ppm), but also within the maximum precision one usually ascribes to the powder method (about 20 ppm). Finally, the resulting lattice parameter value was corrected for refraction [21], which for silicon and Cu$K\alpha$ radiation involves an increase of about 8 ppm.

Single crystal analyses were carried out on specimens previously examined by X-ray Lang and double crystal topography. We used the automated high precision APEX diffractometer designed and set up at the AERE in Harwell [22]. Its characteristics and operating conditions have recently been described [23, 24] and the remarkable performances positively tested [25, 26].

Our (1 1 1)-oriented and mirror-polished crystals were mounted on the sample-holder by silicone grease to avoid mechanical strains. We recorded the Cu$K\alpha_1$ peak of the (444) reflection with a tube working at 40 kV and 24 mA. A

*Analyses performed at the Centre d'Etudes Nucléaires at Saclay (France).

constant temperature of 25.0 ± 0.1 °C during the measurements was insured by the thermostated enclosure of the instrument.

Several determinations were carried out at spots spaced by 1 to 3 mm increments along a diameter of each crystal, using a cylindrical beam with a diameter of 1 mm at the sample. The results were automatically corrected for errors specific to this particular geometry [23, 24] and afterwards a mean value for the crystal was obtained. Lattice parameter oscillations from point to point in fact turned out to be small: the largest ones were observed to occur in the most heavily doped specimens and are reported in Fig. 1.

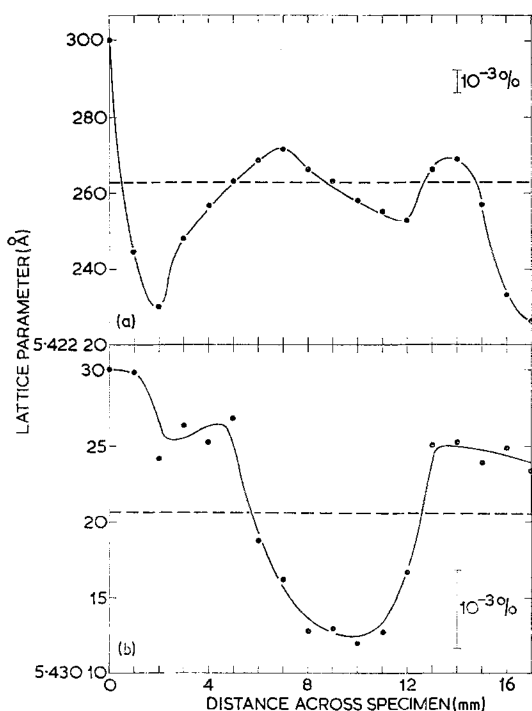

Figure 1 Lattice parameter values across the most heavily doped specimens: (a) boron-doped (B4), (b) phosphorus-doped (P4).

2.4. X-ray effective wavelength

As a preliminary investigation, we performed a precise determination of the effective wavelength of $CuK\alpha_1$ radiation. Substantial corrections had been brought to its traditional value [27] by Bearden [28] and an angular dependence recently found by Barns [29].

We selected a pure silicon crystal (resistivity 3.3×10^3 Ωcm) of very high lattice perfection (both by Lang and double-crystal X-ray topography and by extremely high-precision special measurements of lattice parameter [23, 24]): as shown in Fig. 2, the parameter proved to be constant across the sample within 0.3 ppm. By using a special multiple reflection geometry [30], this crystal was compared with a suitably shaped reference crystal, whose lattice parameter, $a_0 = 5.431\,07 \pm 0.00001$ Å at 25°C, had been determined by Hart and co-workers by means of interferometric experiments absolutely independent of any knowledge of X-ray wavelength [31, 32].

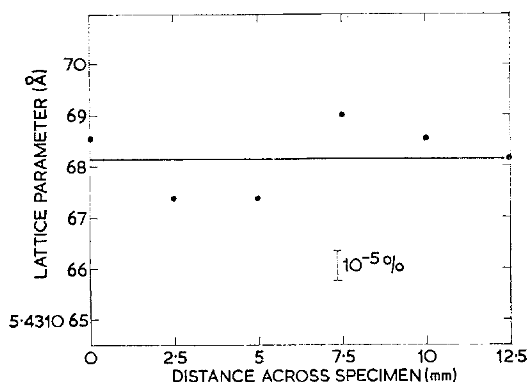

Figure 2 Lattice parameter values across the reference pure silicon crystal (R0) from the special experiment.

Having obtained an absolute value with this procedure, to within 2 ppm, of the lattice parameter of our crystal, it was then examined on the APEX diffractometer to determine the Bragg angle of the (444) reflection with an accuracy comparable with that reported above for lattice spacing. Finally, from Bragg's law, the effective value of $\lambda(CuK\alpha_1)$ was calculated.

The values oftained in the different steps of the procedure are as follows:

$a_0 = 5.43106 \pm 0.00001$ Å

$d_{444} = 0.783906 \pm 0.000002$ Å

$\theta_{444} = 79.3136 \pm 0.0002$ °

$\lambda = 1.540621 \pm 0.000006$ Å.

Our effective wavelength value is about 72 ppm higher than the traditional one and about 38 ppm higher than that proposed by Bearden. It has been employed to calculate our single crystal lattice parameters from measured angular values and also, for uniformity, from the data obtained by the powder method. Specifications and compositions of the analysed specimens are listed in Table I.

TABLE I Specifications and compositions of examined alloys

Sample	Dopant	Conc. (atoms cm^{-3})	Conc. (at. %)
Powders			
r0	n-type	$\simeq 10^{14}$	—
b1	Boron	2.05×10^{19}	0.041
b2	Boron	6.70×10^{19}	0.134
b3	Boron	1.84×10^{20}	0.368
b4	Boron	2.31×10^{20}	0.462
b5	Boron	2.60×10^{20}	0.520
b6	Boron	3.00×10^{20}	0.600
b7	Boron	4.40×10^{20}	0.880
p1	Phosphorus	1.58×10^{19}	0.032
p2	Phosphorus	2.00×10^{19}	0.040
p3	Phosphorus	2.15×10^{19}	0.043
p4	Phosphorus	3.80×10^{19}	0.076
p5	Phosphorus	4.50×10^{19}	0.090
p6	Phosphorus	8.00×10^{19}	0.160
Single crystals			
R0	n-type	$\simeq 10^{14}$	—
B1	Boron	2.00×10^{19}	0.040
B2	Boron	6.60×10^{19}	0.132
B3	Boron	1.90×10^{20}	0.380
B4	Boron	3.00×10^{20}	0.600
P1	Phosphorus	1.45×10^{19}	0.029
P2	Phosphorus	1.83×10^{19}	0.037
P3	Phosphorus	3.80×10^{19}	0.076
P4	Phosphorus	8.05×10^{19}	0.161

3. Results

Our lattice parameter values and the associated standard deviations are reported in Table II. The powder data for the pure silicon reference sample agree well, allowing for the different value employed for the wavelength, with the final result, $a_0 = 5.43054 \pm 0.00017$ Å, obtained for powders by the "Precision Lattice Parameter Project" organized in 1960 by International Union of Crystallography [33] and appears slightly lower than that obtained from single crystals. This has been already observed [34-36]: however, we notice that in our case the discrepancy lies within the error limits of the powder technique.

Since the values of lattice parameters obtained with the two different techniques are in fair agreement, a single plot has been derived from all the data. The plots of lattice parameters a_0 versus dopant concentration c (in at. %) are

TABLE II Lattice parameters of examined alloys

Sample	a_0 (Å)	Sample	a_0 (Å)
Powders (mean standard deviation: 0.0002 Å)			
r0	5.4309	b7	5.4170
b1	5.4302	p1	5.4308
b2	5.4293	p2	5.4307
b3	5.4268	p3	5.4307
b4	5.4256	p4	5.4306
b5	5.4242	p5	5.4305
b6	5.4224	p6	5.4303
Single crystals (standard deviations in parentheses)			
R0	5.431065 (3)	P1	5.430928 (4)
B1	5.43042 (2)	P2	5.43089 (1)
B2	5.42932 (1)	P3	5.43068 (2)
B3	5.42622 (2)	P4	5.43021 (6)
B4	5.42257 (18)		

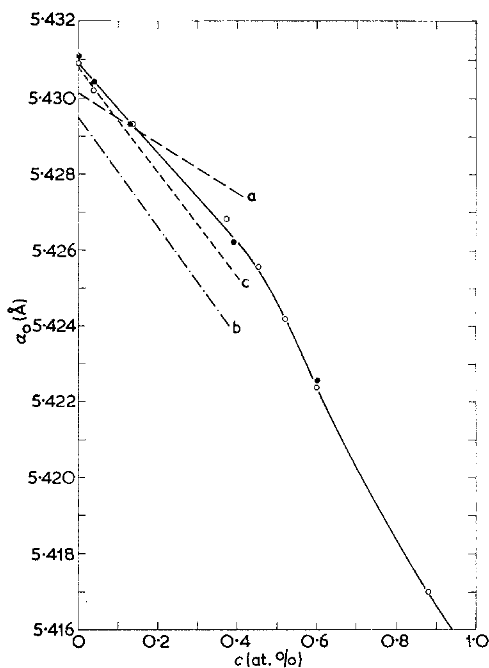

Figure 3 Lattice parameter, a_0 versus concentration, c, for boron-doped specimens (● = single crystals, ○ = powders), in comparison with the data of (a) Pearson and Bardeen, (b) Horn and (c) Kishino.

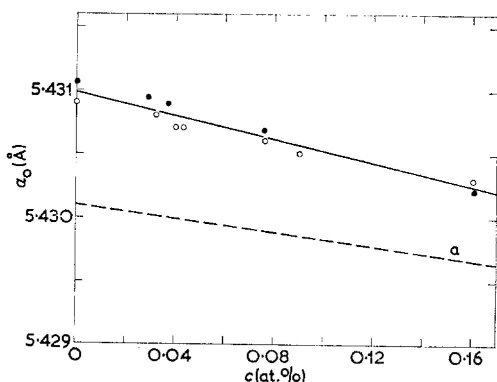

Figure 4 Lattice parameter, a_0, versus concentration, c, for phosphorus-doped specimens (● = single crystals, ○ = powders), in comparison with the data of (a) Pearson and Bardeen.

reported in Figs. 3 and 4 for boron and phosphorus respectively, in comparison with the results of other authors [2, 3, 6, 7]. From the slope of the linear part of these plots we derived the linear lattice contraction β_l for boron and phosphorus in silicon. This coefficient is defined as:

$$\beta_l = \frac{1}{N}\left(1 - \frac{r_{sol}}{r_{Si}}\right)$$

where N is the number of atoms per cm^3 and r the atomic radius.

Our β_l values are reported in Table III and are compared with those determined by different authors [2-5, 7] and those calculated from the data of Pauling [37] and Slater [38]. The values of covalent tetrahedral radii ($r_t = \sqrt{3}\ a_0/8$) resulting from lattice parameter data of pure silicon and from those extrapolated to 100% solute for boron and phosphorus, are reported in Table IV and compared with the values given by Pauling [37] and Slater [38].

As neither boron nor phosphorus have crystal structures of the diamond type and both present several allotropic states, it is believed to be more correct, considering also the arguments put forward by King in his treatment of size factors in alloys [39, 40], to base size correlations in our solid solutions on atomic volumes. This property, defined by taking the unit cell volume divided by the number of atoms in the cell, is particularly well determined in boron, as this element presents allotropic structures of fairly constant density. Plots of mean atomic volumes of our alloys versus concentration of solute in at. % are reported in Fig. 5.

The values of the effective atomic volume Ω^* of the solute, obtained by extrapolation of the linear part of the volume plot to 100% solute, turned out to be 7.16 Å^3 for boron and 15.18 Å^3 for phosphorus. Consideration of our value of the atomic volume for pure silicon, $\Omega_{Si} = 20.02$ Å^3, has allowed the evaluation of the volume size factors proposed by King [39]:

$$\Omega_{sf} = (\Omega^*_{sol} - \Omega_{Si})/\Omega_{Si}\,.$$

Further, on the basis of the data reported by King [39] for the atomic volumes Ω of elementary B and P, we determined the Vegard's law factors:

$$\text{VLF} = (\Omega^* - \Omega)/\Omega\,.$$

These values, together with those of the atomic volumes, are summarized in Table V.

We note that the exact value of the atomic volume of elementary phosphorus is uncertain. Actually, among the allotropic modifications stable at atmospheric pressure of this element, the "black" orthorhombic form (whose structure presents the highest density and is the only well determined one [41]) shows an Ω value, 18.99 Å^3,

TABLE III Linear lattice contraction coefficients for B and P in Si ($\times 10^{24}$ cm^3 atom^{-1})

Atoms	Calc. [37]	Calc. [38]	From [3]	From [2]	From [4]	From [5]	From [7]	Present work
B	5.0	4.5	2.5	5.6	2.3	5.2	4.7	4.5
P	1.2	1.8	1.1	—	0.7	1.0	—	1.8

TABLE IV Atomic radii (Å)

Atoms	Pauling [37]	Slater [38]	Present work
B	0.88	0.85	0.91
P	1.10	1.00	1.07
Si	1.173	1.10	1.176

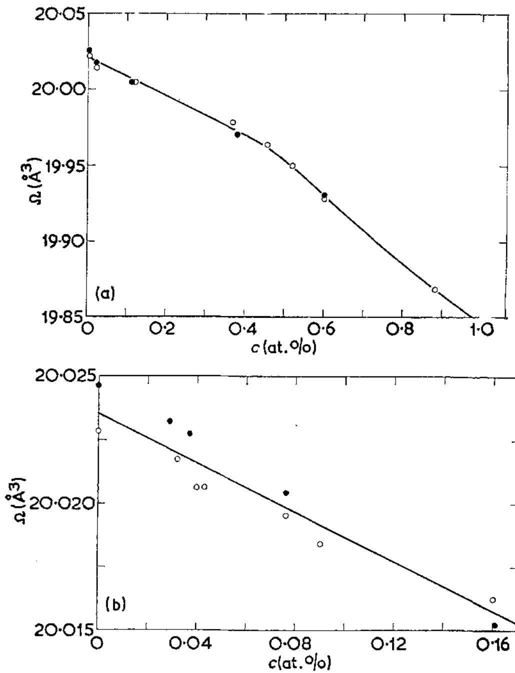

Figure 5 Mean atomic volume, Ω, versus concentration, c, for (a) boron-doped and (b) phosphorus-doped alloys, (● = single crystals, ○ = powders).

considerably larger than that reported by King. However, this simply affects the magnitude of the VLF, but not its sign which remains negative.

4. Discussion

4.1. Atomic radii

First of all we note that our β_l values in Table III agree fairly well with those calculated using the empirical radii given by Pauling and Slater. A satisfactory agreement is also found with the values determined on uniformly doped single crystals by Horn and Kishino, while values derived from surface-diffused specimens are more scattered, and agreement is found only with those reported for boron by McQuhae and Brown. Further, the values of our extrapolated tetrahedral radii agree well with those of Pauling, which were also derived from observation of interatomic distances in crystals of tetrahedral co-ordination. This agreement is a further confirmation that B and P occupy substitutional positions in the silicon lattice or, in any case, the fraction of substitutional solute is large. Considering phosphorus in particular, our results in Fig. 4 indicate that this remains true up to our maximum concentration (8×10^{19} atoms cm^{-3}).

The agreement between our tetrahedral radii and Slater's radii is obviously less good. In fact the empirical radii given by Slater, resulting from consideration of a large number of compounds, do not take into account the co-ordination.

4.2. Elastic strains

Consideration of the Ω_{sf} in Table V indicates that the elastic strain energy is an important factor in limiting the solid solubilities of P and especially of B in silicon. Following the treatment of Eshelby [42] and using the elastic constants of silicon [43] together with the values of Ω_{sf}, we can obtain the strain energy per atom in our dilute alloys:

$$\frac{E(c)}{c(1-c)} = \frac{2}{3}\frac{\mu}{\gamma}\,\Omega_{Si}\,\Omega^2{}_{sf}$$

where c is the atomic fraction of solute, μ the shear modulus of solvent and $\gamma = (3K + 4\mu)/3K$ results from the bulk K and shear moduli of matrix.

TABLE V Volume size factors

Atoms	Ω (Å^3)	Ω^* (Å^3)	Ω_{sf} (%)	VLF (%)	Ω (Å^3) [39]
B	—	7.16	−64.24	−6.65	7.67
P	—	15.18	−24.18	−8.50	16.59
Si	20.02	—	—	—	20.02

The energy term on the right amounts to 0.27×10^{-12} erg for phosphorus and 1.90×10^{-12} erg for boron, assuming an intermediate value for μ, which varies with crystallographic directions. These are high values and, therefore, our solutions are expected to be unstable with respect to intermediate phases in which atomic rearrangement can reduce the elastic energy term and, consequently, the range of primary solid solubility has to be narrow. Further, the negative deviation from the ideal behaviour, expressed quantitatively by the values of VLF in Table V, is also consistent with the observed formation of stable intermediate compounds [44]. It is generally expected that if interatomic forces between unlike species are greater than between like ones, a lattice contraction will occur on homogenization.

4.3. Departure from linear trend for boron in silicon

The plots for the Si-B system in Figs. 3 and 5 show a deviation from linearity at a concentration c_l of about 0.45 at.% solute (2.25×10^{20} atoms cm^{-3}). This phenomenon has been confirmed by comparative X-ray analysis of heavily doped specimens, heat-treated as previously detailed. In any case we have obtained a perfect constancy and coincidence of lattice parameters after quenching or slow cooling.

We notice that previous investigations on homogeneously doped single crystals [2, 6, 7] were carried out on alloys more dilute than those examined in the present investigation. The critical concentration c_l, on the other hand, has been exceeded by Cohen and McQuhae and Brown, who examined surface-diffused specimens, therefore presenting a concentration gradient.

It is unlikely that the deviation from linearity which we observe in determinations performed at room temperature is due to a thermal expansion of the alloy monotonically decreasing with increasing boron content. The lattice parameter expansion of pure silicon from absolute zero to room temperature [45] is smaller than the observed deviation from linearity (see Fig. 3) at the boron-richest composition. The breakaway of the plot from linearity suggests a modification of the electronic environment of both components.

On the other hand, the results of our electrical measurements, consistent with those of Pearson and Bardeen [3] and Chapman *et al* [46], allow us to reject the hypothesis of a complete ionization of the dopant taking place only above 0.45 at.% boron. They confirm that, in the temperature range considered, above 0.05 at.% boron, the semiconductor is fully degenerate. We observed a linear temperature dependence of the resistivity, with a small positive temperature coefficient, similar for all doping levels. This behaviour is like that of an impure metal. Further the concentration of charge carriers, determined by Hall effect measurements, corresponds within a few per cent to the chemical concentration of boron, confirming that the acceptor levels are fully occupied by electrons.

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References

1. E. TANNENBAUM, *Solid-State Electron.* **2** (1961) 123.
2. F. H. HORN, *Phys. Rev.* **97** (1955) 1521.
3. G. L. PEARSON and J. BARDEEN, *ibid* **75** (1949) 865.
4. B. G. COHEN, *Solid-State Electron.* **10** (1967) 33.
5. K. G. MCQUHAE and A. S. BROWN, *ibid* **15** (1972) 259.
6. G. B. DUBROVSKII, Dissertation for Candidate's Degree, Leningrad (1963), quoted in: V. I. FISTUL, Heavily doped semiconductors" (Plenum Press, New York, 1969) pp. 33 ff.
7. S. KISHINO, *Adv. X-ray Anal.* **16** (1973) 367.
8. F. A. TRUMBORE, *Bell Syst. Technol. J.* **39** (1960) 205.
9. N. K. ABRIKOSOV, V. M. GLAZOV and L. CHENG-YÜAN, *Z. Neorg. Khim.* **7** (1962) 831.
10. F. N. SCHWETTMANN and D. L. KENDALL, *Appl. Phys. Letts.* **19** (1971) 218.
11. P. LANZA and P. L. BULDINI, *Anal. Chim. Acta*, in press.
12. J. C. IRVIN, *Bell Syst. Technol. J.* **41** (1962) 387.
13. L. J. VAN DER PAUW, *Philips Res. Repts.* **13** (1958) 1.
14. P. DEBYE and P. SCHERRER, *Physik. Z.* **17** (1916) 277; **18** (1917) 291.
15. W. L. BOND, *Acta Cryst.* **13** (1960) 814.
16. H. P. KLUG and L. E. ALEXANDER, "X-ray diffraction procedures" (Wiley, New York, 1959) pp. 319ff.

17. P. BELLON, V. SCATTURIN and R. ZANNETTI, *Ric. Sci.* **26** (1956) 1732.
18. J. B. NELSON and D. P. RILEY, *Proc. Phys. Soc. (London)* **57** (1945) 160.
19. A. TAYLOR and H. SINCLAIR, *ibid* **57** (1945) 126.
20. M. U. COHEN, *Rev. Sci. Instrum.* **6** (1935) 68; **7** (1936) 155.
21. A. GUINIER, "Théorie et technique de la radiocristallographie" (Dunod, Paris, 1964) p. 2.
22. T. W. BAKER, J. D. GEORGE, B. A. BELLAMY and R. CAUSER, *Adv. X-ray Anal.* **11** (1968) 359.
23. *Idem*, AERE Research Report, Harwell (1969) R-5152.
24. B. A. BELLAMY, *ibid* (1973) R-7311.
25. A. F. W. WILLOUGHBY, C. M. H. DRISCOLL and B. A. BELLAMY, *J. Mater. Sci.* **6** (1971) 1389.
26. C. F. PIHL, R. L. BIEBER and G. H. SCHWUTTKE, *Phys. Stat. Sol. (a)* **17** (1973) 359.
27. K. LONSDALE (ed.), "International Tables for X-ray Crystallography" (Kynoch Press, Birmingham, 1968) Vol. III, p. 60.
28. J. A. BEARDEN, *Rev. Mod. Phys.* **39** (1967) 78.
29. R. L. BARNS, *Adv. X-ray Anal.* **15** (1972) 330.
30. M. HART, unpublished results.
31. *Idem, J. Phys. D: Appl. Phys.* **1** (1968) 1405.
32. I. CURTIS, I. MORGAN, M. HART and A. D. MILNE, in: "Precision measurement and fundamental constants" (edited by D. N. Langenberg and B.N. Taylor) (NBS, Washington, 1971) p. 285.
33. W. PARRISH, *Acta Cryst.* **13** (1960) 838.
34. B. J. ISHERWOOD and C. A. WALLACE, *Nature* **212** (1966) 173.
35. E. D. PIERRON and J. B. MCNEELY, *Adv. X-ray Anal.* **12** (1969) 343.
36. A. SEGMÜLLER, IBM Res. Rept., Yorktown Heights (1969) RC-2640.
37. L. PAULING, "The nature of the chemical bond" (Cornell University Press, Ithaca, 1960) p. 246.
38. J. C. SLATER, *J. Chem. Phys.* **41** (1964) 3199.
39. H. W. KING, *J. Mater. Sci.* **1** (1966) 79.
40. *Idem, ibid* **6** (1971) 1157.
41. A. BROWN and S. RUNDQVIST, *Acta Cryst.* **19** (1965) 684.
42. J. D. ESHELBY, *Solid State Phys.* **3** (1956) 79.
43. H. B. HUNTINGTON, *ibid* **7** (1958) 213.
44. R. P. ELLIOTT, "Constitution of binary alloys", First supplement (McGraw-Hill, New York, 1965) pp. 134 and 716.
45. R. A. EVANS, US Dept. of Commerce, Washington (1964) ASD-TDR-63-316, Vol. V.
46. P. W. CHAPMAN, O. N. TUFTE, J. D. ZOOK and D. LANG, *J. Appl. Phys.* **34** (1963) 3291.

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