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Mössbauer Studies of Implanted I^{129} Ions in Semiconductors and Alkali Halides

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The Groningen isotope separator has been used to implant Te^{129m} into single crystals of Si, Ge, and diamond as well as several alkali halides. The spectra of all semiconducting sources display two well-separated Mössbauer lines of approximately equal intensity. The parameters of the spectra were found to be only slightly dependent on the annealing temperature type of dopant already present in the semiconductors, Mössbauer source temperature, implantation temperature, and Te^{129m} dose. The results obtained for I^{129} in these semiconductors are qualitatively similar to the Fe^{57} data obtained by the Stanford group using the Coulomb excitation implantation technique with a Van de Graaff accelerator. The separation between the lines for the I^{129} sources is seen to be proportional to the separation obtained with the Fe^{57} sources. On the basis of the Mössbauer spectra, as well as the previously published channeling data and the systematics of the I^{129} isomer shifts, the lines are tentatively assigned to be due to iodine atoms in substitutional and interstitial sites. The nature of the interaction causing the very large shifts is briefly discussed. In contrast to the semiconductor results, the Mössbauer spectra obtained with Te^{129m} implanted alkali halide sources are very sensitive to annealing and to the Te^{129m} dose. Both single-line spectra as well as spectra displaying an unresolved structure were obtained. The isomer shifts obtained from the single-line spectra are quite large; about five times larger than the spread of isomer shifts previously obtained from the alkali iodides. For the case of I^{129} in LiF the large shift is probably caused by the large degree of overlap that an iodine ion experiences because of the smaller interatomic spacing in the LiF lattice compared to the alkali iodide lattices.

I. INTRODUCTION

In the last five years ion implantation into semiconductors[1-3] has been widely exploited both by technologists in industry and by solid-state physicists. The technologists have been able to fabricate by implantation new devices in which the high temperatures and long times necessary for diffusion can be avoided and in which at the same time higher-impurity densities can be obtained than normal solubilities would allow. Some of the implanted integrated circuits and MOSFET's have been cheaper to fabricate and they are faster in response time and smaller in size than their diffused counterparts.

The location of these implanted ions and their binding in the lattice are not always well known. Investigations[1-3] of implanted crystals have been carried out mainly by channeling and by Hall-effect measurements. By measuring the angular and energy dependence of back-scattered projectiles the channeling technique mainly tells the investigator which fraction of the impurities is substitutionally imbedded in the crystal, but little is learned about the nature of the local environment of the impurity. Hall-effect measurements determine the number and sign of the electrical carriers and their mobility, but, as in the case of channeling, they give little direct information concerning the microscopic environment of the impurity. In order to obtain information about the electronic interactions between the lattice and the impurity one can complement these investigations with resonance and Mössbauer measurements.

At present most of the implantation-Mössbauer measurements have been carried out in metals in which a large part of the radiation damage rapidly anneals at room temperature and which may display large magnetic hyperfine interactions. The first implantations into semiconductors were carried out by the Oak Ridge group[4] who used a tandem Van de Graaff to Coulomb excite and implant Ge^{73} by recoil into germanium. For these experiments a 25-MeV beam of oxygen ions was directed at a germanium target and the 57-keV γ rays following deexcitation after implantation were analyzed in a Mössbauer spectrometer. A single line was observed having a width consistent with the lifetime of the level, but the intensity of the line was reduced to 8% of its expected value, probably chiefly by radiation damage. A little later the Stanford group[5] used a similar technique to implant Fe^{57} into silicon and germanium. They obtained a two-line spectrum which with the aid of channeling measurements was interpreted in terms of an interstitial and a substitutional site. Similar Mössbauer spectra were obtained[6] with sources prepared by implanting radioactive Co^{57} ions into diamond with an isotope separator.

For the present measurements we have used the Groningen isotope separator to implant Te^{129m} into the semiconductors Si, Ge, and diamond, as well as in the ionic crystals LiF, KCl, KBr, NaCl, and KI. Most of these sources cannot be prepared by normal diffusion; the solubility of tellurium in diamond, for instance, is very small indeed and moreover diffusion techniques may lead to the formation of unwanted compounds. Isotope separator implantation of radioactive nuclei has several advantages over accelerator implantation of nuclei that decay immediately. Apart from difficulties often experienced with accelerator background, isotope separator implanted sources are considerably more convenient to work with since one can prepare sources for measurements lasting several months within a few hours of separator time. In addition, the recoilless fraction is not reduced by thermal spikes and it is possible to anneal the sources in various stages in order to investigate the extent of radiation damage. For the case of the alkali halides annealing proved to be of crucial importance.

II. EXPERIMENTAL PROCEDURE

The 33-day Te^{129m} activity was implanted by accelerating tellurium ions to 110 keV in the Groningen isotope separator. All implantations were done at room temperature except for one implantation of germanium at 330 °C. The ions penetrated to an average depth of 500 Å and stable tellurium beam doses of 5–25 μA h yielded source strengths from 5 to 50 μCi. These strengths correspond to about $(2-20)\times10^{12}$ Te^{129m} ions/cm^2. The rejection ratio for Te^{128} was about one part in 2000 of the primary Te^{128} beam current, raising the total number of impurities to $(1.6-8)\times10^{14}/\text{cm}^2$. The relatively low counting rates from these sources required counting times of several days.

The germanium single-crystal plates used were oriented with the ⟨111⟩ direction normal to the surface. They were etched before implantation in a solution of HF, HNO_3, and acetic acid. The impurities and resistivities of the samples were Ge-*n* (Sb, 0.02 Ω cm), Ge-*p* (Ga, 0.2 Ω cm), Si-*n* (Sb, 0.02 Ω cm), and Si-*p* (B, 600 Ω cm). The diamond plates, oriented with their surface normal to the ⟨100⟩ direction, were obtained from Keppies of Pittsburgh and from Drukker of Amsterdam. The alkali-halide samples were freshly cleaved normal to the ⟨100⟩ direction prior to implantation. No attempt was made to implant the activity into a channeling direction. After implantation some of the samples were annealed in vacuum at temperatures from 400 to 800 °C and for times from 15 min to 25 h. In addition the compound $GeTe^{129m}$ was investigated as well as sources of Te^{129m} diffused into Ge at 400, 600, and 800 °C for 24 h.

The Mössbauer spectra were taken with a 400-channel analyzer in the usual multiscaling mode. Absorbers of 11 and 18 mg/cm^2 of I^{129} in CuI and of 22 mg/cm^2 of I^{129} in KI were used. The source temperature was mostly kept at about 80 °K, but some runs were made at other temperatures between 4 and 270 °K.

III. EXPERIMENTAL RESULTS FOR SEMICONDUCTORS

Examples of spectra obtained with unannealed sources of Te^{129m} implanted into Si, Ge, and diamond are shown in Fig. 1. These spectra have the same general appearance; there are two separate lines of approximately equal intensity and with no evidence for the additional lines expected in the case of a quadrupole interaction. The appearance of two lines, one with a positive and one with a negative shift with respect to the Cu I^{129} absorber, is very consistent for all our measurements on I^{129} implanted semiconductors. In the following, we shall indicate the line with positive shift as line "1," that with negative shift as line "2" and we shall see that these lines correspond to two different sites in the crystal. In order to find a physical interpretation of these spectra the following parameters were varied in our experiment: (i) host lattice (Si, Ge, and diamond), (ii) annealing temperature, (iii) dopants (*n*- and *p*-type), (iv) source temperature, and (v) implantation temperature and dose. A short discussion of these results, that have been compiled in Tables I–III, follows below:

a. Host lattice. From the data given in Table I the difference in the separation between the two lines can be found. The separation between the components in the annealed Si and Ge samples is slightly different, 4.13 ± 0.05 mm/sec and 3.58 ± 0.05 mm/sec, respectively, while the separation for diamond is a factor of 2 larger, namely, 7.24 ± 0.11 mm/sec. The linewidths for diamond (~ 2.1 mm/sec) are slightly larger than for unannealed Ge and Si (~ 1.7 mm/sec). The cubic compound ZnTe yields a width of 1.24 mm/sec for the particular geometry and absorber thickness used in these experiments.

The increased width may be due to one or both of the following effects: (i) a residual unresolved quadrupole splitting and (ii) nonequivalence of occupied sites caused by local damage.

b. Annealing. A considerable number of channeling and Hall-effect measurements[1] has been performed on Ge and Si samples with impurity doses from 10^{12} to $10^{16}/\text{cm}^2$. Annealing experiments on these samples have shown that it is possible to restore crystal damage and that the number of ions in substitutional sites can in certain cases be increased. The greater the dose the crystal has received the higher the annealing temperatures needed to restore the crystal. At very high annealing temperatures the impurities diffuse to the surface and the number of substitutional impurities is again reduced. Channeling and Hall-effect measurements have been carried out for the case of Te implanted into Si after annealing at various temperatures. The channeling measurements indicate that for a room-

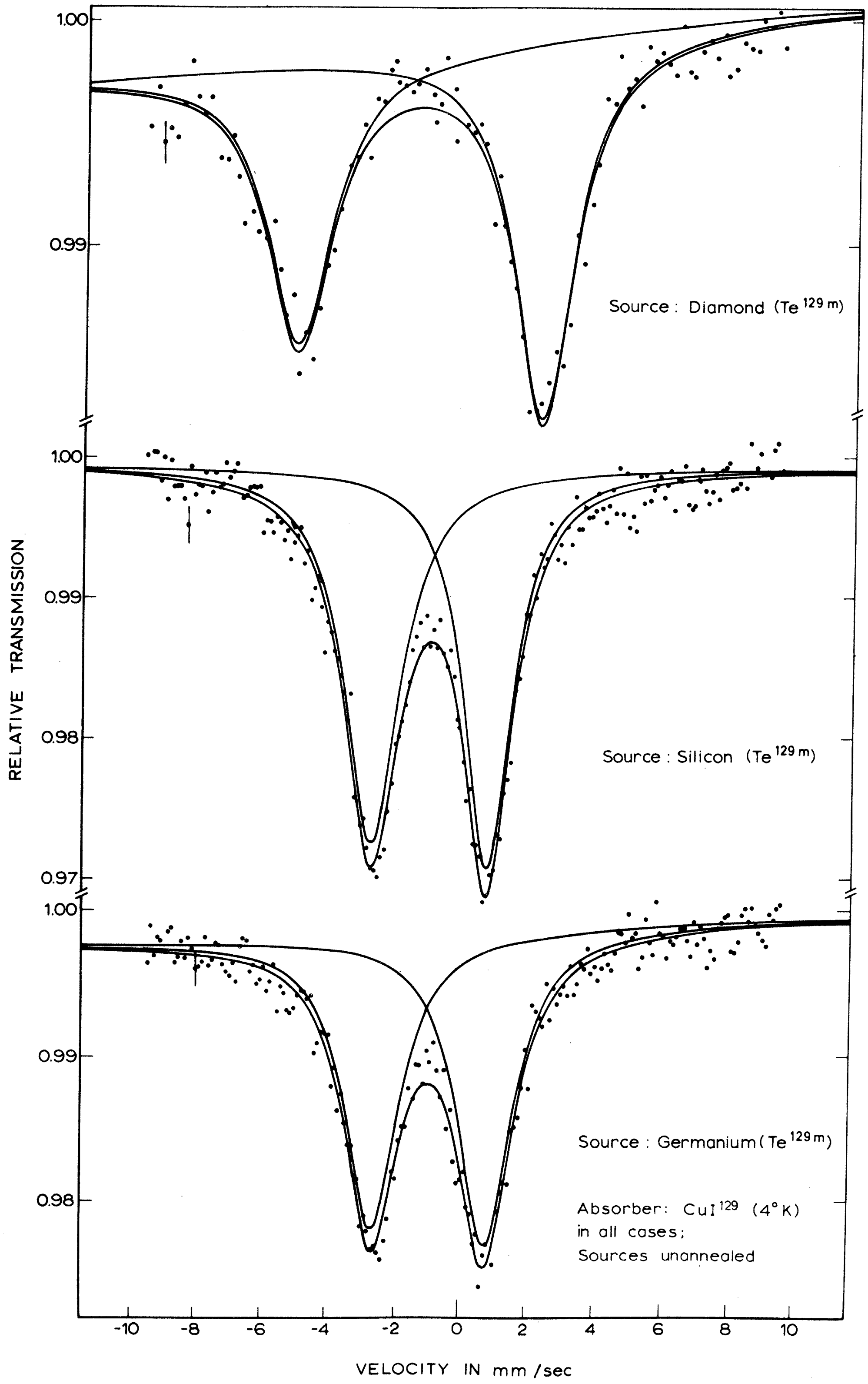

FIG. 1. Mössbauer spectra of the 27.7-keV γ ray of I^{129} obtained with Te^{129m} sources implanted in semiconductors and a Cu I^{129} absorber containing 11 mg/cm^2 of I^{129}.

TABLE I. Isomer shifts δ_1 and δ_2 (vs Cu I^{129} absorber), linewidths Γ_1 and Γ_2 and intensity ratios A_1/A_2 of the two components of the Mössbauer spectrum of I^{129} implanted in diamond, silicon, and germanium single crystals. Source and absorber temperature (T) are equal.

Source	T(°K)	δ_1(mm/sec)	δ_2(mm/sec)	Γ_1(mm/sec)	Γ_2(mm/sec)	A_1/A_2	Annealing condition
Diamond	4.2	2.23 ± 0.06	-5.07 ± 0.08	2.2 ± 0.1	2.3 ± 0.2	1.26 ± 0.06	...
	78	2.25 ± 0.07	-4.00 ± 0.08	1.8 ± 0.1	2.3 ± 0.2	0.99 ± 0.06	...
n silicon	4.2	0.72 ± 0.06	-2.75 ± 0.06	1.73 ± 0.05	2.01 ± 0.06	0.92 ± 0.03	...
	78	0.72 ± 0.06	-2.70 ± 0.06	1.64 ± 0.09	1.68 ± 0.09	0.95 ± 0.05	...
	78	1.10 ± 0.05	-3.05 ± 0.05	1.84 ± 0.15	1.63 ± 0.14	1.11 ± 0.06	750 °C, 15 min
	78	1.08 ± 0.09	-3.03 ± 0.09	1.6 ± 0.2	1.8 ± 0.2	0.89 ± 0.10	850 °C, 15 min
p silicon	78	0.70 ± 0.05	-2.71 ± 0.05	1.6 ± 0.1	1.44 ± 0.07	1.04 ± 0.06	...
p germanium	4.2	0.75 ± 0.06	-2.66 ± 0.06	1.95 ± 0.06	1.94 ± 0.07	1.08 ± 0.03	...
	78	0.69 ± 0.05	-2.55 ± 0.05	1.9 ± 0.1	1.8 ± 0.1	1.09 ± 0.06	...
	78	1.01 ± 0.05	-2.61 ± 0.05	1.5 ± 0.1	1.5 ± 0.1	1.14 ± 0.08	450 °C, 15 min
n germanium	78	0.74 ± 0.06	-2.57 ± 0.06	1.63 ± 0.08	1.8 ± 0.1	0.94 ± 0.06	...
	78	0.84 ± 0.05	-2.71 ± 0.05	1.7 ± 0.1	1.7 ± 0.1	1.02 ± 0.06	400 °C, 15 min

temperature implant of $10^{15}/\mathrm{cm}^2$, annealing at 600 °C was needed to restore a sizeable fraction to the substitutional site while no annealing appeared to be necessary for a 350 °C implantation. At an annealing temperature of about 900 °C Te diffuses to the surface of the substrate and subsequently evaporates. In our experiments the Ge was annealed at 400 and 450 °C and the Si at 700, 750, and 850 °C for 15 min. At the highest annealing temperatures the radioactive strengths of the sources were considerably reduced because of evaporation of Te^{129m}. The diamond sample was not annealed because of the high temperature necessary for diffusion and because a very good vacuum would be needed to prevent graphitization.[7]

The results compiled in Table I show that the intensity ratio A_1/A_2 of the two components of the spectrum is not greatly influenced by the annealing treatment. If anything, a small increase of A_1/A_2 is observed. The width of the components becomes slightly smaller, indicating that a (relatively minor) part of the line broadening is caused by radiation damage. Assuming that the damage close to the iodine impurities is completely annealed, the residual line broadening, which amounts to about 30% compared with a $ZnTe^{129}$ source, should be due to quadrupole interaction. The influence of the annealing treatment on the line positions is considerable, especially for silicon. In this case, the average line distance of 3.43 ± 0.04 mm/sec before annealing is increased to 4.13 ± 0.05 mm/sec after annealing, a 20% change. For germanium an increase of about 10% is found. The cause of this effect will be briefly discussed in Sec. III *d*.

c. Dopants (*n- and p-type*). No discernible differences were observed between spectra of I^{129} in n- and p-type Si and in n- and p-type Ge (Table I). This result implies that the changes in the Fermi levels of these extrinsic semiconductors caused by the n- and p-type dopants do not change the electron configuration of the iodine impurities appreciably. Any direct influence caused if dopant and iodine atoms are nearest neighbors is completely negligible in view of the very low dopant concentration. Similar findings have been reported by the Stanford group for the case of Fe^{57} in Si and Ge.

d. Variation of source temperature. If the spectra of Fig. 1 are interpreted as the result of Te^{129m} residing in two different lattice sites with small electric field gradients that only cause a slight broadening of the lines one would expect to observe a temperature dependence in their intensity ratio. Such a temperature dependence has been observed, for instance, by Mullen[8] for the substitutional site and the vacancy-associated interstitial site of Fe^{57} in NaCl. Among the measurements compiled in Table I, those carried out with Te^{129m} implanted sources in Si, Ge, and diamond at 4 and 78 °K, do not show a clear trend of the intensity ratio. Therefore, additional measurements were performed with a Si (Te^{129m}) sources at 100 and 160 °K. The Si results for all temperatures used are collected in Table II. A slight increase of the intensity ratio A_1/A_2 with temperature may be present,

TABLE II. Intensity ratios of the two lines in the Mössbauer spectra of I^{129} implanted in silicon, measured at different source temperatures T_s with the absorber fixed at 78 °K.

Source Nr.	T_s(°K)	A_1/A_2
3	4.2	0.92 ± 0.03
3	78	0.95 ± 0.04
18	100	0.96 ± 0.04
18	160	1.02 ± 0.06

TABLE III. Isomer shifts (vs CuI^{129} absorber), linewidths and intensity ratios for hot and dirty implants in germanium; isomer shift and linewidth for ZnTe^{129m}, Ge Te^{129m}, and Te^{129m} diffused in Ge at 800 °C. All measurements at 78 °K source temperature. Sources and absorbers were both at 78 °K.

Ge source	δ_1(mm/sec)	δ_2(mm/sec)	Γ_1(mm/sec)	Γ_2(mm/sec)	A_1/A_2	Condition
Ge (Te^{129m})	0.67 ± 0.03	-2.68 ± 0.04	1.38 ± 0.13	1.58 ± 0.13	1.03 ± 0.06	dirty implant (dose 4×10^{17}/cm^{2}Te^{128})
Ge (Te^{129m})	0.76 ± 0.03	-2.97 ± 0.04	1.33 ± 0.10	1.41 ± 0.14	1.16 ± 0.10	hot implant (at 330 °C)
Ge (Te^{129m})	-1.04 ± 0.04		1.54 ± 0.05			Te diffused in Ge
Ge Te^{129m}	-0.96 ± 0.05		1.34 ± 0.03			compound
Zn Te^{129m}	-0.44 ± 0.03		1.24 ± 0.02			compound

but the errors do not allow a quantitative conclusion.

An estimate of the temperature dependence of the second-order Doppler shift yields a value too small to be observed within the statistical accuracy achieved for our measurements with rather weak sources.

e. Variation of implantation temperature and dose rate. Channeling and Hall-effect measurements on silicon and germanium indicate that for implanted isotopes such as Sb it is possible to increase the fraction of ions in the substitutional sites considerably by implanting at about 400 °C (Si) or at about 250 °C (Ge). For implantation of indium, the fraction of ions in the substitutional site is less dependent on the implantation temperature. The In results have been interpreted[9] such that approximately 50% of the ions reside in substitutional sites while the other 50% reside in interstitial sites. In a situation similar to ours Guylai *et al.*[10] found by channeling that 50–60% of the Te ions implanted into Si at 350 °C were in substitutional sites. The Mössbauer spectrum of a source of Te^{129m} implanted in germanium at a temperature of 330 °C shown in Fig. 2 exhibits a line distance $\delta_1 - \delta_2 = 3.73 \pm 0.05$ mm/sec, characteristic of annealed sources [cf. Tables I and II (hot implant)]. The area ratio $A_1/A_2 = 1.16 \pm 0.10$ is slightly larger than the average value $A_1/A_2 = 1.04 \pm 0.05$ obtained for nonannealed sources implanted at room temperature, which may indicate a slightly higher population of site 1 by implanting at a high temperature. The spectrum of a Te^{129m} source implanted at room temperature in germanium together with a dose of stable Te^{128} of about 4×10^{17}/cm^2, i.e., about three orders of magnitude higher than the other sources, is also shown in Fig. 2. The spectrum parameters do not differ from those obtained for the other sources [cf. Tables I and II (dirty implant)]. Apparently, the dose dependence of the character of the sites occupied by the iodine atoms is very small.

f. Compound GeTe^{129m} and Te^{129m} diffused into Ge. The single-line spectrum obtained with a source prepared by diffusing Te^{129m} into Ge at 800 °C for 24 h is compared in Fig. 3 with that of a source of the compound GeTe^{129m}. As seen from the figure and from Table III, the isomer shifts and linewidths for both sources are essentially the same. Presumably, small GeTe crystals are produced during the diffusion of tellurium into germanium. It is clear from Figs. 1–3 and from Table III that the spectra of the diffused and implanted sources are completely different. For the implanted sources there is no GeTe compound formation before or after annealing even at a very high implantation dose. It should be remarked, however, that the annealing temperature of the implanted germanium samples was 450 °C at most. This is too low for diffusion of tellurium as was proved by attempting diffusion of Te^{129m} into germanium at 600 °C. In that case no significant diffusion occurred and practically all activity could be removed from the semiconductor surface with a very light acid etch.

A similar difference as that just reported was found by the Stanford group[5] who also noted that their two-line spectra, obtained with implanted Co^{57} sources, differed considerably from those obtained with a diffused source,[11] which consist of a broad single line.

IV. INTERPRETATION OF SEMICONDUCTOR DATA

a. Are there really two sites? When one observes a one-to-one intensity ratio for two lines found in the Mössbauer spectrum of a spin-$\frac{3}{2}$ to -$\frac{1}{2}$ γ transition, such as in Fe^{57}, Sn^{119}, or Au^{197} it is not obvious whether this spectrum results from a single site with an electric quadrupole interaction or from two sites with different isomer shifts, but each with at most a small field gradient. In such cases, a choice can be made only after studying the influence of an external magnetic field or, in favorable circumstances, by studying the intensity ratio for a single crystal. In fact, a previous measurement of ours[6] on Co^{57} implanted in diamond, which yielded a one-to-one intensity ratio was first thought to be due to ions in a single site experiencing a rather large quadrupole interaction. Channeling measurements by Latshaw and

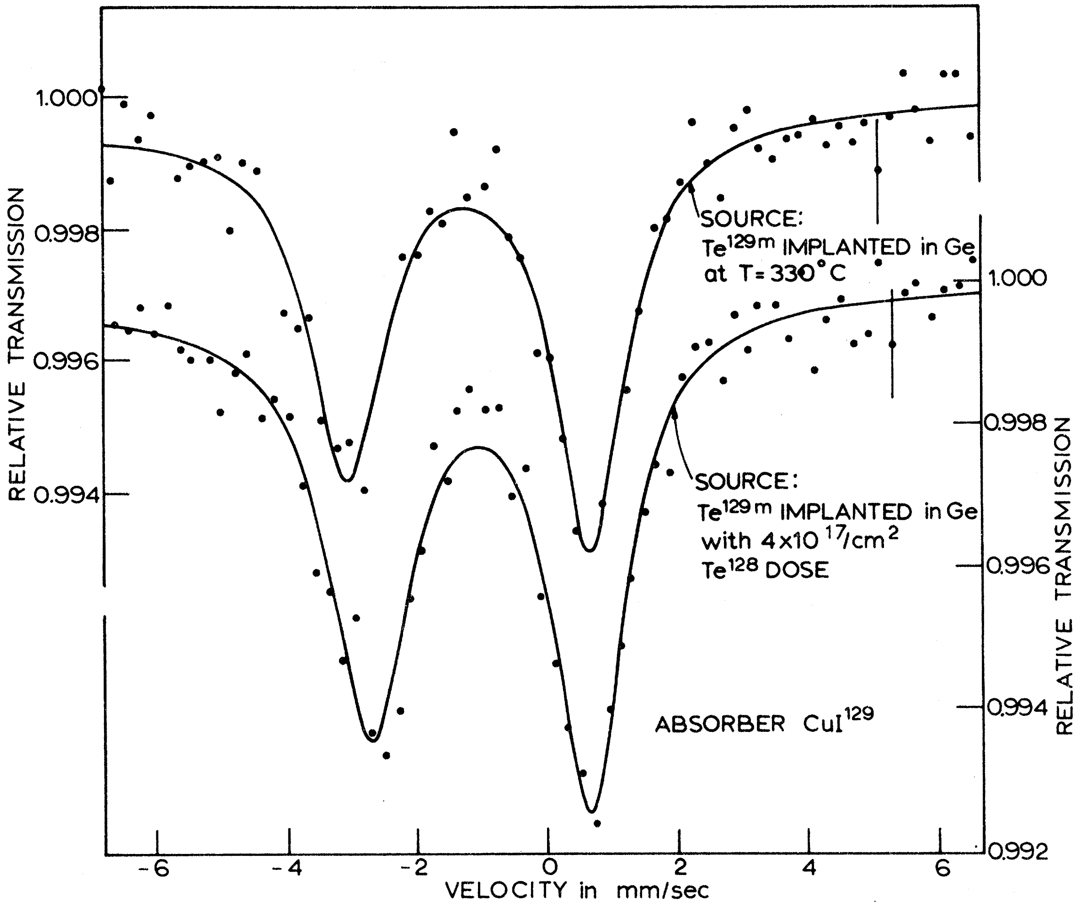

FIG. 2. Mössbauer spectra of the 27.7-keV γ ray of I^{129} with hot and high dose implants of Te^{129m} in germanium at 78 °K.

Hanna[5] indicated, however, that at least two different sites without a substantial quadrupole interaction were present.

For a $\frac{5}{2}$ to $\frac{7}{2}$ transition as in I^{129}, this ambiguity of interpretation is removed by the asymmetry of the quadrupole spectrum. For an I^{129} nucleus in a field gradient comparable to that of one $5p$ electron this spectrum would consist of an asymmetric pattern of eight resolved lines.[12] If the spectrum is only partly resolved, two groups of three lines each would be seen with different shapes and (for a powder sample) with an intensity ratio of 43 to 34. In addition a seventh line of relative intensity 6 should be observable to one side. The characteristic features of the quadrupole spectrum might, however, be washed out by radiation damage effects so that the two observed lines could still be interpreted as smeared out triplets of the quadrupole spectrum. In view of the observed separation of the "triplets," the lines should, however, be much broader in this case. Thus, the spectra shown in Figs. 1 and 2 are incompatible with a quadrupole pattern caused by atoms that are all in substantially equivalent sites.

Another possibility would be that, though all Te^{129m} sites are equivalent, two different charge states of iodine are formed after β decay, giving rise to two single-line components with quite different isomer shifts. This interpretation can be ruled out because different charge states can only be formed in β^- decay by autoionization, the probability for which process is quite small. As a result of β^- emission, the charge of an ion is initially increased by one unit, upsetting the charge equilibrium around the emitting atom. Electrons will be attracted from neighboring atoms, or, if available, from the conduction band. For all ions in equivalent sites, the rate and extent of this attraction of charge will be the same and the only effect on the spectrum could be a distortion if the time scale of the charge attraction happens to be of the order of the lifetime of the nuclear state. Even in this case one would not observe two discrete lines.

Thus, we must conclude that the tellurium atoms have landed in at least two nonequivalent sites, the

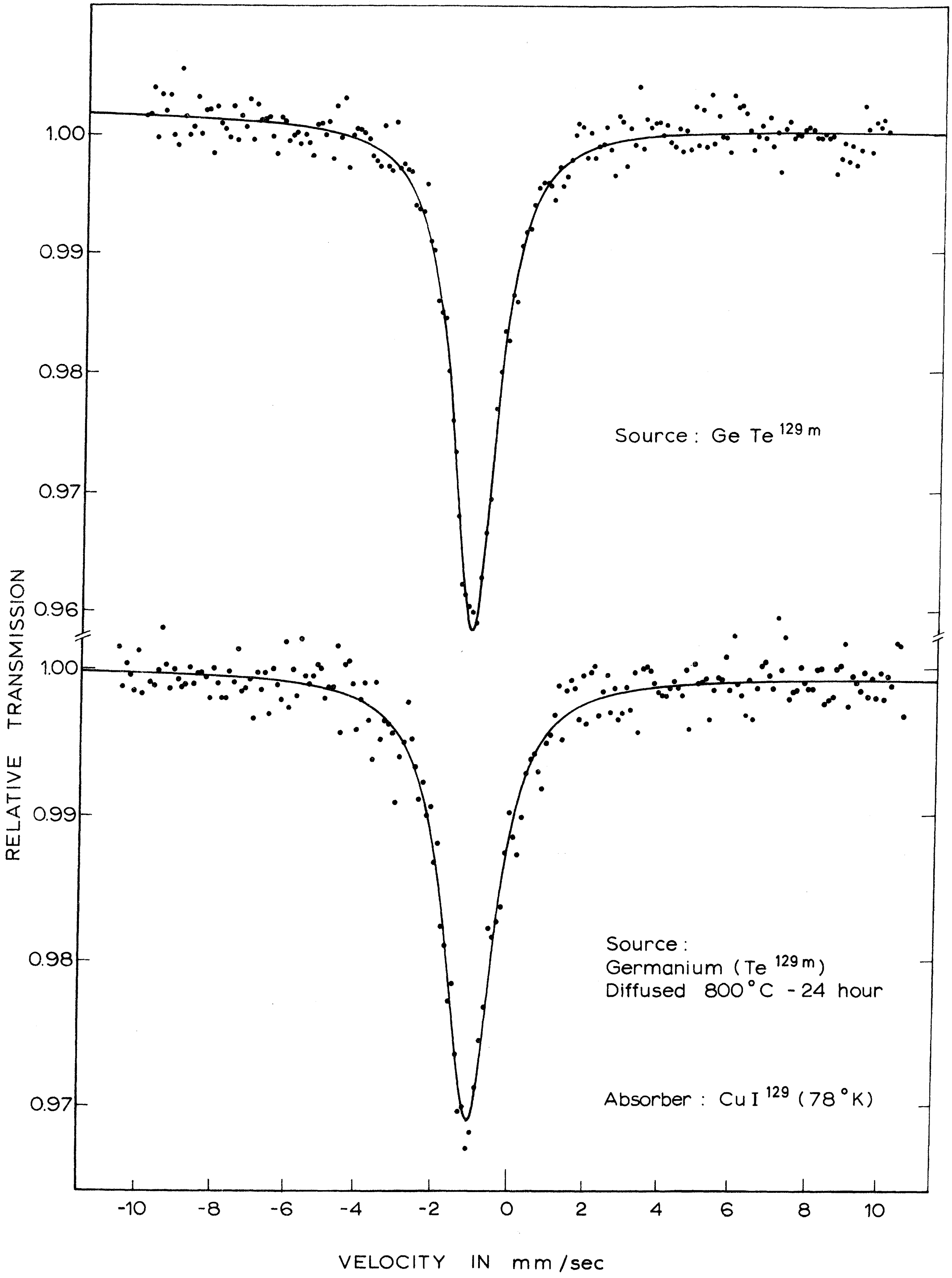

FIG. 3. I^{129} Mössbauer spectra obtained with the compound $GeTe^{129m}$ and with a source of Te^{129m} diffused into Ge.

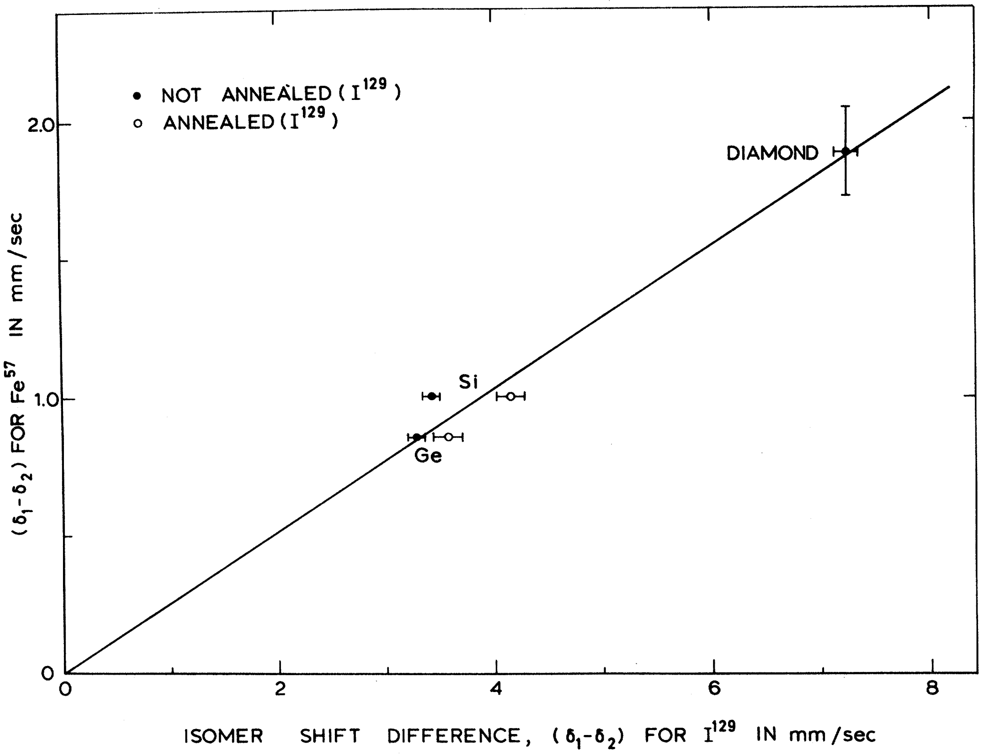

FIG. 4. Separation between the two lines found for implanted Fe^{57} in Si^5, Ge^5, and diamond[6] vs the separation found for the two lines in I^{129} implanted sources in the same lattices.

precise nature of which must as yet be established.

In addition to arguments derived from the Mössbauer spectra, we may consider the channeling and Hall-effect measurements carried out by Gyulai *et al.*[10] and by Picraux *et al.*[13] on samples of Si in which Te was implanted. The channeling results indicate that 50–60% of the Te atoms are in substitutional sites while the remaining 40–50% are in different sites. This result immediately suggests that one of the lines observed in our Mössbauer spectra is due to substitutional Te atoms, the other to interstitial atoms. The Si samples used in the measurements of Gyulai *et al.*, for instance, were subjected to Te doses up to 10^{15} ions/cm^2 using both room temperature and 350 °C implants and they were investigated after annealing at a number of different temperatures. Considerable changes of the channeling results were found as a function of implantation and annealing condition. The dependence of the Hall effect on annealing and implantation temperature, however, is only small. As we have seen in Sec. III, the Mössbauer spectra are almost independent of implantation dose in the range 10^{14}–10^{17} ions/cm^2 and they do not change very much when the sources are annealed or if the implantation temperature is increased to 330 °C.

b. Comparison with other Mössbauer data. Our isomer shift results for I^{129} implanted in semiconductors are compared in Fig. 4 with similar data obtained with Fe^{57} Van de Graaff implantations[5] and with Co^{57} isotope separator implantations.[6] The isomer-shift difference $\Delta\delta = \delta_1 - \delta_2$ has been plotted here rather than the positions of the individual lines. The straight line drawn in Fig. 4 through the origin indicates that the electronic interaction strengths in both sites are more or less proportional for the two implanted isotopes, even though the electron configurations are quite different: for iron, the $3d$ and $4s$ shells are involved, for iodine the $5sp$ shell.

The isomer shifts in diamond are very large for both isotopes. For the case of Fe^{57} in diamond, the separation $\Delta\delta = 1.88$ mm/sec is twice that found between Fe^{2+} and Fe^{3+} compounds (0.9 mm/sec[14]). For the case of I in diamond the separation $\Delta\delta = 7.24$ mm/sec is about the same as the widest separation yet measured for two iodine compounds, i.e., $\Delta\delta = 7.56$ mm/sec between IF_5 and IF_7[15] (see Fig. 5).

The approximate slope of the line in Fig. 4 corresponds to a ratio $\Delta\delta^I/\Delta\delta^{Fe} = 3.9$. In terms of the well-known isomer shift formula given by Shirley,[16] this ratio can be written

$$\frac{\Delta\delta^{I}}{\Delta\delta^{Fe}} = \frac{Z^{I}(A^{I})^{4/3}E_{\gamma}^{Fe}}{Z^{Fe}(A^{Fe})^{4/3}E_{\gamma}^{I}}\,\frac{S(I)\rho^{I}}{S(Fe)\rho^{Fe}}\,\frac{\Delta\psi_{I}^{2}}{\Delta\psi_{Fe}^{2}}, \qquad (1)$$

where Z is the nuclear charge, A is the mass number, E_γ is the energy of the resonant γ ray, $S(Z)$ is the relativistic enhancement factor, and

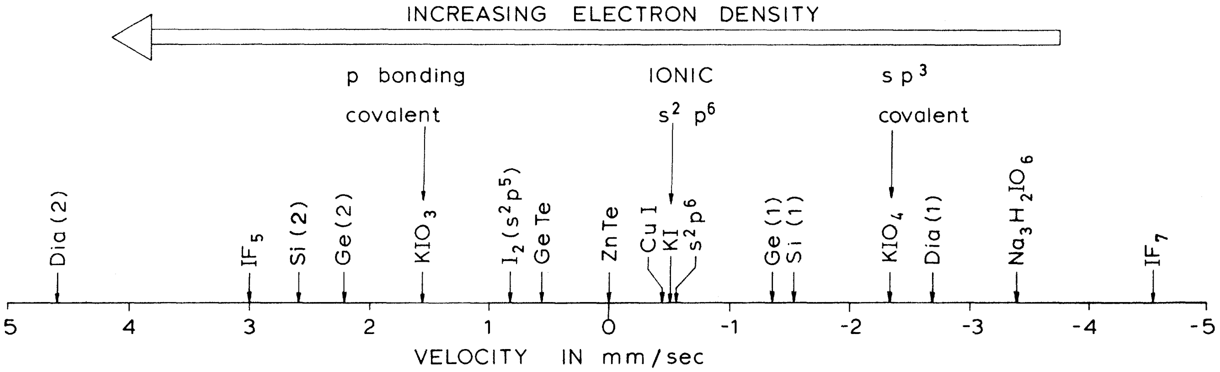

FIG. 5. Isomer shifts of absorbers of I^{129} compounds and of implanted Te^{129m} sources with respect to a $ZnTe^{129m}$ source. Shifts shown for sources implanted in Ge and Si are after annealing.

$\rho = \delta\langle R^2\rangle/\langle R^2\rangle = 2\,(\Delta R/R)$ the fractional difference of the nuclear charge density at the nucleus for the two states. Inserting known values for Z, A, E_γ, and S and $\rho^{I} = 6.4 \times 10^{-4}$ as suggested by Ruby and Shenoy[17] and $\rho^{Fe} = 15 \times 10^{-4}$ obtained from a weighted average of published values for Fe^{57}, we obtain

$$\Delta\psi_I^2 / \Delta\psi_{Fe}^2 \simeq 1.4. \qquad (2)$$

The largest error in this number is due to the uncertainty of ρ^{Fe}, the literature values of which spread by a factor of 2.

c. Interpretation of the I^{129} *isomer shifts.* The 1 : 1 ratio of the intensity of the two components of the Mössbauer spectra is, as we have seen, in satisfactory agreement with channeling measurements[10,13] which have shown that tellurium implants in silicon have two sites with a ratio of about 1 : 1. Unfortunately, this ratio makes it impossible to decide on the basis of channeling results alone which line of the Mössbauer spectrum corresponds to substitutional Te ions and which to interstitial.

Some assistance in assigning the resonance lines to lattice sites is provided by Fig. 5, where I^{129} shifts in various compounds are displayed together with our present data. In order to compare our results with data taken with a $ZnTe^{129}$ source and various absorbers of I^{129} compounds, we must invert the sign of the isomer shifts and then subtract 0.44 ± 0.03 mm/sec, the shift of our CuI absorber with respect to the $ZnTe^{129m}$ source. In this way we have plotted the data of Table I in Fig. 5.

From previous interpretations of the alkali iodide shifts[12] and of the shift for solid iodine,[18] an isomer shift of − 0.54 mm/sec for a "free" I^- ion with closed-shell configuration s^2p^6 relative to a $ZnTe^{129}$ source has been obtained. In addition, a shift of 1.15 mm/sec for removal of one $5p$ electron was obtained from the alkali-halide data, while measurements on isolated iodine molecules in a noble gas matrix[19] yield the probably more accurate value of 1.50 mm/sec. The shift of KIO_3, shown in Fig. 5 at positive velocity, corresponds to an increased electron density with respect to the s^2p^6 configuration. Since the iodine atoms in KIO_3 are almost octahedrally coordinated one expects little sp^3 hybridization and therefore predominantly a transfer of p electrons into covalent I-O bonds. This type of removal of p electrons will allow the s electrons to see a higher effective nuclear charge with the result that the s orbitals contract so that the contract s-electron density is increased. The shift towards higher s-electron density at the nucleus for molecular iodine, where one $5p$ electron is missing from the closed shell, can be understood in the same way. On the other hand, when the iodine atom is tetrahedrally coordinated one expects sp^3 hybridized bonds with the result that the increase in electron density due to removal of $5p$ electrons from the s^2p^6 configuration is overcompensated by direct removal of $5s$ electrons, leading to a reduction of the $5s$-electron density at the nucleus. According to Bukhspan *et al.*,[19] removal of one $5s$ electron entails a change of isomer shift of 9.2 mm/sec in the negative direction. In general, if both s and p electrons are removed, we may write

$$\Delta\delta = -\,9.2\,h_s + 1.5\,h_p \text{ mm/sec}, \qquad (3)$$

where h_s and h_p are the numbers of $5s$ and $5p$ electrons removed from the I^- ion. The effective charge on the iodine ion can be estimated if one knows both the isomer shift and the symmetry of the lattice site, which yields the degree of hybridization. The simple approach outline here and the empirical expression (3) (but with somewhat different coefficients) were first proposed by us in Ref. 12. Though a more thorough theoretical foundation is still lacking, this picture has shown its usefulness in the interpretation of the Mössbauer spectra of many different iodine compounds. It is

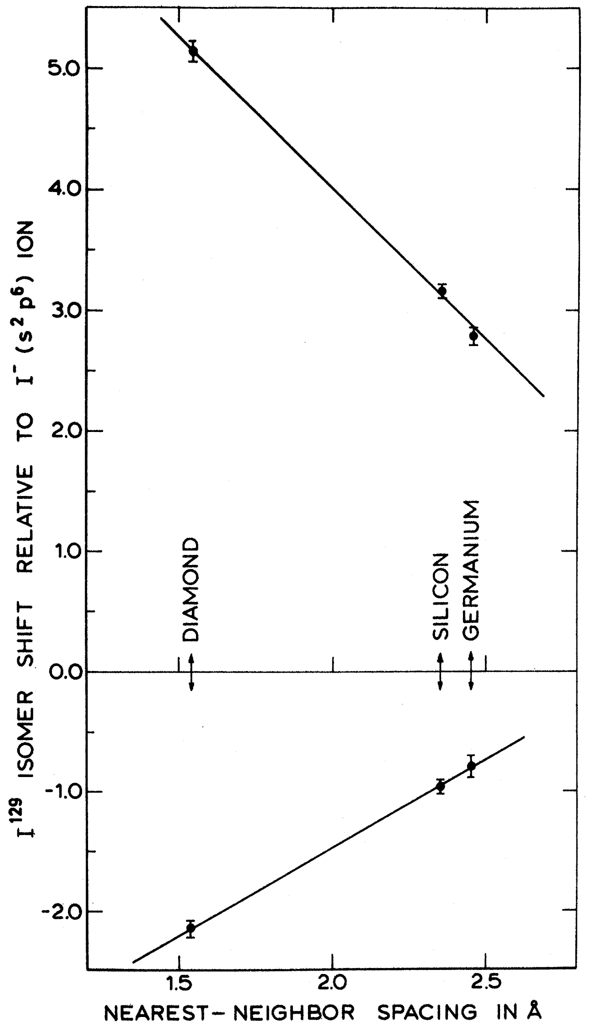

FIG. 6. Isomer shifts for the two lines of annealed Te^{129m} implanted Si, Ge, and diamond sources vs nearest-neighbor spacing in the normal lattice. The straight lines are drawn for visual purposes only. Shifts are given with respect to the shift of a closed-shell I^- configuration (− 0.55 mm/sec with respect to the $ZnTe^{129m}$ source).

well known that *sp* shell substitutional impurities in group-IV semiconductors with tetrahedral coordination exhibit similar sp^3 hybridized bonds as the atoms they replace. For this reason, we tentatively assign the lines denoted in Fig. 5 by Dia (1), Si (1), and Ge (1) at negative velocities (which are the lines at positive velocities in Figs. 1 and 2 and Table I) to the substitutional sites. Taking $h_s = \frac{1}{3} h_p$ for the hybridized bonds of the iodine impurities, we deduce from Eq. (3) that the isomer shift $\Delta\delta$ relative to that for an I^- ion is related to the effective charge $Z_{eff} = h_s + h_p - 1$ on the substitutional iodine ions by $\Delta\delta \simeq -1.2\,(Z_{eff} + 1)$ mm/sec. The measured isomer shift yields, for instance, $Z_{eff} \simeq -0.2$ for iodine implanted in silicon. The estimated value of the effective charge continues the trend of the effective charges of Sb and Te implanted in silicon. These charges can be inferred from Hall-effect measurements. Nelson *et al.*[20] performed such measurements on Sb implanted silicon and found them to be consistent with each substitutional Sb atom donating one electron to the conduction band, so that the effective charge on the antimony is about +1, a well-known result for Sb diffused silicon. The Gyulai *et al.*[10] Hall measurements for Te implanted silicon indicate that only about 5% of the substitutional Te atoms donate electrons to the conduction band, making the Te atoms almost neutral. The negative charge found by us on I implanted silicon forms a logical continuation of this trend, consistent with the increasing electronegativity in the series Sb ($Z_{eff} \sim +1$), Te($Z_{eff} \sim 0$), I($Z_{eff} \sim -0.2$). On the basis of the above interpretation of the site-1 impurities, the site-2 impurities, indicated by Dia (2), Si (2), and Ge (2) in Fig. 5 must correspond to interstitial Te atoms. These lines lie in the region of increased *s* density expected when only *p* electrons are missing from the s^2p^6 shell.

As shown in Fig. 6, the absolute values of the isomer shift increase more or less linearly with decreasing nearest-neighbor spacing, both for the substitutional and the interstitial sites. For the chemically bound substitutional impurities, this change in isomer shift can be viewed as an effect of the change in bond length, which is related to the amount of *s*, *p* charge transferred from the iodine into the bond. The smaller the bond length (as in the case of I in diamond), the larger the interaction and the larger the shift. A quantitative evaluation of this effect is complicated by the fact that the relaxation of the semiconductor lattice around the impurity is unknown. In addition, the interaction between iodine and its neighbors in the Si, Ge, and diamond lattice will be different for the three lattices.

The following remarks can be made about the component of the spectrum that we interpret as due to interstitial impurities. The fact that the observed spectrum consists of a single line with little broadening indicates that the interstitials are in almost equivalent sites with a high degree of symmetry of the surrounding changes. Weiser[21] has pointed out that there are two different interstitial sites with high-charge symmetry: (i) a tetrahedral site with the interstitial ion surrounded by four nearest neighbors at distances of $0.433a_0$ (the same distance as for a substitutional ion) and (ii) a hexagonal site with six nearest neighbors at $0.415a_0$ and eight next-nearest neighbors at $0.649a_0$ (a_0 is the lattice constant). An ion in either of these sites in not expected to experience an appreciable field gradient which agrees with the single-line character of the spectra. Taking into account both the repulsive energy and the polarization energy of the lattice with respect to the impurity, Weiser calculated that the hexagonal site is preferred for small interstitial ions like Li^+ and Cu^+, while larger ions like Ag^+ and Au^+ prefer the tetrahedral site. We will assume, therefore, that the rather large iodine ions occupy the tetrahedral sites so that their nearest-neighbor distances are equal to those for the substitutional iodine ions, if we disregard possible distortions of the lattice. The assumption of locations for the substitutional and interstitial impurities that both have the same space in the lattice is in agreement with the observed small temperature dependence of the intensity ratio of the two components of the Mössbauer spectrum. This indicates that the Debye temperatures and thus the rms vibration amplitudes for both sites are about the same.

The very large difference of the isomer shifts of both components, on the other hand, shows that the electronic configurations must be quite different. A simple qualitative explanation of the isomer shift of the interstitial iodine ions is obtained by assuming that these ions do not disrupt the covalent bonds between the atoms of the host lattice, though they may distort them. This assumption was also made by Weiser[21] in his treatment of the diffusion of interstitial metal atoms. It does not appear unreasonable for the covalent diamond structures considered here, in which the lattice atoms are covalently bonded together in such a way as to have essentially closed shells.

The observed increase of positive isomer shift with decreasing nearest-neighbor spacing can now be interpreted in terms of a compression of the iodine ion by the host lattice. For an I^- ion, with ionic radius $R = 2.2$ Å, the volume excess in a diamond lattice is a factor $(2.2/0.76)^3 = 23$, in a silicon lattice 6.5 and in germanium 5.8. The iodine charge, however, may well be less negative because the implanted Te^{129m} loses an electron on β^- emission. In that case, the volume excess and thus the compression ratio would be smaller since the ionic radius is reduced. For a neutral iodine atom with outer shell configuration s^2p^5, for instance, $R = 1.4$ Å. Then, the absence of p charge from the closed-shell configuration itself would produce a positive isomer shift. From our meaurements, the relative contributions to the isomer shift from compression and from the number of p holes cannot be determined.

On an atomic scale, a compression, leading to an increased s density at the nucleus, must be seen as an overlap distortion of the iodine wave functions. A quantitative calculation of the effect is complicated again by the unknown distortion of the semiconductor lattice by the impurity.

In Sec. III it was observed that the absolute values of the isomer shift of both the substitutional and the interstitial components are increased after annealing of the silicon and germanium sources. This behavior can also be interpreted in terms of compression or of an increased overlap distortion of the wave functions. Upon implantation, host lattice atoms close to the impurity may be displaced because damage sites are formed, e.g., vacancies. By annealing, the lattice reorders, leading to a reduction of the average atom spacing around the impurity and thus to an increased compression.

Finally, we would like to point out that an increase of I^{129} isomer shift with decreasing lattice spacing of the same order of magnitude as observed in the semiconductors has been found by one of us[22] for Te^{129m} sources implanted in a number of metals.

V. IMPLANTATION INTO THE ALKALI HALIDES

A considerable amount of experimental work has been carried out on the mixed alkali-halide systems by such diverse techniques as electric quadrupole resonance,[23,24] NMR chemical shift,[25] and various optical methods. These experiments are appealing because of the possibility of comparing the experimental results with workable theoretical calculations. An impurity of potassium, for example, acts only as a gentle perturbation in a NaCl crystal and one hopes to obtain from these experiments information about this perturbation as well as the interactions of the perfect crystal.

There have been a few Mössbauer studies of Fe^{57} in such alkali halides as NaCl,[8] but because the iron atom is not an alkali or halide ion it creates more than a gentle perturbation in the crystal. Various charge states of iron can be formed in the decay of Co^{57} as well as a vacancy associated state with the Fe^{++} ions. By using a halide such as iodine we hoped to be able to obtain the substitutional state only by implantation and subsequent annealing. So far, our results are not quite consistent, the annealing temperatures and Te^{129m} dose strongly influence the character of the spectra. Single-line spectra as well as spectra with two or more only partly resolved lines were observed. Recently, Seregin and Savin[26] have observed quite complex spectra of I^{129} in the alkali halides. Their samples were prepared by diffusing $H_2(TeCl_6)$ directly into the alkali halides in contrast to our implantation with annealing approach. They interpreted their spectra in terms of two sites, each with a considerable quadrupole splitting. The very marked differences between their complex spectra and our single spectra must be due to the different methods of source preparation.

For our experiments we have chosen to implant Te^{129m} into single crystals of LiF, KCl, KI, and NaCl. The range of mismatch of size for these

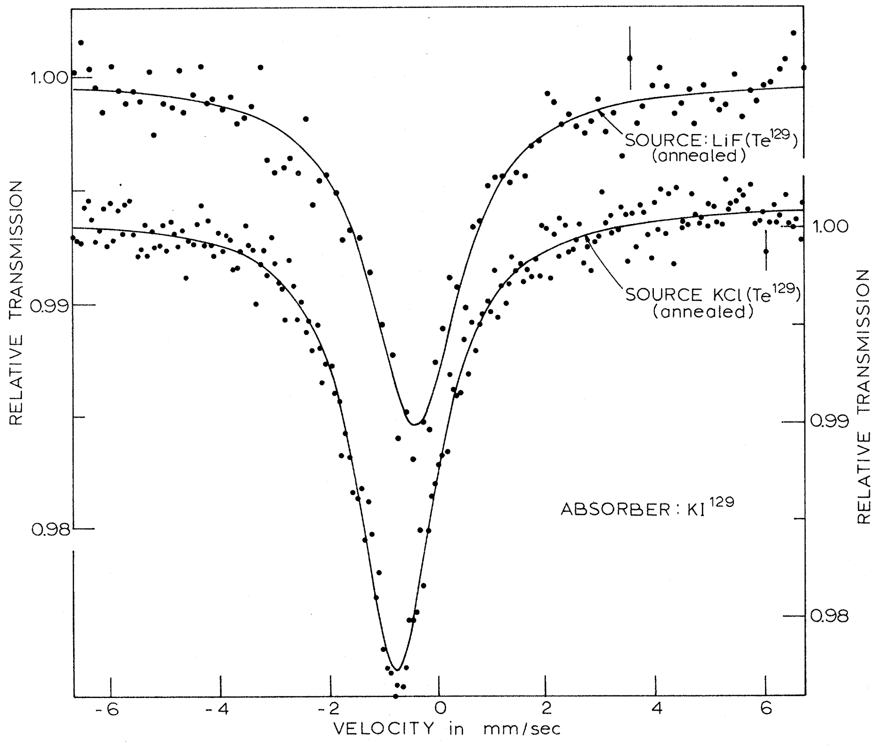

FIG. 7. Spectra obtained with annealed sources (1 h, 500 °C) of Te^{129m} implanted in LiF- and KCl-vs-KI^{129} absorber ($T = 78$ °K).

crystals is very considerable. For the case of I^{129} in LiF the fluorine ion is replaced by an iodine ion which is $(2.2/1.22)^3 = 4.53$ times larger in size, for KCl the ratio is $(2.21/1.81)^3 = 1.80$, while for KI it is, of course, unity.

The alkali halides are much more sensitive to radiation damage than metals or semiconductors and as one might expect the spectra obtained without annealing display several only partly resolved components. However, when the samples were annealed at temperatures of 450–525 °C for 1 h, the spectra usually became considerably sharper and results like those displayed in Fig. 7 were obtained. These spectra are only slightly broader than those of the Ge and Si crystals and most of this broadening can be attributed to the thicker KI absorber used. If one anneals the crystals at temperatures higher than about 600 °C the effective source strength is reduced considerably by evaporation. For the single-line spectra shifts of -0.78 ± 0.03 mm/sec for KCl and of -0.43 ± 0.04 mm/sec for LiF with respect to the KI absorber were obtained. These values are 3–5 times larger than the maximum difference of shifts obtained in our previous work on the alkali iodides: $\delta_{\mathrm{CsI}} - \delta_{\mathrm{KI}} = +0.14 \pm 0.04$ mm/sec. Taking into account the sign reversal of the isomer shift needed because we measure the shift of the source relative to the absorber we see that both the CsI and the implanted halides are shifted in the direction of an increased electron density as compared to the "free" ion (s^2p^6) configuration.

In order to gain some understanding of the magnitudes of these single-line isomer shifts we have tried to apply the formalism of previous work[27] in which the observed alkali iodide isomer shifts were correlated with the overlap of an iodine 5s electron with its neighbors.

$$\Lambda_s = 2\langle I^- 5s \mid s\rangle^2 + 2\langle I^- 5s \mid p\sigma\rangle^2 \tag{4}$$

and then summed over the first and second neighbors in the NaCl lattices to give

$$\Lambda_s^T = 6\Lambda_s^{\mathrm{nn}} + 12\Lambda_s^{\mathrm{nnn}}\,. \tag{5}$$

It was shown in the paper referred to that for these lattices the change of isomer shift relative to the free ion should be proportional to Λ_s^T. In Table IV the results of these calculations are given for a number of lattice constants, corresponding to different expansions of the LiF lattice around the I^{129} impurity. By comparing the total overlaps Λ_s^T given in the last column of Table IV with those pre-

TABLE IV. Outer-shell overlap integrals for iodine in LiF as a function of lattice spacing. Li-I overlaps from Ref. 27.

r_{nnn}	$\Delta r/r$	$\langle 5s^{\mathrm{I}} \mid 2s^{\mathrm{F}}\rangle$	$\langle 5s^{\mathrm{I}} \mid 2p_0^{\mathrm{F}}\rangle$	$12\Lambda_s^{\mathrm{nnn}}$	$6\Lambda_s^{\mathrm{nn}}$	Λ_s^T
2.848	0%	−0.03992	0.09979	0.277	0.065	0.343
3.148	11%	−0.02399	0.07103	0.135	0.029	0.164
3.448	21%	−0.01434	0.04998	0.065	0.013	0.078
3.748	32%	−0.00856	0.03492	0.031	0.006	0.037

viously calculated[27] for I^{129} in LiF and CsI and the isomer shifts relative to the free-ion shift we may estimate the amount of expansion near the I^{129} impurity in LiF, using the proportionality of Λ and δ. In this way we obtain an expansion of about 10% in the LiF lattice constant, consistent with the values obtained from the analysis[23] of the electric quadrupole data of mixed crystals. It is immediately apparent that the larger shift of KCl: I is not compatible with this simple model. Further measurements and calculations should be performed on the mixed alkali-halide systems. The values of the Mössbauer shifts reported here are considerably more accurate than those obtained by the chemical shift technique where the error is approximately one-half of the measured value.

VI. CONCLUSION

Sources of I^{129} in semiconductors and alkali halides have been prepared by implanting Te^{129m} with an isotope separator. In comparison to the accelerator implantation method this technique is less expensive and has lower background counting rates. In addition the separator technique is also more flexible because the samples can be annealed after implantation. For the alkali-halide targets annealing is crucial, while for the semiconductors it produces only minor changes. Mössbauer spectra obtained with I^{129} implanted Ge, Si, and diamond single crystals all displayed two clearly separated lines. The positions and intensities of these resonances were found to be only slightly dependent on the type of dopant (n and p), the dose rate (10^{14} - 10^{17} ions/cm^2), annealing temperature (up to 850 °C), and implantation temperature [(20–330) ° C]. The intensity ratio of the two peaks changes only very little when the sources are measured at temperatures from 4 to 300 °K. The separation between the resonances increases in the sequence from Ge to Si to diamond which indicates that the iodine ions which are most compressed experience the largest interaction. Data[5,6] obtained from Fe^{57} and Co^{57} implanted sources in semiconductors show the same trend. The separation of the Fe^{57} lines is seen to be roughly proportional to that of the I^{129} lines, the change in s-electron density at the Fe and I nuclei being of the same order of magnitude.

The spectra are interpreted in terms of two separate sites, each with only very small quadrupole interaction. This conclusion is based on two pieces of evidence, that of the Mössbauer spectra itself and on the results of the channeling experiments, of Gyulai *et al.*[10] and of Picraux *et al.*[13] that indicate that 50 – 60% of the implanted tellurium atoms reside in substitutional sites. This is in agreement with the one-to-one intensity ratio of the two lines observed in the Mössbauer spectra.

By noting the systematics of the published I^{129} isomer shifts we have been able to assign the line corresponding to increased s density with respect to the I^- ion to the interstitial site and the line with decreased s density to the substitutional site. The latter assignment is consistent with sp^3 hybridized covalent bonds between the iodine and the surrounding atoms.

Spectra obtained from sources of I^{129} implanted into KCl and LiF sometimes display a slightly broadened single-line spectrum after annealing. There is a strong dependence of the spectra on annealing temperature and Te^{129m} dose, which did not always make it possible to obtain single-line spectra. The shifts from the LiF and KCl sources were about 3–5 times larger than the previously measured spread of shifts within the alkali iodides. The magnitude of the shift for LiF (I) can be explained by the overlapping ion model if one assumes that the lattice expands about 10% around the iodine impurity.

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