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Chemical bonding in sulfur, selenium, and tellurium from ^{129}I and ^{125}Te Mössbauer investigations

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^{129}I Mössbauer spectra of plastic and orthorhombic Te_xS_{1-x} ($x = 0.01$), trigonal, monoclinic, and bulk amorphous Te_xSe_{1-x} ($x \leq 0.016$), and trigonal Te have been investigated using ^{129}Te^m labeled sources. From these data, we obtain chemical-bonding information of the I impurity, and show that it is nearly onefold coordinated in all these twofold coordinated hosts. Further, in comparing the measured ^{129}I quadrupole couplings to the known ^{125}Te quadrupole couplings in the chalcogen hosts, a systematic pattern in the ratios of the two couplings emerges. First, a sign reversal of V_{zz} is believed to occur in going from Te to I, and is shown to be a consequence of chemical-bonding rearrangement, viz. the twofold coordination of Te involving π-bonding orbitals with two chalcogens near neighbors, transforms into a nearly onefold coordination of I involving σ-bonding orbitals with a chalcogen neighbor. Second, the ratios R of the ^{125}Te–^{129}I quadrupole couplings are found to be as follows: *t*-Te (-1.12), *t*-Se (-0.65), *m*-Se (-0.55), *a*-Se (-0.52), *r*-S (-0.48), and *p*-S (-0.48). The systematic reduction in the magnitude of R from Te to S is shown to be evidence of an increasingly molecular character of the host chemical bonding. In contrasting the bonding between the Se polymorphs, it is shown that *a*-Se is the most molecular of these solids. The bonding in *a*-Se is shown to be much closer to that in *m*-Se than in *t*-Se.

I. INTRODUCTION

Although there have been numerous efforts to elucidate the structural aspects of amorphous Se (*a*-Se), unique conclusions on the subject have not been unambiguously established. Applications of the Mössbauer effect (ME) to investigate *a*-Se were first pursued in Refs. 1–5, where the ^{125}Te quadrupole interaction (QI) in trigonal (*t*), monoclinic (*m*), and *a*-Se were measured and found to be distinctly different for the various Se polymorphs. In these measurements on polycrystalline samples, only the magnitude of the quadrupole splitting (QS) $\frac{1}{2}[e^2qQ(1+\frac{1}{3}\eta^2)^{1/2}]$ was accessible, and in particular, the asymmetry parameter η and the sign of the electric field gradient (EFG) V_{zz} were not independently available. Understandably, therefore, implications of the ^{125}Te QS data on the nature of the Te chemical bonding in these Se polymorphs remained qualitative.

To complement the ^{125}Te ME measurements on the chalcogens, in the present work we have labeled these hosts by ^{129}Te^m sources and have pursued ^{129}I ME measurements. The conclusions emerging from the present work belong to three domains. The present experiments provide direct chemical-bonding information on the ^{129}I impurity formed as a consequence of nuclear β decay of ^{129}Te^m parent. We show that in each case, I is predominantly onefold coordinated to a chalcogen near neighbor. The present experiments also show, for example, that while I has significant (33%) π-bonding character to its second near neighbor Se in a trigonal chain, this interaction vanishes in *a*-Se and I becomes clearly onefold bonded.[6] Second, the present work dwells on the chemical-bonding rearrangement that ensues when Te impurity is replaced by I in these hosts. In contrasting the ^{129}I QI with the available ^{125}Te QI in these elemental chalcogens, a pattern is strongly suggested. We believe that a sign change of the EFG occurs in all these hosts from a negative V_{zz} at Te to a positive V_{zz} at I. This is an impurity-related property, and it reflects a change in the nature of local bonding at the impurity. These results have a close analogy to the case of Te-thiourea complexes recently investigated by Langouche *et al.*,[7] and we discuss this point appropriately. The positive sign of the iodine V_{zz} in the chalcogen hosts becomes experimentally established from the present work. The negative sign of the tellurium V_{zz} has been experimentally established to date only for the case of *t*-Te from single-crystal measurements.[8,9] As a final conclusion, the present work bears on the nature of the host chemical bonding in the chalcogens. We show that the ratio R of the ^{125}Te to ^{129}I QI provides an experimental parameter that can give a valuable insight in the nature of the host chemical bonding. We propose that the deviation of the measured R value from its critical value of $R_c = -0.48 \pm 0.02$ provides a measure of the nonmolecular character of the host. A systematic reduction in the magnitude of the R value from 1.12 for *t*-Te to 0.48 for the case of *r*-S or *p*-S is taken evidence of an increasingly molecular character in the host bonding in the following sequence: *t*-Te, *t*-Se, *m*-Se, *a*-Se, *r*-S, and *p*-S.

Section II describes the experimental procedure, data handling, and results. In Sec. III, we analyze the ^{129}I quadrupole couplings in terms of Townes and Dailey theory. The chemical-bonding implications of the data are then presented as follows. Section III A focuses on the role of the impurity (Te and I) valence in relation to the QI, and, in particular dwells on the chemical-bonding rearrangement that ensues in going from a Te probe to an I probe. The role of the host chemical bonding to the observed QI in the Se polymorphs (Sec. III B), the elemental chalcogens generally (Sec. III C), and amorphous Se (Sec. III D) in particular, are discussed appropriately. In Sec. III D, we compare the present results on the atomic structure in a-Se to those currently available from x-ray,[10] infrared, and Raman measurements.[11-13] In Sec. III E we discuss results on plastic and orthorhombic S. A summary of conclusions is presented in Sec. IV.

II. EXPERIMENTAL PROCEDURE, DATA HANDLING, AND RESULTS

In a typical experiment, a 10-mg quantity of ^{128}Te in the elemental form was irradiated to a 3×10^{13} neutron flux for a 40-day period to produce about 1-mCi quantity of ^{129}Te^{m} activity. The neutron irradiations were performed at the Nuclear Science and Technology facility at SUNY in Buffalo, New York. The activity was alloyed with 99.9999%-pure Se obtained from Spex Industries, Metuchen, N.J. by heating the elements to 350 °C for 17 h in an evacuated (7×10^{-8} Torr) quartz ampoule.

Bulk a-Se doped with 1.6-at.% ^{129}Te^{m} was then obtained by quenching alloy melts from 350 °C into cold water. The a-Se samples so obtained were crystallized by vacuum annealing at 90 °C for 48 h to produce t-Se.

α-monoclinic Se crystals doped with 0.8-at.% ^{129}Te^{m} were obtained[2] by slow evaporation from a CS$_2$ solution as follows. The a-Se samples doped with ^{129}Te^{m} activity were first produced as outlined above. The a-Se samples were powdered and dissolved in a 800-ml volume of CS$_2$ heated to 70 °C and refluxed using a Soxhlet apparatus. Deep-red m-Se crystals measuring 1–2 mm in length were obtained by slow evaporation (8-ml/h) of the Se-saturated CS$_2$ solution at room temperature.

S samples doped with 1.0-at.% ^{129}Te^{m} were prepared by heating the elements to 500 °C and equilibrating the melt at 350 °C for a 12-h period. Quenching of such melts in cold water yielded samples of noncrystalline S which were purple in color. These samples will hence be labeled as "plastic S" (p-S). The p-S samples were characterized by a differential scanning calorimeter (DSC-Perkin Elmer Model 1B), and exhibited a glass-transition temperature T_g, a crystallization temperature T_x, and a melting temperature T_m of 76 ± 1 °C, 94 ± 1 °C, and 105 ± 1 °C, respectively. A 2-h anneal of the p-S samples at 90 °C crystallized the orthorhombic phase of S (r-S). Prolonged (2–3 days) annealing of the p-S samples at 90 °C slowly precipitated t-Te.

Monoclinic, trigonal, and amorphous Se samples were subjected to x-ray examination and confirmed the anticipated phases. A DSC-scan of the a-Se samples exhibited a glass-transition temperature T_g of 33 ± 1 °C.

A conventional constant-acceleration Mössbauer drive was used to record spectra of the various ^{129}Te^{m} sources using a ^{129}INa absorber (12 mg/cm^2 of ^{129}I). All measurements were performed with the source and absorber cooled to liquid-helium

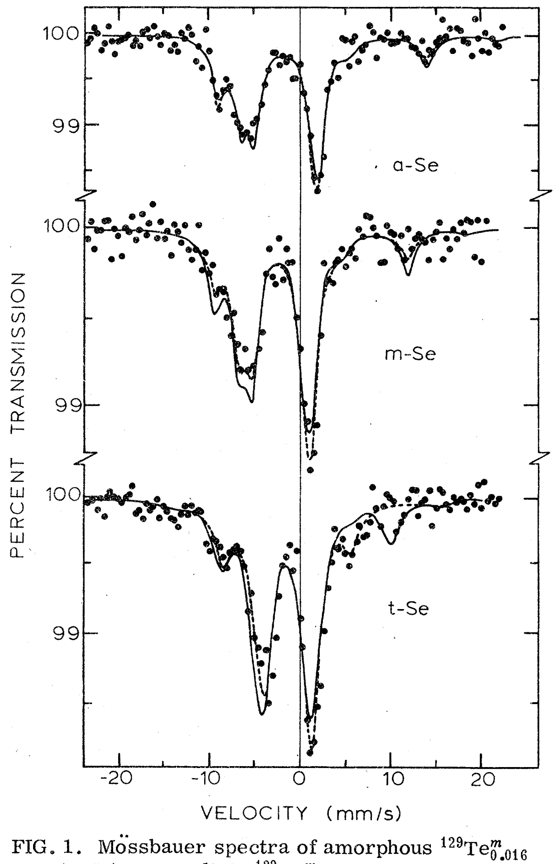

FIG. 1. Mössbauer spectra of amorphous ^{129}Te$^{m}_{0.016}$ Se$_{0.984}$ (a-Se), monoclinic ^{129}Te$^{m}_{0.008}$ Se$_{0.992}$ (m-Se), and trigonal ^{129}Te$^{m}_{0.016}$ Se$_{0.984}$ (t-Se) sources recorded at 4.2 °K. The continuous-line fit represents an analysis of these spectra to a pure ^{129}I quadrupole interaction with constrained line intensities and positions. The broken line fits are obtained when constraints on line intensities are lifted.

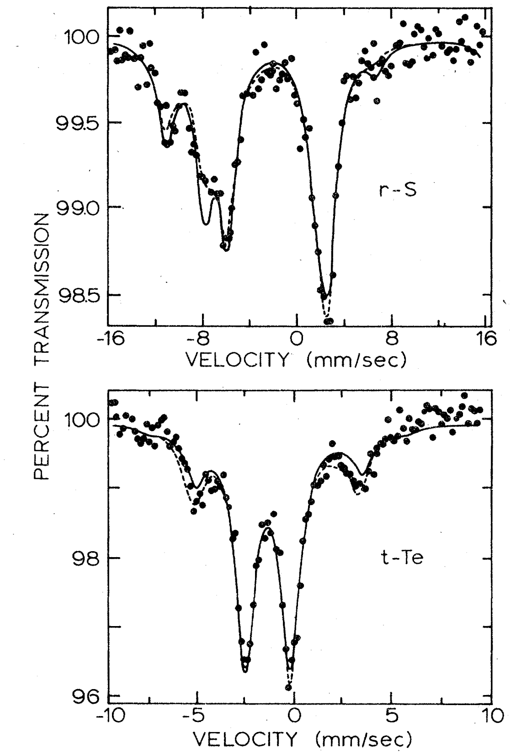

FIG. 2. Mössbauer spectra of orthorhombic $^{129}\mathrm{Te}^{m}_{0.01}\mathrm{S}_{0.99}$ (r-S) and trigonal $^{129}\mathrm{Te}^{m}$ (t-Te) sources recorded at 4.2 °K. The continuous-line fit represents an analysis of these spectra to a pure ^{129}I quadrupole interaction with the line intensities and positions constrained. See Sec. II of text for details. The broken line fit is obtained when constraints on line intensities are lifted.

temperature in a Janis exchange gas Dewar.

Figures 1–3 summarize some of the Mössbauer spectra of $^{129}\mathrm{Te}^{m}$ sources obtained in the present work. The spectra were computer fit by the least-squares method to 12 resonance lines ($I^* = \frac{5}{2}^+ \rightarrow I = \frac{7}{2}^+$, 27.8-keV transition in ^{129}I with a multipolarity $M1 + 0.3\%\ E2$) using the following expression:

$$R(m^*, m) = e^2qQ[(Q^*/Q)p(I^*, m^*) - p(I, m)] + \delta , \qquad (1)$$

where e^2qQ denotes the QI of ^{129}I, Q^*/Q the excited- to ground-state quadrupole moment ratio, and δ the isomer shift (IS). In our fitting routine Q^*/Q was kept fixed at a value of 1.238.[14] As a first step in the analysis of the ^{129}I spectra, we constrained line intensities and line positions $R(m^*/m)$ of the 12 resonance lines, using a polynomial in η from the work of Shenoy and Dunlap,[15] to extract best fit values for e^2qQ, η, and δ. The results are shown as continuous line fits in Figs. 1–3. A noticeable deviation in line intensities between observed and the so obtained theoretical fits is observed. As a second step in the analysis, we then relaxed constraints on line intensities. This procedure yielded significantly better fits to the data which are shown as broken line fits in Figs. 1–3.

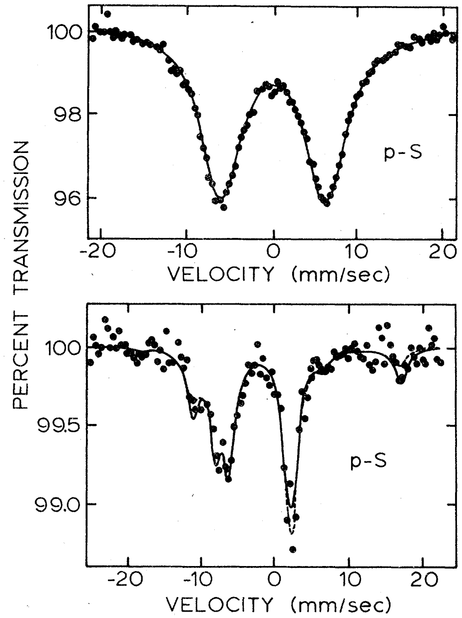

FIG. 3. Mössbauer spectra of plastic $^{125}\mathrm{Te}_{0.01}\mathrm{S}_{0.99}$ absorber (top) and plastic $^{129}\mathrm{Te}^{m}_{0.01}\mathrm{S}_{0.99}$ source (bottom) both recorded at 4.2 °K. The ^{125}Te spectrum (top) was obtained using an ^{125}Sb in Cu source. The ^{129}I spectrum (bottom) shows a fit to a pure ^{129}I quadrupole interaction with constraints on line intensities and positions. See Sec. II of text for details.

Tables I and II give a summary of ^{129}I IS and QI parameters extracted from the spectra of the various hosts. From the asymmetry of the spectra, the sign of the QI (e^2qQ) in each of the chalcogen host is established to be negative. IS of various sources quoted in Table I are relative to ZnTe, and were obtained by subtracting 0.46 mm/sec from the actually measured values relative to the ^{129}INa absorber.

TABLE I. ^{129}I Mössbauer parameters in the chalcogens obtained from data of Figs. 1–3. e^2qQ—quadrupole coupling, η—asymmetry parameter, δ—isomer shift, Γ_{obs}—observed linewidth.

Host	e^2qQ (MHz)	η	δ [a] (mm/sec)	Γ_{obs} (mm/sec)
p-S	−1460 ± 13	0.05 ± 0.05	0.90 ± 0.06	1.86 ± 0.15
r-S	−1426 ± 10	0.14 ± 0.03	0.80 ± 0.04	1.71 ± 0.09
a-Se	−1230 ± 10	< 0.02	0.70 ± 0.04	1.70 ± 0.09
m-Se	−1183 ± 10	0.18 ± 0.03	0.76 ± 0.04	1.88 ± 0.14
t-Se	−925 ± 10	0.50 ± 0.02	1.07 ± 0.04	2.01 ± 0.08
t-Te	−396 ± 3	0.69 ± 0.02	0.80 ± 0.03	1.20 ± 0.03

[a] Converted relative to Zn$^{129}\mathrm{Te}^{m}$ source.

TABLE II. ^{129}I chemical-bonding parameters derived from a Townes-Dailey analysis of quadrupole-coupling data of Table I. U_p—imbalance of $5p$ atomic orbitals, h_p—number of $5p$ holes in I$^-$ configuration $(5s^2p^6)$, $U_{x,y,z}$—electron populations of p_x, p_y, and p_z atomic orbitals, respectively.

Host	U_p	h_p	U_x	U_y	U_z	Iodine configuration	Character of I chemical bond		
							π	σ(ionic)	σ(covalent)
p-S	0.91	0.96	1.99	1.96	1.07	$5s^2p^{5.04}$	0.05	0.07	0.88
r-S	0.89	0.89	2.00	1.92	1.11	$5s^2p^{5.11}$	0.08	0.11	0.81
a-Se	0.76	0.83	1.98	1.97	1.22	$5s^2p^{5.17}$	0.05	0.22	0.73
m-Se	0.74	0.87	1.99	1.92	1.22	$5s^2p^{5.13}$	0.09	0.22	0.69
t-Se	0.58	1.07	1.93	1.74	1.26	$5s^2p^{4.93}$	0.33	0.26	0.41
t-Te	0.25	0.89	1.84	1.73	1.54	$5s^2p^{5.11}$	0.43	0.54	0.03

We believe that the noticeable deviation in line intensities between the observed spectra and the continuous line fit to the data of m-Se, t-Se, and r-S is the result of both texture and Goldanskii-Karyagin effects. It is generally difficult to separate texture from Goldanskii-Karyagin effects in Mössbauer spectra of polycrystalline samples, since both of these effects modify line intensities (from the completely isotropic case as treated in Ref. 15), and can thus either reinforce or cancel one another. We note, however, that the overall agreement between observed and theoretically fitted line intensities (continuous line fit) in the spectrum of a-Se and p-S is noticeably better than the case of their crystalline counterparts. We feel this is most likely due to the lack of texture effects in these noncrystalline hosts.

In the spectra of these two noncrystalline hosts, a striking misfit in the intensity of the prominent line nearest to zero velocity becomes obvious. We note that this misfit is actually present in all the ^{129}I spectra recorded and suggest that it most probably has an origin in a Goldanskii-Karyagin effect. The ^{129}I QI in the chalcogens arise principally due to a onefold-coordinated I$-X_{(1)}$ ($X_{(1)}$ = S, Se, Te) σ bond. The f factor along the I$-X_{(1)}$ molecular axis is expected to be larger than the f factor normal to this axis, leading thus to an angular anisotropy of the f factor about the I$-X_{(1)}$ molecular axis. This anisotropy will, in particular, lead to an enhancement of the $\Delta m = \pm 1$ transitions. The prominent line near zero velocity in the spectra of a-Se, m-Se, r-S, and p-S is the composite[9] of an intense $\Delta m = \pm 1$ transition $(\pm\frac{5}{2} \to \pm\frac{7}{2})$ and a weak $\Delta m = 0$ transition $(\pm\frac{3}{2} \to \pm\frac{3}{2})$. The misfit of this prominent line, we believe, is thus the result of an enhanced $\Delta m = \pm 1$ transition physically arising due to the anisotropy of the I coordination.

III. DISCUSSION OF RESULTS AND INTERPRETATION

The present ^{129}I results on t-Te are in good agreement with the more recent work due to Langouche *et al.*,[9] although there are minor discrepancies with the earlier measurements due to Warren *et al.*[16] and Pasternak and Bukshpan *et al.*[17]

Prior to the present work, to our knowledge there was only one other measurement[18] of the ^{129}I QI in t-Se. These measurements utilized sources of ^{129}Te^m implanted in t-Se at room temperature, and yielded a QI of -1255 ± 15 MHz at 4.2 °K. This interaction strength is significantly different from the value of -925 ± 10 MHz obtained in the present work. This discrepancy may be reconciled as follows. We note that the former QI agrees nicely with the QI in a-Se (-1230 ± 10 MHz) and, on this basis, suggest that in the implantation measurements the ^{129}Te^m ions most probably come to rest in a locally amorphous region. The implantation-induced crystalline disorder persists at room temperature in Se. This is due to the high glass-forming ability of elemental Se and the high crystallization temperature T_c of 94 °C. On the other hand, one does not observe any discrepancy in ^{129}I QI in t-Te between alloyed sources (-396 ± 3 MHz) and implanted sources (-404 ± 4 MHz). This result is again consistent with our existing knowledge of Te as a poor glass former. In elemental Te, we believe that the implantation-induced disorder spontaneously anneals at room temperature, since the crystallization temperature of amorphous Te is known to be less than 10 °C.[19]

Although the Townes and Dailey formalism[20] is strictly applicable to the case of molecules, it can form a starting point for the analysis of ^{129}I QI and IS in the elemental chalcogens. As we show later in this paper, this formalism applies more directly to S and Se than to the case of Te, and this is related to the nature of bonding in the solid state of these elemental chalcogens.

In this formalism, the observed QI ($e^2q_{\text{obs}}Q$) is directly related to the QI in a neutral I atom ($e^2q_{\text{at}}Q$):

$$e^2q_{\text{obs}}Q = U_p e^2 q_{\text{at}} Q\,, \qquad (2)$$

where U_p represents the imbalance of $5p$ atomic orbitals defined as

$$U_p = -U_z + \tfrac{1}{2}(U_x + U_y)\,, \qquad (3)$$

and $e^2q_{\text{at}}Q = -1608$ MHz. U_x, U_y, and U_z give the population of the p_x, p_y, and p_z orbitals. ^{129}I IS are related to the population of the $5s$ and $5p$ orbitals, and, semiempirically, one has established[14] δ relative to Zn ^{129}Te^m as

$$\delta = -(9\pm 1)h_s + (1.5\pm 0.1)h_p - (0.54\pm 0.02)\ \text{mm/sec}\,, \qquad (4)$$

where h_s and h_p designate the numer of $5s$ and $5p$ holes in the I$^-$ configuration ($5s^2 5p^6$);

$$h_p = 6 - (U_x + U_y + U_z)\,. \qquad (5)$$

From the definition of the asymmetry parameter, we have

$$\eta = \tfrac{3}{2}(U_x - U_y)/U_p\,. \qquad (6)$$

The large positive IS in the chalcogen hosts fall in a range which suggests that there is no significant s-electron participation in the chemical bonding. We have therefore assumed $h_s = 0$. In making such an assumption, in effect, one also implies that the chemical bonding is due to p orbitals alone, and that the observed QI and IS are the result of a delicate repopulation of the various p orbitals. It is then possible from the observed e^2qQ, η, and δ, using Eqs. (2)–(6), to uniquely obtain the populations U_x, U_y, and U_z of the p orbitals. We have summarized the results of this calculation in Table II.

A. Te and I chemical-bonding considerations in the elemental chalcogens

To visualize the somewhat exceptional chemical-bonding implications of the ^{129}I Mössbauer-effect data on Te, Se, and S, we have projected the available QI and IS on a U_p vs $\delta - \delta_0$ plot. $\delta - \delta_0$ represents the IS relative to I$^-$ configuration, and is conveniently obtained following Ref. 14 by using $\delta_0 = -0.54$ mm/sec in Eq. (4). On such a plot, a case of pure σ bonding corresponds to $h_p = U_p$ with $\eta = 0$ and lies on the $\delta - \delta_0 = 1.5\,U_p$ line, while the case of a pure π bonding corresponds to $h_p = -2U_p$ with $\eta = 0$ and lies on the $\delta - \delta_0 = -3.0\,U_p$ line. In Fig. 4, open circles represent data points obtained using ^{129}Te^m sources and filled circles represent data points obtained using ^{129}I absorbers. On this plot, we have purposely not included all data corresponding to ^{129}Te^m source experiments performed to data. These data are available in Fig. 6 of Ref. 14, and it is abundantly clear from a quick inspection of the published literature that nearly all ^{129}Te^m source experiments, like the data on the Te-tetrahalides[21] shown in the plot of Fig. 4, belong in the upper left-hand side of this plot. In sharp contrast to these, the available measurements on t-Te and the present measurements on Se and S taken together all appear as notable exceptions, being located in the upper right-hand side of this plot. These results on the elemental chalcogens are, in fact, closely similar to the

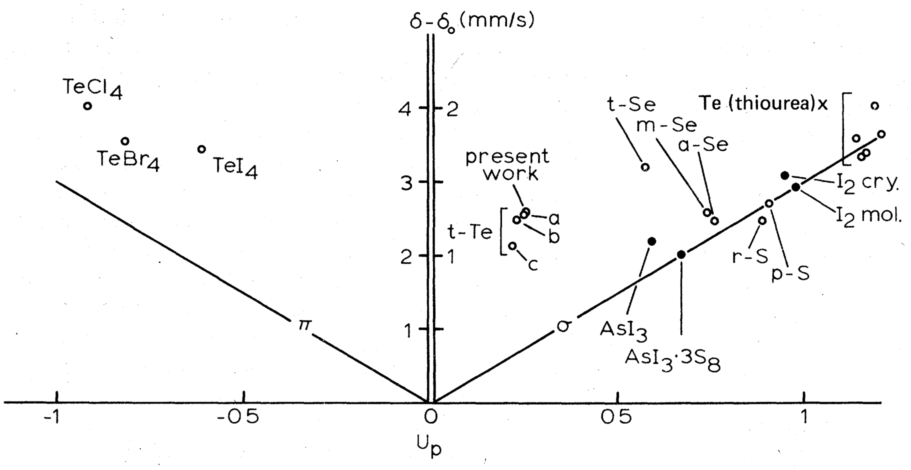

FIG. 4. Plot of U_p vs $\delta - \delta_0$ for the elemental chalcogens. U_p values are taken from Table II, while δ values are taken from Table I. Open circles represent data points obtained using ^{129}Te^m sources, while filled circles were obtained using ^{129}I absorbers. The data on Te-tetrahalides taken from Ref. 21 are representative of typical π bonding observed in source experiments. Data on AsI$_3$, I$_2$ crystals and Te (thiourea)-X complexes are taken from Refs. 23, 22, and 7, respectively. Data on t-Te shown are are taken as follows: a–Ref. 9, b–Ref. 17, and c–Ref. 16.

only other available exception, viz., the one of Te(thiourea)X complexes.[7] In analogy to the case of Te(thiourea)X complexes, we believe that the nature of chemical bonding undergoes a change in character from being predominantly π-like at Te, to becoming predominantly σ-like at I in these chalcogen hosts. We discuss this point in some detail below.

Although the magnitude of the ^{125}Te QI in the elemental chalcogen hosts have been measured, it is only for the case of trigonal Te that the negative sign of V_{zz} has been established from single-crystal measurements of Refs. 8 and 9. The negative sign of V_{zz} in trigonal Te can, in a formal sense, be understood as arising due to a pair of electrons in bonding π-like (p_x and p_y) orbitals with the two Te near neighbors in a chain and a pair of electrons in a p_z orbital normal to the Te-Te-Te plane. Although the sign of V_{zz} at Te impurity in the Se polymorphs and r-S remains to be experimentally established, it seems to us plausible that, in each of these hosts, if Te impurity continues to be twofold bonded, then the sign of V_{zz} will also be negative. In fact, the bonding argument indicated above for the sign of V_{zz} in trigonal Te will be even more applicable for the case of Se and S, since the pair of electrons in the p_z orbital are likely to be more nonbonding.

The electric quadrupole moment (eQ) of the ^{129}I ground state is known to be negative (−0.55 b).[14] The negative sign of ^{129}I QI (e^2qQ) in S, Se, and Te established from the present work, therefore, leads to a positive sign of V_{zz} in each case. Such a result, in our view, can be understood as follows: One of the two Te π bonds transforms into an I σ bond causing V_{zz} to flip by 90°, as shown in Fig. 5. The positive sign of V_{zz} can then be conveniently understood as due to covalent bonding of an iodine p_z hole with its Se or S near neighbor. In these elemental chalcogen hosts, generally speaking, the change in the coordination number from 2, for the case of the isoelectronic Te impurity, to nearly 1, for the case of I impurity, is believed to be responsible for the switching of the chemical-bond character and the sign change of V_{zz}. When Te decays to I in the elemental chalcogens, the bond rearrangement is analogous to that occurring in the Te(thiourea)X hosts. In these complexes, Te is situated at the center of a square planar geometry forming the common center of two mutually perpendicular, three center, two electron bonds. In a formal sense, the negative sign of the Te EFG in this geometry arises due to a pair of 5p electrons in a lone-pair p_z orbital which lies perpendicular to the square planar geometry, and another pair of 5p electrons in π-bonding orbitals in the square planar geometry. When Te is replaced by I, one of the pairs of π-bonding orbitals transforms into a σ-bonding orbital, causing the EFG to flip by 90° and to thus also change sign. In comparing the Te(thiourea)X case to the present case of the elemental chalcogens, the only notable difference is the higher total symmetry in which Te rests in the Te(thiourea)X complexes.

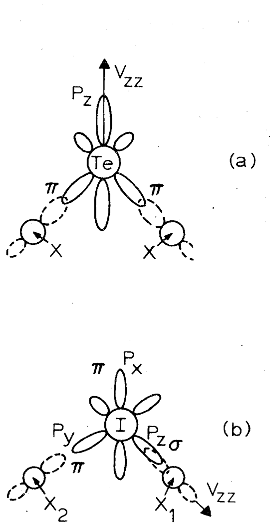

FIG. 5. Schematic diagram of near-neighbor chemical bonding at Te and I impurities in the elemental chalcogens. (a) Te p_z orbitals lie normal to X-Te-X bonding plane (X = S, Se, or Te near neighbors). The Te π bonding to its near neighbors (X) involves p_x and p_y orbitals. (b) The I impurity is shown σ bonded preferentially to one ($X_{(1)}$) of its two near neighbors ($X_{(1)}, X_{(2)}$). Iodine p_z orbital lies along I-$X_{(1)}$ while its bonding to the more distant neighbor ($X_{(2)}$) involving p_x and p_y orbitals reflects π-bonding character. In going from Te to I impurity, a sign change of the EFG results due to a 90° flip of V_{zz} as shown.

B. ^{129}I chemical bonding in trigonal, monoclinic, and amorphous Se

In contrasting the QI parameters for the Se polymorphs given in Table I, a systematic pattern emerges. In going from trigonal to monoclinic and then to amorphous Se, a monotonic increase in the magnitude of e^2qQ, associated with a monotonic decrease in η values, becomes apparent. As we indicated in Sec. III A, the I impurity is preferentially σ bonded to one of its Se neighbors (Se$_{(1)}$). The chemical bonding with its more distant second Se neighbor (Se$_{(2)}$), involving p_x and p_y orbitals must therefore reflect π-bonding character. In going from t-Se to m-Se, we propose that the I-Se$_1$ σ-bond strength grows at the expense of the I-Se$_{(2)}$ π-bond strength, until a nearly pure I-Se$_{(1)}$ σ bond is achieved in a-Se. The small value of η in a-Se clearly supports the presence of a prominent cylindrically symmetric I-Se$_{(1)}$ interaction. On the U_p vs $\delta - \delta_0$ plot in Fig. 4, one can see the trend emerge in going from t-Se to a-Se; the data points move closer to the $\delta - \delta_0 = 1.5U_p$ line, thus indicating a transformation towards a pure σ-like character in a-Se.

These physical ideas evolve in a more quantitative form from the data summarized in Table II, which gives the population U_x, U_y, and U_z of the various p orbitals. From the populations U_x, U_y, and U_z, one can assign the π and σ character to the I bonds. Attention may be drawn to the significant π character (33%) of the I bond in t-Se. In m-Se, the π character sharply reduces to 9% with a consequent increase in the σ character to 91%. This trend continues to the case of a-Se, where the π character reduces further to 5% with a corresponding increase in the σ character to 95%. These results substantiate the claim that I becomes onefold coordinated in a-Se. For the sake of completeness, we have included in Table II chemical-bonding parameters for t-Te. We would like to point out, however, that these parameters on t-Te cannot be taken seriously, since the Townes-Dailey theory has very limited applicability for this host, and we discuss this point in Sec. III C.

In our experiments on Se, we believe that the ^{129}I daughter, formed as a consequence of nuclear β decay of ^{129}Te^m, has developed the chemical-bonding characteristic of an iodine impurity. To illustrate this point, we draw an analogy between the present data on Se and the results of two other ^{129}I absorber experiments shown in Fig. 4. One is the case of crystalline iodine[22] and molecular I_2, and the other that of AsI_3 (Ref. 23) and $AsI_3 \cdot 3S_8$. The change in I chemical bonding from molecular I_2 to crystalline iodine, and likewise, between $AsI_3 \cdot 3S_8$ and AsI_3, is, in fact, the type of change in I chemical bonding undergone from a-Se to m-Se, or a-Se to t-Se. In all these examples outlined, the hosts lying closest to the $\delta - \delta_0 = 1.5\,U_p$ line represent cases where the I bonding is nearly pure σ-like, involving an I-Se$_{(1)}$, I-I$_{(1)}$, or I-As$_{(1)}$ bond. In moving away from the $\delta - \delta_0 = 1.5\,U_p$ line, a familiar pattern emerges; I chemical bonding acquires some π-like character due to the presence of a second more distant neighbor, leading then, generally, to a smaller e^2qQ and a larger δ value.

C. Nature of chemical bonding in S, Se, and Te

The ratio R of the ^{125}Te quadrupole coupling to the ^{129}I quadrupole coupling in a variety of Te(thiourea)X complexes has been reported,[7] and was found to be remarkably constant at $R = -0.48 \pm 0.02$. Two significant features of these complexes which make an interpretation of the quadrupole-coupling data on these systems, somewhat ideally suited for a Townes-Dailey type of analysis may be recalled. The extremely large values of Te and I EFG's in these complexes have: (i) a highly molecular origin which (ii) involves Te bonds that are orthogonal and therefore utilize p orbitals alone. Recognizing that one of the Te π bonds in a Te(thiourea)X complex transforms into an I σ bond, Langouche *et al.*[7] were able to relate the Te EFG to the I EFG as follows:

$$U_p(\mathrm{Te}) = -U_p(\mathrm{I}), \qquad (7)$$

and then proceeded to obtain a new and more reliable value of the ^{125}Te quadrupole moment $eQ = (-0.31\ \mathrm{b})$ from the known ^{129}I ground-state quadrupole moment.

The R value of -0.48 ± 0.02 emerging from the Te(thiourea)X complexes is a significant result for our immediate purpose of understanding the chemical-bonding implications of the QI data on the chalcogens. Having established the ^{125}Te eQ value, one can turn the problem around as follows. One may regard this R value of 0.48(2) as a critical value, R_c, indicating the presence of a strictly molecular origin of EFG's. Bearing in mind that the molecular part of the Te and I EFG's in the chalcogens, in close analogy to the case of Te(thiourea)X complexes, are also related to each other by Eq. (7), we have proceeded to calculate R values for the various chalcogens.

Table III summarizes the available ^{125}Te QI on the chalcogens from previously published data.[1-4] Using our ^{129}I quadrupole couplings from Table I, we have calculated R values for the various chalcogen hosts, and the results appear in Table III. A revealing pattern of R values emerges in going from Te to S. The R value of -0.48 for S coincides with R_c. We take this coincidence to indicate that the EFG in S host has almost entirely a local origin in the imbalance of Te and I p orbitals. This appears to be less true for the Se hosts, where the magnitude of R values are somewhat higher than R_c. In varying degrees, as reflected by the increasing magnitude of R values, the molecular character becomes progressively reduced in t-Se and t-Te. The significantly higher magnitude of R in t-Te is due to the presence of comparable local and nonlocal contributions to the EFG.[4]

In trigonal Te chains an important effect occurs. The "secondary-bonding interactions" which reflect Te interaction with second-near-neighbor sites in adjacent chains become comparable to the "primary-bonding interactions" which reflect interaction with the two near-neighbor Te sites in a chain. We use these "bonding terms" in the way Martin, Lucovsky, and Helliwell[24] have introduced these terms to elucidate intramolecular versus intermolecular forces in these hosts. We should like to suggest that the reduction in ^{125}Te QI in t-Te relative to a-Te,[25] or the reduction in ^{125}Te QI in t-Se relative to a-Se,[3] is a manifesta-

TABLE III. ^{125}Te Mössbauer parameters in indicated chalcogen hosts at 4.2 °K. Δ—^{125}Te quadrupole coupling $[e^2qQ(1+\frac{1}{3}\eta^2)]^{1/2}$, δ—isomer shift, $\Gamma_{\rm obs}$—observed linewidth, R—ratio of ^{125}Te to ^{129}I quadrupole couplings $[\Delta(^{125}\mathrm{Te})/e^2qQ(^{129}\mathrm{I})]$. The value of R was calculated by converting Δ from mm/sec to MHz using 1 mm/sec = 57.24 MHz. The result on Te(thiourea)$_4$Cl$_2$ · 2H$_2$O is included for comparing the R value of this thiourea complex with those obtained on the chalcogens. The R value for this complex is typical of all other thiourea complexes investigated in Ref. 7.

Host	Δ (mm/sec)	δ [a] (mm/sec)	$\Gamma_{\rm obs}$ (mm/sec)	R
Te (thiourea)$_4$Cl$_2$ · 2H$_2$O	15.86 ± 0.07 [b]	0.80 ± 0.06 [b]	5.50 ± 0.20 [b]	−0.48 ± 0.02 [b]
p-S	12.35 ± 0.05	0.38 ± 0.05	5.87 ± 0.06	−0.48 ± 0.02
r-S	11.93 ± 0.06 [c]	0.27 ± 0.07 [c]	6.14 ± 0.09 [c]	−0.48 ± 0.02
a-Se	11.14 ± 0.06 [d]	0.43 ± 0.03 [d]	5.70 ± 0.05 [d]	−0.52 ± 0.02
m-Se	11.33 ± 0.05 [e]	0.33 ± 0.05 [e]	6.15 ± 0.10 [e]	−0.55 ± 0.03
t-Se	10.44 ± 0.05 [c]	0.22 ± 0.07 [c]	6.11 ± 0.08 [c]	−0.65 ± 0.03
t-Te	7.77 ± 0.06 [c]	0.50 ± 0.06 [c]	6.21 ± 0.11 [c]	−1.12 ± 0.04

[a] Relative to Cu(^{125}Sb) source.
[b] Reference 7.
[c] Reference 4.
[d] Reference 3.
[e] Reference 2.

tion of an enhanced secondary-bonding interactions in trigonal chains. The reduction in both ^{125}Te and ^{129}I QI in *t*-Te relative to *t*-Se may be commented upon. In the *t*-Te crystal structure, the four second near neighbors and the two first near neighbors of a given Te site form a slightly distorted octahedron. Application of a 60-kbar pressure to *t*-Te transforms it to a cubic phase in which the ^{125}Te QI has been shown to vanish in the experiments of Berman *et al.*[26] One can visualize *t*-Se, *t*-Te, and the high-pressure phase of Te metal (cubic Te) forming a sequence of solids where in the secondary-bonding interactions become progressively more important until these become indistinguishable from the primary-bonding interactions in cubic Te. In the case of *t*-Te, a significant delocalization of 5*p* electrons occurs, and we believe that the observed EFG is made up of comparable contributions arising from local and nonlocal electrons or band electrons. The large-*R* value for *t*-Te is suggestive of the fact that the nonlocal contribution to the EFG in *t*-Te host has a negative sign.[27] This term would then reinforce the local contribution of the Te EFG (negative) having the same sign, and it will cancel the I EFG (positive) having the opposite sign. One may thus understand the enhancement in the magnitude of *R* above its critical molecular value of 0.48.

In Fig. 6, we have plotted the ratio *R* obtained from Mössbauer measurements against the ratio r_1/r_2. r_1 and r_2 represent the near-neighbor and second-near-neighbor bond lengths in the elemental chalcogen hosts as known from x-ray results.[10,28,29] The correlation of *R* with r_1/r_2 underscores the fact that *R* is a host-dominated property, and, more precisely, its deviation from the critical

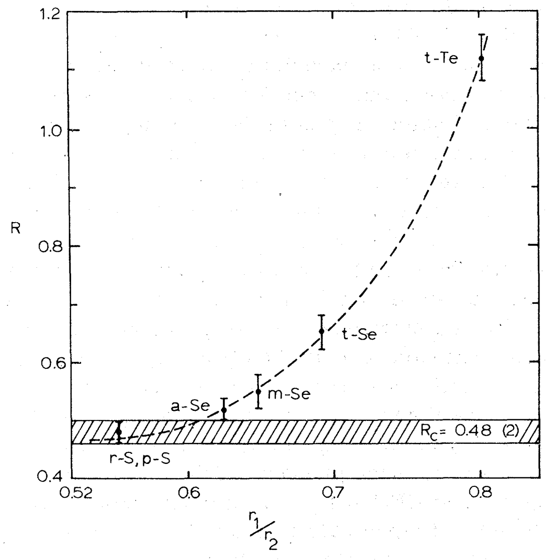

FIG. 6. Ratio of *R* of ^{125}Te to ^{129}I quadrupole coupling plotted against the ratio r_1/r_2 of first-near-neighbor to second-near-neighbor bond lengths in the elemental chalcogen hosts. $R_c = 0.48(2)$ is obtained from Ref. 7 and represents a critical value of *R* when the EFG's have a strictly molecular origin. The r_1 and r_2 values used in this plot are taken from x-ray measurements of Refs. 10, 28, and 29.

value of 0.48(2) is a measure of the nonmolecular character of the host chemical bonding.

D. Atomic structure of amorphous selenium

In this section, we discuss the atomic-structure implications of the present Mössbauer investigations on a-Se, and briefly compare the present results on a-Se with existing ones documented from other types of experiments.

The Mössbauer investigations exhibit the presence of large and rather well defined QI at Te and I impurities in a-Se. From the ^{129}I spectra of Fig. 1 and the earlier reported ^{125}Te spectra of a-Se, it is apparent that one can understand each of these spectra in terms of one predominant site or chemical environment. This is substantiated[4] by the ^{129}I and ^{125}Te linewidths (Γ) observed in a-Se, which compare favorably with those observed in the two crystalline counterparts (see Table I).

We next contrast the ^{129}I and ^{125}Te quadrupole couplings between the Se polymorphs. ^{129}I QI and IS (see Table I) in a-Se of $-1230(10)$ MHz and 0.70(4) mm/sec fall much closer to the values in m-Se of $-1183(10)$ MHz and 0.76(4) mm/sec than to the values in t-Se of $-925(10)$ MHz and 1.07(4) mm/sec. From the ^{125}Te data, one may directly compare the QS in the Se polymorphs, and there again a similar pattern emerges; the ^{125}Te QS in a-Se of 11.14(6) mm/sec falls much closer to the one in m-Se of 11.33(5) mm/sec than to its value in t-Se of 10.44(5) mm/sec. The η values of ^{125}Te EFG remain to be experimentally measured. We feel, however, that since Te is likely to be twofold coordinated in each of these Se hosts, the η values are likely to remain the same. Consequently, we believe that the pattern of ^{125}Te QS indicated above will also be reflected in the e^2qQ values. Thus in contrasting the quadrupole interaction between the Se polymorphs, we can conclude that there is a close similarity in both ^{125}Te and ^{129}I data between a-Se and m-Se, and furthermore, that data on both these Se polymorphs differ significantly from those on t-Se. The values of R in the three Se polymorphs investigated lie reasonably close to R_c, suggesting that the EFG in these hosts have predominantly a molecular origin. The EFG at the $5sp$ impurity atoms (Te, I) is believed to originate primarily in an imbalance (U_p) of the $5p$-like atomic orbitals localized on the impurity, and, furthermore, that contributions to the EFG arising from nonlocalized electrons and more distant lattice ions are less important. The magnitude of the QI thus reflects the primary-bonding and secondary-bonding aspects of the impurity in host molecular units such as Se rings or Se chains.

The R values tabulated in Table III suggest that a-Se is the most covalent or "molecular" of the Se polymorphs. The close similarity of the QI in a-Se to that in m-Se must then also reflect a similarity in the molecular species comprising the two Se hosts. Based on this result and the fact that α-monoclinic Se is known to consist of eightfold Se rings, one therefore concludes that a-Se prepared as a bulk glass must also consist predominantly of Se rings.

There is independent experimental evidence that supports the view that a-Se consists predominantly of Se rings. X-ray radial-distribution-function (RDF) measurements on bulk amorphous Se prepared by quenching the melt from 525 °C were studied by Kaplow *et al.*[10] Kaplow *et al.* found that relatively small static displacements of 0.2 Å were sufficient to convert the α-monoclinic ring structure RDF to that of the a-Se RDF. However, much larger perturbations of 0.7 Å were required to convert the trigonal chain structure to a form that would give a suitable a-Se RDF.

Raman spectra of bulk a-Se reported by Lucovsky *et al.*[11] have shown the close resemblance of vibrational modes in a-Se to those in m-Se. The broad Raman band at a frequency of 250 cm^{-1} in a-Se coincided with several bands present in m-Se. Additionally, the weak Raman bands at 50, 80, and 112 cm^{-1} in a-Se were also observed in m-Se. Raman evidence for the presence of trigonal chains in a-Se is, however, less certain. The frequency mode at 235 cm^{-1}, which appears as a weak shoulder on the 250-cm^{-1} Raman band in a-Se, has been interpreted as an E bending mode (233 cm^{-1}) and an A_1 stretching mode (237 cm^{-1}) of trigonal chains. More recently, Gorman and Solin[12] obtained Raman depolarization spectra of bulk a-Se in the low-frequency region and essentially confirmed the band assignments of Lucovsky *et al.*

The ir spectrum of a-Se is dominated by bands characteristic of Se rings at 95, 120, and 254 cm^{-1}. A weak ir band at 135 cm^{-1} in a-Se is the only one which Lucovsky *et al.*[11] assigned to a bending mode of a trigonal chain. Zirke *et al.*[13] have suggested that this band could conceivably be due to an opened ring rather than a trigonal chain. In conclusion, there appears good evidence that the local order in a-Se consists predominantly of a Se ring specie.

The geometry of Se rings in a-Se has stimulated particular interest, and we address ourselves to this question from the point of view of the present Mössbauer measurements in a separate paper. We have recently examined the compositional variation of the ^{129}I QI in the Te_xSe_{1-x} binary and discuss these results together.

E. Plastic and orthorhombic sulfur

The ^{129}I QI in p-S (-1460 ± 13 MHz) and r-S (-1426 ± 10 MHz) summarized in Table I are the largest of the presently measured QI in the elemental chalcogens. The ^{125}Te QS in p-S resulting from the spectrum of Fig. 4 is 12.35 ± 0.05 mm/sec (see Table III). The ^{125}Te QS in r-S was reported earlier[4] as 11.93 ± 0.06 mm/sec. In contrasting the results on these S polymorphs, we then find that the trend in ^{129}I QI follows closely that of the ^{125}Te QS, viz., the QI in p-S is found to be a few percent larger than in r-S. Furthermore, we also note that the ratio R of the ^{125}Te QS to ^{129}I QI for both p-S and r-S (see Table III) coincides with R_c. This suggests that these S hosts are examples of a highly molecular solid. These R values on S appear as a smooth extrapolation of the R values in Se and Te, and clearly support the correlation of R with the degree of molecular character of the host chemical bonding that we have proposed.

The large values of both the ^{125}Te and ^{129}I QI in the S polymorphs bear a close resemblance to similar data[7,30] on the Te-thiourea complexes. This resemblance is not surprising if it is recognized that in these complexes Te is situated in a square planar arrangement of S atoms. We feel that in both p-S and r-S the ^{125}Te interaction may be attributed to a twofold π-bonded Te site in a C_{2v} symmetry, while the ^{129}I interaction to a onefold-coordinated $\mathrm{I}-\mathrm{S}_{(1)}$ σ bond. The evidence of a nonzero value of η in r-S (Table I) suggests the presence of some π bonding of I to its second neighbor $\mathrm{S}_{(2)}$ in a ring geometry. In p-S, on the other hand, local rearrangement of atomic coordination becomes feasible, and we note that the I impurity tends more toward onefold bonding. This is suggested by the small increase in e^2qQ coupled to a decrease in η value in p-S.

As a final comment, we should like to mention that sources of ^{129}Te^m implanted in r-S platelets were studied by Langouche *et al.*,[18] who reported observing an ^{129}I QI of -1125 ± 34 MHz. This QI is substantially smaller than the one reported in this work for r-S, and thus raises the possibility that this discrepancy is conceivably an implantation-induced artifact. It is possible that a sustained damage may have resulted in the r-S platelets because of implantation, thus causing the ^{129}Te^m ions to come to rest at damaged or defect sites.

IV. CONCLUSIONS

Mössbauer isomer shifts and quadrupole interactions at I and Te impurities measured utilizing ^{129}Te^m-labeled sources and ^{125}Te-labeled absorbers have provided a direct microscopic characterization of the following elemental chalcogens: t-Te, t-Se, m-Se, r-S, and p-S. (i) A sign reversal of V_{zz} is believed to occur in going from Te to I, and is shown to be a consequence of a chemical-bonding rearrangement, viz., the twofold coordination of Te involving π bonding, with two chalcogen near neighbors, transforms into a nearly onefold coordination of I involving σ bonding with a chalcogen near neighbor. (ii) The ratio R of the ^{125}Te$-^{129}$I quadrupole coupling is found to vary as follows: t-Te (-1.12), t-Se (-0.65), m-Se (-0.55), a-Se (-0.52), r-S (-0.48), and p-S (-0.48). The systematic reduction in the magnitude of R from Te to S in the indicated sequence is shown to be evidence of an increasingly molecular character of the host chemical bonding. (iii) In contrasting the host bonding between the Se polymorphs, it is shown that a-Se is the most molecular of these solids, and further, that the molecular unit in a-Se consist predominantly of a Se ring species. (iv) In contrasting the I bonding between the Se polymorphs, it is shown that I has a significant (33%) π-bonding character in a trigonal Se chain, and, furthermore, that this interaction vanishes in a-Se, where I becomes onefold coordinated in a pure σ bond with a Se near neighbor.

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