Fortner, J. M. Khan, E. J. Zaharias, and J. D. Garcia, Phys. Rev. Lett. 25, 1473 (1970).

[5]C. F. Moore, M. Senglaub, B. Johnson, and P. Richard, Phys. Lett. 40A, 107 (1972).

[6]D. Burch, W. B. Ingalls, J. S. Risley, and R. Heffner, Phys. Rev. Lett. 29, 1719 (1972).

[7]C. P. Bhalla and M. Hein, Phys. Rev. Lett. 30, 39 (1973).

[8]W. Bambynek, B. Crasemann, R. W. Fink, H.-U. Freund, H. Mark, C. D. Swift, R. E. Price, and P. Venugopala Rao, Rev. Mod. Phys. 44, 716 (1972).

[9]F. P. Larkins, J. Phys. B: Proc. Phys. Soc., London 4, 14 (1971).

[10]J. D. Garcia, Phys. Rev. A 4, 955 (1971).

[11]F. P. Larkins, J. Phys. B: Proc. Phys. Soc., London 4, L29 (1971).

Nuclear Quadrupole Interactions at Te^{125} in the Isoelectronic Crystalline Hosts of S, Se, and Te†

P. Boolchand, T. Henneberger, and J. Oberschmidt
Physics Department, University of Cincinnati, Cincinnati, Ohio 45221
(Received 13 April 1973)

A systematic increase in Te^{125} quadrupole splitting of up to 54% has been observed in the isoelectronic crystalline hosts of Te, Se, and S. This is attributed to nonlocal and overlap electronic contributions to the electric field gradient q_{el}, which increase as a result of a systematic shortening of the covalent bonds.

We have observed large and unique quadrupole splittings (QS) at Te^{125} in the isoelectronic hosts of orthorhombic S and trigonal Se using the 35.5-keV γ resonance.[1] In conjunction with the measured QS in Te metal,[2,3] these data show a systematic increase of up to 54% in the QS which is found to correlate linearly with the inverse cube of the covalent bond lengths[4] R that Te forms with its two near neighbors in these hosts.

These results are significant, as they will permit an understanding of the origin of the electric field gradient (EFG) in Te metal. It has been pointed out[5] that for semimetals where the density of electron states at the Fermi level is small, the principal mechanism for the origin of the EFG is electronic and comes from all the band electrons below the Fermi surface. For the case of Sb metal where detailed calculations[6] have been made, q_{el} is composed of local, nonlocal, and overlap contributions. Te and Sb both have partially filled $5p$ atomic shells and, in the solid state, are characterized as semimetals. The present results on Te^{125} permit estimating the relative magnitudes of the different contributions to q. In particular these data reveal the existence of sizable contributions of q_{el}(overlap) and q_{el}(nonlocal) and further also suggest that q_{ion} and q_{el}(local) have opposite signs in Te metal. The study of EFG in metals remains a subject of continued interest both experimentally[7,8] and theoretically.[9] The present approach of using isoelectronic hosts in the study of quadrupole interactions using nuclear γ resonance is novel and in a sense complements measurements made using other techniques[10,11] as a function of temperature and pressure. The present measurements are significant in another way. They provide a calibration of covalent bond lengths in terms of QS in Te-based twofold coordinated hosts. This result is of interest in the structure determination of some amorphous semiconductors such as GeTe[12] and Se.[13]

2.7-yr Sb^{125} in Cu was used as a source of monoenergetic γ rays of energy 35.5 keV. The source was prepared by diffusing carrier-free Sb^{125} in high-purity Cu foils. A velocity spectrum of the source taken with a thin ZnTe absorber [Fig. 1(a)] gave an observed full width at half-maximum (FWHM) of 5.95 ± 0.08 mm/sec. In a forthcoming publication[14] we will present details of linewidth measurements using ZnTe absorbers of different thicknesses. The linewidth of the Sb^{125}(Cu) source and the "f" of ZnTe at 78 K were found to be 5.10 ± 0.08 mm/sec and 0.32 ± 0.02, respectively. The linewidth of these sources agrees with $2\Gamma_n = h/\tau = 5.20 \pm 0.04$ mm/sec based on the electronically measured lifetime[15] of the 35.5-keV state. Alloys of the compositions Te$_{0.02}$Se$_{0.98}$ and Te$_{0.014}$S$_{0.986}$ were prepared by melting the elements *in vacuo*, followed by annealing the melt. The Se alloys were annealed at 150°C for 24 h and the S alloys at 50°C for about 6 h. X-ray analysis of the alloys confirmed the trigonal and orthorhombic phases of
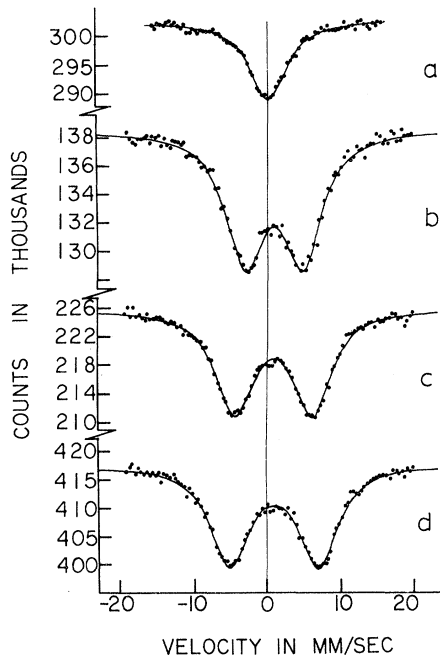
FIG. 1. Te[125] Mössbauer spectra of (a) ZnTe, (b) Te metal, (c) $Te_{0.02}Se_{0.98}$, (d) $Te_{0.014}S_{0.996}$ absorbers. Spectrum (a) was accumulated at 78 K, and spectra (b), (c), and (d) at 4.2 K. Source and absorber were maintained at the same temperature.

Se and S. Velocity spectra of the different Te absorbers are reproduced in Fig. 1. The line-widths of the different spectra (Table I) are the narrowest yet reported for Te[125] and are accountable in terms of the source emission linewidth and finite absorber thickness.

The QS in the 35.5-keV state of spin $I = \frac{3}{2}$ is given by

$$\Delta E_q = \tfrac{1}{2}eqQ(1 + \eta^2/3)^{1/2},\qquad (1)$$

where $Q = -0.2$ b[16] represents the nuclear quadrupole moment, and q and η represent, respectively, the z component and the asymmetry parameter of the EFG tensor. For Te metal, Mössbauer-effect measurements on single-crystal

absorbers[3] have shown that the sign of eqQ is positive and $\eta = 0.64 \pm 0.04$. The result of a positive eqQ was obtained by identifying the positive velocity component of the Te metal quadrupole doublet as the π component. This leads to a negative EFG in Te metal.

Te as a dilute impurity in the hosts of Se and S enters substitutionally and we suggest that the QS observed in these hosts be identified with Te sites covalently bonded to two Se and two S near neighbors in respective molecular units. Recent investigations on Te-Se alloys[17] indeed confirm the view that Te as a dilute impurity in Se has two Se near neighbors. A similar situation is expected for S. It follows that the local twofold symmetry at Te in these isoelectronic hosts is preserved, and that in going from Te to S, one is systematically bringing a smaller-size neighbor closer to a Te site. In the Te metal structure[18] a given Te site sits in a local twofold symmetry with a bond angle $\theta(\text{Te-}\hat{\text{Te}}\text{-Te})$ of 103.2°. The measured value[3] of $\eta = 0.64 \pm 0.04$ in this structure can be well understood as arising because of a bond switching[19] of the two equivalent Te-Te bonds leading to an EFG characterized by an asymmetry parameter η given by

$$\eta = 3\cos\theta.\qquad (2)$$

In hosts of S and Se where a Te impurity also sits in a local twofold symmetry, one may expect a bond-switching mechanism to be operative and, in particular, the η values of the EFG to be given by (2) with θ denoting the appropriate bond angle X-Te-X ($X = $ S and Se). To a first approximation it appears reasonable to assume that θ in the hosts of S and Se will be about the same as in Te metal to within 5°. Under this assumption, a change in the asymmetry parameter η alone cannot account for more than a 6% increase in the QS in going from Te to S. The observed QS increase of 54% consequently must derive primarily from that in q [Eq. (1)].

The net EFG q in Te metal may be written

$$q = (1 - \gamma_\infty)q_{\text{ion}} + (1 - \mathfrak{R})q_{\text{el}}(\text{local}) + (1 - \gamma_{Te\,X})q_{\text{el}}(\text{overlap}) + (1 - \gamma_{XX})q_{\text{el}}(\text{nonlocal}),\qquad (3)$$

where the γ's and R are the appropriate Sternheimer antishielding parameters. The first term represents the EFG due to point ions (Te[6+]) in a uniform negative–charge-density background.[20] A major contribution to q is expected to come

from the aspherical electronic charge density in the central cell arising from the unbalanced p valence electrons. Following Hygh and Das,[6] q_{el} is decomposed in nonlocal and overlap con-

TABLE I. Summary of a least-squares–fit analysis of Te^{125} Mössbauer spectra. Column 2 gives the thickness t of the absorbers; column 3, the observed FWHM; column 4, the QS in the absorber; column 5, the isomer shift (IS) with respect to the source.

Absorber	(mg/cm² of Te^{125})	$FWHM_{obs}$ (mm/sec)	QS (mm/sec)	IS (mm/sec)
$ZnTe$[a]	3	5.84 ± 0.15	$\cdots$	-0.30 ± 0.07
Te metal[b]	4	6.21 ± 0.11	7.77 ± 0.06	$+0.50 \pm 0.06$
$Te_{0.2}Se_{0.98}$[c]	2	6.11 ± 0.08	10.44 ± 0.05	$+0.22 \pm 0.07$
$Te_{0.014}S_{0.996}$[c]	2	6.14 ± 0.09	11.93 ± 0.06	$+0.27 \pm 0.07$

[a]$ZnTe$ crystal chips from Gould Industries, Cleveland, Ohio, were powdered.
[b]99.9999%-pure Te from Spex Industries, Metuchen, N. J., was powdered and annealed.
[c]99.9999%-pure Se and S and isotopically enriched Te^{125} were used as starting materials in the preparation of the alloys.

tributions in Eq. (3).

The analysis of the data was carried out by plotting the QS (Table I) as a function of R^{-3} (Fig. 2), where R represents the length of the Te-X covalent bond lengths. It is pertinent to point out that the electronegativities of Te, Se, and S are about the same, having values[4] of 2.1, 2.4, and 2.5, respectively. This would preclude the pres-
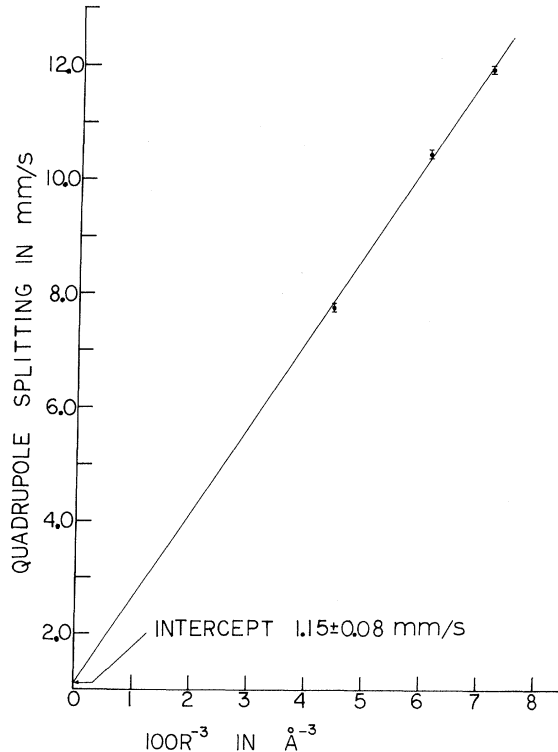

FIG. 2. A plot of observed QS as a function of R^{-3}. R represents the covalent bond lengths Te-X. For the case of Te, Te-Te was taken as 2.83 Å.

ence of any significant double-bond character in the Te-Se and Te-S bonds. Clearly one may then expect that the sum of individual covalent radii will give the Te-Se and Te-S bond lengths quite reliably. Figure 2 reveals a linear relationship of the observed QS as a function of R^{-3}. If one extrapolates linearly to $R^{-3} \to 0$, i.e., $R \to \infty$, one obtains an intercept value of 1.15 ± 0.05 mm/sec for the QS.

The net EFG q is composed of contributions[5] which may have opposite signs. In that sense, the linear relationship of the QS with respect to R^{-3} observed in the present data cannot be uniquely interpreted in the absence of theoretical estimates of the different q terms. In what follows, we outline a likely interpretation of the data.

(a) It is believed that the q_{ion} term in the isoelectronic hosts, much like the case in Sb metal, will represent a small contribution (10%) to q. Its magnitude in the different hosts to a first approximation will be the same. Our recent measurements of the quadrupole interaction at Te^{125} in orthorhombic and plastic sulfur strongly support the view that destruction of long-range order of the host leaves the average EFG unchanged. The minimal role played by the q_{ion} term is thus clear.

(b) A major contribution to q is expected to arise from the aspherical charge density in the central cell if one has, for example, p valence electrons. Sb and Te are cases in point. It is believed that the increase in QS observed here therefore arises primarily because of that in q_{el}. Such a result can be physically understood in terms of an increase in the overlap and nonlocal contributions to q_{el} arising from a shorten-

ing of the Te-X covalent bond lengths. To a first approximation one may expect the q_{el}(local) term to remain unchanged since the local twofold symmetry at Te is preserved in the different hosts. A larger overlap of the $5p$ and np ($n = 3,4$ for S and Se) electron density localized between Te and its near neighbor X, it is expected, will lead to an increase in

$$q_{el}(\text{overlap}) = \langle 5p | (3\cos^2\theta - 1)/r^3 | np \rangle.$$

The presence of a closer near neighbor, it is expected, will lead to an increase in

$$q_{el}(\text{nonlocal}) = \langle np | (3\cos^2\theta - 1)/r^3 | np \rangle.$$

(c) The overlap and nonlocal contributions depend sensitively on R. For the case when $R \rightarrow \infty$, we expect these terms to vanish. The intercept value of the QS therefore represents the contributions $eQ[q_{ion} + q_{el}(\text{local})]$ in Te metal. On removal of the two near neighbors from a Te site in question, one is left with the EFG arising due to the local valence orbitals on Te in a C_{2v} symmetry. The q_{ion} term is assumed to be independent of R in the range $2.8 < R < 2.1$ Å and essentially contributes a constant term.

The net EFG in Te metal is negative while that in Sb metal is positive. The present result of $q_{ion} + q_{el}(\text{local})$, representing 15% of the observed q in Te metal, is quite in contrast to that in Sb metal where calculations show that almost all the q_{net} comes from $q_{ion} + q_{el}(\text{local})$. In Sb metal q_{ion} and $q_{el}(\text{local})$ are both positive. It is likely that (i) q_{ion} and $q_{el}(\text{local})$ have opposite signs in Te metal, with $q_{el}(\text{local})$ being negative, and (ii) sizable $q_{el}(\text{overlap})$ and $q_{el}(\text{nonlocal})$ terms exist in the $P321$ local symmetry of this host.

The present experimental results provide motivation for detailed theoretical calculations of q which are possible from the known band structure[21] of Te metal. A starting point for these calculations could make use of the molecular-orbital approach[22] which has been used to explain the optical properties of S and Se. A meaningful interpretation of the observed isomer shifts would then be possible in terms of $5s$ electron density changes at Te in the isoelectronic hosts. Finally, a measurement of the QS at Te^{125} in oxygen should be quite revealing.

We have benefitted from discussions with Pro-

fessor B. Goodman and Professor P. Suranyi. The encouragement and advice of Professor S. Jha and Professor L. Witten is gratefully acknowledged. We are also thankful to Dr. J. Grover for assistance in x-ray measurements.

---

[1]P. Boolchand, T. Henneberger, and J. Oberschmidt, to be published.

[2]C. E. Violet and R. Booth, Phys. Rev. 144, 225 (1966).

[3]P. Boolchand, B. L. Robinson, and S. Jha, Phys. Rev. B 2, 3463 (1970).

[4]A. F. Wells, Structural Inorganic Chemistry (Clarendon Press, Oxford, England, 1961).

[5]N. C. Mohapatra, C. M. Singal, T. P. Das, and P. Jena, Phys. Rev. Lett. 29, 456 (1972), and references therein.

[6]E. H. Hygh and T. P. Das, Phys. Rev. 143, 452 (1966).

[7]P. Raghavan and R. S. Raghavan, Phys. Rev. Lett. 27, 724 (1971).

[8]P. E. Gregers-Hansen, M. Krusius, and G. R. Pickett, Phys. Rev. Lett. 27, 38 (1971).

[9]R. E. Watson, A. C. Gossard, and Y. Yafet, Phys. Rev. 140, A375 (1965).

[10]P. Raghavan, R. S. Raghavan, and W. B. Holzapfel, Phys. Rev. Lett. 28, 903 (1972).

[11]R. M. Lieder, N. Buttler, K. Killing, K. Beck, and E. Bodenstedt, in Hyperfine Interactions in Excited Nuclei, edited by G. Goldring and R. Kalish (Gordon and Breach, New York, 1971), Vol. 2, p. 449.

[12]D. Adler, M. H. Cohen, E. A. Fagen, and J. C. Thompson, J. Non-Cryst. Solids 3, 402 (1970).

[13]P. Boolchand, Solid State Commun. 12, 753 (1973).

[14]J. Oberschmidt and P. Boolchand, to be published.

[15]C. Hohenemser and R. Rosner, Nucl. Phys. A109, 364 (1968).

[16]M. Pasternak and S. Bukshpan, Phys. Rev. 163, 297 (1967).

[17]P. Boolchand and P. Suranyi, Phys. Rev. B 1, 57 (1973).

[18]P. Unger and P. Cherin, in The Physics of Selenium and Tellurium, edited by W. C. Cooper (Pergamon, New York, 1969), p. 223.

[19]S. Kojima, K. Tsukuda, S. Ogawa, A. Schimauchi, and Y. Abe, J. Phys. Soc. Jap. 9, 805 (1954).

[20]F. W. de Wette, Phys. Rev. 123, 103 (1961).

[21]O. Madelung and J. Treusch, in The Physics of Selenium and Tellurium, edited by W. C. Cooper (Pergamon, New York, 1969), p. 23.

[22]S. Tutihasi and I. Chen, Phys. Rev. 158, 623 (1967).