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# Mössbauer Effect of $I^{127}$ and $Te^{125}$ in Iodine, Tellurium, and Antimony Compounds

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Mössbauer-effect measurements have been carried out to investigate the influence of $\beta^-$ decay and $K$ capture on the electronic structure of the decaying atom. Sources of $I^{125}$ in $NaIO_3$ and $NaIO_4$ showed multiple-line spectra. It was found that through the $K$ capture and the subsequent processes the bonding of the iodine atom is uncoupled and the resulting tellurium atom forms new types of bonds. Sources of $Sb^{125}$ in $NaSbO_3$ and $Sb_2O_3$ exhibited single-line spectra and no evidence for multiple lines was found, which is interpreted as indicating a smaller distortion of the electron shell through $\beta^-$ decay. The Mössbauer effect of the 57.6-keV transition to the ground state of $I^{127}$, which follows the $\beta^-$ decay of the $Te^{127m}$, was used to measure the isomer shift of various iodine compounds at 4.2°K. The linewidths and quadrupole splittings of these compounds were determined in order to check the microscopic stoichiometry, because the same compounds containing $I^{125}$ were then used as sources against a single-line absorber. The isomer-shift scale was calibrated in terms of $s$-, $p$-, and sometimes $d$-electron shielding, according to the atomic configuration and hybridization, respectively. Together with the $s$-electron density of the filled $n=5$ shell, calculated from the Fermi-Segré formula, a value of $\Delta R/R=-2.8\times10^{-5}$ was obtained for $I^{127}$. The 35.5-keV transition in $Te^{125}$ was used to measure the isomer shift and quadrupole splitting of a variety of tellurium compounds at 78°K. A linear relation is found between the isomer shifts of analogous iodine and tellurium compounds, confirming that isoelectronic structures are formed by these elements. Applying the same procedure for the isomer-shift scale calibration as for iodine, $\Delta R/R=+2.4\times10^{-5}$ is derived for $Te^{125}$.

## I. INTRODUCTION

THE technique of resonance absorption of recoil-free $\gamma$ radiation (Mössbauer effect) has been used to study various electric, magnetic, chemical, and lattice dynamic properties of atoms embedded in solids. Included in the broad spectrum of applications is the use of the effect as a means to study processes that occur in the solid or in the atom itself as a result of a preceding nuclear decay. But only such processes can be observed experimentally which occur on time scales comparable with the lifetimes of the particular nuclear level used.

We are here concerned with measurements designed to investigate the influence of two different nuclear decays, i.e., $\beta^-$ decay and $K$-capture decay, on the electronic structure of the decaying atom itself and on its bonding to the neighbor atoms in various chemical compounds. Charge states in diluted gases have been observed in various isotopes and the results for the two decays differ greatly. Snell *et al.*[1] measured the charge states of $Ar^{37}$ atoms following $K$ capture. The highest observed intensity of the charged atoms was associated with charge +3. A maximum intensity for charge +8 was observed for $Xe^{137m}$ atoms following internal conversion; however, charges up to +30 were detected, although with very low intensities. The charge states are mainly created through Auger cascades.[2] Following $\beta^-$ decay in $Kr^{85}$, the rubidium atoms are found with about 80% probability in the charge state +1, and the remaining 20% carry charges up to +10.[3] These higher charges occur primarily through "shake-off" processes.

Delayed-coincidence measurements combined with Mössbauer effect (ME) using $Co^{57}$ embedded in various compounds have shown no time dependence (within $10^{-7}$ sec) of charge states resulting from the preceding $K$-capture process.[4,5] The influence of the preceding nuclear decay can be detected through the ME isomer shift (IS) and quadrupole splitting (QS), which are both dependent on the type and mechanism of the chemical bonding.

The nuclear transition used for our experiments was the 35.5-keV $\gamma$ transition in $Te^{125}$, which is favorable for this type of investigation because the excited $\frac{3}{2}^+$ level is populated as well from $I^{125}$ through $K$ capture as from $Sb^{125}$ through $\beta^-$ decay. In addition, an isomeric state $Te^{125m}$ exists, which also decays via this 35.5-keV

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[1] F. Pleasonton and A. H. Snell, Proc. Roy. Soc. (London) **A241**, 141 (1957); A. H. Snell and F. Pleasonton, Phys. Rev. **111**, 1338 (1958); **100**, 1396 (1955).

[2] *Alpha-, Beta- and Gamma-Ray Spectroscopy*, edited by K. Siegbahn (North-Holland Publishing Co., Amsterdam, 1965).

[3] A. H. Snell and F. Pleasonton, Phys. Rev. **107**, 740 (1957); T. A. Carlson, *ibid.* **130**, 2361 (1963).

[4] W. Triftshäuser and P. P. Craig, Phys. Rev. Letters **16**, 1161 (1966).

[5] W. Triftshäuser and P. P. Craig, Phys. Rev. **162**, 274 (1967).

excited state. Both iodine and antimony form similar chemical compounds and have additional isotopes which exhibit the ME. Thus the specimen used for the investigation can be examined using them first as an absorber against a single-line source and then as a source against a single-line absorber.

Violet *et al.*[6] observed a rather complex Mössbauer spectrum using $I^{125}$ in $NaIO_3$ against a tellurium absorber. They interpreted this spectrum as being due to charge states created as a result of the preceding $K$ capture through the subsequent Auger processes and derived a half-life of $1.6\times10^{-9}$ sec for the $Te^{+6}$ state. Because of the QS of the Te absorber itself it was difficult to determine accurately isomer shifts and line intensities of the expected charge states, and therefore they proposed several pairs of isomer shift and quadrupole splitting which could account for their measured spectrum. We have repeated the measurements of Violet *et al.* and have extended them to include sources of $Te^{127m}$, $I^{125}$, and $Sb^{125}$ as well as measurements with single-line absorbers of $I^{127}$ and $Te^{125}$. The resultant spectra are interpreted in terms of bond modifications without invoking the multiple charge states suggested by Violet *et al.*

## II. EXPERIMENTAL DETAILS

The measurements consist of determinations of IS, QS, and Debye temperatures $\Theta_D$ of the Mössbauer spectra of $I^{127}$ and $Te^{125}$ obtained for analogous iodine and tellurium sources and absorbers.

Iodine and tellurium are neighbors in the periodic system ($5p$ shell), and form chemical compounds that are similar in their electronic configuration. In the measurements we used sources of $Te^{127m}$, $I^{125}$, and $Sb^{125}$. Various iodine compounds were used as absorbers against a single-line source of $Te^{127m}$ in ZnTe.[7] The same compounds, containing $I^{125}$, were then measured as sources against a ZnTe absorber. Thus each compound could be investigated with the ME of two different $\gamma$ transitions.

The isomeric state of $Te^{127m}$ (half-life 105 days) decays with only 1.5% probability to the excited $\frac{7}{2}^+$ state of $I^{127}$ and then to the $\frac{5}{2}^+$ ground state by emission of a 57.6-keV $\gamma$ ray. The mean lifetime of the 57.6-keV level is $(2.68\pm0.16)\times10^{-9}$ sec and the conversion coefficient $\alpha_t$ is 3.75.[8]

$I^{125}$ decays through $K$ capture exclusively to the $\frac{3}{2}^+$ excited level of $Te^{125}$ [$(2.09\pm0.3)\times10^{-9}$ sec mean lifetime]. The decay to the $\frac{1}{2}^+$ ground state occurs either by emission of a 35.5-keV $\gamma$ ray or through internal conversion ($\alpha_t=13.3$).[8] $Sb^{125}$ with half-life 2.8 years decays through $\beta^-$ decay to $Te^{125}$, populating the first excited level with about 21% probability.[9]

The $K$ capture and the internal conversion of the $\gamma$ ray cause strong x-ray radiation background. Because of the close-lying energies, the x rays and the $\gamma$ rays cannot be resolved by a NaI(Tl) scintillator. With a lithium-drifted Si diode, a sufficiently good resolution could be obtained, however, only for very weak sources.

In the case of the 35.5-keV transition, the x-ray energies lie below the $K$-absorption edge of iodine. If $\epsilon_A$ is the absorption probability, then $1-\epsilon_A$ is approximately the escape probability of the x ray. An escape probability of about 80% of the total 35.5-keV $\gamma$ ray intensity was found experimentally for a 0.1-mm thick NaI(Tl) crystal. Therefore, the escape peak at 6.9 keV was used for all the ME measurements. The other escape peak at 3.2 keV was partially covered by the noise background of the photomultiplier tube (RCA 8575) and therefore neglected.

In preparing the iodine, tellurium, and antimony compounds, we followed the techniques described by Gmelin,[10] Brauer,[11] and Bagnall.[12] All samples were investigated by x-ray diffraction using a goniometer x-ray apparatus. No deviation from the regular lattice structure (according to the ASTM catalog[12a]) could be detected by this method, indicating perfect macroscopic stoichiometry of our prepared specimen.

For most of the measurements with the 35.5-keV transition, ZnTe absorbers enriched to 65% in $Te^{125}$ were used. All other absorbers contained the natural abundance of $Te^{125}$ (7%).

The measurements were carried out at liquid-nitrogen or liquid-helium temperature and both source and absorber were held at these temperatures. The sources were driven with sinusoidal velocity and the counts were stored in a 400-channel RIDL multichannel analyzer operated in the multiscaling mode.

## III. RESULTS AND DISCUSSION

### A. Source of $Te^{127m}$ in ZnTe

The isomer shifts and quadrupole splittings of various iodine compounds against a single-line source of $Te^{127m}$ in ZnTe were measured to extract the value of the change of the nuclear radius between the excited and the ground state in $I^{127}$, and to investigate experimentally the local symmetry of the iodine atom in these com-

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[6] C. E. Violet and R. Booth, Phys. Rev. **144**, 225 (1966); **149**, 414(E) (1966).

[7] Obtained from New England Nuclear Corp., Boston, Mass.

[8] J. S. Geiger, R. L. Graham, I. Bergstrom, and F. Brown, Nucl. Phys. **68**, 352 (1965).

[9] *Nuclear Data Sheets*, compiled by K. Way *et al.* (Printing and Publishing Office, National Academy of Sciences–National Research Council, Washington, D.C., 1958).

[10] L. Gmelin, in *Handbuch der Anorganischen Chemie*, edited by Deutsche Chemische Gesellschaft (Verlag Chemie, Leipzig, 1924).

[11] G. Brauer, *Handbuch der Präperativen Anorganischen Chemie* (Ferdinand Enke Verlag, Stuttgart, 1960).

[12] K. W. Bagnall, *The Chemistry of Selenium, Tellurium and Polonium* (Elsevier Publishing Co., Inc., New York, 1966).

[12a] *ASTM Catalog* (The American Society for Testing and Materials, Philadelphia, Pa.).

TABLE I. Experimental values of the linewidths, isomer shifts, and quadrupole splittings of various iodine compounds, measured as absorbers against a $ZnTe^{127m}$ source. The source and the absorbers were held at liquid-helium temperature. $\Gamma_{\text{corr}}$ is the linewidth corrected for finite absorber thickness according to Eq. (2). The ratio $\Gamma_{\text{corr}}/\Gamma_{\text{nat}}$ is given, taking $2\Gamma_{\text{nat}}=2.54$ mm/sec.

| Absorber compounds | Experimentally measured linewidth (mm/sec) | $\Gamma_{\text{corr}}/\Gamma_{\text{nat}}$ | Isomer shift (mm/sec) | $\frac{1}{4}(e^2qQ)$ (mm/sec) |
|---|---|---|---|---|
| $NaIO_3$ | 3.22±0.2 | 1.0±0.08 | −0.44±0.05 | 5.86±0.27 |
| $NaIO_3 \cdot H_2O$ | 3.66±0.2 | 1.15±0.08 | −0.41±0.05 | 5.96±0.27 |
| $Na_2Mn(IO_3)_6$ | 3.34±0.2 | 1.06±0.08 | −0.55±0.04 | 5.81±0.27 |
| $Na_3H_2IO_6$ | 5.26±0.2 | 1.04±0.08 | +1.02±0.04 | 0 |
| $NaIO_4$ | 3.02±0.2 | 1.0±0.08 | +0.85±0.07 | 0 |

pounds. Because the same compounds were also used as sources by incorporating $I^{125}$, it is important to know whether they have perfect microscopic stoichiometry or not, and this is a possibility to prove this. Table I presents the results of the measurements.

A spectrum obtained with a $NaIO_3$ absorber is shown in Fig. 1. In a noncubic lattice symmetry an eight-line spectrum is expected through the $\frac{7}{2}^+ \rightarrow \frac{5}{2}^+$ transition. The spectra were analyzed by the method of least-square fits using an IBM 360 computer. The line positions of the various components are determined through

$$\delta+(ce^2q/4E)(B_eQ_e-B_gQ_g), \qquad (1)$$

where $\delta$ is the isomer shift, $Q$ is the quadrupole moment of the nucleus ($e$ and $g$ refer to the excited and ground states, respectively), and $B$ is defined through

$$B(I,m)=[3m-I(I+1)]/[3I^2-I(I+1)],$$

where $I$ is the spin of the state and $m$ is the quantum number of $I_z$. For the quadrupole moments, we used the values measured by Perlow *et al.*[13] The peak intensities were calculated from the Clebsch-Gordan coefficients.

The experimentally observed linewidth $\Gamma_{\text{expt}}$ increases with the thickness $d$ of the absorber as[14,15]

$$\Gamma_{\text{expt}}=\Gamma_s+\Gamma_a+0.27\Gamma_{\text{nat}}\sigma_0 Nd f_a, \qquad (2)$$

where $\Gamma_s$, $\Gamma_a$, and $\Gamma_{\text{nat}}$ are the source, absorber, and natural linewidths, $Nd$ is the number of resonant atoms per cm², $\sigma_0$ is the resonance absorption cross section, and $f_a$ is the Debye-Waller factor of the absorber. $\Gamma_{\text{nat}}$ is determined by the mean lifetime of the excited nuclear level. In the ideal case, the experimental observed linewidth is twice the natural linewidth. For this transition $2\Gamma_{\text{nat}}$ is equal to 2.54±0.15 mm/sec. Lattice distortions can broaden the linewidths of source and absorber. Therefore, the observation of the ideal linewidth indicates perfect lattice symmetry of source and absorber.

Perlow *et al.*[16] derived a Debye temperature $\Theta_D$ of 280°K for $Na_3H_2IO_6$. Applying the Debye approximation, this corresponds to a recoilless factor of $f_a=0.41$. From Eq. (2), the sum of $\Gamma_s+\Gamma_a$ can be calculated to 2.64±0.2 mm/sec, indicating that the $Te^{127m}$ source and this absorber exhibit nearly the natural linewidth. Taking this result, $\Theta_D$ of the $ZnTe^{127m}$ source can then be deduced to be 102°K. A Debye temperature of about 100°K (with 10% error) is assumed for the other iodine compounds, and with this value the experimentally observed linewidths are corrected for the finite absorber thickness. The results are also presented in Table I as the ratio of $\Gamma_{\text{corr}}/\Gamma_{\text{nat}}$.

For the calibration of the IS scale in terms of $5s$ electron density, we followed the procedure of Hafemeister *et al.*[17] and used the relations which they derived

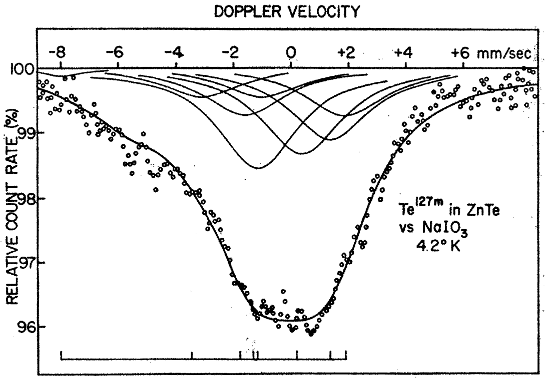

FIG. 1. Mössbauer spectrum at 4.2°K of a $NaIO_3$ absorber and a source of $Te^{127m}$ in ZnTe. The resonance lines obtained through least-square fits are indicated.

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[13] G. J. Perlow and M. R. Perlow, J. Chem. Phys. **45**, 2193 (1966).

[14] S. Margulies and I. R. Ehrman, Nucl. Instr. Methods **12**, 131 (1961).

[15] D. A. O'Connor, Nucl. Instr. Methods **21**, 318 (1963).

[16] G. J. Perlow and M. R. Perlow, Rev. Mod. Phys. **36**, 353 (1964).

[17] D. W. Hafemeister, G. de Pasquali, and H. de Waard, Phys. Rev. **135**, B1089 (1964).

for the number $h_{5s}$ and $h_{5p}$ of $5p$ electrons, removed from the $n=5$ closed shell.

$$h_{5s}=mS^2\Delta Z, \tag{3}$$

$$h_{5p}=m(1-S^2)\Delta Z. \tag{4}$$

$S^2=\cos\alpha/(\cos\alpha-1)$ is the fraction of the removed charge due to $5s$ electrons; $m$ and $\alpha$ are the number and angle, respectively, of the iodine-oxygen bonds in the compound. The Fermi-Segré formula[18] gives the electron density $|\psi(0)|^2$ for an outer $s$ electron at the site of the nucleus as

$$|\psi(0)|^2=[ZZ_{\text{eff}}^2/(\pi a_0^3 n_{\text{eff}}^3)]1-(d\sigma/dn)], \tag{5}$$

where $Z_{\text{eff}}$ is the effective charge seen by the outer $s$ electron, $n_{\text{eff}}$ is the effective quantum number, and $d\sigma/dn$ is the derivative of the quantum defect with respect to the $n$th quantum state. Using this equation and the Slater shielding coefficients,[19] which give

$$Z_{\text{eff}}=7.25+0.35m\Delta Z, \tag{6}$$

we obtain an equation for the IS:

$$\delta-\delta_0=C\{(2-h_{5s})[1+0.097(h_{5s}+h_{5p})]-2\}, \tag{7}$$

where $\delta_0$ is the isomer shift of $I^-$ and $C$ is defined by[20]

$$C=7.8\times10^{-25}|\psi_0(0)|^2(\Delta R/R)[ZA^{2/3}S'(Z)/E_\gamma]. \tag{8}$$

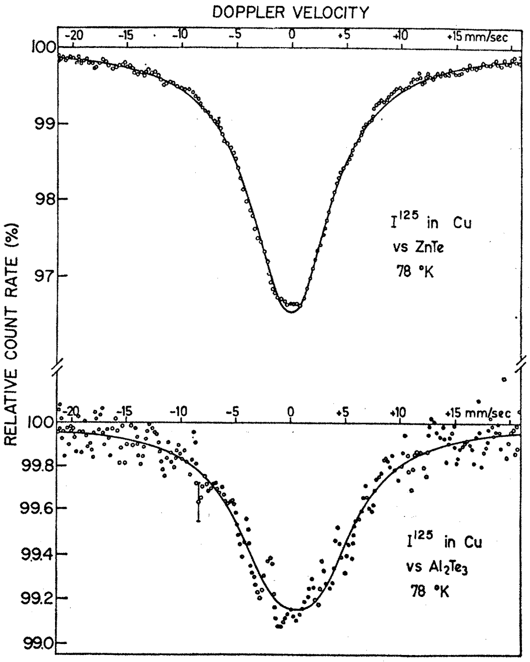

FIG. 2. Mössbauer spectra at 78°K of a ZnTe (top) and a $Al_2Te_3$ absorber (bottom) versus a source of $I^{125}$ in copper.

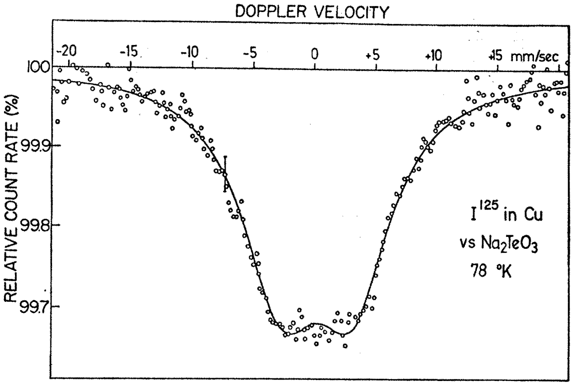

FIG. 3. Mössbauer spectrum at 78°K of a $Na_2TeO_3$ absorber versus a source of $I^{125}$ in copper.

Here $|\psi_0(0)|^2$ is the electron density at the nucleus for the completely filled $s$ and $p$ shells, $Z$ and $A$ are the nuclear charge and mass, respectively, and $S'(Z)$ is a relativistic correction factor.[20] Using our IS data for $NaIO_3$ ($m=3$; $S^2=0.03$), $NaIO_4$ ($m=4$; $S^2=0.25$), and the deduced value for $I^-$ of $\delta_0=0.164$ mm/sec,[13] we get $0.75\pm0.15$ for $\Delta Z$ and $(-1.77\pm0.35)$ mm/sec for $C(I^{127})$. From this calibration, we can determine the $I^{127}$ nuclear radius change $\Delta R/R$. To do this we must know $|\psi_0(0)|^2$, which can be obtained from Eq. (5) with the data $(n_{\text{eff}})^3=6.5$, $[1-(d\sigma/dn)]=1.0975$, and $Z_{\text{eff}}=7.25$. We find $|\psi_0(0)|^2=1.0\times10^{27}\ \text{cm}^{-3}$. (The

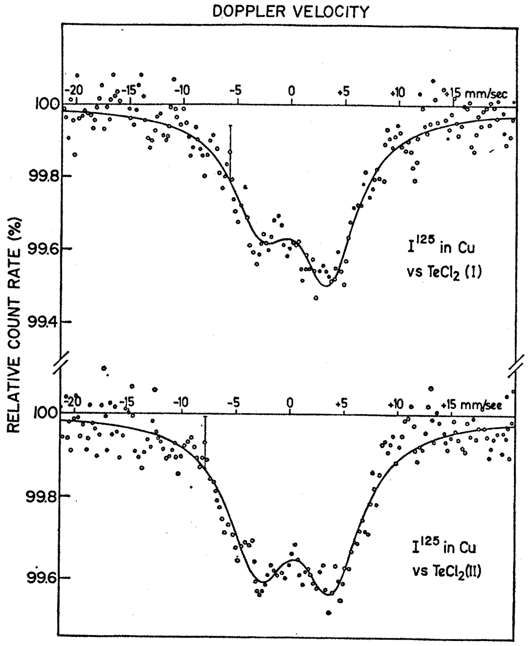

FIG. 4. Mössbauer spectra at 78°K of $TeCl_2$ absorbers versus a source of $I^{125}$ in copper. The observed asymmetric quadrupole splitting of $TeCl_2$(I) is a function of the mechanical treatment of this material. Because of the special crystalline structure of $TeCl_2$, the absorber most probably consisted of small, but oriented, crystallites. Making the absorber more polycrystalline, as in $TeCl_2$(II), caused the asymmetry to vanish.

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[18] H. Kopfermann, *Nuclear Moments* (Academic Press Inc., New York, 1958).

[19] J. Slater, Phys. Rev. **36**, 57 (1930).

[20] D. A. Shirley, Rev. Mod. Phys. **36**, 339 (1964).

TABLE II. Experimental values of the isomer shifts, quadrupole splittings, and recoilless fractions of various tellurium compounds, measured as absorbers against a $I^{125}$ in copper source. The observed linewidths are corrected for finite absorber thickness according to Eq. (2). The ratio $\Gamma_{\text{corr}}/\Gamma_{\text{nat}}$ is given, taking $2\Gamma_{\text{nat}}=5.32$ mm/sec. In the lower part of this table, values for the IS and QS are included which were measured by other authors. Asterisks indicate that the quadrupole splitting is uncertain. The errors in the values of the recoilless fractions are about 15%.

| Absorber compounds | $\Gamma_{\text{corr}}/\Gamma_{\text{nat}}$ | Isomer shift (mm/sec) | $\frac{1}{4}(e^2qQ)$ (mm/sec) | Recoilless fraction (%) |
|---|---|---|---|---|
| $TeCl_4$ | 1.32±0.04 | +1.2±0.1 | 2.0±0.8 | 4.7 |
| $TeBr_4$ | 1.28±0.07 | +1.1±0.1 | 1.9±2.0 | 5.2 |
| $TeI_4$ | 1.33±0.32 | +1.8±0.9 | 2.0* | 4.7 |
| $TeCl_2$ | 1.24±0.07 | +0.48±0.2 | 3.25±0.2 | 3.4 |
| Te | 1.40±0.07 | +0.78±0.1 | 3.55±0.08 | 9.0 |
| $TeO_2$ | 1.30±0.04 | +0.72±0.07 | 3.27±0.06 | 18.2 |
| $Na_2TeO_3$ | 1.21±0.04 | +0.22±0.05 | 2.89±0.04 | 16.2 |
| $Na_2TeO_3\cdot 5H_2O$ | 1.36±0.07 | +0.13±0.1 | 3.36±0.1 | 4.8 |
| $Al_2Te_3$ | 1.56±0.19 | +0.46±0.2 | 2.1±0.3 | 4.5 |
| $Cu_2Te$ | 1.47±0.07 | +0.01±0.08 | 1.0* | 6.8 |
| CaTe | 1.26±0.04 | −0.14±0.07 | 0 | 8.1 |
| PbTe | 1.20±0.07 | −0.15±0.1 | 0 | 15.7 |
| ZnTe | 1.37±0.02 | −0.16±0.04 | * | 15.4 |
| $Na_2TeO_4$ | 1.36±0.01 | −0.99±0.03 | * | 20.5 |
| $K_2TeO_4$ | 1.51±0.04 | −0.98±0.05 | * | 20.2 |
| $TeO_3$ | 1.37±0.07 | −1.07±0.05 | 1.3±0.2 | 24.6 |
| $Te(OH)_6$ | 1.37±0.04 | −1.15±0.04 | 0 | 8.4 |
| MnTe | Ref. 6 | +0.23±0.2 | 1.5±0.5 | |
| βFeTe | Ref. 6 | +0.53±0.2 | 1.5±0.5 | |
| NiTe | Ref. 27 | −0.43±0.1 | 0 | |
| PbTe | Ref. 28 | −0.12 | 0 | |
| Te | Ref. 27 | +0.53±0.1 | 3.7±0.1 | |
| $Na_2TeO_3$ | Ref. 27 | +0.4±0.1 | 3.5±1.0 | |
| $TeF_4$ | Ref. 27 | +0.4±0.5 | 3.5±0.5 | |
| $TeI_4$ | Ref. 27 | +1.0±0.5 | 3.0±1.0 | |

calculated value in Ref. 17 is a factor of 2 too large and thus the derived $\Delta R/R$ for $I^{129}$ is a factor of 2 too small.) By combining these results with Eq. (8), we obtain $\Delta R/R=-2.8\times10^{-5}$. Using the method of Barrett and Shirley,[21] we can also roughly calculate $\Delta R/R$ by considering the collective nuclear deformation $\epsilon$ derived from the quadrupole moments $Q$ of the excited and ground states.

$$Q\simeq P(x)\tfrac{4}{5}ZR_0^2\epsilon(1+\tfrac{1}{2}\epsilon+\cdots), \tag{9}$$

where $P(x)$ is a projection factor discussed by Bohr *et al.*,[22] which is equal to 1 in the limit of weak coupling between core and particle, and $R_0$ is the mean nuclear radius. If the deformed nucleus is assumed to be an incompressible and uniformly charged ellipsoid bound by the surface $R=R_0[1+\frac{2}{3}\epsilon P_2(\cos\theta)]$, we find

$$\begin{aligned}\Delta R/R&=\tfrac{1}{2}(R_e^2-R_g^2)/R_g^2\\&=2(\epsilon_e^2-\epsilon_g^2)/9.\end{aligned} \tag{10}$$

Since $Q$ is known for both states[13] of $I^{127}$, the result is $\Delta R/R=-3\times10^{-4}$. This is about a factor of 10 larger than the experimental value, but it shows the right sign. The values of the quadrupole interaction agree within the limits of experimental error with the quadrupole resonance measurements of Herlach.[23] The electric field gradient (EFG) is directly related to the electronic distribution inside the molecule. According to Townes and Dailey,[24] one may express the measured electric field gradient $eq_{\text{expt}}$ in the following way:

$$eq_{\text{expt}}=U_p\tfrac{4}{5}e\langle 1/r^3\rangle, \tag{11}$$

where $\frac{4}{5}e\langle 1/r^3\rangle$ is the EFG due to the lowest $p$ hole state in the closed shell,[25] and $U_p$ is a quantity depending on the electronic structure of the atomic environment. $U_p$ is related to the $p$-electron distribution in $x$, $y$, and $z$ direction through

$$U_p=\tfrac{1}{2}(U_x+U_y)-U_z, \tag{12}$$

and to Eq. (4) through

$$h_{5p}=U_x+U_y+U_z. \tag{13}$$

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[21] P. Barrett and D. A. Shirley, Phys. Rev. **131,** 123 (1963).

[22] A. Bohr and B. Mottelson, Kgl. Danske Videnskab. Selskab, Mat.-Fys. Medd. **27,** No. 16 (1953).

[23] F. Herlach, Helv. Phys. Acta **34,** 305 (1961).

[24] C. H. Townes and B. P. Dailey, J. Chem. Phys. **17,** 782 (1948).

[25] R. G. Barnes and W. V. Smith, Phys. Rev. **93,** 95 (1954).

TABLE III. Experimental values of the IS and QS of various iodine compounds containing $I^{125}$, measured as sources against a ZnTe absorber. The observed linewidths were corrected for finite absorber thickness according to Eq. (2) and the ratio $\Gamma_{\text{corr}}/\Gamma_{\text{nat}}$ is given, taking $2\Gamma_{\text{nat}}=5.32$ mm/sec. The spectra of $NaIO_3$, $NaIO_3 \cdot H_2O$, $Na_2Mn(IO_3)_6$, and $NaIO_4$ were fitted with two double-line pairs and the isomer shifts, quadrupole splittings, and intensity ratios of the resulting two components are given separately. In order to compare the isomer shifts given in this table with those of Table II, the sign has to be reversed and the IS of ZnTe must be subtracted. Asterisks indicate that the QS is uncertain.

| Sources | $\Gamma_{\text{corr}}/\Gamma_{\text{nat}}$ | Isomer shift (mm/sec) Component 1 | Isomer shift (mm/sec) Component 2 | $\frac{1}{4}(e^2qQ)$ (mm/sec) Component 1 | $\frac{1}{4}(e^2qQ)$ (mm/sec) Component 2 | Intensity ratio Component 1/ Component 2 |
|---|---|---|---|---|---|---|
| $NaIO_3$ | $1.50\pm0.04$ | $-0.45\pm0.15$ | $+0.85\pm0.15$ | $3.2\pm0.1$ | $1.6\pm0.2$ | $2.0\pm0.2$ |
| $NaIO_3 \cdot H_2O$ | $1.35\pm0.07$ | $-0.43\pm0.20$ | $+0.85\pm0.10$ | $3.3\pm0.2$ | $1.5\pm0.2$ | $2.4\pm0.5$ |
| $Na_2Mn(IO_3)_6$ | $1.20\pm0.04$ | $-0.42\pm0.10$ | $+0.80\pm0.15$ | $3.0\pm0.1$ | $0.5\pm0.5$ | $2.0\pm0.1$ |
| $NaIO_4$ | $1.50\pm0.04$ | $-0.47\pm0.1$ | $+0.90\pm0.20$ | $3.2\pm0.2$ | $0.7\pm0.5$ | $2.1\pm0.2$ |
| NaI | $1.88\pm0.11$ | $-0.28\pm0.1$ | | * | | |
| KI | $1.20\pm0.15$ | $-0.43\pm0.2$ | | 0 | | |
| $Na_3H_2IO_6$ | $2.03\pm0.04$ | $+0.88\pm0.02$ | | * | | |

In the iodates the asymmetry parameter $\eta$ is very close to zero ($U_x=U_y$), which is consistent with their molecular structure (iodine-oxygen bonding angles close to 90°),[26] and the bonds will contain chiefly $5p$ electrons ($S^2 \simeq 0$). Then Eq. (12) gives a $U_p$ of $0.47\pm0.02$ for the iodate salts. With the above value $\Delta Z=0.75\pm0.15$ and Eqs. (12) and (13), we may calculate the $p$ electron density in the different directions as $U_x=U_y=1.43$ and $U_z=0.96$. From these results we conclude that the bonding of the iodine in the iodates is primarily along the $z$ direction.

### B. Source of $I^{125}$ in Cu

Spectra obtained with absorbers of various tellurium compounds are shown in Figs. 2–4. Values of the IS, QS, and linewidth for Te and Te compounds at liquid-nitrogen temperature are given in Table II. (Results of other authors are included.[27,28]) A recoil-free fraction of 0.13, corresponding to a Debye temperature $\Theta_D=125$°K is deduced for $I^{125}$ in copper. For the calibration of the IS scale, we proceed analogously to Sec. II A. The IS values considered are those of $TeO_2$, $Na_2TeO_3$, $TeO_3$, and $Na_2TeO_4$. The following configurations are accepted: $TeO_2$ ($p^2$ bonding; $S^2=0$; $m=2$),[12] $Na_2TeO_3$ ($p^2$ bonding; $S^2 \simeq 0$; $m=3$),[29] $TeO_3$ ($sp^2$ bonding; $S^2=0.33$; $m=3$),[30] and $Na_2TeO_4$ ($sp^3$ bonding; $S^2=0.25$; $m=4$).[30] The free $p$ orbital in $TeO_2$ and $TeO_3$ is assumed to make a $\pi$ bonding with oxygen and therefore receives a charge $\Delta p$. Equation (4) is then of the form

$$h_{5p}=m(1-S^2)\Delta Z+2-\Delta p. \qquad (14)$$

We have plotted IS values given in Tables I and II and in Refs. 13 and 17 in graphs comparing the values

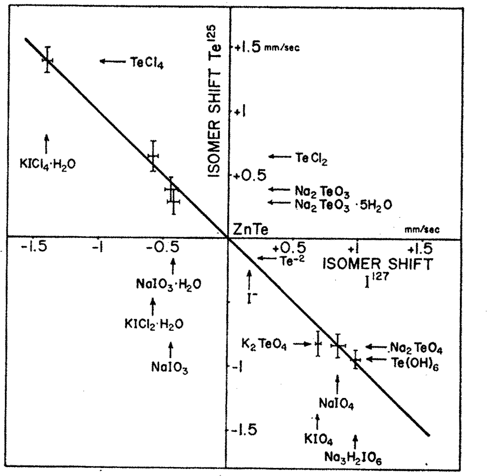

FIG. 5. Measured isomer shifts of iodine compounds are plotted on the horizontal axis relative to a source of $Te^{127m}$ in ZnTe. The isomer shifts of analogous tellurium compounds, measured against a source of $I^{125}$ in copper, are plotted on the vertical axis relative to a ZnTe absorber. The straight line drawn indicates that there is a linear relation between the isomer shifts of these compounds of the two elements.

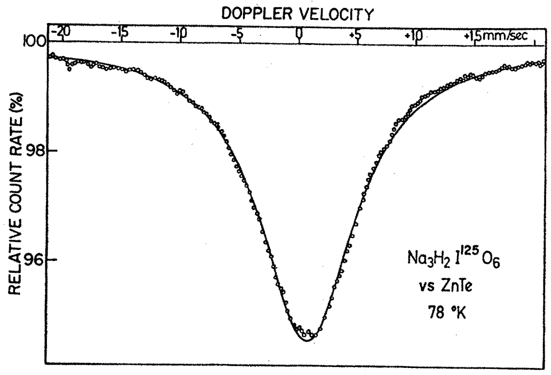

FIG. 6. Mössbauer spectrum at 78°K of a $Na_3H_2IO_6$ source versus a ZnTe absorber.

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[26] T. P. Das and E. L. Hahn, *Nuclear Quadrupole Resonance Spectroscopy* (Academic Press Inc., New York, 1958).

[27] A. B. Buyrn and L. Grodzins, Bull. Am. Phys. Soc. **8**, 43 (1963).

[28] E. P. Stepanov *et al.*, Phys. Letters **6**, 155 (1963).

[29] W. H. Zachariasen and H. E. Buckley, Phys. Rev. **37**, 1295 (1931).

[30] A. F. Wells, *Structural Inorganic Chemistry* (Clarendon Press, Oxford, England, 1962).

TABLE IV. Experimental values of the isomer shifts, quadrupole splittings, recoilless fractions, and corresponding Debye temperatures of $Sb^{125}$ in various antimony compounds, measured as sources against a ZnTe absorber. The observed linewidths are corrected for finite absorber thickness according to Eq. (2), and the ratio $\Gamma_{\mathrm{corr}}/\Gamma_{\mathrm{nat}}$ is given, taking $2\Gamma_{\mathrm{nat}}=5.32$ mm/sec. The errors in the values of the recoilless fractions and Debye temperatures are about 15%. Asterisks indicate that the QS is uncertain.

| Sources | $\Gamma_{\mathrm{corr}}/\Gamma_{\mathrm{nat}}$ | Isomer shift (mm/sec) | $\frac{1}{4}(e^2qQ)$ (mm/sec) | Recoilless fraction (%) | Debye temperature (°K) |
|---|---|---|---|---|---|
| $Sb_2O_3$ | 1.58±0.04 | +0.87±0.04 | 0 | 20.2 | 145 |
| $NaSbO_3$ | 1.50±0.04 | +0.97±0.08 | 0 | 47.5 | 210 |
| $SbCl_3$ | 1.43±0.04 | −0.9±0.1 | 2.8±1.0 | 16.4 | 135 |
| $KSbCl_5$ | 1.73±0.07 | −0.01±0.20 | * | 5.6 | 105 |
| $HSbCl_6$ | 1.73±0.07 | +0.02±0.20 | * | 1.5 | 95 |

for $I^{127}$, $I^{129}$, and $Te^{125}$ with each other. A linear relation is found not only between the isomer shifts of the iodine isotopes, but also between iodine and tellurium. This confirms the assumed similarity of these compounds. A ratio of $-0.65\pm0.05$ is derived for the IS ratio of $I^{127}$ to $I^{129}$, which is slightly different from the ratio of $-0.78\pm0.04$ obtained by Reddy *et al.*,[31] who measured only the IS of $Na_3H_2IO_6$. With the corrected value of Ref. 17 for $\Delta R/R$ of $I^{129}$ we obtain another value for the nuclear radius change in $I^{127}$ to $-3.4\times10^{-5}$ in good agreement with the value calculated in Sec. II A.

The relation between the IS of $I^{127}$ and $Te^{125}$ is shown in Fig. 5. From this proportionality we obtain the IS of the $n=5$ filled shell against $I^{125}$ in Cu as $\delta_0=-0.324$ mm/sec (Ref. 13 and Table II). The ratio $C(Te^{125})/C(I^{127})=-0.96\pm0.05$. By combining $\delta_0$ with Eqs. (4), (7), (8), and (14) we get $\Delta Z=0.77$, $\Delta p=0.13$, $S^2(Na_2TeO_3)=0.03$, and $C(Te^{125})=+1.61\pm0.32$ mm/sec. To extract out of this the change in the nuclear radius of $Te^{125}$ we approximate $|\psi_0(0)|^2$ with the value $1.0\times10^{27}$ cm$^{-3}$ calculated for $I^{127}$ with the Fermi-Segré formula, and obtain $\Delta R/R=+2.4\times10^{-5}$ for $Te^{125}$. On the other hand, with the derived ratio $C(Te^{125})/C(I^{127})$ and the nuclear radius change of $I^{127}$, a value of $+2.7\times10^{-5}$ results. The calculated ratio $C(Te^{125})/C(I^{127})$ gives $-0.91\pm0.18$, in reasonable agreement with the value above. Equations (9) and (10) combined with the quadrupole moment $Q_a(Te^{125})=-(0.19\pm0.02)$ b [32] give a value of $+3.7\times10^{-5}$ for $\Delta R/R$, which agrees fairly in magnitude and sign with the above value.

$Na_3H_2IO_6$ ($sp^3d^2$ bonding)[33] shows a large isomer shift compared to $NaIO_4$ (Table I). So does $Te(OH)_6$ ($sp^3d^2$ bonding)[12] compared to $Na_2TeO_4$ (Table II). This leads to the assumption that the 5*s* electrons of $Na_3H_2IO_6$ and $Te(OH)_6$ are shielded in addition by *d* electrons. This means that $Z_{\mathrm{eff}}$ of Eq. (4) has to be modified to $Z_{\mathrm{eff}}=7.25+0.35m\Delta Z-N_d\Delta d$, where $N_d$ is the number of effective *d* electrons and $\Delta d$ is the shielding of one *d* electron. Together with the corresponding values for $\Delta Z$ and $C$, we then obtain independently the values of 0.12 and 0.13 for $\Delta d$ of $Na_3H_2IO_6$ and $Te(OH)_6$,

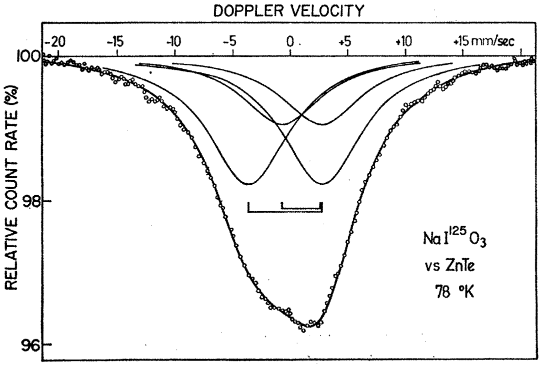

FIG. 7. Mössbauer spectrum at 78°K of a source $I^{125}$ in $NaIO_3$ versus an absorber of ZnTe. The line pair with the large QS, as shown, corresponds in IS and QS to $Na_2TeO_3$ and the pair with the small QS corresponds similarly to $TeO_3$.

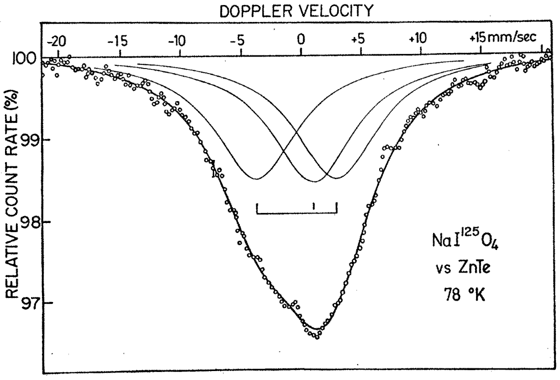

FIG. 8. Mössbauer spectrum at 78°K of a source of $I^{125}$ in $NaIO_4$ versus an absorber of ZnTe. The line pair with the QS, as shown, corresponds in IS and QS to $NaTeO_3$, and the single line corresponds similarly to $Na_2TeO_4$ (see also Ref. 34).

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[31] K. R. Reddy, F. de S. Barros, and S. de Benedetti, Phys. Letters **20**, 297 (1966).

[32] M. Pasternak and S. Bukspan, Phys. Rev. **163**, 297 (1967).

[33] L. Helmholz, J. Am. Chem. Soc. **59**, 2036 (1937).

respectively. The effective shielding of a $5d$ electron is therefore only about $\frac{1}{3}$ of the shielding of a $5p$ or $5s$ electron.

### C. Sources of $I^{125}$ in Iodine Compounds

The ME spectra of $I^{125}$ in various iodine compounds were studied using a single-line absorber of ZnTe (12 mg $Te^{125}/cm^2$). The spectra of $NaIO_3$, $Na_2Mn(IO_3)_6$, and $NaIO_4$ were composed of multiple lines. The results are given in Table III. Figure 6 shows a spectrum obtained from $Na_3H_2IO_6$. The IS differs considerably from that of the isoelectronic compound $Te(OH)_6$ and corresponds rather to the isomer shift of $Na_2TeO_4$, i.e., the Te atom most probably forms a $sp^3$ bond. Attempts were made to fit this relatively broadened spectrum (and also that of NaI) by assuming a small QS, but no definite results could be obtained.

The measurement of $NaIO_3$ against a Te absorber gave qualitatively the same spectrum as given in Ref. 6. The spectra of $NaIO_3$ and $NaIO_4$ against the ZnTe absorber are shown in Figs. 7 and 8, respectively. These measurements were repeated several times with independently prepared samples. No change in the spectra due to different preparation could be detected. The unresolved structure and the asymmetric shape of the spectra remained unchanged, down to liquid-helium temperature. The $K$-capture decay and the subsequent electronic rearrangements induce a distortion of the electron shell and hence of the bonding. Possible stable compounds (according to the starting compound) that the Te atom can form after the $K$ capture has taken place are $Na_2TeO_3$, $TeO_3$, and $Na_2TeO_4$, of which the values for IS and QS (equal intensities of the two lines) have been measured (see Table II). Successful attempts were made to fit the spectrum of $NaIO_3$ with two pairs of lines with symmetric quadrupole splitting, taking for one pair the QS and the IS of $Na_2TeO_3$. Out of the fit we obtained then the IS and the QS for a second pair as well as the intensities (see Fig. 7). The values for IS and QS of the less intense lines correspond to $TeO_3$ or $Na_2TeO_4$ or both. The errors given in Table III are mostly due to uncertainties arising from the fit. These results are not in agreement with the results of Violet *et al.*,[6] who assumed equal intensities of all resonance lines for their fit. Consequently, they derived isomer shifts and quadrupole splittings which could not be ascribed to possible stable tellurium compounds. We made no attempts to fit our spectra under the assumption of four equally intense resonance lines. Similar measurements of $Co^{57}$ in cobaltous compounds have shown that the higher charge states in almost all measured compounds are less intense and that this intensity can depend also on the preparation technique.[4,5] Although this does not have to be the case for the iodine compounds, it at least shows that one must be careful in predicting intensity ratios *a priori*.

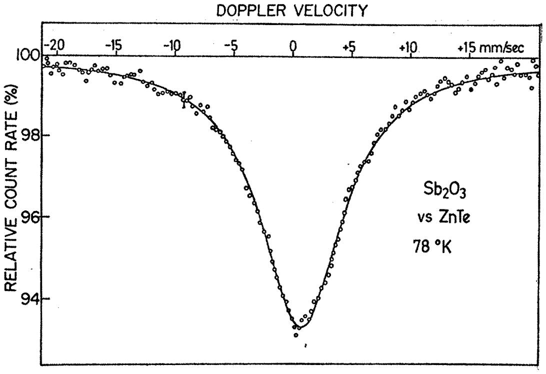

FIG. 9. Mössbauer spectrum at 78°K of a source of $Sb^{125}$ in $Sb_2O_3$ versus an absorber of ZnTe.

The spectrum of $NaIO_4$ can be fitted in the same way with a symmetric pair of lines corresponding to the QS of $Na_2TeO_3$ and a single line (or small QS)[34] corresponding to $Na_2TeO_4$ or $TeO_3$.

The results of these measurements appear to indicate that no higher valence states are established with a measurable intensity and that a description in terms of the $5s$ and $5p$ bonding mechanism can be applied to account for our experimental results. We propose the following alternative model. The recoil of the neutrino accompanying the $K$ capture and the following Auger processes disturb the relatively weak bonding (the weakness is indicated by the low Debye temperature) of the decaying atom to its neighboring atoms in the lattice. The newly created and still excited Te atom then locally forms a possible stable compound for itself. A new short-range lattice rearrangement has to take place in the $NaIO_4$ lattice to account for the observed QS; $NaIO_4$ measured as an absorber exhibits no such splitting (see Table I). In order to account for the 2:1 intensity ratio of the observed line pairs, we propose the following possible explanations.

*$NaIO_3$*. (a) $Na_2TeO_3$ and $TeO_3$ are produced in equal amounts following the $K$-capture decay. $TeO_3$ is, however, fairly isolated in the $NaIO_3$ lattice; hence the recoil-free fraction of 0.25, when measured against the $I^{125}$ in Cu source, may be reduced by about half. (b) $Na_2TeO_3$ is produced preferentially compared to $TeO_3$ because of the similarity of its lattice structure to $NaIO_3$. Therefore the observed intensity of the $TeO_3$ spectrum is reduced in spite of the higher $f$ factor (see Table II).

*$NaIO_4$*. The data indicate that in addition to $TeO_3$, $Na_2TeO_4$ is formed as well. From the above argument of similar lattice structure, the compound $Na_2TeO_4$ should be observed with higher probability than it is actually detected. This fact favors case (a) and indicates that the bonding containing only $p$ electrons is preferred in this process.

The ideal way of carrying out this type of investigation would be to combine the ME measurements with

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[34] Both cases allow equally good fits to the data.

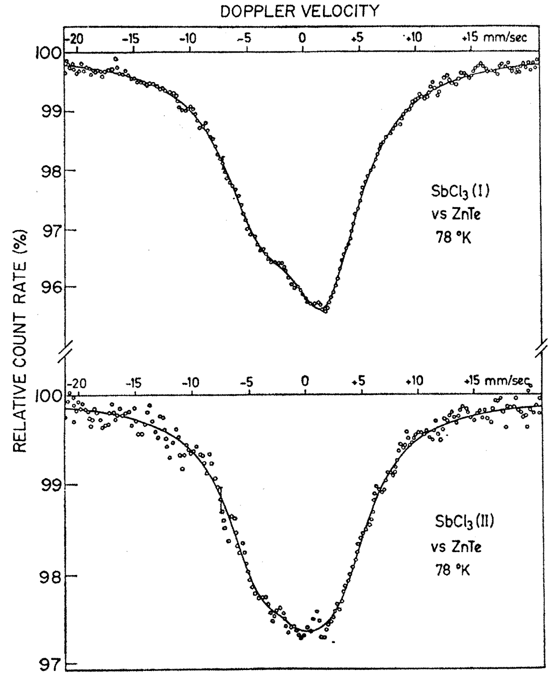

FIG. 10. Mössbauer spectra at 78°K of sources of $Sb^{125}$ in $SbCl_3$ versus an absorber of ZnTe. The observed asymmetric QS of $SbCl_3$(I) (small oriented crystallites) is a function of the mechanical treatment of the material. Making the source more polycrystalline, as in source $SbCl_3$(II), caused the asymmetry to vanish.

delayed-coincidence techniques (similar to those of Refs. 4 and 5). With this method, possible metastable states can be detected if they occur on the time scale of the lifetime of the nuclear level. The only possible coincidences that can be detected in this case are between x rays (about 30 keV) and the 35.5-keV $\gamma$ ray. We attempted such coincidence measurements. Because of the low energies involved and because of the short mean lifetime of the excited state ($2.09\times10^{-9}$ sec), the time resolution obtained was not good enough to achieve definite results

### D. $Sb^{125}$ in Antimony Compounds

The first excited state of $Te^{125}$ is also populated through the $\beta^-$ decay of $Sb^{125}$ and ME measurements can be performed using $Sb^{125}$ in antimony compounds. Combining such measurements with the results obtained with $I^{125}$ in iodine compounds, the difference in the influence of the two nuclear decays on the atomic bonding can be determined experimentally. The isoelectronic configuration, which exists, for example, between $NaIO_3$ and $Na_2TeO_3$, does not exist for the analogous antimony compounds ($Na_3SbO_3$ is unstable) because of the stability of the half-filled $5p$ shell. The values of IS and QS of all measured compounds are presented in Table IV. The compounds $NaSbO_3$ and $Sb_2O_3$ (Fig. 9) were measured against a ZnTe absorber. In both cases, a single-line spectrum was observed. The IS of $NaSbO_3$ and $Sb_2O_3$ corresponds to that of $TeO_3$; however, no QS was detected. No evidence was found that any other tellurium compounds are produced additionally. This suggests that the distortion of the bonding through the $\beta^-$ decay is indeed much smaller than in the case of $K$ capture.

The isomer shifts of $HSbCl_6$ and $KSbCl_6$ are practically equal to those of the telluride compounds (Table II). Initially both compounds have a $sp^3d^2$ configuration, and an IS corresponding to $Te(OH)_6$ might be expected. However, because a compound of the type $TeCl_6$ does not exist and $TeCl_4$ and $TeCl_2$ are not very stable compounds either (low $\Theta_D$), the Te atom apparently becomes separated from the chlorine atoms. The resulting electronic configuration, however, cannot be determined from our measurements.

$SbCl_3$ shows an asymmetric QS (top spectrum of Fig. 10) because it tends to form small single crystals with perferred orientation. The extent of the asymmetry depends on the treatment of the source and vanishes if the source is made more polycrystalline by mechanical means (bottom spectrum of Fig. 10). This indicates that there is no asymmetric Debye-Waller factor.[35] The same behavior is found in $TeCl_2$ (Fig. 4) and has also been reported for similar compounds.[16] The value for the IS of $SbCl_3$ lies between that of $TeCl_2$ and $TeCl_4$. However, because of the effect of mechanical treatment, no attempts were made to fit this spectrum with different lines.

## IV. CONCLUSIONS

From the measurements of a single-line $I^{127}$ source against iodine absorbers and of a single-line $Te^{125}$ source against tellurium absorbers, a linear relation between the isomer shifts of these two nuclear transitions was established. This confirmed the assumption of the isoelectronic structure of iodine and tellurium compounds. The measured isomer shifts are evaluated in terms of the different influence due to $5s$, $5p$, and $5d$ electrons in connection with hybrid configurations. This evaluation procedure gave independently consistent results for iodine and tellurium compounds. The results of the measurements with $I^{125}$ in iodine compounds show that through the $K$-capture process in compounds with relative weak bonding (and hence low Debye temperature) the original bonding is uncoupled and the daughter nucleus tellurium forms new bondings according to its stable configurations. These processes must occur on time scales less than or approximately equal to the nuclear lifetime because in the experiment only these new stable compounds are detected. Through $\beta^-$ decay, on the other hand, no such strong influence on the bonding takes place. The results of $HSbCl_6$ and $KSbCl_6$ might indicate, however, that some distortion takes

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[35] V. I. Goldanskii *et al.*, Phys. Rev. Letters **20,** 137 (1968); V. A. Brynkanov *et al.*, Zh. Eksperim. i Teor. Fiz. **43,** 448 (1962) [English transl.: Soviet Phys. —JETP **16,** 321 (1963)].

place which is only detectable in compounds of very low Debye temperatures.

From these results, conclusions can be drawn to explain qualitatively the observed effects of $Co^{57}$ in cobaltous compounds.[4,5] In the perfectly stoichiometric compounds of $Co^{57}$ in $CoCl_2$, $CoSO_4$, and $(NH_4)_2Fe(SO_4)_2$, all of which have low Debye temperatures, ferrous and ferric ions are observed simultaneously.[5] In CoO doped with $Co^{57}$, which has a high Debye temperature, only $Fe^{2+}$ is observed if the lattice is of perfect stoichiometry.[36] On the other hand, in CoO and NiO samples, which contain cation vacancies, both $Fe^{2+}$ and $Fe^{3+}$ charge states are detected.[5]

This seems to indicate that the distortion through the $Co^{57}$ $K$ capture and subsequent processes is not large enough to destroy the relative strong bonding (high $\Theta_D$) of perfect compounds, and that higher valence states can only be stabilized if vacancies are present. On the other hand, $Fe^{3+}$ charge states can be established in compounds of perfect lattice structure (no vacancies) which have low $\Theta_D$. There the original bonding is decoupled and new types of bonding can be established. This interpretation is consistent with the experimental results and is able to solve most of the controversy concerning the origin of charge states in various compounds containing $Co^{57}$.

Measurements are in progress using $Te^{125m}$ in $Na_2TeO_3$, $TeO_3$, $Na_2TeO_4$, and other tellurium compounds in order to obtain further information about the processes involved.

## ACKNOWLEDGMENTS

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[36] H. N. Ok and J. G. Mullen, Phys. Rev. **168**, 550 (1968).

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# Effective Density of Phonon States for $NdCl_3$ from Vibronic Spectra and Applications to Ion-Lattice Interactions*

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An effective density of phonon states of $NdCl_3$ has been extracted from the vibronic spectra accompanying several electronic transitions of $Pr^{3+}$ and $Nd^{3+}$. The derived $g^*(\omega)$ has a very similar structure for all parent electronic transitions. Anomalies in the vibronic spectra occur for certain optical phonons, and are ascribed to interactions of pairs of $Nd^{3+}$ ions via the phonon field. Use is made of the derived $g^*(\omega)$ in explaining various features of phonon-induced relaxation.

## I. INTRODUCTION

CERTAIN phenomena arising from the interaction of paramagnetic ions with lattice vibrations are strongly dependent on the structure of the phonon frequency distribution function $g(\omega)$ of the particular host crystal. Examples are line broadening, multiphonon relaxation, and vibronic transitions. Therefore, it is essential to know the structure of $g(\omega)$. Common insulating rare-earth crystals have not been generally studied by inelastic neutron scattering. However, the vibronic spectra accompanying rare-earth electronic transitions provide important information regarding the density of phonon states, since the structure of the vibronics is related to the structure of $g(\omega)$.[1-4] In this study, we have extracted an effective density of phonon states $g^*(\omega)$ from several transitions of $Nd^{3+}$ and $Pr^{3+}$ in $NdCl_3$. Although this $g^*(\omega)$ is not intended to replace the detailed density of phonon states, it is nevertheless valuable, because it manifests those features of the true $g(\omega)$ which enter into ion-lattice interaction phenomena.

Although the approximations assumed are in most cases valid, there are irregularities for several particular vibronic transitions of $Nd^{3+}$ involving optical phonons. The energies of the phonons involved are precisely

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[1] W. M. Yen, W. C. Scott, and A. L. Schawlow, Phys. Rev. **136**, A271 (1964).

[2] M. V. Hobden, Phys. Letters **15**, 10 (1965).

[3] E. Cohen and H. W. Moos, Phys. Rev. **161**, 258 (1967); **161**, 268 (1967).

[4] G. F. Imbusch, dissertation, Stanford University, 1964 (unpublished).