PHYSICAL REVIEW B VOLUME 13, NUMBER 1 1 JANUARY 1976

Theory of the ^{125}Te nuclear quadrupole interaction and isomer shifts in tellurium, selenium, and sulfur*

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(Received 2 April 1975)

The electronic wave functions for the systems, tellurium chain and tellurium atom present as a substitutional impurity in a selenium chain and selenium and sulfur rings, are obtained by the extended Hückel procedure. Using these wave functions, the field gradients at the ^{125}Te nucleus in all these four systems is investigated. Very good agreement is found with Mössbauer nuclear quadrupole data in the tellurium chain, both with respect to the magnitude and sign of the quadrupole coupling constant and the asymmetry parameter. For the case ^{125}Te in the rings, the agreement with experiment for the quadrupole coupling constants is not as close but still quite good, the theoretical magnitudes being about 82% for both rings. The signs of the quadrupole coupling constant are not known in these systems, but the theoretical results indicate interestingly that the sign for the selenium ring is the same as in the tellurium chain but opposite in the case of sulfur. The asymmetry parameters are not available experimentally for the rings but are predicted to be very sizable, 0.87 and 0.98, respectively, for selenium and sulfur. For the selenium chain, the sign of the theoretical quadrupole coupling is found in agreement with experiment, but the magnitude is only about one-half the experimental value. The asymmetry parameter is predicted to only be 13% but there is no experimental value available for comparison. Possible reasons are discussed for the less satisfactory agreement with experiment for ^{125}Te in the selenium chain relative to the case of the tellurium chain and the rings. The ratio of the isomer shifts for ^{125}Te in selenium and sulfur ring referred to the tellurium chain is calculated and found to be in good agreement with experiment.

I. INTRODUCTION

There is continuing interest[1] in the understanding of the electronic structures of amorphous materials and in particular of tellurium, selenium, and sulfur, which occur in both crystalline and amorphous phases. Recent extensive experimental investigations[2,3] of the nuclear quadrupole interaction of ^{125}Te in these materials provide an opportunity to obtain valuable information regarding their electronic structures. A theoretical analysis of the ^{125}Te nuclear quadrupole interaction in selenium as well as tellurium and sulfur using calculated electronic structures would considerably strengthen the interpretations[3] of experimental data in amorphous and crystalline materials. In the present work, such a theoretical investigation is undertaken for the first time for ^{125}Te in tellurium and selenium chains and in rings of selenium and sulfur.

Considering the trigonal-chain structures of crystalline tellurium and selenium first, since tellurium is a semimetal and selenium a semiconductor with low conductivity, one expects the Fermi volume to consist of nearly filled Brillouin zones, as in the case[4,5] of antimony or bismuth. In antimony, it was found[5] that using a tight-binding approach based on orthogonalized atomic orbitals, one can obtain very good agreement with the experimental quadrupole coupling constant. In our first analysis[6] of the field-gradient tensor in tellurium, we did employ such an approach and found a theoretical result for the quadrupole coupling constant an order of magnitude smaller than experiment. This indicates then that in contrast to the situation in antimony, there is much more directed character in the electronic distribution in tellurium which is to be expected from its chain-like structure. One should therefore take account of the covalent binding between individual atoms in tellurium in obtaining the electronic wave functions to be used for the evaluation of the field-gradient tensor. This is also expected to be true for the cases of monoclinic selenium and orthorhombic sulfur as well as trigonal selenium.

For the ring structures of selenium and sulfur,[7] we have an assembly of eight atoms and we need the appropriate molecular wave functions for the electrons to calculate the electric field gradient at the ^{125}Te nucleus. For the sake of simplicity and since this is the first investigation of the quadrupole interaction in these systems, to obtain the molecular-orbital wave functions we have utilized the extended Hückel procedure,[8] which has been found to be quite successful for the explanation of hyperfine and magnetic properties[9] of large molecules. For the chains of tellurium and selenium, we have also carried out calculations of the field-gradient tensor using molecular orbitals obtained by the extended Hückel procedure for a number of different lengths and have obtained convergence for chain lengths of 21 and 29 atoms indicating that the result for the latter case should be representative of the infinite chain. We have also evaluated the ^{125}Te isomer shifts for these systems using the electronic wave functions we have obtained.

The procedure for calculation of wave functions and the electronic field-gradient tensor are described in Sec. II. Section III presents the results for the quadrupole coupling constants and isomer shifts, their comparison with experiment and discussion.

II. PROCEDURE

In the extended Hückel procedure, the molecular orbitals (MO) ϕ_μ are expressed as

$$\phi_\mu = \sum_j C_{\mu j} \chi_j \quad , \tag{1}$$

where $C_{\mu j}$ is the coefficient of the jth atomic orbital (AO) χ_j in the μth MO. The AO basis was chosen as real, involving ns, np_x, np_y, and np_z orbitals, with $n = 3$, 4, and 5 for sulfur, selenium, and tellurium, respectively. From the variational form of the one-electron Hartree-Fock equations for ϕ_μ, we arrive at the equations

$$\sum_j C_{\mu j}(\mathcal{H}_{kj} - E_\mu S_{kj}) = 0 \quad , \tag{2}$$

with

$$S_{kj} = \langle \chi_k | \chi_j \rangle \quad ,$$

$$\mathcal{H}_{kj} = \langle \chi_k | \mathcal{H} | \chi_j \rangle \quad .$$

In the EH procedure, the Wolfsberg-Helmholz expression[8] for the Hamiltonian matrix is given by

$$\mathcal{H}_{kj} = \tfrac{1}{2} \kappa S_{kj} (\mathcal{H}_{kk} + \mathcal{H}_{jj}) \tag{3}$$

with

$$\mathcal{H}_{jj} = \epsilon_j^0 + |q_l| (\epsilon_j^\pm - \epsilon_j^0) \; . \tag{4}$$

In Eq. (3), κ is an empirical constant for which the value $\kappa = 1.89$ has been found to be appropriate[8] for calculations involving large molecules. In the expression (4), ϵ_j^0 is the ionization energy of the free atom and ϵ_j^+, is the ionization energies of the positive and negative ions. The quantity q_l is the atomic charge on the lth atom and is obtained by the Mulliken expression

$$q_l = Z_l - \sum_\mu \sum_j \left[|C^l_{\mu j}|^2 + \sum_{m \neq l} \sum_k (C^l_{\mu j} C^m_{\mu k} S_{jk}) \right] n(\mu) \; , \tag{5}$$

with the sum over j referring to the atomic orbitals on atom l while the sum over k refers to the atomic orbitals on atom m. The sum over μ refers to the molecular orbitals, with $n(\mu) = 0$, 1, 2 depending on whether the particular MO is empty, singly occupied, or doubly occupied. Z_l is the core charge on the lth atom, i.e., is the difference between the nuclear charge and the number of core electrons on the atom.

The interactomic distances and angles involved in the calculation were taken from available structural data.[10] As mentioned earlier, the rings of selenium and sulfur consist of eight atoms whose AO have to be included in the MO expression in Eqs. (1) and (2). For the trigonal structure, in addition to the overlap integrals between AO on atoms on a single chain, we have also studied the overlap integrals between AO on atoms on neighboring chains. The latter overlap integrals were found to be rather small compared to those between AO on neighboring atoms on the same chain. It is therefore a good approximation[11] to neglect the chain-chain interactions in this calculation and obtain the wave functions for a single chain.

Once the appropriate electronic wave functions for the chains and rings are obtained, one can calculate the components of the field-gradient tensor by taking the expectation values of the appropriate operators. The ij component of the field-gradient tensor ($i, j = x, y, z$) is given by

$$V_{ij} = \sum_l Z_l \frac{(3 r_{il} r_{jl} - r_l^2 \delta_{ij})}{r_l^5} + \int \frac{\rho(\vec{r})(3 r_i r_j - r^2 \delta_{ij})}{r^5} \, d\tau \quad . \tag{6}$$

In Eq. (6), the summation is over the core charges at various atomic sites l, and the integration is over the electron distribution of the valence electrons on all the atoms. The electron distribution can be split up into

$$\rho(\vec{r}) = \sum_l \rho(\vec{r} - \vec{r}_l) \quad . \tag{7}$$

It was found from the Mulliken charge expression in Eq. (5) that the core charges Z_l are almost completely canceled by the electronic charge at distant ions due to the valence electrons, leading to nearly zero values of q_l. So one really only needs to carry out the integration in (6) using the atomic-orbital components of the central atom in the MO functions, ϕ_μ. By this procedure one obtains

$$q_{jj} = \frac{4}{5} \left\langle \frac{1}{r^3} \right\rangle \sum_\mu (2 C^2_{\mu p_i} - C^2_{\mu p_j} - C^2_{\mu p_k}) \tag{8}$$

and

$$q_{ij} = \frac{12}{5} \left\langle \frac{1}{r^3} \right\rangle \sum_\mu C_{\mu p_i} C_{\mu p_j} \; , \quad i \neq j \quad . \tag{9}$$

In Eqs. (8) and (9), p_i, p_j, and p_k refer to the $5p_x$, $5p_y$, and $5p_z$ orbitals on the central tellurium atom with i, j, and k being taken in cyclic order in Eq. (8). From Eqs. (8) and (9), the field-gradient-tensor components in cgs units with proper sign can be obtained by multiplication with $-ea_0^{-3}$, $-e$ being the charge of the electron and a_0 the Bohr radius.

TABLE I. Field-gradient-tensor parameters for ^{125}Te in tellurium and selenium chains.

Number of atoms	Tellurium chain $V_{z'z'}$ (10^{16} esu/cm^3)	Tellurium chain η	Selenium chain $V_{z'z'}$ (10^{16} esu/cm^3)	Selenium chain η
3	1.15	0.71		
7	−3.16	0.63		
11	−3.29	0.62	−2.01	0.13
21	−3.42	0.61	−2.08	0.13
29	−3.42	0.61	−2.08	0.13
Experiment (Ref. 2)	−3.07	0.64	−4.14	

The value of $\langle 1/r^3\rangle = 11.9335 a_0^{-3}$ for the tellurium $5p$ state is taken from published Hartree-Fock wave functions.[12] For comparison with experiment, one needs to obtain the field-gradient components in the principal-axis system, which can be obtained by diagonalizing the components given in the expressions in Eqs. (8) and (9). In the case of the chains of trigonal tellurium and selenium, it was possible to predict one of the principal axes for any atomic site by symmetry. This axis, which we have chosen here as the x axis, is perpendicular to the chain direction and along the bisector of the angle formed by the lines joining the atomic site to its two nearest neighbors. The other two principal axes were obtained through diagonalization of the field-gradient tensor. From the principal axis components $V_{z'z'}$, $V_{y'y'}$, $V_{x'x'}$ with the usual condition that $|V_{x'x'}| < |V_{y'y'}| < |V_{z'z'}|$, one can obtain the asymmetry parameter η defined by the relation

$$\eta = \left| \frac{V_{y'y'} - V_{x'x'}}{V_{z'z'}} \right| . \tag{10}$$

III. RESULTS AND DISCUSSION

In discussing our results and making comparisons with experiment, we shall first consider the case of trigonal tellurium and selenium. The results we have obtained for $V_{z'z'}$ and η for different chain lengths are presented in Table I. The results show a satisfactory convergence for 11, 21, and 29 atoms in both tellurium and selenium, indicating that the 29-atom result should be quite representative of the infinite chain. Considering the approximate nature of the extended Hückel approach, it is satisfying to find the correct sign[2,13] and very good agreement with the experimental magnitudes of $V_{z'z'}$ and η for pure tellurium chains. This good agreement with experiment indicates that the field gradient indeed owes its origin to the strong covalent bonding between the atoms on the chain. However, it should be noted that the field-gradient result for three atoms is significantly smaller in magnitude and of opposite sign compared to the result for the infinite chain; one has to consider the bonding of each atom with more than just nearest neighbors. Also, the results in Table I indicate that if one has broken chains present in amorphous materials or in other situations, that one should expect to see quite different field-gradient tensors for less than seven atoms in the chain, but that for seven atoms and longer chain lengths the field-gradient tensor should not be very different from the infinite chain.

For ^{125}Te in the selenium chain, the theoretical value of $V_{z'z'}$ is found to be about one-half of the experiment but with agreement in sign. There is no available experimental value for the asymmetry parameter η to compare with theory. It would be interesting to see when η is measured, if the predicted relatively smaller value of η in the selenium chain as compared to tellurium is borne out by experiment or not. In regards to the difference in magnitude between the theoretical and experimental $V_{z'z'}$ for the selenium chain, there could be a number of possible reasons. One reason could be that the tellurium atom does not enter substitutionally but at some interstitial position. Another possibility could be that, although the tellurium atom enters substitutionally, there are significant displacements of the neighboring selenium atoms due to the differences in radii of the tellurium and selenium atoms. Considering the dependence of the off-diagonal Hamiltonian matrix elements $\mathcal{H}_{kj}$ in Eq. (3) on the interatomic distance, through the overlap matrix elements S_{kj}, chain distortions involving displacement of atoms could produce significant changes in the wave functions and hence the field-gradient tensor to explain the difference with experiment.

In the cases of the rings of selenium and sulfur as hosts for the ^{125}Te nucleus, one might expect better agreement with experiment, since in contrast to the open-ended nature of the chain where structural distortion is more likely, the rings are closed structures which are less susceptible to distortions. This expectation is borne out by the results in Table II where good agreement is found with experiment for the magnitudes of $V_{z'z'}$ in the two cases as well as with the trend in going from selenium to sulfur. Additionally, the magnitudes

TABLE II. Field-gradient-tensor parameters for ^{125}Te in selenium and sulfur rings.

	$V_{z'z'}$ (10^{16} esu/cm^3)		
Host	Theory	Experiment	η
Selenium	−3.71	4.49 (Ref. 3)	0.87
Sulfur	3.89	4.73 (Ref. 2)	0.98

of the field gradients at ^{125}Te in the rings are seen from Tables I and II to be larger than in the chains, in agreement with experiment. There are no experimental data available for the asymmetry parameters in the cases of selenium and sulfur rings to compare with our results. Also it would be interesting to have measurements of the signs of the quadrupole coupling constants in the rings, since there is the interesting situation that the theoretically predicted signs for the two cases are opposite to each other, with the sign for the selenium ring agreeing with that in tellurium and selenium chains.

Finally we present a result for the isomer shift for ^{125}Te that can be compared with experiment. Since the isomer-shift constant, relating density differences to isomer shifts, is not accurately known for ^{125}Te, therefore, rather than consider the absolute isomer shifts for ^{125}Te between different systems, it is better to consider the ratio

$$\frac{|\psi(0)|^2_{\mathrm{Te}} - |\psi(0)|^2_{\mathrm{Se\ ring}}}{|\psi(0)|^2_{\mathrm{Te}} - |\psi(0)|^2_{\mathrm{S\ ring}}} = 0.59 \tag{11}$$

from our calculations in good agreement with the experimental value[2,3] of 0.74. This good agreement acts as a verification of the *s* characters of the electronic wave functions in these systems as compared to the *p* character in the case of quadrupole coupling data.

In conclusion, the study of the electronic wave functions for the tellurium atom in several environments has led to satisfactory explanation of available nuclear quadrupole coupling data for ^{125}Te particularly for trigonal tellurium with chain structure. For the cases in which atom enters as a substitutional impurity, the overall agreement of calculated ^{125}Te quadrupole coupling and isomer shift data with experiment indicates that one can use the extended Hückel procedure successfully for these systems and particularly in amorphous materials to obtain valuable information concerning the electronic structure of such systems. Additional experimental data are needed to verify the predicted asymmetry parameters and the signs in some of the systems studied.

ACKNOWLEDGMENT

The authors are very grateful to Professor P. Boolchand for many valuable discussions regarding the experimental Mössbauer data.

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[*] Supported by National Science Foundation.

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[11] It should be pointed out that while the nearest neighbors on adjacent chains are closer than second and further nearest neighbors on the same chain, retaining the latter in the extended Hückel calculation, while dropping fhe former, is not an inconsistency but rather a very essential feature of the calculation. The reason for this is that the distant atoms on the same chain, such as the second nearest neighbor, for example, even though they may be quite distant from the atom at a chosen origin, interact with it indirectly through their strong interaction with their own nearest neighbors, which in turn interact strongly with their nearest neighbors, leading to the delocalized behavior of electrons on the chain. In the present approximation of finite number of atoms on the chain, this delocalization leads to the set of valence-electron energy levels which reduces to bands in the infinite atom chain or Bloch approximation.

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