"Anomalous" variation of the Mossbauer isomer shift of Te^{125} in defective diamond-like semiconductors

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The Mossbauer isomer shift δ of Te^{125} decreases on a decrease of the electronegativity of the surrounding atoms in crystals of diamond-like semiconductors with imperfect crystal lattice structure. A correlation between δ and interatomic distances is found; δ increases with decreasing distance between atoms. It is suggested that such variation of δ may be due to the contribution of the wave functions of neighboring atoms participating in formation of molecular orbitals to the electron density at the Te nucleus.

The Mossbauer isomeric shift δ is connected with the change of the Coulomb interaction following a change of the electron density at the nucleus. In the atomic-orbital approximation, which is widely used to interpret the experimental results, it is proposed that the change δ is connected with a change in the density of the valence electrons of the Mossbauer atom itself. Therefore the change δ is determined mainly by the change in the density of the valence s-electrons, as a result of which the shift δ should increase with this density for nuclei whose radii increase on going to the excited state ($\Delta R/R > 0$)[1].

This approach makes it possible to explain qualitatively or semiquantitatively most experimental data on Mossbauer isomeric shifts. On the other hand, it is only a crude approximation of reality. In a solid, the electrons are collectivized to a lesser or greater degree, so that the wave functions of the valence electrons cannot, strictly speaking, be regarded as belonging to individual atoms. To take this into account, different variants of the molecular-orbital method have recently been used[2-4]. In the widely used approximation in which the molecular orbitals are constructed as linear combinations of atomic orbitals, the electron density at the nucleus can be represented as a sum of three terms: 1) the density of the electrons described by the wave function of the Mossbauer atom, 2) the density resulting from the valence electrons of the neighboring atoms, and 3) the overlap density. In the atomic-orbital approximation, one considers in fact only the first term. In the present article we report experimental results for which an explanation based on the atomic-orbital approximation is patently insufficient, and which apparently constitutes an example in which the change of δ is due mainly to the electron density connected with the last two terms (principally with the overlap density).

We have investigated the Mossbauer spectra of the 35.48-keV γ lines of Te^{125} in diamond-like semiconductors with defects. We expected a decrease of the electronegativity of the surrounding atoms to cause the shift δ to increase as a result of the increased reattraction of the valence electrons of the hybrid sp^3 orbitals to the Te atoms. Experiment revealed an opposite and "anomalous" change in the isomeric shift.

The spectra were investigated with a variable-velocity Mossbauer spectrometer based on the AI-256-1 multichannel analyzer. We used a $ZnTe^{125m}$ source. The investigated compounds were synthesized with tellurium enriched with Te^{125} (77.3%) by melting a stoichiometric mixture of the initial components at high temperature in evacuated quartz ampules. The compounds with aluminum were synthesized under the same conditions, but the components inside the quartz ampule were placed in a corundum crucible. The isotopically enriched tellurium was purified beforehand by recrystallization in a stream of hot hydrogen. The structure of the synthesized compounds was checked with a URS-50-IM x-ray diffractometer. The thickness of the absorbers in terms of the Te^{125} isotope was 1.8–2.5 mg/cm^2. In the measurements of the spectra, the source and the absorber were at 130°K. The moving unit was the source.

The quality of the measurements and the overall appearance of the spectra are illustrated in Fig. 1. In measurements with a source and absorber made of ZnTe, the width 2Γ of the unsplit line was 7.8 mm/sec. The measured spectra were reduced by least squares with a BÉSM-4 computer, using the program for the determination of the parameters of doublet Lorentz lines. The values obtained for the isomeric shift δ (relative to ZnTe) and of the quadrupole splitting Δ are listed in the table.

The crystal structure of the investigated substances is well known[5]. It is derived from the structure of chalcopyrite, one-quarter of the cation sublattice of which is unoccupied. The structure of $CdGa_2Te_4$, $ZnIn_2Te_4$, and $CdIn_2Te_4$ corresponds to the space group S_4^2, that of $ZnGa_2Te_4$ to the group S_4^2 or D_{2d}^{11}, and that of $ZnAl_2Te_4$ and $CdAl_2Te_4$ can be ascribed not only to S_4^2 and D_{2d}^{11}, but also to D_{2d}^1 and D_{2d}^9[5]. The short-

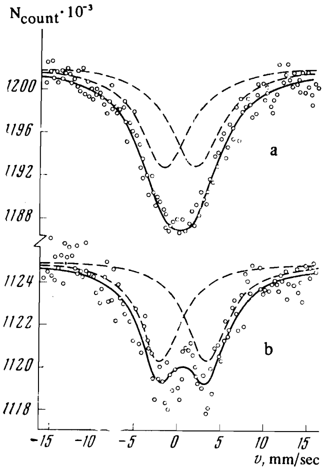

FIG. 1. Mossbauer spectra: a—$ZnGa_2Te_4$, b—$CdAl_2Te_4$. The figure illustrates the separation of the doublet components.

Experimental values of the isomeric shift δ (relative to ZnTe) and of the quadrupole splitting Δ.

Compound	δ, mm/sec	Δ, mm/sec	Compound	δ, mm/sec	Δ, mm/sec
$ZnAl_2Te_4$	0,73±0,11	6,4±0.2	$CdAl_2Te_4$	0,56±0,15	5,6±0,2
$ZnGa_2Te_4$	0,23±0,05	3,5±0.2	$CdGa_2Te_4$	0,23±0,13	3,4±0.2
$ZnIn_2Te_4$	0.17±0,05	3.7±0,2	$CdIn_2Te_4$	0.07±0.15	3,2±0,3

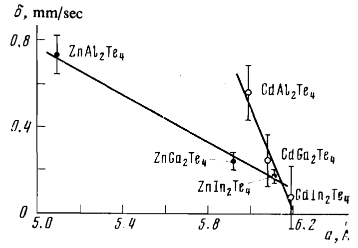

FIG. 2. Correlation between the isomeric shift δ and the interatomic distances.

range order is characterized in all cases by tetrahedral coordination. The hybrid sp^3 orbitals, which are directed towards the vacancies and are occupied by unshared pairs of electrons, are regarded formally as forming a chemical bond with the vacancy.

From the general expression for the Mossbauer isomeric shift[1] and from results of calculation of the influence of screening on the electron densities of the core electrons and of the valence electrons at the nucleus[6], with allowance for the results of estimation of $\Delta R/R$[7], we obtain for the isomeric shift of Te^{125} in the atomic-orbital approximation the formula (δ is in mm/sec):

$$\delta \approx 5[(0.983n_{s1} - 0.065n_{s1}^2 - 0.056n_{s1}n_{p1}) - (0.983n_{s2} - 0.065n_{s2}^2 - 0.056n_{s2}n_{p2})], \tag{1}$$

where n_{s1}, n_{s2}, n_{p1}, and n_{p2} stand for the populations of the s and p orbitals for the Te atoms in the two compared compounds.

The electronegativity increases in the series In-Ga-Al[8]. Therefore the attraction of the coupling electron cloud towards the T atom in the bonds formed by sp^3 electrons should become enhanced on going from the Al-Te bonds to the Ga-Te and In-Te bonds. A corresponding increase should also take place in the density of the s-electrons at the Te nucleus, and since $\Delta R/R$ is positive[7], the isomeric shift should also increase. It is seen from the table that experiment reveals a decrease of δ. The quadrupole splitting Δ changes here as expected, namely it decreases on going from compounds containing Al to compounds with Ga and In, since the number of unbalanced sp^3 electrons decreases[9].

It is seen from (1) that when n_{s1} increases ($n_{s1} \geq n_{s2}$) the value of δ can increase only if n_p decreases strongly at the same time. No such decrease is obtained if the condition $n_p = 3n_s$ is satisfied. If we forgo this condition, then δ should be most sensitive to n_p when n_s remains practically unchanged. Then $\partial\delta/\delta n_p|_{n_s=\text{const}} \approx -0.3n_s$ [mm/sec]. Even in this extreme case, the observed differences of δ between the pairs $ZnAl_2Te_4$ – $ZnIn_2Te_4$ and $CdAl_2Te_4$ – $CdIn_2Te_4$ (see the table) can be explained only if n_p changes by 1.5–2 units. The effective charges should change correspondingly. Such a large change in the effective charges of the Te atoms can obviously not be regarded as realistic.

Calculations[2] with allowance for the exponents of the wave functions of the neighboring atoms show that the electron density at the nucleus should increase rapidly when the atoms come closer together. This is probably the explanation for the observed "anomalous" behavior of δ in the investigated crystals.

From estimates with the aid of the wave functions of Herman and Skillman[10] it follows that the direct contribution of the "tails" of the wave functions of the neighboring atoms to the electron density at the nucleus is of the order of 1% in comparison with the density produced by one valence s-electron, and the contribution due to the overlap can amount to several dozen percent. Both contributions should increase rapidly when the atoms come closer together (more rapidly than $1/r^3$, where r is the interatomic distance).

Figure 2 shows the correlation between δ and the lattice constant a (the values of a were taken from[5], page 172). We see that smaller values of a correspond to larger values of δ. Thus, the experimental data should apparently be regarded as an illustration of how an increase in the density of the 5s electrons at Te nuclei is more than offset, as a result of direct reattraction, by the decrease of the electron density connected with exponents of the wave functions of the neighboring atoms that participate in the formation of the molecular orbitals when the interatomic distances are increased.

Many attempts have been made to estimate the effective electric charges e^{eff} of atoms in crystals with tetrahedral coordination (for example Sn^{119}[11] or Sb^{121}[12]) by measuring the values of δ, and these attempts yielded reasonable values of e^{eff}. Our present results show that this method of determining e^{eff} cannot be used in the case of the Te atoms.

It should be noted that an "anomalous" change of the δ of Te^{125} is also observed for binary defective diamond-like compounds in the series Al_2Te_3 – Ga_2Te_3 – In_2Te_3[13-14], and that the decrease of δ likewise correlates with the increase of the interatomic distances.

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