conservative nonlinear oscillator.

6) The numerical computations were carried out at the computing center of the Physicotechnical Low-Temperature Institute of the Academy of Sciences of the Ukrainian SSR by A. A. Motornaya and V. I. Khatuntsev.

7) Such a magnetization distribution resembles a "spherical domain." We should only bear in mind that, in contrast to the conventional theory of cylindrical domains in thin films, our analysis has been carried out without allowance for the magnetic-dipole interaction.

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Effect of atoms of second coordination sphere on the Mössbauer spectra of ^{119}Sn in diamondlike crystals

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We investigated the Mössbauer spectra of ^{119}Sn in solid solution of diamondlike semiconductors $(\mathrm{Cu_2SnS_3})_x$–$(3\mathrm{ZnS})_{1-x}$ ($x = 1/16$ to 1) and $(\mathrm{Cu_2SnS_3})_x$–$(3\mathrm{CdS})_{1-x}$ ($x = 3/16$ to 1). At values $x < 3/4$, when the probability of the appearance of the tin atoms in the second coordination sphere of the Mössbauer atom is low, the spectra consist of one somewhat broadened line, the parameters of which are practically independent of x. At values $x \geq 3/4$, when a certain fraction of the Mössbauer atoms in the second coordination sphere acquire tin atoms, the line begins to broaden and is transformed into a doublet with further increase of x, while the isomeric shift increases. The results show that large displacements of the electron charges can be induced by the atoms of the second coordination sphere in valence bonds of the atoms situated at the sites of a diamondlike crystal. The observed maximal values of the quadrupole splitting connected with the induce displacement of the electron charges are equivalent to the value of the electric field intensity gradient produced at the nucleus by approximately 1/3 of the unbalanced sp^3 electron. The largest displacements, which lead to a measurable isomeric shift and to a quadrupole splitting of the Mössbauer spectrum line is to be expected in those cases when the second coordination sphere contains atoms elements from far removed groups of the periodic system.

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1. INTRODUCTION

The influence exerted on the structure of the Mössbauer spectrum by atoms that are not directly connected with the Mössbauer atom was observed in tin-organic compounds.[1,2] It was observed in those cases when an atom having large electronegativity or a group of atoms having strongly polar properties is joined to a ligand connected with the Mössbauer atom, and it was attributed to a displacement of the electronic charges of the molecule towards the electronegative center (to the induction effect).

Highly suitable objects for the study of the redistributions of the electronic charges due to the appearance of a great variety of atoms near the Mössbauer atom and at various distances from it, are a complex diamondlike semiconductors.[3,4] In contrast to tin-organic compounds, where the interpretation of the results is frequently made difficult by the lack of structural data, the crystal structures of many diamondlike semiconductors are well known; short-range order is characterized by tetragonal symmetry, while in the case of long-range order the crystal lattices are most frequently of the sphalerite, chalcopyrite, or wurtzite type. In these cases when new complex compounds are synthesized or their solid solutions are produced, the crystal structure is easily obtained by x-ray diffraction. An exceptionally favorable circumstance is the

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possibility of formation of a tremendous number of isostructural solid solutions of diamondlike semiconductors, for it is precisely in such solutions that one can produce for the Mössbauer atom a great variety of environments in the first, second, and more remote coordination spheres.

The idea that the atoms of the second coordination sphere influence the parameters of the Mössbauer spectrum of ^{119}Sn atoms contained in a crystal of a complex diamondlike semiconductor was advanced in the interpretation of the small difference of the isomeric shifts (0.03–0.04 mm/sec) for the compounds $ZnSnAs_2$ and $CdSnAs_2$, in which the tin atoms are directly bound only to the aresenic atoms.[5] This explanation was proposed[6,7] also for the description of the quadrupole splitting observed in the Mössbaer spectra of Cu_2SnS_3, Cu_2SnSe_3 and Cu_2SnTe_3,[6–8] where each tin atom has a tetrahedral surrounding of four chalcogen atoms. However, the large value of the quadrupole splitting (1.07 mm/sec for Cu_2SnS_3[6,7]), was surprising.

We report here a successive investigation of the inductive influence on the parameters of the Mössbauer spectrum of ^{119}Sn contained in a diamondlike crystal of complex composition, by replacing certain atoms of the second coordination sphere by atoms of another chemical element. We studied for this purpose the Mössbauer spectra of the solid solutions $(Cu_2SnS_3)_x$–$(3ZnS)_{1-x}$ and $(Cu_2SnS_3)_x$–$(3CdS)_{1-x}$.

2. PROCEDURE AND EXPERIMENTAL RESULTS

The compounds were synthesized by fusing the components (chemical elements) in vacuum in sealed quartz ampoules. We used tin enriched with ^{119}Sn. It was mixed with tin of natural isotopic composition in a ratio such that Mössbauer absorbers of equal thickness had also equal thicknesses relative to ^{119}Sn(~1 mg/cm^2). The crystal structure of the synthesized compounds was verified against x-ray diffraction patterns. The compounds $(CuSnS_3)_x$–$(3ZnS)_{1-x}$ had a cubic lattice of the sphalerite type in the entire range of concentrations ($x=\frac{1}{16}$ to 1) (the lattice parameter a ranged from 0.542 to 0.544 nm as a function of x). The crystal structure of the synthesized compounds of the system $(Cu_2SnS_3)_x$–$(3CdS)_{1-x}$ depended on the concentration: at values $x<\frac{1}{8}$ these compounds had a hexagonal lattice of the wurtzite type, and at $x=1$ a cubic lattice of the sphalerite type, while at the remaining values of x they had a tetragonal lattice of the chalcopyrite type.

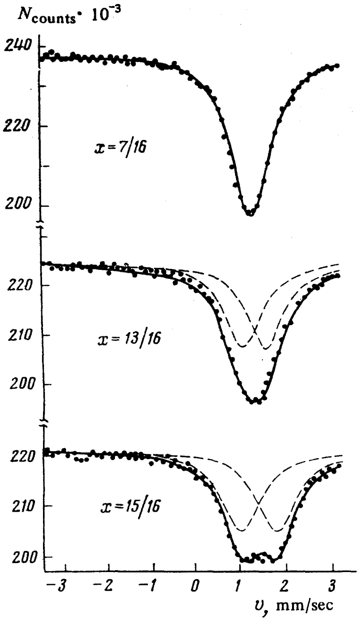

FIG. 1. Examples of Mössbauer spectra of ^{119}Sn in the compounds $(Cu_2SnS_3)_x-(3ZnS)_{1-x}$.

TABLE I.

x	δ, mm/sec	2Γ, mm/sec	Δ, mm/sec	Average number of atoms in second coordination sphere		
				Cu	Zn	Sn
	$(Cu_2SnS_3)_x-(3ZnS)_{1-x}$					
1/16	1.41±0.01	1.07±0.02		0.5	11.5	–
2/8	1.40±0.01	1.06±0.02		1.0	11.0	–
3/16	1.42±0.01	1.08±0.02		1.6	10.4	–
1/4	1.43±0.01	1.09±0.02		2.2	9.8	–
3/8	1.40±0.01	1.09±0.02		3.4	8.6	–
7/16	1.41±0.01	1.04±0.02		4.1	7.9	–
1/2	1.42±0.01	1.07±0.02		4.8	7.2	–
9/16	1.41±0.01	1.08±0.02		5.5	6.5	–
5/8	1.42±0.01	1.09±0.02		6.3	5.7	–
11/16	1.43±0.01	1.10±0.02		7.1	4.9	–
3/4	1.43±0.01	1.20±0.02	0.47±0.02	8.0	4.0	–
13/16	1.44±0.01	1.30±0.02	0.55±0.02	8.7	3.0	0.3
7/8	1.47±0.01	1.45±0.02	0.69±0.02	9.3	2.0	0.7
15/16	1.51±0.01	1.55±0.02	0.84±0.02	10.0	1.0	1.0
1	1.58±0.01	1.90±0.02	1.07±0.02	10.7	–	1.3
	$(Cu_2SnS_3)_x-(3CdS)_{1-x}$					
3/16	1.44±0.01	1.01±0.02		1.6	10.4	–
3/8	1.43±0.01	1.00±0.02		3.4	8.6	–
3/5	1.41±0.01	0.98±0.02		6.0	6.0	–
3/4	1.45±0.01	1.02±0.02		8.0	4.0	–
9/10	1.53±0.01		0.83±0.02	9.6	1.6	0.8
1	1.60±0.01		1.07±0.02	10.7	–	1.3

Note. The indicated errors do not include the systematic error due to the inaccurate graduation of the spectrometer scale.

The Mössbauer spectra were measured with a spectrometer with constant acceleration and registered with an AI-256-1 multichannel analyzer. We used a calcium stannite $Ca^{119m}SnO_3$ source. The source and absorber were at room temperature. The spectra were reduced with a BÉSM-4 computer using the program for the determination of the parameters of singlet and doublet lines.

Typical spectra are shown in Fig. 1. Their parameters (the isomeric shift δ, the line width 2Γ, the quadrupole splitting Δ) are listed in Table I.

3. DISCUSSION OF RESULTS AND CONCLUSIONS

In the range of concentrations x from $\frac{1}{16}$ to $\frac{3}{4}$, the spectrum consists of a single line, whose width and isomeric shift are practically independent of x. The width of this line is somewhat larger than the width measured with the same source and with an absorber of metallic white tin (0.90±0.02 mm/sec). Taking into account the small quadrupole splitting observed in metallic tin[9,10] and the additional line broadening in the investigated compounds, we can assume the existence of an unresolved quadrupole splitting Δ up to 0.3–0.45 mm/sec.

With further increase of x the line broadens and turns into a doublet, while the isomeric shift moves in the positive direction. The qualitative dependence of the Mössbauer-spectrum parameters on x is the same for both systems, despite the presence in the $(Cu_2SnS_3)_x$–$(3CdS)_{1-x}$ system of phase transitions in which the crystal-lattice symmetry is altered. The lowering of the lattice symmetry for the given system in the $\frac{3}{4}$ range does not lead to an additional quadrupole splitting. This shows that the electric field gradient produced at the nucleus by the lattice ions is negligibly small in the considered compounds in comparison with the gradient produced by the valence electrons.

In all the investigated compounds, the tin atoms in the first coordination sphere are surrounded in similar fashion by four sulfur atoms. The numbers of the different atoms in the second coordination sphere depend on the concentration x. The mean values of these numbers are listed in the last columns of the table. It is seen that the parameters of the spectrum do not change in that concentration region in which only the ratio of the numbers of the copper and zinc atoms changes in the second coordination sphere. The appearance of a tin atom in the second coordination sphere produces at the ^{119}Sn nucleus an electric field gradient that splits the line into a duplet and increases the electron density at the nucleus, causing an increase of the isomeric shift.

The observed change of the parameters of the spectrum at concentrations $x > 0.75$ should be connected with the measurement of the ratio of the numbers of the tin atoms, in whose second coordination sphere the tin atoms are present or absent, and to a corresponding superposition of the doublet and singlet lines. At values $x > \frac{15}{16}$ two doublets can become superimposed, inasmuch as certain Mössbauer atoms have two tin atoms in the second coordination spheres.[6] The electric field gradient (EFG) asymmetry parameter η of such atoms, should be close to unity,[11] whereas for atoms with one neighboring tin atom it should be close to zero. Since the quadrupole splitting, at equal values of the maximal EFG component q_{zz}, is proportional to $(1+\eta^2/3)^{1/2}$,[9] it follows that Δ of the second doublet should be somewhat larger. The dependence of the isomeric shift on the concentration x shows that the appearance of one tin atom in the second coordination sphere leads to an increase of the isomeric shift by an amount ≈0.1 mm/sec. One cannot therefore exclude the possiblility that the doublets are shifted relative to one another by the same amount. Superposition of two unequal and somewhat shifted doublets can apparently be the reason of the additional increase of the distance between the peaks of the split line in the interval $x = \frac{15}{16}$ to 1.

The directions of the shift of the electronic charges in the valence bands, which leads (when a tin atom appears in the second coordination sphere) to unequal distribution of the electron density along the different axes of the tetrahedron and to the appearance of an electric field gradient at the nucleus of the central atom, are shown schematically in Fig. 2, where the valence bonds within the confines of two coordination spheres are mapped on a plane. So long as there is no tin atom in the second coordination sphere, the electronic charges are strongly shifted towards the sulfur atoms in the Cu–S and Zn–S bonds, and are shifted little in the Sn–S bond (this is evidenced by the value of the isomeric shift, which is only 0.4 mm/sec smaller than for tetrahedral grey tin α-Sn[6]). The sulfur atom in the bond with the tin atom that has replaced a copper or zinc atom cannot cause such a shift of the charge (owing to the large charge of the core of the tin atom and its larger electronegativity). The sulfur atom makes up the lacking electronic charge by shifting towards itself the charge from the central tin atom until an equilibrium symmetrical distribution of the electron density is established in both S–Sn bonds. Making some realistic assumptions concerning the distribution of the electronic charges at the atoms (i.e., assuming that the charges of all the atoms should be close to zero or that the charges of all the atoms of one chemical element are almost equal), we can readily calculate the charge shifts necessary to attain agreement with these assumptions. It turns out that the required charge shifts are quite large. The shifts of the electronic charges in the Sn–S bonds induce in turn a certain shift of the charges in other bands. The directions of these shifts are shown in Fig. 2 by dashed arrows.

A natural measure of the EFG at a nucleus is the gradient produced by one p-electron (or p-hole), while the measure of the quadrupole splitting is the splitting Δ_p associated with this EFG. In the case of diamond-like crystals it is convenient to use the value of the EFG connected with one sp^3 electron, $\Delta_{sp^3} \approx \frac{3}{4}\Delta_p$.[11,12] For ^{119}Sn we have $\Delta_{sp^3} \approx 3$ mm/sec.[6] It is seen from the table that the observed maximum values of Δ connected with the induced shift of the electronic charges are equivalent to the value of the EFG produced by approximately $\frac{1}{3}$ of the sp^3 electron.

Starting with the scheme of Fig. 2, we can explain also the observed isomeric shifts. There are two pos-

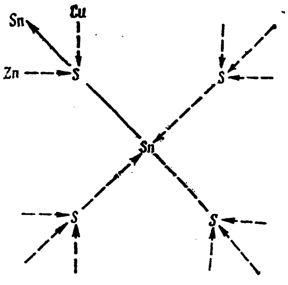

FIG. 2. Electronic-charge shifts induced in the valence bonds by a tin atom of the second coordination sphere and leading to unequal distribution of the electron distribution along the different axes of the tetrahedron and to the appearance of an electric field gradient at the nucleus of the central atom.

sible explanations: 1) the shift of the charge from the tin atom in one Sn–S bond is more than offset by the oppositely directed shift in the three other bonds, and the decisive influence on the increase of the isomeric shift and of the electron density at the nucleus is exerted by the increase in the population of the 5*s* orbital of the tin atom; 2) the shift of the charge from the tin atom in one bond is not compensated by an oppositely directed shift in the three others, and the shift of the *p* electrons and the electron prevails while the electron density at the nucleus is increased because of the decreased screening of the 5*s* electrons by the 5*p* electrons. The choice between these two explanations makes it possible to compare the values of the isomeric shift for the compounds of the two investigated systems. In the compounds $(Cu_2SnS_3)_x-(3CdS)_{1-x}$, owing to the smaller electronegativity of the cadmium atoms compared with zinc atoms,[13] the shift of the charge towards the sulfur atoms in the Cd–S bonds and the induced shift towards the tin atoms in the S–Sn bonds should be stronger than in compounds of the system with ZnS. If the predominant effect on the change of the electron density at the nucleus is furthermore exerted by the increase of the population of the 5*s* orbital of the tin, then the isomeric shift in the compounds $(Cu_2SnS_3)_x-(3CdS)_{1-x}$ should be somewhat larger, as is in fact demonstrated by the table (if we compare the values of the isomeric shift for identical values of x).

On the basis of the obtained experimental data and their analysis we can draw some more general conculsions.

1. In the chemical bonds of atoms situated at the sites of a diamondlike crystal, large shifts of the electronic charges can be induced by atoms of the second coordination sphere. The values of these shifts depend not only on the electronegativities of the atoms, but mainly by the charge of the core (the charge of the atom without the valence electrons) of the atom that causes the shifts. The largest shifts, which lead to a measurable isomeric shift and to a quadrupole splitting of the Mössbauer spectrum line, should be expected in those cases when the second coordination sphere contains atoms of elements from remote groups of the periodic system.

2. A study of the influence of the atoms of the second coordination sphere on the Mössbauer spectrum parameters yields a qualitative picture of the change in the distribution of the electron density in the valence bonds of the Mössbauer atom and its neighbors. In this manner it is possible to obtain information important for the understanding of the structure of the chemical bonds in crystals of a complicated composition, and also information on the distortions produced in the electron-density distributions by various impurity atoms and other crystal-lattice defects. More systematic investigations will apparently make it possible to obtain also the quantitative picture.

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