Effect of optical radiation on the parameters of the Mössbauer spectra of semiconductors

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Mössbauer investigations were made of optically excited single crystals of the semiconductors SnSe and $Pb_{0.2}Sn_{0.8}S$. It is shown for the first time ever that exposure of either sample to light increases appreciably the quadrupole splitting and decreases the shift of the Mössbauer line.

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The parameters of the Mössbauer spectra (the quadrupole splitting ΔE and the absorption line shift δE) depend on the state of the valence shell of the Mössbauer ion, so that changes in the electronic structure of the crystal can lead to a change in the parameters of the Mössbauer spectra. Arguments favoring the possible influence of electromagnetic radiation in the optical band on the parameters of the Mössbauer spectra of a crystal were advanced in[1,2]. There are, as yet, however, no known experiments that confirm this phenomenon.

A convenient object for the investigation of this question, in our opinion, is a semiconductor crystal with clearly pronounced internal photo-effect, so that one can hope to obtain noticeable distortions of the state of the valence shell of the ion under the influence of the optical radiation.

We have carried out Mössbauer investigations of the single crystals SnSe and $Pb_{0.2}Sn_{0.8}S$, which crystallize into an orthorhombic lattice of the SnS type and have a layered structure (space group P_{cmn}). The investigated samples have p-type conductivity with carrier density at room temperature 8.5×10^{17} and 2.8×10^{17} cm^{-3} for SnSe and $Pb_{0.2}Sn_{0.8}S$, respectively. The maximum value of the thermoelectric-power coefficient α is observed for the sample $Pb_{0.2}Sn_{0.8}S$ ($\alpha\cong660$ μV/deg at 350 K).

The Mössbauer measurements were made on single-crystal plates of thickness 20 ± 5 μm, cut perpendicular to the C axis and fastened to a beryllium substrate 220 μm thick. For each sample we obtained the Mössbauer spectra in darkness (the sample was placed in a light-tight wrapper) and at various degrees of exposure to white light. To obtain the Mössbauer spectra we used a constant-acceleration spectrometer based on the NTA-512B analyzer. The variation of the γ-source velocity was 0.05 mm/sec per channel, and the velocity drift did not exceed 0.05 mm/sec in 24 hours of continuous operation of the spectrometer. The γ source was $CaSn^{119m}O_3$ with activity 5 μCi.

The Mössbauer spectra of the sample are shown in Fig. 1. It is seen that the "dark" spectrum of each sample is a quadrupole doublet whose strong asymmetry is apparently due to the angular dependence of the intensity of the absorption lines in single crystals with clearly pronounced anisotropy.[3] The ratio of the areas under the

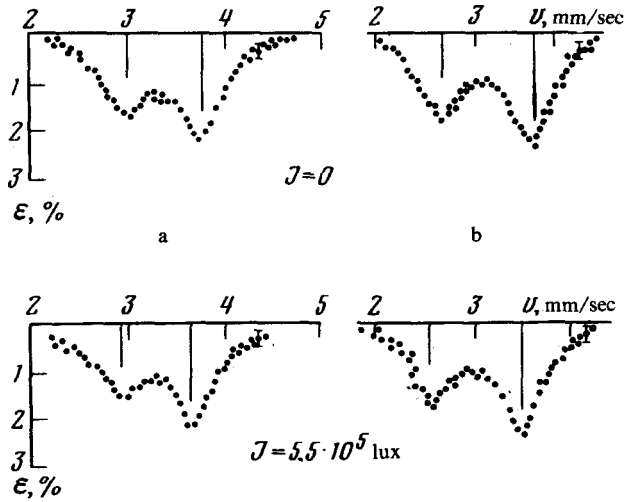

FIG. 1. Mössbauer spectra of single crystals of SnSe(a) and $Pb_{0.2}Sn_{0.8}S$ (b) obtained under various conditions.

right-hand and left-hand peaks of the Mössbauer spectra of the two samples, obtained after a computer reduction, were approximately equal and amounted to 0.53 for SnSe and 0.5 for $Pb_{0.2}Sn_{0.8}S$. The quadrupole splitting and the line shift for the two compounds are listed in Table I.

TABLE I. Parameters of Mössbauer spectra of unexposed samples of semiconducting single crystals and of those exposed to light.

Illumination, lux	Compound			
	SnSe		$Pb_{0.2}Sn_{0.8}S$	
	ΔE ±0.03 mm/sec	δ ±0.02 mm/sec	ΔE ±0.03 mm/sec	δ ±0.02 mm/sec
0	0.65	3.53	0.95	3.25
$1.8 \cdot 10^5$	0.71	3.39	0.97	3.14
$5.5 \cdot 10^5$	0.73	3.32	1.00	3.12
$7.0 \cdot 10^5$	0.74	3.29	1.06	3.11

When the Mössbauer spectra of the illuminated samples were obtained, the latter were placed in a stream of cold air, to prevent heating, and their temperature was monitored with a thermocouple soldered to the surface of the crystal. At all illuminations, the temperature on the sample surface did not exceed 30 °C.

The parameters of the Mössbauer spectra of SnSe and $Pb_{0.2}Sn_{0.8}S$ crystals, corresponding to different illuminations, are listed in Table I. The data obtained show that with increasing illumination the observed absorption-line shift is decreased and the quadrupole splitting is simultaneously increased. It is seen from the table that the changes of the quadrupole splitting are approximately the same for both single crystals ($\sim$0.1 mm/sec), whereas the largest changes of the shift ($\sim$0.2 mm/sec) are observed for the SnSe crystal. To eliminate any doubt that the spectrum parameter may be altered by heating, we performed special temperature measurements. They have shown that the shift δ changes by not more than 0.05 mm/sec in 100°, and the quadrupole splitting remains unchanged within the limits of the eperimental accuracy. Thus, the changes were observed in the parameters of the Mössbauer spectra of single crystals attests to the fact that optical radiation causes transitions of the electrons from the valence to the conduction band, resulting in changes in the electron density and in the symmetry of the electric field at the nucleus of the Mössbauer isotopes.

The observed phenomenon may be useful for the study of the nature of the photoeffect in semiconductors.

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[1]I.B. Bersuker and V.A. Kovarskiĭ, Pis'ma Zh. Eksp. Teor. Fiz. **2**, 286 (1965) [JETP Lett. **2**, 286 (1965)].
[2]Sh.Sh. Bashkirov and E.K. Sadykov, Pis'ma Zh. Eksp. Teor. Fiz. **3**, 240 (1966) [JETP Lett. **3**, 154 (1966)].
[3]Khimicheskie primeneneiya messbauerovskoĭ spektroskopii (Chemical Applications of Mössbauer Spectroscopy (Collection of translations, ed. by V.I. Gol'danskii), Mir, 1968.
[4]E.M. Latypov, N.R. Faĭzullina, V.P. Savel'ev, and R.Yu. Davletshin, Izv. Akad. Nauk SSSR Ser. Neorg. Mater. **12**, 206 (1976).