

Investigation of the influence of a crystal-to-glass transition on the local structure of a semiconductor by the Mössbauer effect on the nuclei ^{125}Te , ^{127}I , and ^{129}I (^{129m}Te)

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It is established by Mössbauer spectroscopy that for compounds obtained in vitreous form in the hard quenching regime the crystal to glass transition is accompanied by a change of the local structure.

The crystal to glass transition is accompanied by changes in many physical properties of semiconductors. It is assumed that the main cause of these changes is the vanishing of the long-range order upon amorphization, but one cannot exclude the possibility that this transition may be accompanied by a restructuring of the short-range order. In spite of the importance of research on the influence of the crystal to glass transition on the local structure of semiconducting compounds, the number of studies in this direction is small, mainly because of experimental difficulties.

The Mössbauer-spectrum parameters are sensitive mainly to the nearest surrounding of the investigated atoms, and it is therefore obvious that Mössbauer spectroscopy can be promising for the study of the structure of disordered systems. We report here the results of a Mössbauer investigation of the influence of the crystal to glass transition on the local surrounding of the atoms ^{125}Te , ^{127}I , and ^{129}I (^{129m}Te) in the semiconducting compounds As_2Te_3 , $\text{As}_4\text{Te}_5\text{I}_2$, AsSI and AsSeI .

The compounds were synthesized by fusing the original components in evacuated quartz ampules. The vitreous samples were obtained by quenching the melts in ice water (in the case of As_2Te_3 —by pouring the melt on a metallic plate), while the crystalline samples were obtained by prolonged annealing of the vitreous alloys.

The Mössbauer spectra were obtained with an electrodynamic-type spectrometer. The sources in the case of ^{125}Te and ^{127}I were ZnTe^{125m} and ZnTe^{127m} , respectively, and in the case of ^{129}I (^{129m}Te) the sources were the investigated compounds (they were synthesized using radioactive ^{129m}Te). In the case of ^{125}Te and ^{127}I the absorbers were the investigated samples (of thickness 3 mg/cm² in terms of ^{125}Te and 20 mg/cm² in terms of ^{127}I), and in the case of ^{129}I (^{129m}Te) the absorber was KI^{129} (thickness 15 mg/cm² in terms of ^{129}I). The spectra of ^{125}Te and of ^{129}I (^{129m}Te) were plotted at 80°K, and those of ^{127}I at 4, 2°K. The results of the reduction of the experimental data are given in the table.

If the crystal to glass transition is accompanied by a change in the short-range order, then one should expect changes in the fine structure of the Mössbauer spectra. Indeed, such changes were observed in the case of As_2Te_3 and $\text{As}_4\text{Te}_5\text{I}_2$, where the Mössbauer spectra for the crystalline alloys were weakly resolved

quadrupole multiplets, whereas their transition to the vitreous state was accompanied by a strong increase of the quadrupole splitting. There is full agreement for all three Mössbauer isotopes (see the table). Thus, it can be concluded that the crystal to glass transition in As_2Te_3 and $\text{As}_4\text{Te}_5\text{I}_2$ is accompanied by a radical rearrangement of the local structure of tellurium and iodine atoms, namely by a decrease in the local coordination numbers.

A different picture is observed in the case of the compounds AsSI and AsSeI , namely, the vitreous and crystalline alloys are characterized by close values of the quadrupole splitting of the Mössbauer spectra (see the table). We can conclude on this basis that for the last two compounds the transition from the crystalline to the vitreous state is not accompanied by a change in the short-range order.

It should be noted that the change of the local surrounding following the crystal to glass transition in As_2Te_3 and $\text{As}_4\text{Te}_5\text{I}_2$ should not be regarded as an anomalous phenomenon. Regel' and co-workers^[1] have shown the crystal to liquid transition in classical semiconductors (silicon, germanium, III-V compounds) is accompanied by a change in the short-range order.

Compounds for which a change in a local structure is observed in the crystal to glass transition are obtained

Compound	State	$\delta(\text{ZnTe}) e^2qQ$		$\delta(\text{KI}) e^2qQ$			
		^{125}Te	^{127}I	^{129}I			
As_2Te_3	Crystal	0.10	3.00	—	—	1.10	7.2
As_2Te_3	Glass	-0.50	7.50	—	—	1.10	36.0
$\text{As}_4\text{Te}_5\text{I}_2$	Crystal	0.00	4.00	-1.35	22.6	1.50	10.6
$\text{As}_4\text{Te}_5\text{I}_2$	Glass	0.30	8.60	-1.50	34.4	1.60	26.6
AsSI	Crystal	—	—	-1.20	43.5	—	—
AsSI	Glass	—	—	-1.30	45.0	—	—
AsSeI	Crystal	—	—	-1.25	42.6	—	—
AsSeI	Glass	—	—	-1.40	43.9	—	—

Note: δ —isomeric shift on mm/sec; e^2qQ —quadrupole-interaction constant, mm/sec (Q —quadrupole moment of the excited nucleus, q —principal value of the electric-field gradient tensor). The error is ± 25 mm/sec in the measurement of δ and ± 0.50 mm/sec in the measurement of e^2qQ .

in the vitreous state only by hard quenching. The same compounds are characterized also by an abrupt change in the electric conductivity parameters following the crystal to glass transition. This also agrees with the results of Regel' and co-workers,^[1] who demonstrated the existence of a correlation between the changes in the electric conductivity parameters and the change in the local structure in the crystal to liquid transition. There exists, however, also a difference between the two indicated mechanisms. Whereas for the crystal to liquid transition the symmetry of the surrounding of the atoms increases (the local coordination number increases), the opposite is observed for the crystal to glass transition (the local coordinate number decreases). In addition, if the short-range order changes in the crystal to liquid transition, then the semiconducting character of the conductivity vanishes. On the other hand, in the case of the crystal to glass transition, even when the short-range order is altered, the semiconducting character of the conductivity remains.

The reason for the change in the local structure following the crystal to glass transition in As_2Te_3 and

$\text{As}_4\text{Te}_5\text{I}_2$ should apparently be sought in the difference between the structures of the liquid and the crystal in the corresponding compounds. The metallization of the chemical bonds in As_2Te_3 and compounds similar to it results, in the case of the liquid to solid transition, in a rapid conversion of the structure of the liquid into the structure of the crystal, and only the strong quenching preserves the structure of the liquid, i. e., produces the disordered structural lattice of glass.

We note in conclusion that the change in the local structure of the compounds As_2Te_3 and $\text{As}_4\text{Te}_5\text{I}_2$, which we observed in the crystal to glass transition, is the first experimental proof of the possibility that not only the long-range order but also the short-range order becomes restructured upon amorphization.

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¹A. R. Regel', in: Stroenie i fizicheskie svoistva veshchestva v zhidkom sostoyanii (Structure and Physical Properties of Matter in the Liquid state), Kiev, 1954, p. 117.