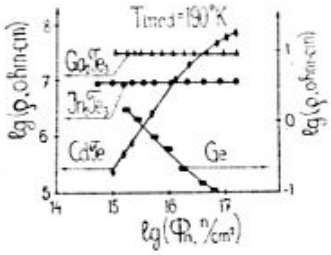

FIGURE 1 The dose of fast neutrons' dependence on the specific resistivity of In_2Te_3, Ga_2Te_3, Ge, Cd and Te. The data are obtained at the temperature 190 K right in the channel of a reactor.

for Ge, Cd and Te are shown in the same figure. It is clear from Figure 1 that crystals without SV markedly change their resistivity with exposure, provided the intensity of γ-radiation is constant, while the specific resistivity of In_2Te_3 and Ga_2Te_3 remains practically constant.

Given in Table 1 are the data concerning the specific resistivity, thermoelectric coefficient, charge carrier concentration and mobility and microhardness of semiconducting crystals reactor-irradiated at $T = 190$ K with a fast neutron dose $\phi_n = 1.84 \cdot 10^{17}$ n/cm².

Measurements were carried out at room temperature. The table shows that after a high dose of neutrons the parameters of In_2Te_3 and Ga_2Te_3 are unchanged and at the same time similar parameters of crystals without SV change appreciably. For In_2Te_3 only the value of the thermo-electric coefficient is subject to a slight change which is due to the radiation-induced disorder of the cations and vacancies in the α-phase of In_2Te_3.[3,6,7]

Shown in Figure 2 are the temperature dependencies

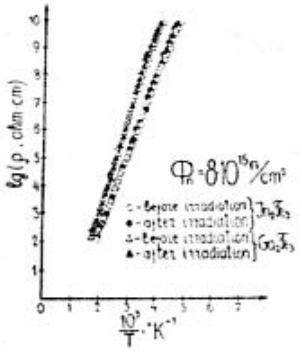

FIGURE 2 The temperature dependence of the specific resistivity of In_2Te_3 and Ga_2Te_3 before and after irradiation of the samples by the dose of fast neutrons $\phi_n = 8 \cdot 10^{15}$ n/cm².

of the specific resistivity of In_2Te_3 and Ga_2Te_3 before and after irradiation. After irradiation the samples, as mentioned above, were not annealed before measuring and their temperature dependence was determined starting with low temperatures. It can be seen from the curves in Figure 2 that the values of conductivity in both In_2Te_3 and Ga_2Te_3 within the temperature range of interest were not affected by irradiation with $1.84 \cdot 10^{17}$ n/cm² fast neutrons.

The conductivity of these semiconducting crystals remained intrinsic as before irradiation. The value of the forbidden energy gap as determined from the slope of the curve (T), as well as from the optical transmission spectrum remained unchanged after irradiation with fast neutrons.†

Thus irradiation with fast neutrons does not result in the production of radiation defects in In_2Te_3 and Ga_2Te_3, at least of such defects whose local levels are in the forbidden energy gap and are filled with electrons (or holes) in equilibrium. It is noteworthy that within the measurement error the values of carrier mobility as well as the value of microhardness in In_2Te_3 and Ga_2Te_3 do not change after the above dose of mixed reactor radiation. Therefore the above experimental data are evidence of the extremely high radiation stability of A_2B_3 semiconductors. As is seen from the results of this paper (Table I) and papers of other authors[10,11] the electrical parameters of other diamond lattice semiconductors markedly change under considerably lower doses of ionizing radiation.

DISCUSSION

It is known that impurity and superstoichiometric atoms in In_2Te_3 and Ga_2Te_3 are localized at SV in equilibrium.[3,4] It may be suggested that the effect of the anomalously high radiation stability of In_2Te_3 type semiconductors is explained by the penetration of the atom knocked from its site into SV and its chemical reaction with neighbouring atoms. Electron redistribution in the crystal occurs, the remaining radiation-induced vacancy (RV) becoming neutral and acquiring SV properties. This mechanism may take place for $A_2^{III}B_3^{VI}$ cations, SV and a cation as if changing places.

† A study of thermally stimulated conductivity in In_2Te_3 leads to the conclusion that after irradiation with fast neutrons the position (0.2 eV) of the peak on the thermally induced conductivity curve remains unchanged. Preliminary data show that the peak intensity is unchanged or becomes slightly higher after irradiation in the reactor. Thus, if radiation-induced traps appear, their number is small.

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RADIATION STABILITY OF $A_2^{III}B_3^{VI}$ SEMICONDUCTORS

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The influence of large doses of fast neutron irradiation on some physical properties of a number of semiconductor materials has been investigated. It is shown that the physical parameters of In_2Te_3 and Ga_2Te_3 semiconducting crystals having loose crystal structure, unlike other semiconductors, possess anomalously high radiation stability. The mechanism of this phenomenon, based on an assumption about large instability zones in the interstitial-vacancy pairs in crystals of In_2Te_3-type, is discussed.

$A_2^{III}B_3^{VI}$ semiconducting compounds belong to the wide class of zinc blende lattice crystals. As is known $A^{II}B^{VI}$, $A^{III}B^{V}$ crystals and the elemental semiconductors Ge and Si also belong to this class. The most important structural peculiarity in the $A_2^{III}B_3^{VI}$ crystals (In_2Te_3, Ga_2Te_3) is that their cation sublattice is only partially filled with atoms and that one third of cation sublattice sites are vacant. The presence and concentration of such vacancies in crystals of this type is exclusively determined by the valence relations. The concentration of the vacancies which are referred to as stoichiometric (SV) does not depend on temperature. It should be emphasized that SV are a structural and "valence" component of the crystal but are not a lattice defect. SV and cations in the cation sublattice may be in both the disordered (Ga_2Te_3, β-In_2Te_3) and ordered state (α-In_2Te_3).

It was shown earlier[1] that SV are neutral. It was also shown that the conductivity of In_2Te_3 and Ga_2Te_3 irrespective of the chemical individualities of the impurity and its concentrations, is purely intrinsic.[1,3] This is due to the fact that the impurity (and superstoichiometric) atoms in such crystals are localized at SV, remaining in the un-ionized state.[4]

In our papers[5–7] it was shown that after bombardment with fast electrons (100 MeV, 10^{19} electrons/cm^2), fast neutrons (1 MeV, 8.10^{16} n/cm^2), γ-quanta (1.2 MeV, 10^{18} q/cm^2) the electrical conductivity, charge carrier concentration and mobility, measured at room temperature do not practically change. This paper reports our further studies of the mechanism of anomalously high radiation stability of semiconducting crystals with stoichiometric vacancies.

EXPERIMENTAL

We studied In_2Te_3 and Ga_2Te_3 samples obtained using the usual technique[8] and In_2Te_3 single crystals grown by the method suggested in Ref. 9. To filtrate slow neutrons the samples were placed in cadmium containers. Since the indium nucleus has a sharp resonance absorption peak at neutron energies of 1.44 ± 0.02 eV, the cadmium containers were coated with a thin indium layer to protect the In_2Te_3 samples. During irradiation the samples had the temperature 190 K. After irradiation they were immersed in liquid nitrogen and kept there until measurements were made. Some measurements were carried out during irradiation.

Apart from the In_2Te_3 and Ga_2Te_3 samples single-crystalline and polycrystalline samples of the semiconducting substances Ge, Cd, Te, Zn and Te were also irradiated under the same conditions. They are diamond-structure crystals (as In_2Te_3 and Ga_2Te_3) but without SV.

In the field of mixed radiation (fast neutrons and gamma rays) all the samples under study have appreciable γ-conductivity. The dose of fast neutrons ϕ_n dependence of specific resistivity ρ measured at 190 K straight in the reactor channel is shown in Figure 1. For comparison the dependencies $\rho(\phi_n)$

TABLE I

Physical properties of some semiconductor crystals before irradiation and after irradiation by the dose of fast neutrons/cm² $\phi_n = 1.84 \cdot 10^{17}$.

Material	Specific resistivity ρ, ohm . cm		Termo EMF α, μV/degree		Microhardness H_μ, kG/mm²	
	Before irradiation	After irradiation	Before irradiation	After irradiation	Before irradiation	After irradiation
In_2Te_3[a] single crystal	$1.6 \cdot 10^6$	$1.7 \cdot 10^6$	−1150	−1000	167 ± 6	166 ± 6
Ga_2Te_3 polycrystal	$1.1 \cdot 10^7$	$1 \cdot 10^7$	+ 800	+ 800	198 ± 6	198 ± 6
Ge polycrystal	27	$4 \cdot 10^{-2}$	− 100	+ 300	761 ± 22	887 ± 37
Si single crystal	$4 \cdot 10^2$	$5.6 \cdot 10^5$	+ 450	+ 250	996 ± 38	1132 ± 72[b]
Cd Te single crystal	$2 \cdot 10^2$	$5 \cdot 10^7$			46.7 ± 0.7	48.8 ± 0.7
Zn Te single crystal	$3 \cdot 10^2$	$4 \cdot 10^4$	+ 750	+ 380	102 ± 1	71.5 ± 1.4[b]

[a] The concentration of charge carriers measured from the Hall constant, in In_2Te_3 is $7 \cdot 10^{10}$ cm^{-3} and remains unchanged after irradiation. The mobility of electrons is also unchanged after irradiation by the same dose of fast neutrons (40 ± 10 cm²/V . sec)
[b] Dose of irradiation $\phi_n = 10^{18}$ n/cm².

This corresponds to disordering in the cation sublattice, if before irradiation the ordering of cations and SV had taken place. This mechanism is undoubtedly operative in α-In_2Te_3 where SV and indium atoms are ordered. As is seen from Table I, the thermoelectric coefficient considerably decreases after fast neutron irradiation. The thermoelectric coefficient in α-In_2Te_3 decreases also after irradiation with fast electrons, It is shown[3] that such a change in the thermoelectric coefficient of In_2Te_3 may be interpreted as an indication of disordering in the cation sublattice. We should note that in Ga_2Te_3 where there is no ordering of cations and SV, irradiation with a high dose of fast neutrons (see the Table) and electrons[6] does not produce any change in the value of the thermoelectric coefficient.

The described mechanism takes place only for cations knocked from their sites. However, this mechanism cannot be extended to anions. Thus irrespective of the fact that an exchange of places between the cations and SV during irradiation with heavy particles is supposed to occur, this mechanism cannot give rise to the effect of radiation stability. Therefore, the physical reason for this effect is associated with one of the two following mechanisms:

1) radiation defects in structures with a great number of vacancies ("loose" structures) are unstable or

2) radiation defects are stable but strictly compensated. Any of these machanisms may explain the preservation of the intrinsic character of the conductivity of such crystals after irradiation.

During irradiation of semiconductors with heavy particles not only the electronic, but also the mechanical properties of the crystals change. The radiation defects in germanium and silicon result in a significant change in microhardness H_μ, since the lattice defects are dislocation stoppers.[12,13] The measurements of the microhardness H_μ in In_2Te_3 and Ga_2Te_3 carried out at room temperature after an irradiation dose of $1.84 \cdot 10^{17}$ n/cm² showed that the microhardness of these crystals does not change after irradiation (see Table I). But it is known that even point defects in In_2Te_3 and Ga_2Te_3 result in a considerable increase in the microhardness.[14] Therefore the fact that no change occurs in H_μ after irradiation is evidence of the absence of radiation-induced damage at least in amounts which might affect H_μ. From Table I it can be seen that the value of electron mobility in In_2Te_3 also remains unchanged. This fact also indicates that after fast neutron irradiation no stable charged lattice defects remain in In_2Te_3 including the compensated ones, since the charged lattice defects should result in a considerable scattering of electrons and reduction of their mobility.

The invariability of H_μ and carrier mobility in In_2Te_3 and Ga_2Te_3 after irradiation with fast neutrons as well as with high energy electrons and

γ-quanta[6] along with the preservation of the charge carrier concentration and the intrinsic character of conductivity show that there is no compensation effect and that the most probable reason for the anomalously high radiation stability is the instability of radiation defects in such loose structures.

ATHERMAL RECOMBINATIONS IN $A_2^{III}B_3^{VI}$

In Vienyard's paper[15] the concept of the interstitial atom instability zone relative to a vacancy is introduced. If the interstitial atom is within the instability zone of a vacancy it recombines with the vacancy athermally (without activation).

In Refs. 16 and 21 it is shown that such unstable pairs can essentially contribute to the equilibrium properties of solids. When the size of the instability zone is large the equilibrium concentration of unstable interstitial-vacancy pairs can greatly exceed the concentration of usual Frenkel pairs, but the unstable pair state of the crystal cannot be preserved by annealing (unlike usual Frenkel defects) because recombination takes place irrespective of temperature.

If the lattice is rather close-packed, then on the line connecting the radiation-induced vacancy and the knock-on atom there are atoms and electronic bridges of covalent bonds, so that even if the interaction between the vacancy and the knock-on atom corresponds to the attraction of elastic or electrostatic origin the knock-on atom may localize in some metastable state. For the recombination to take place thermal activation of this atom would be necessary to take it out of the metastable state. In a loose lattice the knock-on atom which is not very far from "RV" can freely recombine with RV. Let us imagine that a close-packed lattice is a fine mesh net for the knock-on atom where it lingers, a loose lattice being a net with wide meshes through which the knock-on atom falls.

According to Ref. 15 for copper the instability zone contains about 50 atoms, i.e. the instability zone radius (if regarded as spherical) is 2–3 interatomic spacings. The above considerations show that unstable zones in loose lattices of the In_2Te_3 type should be larger. Therefore we can tell for certain that during irradiation with light particles of relatively low energies (γ-quanta, 1 MeV electrons) when the energy E_2 transferred to the lattice atom is only a little above the displacement threshold the interstitial atom and its "own" RV are closely spaced, undoubtedly within the unstable zone. Here athermal (barrierless) recombination of the interstitial atom and the vacancy takes place which causes the radiation stability of such crystals when exposed to γ-quanta and electrons of relatively low energies. As to irradiation with heavy particles when E_2 is large, estimates show that even in cascades initiated by In_2Te_3 and Ga_2Te_3 irradiation with fast neutrons ($E \approx 1$ MeV) and fast electrons ($E = 100$ MeV, the relativistic mass is near the neutron mass) without taking into account the focusing and channelling effects (see below) the maximum distances between an interstitial atom and its "own" RV do not exceed values of the order of several Å, i.e. 2–3 atomic spacings. This is due to the fact that heavy atoms of In_2Te_3 at specific values of the transferred energy $E_2 \sim 50$ KeV have a short free path in the lattice. Therefore, what is said above concerning irradiation with light particles applies also to irradiation with heavy particles.

It is of interest to estimate how the quantity of stable defects in a cascade is affected by the broadening of the unstable zone. For this purpose it is reasonable to compare the A_2B_3 type crystals (In_2Te_3, Ga_2Te_3) with the isoelectronic row of $A^{II}B^{VI}$, $A^{III}B^{V}$ compounds (In_2Te_3, InSb, CdTe, Ga_2Te_3, GaSb, ZnTe). All the isoelectronic row crystals are zinc blende lattice crystals with nearly equal lattice parameters,[18] similar values of covalent bonds[19] and due to the almost complete coincidence of atomic masses, equal values of E_2.

Let v_0 be the size of the unstable zone in a crystal without SV. It follows from the foregoing that the size of the unstable zone increases with decreasing degree of lattice site filling, i.e. with increasing SV concentration. For simplicity we shall assume that the size of the unstable zone for crystals with SV grows linearly with increasing concentration C of these vacancies which characterizes the structure looseness

$$v = v_0 + wC \tag{1}$$

where w is a constant with a volume dimension.

Thompson[20] studied the influence of the unstable zone on the quantity ν' of stable defects in a cascade, provided the interstitial atom can recombine with any of the nearby RV in the cascade.

$$\nu' = \nu e - \nu v/V \tag{2}$$

where ν' is the total number of RV or interstitial atoms in the cascade without taking into account the athermal recombination. The value of ν may be found using for example the Kinchin and Pease model.

V is the volume of a single cascade.

If we substitute the unstable zone size in (2) from (1), then the following will be obtained:

$$\nu' = \nu\, e - \nu v_0/V \,.\, e - \nu w C/V \qquad (3)$$

from which it is seen that the quantity of stable defects exponentially decreases with increasing of SV concentration as compared with the quantity of stable defects in crystals without SV. Thus, intense athermal recombination in loose structures of the In_2T_3 type accounts for the anomalously high radiation stability of such crystals.

The above considerations about the origin of radiation stability in In_2Te_3 and Ga_2Te_3 crystals are mainly based on the fact that according to estimates the distances between RV and interstitial atoms are short. But these distances may appear to be considerably larger if channelling of the knock-on atoms takes place or there are chains of focused collisions in In_2Te_3 and Ga_2Te_3 crystals. Let us evaluate the probability of these effects in loose lattices. The criterion for the focusing is:

$$f = \frac{D}{2R(E_2)} - 1 \qquad (4)$$

where D is the atomic spacing along the chain; R is the effective atomic radius (in the hard-sphere approximation). When $f < 1$ (or $D < 4R$) the focusing occurs, when $f > 1$ the defocusing occurs.

In In_2Te_3 and Ga_2Te_3 crystals where SV constitute one third of the cation sublattice sites the average value of D for many directions (crystallographic directions which pass through the sites of the cation sublattice) in the lattice is higher than in the corresponding crystals of isoelectronic compounds. It follows that at equal E_2 and consequently $R(E_2)$ focusing in crystals with SV is less probable than in crystals without them. It is easy to show that the critical focusing energy

$$E_f = 2A\, e - D/2b \qquad (5)$$

if the atomic repulsive potential is represented in Born's form

$$V(z) = A\, e^{-r/b} \qquad (6)$$

where A, b are constants.

It is seen from Eq. (5) that with increasing D the value of E_f rapidly decreases. The estimates show that under these assumptions E_f is 0.1–1 eV in In_2Te_3 and Ga_2Te_3 crystals in contrast to the usual E_f value reaching approximately tens or hundreds of electron-volt. It can be readily seen that the critical focusing angles in loose structures also diminish.

All this enables us to state that the focusing effect in loose structures is considerably suppressed. The focusing in In_2Te_3 and Ga_2Te_3 can probably take place only along the close-packed layers of tellurium. In a cascade at high E_2 the probability of atom channelling should be taken into account. Using the expression for the amplitude of atom oscillation in the channel I_0 obtained in Ref. 20 in the harmonic approximation for potential (6) and assuming for simplicity that distances between atoms along the axis of the channel and across it are equal we obtain:

$$J_0 \sim D^{1/2}\, e^{D/2b} \qquad (7)$$

As mentioned above, the specific values of D in loose structures of the In_2Te_3 type increase as compared with those having no SV. From Eq. (7) it is seen that with increasing D the amplitude of oscillations in the channel exponentially grows. This leads to the reduction in probability and to the shortening of the length of channelling in loose structures, since (see Ref. 20) after a certain critical value of oscillation amplitude has been reached the passing atom destroys the channel.

Therefore, the channelling and focusing effects in loose structures of the In_2Te_3 type are considerably suppressed; so that practically there is no interstitial atoms and their "own" RV located far from each other.

Thus, consideration of radiation defects in loose structures is restricted to consideration of closely located RV-atom pairs which, as shown above, recombine athermally.

It is exactly this that determines the anomalously high radiation stability of the structures of the In_2Te_3 type. It can be expected that high radiation stability is the property characteristic not only of In_2Te_3 and Ga_2Te_3 but in general of all loose structures.

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