Neutrino-Recoil-Induced Frenkel Pairs in InSb Observed by Mössbauer Spectroscopy

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The decay of ^{119}Te to ^{119}Sb via electron capture is utilized to produce isolated, single Frenkel pairs in InSb. This is caused by neutrino emission, which imparts a recoil of 12 eV to the ^{119}Sb atoms, thereby displacing about 20% of them into interstitial sites. The effect is traced by Mössbauer emission spectroscopy following the decay of ^{119}Sb to ^{119}Sn. The displacement threshold E_d is confined to $6 < E_d < 12$ eV from auxiliary experiments employing ^{119m}Te isotopes.

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The study of elementary defects in semiconductors requires information on an atomic level and, above all, identification of the defect under study which often is a major problem in defect physics. The method which has mainly contributed to the understanding of the electronic and structural defect properties is electron paramagnetic resonance (EPR) and its related techniques with particular success for silicon and II-VI semiconductors; for a comprehensive review see [1]. But even for the best studied material, silicon, an isolated interstitial has not been identified and for the III-V semiconductors, where the impact of EPR is more limited, "no direct identification of any group-V vacancy or interstitial exists" [1]. In the following, we describe another experimental approach: We have correlated production of isolated Frenkel pairs in InSb with a study of these pairs by Mössbauer spectroscopy, which provides information on the elementary defects on an atomic level.

In our experiment we utilize the Mössbauer effect on the probe ^{119}Sn, which is fed by its radioactive parent ^{119}Sb. The Mössbauer effect is observed on the 24 keV transition in ^{119}Sn, which by way of the nuclear hyperfine interaction is sensitive to the immediate environment of the probe atom. In this way information on its lattice position and possible defects associated with it can be obtained. Details on the application of the Mössbauer effect to semiconductor defect studies may be found in [2]. Combination of Mössbauer spectroscopy with Frenkel pair production is achieved by starting with the radioactive precursor ^{119}Te resulting in two successive β decays:

$$^{119}\mathrm{Te}(16\ \mathrm{h}) \rightarrow {}^{119}\mathrm{Sb}(38\ \mathrm{h}) \rightarrow {}^{119}\mathrm{Sn} \qquad (1)$$

(half-lives given in parentheses); see Fig. 1. 80% of the ^{119}Te ground state nuclei decay to an excited state at 644 keV in ^{119}Sb via electron capture, emitting a neutrino that almost completely carries the decay energy Q_{EC} [3]. For the resulting recoil energy E_R of the Sb atoms one obtains

$$E_R = (Q_{\mathrm{EC}} - E_{\mathrm{ex}} - E_b)^2/2Mc^2 = 12\ \mathrm{eV}. \qquad (2)$$

Q_{EC} is the mass difference between neutral ^{119}Te and ^{119}Sb, E_{ex} is the energy of the excited state in Sb, M denotes the mass of ^{119}Sb, and E_b is the binding energy of the ^{119}Te K electron. Two weak decay branches also contribute recoil energy: a 10% decay to an excited state at 700 keV resulting in 11 eV and a high energy γ decay (1.75 MeV) with 14 eV (5%) [3]. Thus a total of 95% of the ^{119}Te disintegrations proceeds with close to 12 eV recoil energy on the Mössbauer probe. In the final decay $^{119}\mathrm{Sb} \rightarrow {}^{119}\mathrm{Sn}$, the "proper" Mössbauer decay, only 1.3 eV recoil energy results due to neutrino emission that cannot contribute to defect production. Therefore the Mössbauer effect on ^{119}Sn is a true "analyzer" of the preceding events. We chose the III-V semiconductor InSb for our experiment because it offers several attractive features: According to [4], the threshold energy E_d for Frenkel pair production is expected to be extremely low, around 6–10 eV. Thus, the 12 eV recoil energy imparted to ^{119}Sb should just be sufficient for the exclusive production of single Frenkel pairs. Additionally, Te is a common donor in III-V semiconductors and can be

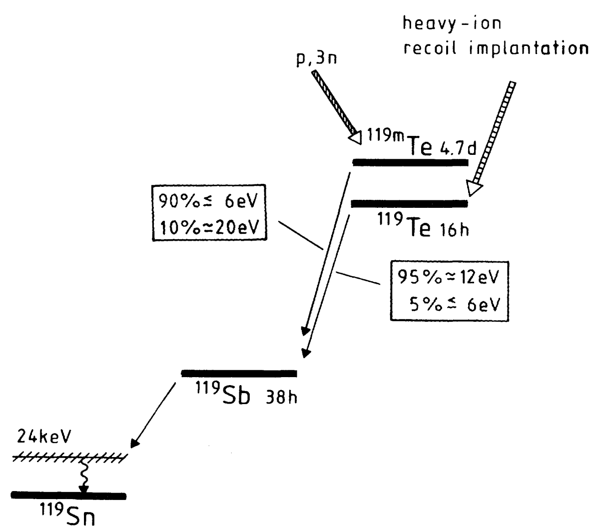

FIG. 1. Partial decay schemes of ^{119}Te and ^{119m}Te showing the feeding of the Mössbauer state in ^{119}Sn. The insets show the fractions of decays leading to recoil energies as indicated (mainly due to neutrino recoil).

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incorporated on substitutional V sites [5]. After its decay to Sb it becomes an eigenatom of the InSb crystal and therefore is either a native substitutional atom or part of an intrinsic defect configuration. The Mössbauer effect is measured after the final decay proceeding from Sb to Sn. The electronic rearrangement associated with the nuclear transmutation is expected to be sufficiently fast that the hyperfine parameters measured are characteristic for the Sn state: for further details see [2].

We used single-crystalline InSb wafers, 1.5 cm in diameter and 500 μm thick, characterized as intrinsic material by the supplier (MCP). These were recoil implanted with radioactive ^{119}Xe ions produced by the reaction ^{105}Pd(^{18}O,4n)^{119}Xe with a 77 MeV ^{18}O beam from the heavy-ion accelerator of the Hahn-Meitner-Institut. A ^{105}Pd foil of 2 mg/cm^2 thickness was bombarded, resulting in an energy distribution of the recoiling ^{119}Xe ions between 1 and 10 MeV. This leads to an almost constant implantation profile of 10^{14} probe atoms/cm^3 in InSb to a depth of 3 μm. A special scattering geometry separated the recoiling ^{119}Xe ions from the primary beam to avoid direct implantation of ^{18}O into the InSb samples. ^{119}Xe decays to ^{119}Te via ^{119}I with half-lives of 6 and 19 min, respectively.

In the following the time elapsed after the production of the ^{119}Te activity is the important parameter that governs the observable effects of the neutrino-recoil process. An InSb sample was recoil implanted for about 24 h. After complete decay of ^{119}Xe/^{119}I to ^{119}Te the sample was annealed at 420 °C under Ar atmosphere for 10 min to remove all defects from implantation and from possible defects due to the ^{119}Xe/^{119}I decays. This annealing procedure is expected to result in the substitutional incorporation of the ^{119}Te atoms on Sb sites [5,6]. The sample was then cooled to 4.2 K, which marks the time zero of the experiment. At this time most of the radioactive probes ($\approx$70%) are still ^{119}Te ($T_{1/2}$ = 16 h). Mössbauer spectra measured subsequently probe the lattice location of ^{119}Te and possible site changes due to the $^{119}\text{Te} \rightarrow {}^{119}\text{Sb}$ decay. Figure 2 (top) shows the following result: The spectrum consists of two resolved lines, the well known line for substitutional Sn [5] (δ = 1.98 mm/s) and a smaller second component with a large isomer shift δ = 3.5 mm/s (corresponding to higher s-electron density) comprising 12(2)% of the spectral intensity. Corrected for decays of ^{119}Te to ^{119}Sb already occurring before time zero, one obtains an intensity F_0 = 17(4)%. This line is assigned to interstitial Sn as discussed below and in the following termed "defect line." The sample was then annealed a second time (10 min at 420 °C) 80 h after time zero and recooled to 4.2 K. At this time, after 5 half-lives of ^{119}Te, it contains almost entirely ^{119}Sb (>95%). Now, the spectrum measured [Fig. 2 (middle)] shows only the substitutional line, a defect line is no longer present. Since this time the lattice location of ^{119}Sb is explored, it is clear that the defect

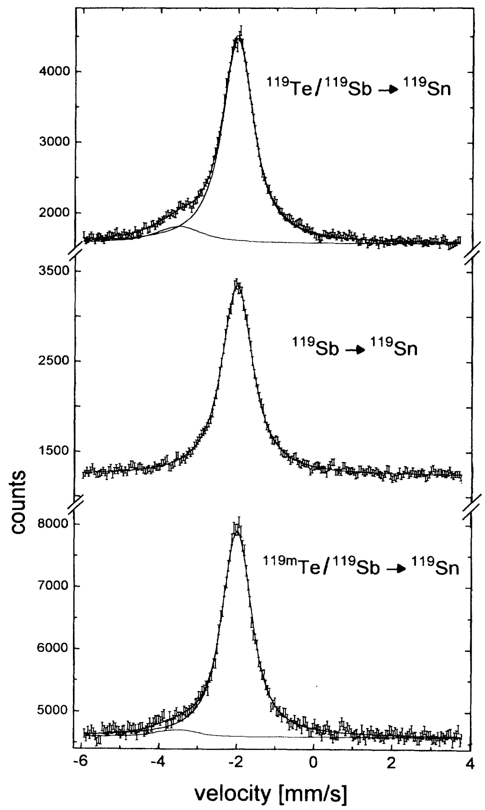

FIG. 2. Mössbauer emission spectra of ^{119}Sn in InSb for various parent activities: ^{119}Te (top), ^{119}Sb (middle), ^{119m}Te (bottom); for details see text. The spectra were measured at 4.2 K versus a $CaSnO_3$ absorber incorporated in a resonance detector at room temperature [2].

line has its origin in the Te nature of the Mössbauer probes. As both ^{119}Te and ^{119}Sb are expected to be incorporated substitutionally [5,6], the defect line in the former spectrum is supposedly created as a result of the ^{119}Te nuclear decay, i.e., by the neutrino recoil effect.

To prove this origin unambiguously, we performed a second type of experiment: the radioactive ^{119m}Te precursor was produced; i.e., a state which is chemically identical to ^{119}Te but differs in the nuclear decay properties. The state is produced by using the InSb samples as targets for 30 MeV protons to induce the reaction ^{121}Sb(p, 3n)^{119m}Te, the protons passing through the samples. In comparison with the ^{119}Te ground state decay the main part of the ^{119m}Te decay imparts much lower recoil energy to its ^{119}Sb daughter (Fig. 1): almost 90% of the decays lead to recoil energies around 6 eV or less and only a fraction of 10% causes recoil energies around 20 eV (5% at 23 eV; 5% at 20 eV) due to high-energy neutrinos and γ's [3].

After irradiation for 4 h the sample was stored for 80 h to let all unwanted radioactivities decay. Then it was annealed as described earlier and held at 4.2 K from then on (time zero). Because of the characteristics of a long-lived state (^{119m}Te, $T_{1/2} = 4.7$ d) decaying into a shorter-lived one (^{119}Sb, $T_{1/2} = 38$ h), suitable timing of the Mössbauer measurements permits one to again probe the behavior of both Te and Sb atoms in the InSb matrix separately [2]. At time zero the ^{119m}Te activity is almost in equilibrium with its decay product ^{119}Sb. Thus a spectrum measured immediately after the annealing (for a time short compared to the ^{119}Sb half-life) comprises mainly those atoms that were ^{119}Sb at time zero, whereas a spectrum taken after several half-lives of ^{119}Sb makes those Mössbauer atoms visible that were still ^{119m}Te at time zero [2]. A measurement with the first time condition shows only the substitutional line, which proves again that Sb is incorporated substitutionally. However, also the spectrum comprising >80% ^{119m}Te at time zero gives hardly any evidence of any other than the substitutional line, Fig. 2 (bottom). Analysis with the same two lines as for spectrum 2 (top) yields 3(2)% spectral intensity for the defect line, proving that Te is practically also entirely incorporated substitutionally. This result proves unambiguously that the defect line in Fig. 2 (top) is due to the neutrino recoil; the small hint of a defect fraction in Fig. 2 (bottom) might be due to the 10% recoil events in the ^{119m}Te decay with E_R around 20 eV. The majority of decays with $E_R \approx 6$ eV (90%), however, does not lead to defect production, showing that E_R must exceed 6 eV to create Frenkel pairs.

With the recoil energy so close to the displacement threshold, one can safely assume that our experiment produces exclusively *single* Frenkel pairs. Thus three configurations of the ^{119}Sb probe atoms giving rise to the defect line appear conceivable: (1) A substitutional location possibly on a neighboring In site with an adjacent Sb vacancy due to a replacement collision with a neighboring atom. (2) An interstitial location with a Sb vacancy close by, i.e., a close Frenkel pair configuration. (3) An interstitial configuration with a larger distance to the Sb vacancy, i.e., outside the nearest-neighbor range of the hyperfine interaction. Configuration (1) appears unlikely for recoil energies hardly exceeding the displacement energy. Indeed, ^{119}Sn Mössbauer lines attributed to this configuration in ion-implanted III-V compounds show a systematic increase of the isomer shift $\Delta\delta$ by only ≈0.3 mm/s as compared to substitutional V sites [5,7,8], which is incompatible with the present value of $\Delta\delta = 1.52$ mm/s (Table I). The large isomer shift for the defect line is, however, compatible with shifts found both experimentally and theoretically for interstitial Sn in various semiconductors [5,7,8,9]. From the theoretical results [8] it can be inferred that a $\Delta\delta$ of about 1.5 mm/s reflects a substantial electron transfer from an approximate $5sp^3$ bonding configuration (substitutional) towards a $5s^2p^2$ nonbonding state (interstitial).

These results allow us to assign the defect line to ^{119}Sb atoms directly displaced into interstitial sites. Since free interstitial sites are available in ⟨111⟩ and ⟨100⟩ directions, primary displacements near threshold energies might preferentially proceed along these axes [10–12], a sketch of the recoil scenario is shown in Fig. 3. The considerable broadening $\Delta\Gamma$ of 0.52 mm/s associated with the defect line (Table I) indicates that it contains more than one component. Our most recent experiments probing the thermal stability show that the defect line disappears in two almost equal steps around 140 and 390 K, respectively. This fact allows a separation of the defect line in two closely spaced fractions around $\delta = 3.5$ mm/s. The annealing state at 140 K is certainly due to correlated Frenkel pair recombination; a detailed discussion of these facts will be given in a later publication.

TABLE I. Mössbauer parameters for ^{119}Sn in InSb after electron capture decay of ^{119}Te measured at 4.2 K. The isomer shift δ is given relative to $CaSnO_3$ at room temperature. Γ is the linewidth (FWHM) fitted as a Lorentzian not including a small Gaussian contribution, which accounts for the special line shape of the $CaSnO_3$ absorber. F is the fractional resonance area.

δ (mm/s)	Γ (mm/s)	F (%)	Assignment
1.98(2)	0.88(3)	88(4)	Site-V substitutional
3.50(5)	1.40(10)	12(2)	Interstitial

In summary, we have shown that an energy of 12 eV due to neutrino recoil leads to Frenkel pair formation in an otherwise perfect crystal of InSb, which can be traced by Mössbauer emission spectroscopy with the probe atom taking the part of the primary knock-on atom (PKA). Our study provides the first observation of a Frenkel pair in a III-V semiconductor by a microscopic technique.

Finally, we would like to add some remarks with regard to the neutrino recoil effect. Already very early Gonser [13] hinted at the possibility that a low energy nuclear decay process could possibly be used for defect studies correlated to the Mössbauer probe atom. Experiments in that direction were first performed utilizing recoil energies distributed between 0 and 200 eV following neutron capture with subsequent γ decay as reviewed by Vogl [14]. An experiment employing the β-NMR technique on InSb following neutron capture also belongs to this category [15]. The first definitive defect resulting from monoenergetic neutrino recoil was reported in 1984 [16,17], the analyzing technique in this case was the perturbed angular correlation method (PAC). In those experiments it was shown that in the close-packed metal Cu Frenkel pair production proceeds via replacement collisions, making a single vacancy nearest neighbor to the substitutional PAC probe. In germanium with its open structure indirect evidence also points to a replacement mechanism leaving a vacancy adjacent to the PAC probe [18]. It should be pointed out, however, that a direct displacement to an interstitial site with

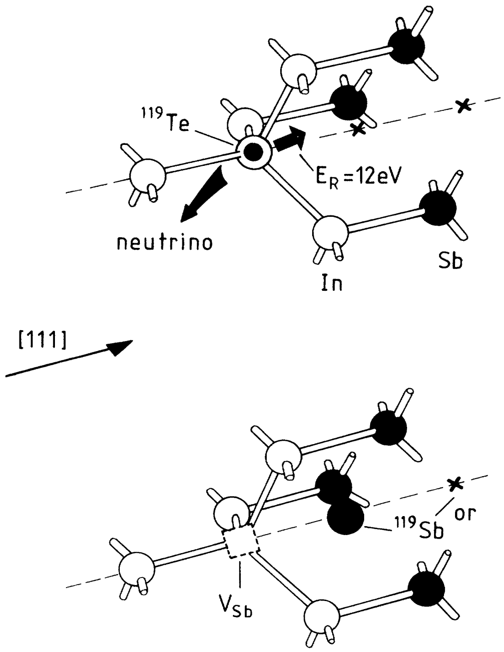

FIG. 3. Sketch of the neutrino recoil process. ^{119}Te is incorporated on a substitutional Sb site receiving 12 eV recoil energy from neutrino emission (top). After the decay ^{119}Sb is in an interstitial position with a vacancy nearby (bottom). ⟨111⟩ is a likely direction for the Frenkel pair production; other directions may also contribute. The crosses indicate two principally different interstitial positions for the probe atom from the standpoint of the hyperfine interaction: the left cross marks a close Frenkel pair configuration and the right is representative of all interstitial positions with a larger distance to the Sb vacancy, i.e., outside the nearest-neighbor range of the hyperfine interaction.

cubic symmetry would be invisible to PAC since an electric field gradient is required to mark a defect site. This might be one of the reasons why PAC experiments employing the neutrino-recoil technique failed to detect a defect in III-V compounds [18]. The present experiment, however, shows for the first time experimentally that in a semiconductor very close to the defect threshold the basic Frenkel pair production mechanism is the direct displacement of the PKA to an interstitial site.

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