Nuclear gamma resonance in neutral tin atoms in the crystal matrix of In_2Te_3

V. M. Koshkin, E. E. Ovechkina, and V. P. Romanov

Physico-technical Institute of Low Temperatures, Ukrainian Academy of Sciences, Kharkov

(Submitted July 3, 1975)
Zh. Eksp. Teor. Fiz. **69**, 2218–2221 (December 1975)

The nuclear gamma-resonance (Mössbauer) method was used in an investigation of the electron states of tin impurity atoms in the crystal lattice of In_2Te_3. It was found that, in the investigated range of concentrations (1–8 at.%), the tin atoms introduced into the In_2Te_3 lattice remained neutral and this accounted for the unusual (for semiconductors) absence of extrinsic conduction in In_2Te_3-type crystals doped with elements belonging to various groups of the periodic system. A scale was derived for the isomeric shift as a function of the effective charge of the *s* valence electrons in tetrahedrally coordinated compounds of tin.

PACS numbers: 76.80.+y, 71.55.Dp

The introduction of impurities into inorganic crystals results, irrespective of the dissolution mechanism, either in ionization or formation of covalent bonds with the crystal matrix atoms. This applies particularly to any semiconductor crystals with the diamond-type lattice (Ge, Si, α-Sn) and to similar—in respect of their structure and nature of the bonds—crystals with the sphalerite lattice (CdTe, GaAs, ZnS, etc.). All these crystals are characterized by the tetrahedral coordination of atoms and sp^3 bonds. Crystals of the In_2Te_3 type occupy a special place in this class of substances: they also have the sphalerite lattice but the cation sublattice includes additional tetrahedral voids (one third of the total number of cation sites).

Earlier theoretical and experimental studies of the dissolution of impurities in In_2Te_3-type crystals and the electron properties of these crystals[1,2] showed that the equilibrium states of impurity atoms in these additional tetrahedral voids were neutral and that such atoms did not interact chemically with the matrix atoms. However, these investigations yielded only an indirect proof of the neutral state of impurity atoms in the investigated crystals. Therefore, it would be interesting to confirm this conclusion by a direct method. Direct evidence on the electron states of atoms in a crystal lattice can be obtained from the isomeric shift in the nuclear gamma resonance (Mössbauer) spectra. The present paper reports an investigation of electron states of impurity atoms of tin in indium telluride by the Mössbauer method.

The technology of preparation of $In_2Te_3Sn_x$ alloys and the control of the single-phase nature and homogeneity of these alloys were the same as in[3]. Samples were doped with tin enriched (to 85%) with Sn^{119}. X-ray phase and microstructure analyses showed that all the samples consisted of just one phase. The Mössbauer absorption was determined using a constant-acceleration spectrometer based on an AI-256-1 analyzer whose address register was changed to the reversible form.[4] The source of the γ rays was $BaSn^{119}O_3$.

The Mössbauer spectra were recorded for $In_2Te_3Sn_x$ samples with three different concentrations of tin ($x = 0.015, 0.04, 0.08$) at room temperature. Figure 1 shows the absorption spectrum of $In_2Te_3Sn_{0.08}$; the spectra of the samples with the other concentrations of tin were similar. The absorption spectra were single lines ($\Delta\Gamma = 0.76$ mm/sec) with an isomeric shift $\delta = +(3.58 \pm 0.08)$ mm/sec, which was the same for all the investigated Sn^{119} concentrations. Thus, the electron state of the tin atoms was the same throughout the investigated range of tin concentrations, which indicated that the dissolution mechanism was the same in all cases.

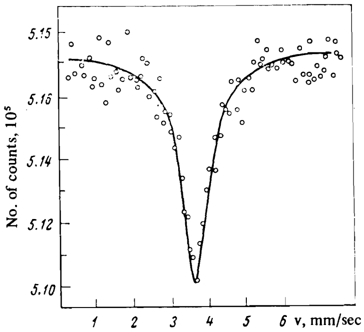

FIG. 1. Absorption spectrum of Sn^{119}-doped In_2Te_3.

The electron state of tin corresponding to $\delta = +3.58$ mm/sec was found by plotting a scale of isomeric shifts as a function of the effective charge e_s^* of the s valence electrons at the tin nuclei. In plotting the scale, it was necessary to bear in mind certain points which had not been considered in the derivation of similar scales in the past.

1. The scale should be the dependence of the isomeric shift on e_s^* and not on the difference between electronegativities,[5,6] because the linearity of the dependence of the degree of ionicity λ on the difference between electronegativities is usually observed for these compounds only in a narrow range of this difference. Moreover, plotting the dependence of the isomeric shift on e_s^* makes it possible to include in the same scale the neutral tin atoms when $e_s^* = 2$ (the electron configuration of a neutral atom of tin is $4d^{10}5s^25p^2$). In the case of atoms in the sp^3 bonds, we have $e_s^* = 1 \pm \lambda$ (in electron charge units), where the "+" and "–" signs correspond to the behavior of tin as an anion or cation.

2. It is shown in[7] that the definition of λ for crystals with sp^3 bonds based on the well-known Pauling formula

$$\lambda = 1 - \exp(-0.18\Delta x^2), \tag{1}$$

where Δx is the difference between electronegativities, gives incorrect results. The expression (1) was obtained by Pauling for hydrogen halides (sp bonds) and, strictly speaking, it is valid only for this class of compounds. In

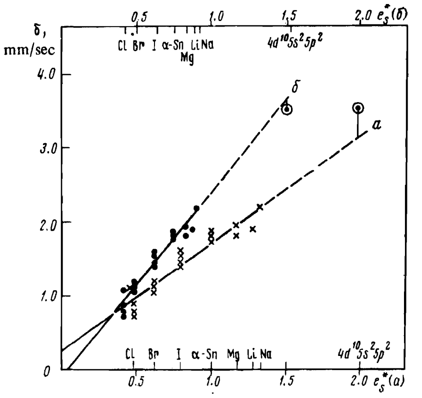

FIG. 2. Dependence of the isomeric shift (relative to an $Sn^{119}O_2$ source) in tin compounds ($SnCl_4$, $SnBr_4$, SnI_4, α-Sn, Mg_2Sn, Li_4Sn, Na_4Sn) on the effective charge of the s valence electrons: a) without allowance for screening, $\delta = 1.47e_s^* + 0.24$; b) with allowance for screening, $\delta = 2.50e_s^* - 0.13$.

the case of crystals with sp^3 bonds, the degree of ionicity is given by [7]

$$\lambda(sp^3) = 1 - \exp(-0.5\Delta x^2), \qquad (2)$$

where, instead of the constant 0.18 in Eq. (1), we now have 0.5 and we then find that λ describes well the ionicity of crystals with sp^3 bonds.

3. Finally, in the determination of the electron density at tin nuclei, we must allow for the screening effects. [5,8] Figure 2 shows the dependence of the isomeric shift for several tin compounds with sp^3 bonds[1] on the value of e_s^* without allowance for the screening effect (a) and with allowance for this effect (b). The straight lines in Fig. 2 were obtained on a computer by the least-squares analysis of all the published values of δ. Extrapolation of the line a to $e_s^* = 2$, corresponding to the neutral state of tin, gave $\delta = +3.19$ mm/sec for Sn^{119} atoms in the In_2Te_3 lattice, which differed considerably from our experimental value. However, the extrapolation of line b to $e_s^* = 1.51$ (corresponding to the neutral state of tin subject to a correction for screening in accordance with Shpinel' [5]) gave $\delta = +3.65$ mm/sec, which agreed (within the limits of the rms error $\Delta\delta = 0.11$ mm/sec) with our isomeric shift of 3.58 mm/sec. This indicated that the screening effect was important.

Thus, an investigation of the Mössbauer effect in Sn^{119} nuclei introduced into the In_2Te_3 lattice shows that the tin atom remains in the neutral state. This accounts for the unusual (in the case of semiconductors) absence of extrinsic conduction when In_2Te_3-type crystals are doped with elements belonging to different groups in the periodic system. [2]

Studies of doped In_2Te_3-type crystals provide, in a sense, a unique opportunity for investigating the electron states of neutral atoms which are in equilibrium with the host lattice. In particular, the isomeric shift obtained for neutral tin atoms makes it possible to establish a scale for the determination of δ (or e_s^*) throughout the full range of ionicity in any tin compound in which tin atoms are tetrahedrally coordinated.

The application of the scale of isomeric shifts together with the calculated electron density $\psi_s^2(0)$ at a tin nucleus [8] to the $4d^{10}5s^25p^2$ and $4d^{10}5s5p^3$ configurations gives the following change in the charge radius of the tin nucleus in the case of a γ transition of 23.8 keV energy: $\delta R/R = +7.9 \times 10^{-5}$.

It should be noted that our experimental value of the isomeric shift of the neutral state of tin is in agreement with an estimate of the isotopic shift obtained by Bryukhanov et al.: [10] $\delta = +(3.5-3.6)$ mm/sec, found by extrapolation from the values of the isomeric shifts of tin atoms introduced into various metallic matrices.

The authors are grateful to V. V. Eremenko for valuable discussion of the results.

---

[1] The compound SnF_4 is not included in the $SnHal_4$ series because Gol'danskiĭ [9] shows that the coordination number of tin in this compound is 6 and the Sn–F bonds are due to electrons which are not in the sp^3 state.

[1] V. M. Koshkin and L. V. Atroshchenko, Fiz. Tverd. Tela (Leningrad) **11**, 816 (1969) [Sov. Phys.-Solid State **11**, 667 (1969)].
[2] V. M. Koshkin, L. P. Gal'chinetskiĭ, and A. I. Korin, Fiz. Tekh. Poluprovodn. **5**, 1983 (1971) [Sov. Phys.-Semicond. **5**, 1718 (1972)].
[3] E. E. Ovechkina and L. V. Atroshchenko, in: Monokristally i tekhnika (Single Crystals and Technology), No. 7, 1972, p. 50.
[4] V. L. Ponomarchuk and V. P. Romanov, Prib. Tekh. Eksp. No. 5, 31 (1972).
[5] V. S. Shpinel', Rezonans γ-lucheĭ v kristallakh (Resonance of γ Rays in Crystals), Nauka, M., 1969.
[6] D. A. Shirley, Rev. Mod. Phys. **36**, 339 (1964).
[7] E. E. Ovechkina, V. M. Koshkin, and L. A. Sysoev, Zh. Strukt. Khim. **10**, 156 (1969).
[8] J. K. Lees and P. A. Flinn, J. Chem. Phys. **48**, 882 (1968).
[9] V. I. Gol'danskiĭ, Usp. Fiz. Nauk **89**, 333 (1966) [Sov. Phys.-Usp. **9**, 461 (1967)].
[10] V. A. Bryukhanov, N. N. Delyagin, and V. S. Shpinel', Zh. Eksp. Teor. Fiz. **47**, 80 (1964) [Sov. Phys.-JETP **20**, 55 (1964)].

Translated by A. Tybulewicz
239