

Electron spin resonance of the intrinsic defects in TlSe crystals

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The electron spin resonance of undoped thallium selenide in the temperature interval 3.8–8.2 K is described and the temperature dependence of the paramagnetic relaxation rate is determined. Analysis of the allowed superhyperfine structure and the large hyperfine structure constant suggest that the model for the intrinsic defect of the TlSe structure can be used.

Anisotropic III-VI crystals have unique optical properties¹ which are attributable, as seems to be the case, to the intrinsic lattice defects. In view of this circumstance, it would be of interest to study the nature of such defects and their local structure. In this letter we present the results of an experimental study of the electron

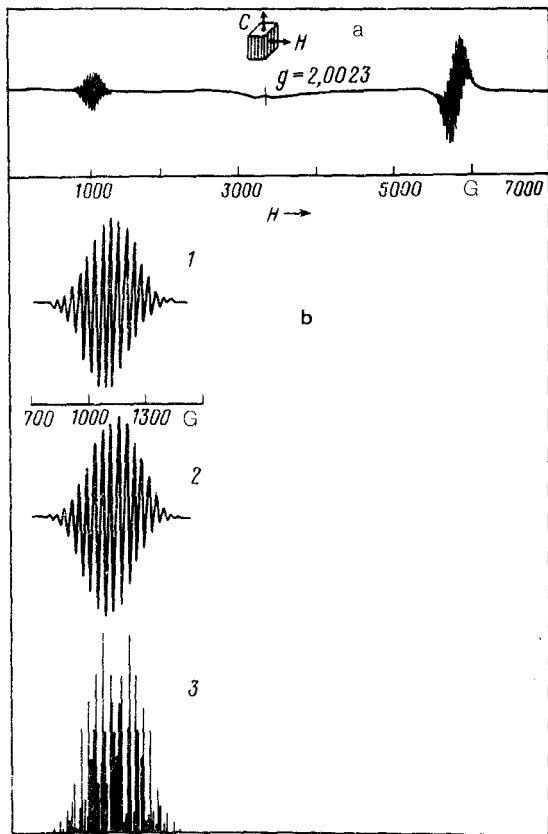


FIG. 1. The EPR spectra of thallium selenide. (a) The EPR spectrum of TlSe when the c axis of the crystal is oriented perpendicular to the direction of the magnetic field; (b) experimental superhyperfine transition (1) and theoretical superhyperfine transitions (2,3).

spin resonance, which was initially detected in thallium selenide crystals, and we propose a model for the paramagnetic (spin) center.

The p -TlSe crystals were grown by the zone-melting method. The hole density was 10^{13} cm^{-3} at room temperature. The thallium selenide single crystals crystallize in the tetragonal structure (space group $I4/mcm$). We used the Bruker ER220D-LR spectrometer to study the electron spin resonance. The spin relaxation rate was determined by the method of continuous resonance-transition saturation.

The ESR spectrum for the orientation of the c axis of the crystal perpendicular to the direction of the magnetic field is shown in Fig. 1a. The spectrum consists of two hyperfine-structure components, each of which is split into 18 superhyperfine-structure lines. This spectrum can be described by a spin Hamiltonian of the type

$$\mathcal{H} = \tilde{S}\tilde{A}I + g\beta\mathbf{H}\mathbf{S} + g_N\beta_N\mathbf{H}\mathbf{I} + \sum_i \tilde{S}\tilde{B}_i\mathbf{I}_i, \quad (1)$$

where g and g_N are the electron and nuclear g -factors, \tilde{A} and \tilde{B}_i are the hyperfine and superhyperfine interaction tensors, I is the nuclear spin of the thallium atom on which

the unpaired electron is localized, I_i are the nuclear spins of the thallium atoms in the nearest neighborhood, and β and β_N are the Bohr magneton and the nuclear magneton.

The angular dependence of the hyperfine structure of the spectrum is seen when the crystal rotates in the plane of the c axis. The large value of the hyperfine-interaction constant and its anisotropy are evidence that the unpaired electron is probably localized on the hybrid sp^3 orbital of the thallium atom. The Tl^{203} and Tl^{205} isotopes have the same nuclear spin, $I = 1/2$, and approximately equal value of the gyromagnetic ratio² ($\gamma/2\pi$) (Tl^{203}) = 2456 Hz/G; ($\gamma/2\pi$) (Tl^{205}) = 2480 Hz/G. If the scarce Se^{77} isotope (8.3% natural abundance) is disregarded, we can assume that the thallium nuclei in the nearest neighborhood of the paramagnetic defect account for the superhyperfine-structure. From the number of superhyperfine-structure lines and the relative intensity of these lines we can suggest the most likely environment of the magnetic electron. Let us examine a fragment of the crystal structure of thallium selenide, shown in Fig. 2a. Two thallium atoms $Tl(III)$, separated a distance $c/s = 3.5 \text{ \AA}$ on the c axis, are the nearest neighbors of the unpaired electron which is localized on the thallium atom. Next we have four Tl^+ atoms, separated a distance $a/2 = 4.02 \text{ \AA}$, and finally we have eight Tl^+ atoms spaced 5.33 \AA apart. If the interaction is assumed to be a superhyperfine dipole-dipole interaction, the corresponding constants are $B_1:B_2:B_3 = 1:0.66:0.29$. The interaction with the more-distant neighbors is taken into account in the superhyperfine structure linewidth $\delta = 0.24B_1$, and the anisotropy of the superhyperfine interaction can be ignored, which is quite legitimate in the case of the low-field hyperfine-structure component (Fig. 1a). In order to have an even number of superhyperfine-structure lines, there must be only one thallium atom, rather than two, in the nearest neighborhood. The superhyperfine transitions calculated in the approximation indicated above are shown in Fig. 1b. Also shown in this figure is a

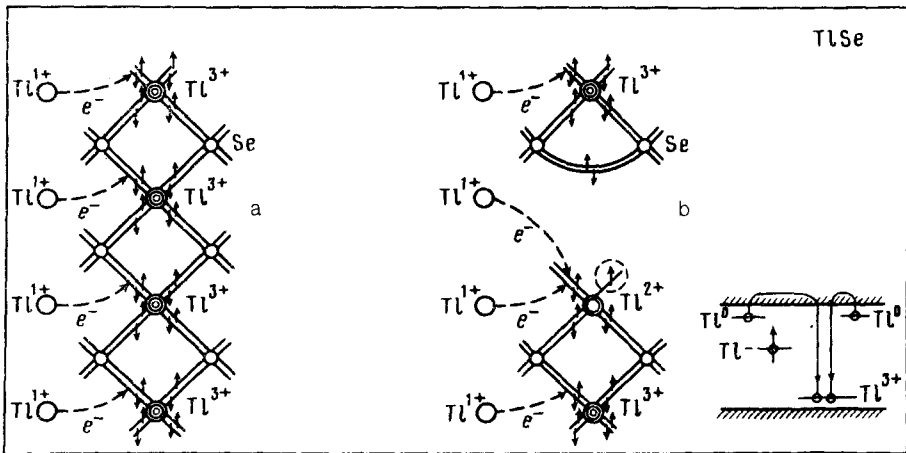


FIG. 2. The crystal structure of TlSe. (a) A fragment of the crystal structure of thallium selenide; (b) a model of the defect showing the absence of one of the links in the TlSe chain.

computer-simulated spectrum of the superhyperfine structure with $\delta = 0.24B_1$. The values of the constants determined from the experimental spectrum are $B_1 = 115$ G, $B_2 = 76$ G, and $B_3 = 33$ G.

Agreement between the experimental and calculated spectra of the superhyperfine structure is evidence that one of the Tl(III) atoms is absent in the nearest neighborhood of the magnetic electron.

Taking into account the above-mentioned remark concerning the sp nature of the orbital of the thallium atom, in which the unpaired electron is localized, it would seem that the most probable model for the defect would be the absence of one of the links of the Tl-Se chain (Fig. 2b). In this case three electrons would be localized in the two "free" sp^3 orbitals of the defect, so that one of the orbitals would always have an unpaired electron. In general, an unpaired electron may be found in a "resonant" state between two links, which accounts for the anisotropy of the hyperfine interaction with the axial axis which runs in the same direction as the Tl-Se chain in the crystal, consistent with the results of the experiment.

Study of the temperature dependence of the spin-lattice relaxation of a paramagnetic defect at temperatures in the interval 3.8–8.2 K showed that the relaxation rate τ^{-1} is described by the expression

$$\tau^{-1} = [(8.1 \pm 0.3) \times 10^3 T^{0.5} + (4 \pm 3) \times 10^4 T^5] c^{-1} \text{ s}^{-1}. \quad (2)$$

The presence of the Orbach-Blume process (the T^5 number) in the spin-lattice-relaxation mechanism confirms that the magnetic state of the defect has a high multiplicity which stems from the strong hyperfine interaction. The process described by $T^{0.5}$, however, remains unclear.

¹G. L. Belen'kiĭ and V. B. Stopachinskiĭ, Usp. Fiz. Nauk **140**, 233 (1983) [Sov. Phys. Usp. **26**, 497 (1983)].

²A. Lösche, Kerninduktion (in German), Deutsche Verlag der Wissenschaften, Berlin (1957).

Translated by S. J. Amoretty