

Oscillatory nature of the relaxation to equilibrium in the system of intrinsic defects of nonstoichiometric lead and tin tellurides

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Experiments demonstrate that there are semiconductor crystals in which the relaxation of the intrinsic defects to an equilibrium distribution at a fixed temperature is of the nature of an oscillatory process in a nonlinear system with a pronounced friction. Tellurides of lead and tin were studied as particular examples.

The defects in a material with a defect concentration above the thermodynamic—equilibrium level anneal out at some rate or other. In other words, the concentration of these defects decreases. Under fixed external conditions the theory predicts a monotonic relaxation to an equilibrium defect distribution in crystals in the course of this annealing.¹

In a study of the electronic conductivity of various crystals of lead and tin tellurides, we have observed a different relaxation kinetics in the system of intrinsic defects in semiconductor crystals. Specifically, the relaxation to equilibrium occurs through a rapidly damped oscillatory process as in a nonlinear system with a pronounced friction. This process is illustrated in Fig. 1 as a plot of the Hall coefficient versus the time at room temperature for one of these samples, with the composition $\text{Pb}_{0.9}\text{Sn}_{0.1}\text{Te}$. We selected this sample for the most extensive and most detailed experiments. Since the free carriers in the tellurides of lead and tin result from intrinsic lattice defects, this curve reflects the kinetics of the relaxation to equilibrium in the defect subsystem of these crystals.

A relaxation process of an oscillatory nature was observed in crystals grown from highly nonstoichiometric melts, enriched in the metallic components, like those studied in Ref. 2. The ends of these bars have an *n*-type conductivity. According to Ref. 2, the end region contains a large number of interstitial tin atoms. The present experiments showed that the *n*-type region directly adjacent to the growth *p-n* junction in these crystals is in an unstable-equilibrium state, which is a consequence of the crystal growth conditions. It may persist for a long time if the crystal is held near room temperature. This state will be destroyed if the crystal temperature is lowered substantially and rapidly, by immersion in liquid nitrogen, for example. After such a cooling, and after a subsequent slow heating back to room temperature, the density of free carriers in these crystals (and thus the density of the intrinsic defects associated with these carriers) behaves in an extremely distinctive way as a function of the temperature. Curve 1 in Fig. 2 shows this density as a function of the temperature *T*. At room temperature the electron density becomes greater than its original value. It undergoes similar changes after a slight heating of the crystal from room temperature to 80–

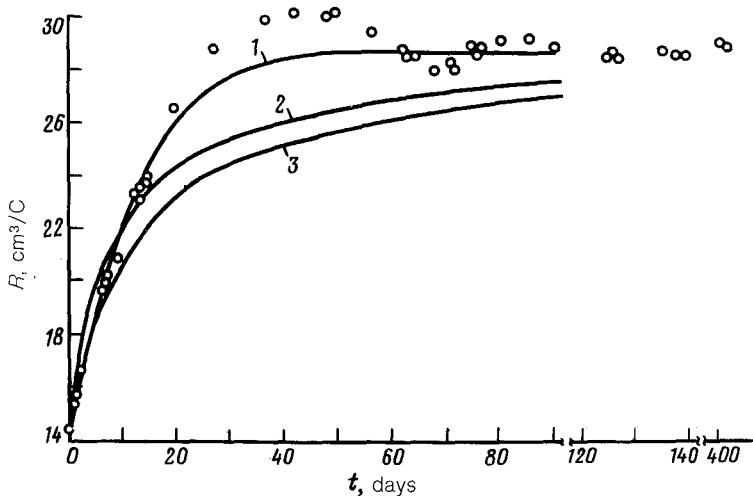


FIG. 1. Time evolution of the Hall coefficient in a $\text{Pb}_{0.9}\text{Sn}_{0.1}\text{Te}$ sample at room temperature (see the text proper for an explanation). Circles—Experimental results; solid lines—theoretical predictions (see the text proper) for the values $\alpha = 1$ (curve 1) and $\alpha = 2$ [curves 2 and 3, for different values of the coefficient K in Eq. (1)].

100 °C, followed by a cooling. When the cooling–heating cycles are repeated, the non-monotonic temperature dependence of the Hall coefficient disappears (curves 2–4 in Fig. 2).

If the temperature cycling is stopped at room temperature at any point, the elec-

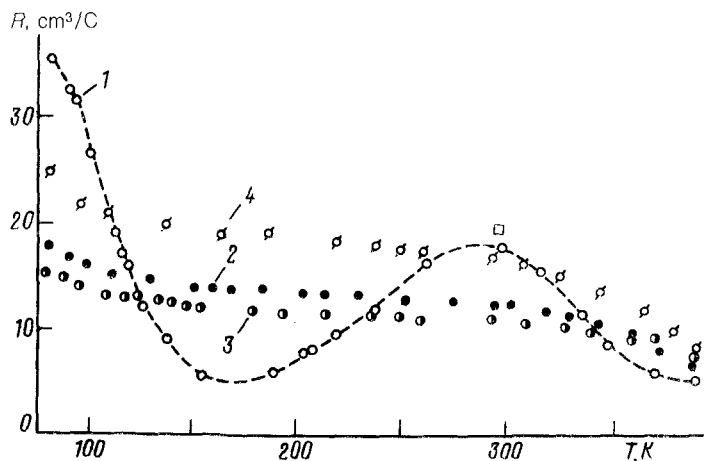


FIG. 2. Temperature dependence of the Hall coefficient for the same sample as in Fig. 1. The curve labels show the order of the temperature cycle (see the text proper for an explanation). The time interval between temperature cycles 1 and 2 was 6 days, that between cycles 2 and 3 was 1 day, and that between cycles 3 and 4 was 7 days. The crystal was held at room temperature between cycles. The square shows the value of R at the same temperature before the first rapid cooling of the crystal.

trical properties of the crystals with the temperature dependence of the carrier density described above do not remain constant over time. At first, the density of free carriers (and thus the density of the intrinsic defects responsible for these carriers) decreases substantially and rapidly with the time. The process slows down as the equilibrium state is approached. The system tends toward a given equilibrium state not in a monotonic way but by oscillating around the equilibrium state. At room temperature the duration of this relaxation is very long—a matter of several months. We were unable to clearly and reliably observe more than two excursions in different directions from the equilibrium position toward which the system was relaxing. The remaining changes with the time were of a nature which could be attributed to the experimental errors in the determination of the Hall coefficient. As Fig. 1 shows, the nominal period of this oscillation in the carrier (or defect) density decreases as the process proceeds and also with decreasing amplitude of the excursion of the density from its equilibrium value. In other words, the crystal behaves as a typical nonlinear oscillator system with a pronounced friction.

To study the mechanism for the change in the state of the defect subsystem of the crystals which had been driven from their unstable-equilibrium state, in the initial stage of the annealing, we compared the experimental results with theoretical predictions of the time dependence of a nonequilibrium parameter for reactions of various orders.¹ We assumed that the time dependence of the Hall coefficient, $R(t)$, can be represented by $R(t) = 1/\{e[n_\infty + N(t)]\}$, where n_∞ is the equilibrium density toward which the system is tending, and N is the density of nonequilibrium carriers (or defects). The time dependence of the latter density, $N(t)$, is the solution of the differential equation

$$\frac{dN(t)}{dt} = -KN^\alpha(t). \quad (1)$$

The parameter α specifies the order of the reaction. It embodies information on the mechanism for the time evolution of the defect density.¹

We see from Fig. 1 that in the initial stage of the relaxation to equilibrium the experimental results can be described well by the curve of a first-order reaction. The results are described considerably less well by the curves for a second-order reaction. The meaning here, according to Ref. 1, is that the time evolution of the density of defects responsible for the free carriers is governed not by the direct recombination of randomly distributed point defects, e.g., (interstitial atom)-vacancy defects, but more probably by a capture of donor centers by certain capture centers. The latter may be the surface of the crystal, interfaces of some sort, etc. In light of the earlier discussion of the properties of the crystals in which this effect is observed, this result correlates with data³ showing a high probability for the excess tin in PbSnTe to move to the surface of the crystal as it is being grown from a material highly enriched in the metallic components. At this point, the reasons why the relaxation to an equilibrium defect distribution in such crystals can take on the features of an oscillation process are not clear.

¹J. Bourgoin and M. Lannoo, *Point Defects in Semiconductors II: Experimental Aspects*, Springer-Verlag, New York, 1983.

²P. M. Starik, D. M. Zayachuk, V. I. Lastivka, and S. A. Chornei, *Pis'ma Zh. Tekh. Fiz.* **13**, 439 (1987) [*Sov. Tech. Phys. Lett.* **13**, 181 (1987)].

³V. A. Shenderovskii, P. M. Starik, V. I. Mikityuk, *et al.*, *Dokl. Akad. Nauk UkrSSR A*, No. 2, 61 (1989).

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