

# Deep and shallow acceptor levels in solid solutions of lead and tin chalcogenides, $\text{Pb}_{0.92}\text{Sn}_{0.08}\text{S}_{0.8}\text{Se}_{0.2}$

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A study of the Hall effect in  $\text{Pb}_{0.92}\text{Sn}_{0.08}\text{S}_{0.8}\text{Se}_{0.2}$  has revealed acceptor states, which form deep ( $\epsilon_a \sim 0.085$  eV) and shallow ( $\epsilon_a \sim 0.025$  eV) energy levels in the band gap.

The primary acceptor centers in lead salts and solid solutions containing them are metal vacancies whose energy levels lie against a background of the allowed energies of the valence band.<sup>1,2</sup> To the best of our knowledge, acceptor levels of a different type have yet to be observed in undoped crystals of lead–tin chalcogenides. In the present

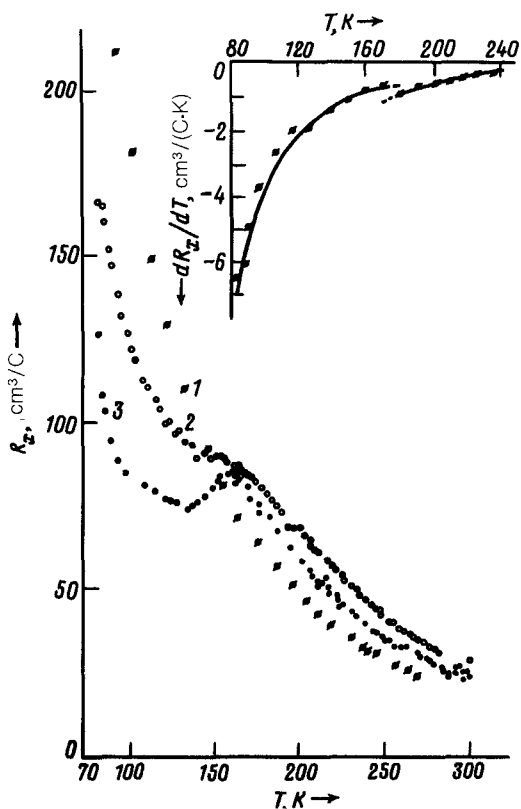


FIG. 1. Characteristic temperature dependence of the Hall coefficient for various groups of  $\text{Pb}_{0.92}\text{Sn}_{0.08}\text{S}_{0.8}\text{Se}_{0.2}$  crystals. The inset shows the temperature dependence of the first derivative  $dR_x/dT$  for the crystals of the first group, which are represented by curve 1 in the main part of the figure.

study we have observed such levels, in measurements of the Hall effect in a  $\text{Pb}_{0.92}\text{Sn}_{0.08}\text{S}_{0.8}\text{Se}_{0.2}$  solid solution with low charge-carrier densities (down to values on the order of  $10^{15} \text{ cm}^{-3}$ ) in the crystals immediately after their growth.<sup>3</sup>

We studied several dozen samples over the density range  $5 \times 10^{15} - 3 \times 10^{17} \text{ cm}^{-3}$ . The statistical nature of this study made it possible to lump all these crystals into three groups on the basis of the temperature dependence of the Hall coefficient. Each of the groups is represented by a curve in Fig. 1. Of interest in connection with the present study are two aspects of these curves. First, the Hall coefficient increases with decreasing temperature for all crystals, and the increase is extremely substantial (the ratio  $R_{77}/R_{300}$  for the samples with the lowest density reaches values of 1.5 orders of magnitude). Second, the curves of  $R_x(T)$  are not monotonic for any of the crystals, although the nature and the extent of the deviation from a monotonic behavior are different for the different groups of samples. The monotonic behavior is disrupted in the temperature interval<sup>1)</sup>  $\sim 140-180 \text{ K}$ .

The nature of the temperature dependence of  $R_x$  clearly indicates that these

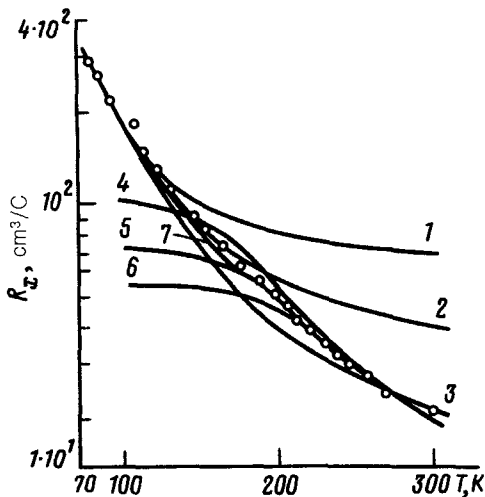


FIG. 2. Temperature dependence of the Hall coefficient. The points are experimental. The solid lines are theoretical, calculated from expressions (1) and (2) with the following values of the activation energy  $\epsilon_a$ , eV: 1—0.02; 2—0.03; 3—0.04; 4—0.08; 5—0.089; 6—0.1. Curve 7 corresponds to the simultaneous operation of two acceptor levels, with activation energies of 0.025 and 0.085 eV.

materials contain acceptor centers with a nonzero activation energy and are thus distinguished from binary compounds and most IV–VI solid solutions. Furthermore, the large drop in the values of  $R_x$  and the fairly rapid change in this coefficient at both low and high temperatures lead to the conclusion that we are dealing with more than a single acceptor level of this type. This conclusion is supported by a quantitative analysis whose results are shown in Fig. 2 for the particular case of one of the samples of the group of crystals for which the  $R_x(T)$  curves are of the type shown by the curve 1 in Fig. 1. The temperature dependence of the hole density (and thus that of the Hall coefficient) was calculated on the basis of the standard equations for electrical neutrality and an expression for the hole density in the approximation of a Kane dispersion:

$$p = \Delta + N_a \left( 1 - \frac{1}{1 + \frac{1}{2} \exp(-\epsilon_a^* - \eta^*)} \right), \quad (1)$$

$$p = \frac{(2m_d k_0 T)^{3/2}}{3\pi^2 \hbar^3} S_{3/2,0}^0(\eta, \beta). \quad (2)$$

Here  $N_a$  and  $\epsilon_a$  are the concentration and activation energy of the acceptor centers, and  $\Delta$  is the difference between the densities of holes which are not frozen out at the lowest temperatures (their presence is confirmed by measurements of the Hall coefficient carried out at liquid-helium temperature for several of the samples) and possible donor centers. The effective mass of the density of states,  $m_d$  was taken to be the same as in calculations of the mobility:  $m_d(T) = 0.14(T/77)^{0.6} m_0$ .

It can be seen from Fig. 2 that only a small part of the  $R_x(T)$  curve along the temperature scale can be described satisfactorily under the assumption that there ex-

ists only a single acceptor level with a nonzero activation energy. In order to explain the low-temperature part of a curve, it is necessary to assume that there exists a "shallow" level, while an explanation of the high-temperature part of the curve requires the assumption of a "deep" level. The activation energy  $\epsilon_a$ , which leads to the best description of the low-temperature parts of the  $R_x(T)$  curves, is  $\sim 0.25$  eV; the corresponding activation energy for the high-temperature region is  $\sim 0.085$  eV. These activation energies are averages over the results on a large number of samples of this group of crystals. With the latter value of  $\epsilon_a$  it is also possible to find a good description of the high-temperature parts of the  $R_x(T)$  curves for the other two groups of samples, shown by curves 2 and 3 in Fig. 1.

At this point the nature of these acceptor centers is unknown. All that can be asserted is that they are associated with intrinsic defects, since these crystals were grown from highly pure starting materials and contained no impurities. These centers are probably large complexes. We attribute their appearance to the tendency of this particular material to undergo a self-compensation.<sup>3</sup> We have not seen such acceptor levels, at least in a study of  $\text{Pb}_{1-x}\text{Sn}_x\text{S}_{1-y}\text{Se}_y$  solid solutions close in composition to that studied here, whose crystals exhibit no characteristics of compensated materials. On the other hand, the activation energy of the deep level which we did observe correlates very well with that of acceptor centers in sulfur-rich  $\text{PbS}_{1-x}\text{Se}_x$  crystals heavily doped with compensating impurities. Those centers are also attributed to large complexes of unknown origin.<sup>5</sup> Comparing our data with the data of Ref. 5, we might suggest that compensation processes lead to the formation of acceptor centers which create deep levels in the band gap in complex systems based on the selenides and sulfides of lead, regardless of whether they result from an interaction of intrinsic components or foreign impurities.

We would like to conclude with the following comments. At this point there is uncertainty regarding not only the nature of the acceptor centers which have been observed but also regarding the question of whether we are dealing with the simultaneous operation of two acceptor levels or a conversion of certain acceptor complexes (or parts thereof) into each other as the temperature is varied. In principle, the first of these suggestions would permit a completely satisfactory theoretical description of the entire temperature dependence  $R_x(T)$  for the crystals of the first group (curve 7 in Fig. 2), but without additional assumptions it would not be possible to explain the  $R_x(T)$  curves for the group of crystals represented by curve 3 in Fig. 1. If it is instead assumed that certain complexes undergo a conversion (complete or partial) into others as the temperature is varied, then this behavior of  $R_x(T)$  would become completely understandable, at least at a qualitative level. A final resolution of this question will require further study, primarily a theoretical derivation of the energy states of complexes of intrinsic defects in IV-VI compounds.

<sup>1</sup>A nonmonotonic temperature dependence is also characteristic of many other physical properties of these materials.<sup>4</sup>

<sup>3</sup>J. N. Parada and G. W. Pratt, Phys. Rev. Lett. **22**, 180 (1969).

<sup>5</sup>B. A. Volkov and O. A. Pankratov, Zh. Eksp. Teor. Fiz. **88**, 280 (1985) [Sov. Phys. JETP **61**, 164 (1985)].

<sup>3</sup>V. I. Gerasimov and Z. T. Drapak *et al.*, *Izd. Akad Nauk SSSR, Neorgan. Mater.* **21**, 910 (1985).

<sup>4</sup>V. J. Garasim, D. M. Zayachuk, R. D. Ivanchuk *et al.*, *Phys. Status Solidi A* **111**, K99 (1989).

<sup>5</sup>A. N. Veiš, V. I. Kaïdanov, R. Yu. Krupitskaya *et al.*, *Fiz. Tekh. Poluprovodn.* **14**, 2349 (1980) [*Sov. Phys. Semicond.* **14**, 1392 (1980)].

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