Precipitation of Te and Pb in PbTe Crystals

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Precipitation rates of Te and Pb in supersaturated PbTe crystals have been studied in the temperature range from 180° to 400°C. The experimental results are interpreted as evidence that the dislocation and its interacting field may be considered as a simple cylinder sink with an effective capture radius R. The activation energy associated with precipitation was found to be 0.88 ev. Thermoelectric power measurements were used to monitor the precipitation process in p-type PbTe. Precipitation is shown to be a simple means for controlling the carrier concentration in nonstoichiometric crystals displaying retrograde solubility in their phase diagrams. From Hall data on near intrinsic crystals, the intrinsic carrier concentration and resistivity for PbTe are estimated to be $n_i = 2 \times 10^{16}/\text{cm}^3$, and $\rho_i = 0.2$ ohm cm.

INTRODUCTION

COMPOUND semiconductor crystals may exist over a range of composition near the stoichiometric proportions, through the incorporation of interstitial atoms, place exchange or creation of lattice vacancies. In the case of the lead salt semiconductors PbS, PbSe, and PbTe the vacancy model is believed to be appropriate.[1] Since vacancies contribute donor or acceptor levels in the band structure of these semiconductors, a knowledge of the rules governing the concentration and kind of vacancies in the crystal, contributes to the understanding of their various electrical and optical properties.

One of the important characteristics of nonstoichiometric crystals, is the maximum concentration of vacancies or equivalently the concentration of excess ions which can be incorporated into the crystal lattice. This should, in general, be a temperature dependent quantity and will generally be different for vacancies or excess ions in the anion or cation sublattices.

Experimental studies of the maximum deviation from the stoichiometric composition of PbTe have been made in the temperature range from 400°C to the maximum melting temperature of the crystal.[2] The composition of the crystal in equilibrium with the lead-rich liquid, or tellurium-rich liquid, was established through a vapor diffusion process. The resulting composition, as a function of temperature, reveals regions of retrograde solubility for both the excess lead and excess tellurium crystals. For example, at about 775°C the crystal may incorporate maximum excesses of about 0.013 at. %. Te and 0.006 at.% Pb. These correspond to carrier concentrations of 7.6×10^{18} holes/cm³ and 3.3×10^{18} electrons/cm³, respectively. At 500°C, the solubility of the atoms is reduced to 4.5×10^{18} excess Te/cm³, and 7×10^{17} excess Pb/cm³. At 400°C, the solubilities are 1.5×10^{18} excess Te/cm³, and 1.5×10^{17} excess Pb/cm³, and the time for the crystals to come into equilibrium with the vapor, through diffusion, was believed to be of the order of 500 to 1000 hr.[2]

Within the retrograde solubility region, a crystal possessing the maximum excess concentration of cations or anions at a given temperature will become supersaturated in that ion upon cooling the crystal to a lower temperature. The excess ions may be disposed of by an internal precipitation process, in which the excess atoms diffuse from normal sites to precipitation centers, where they deposit out as neutral atoms. In this process, the concentration of donor or acceptor levels in the crystal is reduced to the maximum value appropriate for the lower temperature. The average distance an atom must diffuse to an internal precipitation center, such as a dislocation, will generally be much shorter than the corresponding distance to the surface in crystals treated by the vapor diffusion process. Hence, the equilibrium times for the internal process will be less than for the process involving diffusion from the vapor or liquid state.

The present experiments were designed to study the rates of precipitation of excess Pb and Te in PbTe crystals at relatively low temperatures, where the vapor diffusion process is excessively slow. From the precipitation rate curve for a given temperature, one can establish the nature of the precipitation center. A second objective in these experiments is to utilize this very simple internal precipitation process for preparing crystals of PbTe with controlled carrier concentration approaching the stoichiometric limits.

EXPERIMENTAL METHOD

Changes in crystal composition resulting from the precipitation of one of the components of a compound may be revealed by changes in some of the electrical properties of the crystal. Experiments designed to study the precipitation rate, therefore, should utilize an electrical property that is highly sensitive to crystal composition at the temperature at which precipitation occurs. In addition, it would be desirable for the electrical property selected to be a simple quantity that could be recorded as a function of time. In p-type PbTe the thermoelectric power satisfies these requirements better than any other electrical property.

The thermoelectric power α in p-type crystals is posi-

[1] W. W. Scanlon, *Properties of Elemental and Compound Semiconductors*, edited by H. Gatos (Interscience Publishers, Inc., New York, 1959), p. 185.

[2] R. F. Brebrick and R. S. Allgaier, J. Chem. Phys. **32**, 1826 (1960).

tive at low temperatures, and rises with increasing temperature to a maximum value. With further increase in temperature, α decreases rapidly through zero to a negative maximum. Thermoelectric power curves for crystals of different acceptor concentrations are similar in shape, but the temperature at which α crosses over from positive to negative values decreases with decreasing acceptor concentration. In this steep portion of the thermoelectric power curve near the crossover temperature, the value of α is very sensitive to the acceptor concentration. Changes in the acceptor concentration in p-type PbTe crystals caused by precipitation of excess Te may be evaluated by studying the rate of change in α as the supersaturated crystal is held at a fixed temperature in the α crossover region.

The problem of converting values of α to acceptor concentrations in the transition region between extrinsic and intrinsic conduction is a difficult one to solve using theoretical expressions for the thermoelectric power in semiconductors. Fortunately, it is possible to evaluate the data much more simply by an experimental method. Thermoelectric power vs temperature curves may be obtained for a group of crystals having acceptor concentrations, based upon room temperature Hall data, within the range of values encountered in the precipitation experiments. Since the time required to obtain the α curves is negligibly small compared to the times involved in precipitation, one may safely assume the crystal compositions are fixed in these experiments. In the vicinity of temperatures where α changes from positive to negative values, the thermoelectric power curves are approximately parallel and linear over an appreciable range of temperatures. A plot of α against acceptor concentration at a given temperature in this region can be used to convert values of α obtained in precipitation experiments into acceptor concentrations. These data may then be used to give the rate of precipitation of excess Te at the temperature under investigation. Extrapolating the data at various precipitation temperatures to infinite time gives values for saturation concentration of Te in the PbTe lattice as a function of temperature.

In the case of n-type PbTe crystals containing an excess of Pb in the lattice over the stoichiometric proportions, the saturation concentration of Pb also decreases below about 700°C with decreasing temperature. A crystal saturated with Pb at one temperature in this region may dispose of the excess Pb by precipitation when cooled to a lower temperature. Unfortunately, there is no convenient electrical property known which can be measured at the precipitation temperature to monitor the concentration of donors in the crystal. At the precipitation temperatures of interest, the n-type crystals are well into the intrinsic region. Thus, crystals must be periodically quenched to room temperature, where measurements such as the Hall effect may be taken to evaluate the progress of the precipitation. Ex-

periments of this type have been carried out by Pell[3] in studying precipitation of Li and Ge.

THE EXPERIMENT

Pulled single crystals of p-type PbTe prepared by Dr. Houston of this Laboratory have acceptor concentrations of about $3 \times 10^{18}/cm^3$ due to nonstoichiometry. Etch pit counts on these crystals give dislocation densities of about $10^5/cm^2$. Specimen dimensions of about $3 \times 3 \times 15$-mm^3 are used in thermoelectric power studies. The n-type specimens were prepared by Dr. Brebrick by diffusion treatments in a system containing a lead rich alloy of PbTe. The details of this process are given elsewhere.[2]

For the p-type material, the initial acceptor concentration and mobility were obtained from room temperature Hall effect and resistivity measurements. The sample was then mounted for thermoelectric power measurements. Iron-Constantan thermocouples were pressed against each end, and a heater near one end provided a temperature difference of about 1°C along the sample. The thermoelectric voltage was measured with reference to the iron thermocouple leads. For the investigations carried out here, sample temperatures were sufficiently low that there was no need to surround them in a nonoxidizing atmosphere. Similar runs in $vacuo$ yielded the same results as were obtained in air.[4] In the initial run, thermoelectric power data were taken from $-196°$ to about 400°C. The crystal was then held at 385°C. The thermoelectric power changed gradually over a period of 2 hr, approaching a stable value for the saturation concentration of Te at that temperature. The thermoelectric power curve was then obtained from 385° down to $-196°$C. Room temperature Hall and resistivity data were taken for the crystal to evaluate the composition change incurred. The crystal was then remounted for thermoelectric power studies, and it was held at a fixed temperature of 370°C until thermoelectric
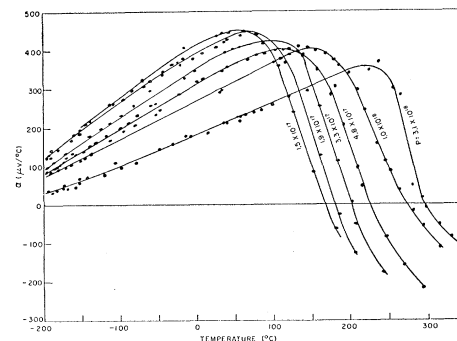

FIG. 1. Thermoelectric power vs temperature for p-type PbTe crystals having acceptor concentrations in the range from $3 \times 10^{18}/cm^3$ to $1.5 \times 10^{17}/cm^3$.

[3] E. Pell, $Solid$ $State$ $Physics$ in $Electronics$ and $Communications—Semiconductors$, edited by M. Deserant and J. L. Michiels (Academic Press, Inc., New York, 1960), Vol. 1, p. 261.
[4] R. Riedl (private communication).

power showed no further change; this time, 4 hr were required. Subsequent experiments of a similar type at 294°, 245°, 204°, and 181°C were made requiring increasing times to reach equilibrium. For the lower temperature experiments, times of the order of days or weeks were required in order to come to equilibrium. For these long runs the thermal emf from the sample with a fixed 1°C temperature gradient was put on a recording potentiometer to indicate the progress of the composition change. Periodic measurements of α by the standard technique with a Leeds & Northrup type K potentiometer gave more precise values of α as a function of time for the precipitation rate studies.

RESULTS

p-Type Crystals

Thermoelectric power curves obtained for crystals of various acceptor concentrations are shown in Fig. 1. The general behavior is normal for a p-type semiconductor. In the case of the crystal with an acceptor concentration of 3×10^{18} for which α data was taken at temperatures exceeding 300° or 350°C, there is evidence that composition changes were occurring during the course of the α measurements at these high temperatures, even though such measurements required but a few minutes. In this case, the high temperature portion of the curve shows deviations from the general behavior expected for crystals which maintain a fixed composition throughout the time required to obtain the curve.

The values of carrier concentration, mobility, and resistivity for the crystals at room temperature are listed in Table I. The time required to reach 95% of the saturation concentration of acceptors for various temperatures, is shown in Fig. 2. The saturation concentration of excess Te, as a function of temperature is shown in Fig. 3. Assuming an exponential law of the form $n = n_0 e^{(-w/kT)}$, one finds that the energy w is 0.88 ev which is larger than the value of 0.62 ev obtained in the vapor diffusion process.[2]

The data on precipitation rate are analyzed in detail for a typical experimental run for the equilibrium temperature of 204°C. The results are compared to Ham's
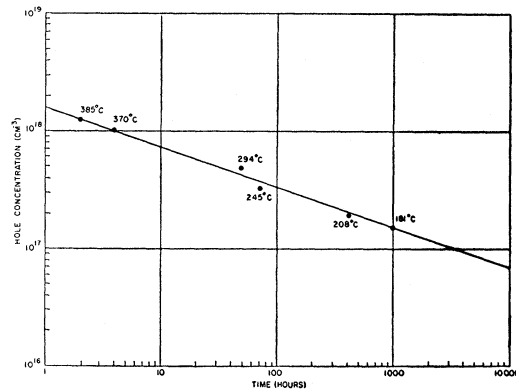
FIG. 2. Equilibrium time and temperatures for various acceptor concentrations in PbTe crystals.

theory of stress-assisted precipitation on dislocations.[5] This theory includes the effects of both drift and diffusion to a dislocation with its associated stress field. The stress field is characterized by a cylinder around the dislocation having an effective capture radius R. The time t from precipitation experiments is expressed in terms of a reduced time factor $T = Dt/r_s^2$, where D is the diffusion coefficient and r_s is the radius of a cylinder concentric with the dislocation such that $\pi r_s^2 = 1/L$, where L is the number of edge dislocations per unit area. Data of Boltaks and Mokhov[6] on self-diffusion in PbTe were used for calculating D at various temperatures.
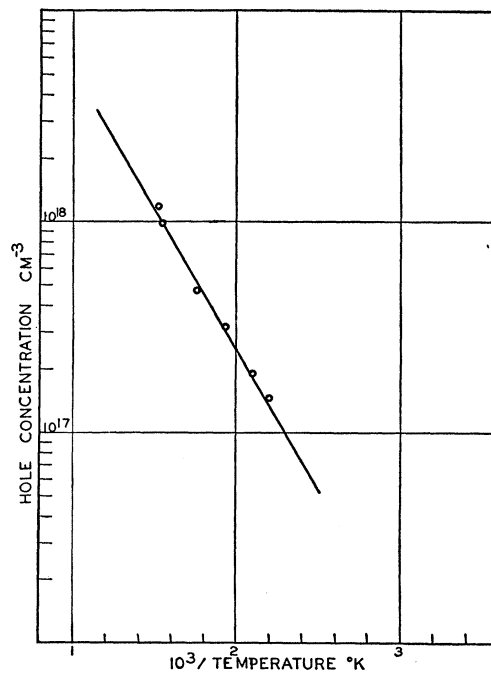
TABLE I. Values of room temperature carrier concentration, mobility, and resistivity in PbTe crystals annealed at various temperatures.

Annealing temperature (deg C)	p (10^{17}/cm³)	μ (cm²/v-sec)	ρ (10^{-3} ohm-cm)
(initial condition)	31	870	2.3
385	12	760	6.7
370	10	680	9.1
294	4.8	690	19
245	3.3	730	26
204	1.95	790	41
181	1.5	715	58

FIG. 3. The saturation concentration of excess Te in PbTe crystals as a function of reciprocal temperature.

[5] F. S. Ham, J. Appl. Phys. **30**, 915 (1959).
[6] S. I. Boltaks and Iu. N. Mokhov, Soviet Phys.—Tech. Phys. **3**, 974 (1958).
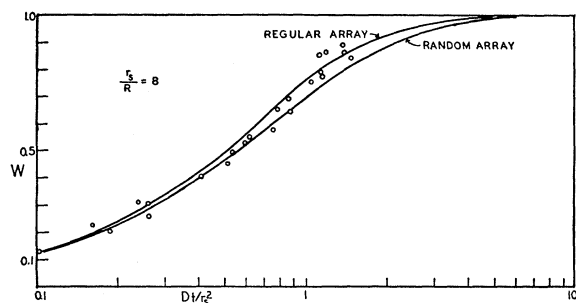
FIG. 4. Precipitated fraction (W) as a function of reduced time $(Dt/r^2{}_s)$ in PbTe crystals at 204°C.

The precipitated fraction W is then plotted as a function of the reduced time giving the points shown in Fig. 4. From the value of T for which W rises to $1-e^{-1}$ of the maximum value, one may obtain the value of r_s/R by using Fig. 5 of reference 5. The experimental data indicate a ratio $r_s/R=8$.

Ham's theoretically calculated curve for the unprecipitated fraction, as a function of the reduced time for $r_s/R=8$, is shown by the full lines in Fig. 4. Two curves are given, one for a regular and the other for a random array of dislocations. The experimental points appear to agree somewhat better with the regular array curve, but this conclusion is not decisive due to the similarity of the two curves and scatter of experimental points.

n-Type PbTe

The precipitation of excess Pb in n-type PbTe has not been investigated in as much detail as the precipitation
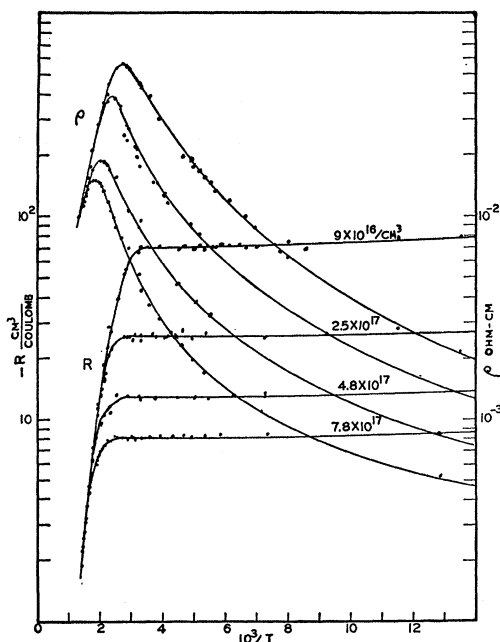

FIG. 5. Hall effect and resistivity as a function of reciprocal temperature for n type PbTe crystals after various precipitation times at 400°C.

of Te in p-type PbTe. At the precipitation temperature, n-type crystals are in the intrinsic region and must be quenched periodically to room temperature for measurements of the composition change. Experiments were conducted only to demonstrate the effects of precipitation in n-type crystals, but no conclusions were drawn regarding the equilibrium concentrations of excess Pb at various temperatures or precipitation rates. n-type PbTe material was prepared by Dr. Brebrick by the vapor diffusion process with a donor concentration of $7.8\times10^{17}/cm^3$ based upon Hall effect data. Hall effect and resistivity, as functions of temperature, were measured on the starting material and the results are shown on the lowest set of curves in Fig. 5. After holding the crystal at 400°C for 15 hr the room temperature Hall data indicated a reduction in donor concentration to about $4.8\times10^{17}/cm^3$. Following another 20 hr at 400°C the donor concentration was reduced to 2.5 $\times10^{17}/cm^3$ and with an additional 24 hr it was $9\times10^{16}/cm^3$. There was no evidence of approaching the equilibrium concentration appropriate for 400°C in these studies. By comparison, crystals treated by the vapor process at this temperature, have a donor concentration of 1.5×10^{17} and require from 500 to 1000 hr to reach equilibrium.[2]

CONCLUSIONS

The precipitation of Te in PbTe crystals can be interpreted as evidence that the dislocation and its interacting field may be considered as a simple cylindrical sink with an effective capture radius R. The shape of the precipitation curves resembles those calculated by Ham for the case of stress-assisted precipitation on dislocations.

Precipitation of atoms in excess of the stoichiometric proportions in compound semiconductors displaying retrograde solubility in their phase diagram, is shown to be a simple means for obtaining crystals of controlled donor or acceptor concentrations. Previous methods in which the crystal's internal composition is controlled through a vapor diffusion process in a controlled atmosphere, generally require much higher temperatures and longer times than this internal process.[2,7,8] It is often difficult to quench the crystal sufficiently rapidly from the high temperature to freeze in the composition established at the high temperature. The present experiments show that precipitation occurs very rapidly at the high temperatures used in vapor treatment experiments, and can modify the equilibrium composition, established with the vapor as the crystal is quenched.[9]

These experiments also account for the "irreversibility" in the electrical conductivity and thermoelectric power in p-type PbTe observed by Kovalchik and

[7] J. Bloem, Philips Research Repts. 11, 273 (1956).
[8] R. F. Brebrick and W. W. Scanlon, Phys. Rev. 96, 598 (1954).
[9] R. F. Brebrick (private communication).

Maslakovets[10] upon heating and cooling crystals. They, however, only observe such effects in p-type crystals of PbTe with practically no effect being observed in n-type crystals. Our results, on the other hand, show precipitation effects in both n and p-type crystals. In the n-type crystals, much longer annealing times at a given temperature were required for the effects to be observed than in p-type crystals.

[10] T. L. Kovalchik and Iu. P. Maslakovets, J. Tech. Phys. (U. S. S. R.) **26**, 2417 (1956) [Soviet Phys.—Tech. Phys. **1**, 2337 (1957)].

From Hall effect data on n-type PbTe crystals, the intrinsic carrier concentration and resistivity at room temperature are estimated to be $n_i = 2 \times 10^{16}/\text{cm}^3$ and $\rho_i = 0.2$ ohm cm.

ACKNOWLEDGMENTS

Anomalous Lattice Specific Heat of Gold and Zinc at Liquid Helium Temperatures

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The heat capacities of both single-crystal and polycrystalline samples of gold and of zinc have been measured between 1.5 and 4.2°K. For gold the results may be represented accurately by an equation of the form $C = \gamma T + \beta T^3$, but the coefficient β of the cubic term is significantly smaller than the value derived from low-temperature elastic constants measured on the same specimen. For zinc a polynominal expression of the results requires a T^5 term in addition to the usual linear and cubic terms. The T^5 term is positive, as in most other solids upon which measurements have been made, but is very large in magnitude, amounting to about one-fifth of the total heat capacity at 4°K. The agreement between the Debye temperatures near 0°K calculated from heat capacity and from low-temperature elastic constants measured on the same specimen may be within experimental error.

INTRODUCTION

THE work reported in this paper was undertaken in an effort to resolve some of the inconsistencies between the lattice specific heats of certain metals as determined directly by heat capacity measurements and as derived from low-temperature elastic constants. An impetus was provided by the availability of the large single-crystal specimens of gold and zinc used by Alers and Neighbours[1,2] for elastic constant determinations. We were thus able to eliminate one source of experimental uncertainty by making both of the essential measurements on the same set of specimens. Since these measurements did nothing to resolve the inconsistencies, heat capacity measurements were made later on polycrystalline specimens to see if this sort of change of macrostructure might affect the lattice specific heat, unlikely though it seemed.

The measurements reported here on gold are largely in agreement with previous accurate helium temperature results. On zinc, our measurements show some detail not apparent in earlier work.

It is assumed that in these two metals, gold and

[1] G. A. Alers and J. Neighbours, J. Phys. Chem. Solids **7**, 58 (1958).
[2] J. Neighbours and G. A. Alers, Phys. Rev. **111**, 707 (1958).

zinc, the specific heat C is the sum of an electronic component linear in temperature and denoted by γT, and a lattice component making up the remainder. Conventionally at low temperatures one assumes also that the lattice component is cubic and may be denoted by βT^3, where theoretically $\beta = 1943(1/\theta_0)^3 \times 10^{-6}$ joules per mole deg^4 and T is small compared to θ_0, the "Debye characteristic temperature." Thus, if one plots experimental values of C/T vs T^2, the points are expected to fall on a straight line of the form $C/T = \gamma + \beta T^2$, from which the coefficients γ and β, and θ_0, are determined. The Debye temperature θ_0 is also calculable from low-temperature elastic constants. Alers and Neighbours[3] in a review article have given a comprehensive discussion of various ways of doing this and have made a comparison between Debye temperatures derived from heat capacities and from elastic constants for all the solids for which data were available.

As we shall see, the specific heat of zinc cannot be fitted by linear plus cubic terms alone even at temperatures below $\theta_0/100$. Empirically, therefore, we have added a term δT^5 to the specific heat equation. Qualitatively this is justified by much theoretical and

[3] G. A. Alers and J. Neighbours, Revs. Modern Phys. **31**, 675 (1959).