Electrical and Optical Properties of Epitaxial Films of PbS, PbSe, PbTe, and SnTe†

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Single-crystal films of PbS, PbTe, PbSe, and SnTe have been grown on heated alkali-halide substrates. The temperature dependence of the mobility, Hall coefficient, and resistivity between 77°K and 300°K and the dependence of the magnetoresistance upon sample orientation and magnetic field strength at 77°K have been studied. Analysis of the refractive indices, measured interferometrically in the 2.0- to 15.0-μ region, has yielded optical dielectric constants and the direct energy gaps as functions of temperature. These studies indicate that the single-crystal films have electrical and optical properties comparable to those found in bulk material. Discussions of film formation and strain phenomena are presented and compared with the experimental results. Some of the limitations of these materials are discussed with particular emphasis on the role of structure of the films on the electrical properties.

INTRODUCTION

IT has been known for many years that single-crystal films of the lead salts, PbS and PbSe, could be grown on heated rock-salt substrates.[1,2] Several investigations have been carried out with these films, but they have been restricted to the examination of the nucleation and growth of epitaxial films.[3-7] The primary tools in these studies have been electron-transmission microscopy and diffraction. While considerable structural information has been obtained, no attempts have been made to use these films in more general solid-state investigations. In this paper we report on a variety of experiments dealing with the electrical, optical and mechanical properties of these films. These experiments indicate that the films behave like thin single crystals having band structure, crystal perfection, dielectric, transport and mechanical properties comparable to the best available single crystals. These measurements are discussed in terms of the currently accepted mechanisms of heteroepitaxial growth.

The procedure used in producing these films was described recently by Schoolar and Zemel.[8] In general, the methods are similar to those used by Elleman and Wilman.[1] These authors used electron-diffraction data

as a criterion of crystal quality. In the following we will use electrical measurements, in particular the Hall mobility, as the measure of film quality.

Polycrystalline evaporated films of PbS, PbSe, and PbTe have been used for many years as infrared photoconductive detectors. Despite their widespread use, the mechanism of sensitivity is poorly understood. The structure, electrical properties, and recombination processes of the films have never been resolved satisfactorily. The study of the epitaxial films was originally undertaken to shed some light on these various processes. It became apparent from the outset, that the properties of the photoconductive and epitaxial films are radically different. Among these differences is that no measurable photoconductivity has been observed in any epitaxial film grown to date. However, no attempt has been made to sensitize the films, so that this does not preclude the possibility that sensitive infrared photodetectors could be produced by epitaxial techniques.

There are several characteristics of the epitaxial films that make them attractive for solid-state investigations:

1. Only small amounts of material are needed to produce usable single crystals.

2. If the impurities in the starting material have higher vapor pressures than the compound to be deposited, then these impurities will evaporate preferentially from the beam source used.[8] If the impurities have vapor pressures significantly lower than the material of interest, the deposit will be purer.

3. The films grown this way have very uniform thickness. Furthermore, the surfaces require no further treatment to make them suitable for either optical-transmission or reflection measurements.

4. The relatively high resistance of the thin samples reduces the difficulties associated with contact resistance experienced in making bulk electrical measurements.

For these reasons, the epitaxial films deposited on suitable substrates are almost ideal for a variety of electrical and optical measurements. The main drawback is variations in the density of impurities as the film grows. The electrical measurements provide a

† A brief account of this work has been presented in a series of talks before the American Physical Society: J. D. Jensen and J. N. Zemel, Bull. Am. Phys. Soc. 6, 437 (1961). R. B. Schoolar, J. D. Jensen, and J. N. Zemel, Bull. Am. Phys. Soc. 8, 63 (1963). J. D. Jensen, R. B. Schoolar, and J. N. Zemel, Bull. Am. Phys. Soc. 8, 63 (1963). J. D. Jensen and R. B. Schoolar, Bull. Am. Phys. Soc. 8, 198 (1963). D. L. Mitchell, E. D. Palik, J. D. Jensen, R. B. Schoolar, and J. N. Zemel, Bull. Am. Phys. Soc. 8, 309 (1963). R. B. Schoolar, Bull. Am. Phys. Soc. 8, 516 (1963). J. N. Zemel and J. D. Jensen, Bull. Am. Phys. Soc. 8, 517 (1963). D. L. Mitchell, E. D. Palik, J. D. Jensen, R. B. Schoolar, and J. N. Zemel, Bull. Am. Phys. Soc. 9, 292 (1964). J. N. Zemel, Bull. Am. Phys. Soc. 9, 493 (1964).

[1] A. J. Elleman and H. Wilman, Proc. Phys. Soc. (London) 61, 164 (1948).
[2] D. W. Pashley, Advan. Phys. 5, 174 (1954).
[3] J. W. Matthews, Phil. Mag. 76, 1347 (1961).
[4] J. W. Matthews, and K. Iseback, Phil. Mag. 8, 469 (1963).
[5] J. W. Matthews, Phil. Mag. 8, 711 (1963).
[6] A. D. Wilson, R. C. Newman, and R. Bullough, Phil. Mag. 8, 2035 (1963).
[7] L. O. Brockway and M. S. Wasserman, University of Michigan, 5th Quarterly Report AF-18 (600) 175, 1953 (unpublished).
[8] R. B. Schoolar and J. N. Zemel, J. Appl. Phys. 35, 1848 (1964).

sensitive means for deciding whether there are any serious gradients in the carrier concentration. The optical properties would not be affected by minor impurity gradients.

The galvanomagnetic properties to be reported here are: the temperature dependence of the resistivity, Hall coefficient and the derived Hall mobility, the angular and field dependence of the magnetoresistance, and the time variation of selected properties occurring in several films. In general, these properties clearly reflect the high degree of perfection of the films. On some films, a residual resistance is found which is ascribed to internal boundaries arising from the growth process. In two recent publications, the temperature dependence of the resistivity and Hall coefficient of epitaxial PbTe films grown on mica are discussed.[9,10] The results are in general agreement with the work to be reported here. Some work on PbSe grown on NaCl, LiF, and glass substrates has also been reported.[11]

Riedl and Schoolar[12] have shown that precise index-of-refraction measurements are possible on PbS epi-
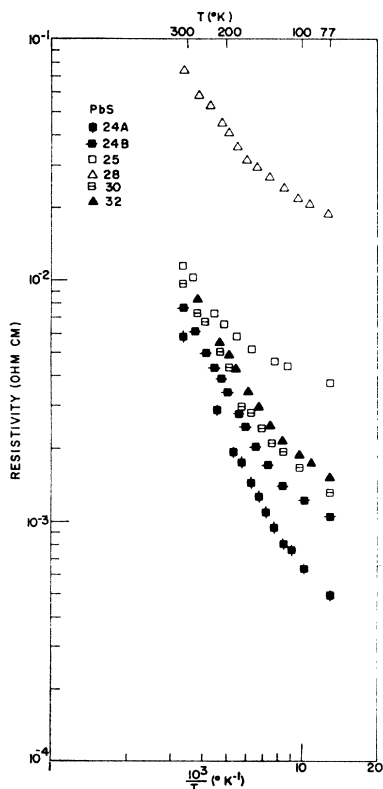

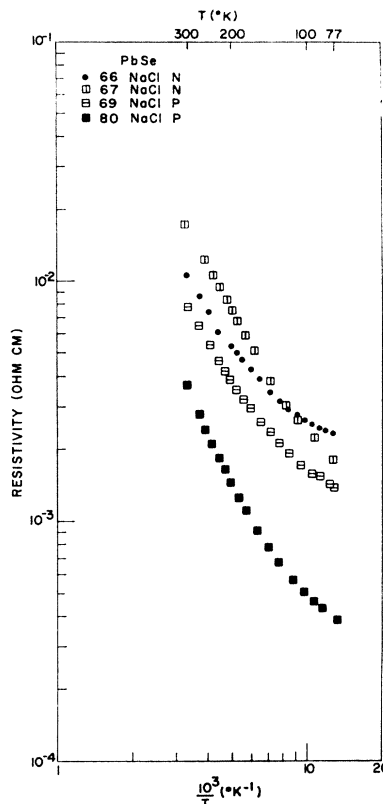FIG. 1. Temperature dependence of the resistivity of PbS.

FIG. 2. Temperature dependence of the resistivity of PbSe.

taxial films in the near-infrared spectral region. The excellent agreement between the refractive indices obtained from bulk-reflectivity data and from thin-film multiple interference patterns taken at room temperature encouraged additional measurements on the films. As an example, Schoolar and Dixon[13] have reported recently on the detailed structure of the fundamental absorption edge in PbS using epitaxial films.

In a series of recent publications, Mitchell et al.[14–17] have discussed the interband magneto-optic (IMO) phenomena in the lead salts, PbS, PbSe, and PbTe. These measurements have been instrumental in establishing the band structure of these materials. The band model that emerges from these measurements is that all three substances have multivalley structures with minima at the (111) Brillouin-zone edge for both the conduction and valence bands. This picture is con-

[9] Y. Makino, J. Phys. Soc. Japan 19, 580 (1964).

[10] Y. Makino and T. Hoshina, J. Phys. Soc. Japan 19, 1242 (1964).

[11] S. A. Semiletov and I. P. Voronina, Dokl. Akad. Nauk. SSSR 152, 1350 (1963) [English transl.: Soviet Phys.—Doklady 8, 960 (1964)].

[12] H. R. Riedl and R. B. Schoolar, Phys. Rev. 131, 2082 (1963).

[13] R. B. Schoolar and J. R. Dixon, Phys. Rev. 137, A667 (1965).

[14] D. L. Mitchell, E. D. Palik, J. D. Jensen, R. B. Schoolar, and J. N. Zemel, Phys. Letters 4, 262 (1963).

[15] D. L. Mitchell and E. D. Palik, Conference on High Magnetic Fields, Clarendon Laboratory, University of Oxford, 1963 (unpublished).

[16] E. D. Palik, D. L. Mitchell, and J. N. Zemel, Phys. Rev. 135, A763 (1964).

[17] D. L. Mitchell, E. D. Palik, and J. N. Zemel, in Proceedings of the International Conference on the Physics of Semiconductors, Paris, 1964 (Dunod Cie., Paris. 1964), p. 325.
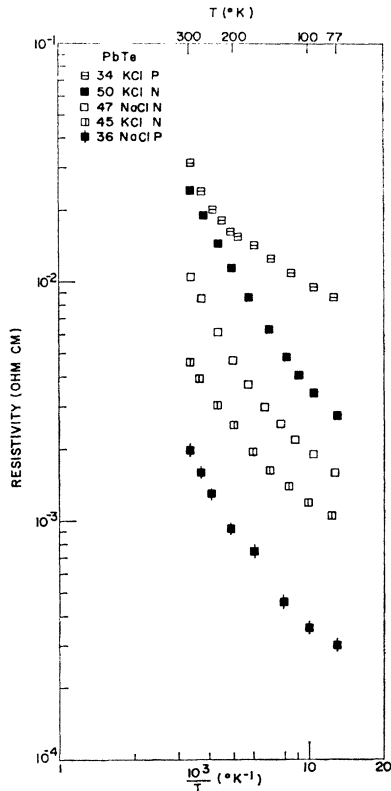
FIG. 3. Temperature dependence of the resistivity of PbTe.

have examined the reflectivity of thick epitaxial films of the lead salts from 1 to 5.0 eV. Their results are in qualitative agreement with the reflectivity data of Cardona and Greenaway.

Recently, Zemel[26] has measured the transverse optical (TO) phonon frequency of zero wave number in epitaxial films of PbS and found it to be 0.2×10^{12} sec^{-1}. This problem is related to the long standing uncertainty in the static dielectric constant. The relationship between the static dielectric constant ϵ_0 and the transverse optical frequency ω_T is given by the Lyddane-Sachs-Teller equation[27]

$$\epsilon_0 = \epsilon_\infty (\omega_L/\omega_T)^2, \tag{1}$$

where ϵ_∞ is the high-frequency dielectric constant and ω_L is the longitudinal-optical phonon frequency of zero wave number. The high-frequency dielectric constant was obtained during the present measurements (see Table II). The longitudinal-optical phonon was obtained by Hall and Racette from phonon-assisted tunneling at 4.2°K.[28] Assuming that the energy of this phonon is independent of temperature and using Eq. (1), Zemel obtained a value of about 175 for the room temperature static dielectric constant. This confirms the earlier speculation of several authors that the static dielectric constant of these materials would have to be very large to account for the observed low-temperature electrical properties.[29]
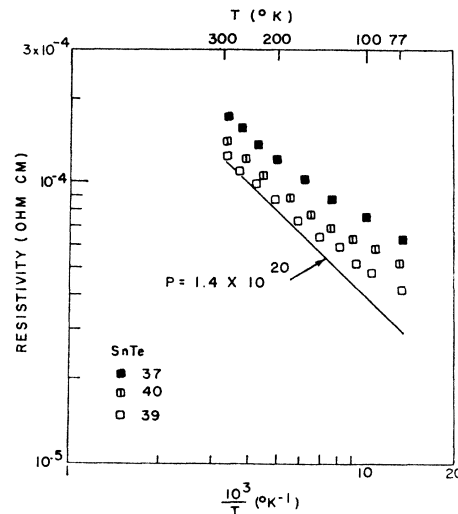
E. Burstein, R. Wheeler, and J. Zemel[30] have shown

sistent with the conclusions drawn by other authors.[18-22] Furthermore, the anisotropy of the bands increases as one goes from PbS to PbSe with the greatest anisotropy in PbTe.[17]

Some indications of deeper-lying bands in the lead salts PbS, PbSe, PbTe and the tin salt SnTe have been obtained recently by Cardona and Greenaway.[23] They measured the transmittance of very thin epitaxial films and the reflectivity of cleaved bulk samples from 0.5 to 6.0 eV. They extended their reflectivity data to 25 eV using thick epitaxial films. The absorption coefficient α was determined from 0.5 to 15 eV using their data and the Kramers-Kronig relationship.[24] Pronounced peaks were obtained in α which agreed well with minima in the transmittance. Wessel et al.[25] at this Laboratory

FIG. 4. Temperature dependence of the resistivity of SnTe.

[18] W. W. Scanlon, Solid State Phys. 9, 83 (1959).
[19] L. E. Johnson, J. B. Conklin, and G. W. Pratt, Jr., Phys. Rev. Letters 11, 538 (1963).
[20] G. W. Pratt, Jr. and L. G. Ferreira, in Proceedings of the International Conference on the Physics of Semiconductors, Paris, 1964 (Dunod Cie., Paris, 1964), p. 69; L. Kleinman and P. J. Lin, ibid., p. 63.
[21] J. O. Dimmock and G. B. Wright, Phys. Rev. 135, A821 (1964).
[22] K. F. Cuff, M. A. Ellet, C. D. Kuglin, and L. R. Williams, in Proceedings of the International Conference on the Physics of Semiconductors, Paris, 1964 (Dunod Cie., Paris, 1964), p. 677.
[23] M. Cardonna and D. L. Greenaway, Phys. Rev. 133, A1685 (1964).
[24] F. Stern, Solid State Phys. 15, 299 (1964).
[25] P. R. Wessel, J. R. Dixon, J. N. Zemel, R. B. Schoolar, and J. D. Jensen, Bull. Am. Phys. Soc. 8, 517 (1963).

[26] J. N. Zemel, in Proceedings of the International Conference on the Physics of Semiconductors, Paris, 1964 (Dunod Cie., Paris, 1964), p. 1061.
[27] R. H. Lyddane, R. G. Sachs, and E. Teller, Phys. Rev. 59, 673 (1941).
[28] R. N. Hall and J. H. Racette, J. Appl. Phys. 32, 2078 (1961).
[29] E. Burstein and P. H. Egli, Advances in Electronics, edited by L. Marton (Academic Press Inc., New York, 1955), Vol. 7, p. 1.
[30] E. Burstein, R. G. Wheeler, and J. N. Zemel, in Proceedings of the International Conference on the Physics of Semiconductors, Paris, 1964 (Dunod Cie., Paris, 1964), p. 1065.

that the TO phonon in PbSe at liquid helium temperatures is 1.2×10^{12} sec^{-1}. Using the data of Hall and Racette[28] for ω_L and ϵ_∞ given in this paper, they calculated ϵ_0 to be 250.

Bis and Zemel[31] have obtained single-crystal, single-phase epitaxial films of the system $PbSe_xTe_{1-x}$. It is clear from this work that many other substitutional alloy systems can be prepared using their techniques.

This survey of the various areas where epitaxial films of the lead salts can be used to clarify the properties of these materials is far from complete. Other uses can be envisaged providing the films have physical and electrical properties comparable to bulk material. If other materials can be prepared in this form, similar measurements are possible. For example Iwasa, Balslev, and Burstein[32] have used ground and polished bulk material as well as epitaxial films deposited on germanium to measure the infrared lattice-vibration transmission spectrum of GaAs. Their calculation of (ω_L/ω_T) is in excellent agreement with the value based on bulk reflectivity data reported by Hass and Henvis.[33]
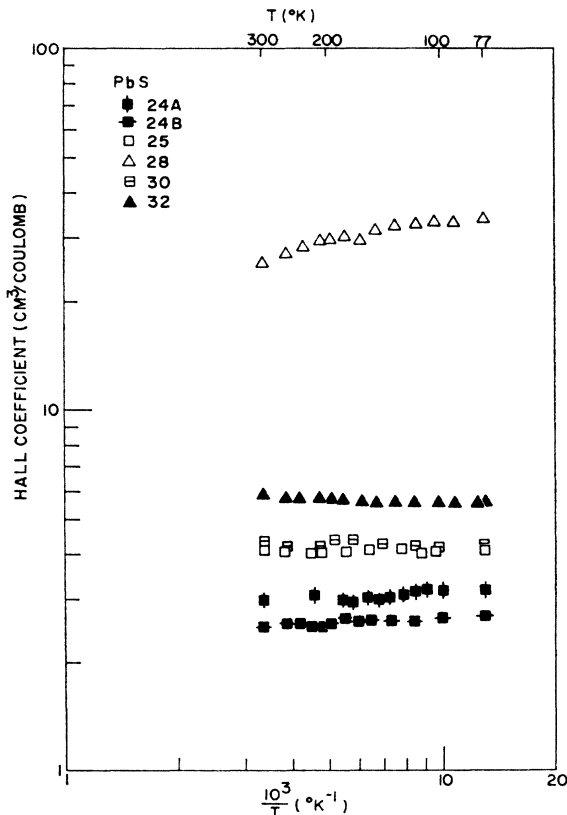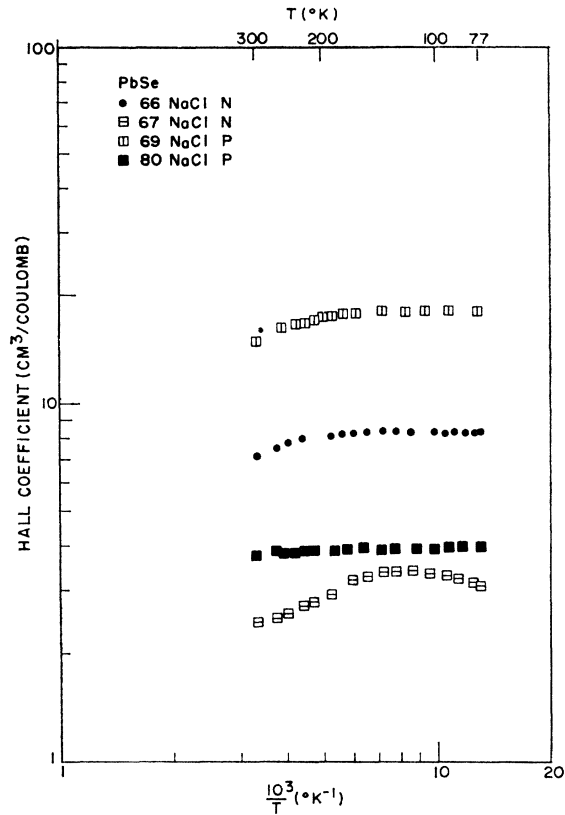

FIG. 6. Temperature dependence of the Hall coefficient of PbSe.

EXPERIMENTAL PROCEDURES

Film Preparation

Epitaxial films of PbS, PbSe, PbTe, and SnTe were prepared using the methods and equipment described elsewhere.[8] Immediately after removal of the films from the system, the thickness was determined by interferometric methods described by Schoolar and Zemel.[8] The uncertainty in the thickness measurement is estimated to be $\pm 3\%$ for the lead salts and $\pm 10\%$ for SnTe. The thickness determination of SnTe was limited by the high free-carrier density which masked the interference fringes in the rocksalt spectral region.

Electrical measurements were made on a sample cleaved from the film-substrate specimen. The length-to-width ratio of these samples was usually $4:1$. For the optical measurements, a broad-area specimen was desirable. It was found that two films deposited on different rocksalt substrates at the same time had essentially identical properties. One film was used for the optical measurements and the other reserved for the electrical measurements.

Electrical Measurements

The resistivity, Hall coefficient, and the angular- and magnetic-field dependence of the magnetoresistance
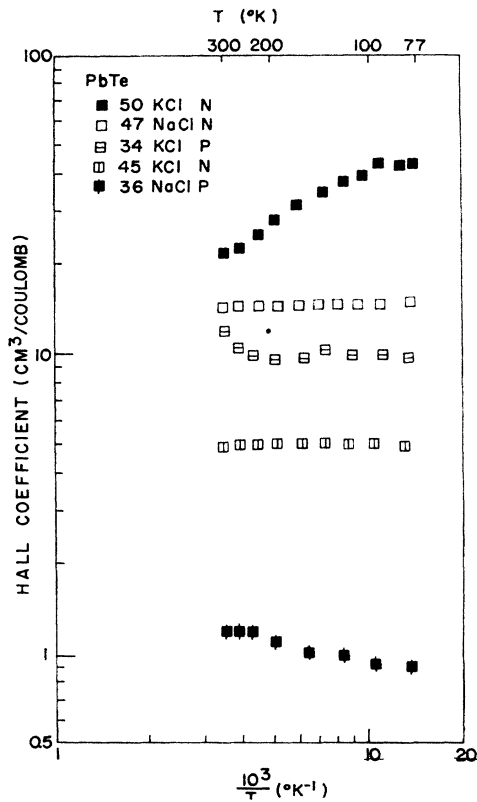

FIG. 5. Temperature dependence of the Hall coefficient of PbS.

[31] R. F. Bis and J. N. Zemel (to be published).
[32] S. Iwasa, I. Balslev, and E. Burstein, Bull. Am. Phys. Soc. 9, 237 (1964).
[33] M. Hass and B. W. Henvis, J. Phys. Chem. Solids 23, 1099 (1962).

FIG. 7. Temperature dependence of the Hall coefficient of PbTe.

were measured using dc techniques as described by
Putley.[34] These quantities and the derived Hall mo-
bility were obtained at different temperatures between
300 and 77°K. The measurements were made with the
sample in a stainless steel Dewar. The sample was
cemented to a copper cold finger with a mixture of high-
vacuum grease and copper dust to provide good
thermal contact. The cold finger was the bottom of the
liquid-nitrogen reservoir which had a double chamber—
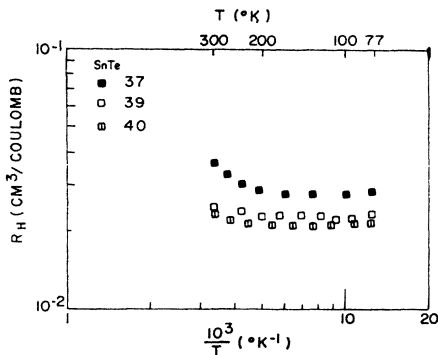the lower chamber being used primarily as a thermal

FIG. 8. Temperature dependence of the Hall coefficient of SnTe.

[34] E. H. Putley, *The Hall Effect and Related Phenomena* (Butter-
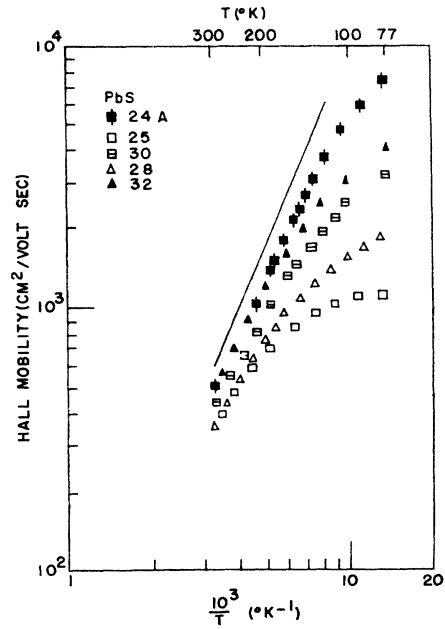worths Scientific Publications Ltd., London, 1960), Chap. 2, p. 42.

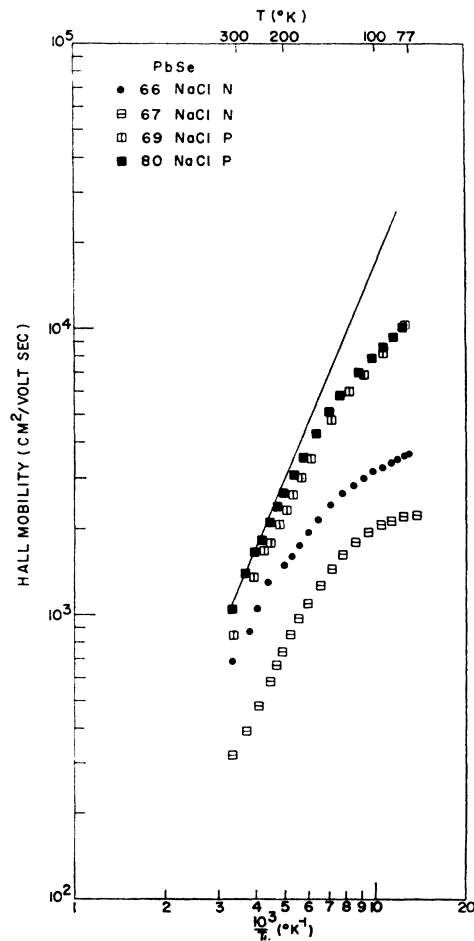FIG. 9. Temperature dependence of the Hall mobility of PbS.

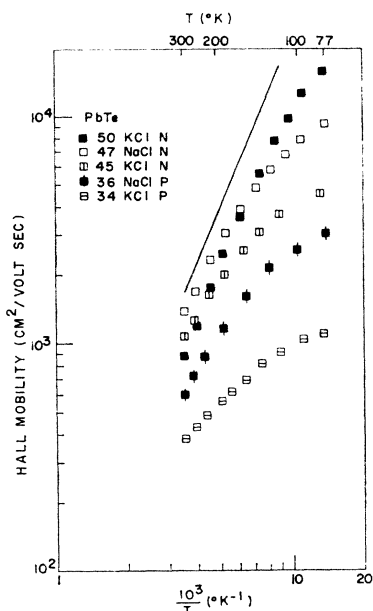FIG. 10. Temperature dependence of the Hall mobility of PbSe.

FIG. 11. Temperature dependence of the Hall mobility of PbTe.

resistor between the liquid nitrogen in the upper chamber and the sample on the cold finger. As a result, the sample cooled sufficiently slowly so that the temperature dependence of the electrical properties could be measured. Copper wire leads were attached to the sample with an air drying silver paste (Dupont Conductive Silver 487). The contact resistance was negligible compared to the sample resistance. Pressures in the Dewar were maintained at 10^{-5} Torr. The uncertainty in the resistivity and Hall-coefficient measurements was $\pm 10\%$ for the lead salts and $\pm 15\%$ for SnTe. The magnetoresistance measurement had an
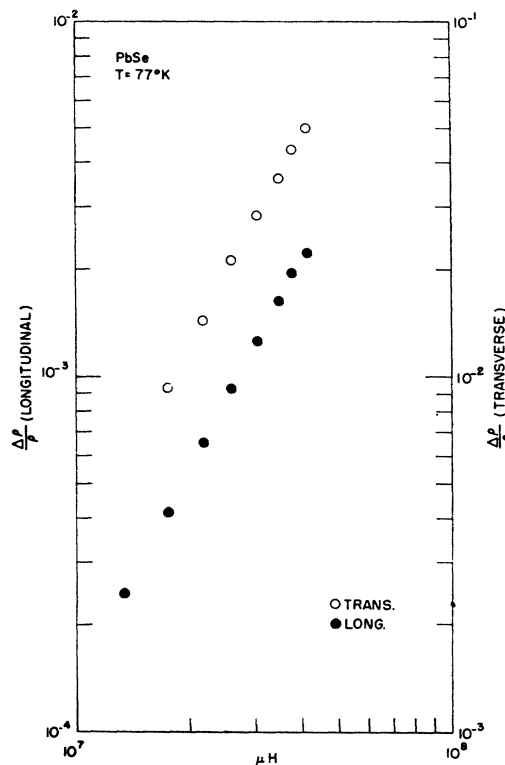

FIG. 12. Temperature dependence of the Hall mobility of SnTe.

FIG. 13. Magnetic-field dependence of the magnetoresistance of PbSe.

error of $\pm 6\%$. The temperature was accurate within $\pm 3°K$.

Optical Measurements

Optical measurements of several samples of each material were carried out using a Perkin Elmer Model 21 spectrophotometer equipped with NaCl optics. The reflectivity attachment for the spectrophotometer was modified so that a small Dewar could be mounted on it.
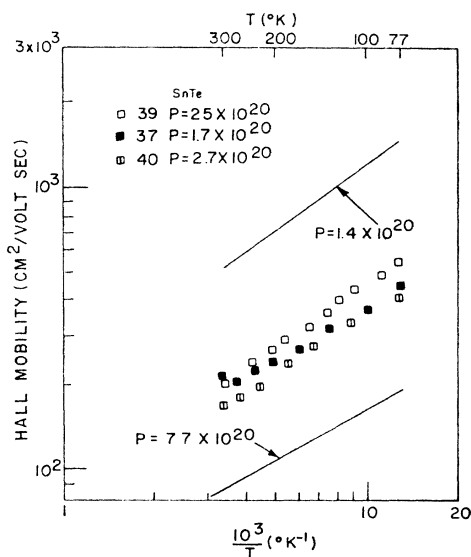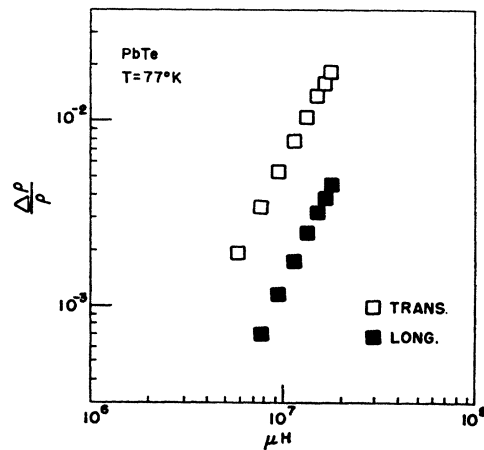

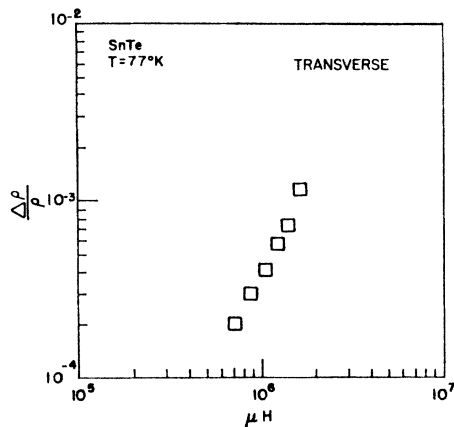FIG. 14. Magnetic-field dependence of the magnetoresistance of PbTe.

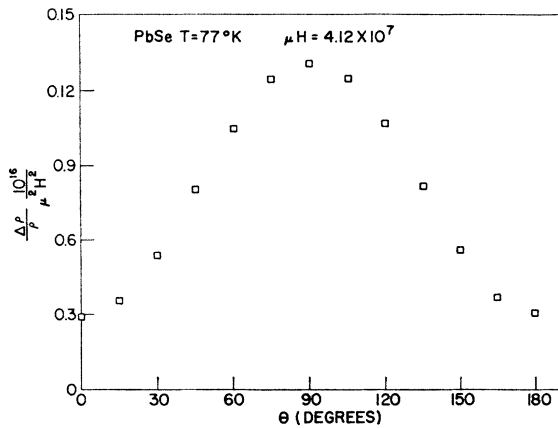FIG. 15. Magnetic-field dependence of the magnetoresistance of SnTe.

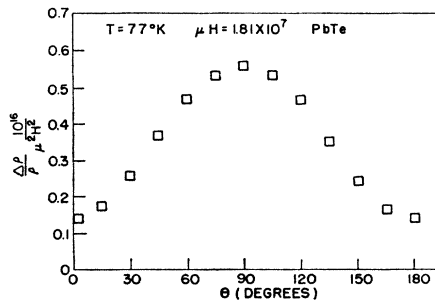FIG. 16. Angular dependence of the magnetoresistance of PbSe.

FIG. 17. Angular dependence of the magnetoresistance of PbTe.

The films (on substrates) were cemented to the bottom of the cold finger using the vacuum grease and copper dust mixture for good thermal contact. Reflectivity measurements were made at room temperature and at liquid-nitrogen and steam points. Sample temperatures were stable and within $\pm 4°K$ of the bath temperature. Absolute-reflectivity measurements were accurate to within 10%.

EXPERIMENTAL RESULTS

Electrical Properties

The temperature dependence of the resistivity of PbS, PbSe, PbTe, and SnTe is shown in Figs. 1, 2, 3, and 4, respectively. The Hall coefficient for these materials is given in Figs. 5, 6, 7, and 8. And the Hall mobility is shown in Figs. 9, 10, 11, and 12. Typical bulk behavior is shown as the solid lines in Figs. 9, 10, 11, and 12 for comparison. The magnetic-field dependence of the magnetoresistance is given in Figs. 13, 14, and 15 for PbSe, PbTe, and SnTe, respectively. The angular dependence of the magnetoresistance of PbSe, PbTe, and SnTe is presented in Figs. 16, 17, and 18. θ is the angle between the sample current and the magnetic field. The magnetic field varies in a plane defined
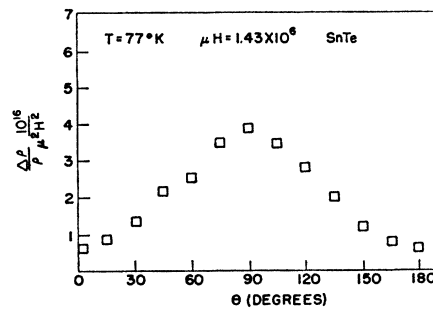

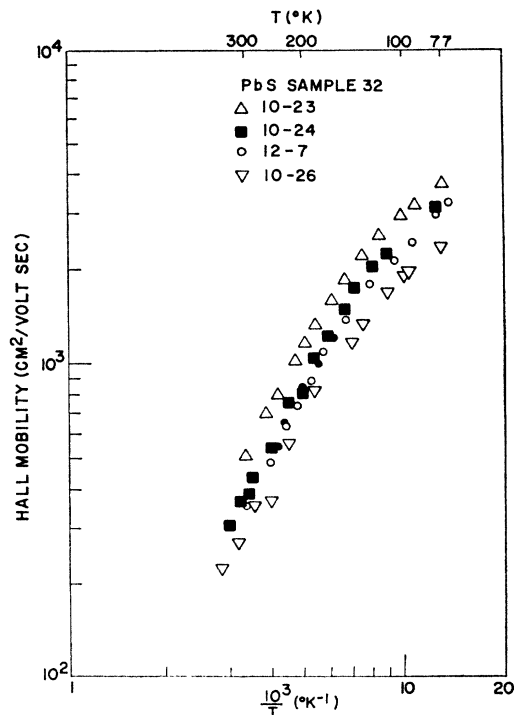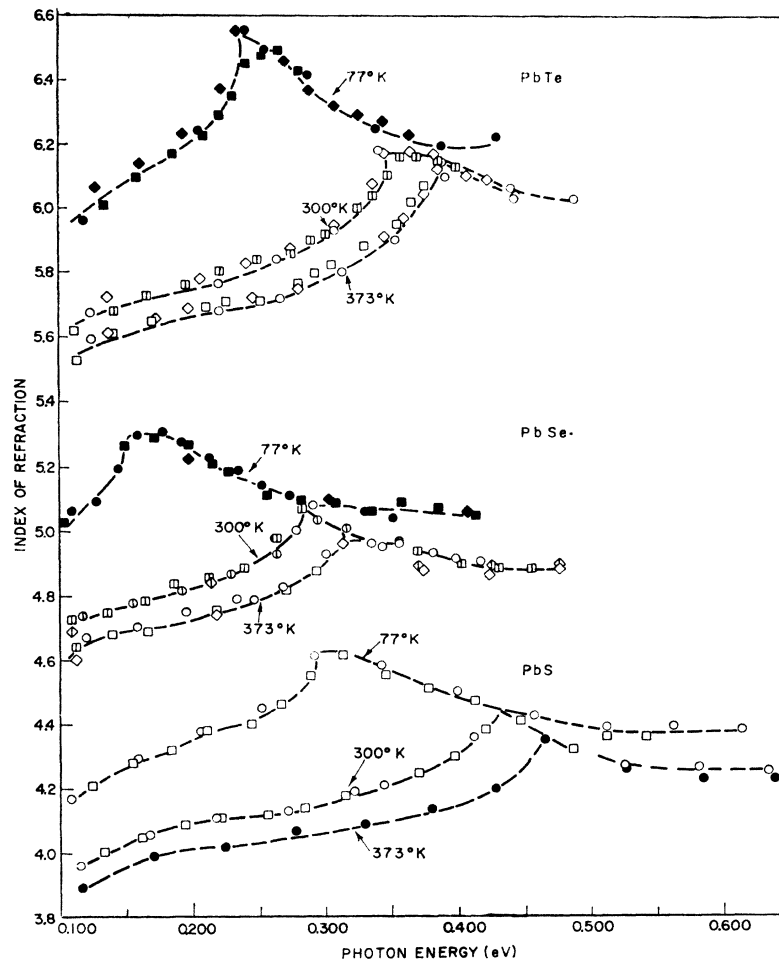Fig. 18. Angular dependence of the magnetoresistance of SnTe.

FIG. 19. Temperature dependence of the Hall mobility of PbS No. 32 showing time-dependent behavior.

FIG. 20. Photon-energy dependence of the index of refraction of PbS, PbSe, and PbTe at 77, 300, and 373°K.

by the vector normal to the surface and the current density. μ is the Hall mobility at the specified temperature. These data show no correlation to the sample thickness.

While the electrical properties of the films were generally quite stable, some time dependent behavior was observed. In Fig. 19, the mobility of a PbS film (PbS 32) is shown. When originally grown, the mobility displayed the temperature dependent behavior indicated by 10–23. An attempt was made to improve the mobility by annealing the film overnight at a temperature slightly above room temperature. When measured the next day, the mobility had decreased as seen in the data marked 10–24. A repetition of the measurements on the following day (no additional heat treatment) indicated no further change in the mobility. When again subjected to an overnight anneal, the data marked 10–26 were obtained. The sample was then removed from the system and stored for over a month in a desiccator. The mobility was then remeasured, and it was observed that there was some recovery as indicated by the 12–7 data. Throughout these measurements, the Hall coefficient remained unchanged.

The analysis of the data for SnTe was different from that employed for the lead salts. Because of the very high carrier concentration, it was difficult to determine the thickness optically and the films were so thin that they could not be weighed accurately. To determine the carrier concentration we made use of the fact that the mobility in the bulk crystals of SnTe is inversely proportional to the carrier concentration. As a result, the conductivity of SnTe is independent of carrier concentration to a fair degree of approximation. Therefore we can determine the thickness of the SnTe sample from a measurement of the resistance, which is a function only of the thickness and length-to-width ratio.

The electrical data indicate that the films fall into two general classes. The first class, to which film 24A of Fig. 9 belongs, has properties comparable to bulk material. Film 25 of Fig. 9 is an example of the second class which displays properties related to the defect structure of the films. This class is characterized by a Hall mobility which increases more slowly with decreasing temperature than class-one films. We attempt to explain this behavior in the discussion section below.
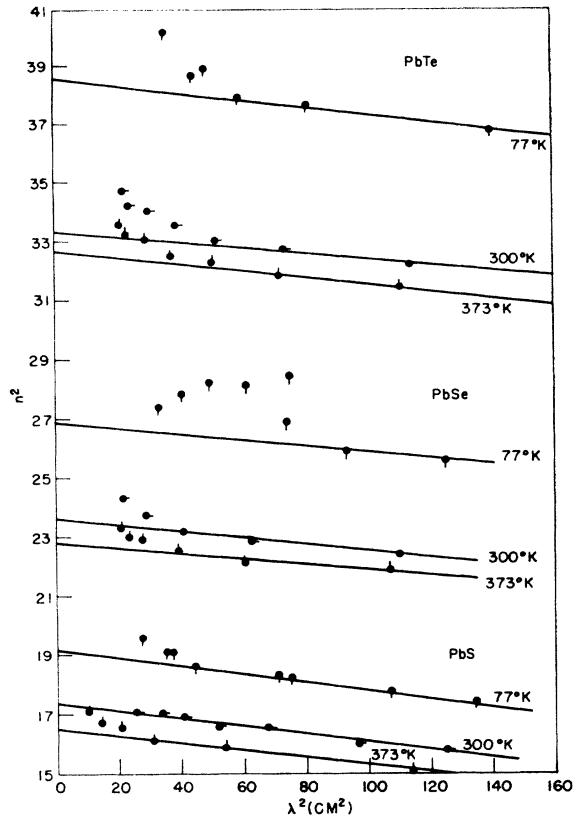
FIG. 21. Square of the index of refraction versus the square of wavelength for PbS, PbSe, and PbTe at 77, 300, and 373°K.

A summary of the room-temperature and liquid-nitrogen-temperature data is given in Table I.

Optical Properties

The refractive indices n of the lead-salt films were determined at 77, 300, and 373°K from the reflectivity data using the interferometric and weighing technique described by Riedl and Schoolar.[12] These techniques were not applicable to SnTe because the high carrier density $(1 \times 10^{20}$ cm$^{-3})$ masked a large portion of the rocksalt spectral region. The experimental error in these measurements is $\pm 3\%$. The energy dependence of the refractive indices at these temperatures is presented in Fig. 20. A peak appears in the index of each material which is associated with the rapid change in the absorption coefficient in the fundamental absorption edge.[12,13,24] It is clearly evident that this peak shifts to lower energies as the temperature decreases. This shift is associated with the decrease in the direct energy gap E_g with temperature. It can be shown that E_g is at a somewhat lower energy than the position of the peak. Estimates of the direct gap E_g^* based upon the relative positions of the peaks are presented in Table II. They are compared with the direct gaps of strained and unstrained films measured at 77°K using IMO techniques in Table III.

TABLE I. Hall mobilities and typical carrier concentrations for various types of PbS, PbTe, PbSe, and SnTe at 77 and 300°K.

Material	Hall mobility at 300°K (cm²/V sec)	Hall mobility at 77°K (cm²/V sec)	Typical carrier concentration
PbS			
Synthetic (as grown)	700	13 500	2×10^{18} electrons/cm³
Natural	500	6000	5×10^{17} electrons/cm³
Epitaxial film	500	9000	2×10^{18} electrons/cm³
Nonepitaxial film[a]	10	<1	2×10^{18} holes/cm³
PbSe			
Synthetic (as grown)	1000	16 000	3×10^{18} holes/cm³
Epitaxial film	1000	11 000	7×10^{17} electrons/cm³
Nonepitaxial film[a]	20	<1	$\cdots$
PbTe			
Synthetic (as grown)	900	20 000	2×10^{18} holes/cm³
Epitaxial film	1100	16 000	5×10^{17} electrons/cm³
Nonepitaxial film[a]	20	$\cdots$	$\cdots$
SnTe			
Synthetic (as grown)	200	450	2.5×10^{20} holes/cm³
Epitaxial film	200	450	2.5×10^{20} holes/cm³
Nonepitaxial film	$\cdots$	$\cdots$	$\cdots$

[a] Nonepitaxial film data is from various types of photosensitive films produced at the U. S. Naval Ordnance Laboratory.

TABLE II. A comparison of the parameters $\epsilon_\infty(1)$, $\epsilon_\infty(2)$, λ_0, and E_g^* for PbS, PbSe, and PbTe at 77°, 300°, and 373°K.

Material	$\epsilon_\infty(1)$	$\epsilon_\infty(2)$	$\lambda_0(\mu)$	E_g^*(eV)
	373°K			
PbS	16.5	15.8	0.68	0.44
PbSe	22.8	21.6	1.20	0.31
PbTe	32.6	31.3	1.16	0.34
	300°K			
PbS	17.4	16.9	0.77	0.41
PbSe	23.6	22.1	1.37	0.27
PbTe	33.4	32.2	1.26	0.31
	77°K			
PbS	19.2	17.6	1.47	0.28
PbSe	26.9	23.5	3.16	0.15
PbTe	38.5	35.3	2.88	0.20

TABLE III. Band-edge parameters for PbS, PbSe, and PbTe at 77°K.

Material	Dispersion-peak data $E_g^*(S)$[a] $(10^{-3}$ eV)	IMO Data[b] $E_g(S)$[a] $(10^{-3}$ eV)	$E_g(U)$[a] $(10^{-3}$ eV)
PbS	280±10	278±2	307±3
PbSe	150±10	159±3	176±5
PbTe	200±10	203±2	217±2

[a] (S)—film on substrate; (U)—film removed from substrate.
[b] See Ref. 17.

The refractive indices have been analyzed to yield the high frequency dielectric constants ϵ_∞. Two procedures have been followed. The first was to extrapolate the free carrier and lattice dispersion to infinite energy. This was done by plotting n^2 versus λ^2 and extrapolating

FIG. 22. Temperature dependence of the optical dielectric constants and the energy gaps of the lead salts, uncorrected for thermal-expansion strain.
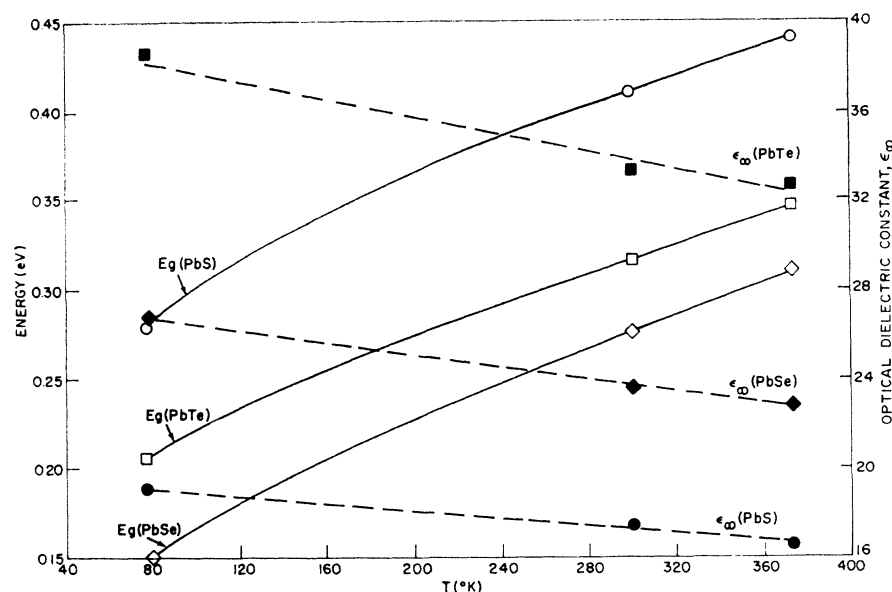
the long wavelength linear region to zero wavelength which yielded $n_0^2 = \epsilon_\infty$, as shown in Fig. 21. The second procedure, one employed by Walton and Moss[35] recently, was to assume the high-frequency properties of the lead salts could be treated as a single oscillator at wavelength λ_0 and apply the simple classical dispersion relation.[36] If n_0 is the refractive index of an empty lattice at infinite wavelength, the index will vary as

$$(n_0^2 - 1)/(n^2 - 1) = 1 - (\lambda_0/\lambda)^2. \qquad (2)$$

The λ_0's and n_0's have been evaluated from plots of $(n^2 - 1)^{-1}$ versus λ^{-2} for the lead salts at three temperatures. The values for $\epsilon_\infty(1)$ and $\epsilon_\infty(2)$ obtained at three temperatures, using the first and second procedures respectively, are presented in Table II along with the values for λ_0 and E_g^*. The average values for ϵ_∞ and E_g^* are plotted as a function of temperature in Fig. 22 for comparison.

DISCUSSION

The behavior of the first class of films requires very little discussion. They behave like single-crystal material showing the degenerate behavior of the Hall coefficient, the $T^{-5/2}$ power law temperature dependence of the Hall mobility, and the positive change in the band gap with temperature. The second class of films displays a less conventional behavior which sheds some light on a number of basic transport processes occurring in the lead salts.

[35] A. K. Walton and T. S. Moss, Proc. Phys. Soc. (London) 81, 509 (1963).

[36] T. S. Moss, *Optical Properties of Semiconductors* (Butterworths Scientific Publications Ltd., London, 1959), Chap. 2, p. 17.

A. Film Formation

Let us consider the generally accepted model for the formation of the films on heated alkali halide substrates.[37] As the lead salt condenses on the substrate, elementary nuclei are formed at preferred sites on the surfaces. These nuclei are strongly oriented with respect to the substrate in the (100) direction. As the nuclei grow they start to impinge on neighboring nuclei. At the boundaries of the crystallites, the matching of the
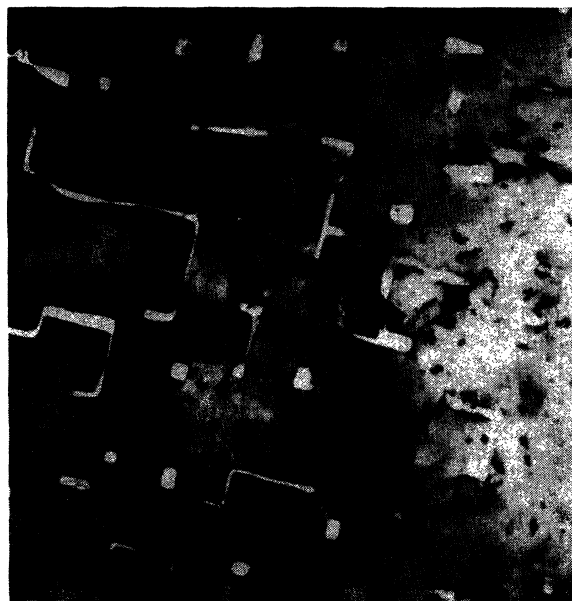

FIG. 23. Electron micrograph of a 800-Å-thick PbS film, 45 000×.

[37] D. W. Pashley, *Metallurgy of Advanced Electronic Materials* (Interscience Publishers, Inc., New York, 1963), Vol. 19.
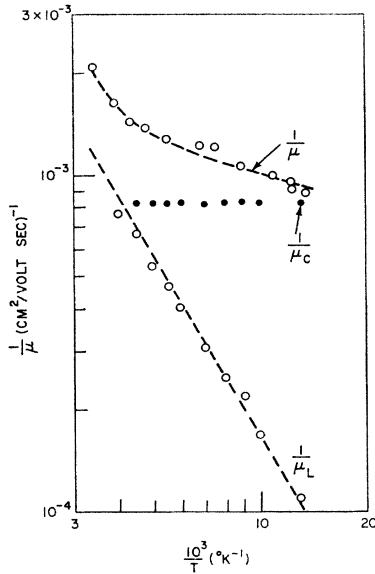
FIG. 24. Temperature dependence of the mobility of two thin PbTe films which display pronounced boundary scattering. μ_L represents the conventional $T^{-5/2}$ power-law dependence of the bulk mobility, and μ_c is the boundary-limited mobility.

atomic spacings will not be perfect. This mismatch of the spacings at the boundaries can lead to voids when more than two crystallites overlap. Electron micrographs of thin lead salt films confirm the existence of such voids, and an example of this type of structure is shown in Fig. 23.[38] Similar structures have been reported by other authors.[4,6]

B. Scattering Process

The boundary region between the crystallites should exert a pronounced influence on various properties of the films. If the boundaries constitute a small fraction of the total area of the film, the normal optical properties should not be severely affected by them. However, because of the mismatch in the lattice spacing, the boundary region should be very effective in scattering the current carriers. This should lead to a reduction in the mobility μ of the carriers. Because of the need to satisfy the cyclotron condition, $\mu H \geq 1$, the magneto-optic properties of the films will also be sensitive to the presence of the intercrystalline zones.[17]

If the boundary is effective as a scattering region, the upper limit on the mean free path of the carriers will be the average dimension of the crystallites. Let us call this dimension L_c. The time between scatterings τ_c will then be

$$\tau_c = L_c/v, \qquad (3)$$

where v is the velocity of the carriers. This velocity will depend on the statistics of the carriers, i.e., whether Boltzmann or Fermi-Dirac statistics are obeyed. In

[38] This photograph was supplied by E. G. Bylander of this Laboratory.

turn, this will depend on the carrier concentration and the electron-gas temperature. For the films being considered, it will be safe to assume that the carrier concentration is sufficiently high so that Fermi-Dirac statistics apply. Under such circumstances, the velocity is independent of temperature and will be given by the expression[39]

$$v = (h/2m^*)(3n/\pi)^{1/3}, \qquad (4)$$

where m^* is the carrier effective mass, n is the carrier concentration, and h is Planck's constant. The mobility μ is given by

$$\mu = q\tau/m^*, \qquad (5)$$

where τ is the mean free time. At sufficiently low temperatures, τ will be limited by boundary scattering and will be τ_c. Since both v and L_c are independent of temperature, τ_c will be temperature independent according to Eq. (3). Neglecting the temperature dependence of the effective mass, this implies that μ_c will be temperature, independent.

Aside from the boundary scattering, we expect that the free carriers will be subject to the same scattering processes that occur in the bulk. At high temperatures, there is scattering by lattice vibrations which is assumed to give rise to the $T^{-5/2}$ temperature dependence of the bulk mobility. If the boundary and lattice scattering processes are independent of each other, the measured mobility μ will obey the following relationship

$$1/\mu = 1/\mu_L + 1/\mu_c, \qquad (6)$$

where μ_L is the lattice mobility and μ_c is the boundary-limited mobility. Experimental values of $1/\mu$ are plotted in Fig. 24 for two PbTe Hall samples from films of different thickness. In addition, experimental values of $1/\mu_L$ obtained from the temperature behavior of bulk material are plotted in Fig. 24. The values of $1/\mu_c$ have been calculated using these data and Eq. (6). They are independent of temperature in accordance with the discussion above. These results show that for class-two films the relative significance of the boundary scattering is large at low temperatures.

From the Hall coefficient R of the films we can get the carrier concentration using the one-band expression

$$R = 1/nq. \qquad (7)$$

From Eqs. (3), (4), (5), and (7) we obtain a relationship between the boundary-limited mobility and the average crystallite size

$$L_c = (h\mu_c/2q)(3/\pi qR)^{1/3}. \qquad (8)$$

From the data in Fig. 24, we get a mean free path at low temperatures of approximately 250 Å. This value is in moderate agreement with the average spacing of 500 Å between voids observed in Fig. 23. Although

[39] W. Shockley, *Electrons and Holes in Semiconductors* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950), Chap 11, p. 281.

PbS was used to make the micrograph and PbTe was used in the electrical measurements, we assume that the average spacing between the voids is approximately the same for both materials.

We conclude that boundary scattering is an important mechanism for limiting the mobilities of the lead salts at low temperatures. It is also clear from this discussion that higher mobilities at low temperatures should be possible if two conditions are met. First, the alignment of the mosaic structure of the substrate crystal must be exceptionally good. If there are any low-angle grain boundaries in the substrate, they will have a pronounced effect on the electrical properties of the films. Second, the number of nucleation sites must be kept as small as possible. This number will be a property of the substrate material. A study of the influence of the substrate on the properties of the films would be of definite interest.

Figures 13, 14, and 15 show that the magnetoresistance was always proportional to the square of the magnetic field, as it should be for the field intensities used. Figures 16, 17, and 18 reveal the longitudinal magnetoresistance was considerably smaller than the transverse effect in all the materials studied. This behavior is characteristic of spherical energy surfaces, and in the case of PbSe is in accord with measurements made on bulk material.[40] However, the present results do not agree with bulk magnetoresistance data on PbTe[40] and SnTe.[41] These discrepancies may be due to boundary scattering and/or large strains at low temperatures. A more extensive investigation of magnetoresistance in these films would also be of interest.

C. Strain Phenomena

Whenever one discusses the temperature dependence of the various properties of epitaxial films the strain produced by the thermal expansion differences between the film and the substrate must be considered. A general discussion of the origin of the strain is given by Mitchell et al.[16] The strain plays an important role in the magneto-optical studies because of its influence on the position of the band gap.

In the lead salts, the conduction- and valence-band extrema lie at the (111) Brillouin-zone edge point L.[19—22] The films grow with a (100) orientation so the thermal expansion mismatch produces a strain with 4-fold symmetry about the growth axis. Such a strain does not lift the degeneracy of the extrema nor produce relative changes in the populations of the valleys of a band. The mobility therefore remains a scalar quantity for film thickness where the size effect is unimportant.

To a first order, the strain effect on the electrical properties arises from the changes in the effective mass of the carriers due to the change in the band gap. Since these bands are nondegenerate and appear to interact

we would expect that the effect of the thermally induced strain would be the same for both hole and electron mobilities. Mitchell, Palik, and Zemel[16,17] have shown that the reduced effective mass found in the IMO experiments changes by about 5%. This corresponds to the change in mobility observed by Paul, DeMeis, and Finegold[42] for the same equivalent pressure of 5 kbar. The observed mobilities in the films should be subject to a small downward correction due to this pressure effect on the effective mass. The maximum correction should be of the order of the 5% change in the effective masses of the carriers. This small correction has not been included in the data presented.

So far we have not considered an important question concerning the thermal strain: At what temperature is the thermal strain zero? The experimental evidence indicates that the strain is zero at room temperature. This is a rather surprising result on several counts. The films are grown on substrates heated to about 300°C. The films should be strained at room temperature unless the substrate behaved in an anomalous fashion. Otherwise, strain relief in the films would have to take place through slippage. This is not reasonable since that type of deformation would have a marked effect on the electrical properties of the samples. The calculated stress in the sample due to the thermal strain (this strain is obtained by a numerical integration of the differences in the coefficients of thermal expansion from the growth temperature down to room temperature) is approximately 5 kbar. A stress as large as this would produce easily observed changes in the optical properties. Riedl and Schoolar[12] have presented data showing that the position of the energy gap in epitaxial PbS is within experimental error of the gap of natural PbS. Thus, it appears that there is not any strain at room temperature. This is borne out by the fact that cycling samples from room temperature down to liquid-nitrogen temperature does not seem to produce any changes in the electrical, optical, or magneto-optical properties of the films.

An insight into the lack of room-temperature strain may be found in the paper of Stearns, Pack, and Lad.[43] They observed that cleaved and annealed single crystals of rocksalt displayed anelastic behavior at very low strain levels in flexure tests. The anelastic behavior disappears when the surface region of the cleaved crystal is removed by a water etch. Stearns, Pack, and Lad account for the anelasticity of the cleaved surface of the rocksalt in terms of the motion of dislocation loops in the surface. On cooling the samples from their growth temperature, the epitaxial film generates a stress in the substrate that causes the dislocation loops in the substrate to expand, thereby relieving the stress. As a

[40] R. S. Allgaier, Proceedings of the International Conference on Semiconductor Physics, Prague, 1960 (Czechoslovak Academy of Sciences, Prague, 1961), p. 1037.

[41] B. B. Houston and R. S. Allgaier (to be published).

[42] W. Paul, M. DeMeis, and L. X. Finegold, Proceedings of the International Conference on the Physics Semiconductor, Exeter, 1962 (The Institute of Physics and the Physical Society, London, 1962), p. 712.

[43] C. A. Stearns, A. E. Pack, and R. A. Lad, J. Appl. Phys. 31, 231 (1960).

result, there is no significant strain on the sample at room temperature. When the film is cooled to liquid-nitrogen temperatures, the dislocation-loop velocity is negligible because they do not have the thermal energy to move. This would account for the reproducibility of the electrical and IMO properties when the film is cycled down to liquid-nitrogen temperatures. The dislocation-loop model is quite capable of accounting for most of the observed strain-relief effects.

We have observed some effects in the electrical properties of the films that can be ascribed to the motion of defects of various types in the films. On PbS 32 in Fig. 19, we have observed the appearance and disappearance of scattering centers. The explanation for the behavior of PbS 32 rests on an observation made by Scanlon.[44] He found that there was a marked difference in the mobility of a natural PbS crystal depending on whether the measurement of the conductivity was made parallel or perpendicular to some low angle grain boundaries that were predominant in one direction. If, when the films are heated to the annealing temperature, there is a tensile stress placed on the film due to the difference in the thermal expansion coefficients, then the PbS would be expected to slip. In order for this to happen we must assume that the dislocation loops in the substrate have interacted as a result of the initial cooling to room temperature and they can no longer expand or contract, i.e., they are locked. The slip bands in the PbS film, like the low angle grain boundaries, should be effective as scattering regions. There is no particular reason for the slip band to act as bulk trapping sites because of the very large static dielectric constant of the lead salts. This large dielectric constant would reduce the binding energy of the traps so that they could be expected to be thermally ionized at all reasonable temperatures. As was the case in Sec. B, we see that grain-boundary scattering plays an important role in the electrical properties of the lead salts.

D. Optical Properties

The significant property obtained from the optical measurements is the dependence of the index of refraction of these materials on the wavelength at different temperatures. From these measurements, one can obtain the high frequency dielectric constant ϵ_∞ as a function of temperature. The precise method of analyzing the data to obtain ϵ_∞ depends on the data that is available. As described earlier, we have used two different procedures to obtain ϵ_∞: the conventional extrapolation of n^2 versus λ^2 to $\lambda^2 = 0$ and the procedure used by Walton and Moss. These two procedures employ data from different parts of the spectrum. The n^2 versus λ^2 plot in Fig. 21 describes the contribution of the free

[44] W. W. Scanlon, Phys. Rev. **106**, 718 (1957).

carriers and the lattice vibrational modes to the dispersion. The Walton-Moss procedure, on the other hand, is based upon the dispersion arising from the bound carriers in an empty lattice. To obtain a reliable value for the high frequency dielectric constant, we have employed both procedures. The values obtained agree to within 8% in the worst case and are within 4% for most of the values obtained. The reason for this agreement despite the difference in procedures used is that the lattice–vibrational and plasma frequencies are well separated from the absorption band-edge frequency. Because the n^2 versus λ^2 method employs only the lattice and free-carrier dispersion, one should use data from a wavelength region well below the absorption edge. On the other hand, the Walton-Moss procedure requires one to use data where the dispersion due to free carriers and the lattice will be relatively small. The properties of the films were such that both requirements were fulfilled in most instances.

CONCLUSIONS

The results of this work clearly indicate that epitaxial films of the lead salts, PbS, PbSe, and PbTe and the tin salt SnTe have properties equivalent to bulk material. Because of the form in which they are grown, they are well suited for a variety of experiments. We have employed a number of conventional techniques for studying these materials. The low-temperature mobility and the carrier concentrations initially obtained are quite comparable to the bulk. The optical properties of these materials can be easily studied. Strain effects due to the difference in thermal expansion coefficients of the film and the substrate play an important role on the optical behavior near the absorption edge, but the effects on the electrical properties are much less severe. Experimental evidence indicates that inhomogeneities are not a serious problem in most of the films grown. We have evidence that boundary scattering plays a very important role in determining the low-temperature mobility in the lead salts.
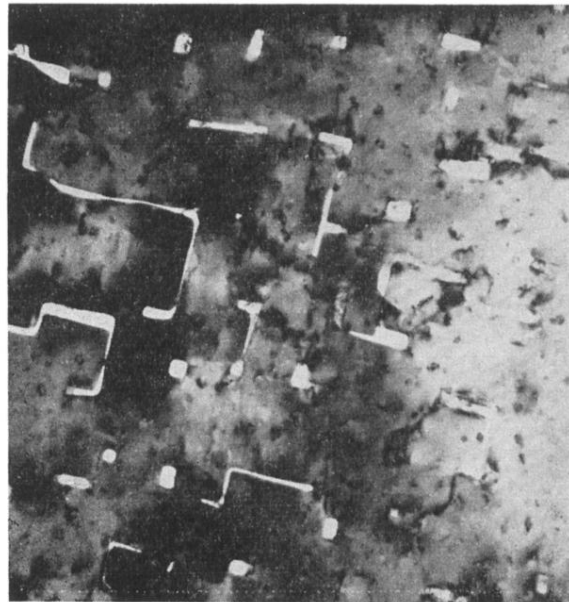
FIG. 23. Electron micrograph of a 800-Å-thick PbS film, 45 000×.