are optically positive with similar birefringence, and both display twinning that causes the crystals to mimic hexagonal symmetry. The powder patterns for the two salts are dissimilar, but they both contain a prominent set of lines, which in $CaK_3H(PO_4)_2$ correspond to the first four orders of the $00l$ reflections. In the tracing for one preparation of $MgNa_3H(PO_4)_2$, all four of these reflections appeared with greatly enhanced intensities because of an orientation or particle size effect, showing that they were orders of the same plane. These spacings are 7.7% smaller in $MgNa_3H(PO_4)_2$ than in $CaK_3H(PO_4)_2$. A comparison of the densities of the two salts, along with the apparent decrease in the length of c, indicates that the a and b axes of $MgNa_3H(PO_4)_2$ are smaller by an average of 7%. When allowance is made for differences of this magnitude in the dimensions of the two cells, a similarity in groupings of lines in the two powder patterns is discernible.

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Preparation of Indium Antimonide and Gallium Arsenide Films

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This note describes a chemical method of making multicrystalline films of semiconductors such as InSb and GaAs which appears general for III–V compounds and which may also be useful in a modified form for compounds such as PbSe, HgSe, and Zn_3As_2. The basic approach is to form a film of a coördination compound containing elements from the IIIA and Va columns of the periodic table and to decompose this thermally into a film of the corresponding III–V semiconductor. The following equations for boron–antimony[2] and indium phosphide[3] summarize the more closely related past work on reactions of this type

$$Sb_2(CH_3)_4 + B_2H_6 \xrightarrow{100^\circ} 2(CH_3)_2SbBH_2 + H_2 \quad (1)$$

$$(CH_3)_2SbBH_2 \xrightarrow{210^\circ} \text{SbB (black solid of this composition)} \quad (2)$$

$$In(CH_3)_3 + PH_3 \longrightarrow In(CH_3)_3PH_3 \quad (3)$$

$$In(CH_3)_3PH_3 \xrightarrow{-80^\circ} (InCH_3PH)_x \quad (4)$$

$$(InCH_3PH)_x \xrightarrow{300^\circ} InP \quad (5)$$

Experimental

Because of the inflammability of the compounds used and their reactivity with stopcock grease, most of the compounds were prepared and manipulated in a standard vacuum line equipped with mercury float valves and consisting of three main sections: (1) a storage system, (2) a tensimeter and measurement section, and (3) a reaction system.

Materials.—Stibine was prepared by the reaction of concentrated hydrochloric acid on a magnesium–antimony alloy, Mg_3Sb_2. The SbH_3 was purified by fractional distillation and condensation. The material which distilled through a trap at −139° and condensed in a trap at −159° was found to be tensimetrically homogeneous with a vapor pressure of 227 mm. at −45.2°. This is in agreement with the published value[4] of 224 mm. at the same temperature for SbH_3.

Trimethylindium was prepared by the reaction of dimethylmercury and indium metal in a sealed tube at 100°. The excess dimethylmercury was removed from the reaction product by fractional distillation. The trimethylindium condensed as large crystals, highly refractive to visible light, with a melting point of 88°, in good agreement with the published value[5] of 88.4°.

Trimethylstibine was prepared by the reaction of excess trimethylaluminum with SbF_3 at room temperature. The purified product had a vapor pressure of 30 mm. at 0°, which is in agreement with the literature value of 29.7 mm.[5]

Arsine was prepared in poor yield by the reaction of $LiBH_4$ with $AsCl_3$ in ether. Trimethylgallium was made by heating $Hg(CH_3)_2$ with Ga metal in a sealed tube at 130° for 1 week. The measured vapor pressure of the trimethylgallium was 65.0 mm. (lit. value[6] 64.5 mm.).

The Reaction of Stibine with Trimethylindium.—Stibine and trimethylindium were condensed at liquid nitrogen temperature in separate bulbs on each side of a U-tube connected to a mercury manometer. The SbH_3 bulb was brought to about −112° by means of a carbon disulfide slush bath, and the $In(CH_3)_3$ bulb was brought to room temperature. Thus, the $In(CH_3)_3$ sublimed through an atmosphere of about 2 mm. of SbH_3 at room temperature (26 to 28°) to the bulb at −112°. After three such passes a visible orange film formed on the U-tube between the bulbs, and an increase in the total pressure of the system was observed. Twelve or more passes were made to obtain films for tests. The orange film did not change in appearance when a boiling water bath was placed around

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the U-tube, but when the evacuated and sealed U-tube was placed in an oven at 150 to 160° the orange film darkened to a reflective gray film in about 0.5 hr. The pressure rise during the formation of the orange film was shown to be due to methane. The vapor pressure of the fractions non-condensable at −196° was found to be 10.5 mm. at −196° (lit. value[7] is 10 mm. for methane). The gray film was shown to be crystalline InSb by X-ray diffraction analysis, and the elements were identified qualitatively by spot tests. The gas evolved when the orange film was heated was shown to be mostly methane. Thicker orange films and InSb films were prepared by passing the $In(CH_3)_3$ through SbH_3 vapor at 30 mm. pressure.

The Reaction of Trimethylstibine with Trimethylindium.—The coördination compound of $Sb(CH_3)_3$ and $In(CH_3)_3$ was prepared by mixing the vapors of the two compounds. The coördination compound was a colorless solid at 0°, but a liquid at room temperature (26°). When the tube containing the coördination compound was heated at 100° for 100 hr., and then cooled back to room temperature, the pressure was found to have risen slightly, but no ethane could be detected by tensimetric analysis. In order to determine the degree of dissociation of the coördination compound into $In(CH_3)_3$ + $Sb(CH_3)_3$ a small sample was condensed in a tensimeter and pressure was recorded as a function of temperature. The compound was completely vaporized at 65°. Between 60 and 100° the vapor behaved as if completely dissociated into an ideal gas mixture (P/T = constant). This experiment alone does not prove the coördination compound to be dissociated in the vapor phase, but at least partial dissociation is to be expected from the behavior of other compounds of this type.

The Reaction of Arsine with Trimethylgallium.—Mixtures of vapors of these two compounds in 1:1 molecular proportions were allowed to react in Pyrex tubes at room temperature (25 to 28°). After the tube stood for 18 hr., a gray film was observed on the walls of the tube. When heated to 150 to 200° the film turned red, and methane was found to be the chief component in the gaseous reaction products. The red film was not changed by heating at 150° for several hours under vacuum, and its resistance was too large to be measurable with two probes and a vacuum-tube ohmmeter. The red color, high resistivity, and the method of preparation are all consistent with the film being stoichiometric GaAs. More work is planned on this.

Electrical Measurements.—Some resistance measurements were made on the InSb films in order to characterize them further. In Fig. 1 are plotted resistances *vs.* temperature for three of the films with two indium electrodes. Four-probe measurements on one of the films gave the same resistance ratio for two temperatures as the two probes. The films (on Pyrex substrates) were suspended in dry air inside a bulb which was immersed in a cryostat.

The slopes of the curves at the higher temperature correspond to a band gap of 0.23 e.v. (from $\sigma = \sigma_0 \exp (\Delta E/2kT)$). Although this value is larger than the band gap for pure, single-crystal InSb at 300°K. (0.17 e.v.), the break in the curve due to impurity conduction occurs at −130° or lower, indicating a highly stoichiometric material. Surface conduction, crystal boundary imperfections, and possibly some unconverted coördination complex probably raise the apparent band gap. The crystals were large enough to give an X-ray diffraction pattern, but the films showed no crystalline surface structure when inspected under an optical microscope.

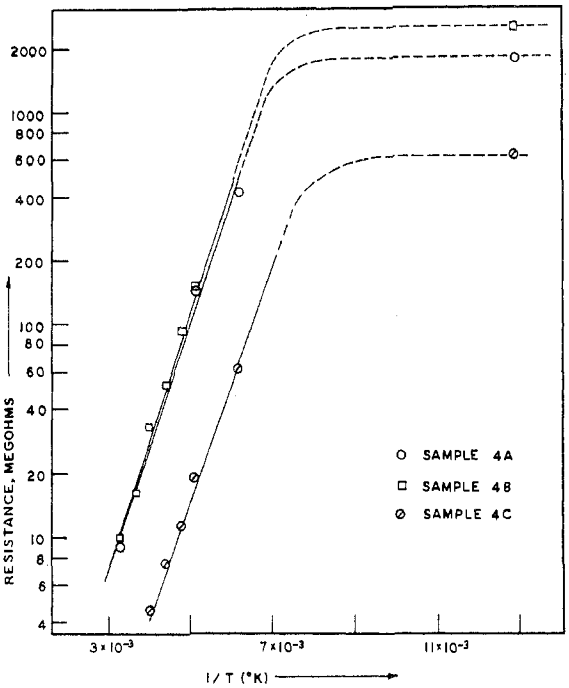

Fig. 1.—Resistances of InSb film *vs.* temperature.

In one experiment the orange film obtained from $In(CH_3)_3$ + SbH_3 was heated *in vacuo* at 140 and 155° for periods of 1 to 22 hr. At 140° the film resistance did not decrease detectably in 20 hr. from essentially infinity, but at 155° square area resistances dropped to 5 megohms in one film in the same time. In another film 22 hr. was required at 155° to reduce the resistance to 15 megohms.

Discussion

The orange film obtained from $In(CH_3)_3$ + SbH_3 appears to be $(CH_3InSbH)_x$. This is indicated by its color, its lack of volatility, by the evolution of methane during its formation, by its high electrical resistivity, and by its dissociation into stoichiometric InSb. The gradual decrease in resistivity of the orange film with time when heated at 155° is of interest because the material seems to be transforming from an organic to an inorganic semiconductor.

The slopes of the resistance–temperature curves in the 200 to 300°K. region for the InSb films appear to be determined partly by surface impurity states because further exposure to air reduced the slopes considerably. However, the low temperature at which the curves break over to constant impurity conduction is a good indication of the

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(7) F. D. Rossini, *et al.*, Natl. Bur. Standards Circ. 461, U. S. Government Printing Office, Washington, D. C., 1947.

stoichiometry of the films. The knee in the curve corresponds to a change from intrinsic conductivity at the higher temperatures to impurity or extrinsic conductivity at the lower temperatures.[8] When too high a pressure of SbH_3 was used in preparing the films the resistances were almost independent of temperature (up to 300°K., the highest temperature used), apparently because excess antimony was produced. A heated probe on the purer films gave a potential corresponding to a p-type semiconductor at room temperature, so that again we conclude that the high-temperature slopes in Fig. 1 are partly due to surface impurities (principally oxygen). The resistances were too high for conventional Hall effect measurements.

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Preparation of Ruthenium(II) by Controlled Potential Reduction

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Complexes of ruthenium(III) and (IV) have received considerable attention in the modern literature with regard to their solution chemistry and spectral characteristics.[1–5] Relatively little is known about the behavior of ruthenium(II) in solution, however. Jørgensen[6] has critically discussed the spectra of ruthenium(II) halide complexes in terms of crystal field theory.

Ruthenium(II) is commonly prepared in acid solution by reduction of ruthenium(III) or (IV) with zinc or cadmium amalgams, resulting in the inevitable introduction of foreign cations. While ruthenium(II) has been produced polarographically at microelectrodes,[7] attempts to prepare this species in perchloric acid media by controlled potential reduction at macroelectrodes[8] have been unsuccessful.

This author has found it possible to prepare stable solutions of ruthenium(II) in acidic chloride media by controlled potential reduction of ruthenium(IV) at a mercury pool electrode by accurate control of several critical factors. Polarographic work[7] has shown that ruthenium catalyzes the reduction of H^+ at mercury electrodes at surprisingly positive potentials in perchloric acid media. Preliminary polarographic experiments in hydrochloric acid media have shown similar effects. As a result, accurate control of the cathode potential is required in order to avoid hydrogen evolution while operating at potentials corresponding to the diffusion plateau of the ruthenium wave. The pH of the medium must be kept below 2.5 to avoid hydrolysis of ruthenium species.

The optimum conditions for the electrolytic production of ruthenium(II) at an applied potential of -0.470 ± 0.001 volts *vs.* s.c.e. were found in 4 *M* KCl solutions adjusted to pH 1.5 with HCl. Best results were obtained in solvent deaerated with N_2 and pre-electrolyzed under experimental conditions to remove reducible impurities. Under these conditions, lavender-blue solutions of $RuCl_4^{-2}$, having characteristic absorption maxima at 538 and 610 mμ, were produced. The spectra obtained are in good agreement with those of Jørgensen,[6] who prepared ruthenium(II) in 2 and 6 *M* HCl by reduction with zinc amalgam. No spectral evidence for the presence of ruthenium(III) or (IV) was found after completion of electrolysis.

Graphical integration of current–time curves for the reduction of K_2RuCl_6 by this method yielded values of 2.01 ± 0.01 for *n*, the number of electrons involved in the electrode process. Plots of log current *vs.* time gave good straight lines as a further indication of 100% current efficiency. The coulometric data are summarized in Table I.

Experimental

K_2RuCl_6 (A. D. MacKay, Inc., New York, N. Y.) was used as a source of ruthenium(IV). All other chemicals

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