than BF_3 in liquid hydrogen fluoride, using fluoride ion as the reference base.

The heat of solution of $SbCl_5$ in nitrobenzene (10.4 kcal./mole) approximates the corresponding value[8] for BCl_3 (8.7 kcal./mole). In view of their similar acid strength in pyridine, $SbCl_5$ most likely is present in the form of its adduct, $C_6H_5NO_2 \cdot SbCl_5$, similar to that postulated for BCl_3 in nitrobenzene.[24]

The heats of solution of PCl_4F and PCl_3F_2 in nitrobenzene (Table III) are lower than expected if a parallel in acid strength with the two bases, nitrobenzene and pyridine, is assumed. A value near 7 kcal./mole would be expected instead of the observed 2–3 kcal./mole. Hence, if adduct formation is taking place with the weak base, nitrobenzene, it must be doing so to a limited extent. Further, there is the possibility of the presence of an equilibrium ionization in the case of PCl_4F and PCl_3F_2 in nitrobenzene; however, further work is necessary to resolve the situation. In any case the over-all heat of reaction of the pure liquid halides with pyridine in nitrobenzene is independent of the state of the halide in nitrobenzene solution.

Considering the heats of reaction of $SbCl_5$ with alkylpyridine compounds in nitrobenzene, it is seen (Table V) that 2-methylpyridine produces a lower value than that obtained with pyridine. Such a lowering may serve to show the operation of a steric effect between the methyl group and neighboring chlorine atoms attached to antimony, especially since substitution of a methyl, ethyl, or isopropyl group in the 4 position gave similar heats of reaction, approximately 2 to 2.5 kcal./mole higher than the value observed with pyridine. The higher values found for alkyl substitution in the 4-position indicate the presence of an inductive effect. These changes parallel those observed[25] with BF_3 and monoalkyl pyridines studied by analogous methods.

Although it was possible to characterize 1:1 adducts containing $SbCl_5$ and either 2-ethyl or 2-isopropylpyridine, the heats of reactions involving these systems in nitrobenzene were not reproducible, suggesting the presence of competing reactions. $SbCl_5$ reacted with 2,6-lutidine but no characterizable product was isolated.

Acknowledgment.—The authors wish to express their appreciation to the National Science Foundation for a grant supporting this work.

[24] R. F. Grossman, *J. Org. Chem.*, **22**, 581 (1957), reported the isolation of $C_6H_5NO_2 \cdot SbCl_5$. We confirmed the preparation by precipitating it out of nitrobenzene solution by the addition of excess $SbCl_5$. *Anal.* Calcd. for $C_6H_5NO_2 \cdot SbCl_5$: C, 17.16; H, 1.19; N, 3.39; Cl, 41.99; Sb, 28.84. Found: C, 16.91; H, 1.39; N, 3.30; Cl, 41.89; Sb, 29.01. From infrared data, Grossman concluded that the structure was a simple addition compound involving Sb–O coördination.

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Zinc Phosphide Iodide (Zn_3PI_3) and Zinc Arsenide Iodide (Zn_3AsI_3): New Compounds with Disordered Defect Zincblende Structure

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New compounds, Zn_3PI_3 and Zn_3AsI_3, have been synthesized by the reaction of Zn_3P_2 or Zn_3As_2 with ZnI_2 in evacuated sealed quartz tubes at 475°. They have disordered defect zincblende structures (space group F$\bar{4}$3m) in which three zinc atoms and one vacancy are disordered over four cation sites, and three iodine atoms and one phosphorus (or arsenic) atom are disordered over four anion sites. A high Debye parameter for the zinc atoms is attributed to vibrations in the direction of the vacancies. The lattice constants compare favorably with values calculated from atomic radii. Relationships among this new modification of the zincblende structure and other structures are discussed. The compounds reported are the only ones found in the pseudobinary systems studied; compounds with the antichalcopyrite structure have not been observed. Some chemical and physical properties of the new compounds are given.

Introduction

The chalcopyrite ($CuFeS_2$) structure (space group I$\bar{4}$2d) is related to the zincblende (cubic ZnS) structure (space group F$\bar{4}$3m) in that the metal atoms of the former are so ordered in the zincblende-type structure that zinc atoms are alternately replaced by copper and iron atoms. This results in tetragonal symmetry with a doubling of the number of formula weights per unit cell but with the c/a ratio of the unit cell slightly less than two.

In addition to $CuFeS_2$, chalcopyrite structures are found in many other compounds of the type $A^{I}B^{III}C_2^{VI}$[1] as well as of the type $A^{II}B^{IV}C_2^{V}$[2] (*e.g.*, $ZnGeP_2$). On the other hand, $MgGeP_2$ has been reported[3] to crystallize with the cubic zincblende structure wherein the metal ions are totally disordered on the site corresponding to that of Zn in zincblende.

[1] See, for instance, H. Hahn, G. Frank, W. Klingler, A. D. Meyer, and G. Störger, *Z. anorg. allgem. Chem.*, **271**, 153 (1953).

[2] See, for instance, H. Pfister, *Acta Cryst.*, **11**, 221 (1958).

[3] O. G. Folberth and H. Pfister, *ibid.*, **14**, 325 (1961).

Folberth and Pfister[4] reported that $ZnSnAs_2$ has the same disordered structure as $MgGeP_2$, but Gasson, *et al.*,[5] now state that this is the high temperature form, designated α', and that the stable form at room temperature, designated α, has the chalcopyrite structure.

The present work was initiated in an attempt to synthesize compounds with an antichalcopyrite structure, *i.e.*, compounds in which two anions of different valence would be alternately substituted for the sulfur atoms in zincblende, while all the metal atoms on the other site would be identical.

Attempts to prepare compounds with an antichalcopyrite structure have been made previously, but without success, by Goodman[6] and by Folberth.[7] Goodman states that the possibility of obtaining compounds with this structure "cannot be entirely ruled out" but that his results "can be interpreted as indicating that the anionic sub-lattice with its relatively large atoms provides the stable framework for the various compound diamond structures." Both Goodman[6] and Folberth,[8] however, worked only with proposed compounds of the type $A_2^{III}B^{IV}C^{VI}$.

In the present work it was decided to seek compounds of the type $A_2^{II}B^{V}C^{VII}$. This paper therefore deals with results obtained in binary systems of Zn_3P_2, Zn_3As_2, or Zn_3Sb_2 with zinc dihalides.

Experimental

Syntheses.—The zinc halides used were the best laboratory grades commercially available. Zn_3P_2, Zn_3As_2, and Zn_3Sb_2 were synthesized by reaction of stoichiometric quantities of extremely pure powders of the constituent elements in evacuated sealed quartz tubes. The powder mixtures were brought up to temperature gradually and kept at the maximum for several hours; the maximum for Zn_3P_2 and Zn_3As_2 was 750° and for Zn_3Sb_2 850°. The X-ray diffraction powder pattern of the pure Zn_3P_2 prepared was identical with that of "Purified" Zn_3P_2 available from Fisher Scientific Company, and preparations made from both were also identical.

Equimolar combinations of either Zn_3P_2, Zn_3As_2, or Zn_3Sb_2 together with $ZnCl_2$, $ZnBr_2$, or ZnI_2 were heated for from 2 to 24 hr. in evacuated sealed quartz tubes at temperatures ranging from about 350 to 1000°. In most cases, the X-ray diffraction powder pattern of the product indicated no formation of compounds of the type sought, but interesting new compounds were formed in two systems. These systems were Zn_3P_2–ZnI_2 and Zn_3As_2–ZnI_2, and the optimum temperature for formation was found to be 475°. It was found, however, that the new phases always were accompanied by excess Zn_3P_2 or Zn_3As_2 if reactants were present in a 1:1 molar ratio. This indicated that the compounds were not Zn_2PI and Zn_2AsI, and further work established the formulas as Zn_3PI_3 and Zn_3AsI_3, which could be formed by the reactions

$$Zn_3P_2 + 3ZnI_2 \longrightarrow 2Zn_3PI_3$$

and

$$Zn_3As_2 + 3ZnI_2 \longrightarrow 2Zn_3AsI_3$$

Optimum synthesis temperature was again 475°, and the reactions were found to occur rapidly. The products formed and their observed properties were found to be independent of cooling rate. Although a much shorter period was required for complete reaction, 24 hr. was chosen as a standard time of preparation, and this was followed by slow cooling in the muffle furnace after cutting off the power.

With stoichiometric quantities of the reactants the X-ray diffraction powder patterns contained only lines of the new compounds; with a larger amount of either reactant, the pattern of the excess could be seen. Therefore, no other compounds exist in these pseudobinary systems. No shifts in lattice constants were observed, indicating either that little if any solid solution occurs or that, if there is a small region of solid solution formation, the lattice constant is insensitive to it.

Results

Crystal Structure of the New Compounds.—All the lines in the X-ray diffraction powder photographs of Zn_3PI_3 and Zn_3AsI_3 could be easily indexed on the basis of face-centered cubic unit cells (see Table I). Comparison with an X-ray diffraction powder photograph of cubic ZnTe revealed that the structure must be that of zincblende, for extinctions were identical and intensities nearly so. In order to fit a formula such as Zn_3PI_3 into the zincblende structure, it is necessary for the three zinc atoms to be statistically distributed over the four zinc sites in the zincblende unit cell (that is, the one vacancy is disordered). It is also necessary for the three iodine atoms and the one phosphorus atom to be disordered over the four sulfur sites. Any ordering of vacancies or anions would be expected to change the structure from cubic to something lower in symmetry and this would be evidenced by additional lines in the X-ray pattern.

In order to check the structure more quantitatively, intensity measurements of a powder sample of Zn_3PI_3

Table I

X-Ray Diffraction Powder Patterns of Zn_3PI_3 and Zn_3AsI_3

(Cu Kα radiation, 57.3 mm. radius camera)

hkl	Zn_3PI_3 *d*, Å.	Zn_3AsI_3 *d*, Å.	Intensity[a] (both new compounds)	Intensity of corresp. cubic ZnTe line
111	3.42	3.43	vs	vs
200	2.96	2.98	w+	w+
220	2.10	2.12	s	s
311	1.79	1.81	s−	s−
222	1.718	1.73	vw	vw
400	1.485	1.500	w	w+
331	1.365	1.377	m	m
420	1.329	1.342	w	w
422	1.215	1.226	m	m
333,511	1.145	1.158	w	w+
440	1.051	1.061	vw	w
531	1.007	1.017	w+	m−
600,442	0.991	1.001	w−	vw
620	.941	0.950	w−	w+
533	.909	.918	vw	w
622	.897	.906	vw	vvw
444	.859	.867	vvw	vw
551,711	.8335	.8415	w	w+
640	.8251	.8339	vw	vvw
642	.7946	.8025	m	m
553,731	.7739	.7820	m	m

[a] Intensity abbreviations: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; vvw, very very weak.

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(4) O. G. Folberth and H. Pfister, *Acta Cryst.*, **13**, 199 (1960).

(5) D. B. Gasson, P. J. Holmes, I. C. Jennings, B. R. Marathe, and J. E. Parrott, *J. Phys. Chem. Solids*, **23**, 1291 (1962).

(6) C. H. L. Goodman, *ibid.*, **6**, 305 (1958).

(7) O. G. Folberth, *Z. Naturforsch.*, **14a**, 94 (1959).

(8) O. G. Folberth, private communication.

were taken with a standard Norelco diffractometer, and these intensities were corrected for Lorentz and polarization factors (see Table II). Correction for absorption is not necessary with diffractometer data because the correction is a constant for all reflections. The calculated intensities for the zincblende structure fall into three types: *h*, *k*, *l*, all odd

$$F^2 = 16({}^3/_4 f_{\mathrm{Zn}} e^{-M_{\mathrm{Zn}}})^2 + 16({}^1/_4 f_{\mathrm{P}} e^{-M_{\mathrm{P}}} + {}^3/_4 f_{\mathrm{I}} e^{-M_{\mathrm{I}}})^2$$

$h + k + l = 4n$

$$F^2 = 16({}^3/_4 f_{\mathrm{Zn}} e^{-M_{\mathrm{Zn}}} + {}^1/_4 f_{\mathrm{P}} e^{-M_{\mathrm{P}}} + {}^3/_4 f_{\mathrm{I}} e^{-M_{\mathrm{I}}})^2$$

and $h + k + l = 4n + 2$

$$F^2 = 16({}^3/_4 f_{\mathrm{Zn}} e^{-M_{\mathrm{Zn}}} - {}^1/_4 f_{\mathrm{P}} e^{-M_{\mathrm{P}}} - {}^3/_4 f_{\mathrm{I}} e^{-M_{\mathrm{I}}})^2$$

where F is the structure factor, f is the atomic scattering factor, and $M = B(\sin \theta/\lambda)^2$, where B is the Debye parameter $8\pi^2\bar{U}^2$ for isotropic displacement, and $\bar{U}^2$ is the mean square displacement of the atoms from their mean positions. The expression e^{-M} is known as the temperature factor.

Intensities including multiplicity factors were calculated with an IBM 7090 computer. A calculation based on an over-all temperature factor with $B = 1.5$ Å.^{2} (a rather average value for inorganic compounds) led to good agreement for low angle lines but very poor agreement for some at high angles, and the agreement between observed and calculated intensities (the R-factor

$$\left.\frac{\Sigma(F^2_{\mathrm{obsd}} - F^2_{\mathrm{calcd}})}{\Sigma F^2_{\mathrm{calcd}}} \times 100\right)$$

was 23.7%. For example, the 600 and 620 lines were observed to have relative intensities of 62 and 41, while the calculated values were 16 and 84, respectively. Since F (600) equals the difference in atomic scattering factors of Zn and the average of I and P, but F (620) equals the sum, the two can be brought close to observed values only if an anomalously high temperature factor exists for the Zn atoms. This type of behavior has been observed in AgI,[9–11] CuI,[12] and CuBr.[13] A least-squares refinement program was written to refine the Zn and I temperature factors, with the phosphorus atom given the same temperature factor as iodine. The best agreement ($R = 16.9\%$; see Table II) was obtained with $B_{\mathrm{Zn}} = 7.4$ Å.^{2} and $B_{\mathrm{I,P}} = 1.4$ Å.^{2}. The remaining error is thought to be due to the difficulty in obtaining good data from powder samples.

Each Zn in $\mathrm{Zn_3PI_3}$ is surrounded by four anionic nearest neighbors and then there are twelve cationic positions as next-nearest neighbors. Since the twelve cationic positions are on the average nine Zn atoms and three vacancies, it might be expected that Zn atoms would tend to move in the direction of the high negative charge regions of each of the three vacancies (and, of course, each vacancy would have an attraction for an average of nine Zn atoms). Since the vacancies are actually distributed randomly, the vibration would appear to take place in all twelve directions so that the effect would appear isotropic and the crystal symmetry would not be lowered by the displacement. Such an effect does, however, explain the unusually high temperature factor found for Zn. The root mean square displacement, $\sqrt{\bar{U}^2}$, of a Zn atom from its ideal zincblende position is found to be 0.3 Å. The structure is illustrated in Fig. 1.

TABLE II

CALCULATED *vs.* OBSERVED INTENSITIES FOR $\mathrm{Zn_3PI_3}$

hkl	Intensity[a]	F^2_{obsd}[b]	F^2_{calcd}[c]	F^2_{calcd}[d]
111	100	101	107	116
200	12	17	14	21
220	44	174	198	185
311	32	161	180	182
222	10	40	11	25
400	7	45	61	49
331	11	125	116	114
420	4	53	22	65
422	13	138	163	119
333,511	6	79	107	104
440	3	47	58	40
531	9	121	115	114
600,442	5	62	16	56
620	3	41	84	55
533	6	51	43	43
622	4	23	10	36
444	5	33	21	14
551,711	10	71	64	66
640	5	23	8	29
642	11	91	94	61
			$R = 23.7\%$	$R = 16.9\%$

[a] From diffractometer trace. [b] L. P. corrected. [c] $B_{\mathrm{Zn}} = 1.5$; $B_{\mathrm{P,I}} = 1.5$. [d] $B_{\mathrm{Zn}} = 7.4$; $B_{\mathrm{P,I}} = 1.4$.

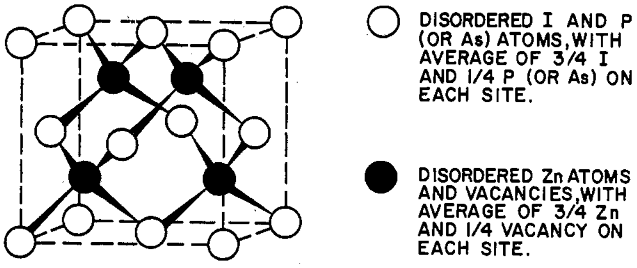

Fig. 1.—Crystal structure of $\mathrm{Zn_3PI_3}$ and $\mathrm{Zn_3AsI_3}$.

The lattice constants are given in Table III along with values calculated from radii given in the literature. In making this calculation, a weighted average of three I and one P (or As) was used for the anion, but it was difficult to decide just how to treat the disordered vacancy. Probably the presence of disordered vacancies will tend to affect the value of the lattice constant but just how much cannot be properly estimated. The calculations on which Table III is based were made as if all vacancies were actually filled with zinc atoms. The calculated lattice constant is therefore taken as being $4/\sqrt{3}$ times the average distance between zinc and iodine or phosphorus (or arsenic). It will be seen from Table III that agreement between experimental and calculated values is quite good. The values calculated from Wyckoff's radii are exceptionally good.

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(11) S. Hoshino, *J. Phys. Soc. Japan*, **12**, 315 (1957).
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(13) S. Hoshino, *ibid.*, **7**, 560 (1952).

TABLE III

LATTICE CONSTANTS OBSERVED AND CALCULATED, Å.

Compound	Observed	Calcd. from Pauling[a]	Calcd. from Wyckoff[b]
Zn_3PI_3	5.945	5.88	5.96
Zn_3AsI_3	6.006	5.92	6.01

[a] Calculated from Pauling's tetrahedral covalent radii [L. Pauling, "The Nature of the Chemical Bond," Third Edition, Cornell University Press, Ithaca, N. Y., 1960, p. 246]. [b] Calculated from Wyckoff's neutral atomic radii from tetrahedral crystals [R. W. G. Wyckoff, "Crystal Structures," Interscience Publishers, Inc., New York, N. Y., 1960, Table III, 13, Chapter III, Table p. 33].

The density calculated for Zn_3PI_3 from the lattice constants and the structure (with one formula weight per unit cell) is 4.81, while the value determined by displacement of benzene in a specific gravity bottle is 4.87 g./ml. It may be of interest to note that this value is higher than the reported density of either of the reactants, Zn_3P_2 (4.55) and ZnI_2 (4.666).

Physical and Chemical Properties.—Both new compounds are dark gray. They do not melt but rather decompose into the compounds from which they were formed starting at about 600° when sealed under vacuum. Under "open" vacuum they begin to lose ZnI_2 at about 300°. Alcohol dissolves out ZnI_2, leaving Zn_3P_2 (or Zn_3As_2) behind. These chemical properties are very similar to those of Ag_2HgI_4. On exposure to moist air, deliquescence occurs.

No tendency for the new compounds to form single crystals was observed. Crystals could not be grown from solution in excess molten ZnI_2 or from the vapor phase. Attempts were made to measure electrical conductivity of pressed pellets of the powder as a function of temperature, but only erratic behavior was observed. This may have been due to changes in composition resulting from absorption of water even though the pellet was kept in a stream of nitrogen dried with Drierite and from loss of ZnI_2 as the pellet was heated. At room temperature, the conductivity of the compounds is of the order of 10^{-10} ohm^{-1} cm.$^{-1}$.

Discussion

The synthesis of compounds with an antichalcopyrite structure remains unattained. However the new compounds reported here represent a closely related new modification of the zincblende structure. They are chemically related to antichalcopyrite in that the cation sublattice consists entirely of zinc and the anion sublattice is shared by elements from groups V and VII of the periodic table. They are structurally related to an anti-$MgGeP_2$ (or anti-α'-$ZnSnAs_2$) structure in that their anions are disordered in one of the zincblende sublattices. They are structurally related to γ-Ga_2Se_3[14] in that cations and vacancies are disordered in the other sublattice of the zincblende structure. Finally, they are related to the zincblende type "Phase I" which extends from 10 to 20 mole % Ag_2S in the Ag_2S–HgI_2 system[15] in that disordered anions of two different valence states and disordered cations and vacancies are present; these differ however in the number of unlike cations present and the valence states of some of the elements involved.

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Copper(II) Bromide Complexes. I. A Spectrophotometric Study

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Spectrophotometric studies on copper(II) bromide–lithium bromide mixtures in aqueous and organic solvents and on solid bromocuprates of known structure have shown that the highest bromide complex formed is the $CuBr_4^{-2}$ ion. This species is purple. The green color observed at lower bromide concentrations in various solvents is felt to be $CuBr_3^{-}\cdot 2$ solvent.

The striking color changes when solutions of copper(II) bromide, particularly in non-aqueous media, are treated with hydrogen or alkali bromide have attracted the interest of a number of investigators. Kosower, Martin, and Meloche[3] interpreted the spectral changes observed in an alcoholic copper(II) bromide solution on addition of hydrogen bromide in terms of a series of six mononuclear copper(II) bromide complexes. The low stability in aqueous solution of the $CuBr^+$ ion,[4] which we have found not to be changed significantly in going to alcoholic medium,[5] suggests that an alternative interpretation might better explain the observed

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