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Mixed-Cation Transition Metal Pyrite Dichalcogenides—High Pressure Synthesis and Properties

T. A. BITHER, P. C. DONOHUE, W. H. CLOUD, P. E. BIERSTEDT, AND H. S. YOUNG

Central Research Department,† *E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware 19898*

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Ternary, pyrite-type dichalcogenides $Zn_yMn_{1-y}X_2$, $Cd_yMn_{1-y}X_2$, $Zn_yCd_{1-y}X_2$, $Zn_yCu_{1-y}X_2$, $Cd_yCu_{1-y}X_2$, $Mn_yCu_{1-y}X_2$, $Cu_{\sim0.75}Fe_{\sim0.25}S_2$, and $Ni_{0.4-0.6}Fe_{0.6-0.4}X_2$ ($0 < y < 1$, X = S, Se, Te) have been synthesized at high pressure (65–89 kbars). Semiconductor behavior was observed in the first three compositions. The ternaries rich in Cu were metallic, and the superconducting transition temperature of CuS_2 was elevated upon substitution with less than 20 *a/o* of Zn or Cd. A noncolinear spin structure is proposed to explain the ferromagnetism observed in the $Mn_yCu_{1-y}X_2$ compounds.

Introduction

Preparation of the transition metal pyrite-type compounds CuS_2, $CuSe_2$, $CuTe_2$, ZnS_2, $ZnSe_2$, CdS_2, and $CdSe_2$ under high pressure has been reported by us (*1*), (*2*). Of these three cations, only ternary pyrite phases containing Cu have been described. Thus, the mineral penroseite, $(Cu,Ni)Se_2$, is discussed by Earley (*3*) who also prepared synthetic analogs, $Cu_yNi_{1-y}Se_2$ ($y \leqslant 0.24$), by reaction of the elements in sealed, evacuated silica tubes. Moh (*4*) and Bouchard (*5*) examined the analogous sulfide system and found that $Cu_yNi_{1-y}S_2$ ($y \leqslant 0.33$) could be prepared at autogenous pressures. Other copper-containing, pyrite-type minerals include cuprian bravoite and villamaninite (*6*), $Cu_wNi_xCo_yFe_zS_2$ ($w+x+y+z=1$, $w \leqslant 0.6$) with variable amounts of these four cations. In addition, Hull and Hulliger (*7*) have recently reported the selenides $(Cu,M)Se_2$ (M = Fe, Co, Ni).

Ternary pyrite dichalcogenides $M_yM'_{1-y}X_2$ containing these three *high-pressure pyrite cations*, both in combinations with each other as well as with other transition metals including Mn and Fe, have now been synthesized in a tetrahedral anvil apparatus. Electrical and magnetic properties of these compositions have been measured and, as has been observed in the binary pyrites MnX_2 to ZnX_2 (*2*), the mixed-cation isotypes also occur as a group having properties that vary from (1) superconductors to (2) weak paramagnetic to ferromagnetic metallic conductors to (3) semiconductors.

Experimental Section

Preparation of Compounds

Reactions were carried out at 60–65-kbars pressure, unless otherwise indicated, in a tetrahedral anvil apparatus of National Bureau of Standards design (*8*) using a cylindrical boron nitride crucible surrounded by a graphite-sleeve resistance heater inserted in a pyrophyllite tetrahedron. The calibration points used to establish the pressure developed were the transitions Bi(I) → Bi(II) (25.37 ± 0.02 kbars), Bi(II) → Bi(III) (26.96 ± 0.18 kbars), Tl(II) → Tl(III) (36.69 ± 0.11 kbars), and Ba(II) → Ba(III) (59.0 ± 1.0 kbars). All compressions were made on the assembly at room temperature, and the charge was then heated to the desired temperature which was measured with a Pt–Rh thermocouple, uncorrected for pressure effects. The thermocouple was adjacent to the center of the graphite heater.

High purity reactants (> 99.99% pure) were ground together and pelleted prior to reaction. Depending on reactant densities, pellets weighed 0.1–0.9 g. This technique was used to prepare ternary pyrites of the type $M_yM'_{1-y}X_2$ in which M and M' included selected combinations of the cations Zn, Cd, Cu, Ni, Fe, and Mn and X was S, Se, or Te. Parameters such as reactant ratios, temperature cycles, and pressures were dependent upon the compound being prepared and are given in the section on Results. Sulfides were extracted with CS_2 to remove the soluble form of unreacted sulfur.

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The chemical compositions of most of these $M_yM'_{1-y}X_2$ compounds were estimated by Vegard's rule (*9*). Where chemical analyses or density measurements were obtained, the reliability of this method for the estimation of composition was confirmed.

X-Ray Data

Debye–Scherrer X-ray diffraction powder data were obtained at 25°C on the reaction products. Patterns that showed the pyrite-type structure were indexed, and the unit-cell dimensions were refined by a least-squares method (*2*). Cell dimensions showed a standard deviation of ± 0.001 Å or less.

Electrical and Meissner Measurements

Electrical resistivity was measured on reasonably well-shaped single crystals using a four-probe technique (*2*). Activation energy of resistivity, E_a, is defined by the relation $\rho = \rho_0 e^{E_a/kT}$.

Superconductivity was determined magnetically by the Meissner effect in which the self-inductance of a coil containing the sample was observed (*10*). Measurements could be made to a lowest temperature of 1.25°K.

Magnetic Measurements

A vibrating sample magnetometer and/or a Faraday balance were used to measure magnetic properties. Saturation magnetizations were determined in fields up to 17,500 Oe, Curie temperatures in fields of 50–300 Oe, and susceptibilities in fields of 2000–17,500 Oe. Measurements were usually made in the range 4.2–300°K.

Results

$Zn_yMn_{1-y}X_2$

Pyrite-type $Zn_yMn_{1-y}S_2$ compounds ($y \simeq 0.35$, 0.53, and 0.70) were obtained as dark-red crystals at the sample ends by reactions of 0.5 ZnS/1.5 MnS/2.5 S, ZnS/MnS/2.5 S, and 1.5 ZnS/0.5 MnS/2.5 S, respectively, for 1 h at 1000°C, a 5-h cool to 875°C, and a subsequent quench to room temperature, all at 65 kbars. Chemical analyses on the most zinc-rich compound agreed well with the *y* value of 0.70 estimated from Vegard's rule (Anal. calcd. for $Zn_{0.70}Mn_{0.30}S_2$: Zn, 36.22; S, 50.74. Found: Zn, 37.5; S, 50.7) and indicated the formula $Zn_{0.73}Mn_{0.27}S_2$. Similarly, black crystals having the pyrite-type structure with the estimated composition $Zn_{0.5}Mn_{0.5}Se_2$ were obtained at the sample ends by reaction of 0.5 Zn/0.5 Mn/2.2 Se at 65 kbars for 1 h at 800°C, a 2-h cool to 700°C, and a subsequent quench to room temperature. In the telluride system, reaction of 0.5 Zn/0.5 Mn/2 Te at 65 kbars for 2 h at 800°C, a 4-h cool to 400°C, and a quench to room temperature gave a product comprising red crystals of ZnTe at the sample ends adjoined by silver crystals with a granular mixture containing Te in the center. The X-ray powder pattern of the silver crystals could be indexed on the basis of a pyrite-type structure having a unit cell smaller than that of $MnTe_2$ and indicating a ternary approximating the composition $Zn_{0.5}Mn_{0.5}Te_2$.

These $Zn_yMn_{1-y}X_2$ compounds are semiconductors with relatively low activation energies of resistivity. Magnetic susceptibility measurements from 300°K showed Curie–Weiss behavior. A small, spontaneous moment of 0.05 μB appeared at 55°K in the telluride. No identifiable ordering temperatures were observed in the selenide and sulfide ternaries (Table I).

$Cd_yMn_{1-y}X_2$

The phase relationships involved in the formation of pyrite-type Cd–Mn dichalcogenides appear to be more complex than those in the analogous Zn–Mn systems, and only $Cd_yMn_{1-y}Se_2$ was isolated in single crystal form suitable for characterization. In the sulfide system, reaction of CdS_x (amorphous)/MnS/1.5 S at 65 kbars for 1 h at 700°C followed by a quench to room temperature gave an orange powder interspersed with tiny black crystallites. X-ray diffraction powder data indicated a polyphase product that comprised (a) pyrite-type $Cd_{0.35}Mn_{0.65}S_2$ ($a = 6.176$ Å), (b) a rock salt-type $\sim Cd_{0.5}Mn_{0.5}S$ ($a = 5.340$ Å), and (c) a wurtzite-type $\sim Cd_{0.6}Mn_{0.4}S$ ($a = 4.07$, $c = 6.62$ Å). Miller et al., (*11*) have reported the formation of this mixed (Cd,Mn)S rock salt-type phase at pressures up to 40 kbars. Similarly, a polyphase red-orange powder resulted from reaction of the same starting materials at 65 kbars for 2 h at 700°C, a 6-h cool to 400°C, and a subsequent quench to room temperature. This product was observed to contain pyrite-type $Cd_{0.6}Mn_{0.4}S_2$ ($a = 6.228$ Å) as the main phase mixed with α-MnS and (Mn,Cd)S products as above.

In contrast, the reaction of 0.5 Cd/0.5 Mn/3.2 Se at 65 kbars for 2 h at 1000°C, a 6-h cool to 400°C, and a quench to room temperature gave red-brown crystals of wurtzite-type (Cd,Mn)Se ($a = 4.21$, $c = 6.94$ Å) at the sample ends adjoined by black crystals having the pyrite-type structure and with the estimated composition $Cd_{0.44}Mn_{0.56}Se_2$. Excess Se was present in the center of the sample. A density measurement on this pyrite phase was in good

TABLE I

SEMICONDUCTING $(Zn,Mn)X_2$ AND $(Cd,Mn)X_2$ PYRITES

		Electrical		Magnetic			
$(M,Mn)X_2$	a, Å	E_a, eV	$\rho_{25°}$, Ω cm	p^2_{eff}, μ^2_B	No. spins/Mn	θ, °K	Remarks
$Zn_yMn_{1-y}S_2$							
$y = 0$, MnS_2	6.109			37.9	5.2	−598	Antiferro., $T_N = 48°K$[a].
0.35	6.055	0.14	4.0×10^{-1}	27.6	5.6	−463	Curie–Weiss behavior but no max. in χ vs T curve to 10°K. $\chi_{300°K} = 37 \times 10^{-6}$ emu/g
0.53	6.027	0.14	1.0×10^{0}				
0.73	6.000	0.17	2.7×10^{1}				
1, ZnS_2[b]	5.954	($\Delta E > 2.5$)	1.0×10^{6}				Diamagnetic
$Zn_yMn_{1-y}Se_2$							
$y = 0$, $MnSe_2$	6.430	($\Delta E = 0.2$)[c]		35.2	5.0	−483	Antiferro., $T_N \sim 100°K$[d].
0.5	6.360	0.07 ($\alpha = +220$ μV/°)[e]	9.0×10^{-3}	21.1	5.5	−267	Slight departure from C–W law < 30°K. $\chi_{300°K} = 21 \times 10^{-6}$ emu/g
1, $ZnSe_2$[b]	6.293	0.24	2.0×10^{6}				Diamagnetic
$Zn_yMn_{1-y}Te_2$							
$y = 0$, $MnTe_2$	6.951	($\Delta E = 0.2$)[c]		34.1	4.9	−528	Antiferro., $T_N = 87°K$[a].
$\simeq 0.5$	6.874	0.003	4.6×10^{-3}	9.7	3.5	+ 30	C–W behavior. Spontaneous moment (0.05 μB) appears at 55°K. $\chi_{100°K} = 55 \times 10^{-6}$ emu/g
$Cd_yMn_{1-y}Se_2$							
$y = 0.48$	6.511	0.10 ($\alpha = +300$ μV/°)[e]	1.0×10^{0}	20.2	5.3	−308	C–W behavior but no max. in χ vs. T curve to 4.2°K. $\chi_{297°K} = 18 \times 10^{-6}$ emu/g
1, $CdSe_2$[b]	6.615						Diamagnetic

[a] M. S. Lin and H. Hacker, *J. Solid State Commun.* **6**, 687 (1968).

[b] Ref. (*2*).

[c] F. Hulliger, *Helv. Phys. Acta* **32**, 615 (1959).

[d] J. M. Hastings, N. Elliot, and L. M. Corliss, *Phys. Rev.* **115**, 13 (1959).

[e] α—Seebeck coefficient.

agreement with that calculated for the above formula estimated by Vegard's rule (Dens. calcd. for $Cd_{0.44}Mn_{0.56}Se_2$ with $a = 6.511$ Å: 5.730 g/cm³. Found 5.789 g/cm³) and indicates the formula $Cd_{0.48}Mn_{0.52}Se_2$. In the telluride system, reaction of 0.5 Cd/0.5 Mn/2 Te under the same conditions as used for the selenide gave a heterogeneous product comprising (a) a sphalerite-type (Cd,Mn)Te ($a = 6.417$ Å), (b) a pyrite-type $(Cd,Mn)Te_2$ ($a = 6.979$ Å), and (c) unreacted Te. The pyrite phase could not be isolated for characterization.

Like the $Zn_yMn_{1-y}X_2$ compounds, the $Cd_{0.48}Mn_{0.52}Se_2$ product was a semiconductor. Magnetic susceptibility measurements from 300–4°K showed Curie–Weiss type behavior, but a maximum in the susceptibility indicative of a Néel point was not observed (Table I).

$Zn_yCd_{1-y}X_2$

Reactions at 65 kbars of equimolal amounts of crystalline or amorphous ZnS/CdS plus excess sulfur gave microcrystalline yellow to orange matrices which, from their X-ray diffraction patterns, comprised $Zn_yCd_{1-y}S_2$ pyrite-type phases mixed with unreacted ZnS and CdS. Thus reaction at (a) 700°C for 3 h, a 3-h cool to 400°C, and a quench to room temperature gave $Zn_{0.56}Cd_{0.44}S_2$ ($a = 6.110$ Å) and $Zn_{0.71}Cd_{0.29}S_2$ ($a = 6.056$ Å); (b) 600°C for 3 h, a 3-h cool to 300°C, and a quench gave $Zn_{0.5}Cd_{0.5}S_2$ ($a = 6.125$ Å); and (c) 500°C for 5 h followed by a quench gave $Zn_{0.7}Cd_{0.3}S_2$ ($a = 6.059$ Å). Comparable reactions of Zn/Cd/4 Se at 65 kbars gave microcrystalline black matrices which consisted of mixtures of $Zn_yCd_{1-y}Se_2$ pyrite-type phases as well as ZnSe, CdSe, and Se. For example, reaction at (a) 800°C for 1 h, a 4-h cool to 400°C, a 1-h hold at 400°C, and a quench gave $Zn_{0.32}Cd_{0.68}Se_2$ ($a = 6.510$ Å); and (b) 600°C for 4 h, a 2-h cool to 400°C, and a quench gave $Zn_{0.46}Cd_{0.54}Se_2$ ($a = 6.464$ Å).

These products all showed very high electrical resistance in agreement with the semiconducting properties of their respective binary end members (*2*), but single crystal sections could not be isolated for characterization.

$Zn_yCu_{1-y}X_2$

Pyrite-type $Zn_yCu_{1-y}S_2$ compounds ($y \simeq 0.05$, 0.07, 0.09, and 0.20) were obtained as purple to blue-black microcrystals by reaction of ZnS with either Cu_2S or CuS plus sulfur in the elemental ratios Zn:Cu:S = 0.05:0.95:2.0, 0.10:0.90:2.0, 0.20:0.80:2.0, and 0.25:0.75:2.3 at 65 kbars for 2–3 h at 600–800°C, a 2-h cool to 400°C, and quench to room temperature. As the Zn content of the pyrite phase decreased from that of the initial charge, ZnS (sphalerite-type) was also observed in the X-ray diffraction patterns of the products. At a charge of 0.5 ZnS/0.5 CuS/S, reaction at 89 kbars for 2 h at 1000°C with a quench to room temperature gave a similar blue-black microcrystalline product that comprised two intermixed pyrite phases ($y \simeq 0.4$ and 0.8) rather than a single species. A single pyrite phase ($y \simeq 0.97$) was again formed in the high Zn region of this ternary from 0.95 ZnS/0.05 CuS/1.55 S under reaction conditions similar to those used to prepare phases of low Zn content. Although ZnS_2 is bright yellow, microcrystalline $Zn_{0.97}Cu_{0.03}S_2$ was black.

Reaction of 0.5 Zn/0.5 Cu/2–2.2 Se at 65 kbars gave segregated products from which different pyrite phases were isolated depending upon the heating cycle. Thus a 1-h heat at 1000°C, a 3-h cool to 400°C, and a quench to room temperature gave a banded product with (a) yellow-brown ZnSe at the sample ends, (b) an adjoining zone of blue pyrite-type crystals ($y \simeq 0.05$), and (c) an Se-rich center. With a 1-h heat at 800°C, a 2-h cool to 700°C, and a quench, a black pyrite phase ($y \simeq 0.95$) formed at the extreme ends of the sample in addition to the three sections noted above. With a 4-h heat at 800°C, a 4-h cool to 400°C, and a quench, two pyrite phases ($y \simeq 0.4$ and 0.9) were formed in the initial zone of black microcrystals.

These $Zn_yCu_{1-y}X_2$ compounds showed metallic-type conduction and with $y < 0.2$, they were also superconductors (Table II).

$Cd_yCu_{1-y}X_2$

Reaction of 0.1 CdS_x (amorphous)/0.9 CuS/S at 65 kbars for 2 h at 700°C, a 6-h cool to 400°C, and a quench to room temperature gave a purple, microcrystalline pyrite-type product ($y \simeq 0.04$) containing a small amount of CdS. In the selenide system, reaction of 0.1 Cd/0.9 Cu/2 Se at 65 kbars for 2 h at 1000°C, a 6-h cool to 400°C, and a quench gave dark-blue crystals of pyrite-type structure ($y \simeq 0.04$). Under the same conditions, reaction of 0.5 Cd/0.5 Cu/2 Se gave a zoned product comprising (a) black crystals of CdSe at the sample ends, (b) an adjoining region of blue crystals of pyrite-type structure ($y \simeq 0.06$), and (c) a center of unreacted Se. Superconductivity was also observed in these compounds (Table II).

$Mn_yCu_{1-y}X_2$

Pyrite-type $Mn_yCu_{1-y}S_2$ compounds ($y \simeq 0.01$–0.8) were obtained as dark purple to purple-black to black crystals (blackness increased with increasing Mn content) by reaction of yMnS/$(1-y)$CuS/S at 65 kbars for 2–14 h at 800°C followed either by a direct quench to room temperature or a slow cool for 4–8 h to 400°C and a subsequent quench. At an MnS charge in the range $y \simeq 0.15$–0.4, sharp separation into two pyrite phases frequently occurred. At higher charges of MnS, this component reacted incompletely and appeared throughout the ternary pyrite phase.

Black crystals having the pyrite-type structure with an estimated composition $Mn_{0.55}Cu_{0.45}Se_2$ were obtained at the sample ends by reaction of 0.5 Mn/0.5 Cu/2.2 Se at 65 kbars for 1 h at 800°C,

TABLE II

SUPERCONDUCTING $(Zn,Cu)X_2$ AND $(Cd,Cu)X_2$ PYRITES

$(M,Cu)X_2$	a, Å	Color	Meissner Superconducting Transition Range, °K
$Zn_yCu_{1-y}S_2$			
$y = 0$, CuS_2[a]	5.790	Purple	1.48–1.53
0.05	5.798	Purple	1.9 –2.3
0.07	5.801	Blue-Purple	1.5 –2.5
0.09	5.805	Blue-Purple	2.0 –2.5
0.2	5.823	Blue-Black	1.5 –2.5
0.4, 0.8 [b]	5.851, 5.926 [b]	Blue-Black	Metallic–none to 1.3
0.97	5.949	Black	Degenerate semiconductor
1, ZnS_2[a]	5.954	Yellow	Semiconductor
$Zn_yCu_{1-y}Se_2$			
$y = 0$, $CuSe_2$[a]	6.117	Blue	2.30–2.43
0.05	6.126	Blue	1.60–2.45
0.4, 0.9 [b]	6.186, 6.274 [b]	Black	Metallic–none to 1.3
0.95	6.285	Black	Degenerate semiconductor
1, $ZnSe_2$[a]	6.293	Silver	Semiconductor
$Cd_yCu_{1-y}X_2$			
$Cd_{0.04}Cu_{0.96}S_2$	5.809	Purple	1.3–2.0
CdS_2[a]	6.303	Yellow	Semiconductor
$Cd_{0.04}Cu_{0.96}Se_2$	6.138	Blue	
$Cd_{0.06}Cu_{0.94}Se_2$	6.146	Blue	1.3–2.1
$CdSe_2$[a]	6.615	Black	Semiconductor

[a] Ref. (*2*).

[b] Two pyrite phases, intimately mixed.

a 2-h cool to 700°C, and a subsequent quench to room temperature. In the telluride system, reaction of 0.5 Mn/0.5 Cu/2 Te at 65 kbars for 2 h at 800°C, a 4-h cool to 400°C, and a quench to room temperature gave silvery crystals at the sample ends. A Debye–Scherrer powder pattern on these showed some broadness of lines but could be indexed on the basis of the pyrite-type structure. The unit cell dimension indicated the approximate composition $Mn_{0.65}Cu_{0.35}Te_2$.

These $Mn_yCu_{1-y}X_2$ compounds were metallic conductors like CuS_2, but only traces of Mn were required to introduce a localized moment sufficient to destroy the superconductivity observed in unmodified CuS_2. Departures from Curie–Weiss-type behavior were noted at low temperatures in the dilute (in Mn) compositions, and at higher Mn concentrations ferromagnetism was observed (Table III).

$Cu_yFe_{1-y}S_2$

At 65 kbars the system yCu/$(1-y)$Fe/2S gave varied products depending upon the heating cycles used. Thus melt reactions of Cu_2S–FeS–S or Cu–Fe–S in the elemental ratios Cu:Fe:S = 0.33:0.67:2.2, 0.5:0.5:2.2, 0.67:0.33:2.2, or 0.75:0.25:2.2 at 1200–1000°C for 2 h followed by either a direct quench to room temperature or a slow cool to 400°C prior to quenching gave heterogeneous mixtures of products. These comprised CuS_2 and FeS_2 doped with minor amounts of Fe or Cu, respectively, plus intermediate pyrite-type phases (purple-black color) with cell dimensions in the range $a = 5.69$–5.73 Å. Very small amounts of the $Cu_yFe_{1-y}S_2$ pyrites were formed upon quenching from high temperature, but the yield increased in runs involving a slow cool. Ratios of Cu:Fe varying widely from 1:2 to 3:1 thus gave ternaries high in Cu over the relatively narrow compositional limit $Cu_{0.73-0.84}Fe_{0.27-0.16}S_2$ rather than a broad range of solid solutions. This suggests a compound approximating the composition Cu_3FeS_8 (four molecules of MX_2 are present in the pyrite unit cell).

The solid-state reaction at 65 kbars of CuS/FeS/2S

TABLE III

MAGNETIC (Mn,Cu)X_2 PYRITES

Composition y	a, Å	$\chi_{300°K} \times 10^6$ emu/g	p^2_{eff}	No. Spins/Mn (from p^2_{eff})	θ, °K	μ_s	No. Spins/Mn (from μ_s)	T_c °K	Remarks
$Mn_yCu_{1-y}S_2$									
0, CuS_2	5.790	0.3							Temp. independent χ. Supercond., T_s[a] 1.53°K
< 0.01	5.792	0.7	0.28	> 4.4					No ordering trans., wk. interaction < 75°K. No T_s to 1.3°K. Metallic
0.03	5.798	3.3	1.02	4.9					No ordering trans., wk. interaction < 140°K. No T_s to 1.3°K
0.05	5.806	7.7	2.01	5.4	40	0.06	1.2	44	Field dependent χ. $\sigma_s = 3$ emu/g
0.12	5.828	13.1	3.48	4.5	39	0.16	1.3	< 4	Field dependent χ. $\sigma_s = 7$ emu/g
0.15	5.838		7.10	5.9	67	0.30	2.0	62	$\sigma_s = 13$ emu/g. Metallic
0.25	5.869	43	6.81	4.3	139	0.70	2.8	102	$\sigma_s = 31$ emu/g. Metallic
0.28	5.880	44	7.95	4.4	119	0.63	2.3	106	$\sigma_s = 28$ emu/g. Metallic
0.66	6.002	83	19.5	4.5	60	0.34	0.5	108	$\sigma_s = 16$ emu/g. Minor MnS present
0.78	6.039							112	Still ferrimag. Contains MnS
1, MnS_2[b]	6.109	46	37.9	5.2	−598				Antiferro., $T_N = 48$°K
$Mn_{0.56}Cu_{0.44}Se_2$	6.293	37	14.7	4.2	68	0.50	0.9	89	$\sigma_s = 13$ emu/g. Metallic. $\rho_{300°K} = 8 \times 10^{-4}\ \Omega$ cm
$Mn_{0.67}Cu_{0.33}Te_2$	6.838	25	18.8	4.4	3	0.05	0.075	60	$\sigma_s \simeq 1$ emu/g. $\rho_{300°K} = 1 \times 10^{-3}\ \Omega$ cm

[a] Superconducting transition.

[b] M. S. Lin and H. Hacker, *J. Solid State Commun.* 6, 687 (1968).

for 3 h at 800°C followed by a 3-h cool to 400°C and a quench to room temperature again gave the ternary $Cu_{0.75}Fe_{0.25}S_2$ ($a = 5.695$ Å) in microcrystalline form mixed with FeS_2. The reactants 3 CuS/FeS/4S were treated similarly for 14 h at 800°C followed by an 8-h cool to 200°C in an attempt to obtain single crystals. Microcrystalline $Cu_{0.76}Fe_{0.24}S_2$ ($a = 5.702$ Å) was isolated.

Although single crystals were not available, qualitative measurements indicated metallic-type conduction for $Cu_{0.76}Fe_{0.24}S_2$. A broad superconducting transition was observed to start at 1.7°K and was still rising at 1.3°K, the lowest temperature of measurement. Weak, essentially temperature-independent magnetic susceptibility was also observed (Table IV).

$Ni_yFe_{1-y}X_2$

Studies on the Fe–Ni–S ternary have been reported by Clark and Kullerud (*12*). Data taken along the FeS_2–NiS_2-join in the presence of sulfur-rich liquid and vapor showed that this pair of pyrite-type disulfides is stable below 729°C. The solubility of NiS_2 in FeS_2 was limited (less than 10%), whereas about 25% of FeS_2 was soluble in NiS_2. By reactions of 0.5–0.6 Fe/0.5–0.4 Ni/2.2 S at 65 kbars for 1 h at 1000°C, a 3-h cool to 800°C, and a quench to room temperature, this solubility region was extended to give silvery crystals of pyrite-type $Ni_yFe_{1-y}S_2$ having essentially the composition of their respective fusion charges. Columnar, silvery crystals of the ternary selenide $Fe_{0.4}Ni_{0.6}Se_2$ were also prepared under similar high-pressure conditions. These ternary compounds were weakly paramagnetic, metallic conductors (Table IV).

Discussion

To explain and correlate the magnetic and electrical properties of the binary, pyrite-type dichalcogenides of Mn through Zn, a qualitative

TABLE IV

PARAMAGNETIC (M,Fe)X_2 PYRITES

(M,Fe)X_2	a, Å	$\chi \times 10^6$, emu/g		p_{eff}^{2}[a]	θ, °K	Remarks
		4.2°K	300°K			
$Cu_{0.76}Fe_{0.24}S_2$	5.702	1.3	0.9			Weak, essentially temp. ind. χ. Metallic. Superconducting transition, 1.3–1.7°K
$Ni_{0.5}Fe_{0.5}S_2$	5.545	5.8(77°K)	4.7	5.2	−860	Metallic
$Ni_{0.45}Fe_{0.55}S_2$	5.531	14.7	9.1	5.5	−345	Metallic
$Ni_{0.4}Fe_{0.6}S_2$	5.525	8.7	5.1	3.0	−280	Metallic
$Ni_{0.6}Fe_{0.4}Se_2$	5.890	2.4	1.5			Weak, essentially temp. ind. χ. Metallic. $\rho_{298°K} = 5.5 \times 10^{-4}\ \Omega$ cm

[a] Least squares, 77–300°K.

band model emphasizing covalent cation-anion interactions was used (*2*). Features of this model have now been found helpful in understanding the physical properties of some of the ternary compositions described herein, but in other cases this simple band picture does not seem to apply.

Pyrite-type solid solutions formed readily under pressure (Table I) between the diamagnetic semiconductor ZnS_2 (filled d states) and the antiferromagnetic semiconductor MnS_2 (localized d electrons arising from the intraatomic exchange stabilization of the high-spin d^5 configuration). The resultant paramagnetic, semiconductor ternaries, however, cannot be described in terms of the band model used for the binaries. No maximum in the χ vs T curve was observed down to 10°K in $Zn_{0.35}Mn_{0.65}S_2$, for example, and in these ternaries both end members appear to act as mutual diluents with no interaction taking place between the filled d states in ZnS_2 and the localized d electrons in MnS_2. The same situation also appears to pertain for the ternary selenides $M_yMn_{1-y}Se_2$ (M = Zn,Cd). In $Zn_{0.5}Mn_{0.5}Te_2$, however, a small spontaneous moment near 55°K was observed, and some interaction between the d electrons of Zn and Mn may be occurring in this more covalent telluride.

Solid solutions also formed under pressure between ZnX_2 and CdX_2 (X = S, Se), having respectively filled 3d and 4d shells, but single crystals could not be isolated to confirm the expected similarities in properties to those of the end members.

Copper disulfide, with a three-quarters-filled e_g band, is an excellent metallic conductor (superconducting transition at 1.5°K). Although the unit cell dimension is within 3 % of that of semiconductor ZnS_2, complete solid solution between these two binary sulfides was not observed (Table II). Disproportionation into two pyrite-type phases occurred near the midpoint of the series, an effect which may relate to the difference in conductivity types.

In the Cu-rich region of the $Zn_yCu_{1-y}S_2$ compositions, the band model is operative. Metallic properties still prevail, and in addition the unusual effect of an increase in the superconducting transition temperature of CuS_2 by substitution of up to 20 *a/o* of Cu by Zn is observed. Cadmium shows the same properties but to a lesser degree. A basic knowledge of the superconducting mechanism would be required to interpret this effect. The same general properties are also observed in the isotypic selenide ternaries (Table II) except the increase in superconducting transition temperature. At the high Zn end of these series, the compositions behave as degenerate semiconductors. The band model is still operative with Cu introducing holes into the filled e_g band of ZnX_2. Interestingly, only a small amount of Cu ($\leqslant$ 3 *a/o*) is required to change ZnS_2 from yellow to black.

Solid solutions of CuS_2 with FeS_2 offer an interesting contrast to those of CuS_2 with ZnS_2. Both FeS_2 and ZnS_2 are semiconductors with filled t_{2g} levels, but FeS_2 has an empty rather than a filled e_g band. In the $Cu_yFe_{1-y}S_2$ system, each cation had very limited solubility in the reciprocal binary. In addition, only one intermediate composition formed having a modest range of stoichiometry, i.e., $x =$ 0.73–0.84, near Cu_3FeS_8. This phase may result from a favorable electron-to-atom ratio. Although the compositional behavior of this ternary is not explained by the band model, its metallic-type conduction coupled with temperature-independent magnetic susceptibility is compatible therewith. Hull and Hulliger (*7*) observed similar magnetic and electrical properties in the isotypic pyrite-type ternary $Cu_yFe_{1-y}Se_2$ ($y \leqslant 0.75$) in which a broad range of solid solubility is indicated. They observed no superconducting transition in these selenides, in contrast to our result on $Cu_{0.76}Fe_{0.24}S_2$ ($T_s \sim 1.7°K$).

Based upon the experimental data of Table III, the following qualitative conclusions can be drawn about the magnetic properties of the $Mn_yCu_{1-y}S_2$ ternary system. It appears that the Mn retains a local moment when substituted into CuS_2 in very low concentrations ($y < 0.05$). With increasing Mn concentration, the magnetic structure appears to be determined by long-range, ferromagnetic indirect exchange through the CuS_2 conduction electrons. As the Mn concentration is further increased, the antiferromagnetic superexchange interaction, as in MnS_2, becomes increasingly important. The competition between the two types of exchange should lead to a noncolinear spin structure. The net spontaneous moment should first increase with initial Mn concentration and then decrease for larger concentrations. The Weiss constant should also reflect the competition between ferromagnetic and antiferromagnetic exchange interactions; and as can be seen in Table III, the correlation between μ_s and θ is rather good, even for the selenide and telluride.

If the magnetic structure is a canted or noncolinear one with a cant angle that increases with increasing Mn concentration, the spontaneous magnetization will have no simple relationship with Mn concentration except that it will be less than $5\mu B$ per Mn ion and should be considerably less for the higher Mn concentrations. Such behavior is seen in Table III. The value of p_{eff}^2 should scale linearly with Mn concentration as 35 μB^2 per Mn ion. The data of Table III give an average of 28 μB^2 per Mn ion, a value that is not unreasonable considering possible irregularities in stoichiometry.

Of the first-row transition metal pyrite disulfides, only CoS_2 with one e_g electron is a metallic ferromagnet. In terms of the band model used to describe the behavior of the series MnS_2 to ZnS_2, (*2*) it is interesting to compare the properties of the ternary $Ni_{0.5}Fe_{0.5}S_2$, having an average of one e_g electron, to those of CoS_2. This ternary, and adjacent compositions richer in Fe, which required synthesis under pressure to bring about solid solution formation in this intermediate range, are metallic (Table IV), but weak paramagnetism rather than ferromagnetism was observed. These data are compatible with observed properties of the $Ni_yCo_{1-y}S_2$ system (*13*) which exhibits strong antiferromagnetic Ni–Ni interactions as evidenced by large negative Weiss constants (θ) that increase in magnitude with increasing Ni concentration.

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