

Behavior of the AB₂-Type Compounds at High Pressures and High Temperatures

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Behavior of the AB₂ Type Compounds at High Pressures and High Temperatures

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Data on the polymorphic phase transformations of known compounds and new synthetic compounds of the type AB₂ have been compiled and evaluated. All available pressure studies have been included and referenced. Pressure-temperature phase diagrams showing first order solid-solid phase boundaries and/or melting curves showing the best fit to the experimental data are included. For some materials which can be produced only by chemical synthesis techniques at high pressures and high temperatures, reaction-product diagrams have been employed to estimate the region of thermodynamic stability. Crystallographic data of all the known phases of each material have been tabulated and evaluated. This review covers 168 compounds and 332 phases including the room temperature atmospheric pressure phase for each compound when it exists.

Key words: AB₂-type compounds; calibration; critically evaluated data; crystallographic data; experimental melting curves; p, T phase diagrams; polymorphism; solid-solid phase boundaries; high pressure; high temperature.

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1. Introduction

This review of the behavior of the AB₂-type compounds is the third in a series of papers on the subject of material phases at high pressures and high temperatures. The two preceding papers were concerned with the pressure-temperature induced modifications and the phase diagrams for the elements [64] and AB-type compounds [172]. This paper will follow a similar format and will emphasize thermodynamic parameters of the solid-state equilibrium phase boundaries and melting curves. For most of the high pressure phases discussed within the context of this review, crystallographic data are reported. The results of the crystallographic investigations are evaluated and the numerical data are presented in table 2.

In comparing this review to the previous two it will be noted that there are fewer phase diagrams even though more compounds are discussed. The materials studied may be classified in three principal groups in regard to the preparation of the high pressure phases.

1. Materials whose kinetics are relatively rapid not allowing high pressure phases to be retained metastably at atmospheric pressure: In such compounds *P*, *T* phase boundaries are measured in situ by differential thermal analysis or by the detection of discontinuities in certain physical or transport properties such as measurement of compression or electrical resistance respectively. Crystallographic data of high pressure phases must be collected at pressure.

2. Materials whose kinetics are relatively sluggish allowing high pressure-high temperature phases produced to be retained metastably at atmospheric pressure and room temperature: High pressure phases in this category may be produced by static or dynamic pressure experiments. The crystallographic data is collected at room temperature atmospheric pressure conditions. For this type of material it is much more difficult to obtain a phase diagram. Generally, what one attempts to do is to obtain enough points on a reaction product diagram to make a reasonable evaluation of the phase diagram. The limitation is that this procedure has been carried out for very few materials. Another problem is based on the objective of the experiment. Some researchers desire only to produce the new phase and unfortunately are not concerned about its stability field. Another limitation for the reviewer is the limited number of experimental data for good intercomparison.

3. Compounds which hitherto did not exist: This type of compound especially typified by various series such as the rare earth di-antimonides RSb₂: R = Dy, Ho, Er, Tm, Lu, Y), the cubic rare earth iron Laves phases RFe₂ R = Pr, Nd, Sm, Gd, Tb, Ho, Yb, Lu), and numerous di-chalcogenide compounds. For this class of compounds which can only be synthesized at high pressure, the successful synthesis may be due to one of the following factors [15].

(a) The size ratio of the atoms might be unfavorable at 1 bar and the differential compressibilities may be such that at higher pressure the radius ratios will improve. This point of view apparently holds for the rare earth di-tellurides. This series RTe_{2-x} was known for R = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy and Yb. With high pressure synthesis the added

members YTe_{2-x}, HoTe_{2-x}, ErTe_{2-x} were also synthesized. Since Te is more compressible than the RE component, the radius ratio $r(R)/r(Te)$ for the smaller rare earth elements should be comparable to that of the larger rare earth element.

(b) At atmospheric pressure the vapor pressure of one component in the system might be too high at the synthesis temperature, and very high pressure would be necessary to contain it.

(c) Pressure might alter the phase diagram such as occurs in the Ni-C system [247] making possible the synthesis of diamond in a region where diamond and Ni-liquid coexist, which is not part of the normal atmospheric pressure phase (*T*, *x*) diagram. Such phenomena are most likely to occur in *P*, *T*, *x* diagrams.

Since the majority of the compounds discussed in this report fall into the classification (2) and (3) above relatively few phase diagrams are possible. These data range from a single data point to fairly extensive reaction product diagrams. A few of the characteristic reaction product diagrams have been included but those with fewer than 5 data points have been omitted.

The scope of this review includes 168 AB₂-type compounds representing some 332 separate phases. A fairly complete compilation of crystallographic data for these phases has been included in Appendix A (Table 1: (Crystallographic Data for AB₂-Type Compounds)). The pressure (kbar) and temperature (°C) headings of columns 2 and 3, respectively, of the crystallographic tables refer to the pressure-temperature conditions under which the data were analyzed. The temperature and pressure at which a particular phase was prepared or its stability can be found in the text. Those phases for which either the crystal system and/or unit cell dimensions are not known are indicated by an asterisk in the particular column.

Discussions of pressure calibration can be found in previous reports by Decker et al. [91] and Merrill [172]. Table 1 contains a list of the presently accepted best values of the fixed pressure transition points for the recommended pressure calibration standards up to 80 kbar. The recommended SI unit of pressure is the pascal (newton/meter²). Since the bar (10⁵ pascal) has been used almost exclusively in the high pressure literature as the unit of pressure, the units "bar" and "kbar" have been used throughout this report. For ease in converting to GPa (giga pascal) from kbar use the following conversion: 1 GPa = 10 kbar.

TABLE 1. Pressure fixed points

Transition	Pressure (kbar) at RT	Reference
Hg(L-I)	7.57(0 °C)	172
Hg(L-I)	12.55(25 °C)	172
Bi(I-II)	25.5	172
11(II-III)	36.7	172
Ba(I-II)	55.3	172
Bi(III-V)	76.7	172

Table 2

CRYSTALLOGRAPHIC DATA

COMPOUND	Pressure (kbar)	Temperature (°C)	Crystal System	Structure Type	a (Å)	b (Å)	c (Å)	Angle (°)	Z	Space Group	Density (g/cm ³)	Ref.
<u>Antimonides</u>												
LaSb ₂ (I)	N	R	Orthorhombic	LaSb ₂	6.314	6.175	18.56		8	Cmca	7.00	258
CeSb ₂ (I)	N	R	Orthorhombic	LaSb ₂	6.295	6.124	18.21		8	Cmca	7.25	183a
PrSb ₂ (I)	N	R	Orthorhombic	LaSb ₂	6.230	6.063	17.89		8	Cmca	7.56	96
NdSb ₂ (I)	N	R	Orthorhombic	LaSb ₂	6.207	6.098	18.08		8	Cmca	7.53	260
SmSb ₂ (I)	N	R	Orthorhombic	LaSb ₂	6.151	6.051	17.89		8	Cmca	7.83	260
GdSb ₂ (I)	N	R	Orthorhombic	LaSb ₂	6.157	5.986	17.83		8	Cmca	8.10	96
GdSb ₂ (II)	N	R	Orthorhombic	HoSb ₂	3.373	5.986	7.926		2	C222	8.52	66
TbSb ₂ (I)	N	R	Orthorhombic	LaSb ₂	6.123	5.969	17.72		8	Cmca	8.25	96
TbSb ₂ (II)	N	R	Orthorhombic	HoSb ₂	3.359	5.817	7.887		2	C222	8.67	66
DySb ₂ (II)	N	R	Orthorhombic	HoSb ₂	3.350	5.802	7.862		2	C222	8.82	66
HoSb ₂ (II)	N	R	Orthorhombic	HoSb ₂	3.343	5.790	7.842		2	C222	8.94	66
ErSb ₂ (II)	N	R	Orthorhombic	HoSb ₂	3.337	5.780	7.820		2	C222	9.04	66

Table 2

CRYSTALLOGRAPHIC DATA (Continued)

COMPOUND	Pressure (kbar)	Temperature (°C)	Crystal System	Structure Type	a (Å)	b (Å)	c (Å)	Angle (°)	Z	Space Group	Density (g/cm ³)	Ref.
<u>Antimonides (Cont'd)</u>												
TmSb ₂ (II)	N	R	Orthorhombic	HoSb ₂	3.330	5.768	7.807		2	C222	9.13	66
LuSb ₂ (II)	N	R	Orthorhombic	HoSb ₂	3.321	5.752	7.780		2	C222	9.35	66
YSb ₂ (II)	N	R	Orthorhombic	HoSb ₂	3.362	5.823	7.876		2	C222	7.16	66
<u>Arsenides</u>												
CdAs ₂ (I)	N	R	Tetragonal		7.96		4.67		4	I4 ₁ 22	5.8	68
CdAs ₂ (II)			*									77
Mn ₂ As(I)	N	R	Tetragonal	Cu ₂ Sb	3.769		6.278		2	P4/mmm	6.88	93
Mn ₂ As(II)	N	R	Tetragonal	Fe ₂ P	6.363		3.678		3	P6 ₂ m	7.13	126
NiAs ₂ (I)	N	R	Orthorhombic	Anomalous marcasite	4.78	5.78	3.53		2	Pnrm	7.10	273
NiAs ₂ (II)	N	R	Cubic	Pyrite	5.77				4	Pa ₃	7.21	179
SiAs ₂	N	R	Cubic	Pyrite	6.023				4	Pa ₃	5.41	94
ZnAs ₂ (I)	N	R	Monoclinic		9.28	7.68	8.03	102.3	8	P2 ₁ /c	5.1	221
AnAs ₂ (II)			*									77
<u>Borides</u>												
SmB ₂	N	R	Hexagonal	AlB ₂	3.310		4.019		1	P6/mmm	14.04	65

Table 2

CRYSTALLOGRAPHIC DATA (Continued)

COMPOUND	Pressure (kbar)	Temperature (°C)	Crystal System	Structure Type	a (Å)	b (Å)	c (Å)	Angle (°)	Z	Space Group	Density (g/cm ³)	Ref.
<u>Carbides</u>												
TbC ₂ (I)	N	R	Tetragonal	CaC ₂	3.692		6.210		2	I4/mmm	7.18	149
TbC ₂ (II)	N	R	Orthorhombic		13.45	27.28	7.16		64		7.40	149
DyC ₂ (I)	N	R	Tetragonal	CaC ₂	3.666		6.162		2	I4/mmm	7.48	149
DyC ₂ (II)	N	R	Orthorhombic		13.55	26.97	7.10		64		7.64	149
HoC ₂ (I)	N	R	Tetragonal	CaC ₂	3.644		6.139		2	I4/mmm	7.70	149
HoC ₂ (II)	N	R	Orthorhombic		13.07	27.02	7.53		64		7.55	149
ErC ₂ (I)	N	R	Tetragonal	CaC ₂	3.617		6.059		2	I4/mmm	7.96	149
ErC ₂ (II)	N	R	Orthorhombic		13.28	27.24	7.02		64		8.00	149
TmC ₂ (I)	N	R	Tetragonal	CaC ₂	3.602		6.012		2	I4/mmm	8.21	149
TmC ₂ (II)	N	R	Orthorhombic		13.25	26.55	7.36		64		7.92	149
YbC ₂ (I)	N	R	Tetragonal	CaC ₂	3.649		6.133		2	I4/mmm	8.01	149
YbC ₂ (II)			*									149
LuC ₂ (I)	N	R	Tetragonal	CaC ₂	3.563		5.964		2	I4/mmm	8.73	149
LuC ₂ (II)	N	R	Orthorhombic		12.40	27.30	6.87		64		9.09	149
YC ₂ (I)	N	R	Tetragonal	CaC ₂	3.665		6.169		2	I4/mmm	4.53	149
YC ₂ (II)	N	R	Orthorhombic		13.42	27.64	7.13		64		4.54	149

Table 2

CRYSTALLOGRAPHIC DATA (Continued)

COMPOUND	Pressure (kbar)	Temperature (°C)	Crystal System	Structure Type	a (Å)	b (Å)	c (Å)	Angle (°)	Z	Space Group	Density (g/cm ³)	Ref.
<u>Halides</u>												
BaF ₂ (I)	N	R	Cubic	CaF ₂	6.196				4	Fm3m	4.89	95
BaF ₂ (II)	N	R	Orthorhombic	αPbCl ₂	4.039	6.705	7.911		4	Pbnm	5.49	89
BeF ₂ (I)	N	R	Hexagonal	αQuartz	4.74		5.15		3	P3 ₁ 21	2.34	373
BeF ₂ (II)	N	R	Tetragonal	αCristobalite	6.60		6.74		8	P4 ₁ 2 ₁	2.13	273
BeF ₂ (III)	N	R	Cubic	βCristobalite	7.16				8	Fd3m	1.70	273
BeF ₂ (IV)	N	R	Monoclinic	Coesite	6.88	11.92	6.88		16	C2/c	2.55	85
CaF ₂ (I)	N	R	Cubic	CaF ₂	5.462				4	Fm3m	3.18	95
CaF ₂ (II)	N	R	Orthorhombic	αPbCl ₂	3.581	5.959	7.009		4	Pbnm	3.77	219
CdF ₂ (I)	N	R	Cubic	CaF ₂	5.388				4	Fm3m	6.39	95
CdF ₂ (II)	N	R	Orthorhombic	αPbCl ₂	3.368	5.690	6.454		4	Pbnm	8.08	219
CoF ₂ (I)	N	R	Tetragonal	Rutile	4.54		3.32		2	P4 ₂ /mnm	4.70	95
CoF ₂ (II)	N	R	Cubic	CaF ₂	4.91				4	Fm3m	5.44	7
EuF ₂ (I)	N	R	Cubic	CaF ₂	5.808				4	Fm3m	6.49	219
EuF ₂ (II)	N	R	Orthorhombic	αPbCl ₂	3.803	6.324	7.435		4	Pbnm	7.06	219
MnF ₂ (I)	N	R	Tetragonal	Rutile	4.873		3.310		3	P4 ₂ /mnm	3.92	95
MnF ₂ (II)	N	R	Orthorhombic		5.03	5.03	5.28		4		4.62	132
MnF ₂ (III)	N	R	Orthorhombic	αPbCl ₂	3.25	5.54	6.88		4	Pbnm	4.98	132
MnF ₂ (IV)	N	R	Orthorhombic	αPbO ₂	4.96	5.80	5.359		4	Pnab	3.99	6

Table 2

CRYSTALLOGRAPHIC DATA (Continued)

COMPOUND	Pressure (kbar)	Temperature (°C)	Crystal System	Structure Type	a (Å)	b (Å)	c (Å)	Angle (°)	Z	Space Group	Density (g/cm ³)	Ref.
<u>Halides (Cont'd)</u>												
MnF ₂ (V)	40	400	Cubic	CaF ₂	5.192				4	Fm3m	4.41	133
NiF ₂ (I)	N	R	Tetragonal	Rutile	4.51		3.30		2	P4 ₂ /mnm	4.78	78
NiF ₂ (II)	130-150	R	Cubic	CaF ₂	4.84				4	Fm3m	5.66	7
PbF ₂ (I)	N	R	Cubic	CaF ₂	5.939				4	Fm3m	7.77	95
PbF ₂ (II)	N	R	Orthorhombic	αPbCl ₂	3.899	6.442	7.651		4	Pbnm	8.48	219
SrF ₂ (I)	N	R	Cubic	CaF ₂	5.794				4	Fm3m	4.28	95
SrF ₂ (II)	N	R	Orthorhombic	αPbCl ₂	3.804	6.287	7.469		4	Pbnm	4.67	219
ZnF ₂ (I)	N	R	Tetragonal	Rutile	4.711		3.132		2	P4 ₂ /mnm	4.94	95
ZnF ₂ (II)	110	R	Monoclinic	ZrO ₂	5.29	4.96	5.05		4		5.27	131
ZnF ₂ (III)	80	300	Cubic	CaF ₂	4.92				4	Fm3m	5.77	131
ZnF ₂ (IV)	N	R	Orthorhombic	αPbCl ₂	4.683	5.658	5.166		4	Pbnm	5.01	131
FeCl ₂ (I)	N	R	Rhombohedral	CdI ₂	3.598		17.536		3	R3m	3.25	257
FeCl ₂ (II)	6.4	R	Rhombohedral	FeBr ₂	3.585		5.735		1	R3m	3.30	257
HgCl ₂ (I)	N	R	Orthorhombic	αPbCl ₂	5.963	12.735	4.325		4	Pbnm	5.45	95
HgCl ₂ (II)			*		*							19
HgCl ₂ (III)	90	R	*		*							19

Table 2

CRYSTALLOGRAPHIC DATA (Continued)

COMPOUND	Pressure (kbar)	Temperature (°C)	Crystal System	Structure Type	a (Å)	b (Å)	c (Å)	Angle (°)	Z	Space Group	Density (g/cm ³)	Ref.
<u>Halides (Cont'd)</u>												
HgBr ₂ (I)	N	R	Orthorhombic	HgBr ₂ (C24)	6.798	12.445	4.624		4	Bb2 ₁ m	6.08	95
HgBr ₂ (II)	1.7	R	*		*							19
HgBr ₂ (III)	23	R	*		*							19
HgBr ₂ (IV)	38.7	R	*		*							19
ZnBr ₂ (I)	N	R	Rhombohedral	CdCl ₂	3.92		18.73		3	R $\bar{3}$ m	4.50	95
ZnBr ₂ (II)	25	R	Tetragonal		10.83		21.66		32		4.71	171
ZnBr ₂ (III)	80	R	Hexagonal	CdI ₂	3.65		5.73	1	1	P $\bar{3}$ m1	5.65	171
HgI ₂ (I)	N	26	Tetragonal		4.39		12.38		2	P4 ₂ /nmc	6.33	95
HgI ₂ (II)	N	130	Orthorhombic	HgBr ₂ (C24)	7.32	13.76	4.67		4	A2 ₁ mc	6.41	95
HgI ₂ (III)	6	R	*		*							252
HgI ₂ (IV)	5	375	*		*							18
HgI ₂ (V)	75	R	Hexagonal		4.22		23.70		4	P $\bar{3}$ c1	8.25	173
GeI ₂ (I)	N	R	Hexagonal		4.13		6.79		1	P $\bar{3}$ m1	5.37	95
GeI ₂ (II)	20	R	*		*							52

Table 2

CRYSTALLOGRAPHIC DATA (Continued)

COMPOUND	Pressure (kbar)	Temperature (°C)	Crystal System	Structure Type	a (Å)	b (Å)	c (Å)	Angle (°)	Z	Space Group	Density (g/cm ³)	Ref.
<u>Oxides</u>												
Ag ₂ O(I)	N	R	Cubic	Cuprite	4.728				2	Pn3m	7.28	95
Ag ₂ O(II)	115	1400	Hexagonal	CdI ₂	3.072		4.941		1	C3n	9.53	130
CrO ₂	N	R	Tetragonal	Rutile	4.419		2.915		2	P4 ₂ /mnm	4.90	196
H ₂ O(Ih)	N	-162	Hexagonal		4.499		7.324		4	P6 ₃ /mmc	0.93	138
H ₂ O(Ih)	N	10	Hexagonal		4.519		7.362		4	P6 ₃ /mmc	0.917	138
H ₂ O(Ic)	N	-162	Cubic		6.35				8	Fd3m	0.93	138
H ₂ O(Ic)	N	-130	Cubic		6.352				8	Fd3m	0.933	138
H ₂ O(II)	N	-162	Rhombohedral		7.79			113.1		R3	1.18	138
H ₂ O(II)	3	-38	Rhombohedral		7.73			113.0		R3	1.18	138
H ₂ O(III)	2	-22	Tetragonal		6.674		6.97		12	P4 ₁ ² ₁ ²	1.15	138
H ₂ O(IV)	5	-6									1.29	138
H ₂ O(low V)	N	-162	Monoclinic		9.22	7.54	10.35	109.2	28	A2/a	1.23	138
H ₂ O(high V)	5	-50	Monoclinic		9.08	7.42	10.20	109	28	A2/a	1.28	138
H ₂ O(low VI)	N	-162	Orthorhombic		6.27	6.27	5.79		10	Pn3m	1.37	138
H ₂ O(high VI)	8	-50	Tetragonal		6.17		5.70		10	P4 ₂ /nmc	1.38	138
H ₂ O(VII)	25	25	Cubic		3.40				2	Pn3n	1.52	138
H ₂ O(VIII)	N	-162	Tetragonal		4.80		6.99		8	I4 ₁ /amd	1.49	138
H ₂ O(VIII)	25	-50	Tetragonal		4.65		6.79		8	I4 ₁ /amd	1.63	138
H ₂ O(IX)	N	-162	Tetragonal		6.73		6.83		12	P4 ₁ ² ₁ ²	1.16	138

Table 2

CRYSTALLOGRAPHIC DATA (Continued)

COMPOUND	Pressure (kbar)	Temperature (°C)	Crystal System	Structure Type	a (Å)	b (Å)	c (Å)	Angle (°)	Z	Space Group	Density (g/cm ³)	Ref.
<u>Oxides (Cont'd)</u>												
GeO ₂ (I)	N	R	Hexagonal	αQuartz	4.972		5.638		3	P3 ₁ 21	4.28	95
GeO ₂ (II)	N	R	Tetragonal	Rutile	4.395		2.850		2	P4 ₂ /mnm	6.28	95
GeO ₂ (III)	N	R	Orthorhombic	αPbO ₂					4	Pnab		215
GeO ₂ (IV)	N	R	Hexagonal	Fe ₂ N	2.729		4.312		1	P312 or P31m		
HfO ₂ (I)	N	R	Monoclinic		5.25	5.18	5.12	99.2	4	P2 ₁ /c	10.3	95
HfO ₂ (II)	N	1920	Tetragonal		5.14		5.25		4	I4 ₁ /amd	10.03	26
HfO ₂ (III)	N	R	Orthorhombic		5.056	5.006	5.224		4	P2 ₁ 2 ₁ 2 ₁	10.58	26
HfO ₂ (IV)	N	2750	Cubic	CaF ₂	5.30				4	Fm3m	9.39	95
MnO ₂ (I)	N	R	Tetragonal	Rutile	4.386		2.856		2	P4 ₂ /mnm	5.27	95
MnO ₂ (II)	N	R	Orthorhombic	αPbCl ₂	4.46	9.32	2.85		4	Pbnm	4.87	95
MnO ₂ (III)	140	R	*	*	*							79
MnO ₂ (IV)	N	R	Cubic		9.868				32		4.81	79
PbO ₂ (I)	N	R	Tetragonal	Rutile	4.955		3.332		2	P4 ₂ /mnm	9.56	95
PbO ₂ (II)	N	R	Orthorhombic	αPbO ₂	5.497	5.951	4.948		4	Pnab	9.81	95
PbO ₂ (III)	N	R	Cubic	CaF ₂	5.349				4	Fm3m	10.34	249
PtO ₂ (I)	N	R	Hexagonal		3.08		4.19		1	P6/mmm	11.1	95
PtO ₂ (II)	N	R	Orthorhombic	Disordered Rutile	4.487	4.536	3.137		2	Pnn2 or Pnnm	11.8	223
RhO ₂	N	R	Tetragonal	Rutile	4.486		3.088		2	P4 ₂ /mnm	7.16	223

Table 2

CRYSTALLOGRAPHIC DATA (Continued)

COMPOUND	Pressure (kbar)	Temperature (°C)	Crystal System	Structure Type	a (Å)	b (Å)	c (Å)	Angle (°)	Z	Space Group	Density (g/cm ³)	Ref.
Oxides (Cont'd)												
SiO ₂ (I)	N	R	Rhombohedral	αQuartz	4.913		5.394		3	P3 ₁ 21	2.65	219
SiO ₂ (II)	N	R	Hexagonal	βQuartz	5.01		5.47		3	P6 ₂ 22	2.52	95
SiO ₂ (IIIa)	N	R	Orthorhombic	αTridymite	9.88	17.1	16.3		64		2.32	95
SiO ₂ (IIIb)	N	R	Hexagonal	βTridymite	5.03		8.22		4		2.21	95
SiO ₂ (IVa)	N	R	Tetragonal	αCristobalite	4.97		6.92		4	P4 ₁ 2 ₁	2.34	219
SiO ₂ (IVb)	N	R	Cubic	βCristobalite	7.13				8	Fd3m	2.20	95
SiO ₂ (V)	N	R	Monoclinic	Coesite	7.17	7.17	12.38	120	16	C2/c	2.90	199
SiO ₂ (VI)	N	R	Tetragonal	Stishovite	4.179		2.665		2	P4 ₂ /mnm	4.29	242
SiO ₂ (VII)	N	R	Tetragonal	Keatite	7.456		8.604		12	P4 ₁ 2 ₁ 2	4.39	219
SiO ₂ (VIII)	N	R	Orthorhombic	αPbO ₂	4.30	4.70	4.50		4	Pnab	4.27	109
SiO ₂ (IX)	N	R	Hexagonal	Fe ₂ N	2.561		4.112		1	P312 or P31m	4.27	160
SnO ₂ (I)	N	R	Tetragonal	Rutile	4.67		3.14		2	P4 ₂ /mnm	7.26	95
SnO ₂ (II)	N	R	Orthorhombic	αPbO ₂	4.719	5.714	5.223		4	Pban	7.11	248
SnO ₂ (III)	250	R	Cubic	CaF ₂	4.925				4	Fm3m	8.38	159
TeO ₂ (I)	N	R	Orthorhombic	Brookite	5.59	11.75	5.50		8	Pbca	5.83	95
TeO ₂ (II)	N	R	Tetragonal	Rutile	4.79		3.77		2	P4 ₂ /mnm	6.09	95
TeO ₂ (III)	N	R	Tetragonal	Paratellurite	4.810		7.613		4	P4 ₁ 2 ₁ 2	6.01	95
TeO ₂ (IV)	10.1	R	Orthorhombic		4.728	4.823	7.581		4	P2 ₁ 2 ₁ 2 ₁	6.13	272

Table 2

CRYSTALLOGRAPHIC DATA (Continued)

COMPOUND	Pressure (kbar)	Temperature (°C)	Crystal System	Structure Type	a (Å)	b (Å)	c (Å)	Angle (°)	Z	Space Group	Density (g/cm ³)	Ref.
<u>Oxides (Cont'd)</u>												
TiO ₂ (I)	N	R	Tetragonal	Anatase	3.73		9.37		4	I4 ₁ /amd	4.05	95
TiO ₂ (II)	N	R	Orthorhombic	Brookite	5.456	9.132	5.143		8	Pbca	4.12	95
TiO ₂ (III)	N	R	Tetragonal	Rutile	4.589		2.954		2	P4 ₂ /nnm	4.24	95
TiO ₂ (IV)	N	R	Orthorhombic	αPbO ₂	4.532	5.513	4.896		4	Pnab	4.34	155
TiO ₂ (V)	N	R	Cubic		4.455				4	Fm3n	6.14	156
TiO ₂ (VI)	250	R	Hexagonal		9.22		5.685		16		5.07	159
ZrO ₂ (I)	N	R	Monoclinic		5.164	5.255	5.297	99.2	4	P2 ₁ /c	5.77	95
ZrO ₂ (II)	N	R	Tetragonal		5.071		5.27		4	P4 ₂ /nmc	6.03	95
ZrO ₂ (III)	35	800	Orthorhombic		5.110	5.076	5.267		4	P2 ₁ ² ₁ ² ₁	5.99	27
ZrO ₂ (IV)	N	2330	Cubic		5.256				4		5.64	95
Zn(OH) ₂ (I)	N	R	Orthorhombic	C31	8.53	5.15	4.92		4	P2 ₁ ² ₁ ² ₁	3.05	95
Zn(OH) ₂ (II)	N	R	Orthorhombic		6.73	7.33	8.47		8		3.16	11
Zn(OH) ₂ (III)	N	R	Hexagonal		3.11		7.80		3		2.40	11
Zn(OH) ₂ (IV)	N	R	*		*							11
Zn(OH) ₂ (V)	N	R	Hexagonal	CdI ₂	3.194		4.714		1	C3m	3.96	11

Table 2

CRYSTALLOGRAPHIC DATA (Continued)

COMPOUND	Pressure (kbar)	Temperature (°C)	Crystal System	Structure Type	a (Å)	b (Å)	c (Å)	Angle (°)	Z	Space Group	Density (g/cm ³)	Ref.
<u>Phosphides</u>												
GeP ₂	N	R	Cubic		5.619				4		5.04	188
NbP _{1.70}	N	R	Tetragonal	PbFC1	3.339		7.649		2		5.65	126a
SiP ₂	N	R	Cubic	Pyrite	5.7045				4	Pa3	3.22	94
VP _{1.75}	N	R	Tetragonal	PbFC1	6.3237		7.2671		8	P4m2	4.81	126a
ZnP ₂ (I)	N	R	Monoclinic		8.85	7.29	7.56	102	8	P2 ₁ /c	3.55	95
ZnP ₂ (II)	N	R	Tetragonal		5.08		18.59		8	P4 ₁ 2 ₁ 2 or P4 ₃ 2 ₁ 2		
ZnP ₂ (III)	N	R	Cubic		5.322				4		3.55	189
CoP ₂	N	R	Monoclinic	Arsenopyrite	5.610	5.591	5.64	116.8	4	P2 ₁ /c	5.09	93

Table 2

CRYSTALLOGRAPHIC DATA (Continued)

COMPOUND	Pressure (kbar)	Temperature (°C)	Crystal System	Structure Type	a (Å)	b (Å)	c (Å)	Angle (°)	Z	Space Group	Density (g / cm ³)	Ref.
<u>Germanides and Silicides</u>												
BaGe ₂ (I)	N	R	Orthorhombic		9.05	6.83	11.65		8	Pnma or Pna2 ₁	5.21	102
BaGe ₂ (II)	N	R	Tetragonal	αThSi ₂	4.755		14.73		4	I4 ₁ /amd	5.63	102
BaSi ₂ (I)	N	R	Orthorhombic		8.92	6.75	11.57		8	Pnma or Pna2 ₁	3.69	95
BaSi ₂ (II)	N	R	Rhombohedral		4.047		5.330		1	P $\bar{3}$ m1	4.25	100
CaSi ₂ (I)	N	R	Rhombohedral		3.855		30.6		6	R $\bar{3}$ m	2.46	169
CaSi ₂ (II)	N	R	Tetragonal	αThSi ₂	4.283		13.54		4	I4 ₁ /amd	2.47	169
EuSi ₂	N	R	Tetragonal	αThSi ₂	4.304		13.65		4	I4 ₁ /amd	5.47	101
SrSi ₂ (I)	N	R	Cubic		6.535				4		3.42	95
SrSi ₂ (II)	N	R	Tetragonal	αThSi ₂	4.430		13.83		4	I4 ₁ /amd	3.51	101

Table 2

CRYSTALLOGRAPHIC DATA (Continued)

COMPOUND	Pressure (kbar)	Temperature (°C)	Crystal System	Structure Type	a (Å)	b (Å)	c (Å)	Angle (°)	Z	Space Group	Density (g/cm ³)	Ref.
<u>Sulfides</u>												
Ag ₂ S(I)	N	R	Monoclinic	Acanthite	7.87	6.91	4.23	99.6	4	P2 ₁ /n	7.25	95
Ag ₂ S(II)	N	189	Cubic	Argentite	4.870				2	Im $\bar{3}$ m	7.12	95
Ag ₂ S(III)	N	600	Cubic	High Argentite	6.269				4		6.68	95
Ag ₂ S(IV)	20	R	*	*	*							76
BiS ₂	N	R	*	<u>d-values</u>								
				3.11(100)								
				2.97(60)								
				2.62(65)								
				1.88(70)								
				1.81(70)								
				1.504(60)								
CS ₂ (I)	N	-114	Orthorhombic		6.455	5.596	8.939		4	Cmca	1.566	10
CS ₂ (I)	N	-214	Orthorhombic		6.215	5.404	9.280		4	Cmca	1.623	10
CS ₂ (I)	20	R	Orthorhombic		6.16	5.38	8.53		4	Cmca	1.79	263
Cu ₂ S(I)	N	R	Orthorhombic		13.491	27.323	11.881		96	Ab2m	5.79	95
Cu ₂ S(II)	N	152	Hexagonal	Chalcocite	3.961		6.722		2	P6 ₃ /mmc	5.74	95
Cu ₂ S(III)	N	456	Cubic		5.725				4	F . .	5.63	95
Cu _{1.96} S(I)	N	R	Tetragonal		3.996		11.287		4	P4 ₃ ² ₁ 2	5.86	95
Cu _{1.96} S(II)	N	220	Cubic		~ 5.6							76
CuS ₂	N	R	Cubic	Pyrite	5.796				4	Pa $\bar{3}$	4.44	32

Table 2

CRYSTALLOGRAPHIC DATA (Continued)

COMPOUND	Pressure (kbar)	Temperature (°C)	Crystal System	Structure Type	a (Å)	b (Å)	c (Å)	Angle (°)	Z	Space Group	Density (g/cm ³)	Ref.
<u>Sulfides (Cont'd)</u>												
GeS ₂ (I)	N	R	Orthorhombic	C44	11.66	22.34	6.86		24	Fdd2	3.03	95
GeS ₂ (II)	N	R	Tetragonal		5.480		9.143		4	I4̄2d	3.30	198
H ₂ S(I)	N	-120	*		*							240
H ₂ S(II)	N	-160	*		*							240
H ₂ S(III)	N	-175	*		*							240
H ₂ S(IV)	6	-140	*		*							240
H ₂ S(V)	8	-120	*		*							9
IrS ₂ (I)	N	R	Orthorhombic	IrSe ₂	19.78	5.624	3.565		8	Pnam	8.59	121
IrS ₂ (II)	N	R	Cubic	Pyrite	5.68				4	Pa3	9.22	179
MoS ₂ (I)	N	R	Rhombohedral	3R	3.15		12.30		2	P6 ₃ /mmc	4.98	95
MoS ₂ (II)	20	R	*		*							54
NbS ₂ (I)	N	R	Hexagonal	2H	3.31		11.89		2	P6 ₃ /mmc	4.62	95
NbS ₂ (II)	N	R	Rhombohedral	CdCl ₂	3.33		17.80		3	R3̄m	4.57	95
NbS ₂ (III)	N	R	Hexagonal	4H-TaSe ₂	3.33		23.8		4	P6 ₃ /mmc	4.56	151
PdS ₂ (I)	N	R	Orthorhombic		5.54	7.53	5.46		4	Pbca	4.95	95
PdS ₂ (II)	N	R	Orthorhombic		5.51	7.16	5.56		4		5.16	180
SiS ₂ (I)	N	R	Orthorhombic		5.60	9.55	5.53		4	Ibam	2.06	95
SiS ₂ (II)	N	R	Tetragonal		5.420		8.718		4	I4̄2d	2.37	198

Table 2

CRYSTALLOGRAPHIC DATA (Continued)

COMPOUND	Pressure (kbar)	Temperature (°C)	Crystal System	Structure Type	a (Å)	b (Å)	c (Å)	Angle (°)	Z	Space Group	Density (g/cm ³)	Ref.
<u>Sulfides (Cont'd)</u>												
SrS ₂	N	R	Tetragonal	CuAl ₂	6.095		7.616		4	I4/mcm	3.56	139
ZnS ₂	N	R	Cubic	Pyrite	5.954				4	Pa3	5.56	33
<u>Rare Earth Sulfides</u>												
LaS ₂ (I)	N	R	Tetragonal		8.23		8.13		8	P4/nmm	4.90	31
LaS ₂ (II)	N	R	Cubic		8.20				8		4.90	104
CeS ₂ (I)	N	R	Tetragonal		8.115		8.115		8		5.08	31
CeS ₂ (II)	N	R	Cubic		8.12				8		5.67	105
FrS ₂	N	R	Cubic		8.08				8		5.16	104
NdS ₂	N	R	Cubic		8.011				8		5.38	104
GdS ₂ (I)	N	R	Tetragonal	LaS ₂	7.796		7.196		8		6.72	107
GdS ₂ (II)	N	R	Cubic		7.882				8		6.96	262
TbS ₂ (I)	N	R	Tetragonal	LaS ₂	7.754		7.864		8		6.27	262
TbS ₂ (II)	N	R	Cubic		7.845				8		6.14	262

Table 2

CRYSTALLOGRAPHIC DATA (Continued)

COMPOUND	Pressure (kbar)	Temperature (°C)	Crystal System	Structure Type	a (Å)	b (Å)	c (Å)	Angle (°)	Z	Space Group	Density (g/cm ³)	Ref.
Rare Earth Sulfides (Cont'd)												
DyS ₂ (I)	N	R	Tetragonal	LaS ₂	7.696		7.861		8		6.47	104
DyS ₂ (II)	N	R	Cubic		7.809				8		6.32	262
YS ₂ (I)	N	R	Tetragonal	LaS ₂	7.720		7.846		8		4.348	104
YS ₂ (II)	N	R	Cubic		7.797				8		4.289	262
HoS ₂ (I)	N	R	Tetragonal	LaS ₂	7.649		7.839		8		6.645	202
HoS ₂ (II)	N	R	Cubic		7.784				8		6.45	262
ErS ₂ (I)	N	R	Tetragonal	LaS ₂	7.636		7.811		8		6.75	202
ErS ₂ (II)	N	R	Cubic		7.745				8		6.62	262
TmS ₂ (I)	N	R	Tetragonal	LaS ₂	7.610		7.784		8		6.86	262
TmS ₂ (II)	N	R	Cubic		7.745				8		6.66	262
YbS ₂ (I)	N	R	Tetragonal	LaS ₂	7.578		7.767		8		7.06	262
YbS ₂ (II)	N	R	Cubic		7.722				8		6.84	262
LuS ₂ (I)	N	R	Tetragonal	LaS ₂	7.560		7.751		8		7.17	262
LuS ₂ (II)	N	R	Cubic		7.687				8		6.99	262

Table 2

CRYSTALLOGRAPHIC DATA (Continued)

COMPOUND	Pressure (kbar)	Temperature (°C)	Crystal System	Structure Type	a (Å)	b (Å)	c (Å)	Angle (°)	Z	Space Group	Density (g/cm ³)	Ref.
<u>Selenides</u>												
Ag ₂ Se(I)	N	R	Orthorhombic		4.344	7.111	7.790		4	P222	8.14	82
Ag ₂ Se(II)	N	173	Cubic		4.993				2	Im3m	7.86	82
BiSe ₂	N	R	*		*							229
CdSe ₂	N	R	Cubic	Pyrite	6.615				4	Pa3	6.20	33
Cu ₂ Se(I)	N	R	Tetragonal		8.12		11.17		16		7.09	95
Cu ₂ Se(II)	N	170	Cubic	Sphalerite	5.852				4	F43m	6.83	95
Cu ₂ Se(III)	32	R	*		*							76
CuSe ₂ (I)	N	R	Orthorhombic	Marcasite	5.017	6.198	3.741		2	Pnmm	6.32	95
CuSe ₂ (II)	N	R	Cubic	Pyrite	6.123				4	Pa3	6.41	33
FeSe ₂ (I)	N	R	Orthorhombic	Marcasite	4.799	5.714	3.557		2	Pnmm	7.28	95
FeSe ₂ (II)	N	R	Cubic	Pyrite	5.783				4	Pa3	7.34	32
MoSe ₂	N	R	Rhombohedral	3R	3.292		19.392		3		6.94	253
ZnSe ₂	N	R	Cubic	Pyrite	6.615				4	Pa3	5.124	33
NdSe ₂ (I)	N	R	Hexagonal	2H	3.45		12.54		2	P6 ₃ /mmc	7.75	95
NdSe ₂ (II)	N	R	Rhombohedral	3R	3.45		18.88		3	R3m	7.73	95
NdSe ₂ (III)	N	R	Hexagonal	4H _p	3.349		25.188		4	P6 ₃ /mmc	7.77	95
NdSe ₂ (IV)	N	R	Hexagonal	4H _o	3.46		24.8		4	P6 ₃ /mmc	7.80	98

Table 2

CRYSTALLOGRAPHIC DATA (Continued)

COMPOUND	Pressure (kbar)	Temperature (°C)	Crystal System	Structure Type	a (Å)	b (Å)	c (Å)	Angle (°)	Z	Space Group	Density (g/cm ³)	Ref.
<u>Selenides (Cont'd)</u>												
SmSe ₂	N	R	Tetragonal	LaTe ₂	4.110		8.275		2	P4/nmm	7.32	13
TmSe ₂	N	R	Tetragonal	LaTe ₂	3.961		8.188		2	P4/nmm	8.45	261
YbSe ₂	N	R	Tetragonal	LaTe ₂	3.970		8.151		2	P4/nmm	8.56	261
LuSe ₂	N	R	Tetragonal	LaTe ₂	3.939		8.147		2	P4/nmm	8.86	261
<u>Tellurides</u>												
Ag ₂ Te(I)	N	R	Monoclinic		8.13	4.48	8.09	112.9	4	P2 ₁ /n	8.40	14
Ag ₂ Te(II)	N	155	Cubic	Disordered(fcc)	6.64				4	F ₄₃₂	7.79	95
Ag ₂ Te(III)	24	R	Tetragonal		8.92		6.09		8		9.41	14
Ag ₂ Te(IV)	40	R	Tetragonal		8.68		6.09		8		9.91	14
Ag ₂ Te(V)	30	300	*		*							14
Ag ₂ Te(VI)	N	825	Cubic		5.29				2	I ₄₃₂	7.70	95
AuTe ₂ (I)	N	R	Monoclinic	Calaverite	7.18	4.40	5.07	90.0	2	C2/m	9.38	273
AuTe ₂ (II)	N	R	Orthorhombic	Krennerite	16.51	8.80	4.45		8	Pma	9.29	273
AuTe ₂ (III)	20	R	Tetragonal	Two possible unit cells	5.25 6.13		5.48 3.72		2 2		9.94 10.74	2 2
CuTe ₂	N	R	Cubic	Pyrite	6.60				4	Pa ₃	7.36	34

Table 2

CRYSTALLOGRAPHIC DATA (Continued)

COMPOUND	Pressure (kbar)	Temperature (°C)	Crystal System	Structure Type	a (Å)	b (Å)	c (Å)	Angle (°)	Z	Space Group	Density (g/cm ³)	Ref.
<u>Tellurides (Cont'd)</u>												
CoTe ₂ (I)	N	R	Orthorhombic	Marcasite	5.319	6.319	3.897		2	Pnmm	7.96	95
CoTe ₂ (II)	N	R	Hexagonal	CdI ₂	3.784		5.403		1	P $\bar{3}$ m1	7.74	95
CoTe ₂ (III)	N	R	Cubic	6.310					4	Pa3	8.31	32
FeTe ₂ (I)	N	R	Orthorhombic	Marcasite	5.340	6.26	3.849		2	Pnmm	7.98	95
FeTe ₂ (II)	N	R	Cubic	Pyrite	6.292				4	Pa3	8.29	32
NiTe ₂ (I)	N	R	Hexagonal	CdI ₂	3.385		5.255		2	P $\bar{3}$ m1	7.73	95
NiTe ₂ (II)	N	R	Cubic	Pyrite	6.374				4	Pa3	8.05	34
<u>Rare Earth Tellurides</u>												
YTe _{2-x}	N	R	Tetragonal	Cu ₂ Sb	4.291		8.912		2	P4/nmm	6.96 (6.19) ^a	60
HoTe _{2-x}	N	R	Tetragonal	Cu ₂ Sb	4.264		8.872		2	P4/nmm	8.65 (7.86) ^a	60
ErTe _{2-x}	N	R	Tetragonal	Cu ₂ Sb	4.248		8.865		2	P4/nmm	8.77 (7.98) ^a	60
TmTe _{2-x}	N	R	Tetragonal	Cu ₂ Sb	4.240		8.831		2	P4/nmm	8.87 (8.07) ^a	60
LuTe _{2-x}	N	R	Tetragonal	Cu ₂ Sb	4.322		8.807		2	P4/nmm	9.10 (8.29) ^a	60
() ^a - calculated for x = 0.3												

Table 2

CRYSTALLOGRAPHIC DATA (Continued)

COMPOUND	Pressure (kbar)	Temperature (°C)	Crystal System	Structure Type	a (Å)	b (Å)	c (Å)	Angle (°)	Z	Space Group	Density (g/cm ³)	Ref.
Mixed Cation Transition Metal Chalcogenides												
Cd _{0.04} Cu _{0.96} S ₂	N	R	Cubic	Pyrite	5.089				4	Pa3	4.24	34
Cd _{0.35} Mn _{0.65} S ₂	N	R	Cubic	Pyrite	6.055				4	Pa3	4.16	34
Cr _{0.39} Co _{0.61} S ₂	N	R	Cubic	Pyrite	5.558				4	Pa3	4.66	92a
Cu _{0.76} Fe _{0.24} S ₂	N	R	Cubic	Pyrite	5.702				4	Pa3	4.51	34
Mn _{0.25} Cu _{0.75} S ₂	N	R	Cubic	Pyrite	5.869				4	Pa3	4.12	34
Ni _{0.50} Fe _{0.50} S ₂	N	R	Cubic	Pyrite	5.545				4	Pa3	4.69	34
Zn _{0.50} Cd _{0.50} S ₂	N	R	Cubic	Pyrite	6.125				4	Pa3	4.42	34
Zn _{0.20} Cu _{0.80} S ₂	N	R	Cubic	Pyrite	5.825				4	Pa3	4.62	34
Zn _{0.35} Mn _{0.65} S ₂	N	R	Cubic	Pyrite	6.055				4	Pa3	4.16	34
Cd _{0.06} Cu _{0.94} Se ₂	N	R	Cubic	Pyrite	6.146				4	Pa3	6.42	34
Cd _{0.48} Mn _{0.52} Se ₂	N	R	Cubic	Pyrite	6.511				4	Pa3	5.71	34

Table 2

CRYSTALLOGRAPHIC DATA (Continued)

COMPOUND	Pressure (kbar)	Temperature (°C)	Crystal System	Structure Type	a (Å)	b (Å)	c (Å)	Angle (°)	Z	Space Group	Density (g/cm ³)	Ref.
Mixed Cation Transition Metal Chalcogenides (Cont'd)												
Mn _{0.56} Cu _{0.44} Se ₂	N	R	Cubic	Pyrite	6.293				4	Pa3	5.77	34
Ni _{0.60} Fe _{0.40} Se ₂	N	R	Cubic	Pyrite	5.890				4	Pa3	7.01	34
Zn _{0.32} Cd _{0.68} Se ₂	N	R	Cubic	Pyrite	6.510				4	Pa3	6.15	34
Zn _{0.40} Cu _{0.60} Se ₂	N	R	Cubic	Pyrite	6.186				4	Pa3	6.23	34
Zn _{0.50} Mn _{0.50} Se ₂	N	R	Cubic	Pyrite	6.360				4	Pa3	5.63	34
Mn _{0.67} Cu _{0.33} Te ₂	N	R	Cubic	Pyrite	6.838				4	Pa3	6.50	34
Zn _{0.50} Mn _{0.50} Te ₂	N	R	Cubic	Pyrite	6.874				4	Pa3	6.45	34

Table 2

CRYSTALLOGRAPHIC DATA (Continued)

COMPOUND	Pressure (kbar)	Temperature (°C)	Crystal System	Structure Type	a (Å)	b (Å)	c (Å)	Angle (°)	Z	Space Group	Density (g/cm ³)	Ref.
<u>Alloy and Intermetallic Compounds</u>												
AuAl ₂	N	R	Cubic	CaF ₂	6.00				4	Fm3m	7.12	95
AuGa ₂	N	R	Cubic	CaF ₂	6.075				4	Fm3m	9.97	95
AuIn ₂ (I)	N	R	Cubic	CaF ₂	6.515				4	Fm3m	10.25	95
AuIn ₂ (II)	N	R	*		*							211
LaCo ₂	N	R	Cubic	MgCu ₂	7.449				8	Fd3m	8.25	204
LaOs ₂ (I)	N	R	Cubic	MgCu ₂	7.743				8	Fd3m	14.86	63
LaOs ₂ (II)	N	R	Hexagonal	MgZn ₂	5.419		9.083		4	P6 ₃ /mnc	14.92	63
CeOs ₂ (I)	N	R	Cubic	MgCu ₂	7.593				8	Fd3m	15.80	63
CeOs ₂ (II)	N	R	Hexagonal	MgZn ₂	5.355		8.816		4	P6 ₃ /mnc	15.78	63
SmRu ₂ (I)	N	R	Cubic	MgCu ₂	7.577				8	Fd3m	10.81	62
SmRu ₂ (II)	N	R	Hexagonal	MgAn ₂	5.298		8.939		4	P6 ₃ /mnc	10.81	62
NdRu ₂ (I)	N	R	Cubic	MgCu ₂	7.612				8	Fd3m	10.47	62
NdRu ₂ (II)	N	R	Hexagonal	MgZn ₂	5.323		9.004		4	P6 ₃ /mnc	10.44	62
MnAu ₂ (I)	N	R	Tetragonal	CaC ₂	3.363		8.592		2	I4/mnm	15.33	95
MnAu ₂ (II)	N	R	Tetragonal		*							62

Table 2

CRYSTALLOGRAPHIC DATA (Continued)

COMPOUND	Pressure (kbar)	Temperature (°C)	Crystal System	Structure Type	a (Å)	b (Å)	c (Å)	Angle (°)	Z	Space Group	Density (g/cm ³)	Ref.
<u>Iron Compounds</u>												
PrFe ₂	N	R	Cubic	MgCu ₂	7.467				8	Fd3m	8.06	61
NdFe ₂	N	R	Cubic	MgCu ₂	7.452				8	Fd3m	8.21	61
SmFe ₂	N	R	Cubic	MgCu ₂	7.415				8	Fd3m	8.54	61
GdFe ₂	N	R	Cubic	MgCu ₂	7.394				8	Fd3m	8.84	61
TbFe ₂	N	R	Cubic	MgCu ₂	7.354				8	Fd3m	9.07	61
HoFe ₂	N	R	Cubic	MgCu ₂	7.303				8	Fd3m	9.43	61
YbFe ₂	N	R	Cubic	MgCu ₂	7.239				8	Fd3m	9.97	61
LuFe ₂	N	R	Cubic	MgCu ₂	7.229				8	Fd3m	10.08	61
<u>Magnesium Compounds</u>												
Mg ₂ Si(I)	N	R	Cubic	CaF ₂	6.404				4	Fm3m	1.94	95
Mg ₂ Si(II)	N	R	Orthorhombic	Ni ₂ Si	4.48	5.94	8.22		4	Pnmb	2.34	219
Mg ₂ Ge(I)	N	R	Cubic	CaF ₂	6.378				4	Fm3m	3.10	95
Mg ₂ Ge(II)	N	R	Orthorhombic	Ni ₂ Si	4.57	5.96	8.50		4	Pnmb	3.47	219

Table 2

CRYSTALLOGRAPHIC DATA (Continued)

COMPOUND	Pressure (kbar)	Temperature (°C)	Crystal System	Structure Type	a (Å)	b (Å)	c (Å)	Angle (°)	Z	Space Group	Density (g/cm ³)	Ref.
Magnesium Compounds (Cont'd)												
Mg ₂ Sn(I)	N	R	Cubic	CaF ₂	6.765				4	Fm3m	3.60	95
Mg ₂ Sn(II)	N	R	Orthorhombic	Ni ₂ Si	4.82	6.25	9.14		4	Pmnb	4.03	219
Manganese Compounds												
SrMn ₂ (I)	N	R	Cubic	MgCu ₂	7.79				8	Fd3m	7.31	153a
SrMn ₂ (II)	N	R	Hexagonal	MgZn ₂	5.501		8.968		4	P6 ₃ /mmc	7.35	97a
GdMn ₂ (I)	N	R	Cubic	MgCu ₂	7.724				8	Fd3m	7.70	264a
GdMn ₂ (II)	N	R	Hexagonal	MgZn ₂	5.447		8.893		4	P6 ₃ /mmc	7.76	97a
TbMn ₂ (I)	N	R	Cubic	MgCu ₂	7.620				8	Fd3m	8.07	264a
TbMn ₂ (II)	N	R	Hexagonal	MgZn ₂	5.390		8.786		4	P6 ₃ /mmc	8.07	97a
DyMn ₂ (I)	N	R	Cubic	MgCu ₂	7.573				8	Fd3m	8.33	264a
DyMn ₂ (II)	N	R	Hexagonal	MgZn ₂	5.356		8.744		4	P6 ₃ /mmc	8.32	97a
HoMn ₂ (I)	N	R	Cubic	MgCu ₂	7.507				8	Fd3m	8.63	264a
HoMn ₂ (II)	N	R	Hexagonal	MgZn ₂	5.316		8.672		4	P6 ₃ /mmc	8.59	97a
YBMn ₂	N	R	Hexagonal	MgZn ₂	5.233		8.561		4	P6 ₃ /mmc	9.25	97a
YMn ₂ (I)	N	R	Cubic	MgCu ₂	7.678				8	Fd3m	5.83	95
YMn ₂ (II)	N	R	Hexagonal	MgZn ₂	5.404		8.848		4	P6 ₃ /mmc	5.87	97a

2. Antimonides

In a series of rare earth compounds RX_2 where the rare earth element R is varied, it is common to find that compounds can be prepared for only a certain range of the elements of the rare earth series. Prior to synthesis studies conducted at high pressure, for example, rare earth diantimonides were known for the lighter rare earths. The first rare earth diantimonide discovered was $LaSb_2$ by Vogel and Klose [258]. In 1966, Olcese [183a] reported $CeSb_2$ and in 1967 $YbSb_2$, $NdSb_2$, and $SmSb_2$ were reported by Wang and Steinfink [260]. Wang and Steinfink [260] attempted the synthesis of the antimonides of Gd, Dy, Ho, and Er but were unsuccessful. By single crystal x-ray diffraction techniques $LaSb_2$, $CeSb_2$, $NdSb_2$, and $SmSb_2$ were found to have an orthorhombic structure [26] designated the $LaSb_2$ -type. In this structure it was found that the Sb-Sb bond distance was short, suggesting that beyond a certain limit the structure would become unstable.

High pressure high temperature synthesis studies by Eatough and Hall [96] have extended the $LaSb_2$ -type structure to include $PrSb_2$, $GdSb_2$ and $TbSb_2$. The synthesis of these diantimonides takes place at approximately 35 kbar and 1200 °C to 1500 °C. A new high pressure phase referred to as the $HoSb_2$ -type was discovered by Eatough and Hall [96] which extends the diantimonide series to include the heavier rare earth elements. Synthesis of the $HoSb_2$ -type rare earth diantimonide has been reported for $GdSb_2$, $TbSb_2$, $DySb_2$, $HoSb_2$, $TmSb_2$, $LuSb_2$ and YSb_2 . The range of pressure and temperature for the synthesis of this series is 40–60

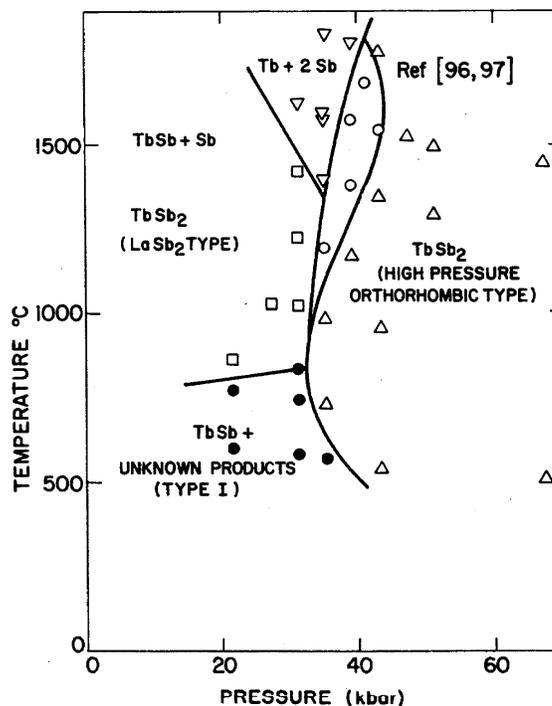


FIGURE 2. Reaction product diagram for $Tb + 2Sb$.

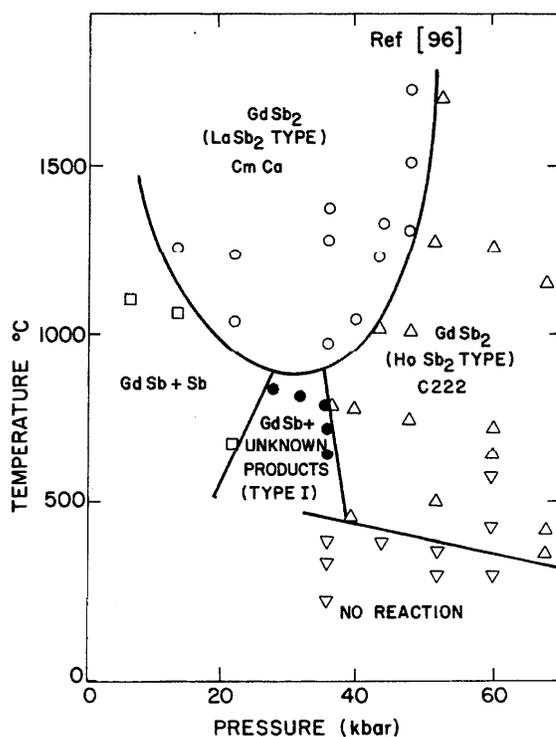


FIGURE 1. Reaction product diagram for $Gd + 2Sb$.

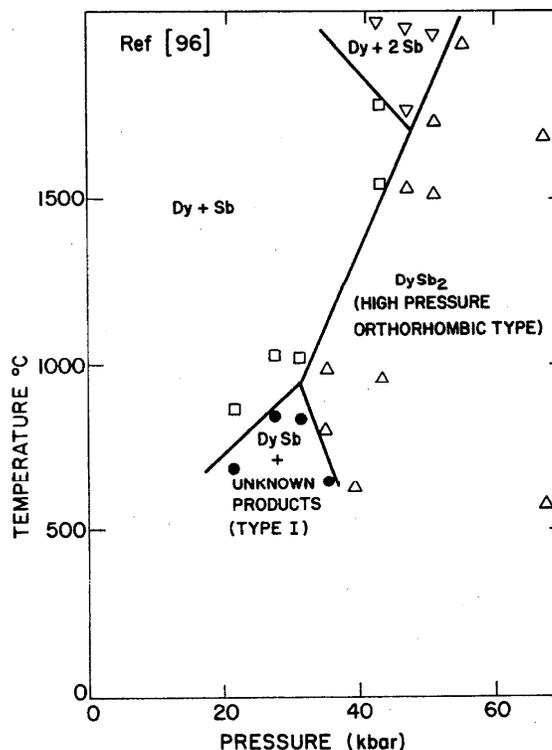


FIGURE 3. Reaction product diagram for $Dy + 2Sb$.

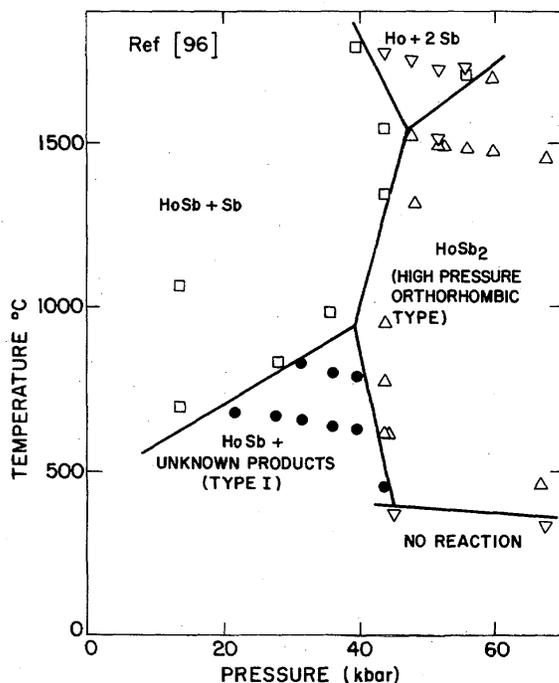


FIGURE 4. Reaction product diagram for Ho + 2Sb.

kbar and 500–1500 °C. The approximate stability fields of these phases are shown in figures 1 through 4. The crystallographic data on the HoSb₂-type structure is based on powder diffraction studies. Eatough and Hall [96] indexed it as orthorhombic and Johnson [127] proposed the structure whose space group is C222.

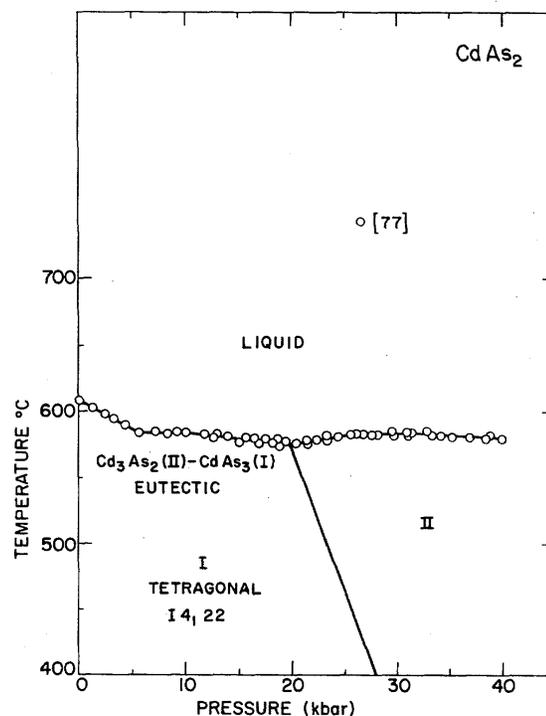
The HoSb₂-type structure ($Z = 2$) is made up of hexagonal layers of Ho and Sb atoms with a layer stacking sequence Ho-Sb(1)-Sb(2). These layers are stacked in such a way that the expected hexagonal symmetry is reduced to orthorhombic (pseudohexagonal). The Sb atoms of one layer are lined up over the midpoint of the lines connecting the hexagonal array of Ho atoms in an adjacent layer. If the Sb atoms were situated over the center of alternate triangles of Ho, the CdI₂-type structure would be obtained. The HoSb₂-type structure results in a 10 percent increase in Sb-Sb bond length over the LaSb₂-type structure but a 20 percent decrease in R-R bond length.

The crystallographic unit cell dimensions of the high pressure HoSb₂-type compounds prepared by Eatough and Hall [96,97] have been recalculated by Cannon [66] using the structure proposed by Johnson [108] and the original x-ray data of Eatough and Hall [96,97]. The calculations of Cannon [66] confirm that Johnson's HoSb₂-type structure fits the experimental data much better than that proposed by Eatough and Hall [96,97] and is probably correct.

3. Arsenides

3.1. CdAs₂

The CdAs₂ phase diagram (fig. 5) has been investigated by Clark and Pistorius [77]. CdAs₂ was prepared by direct

FIGURE 5. Phase diagram for CdAs₂.

synthesis of stoichiometric quantities of the elements in evacuated quartz ampoules which were heated to 850 °C and cooled slowly. Measurements of the resistance (four wire method) of a sliver of CdAs₂ as a function of pressure in a Bridgman anvil device reveal a phase transition at approximately 60 kbar at 25 °C. The resistance dropped by a factor of 30 in separate experiments. At higher temperatures the transition was observed by means of DTA (using Chromel-Alumel thermocouples) at constant temperature while the pressure was cycled through the transition. The CdAs₂(I)-CdAs₂(II) phase boundary has an approximate slope of -10 K/kbar. It intersects the melting curve at 19.8 kbar and 579.5 °C.

The melting curve of CdAs₂ was studied to 45 kbar. The melting of CdAs₂(I) yielded sharp and strong DTA signals. The melting curve drops with pressure with an initial slope of -1.6 K/kbar from 621 °C at atmospheric pressure to the triple point at 19.8 kbar and 579.5 °C. Melting of the denser CdAs₂(II) phase initially rises with pressure with a slope of 1.8 K/kbar, passes through a broad maximum at ~ 30 kbar and 591.5 °C and then falls with increasing pressure. Upon decreasing pressure the CdAs₂(II) melting curve could be followed to ~ 5 kbar below the triple point. No metastable extension of the CdAs₂(I) melting curve could be observed on the up cycle.

The DTA signals of the CdAs₂(I) melting curve exhibit interesting metastable behavior on the decreasing temperature cycle. The phase boundary initially drops with pressure from 610 °C at atmospheric pressure to 589.5 °C, at 5.9 kbar, where the slope of the curve sharply changes from -4.2 K/kbar to 10.4 K/kbar. The initial part of the curve is attrib-

ed to the Cd_3As_2 - CdAs_2 eutectic at 610°C at atmospheric pressure (56 at. percent As). The abrupt change in the slope at 589.5°C and 8.4 kbar is due to the $\text{CdAs}_2(\text{I})$ -As eutectic.

Each phase boundary in this work was based on several separate runs. For melting curve determinations, the results are believed to be within ± 0.5 kbar and ± 0.5 K. In the determinations of the $\text{CdAs}_2(\text{I})$ - $\text{CdAs}_2(\text{II})$ boundary the accuracy of the pressures are estimated to be within ± 2 kbar. Experimental corrections described by Pistorius and Clark (194) and Richter and Pistorius [201] have been applied.

$\text{CdAs}_2(\text{I})$ is tetragonal, space group $I4_122 - D_{10}^4$ with Cd atoms in 4(b) positions and As atoms in 8(f) positions. The structure of $\text{CdAs}_2(\text{II})$ has not been determined.

3.2. Mn_2As

Both Cr_2As and Mn_2As have been prepared at atmospheric pressure with the Cu_2Sb -type structure. In addition, Cr_2As was synthesized with the Fe-P-type structure by quenching from high temperature. The Fe_2P -type phase of Mn_2As could not be prepared in this manner but was synthesized from samples subjected to simultaneous high temperature and high pressure [126].

The Cu_2Sb -type of Mn_2As was prepared by slowly heating stoichiometric mixtures of the elements to 700°C in evacuated silica tubes. The samples were afterwards held at 1100°C for a few hours and then quenched in water. The Fe_2P -type modification of Mn_2As formed at a temperature of 1200°C and pressure of 65 kbar held for 2 hours. The product was allowed to cool to 1100°C and quenched to room temperature under pressure.

The crystallography of Fe_2P -type Mn_2As was determined by standard single crystal techniques. The hexagonal unit cell dimensions are $a = 6.363 \text{ \AA}$, $c = 3.678 \text{ \AA}$, $z = 3$ and $\rho_c = 7.13 \text{ g/cm}^3$. The space group is $P\bar{6}2m$. $\text{Mn}_2\text{As}(\text{II})$ is antiferromagnetic with a Neel temperature of $50 \pm 10 \text{ K}$.

3.3. NiAs_2

The pyrite-type crystal structure is exhibited by a wide variety of compounds, many of which are of interest because of their varied electrical and magnetic properties. The pyrite structure (space group $\text{Pa}\bar{3}$) is in general a densely packed arrangement and therefore tends to be formed when synthesis is attempted between the transition metals and groups Va or VIa elements at high pressure.

Nickel diarsenide crystallizes in an anomalous marcasite structure which differs from the normal marcasite by small angular distortions about the cation octahedra. Since the marcasite structure has a less dense packing arrangement, a transformation to the pyrite structure should be induced by the action of high pressure.

The pyrite phase of NiAs_2 was prepared by Munson [179] from the reaction of a mixture of powdered Ni and As in a 1:1.22 mole ratio. The sample in the high pressure chamber was held at a temperature of 1400°C and a pressure of 65 kbar for a period of one half hour. The presence of the pyrite-type NiAs_2 was confirmed by powder x-ray examination. Cubic NiAs_2 is gray with unit cell dimension $a = 5.77 \text{ \AA}$ and densities $\rho_c = 7.15 \text{ g/cm}^3$ and $\rho_c = 7.21 \text{ g/cm}^3$.

3.4. SiAs_2

Silicon diarsenide has been synthesized with the pyrite-type crystal structure, space group $\text{Pa}\bar{3}$. This is the only known phase of SiAs_2 and requires elevated pressure for its preparation. Successful syntheses were carried out [94] from 45 and 65 kbar at 1300°C with reaction times of one hour, then cooled slowly to 1100°C at the rate 50°C/h quenched. The crystal structure and space group of SiAs_2 were verified by single crystal techniques.

Silicon atoms are located in special positions 4(a), while arsenic atoms occupy eightfold position 8(c) for which $x = 0.384$. The unit cell data are $a = 6.023 \text{ \AA}$, $z = 4$, and $\rho_c = 5.41 \text{ g/cm}^3$. SiAs_2 , along with SiP_2 , GeAs_2 , GeP_2 , unusual due to the fact that they are the only examples of pyrite type compounds of nonmetallic elements. They are also unusual in that silicon is octahedrally coordinated. The unit cell dimension of PtAs_2 and PdAs_2 ($a = 5.965 \text{ \AA}$ and 5.985 \AA , respectively) are very close to that of SiAs_2 and the bond distances of SiAs_2 are within experimental error equal to their counterparts in PtAs_2 and PdAs_2 .

3.5. ZnAs_2

The phase diagram of ZnAs_2 has been studied by Clark and Pistorius [77] in a piston-cylinder device by means of differential thermal analysis using chromel-alumel thermocouples. The ZnAs_2 samples were prepared by direct synthesis of stoichiometric quantities of the elements.

The melting curve of $\text{ZnAs}_2(\text{I})$ is nearly linear with a slope of -4.7 K/kbar and terminates at the triple point which is located at 19 kbar, 679°C . The melting curve of

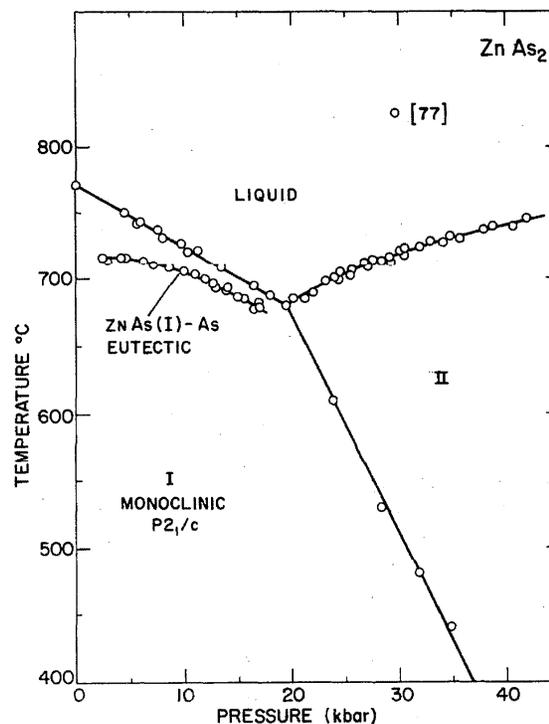


FIGURE 6. Phase diagram for ZnAs_2 .

ZnAs₂(II) rises with pressure with an initial slope of + 4.0 K/kbar and considerable curvature. The ZnAs₂(II) melting curve was determined up to 45 kbar. The experimental uncertainties of the melting point determinations are estimated to be ± 0.5 kbar and ± 0.5 K. (fig. 6).

Resistance measurements in a Bridgman anvil device at 25 °C showed no polymorphic transitions up to an estimated pressure of 110 kbar. At higher temperatures the ZnAs₂(I)-ZnAs₂(II) phase boundary was observed by means of DTA at constant temperature while the pressure was cycled across the transition. Using this technique the phase boundary was traced from the triple point (679 °C) down to 450 °C. A linear extrapolation of this phase boundary intersects the room temperature pressure axis at approximately 70 kbar. The failure to detect the transition by electrical resistance methods may be due to poor kinetics associated with this transition at room temperature.

Along the ZnAs₂(I) melting curve metastable behavior is observed not identical to that noted in CdAs₂(I). The metastable phase boundary is due to the ZnAs₂(I)-As eutectic. No ZnAs₂(II)-As eutectic was observed at pressures above the triple point. However, signals due to the ZnAs₂(I)-As reappeared upon lowering the pressure past the triple point.

ZnAs₂(I) is primitive monoclinic, space group P2₁/c (C_{2h}⁵). The structure of ZnAs₂(II) has not been determined.

4. Borides

4.1. SmB₂

Rare earth borides of the composition RB₂ have been prepared at atmospheric pressure for all the heavier rare earth members from gadolinium through lutetium including yttrium and scandium. These diborides are isomorphous and have the AlB₂-type structure (C32). This structure is hexagonal (P6/mmm) and consists of alternating layers of metal and boron atoms. Previous attempts to synthesize the diborides with rare earth component larger than gadolinium have been unsuccessful. Cannon et al. [65] suggested that since the compressibilities of the lanthanides are greater than that of boron, then pressure would tend to make the lanthanides behave like the smaller ones.

Of the seven lanthanid elements which are larger than gadolinium, simultaneous high pressure-high temperature conditions were successful in synthesizing one new diboride phase, SmB₂. SmB₂ was prepared from a stoichiometric ratio of the elements reacted at 65 kbar and 1140–1240 °C for 75 minutes. The AlB₂-type cell of SmB₂ has the dimensions $a = 3.310$ Å and $c = 4.019$ Å. Intensity data from the powder x-ray diffraction patterns indicate that the samarium atom in SmB₂ is flattened in the *c*-crystallographic direction.

5. Carbides

The heavy rare earth dicarbides have been shown to exist in both cubic and hexagonal modifications and have been studied extensively [46,237,238]. In LuC₂ a transformation was observed to proceed from cubic to a low order symmetry which was tentatively identified as tetragonal with an unusually large unit cell. High pressure studies of the lanthanum dicarbides were carried out in an attempt to

synthesize this lattice type. The normal stable modifier of the lanthanum dicarbides of (Tb, Dy, Ho, Er, Tm, Yb, Lu, Y:C₂) is body centered tetragonal CaC₂-type, space group I4/mmm.

Dicarbides of the rare earth metals were prepared by arc melting the elements together in a helium atmosphere. Synthesis of the possible high pressure phases were carried out in the pressure range 15–34 kbar and temperature range 850 and 1200 °C and time intervals of 5 to 30 minutes [176a]. While all of the dicarbides listed above could be made successfully by high pressure techniques, three of them, LuC₂, YbC₂ and TmC₂ were prepared by high temperature annealing techniques. The powder diffraction patterns of the high pressure phase were complex containing very many lines. The data were fit to the orthorhombic crystal system with a large unit cell size ($Z = 64$). There is no sequential trend of the density with increasing atomic number of the rare earth metal which casts some doubt on the orthorhombic crystal system.

6. Germanides

6.1. BaGe₂

At atmospheric pressure BaGe₂ crystallizes in an orthorhombic Pnma (or Pna2₁) structure made of isolated Ge₄ tetrahedra. At a pressure of 40 kbar and temperature of 1000 °C BaGe₂(I) transforms to a tetragonal modification of the α -ThSi₂-type which can be retained metastably at atmospheric pressure [102]. BaGe₂(II) is isomorphous with the high pressure phase of CaSi₂ and SrSi₂, while the high pressure form of BaSi₂ is rhombohedral (space group P3m1). In the presence of air and moisture BaGe₃(II) decomposes and when heated to 350 °C it reverts to the atmospheric pressure form. The decrease in volume in the GaGe₂-BaGe₂(II) transition amounts to 8 percent. The tetragonal unit cell dimensions of BaGe₂(II) are $a = 4.755$ Å, $c = 14.73$ Å with $Z = 4$ and $\rho_c = 5.63$ g/cm³.

In the BaSi₂(I)-BaSi₂(II) transformation the isolated Si₄ tetrahedra change so as to appear to lie in wavy Si-layers. Actually the Si₄ tetrahedra in BaSi₂(II) may be described as corner shared in a two dimensional array involving only the silicon atoms in the basal plane of the tetrahedra. In contrast to BaSi₂(II) the Si-layers in BaGe₂(II) are made up to planar Si₄ groups in which the adjacent layers are rotated by 90°. The coordination polyhedra in BaSi₂(II) (rhombohedral) and BaGe₂(II) (tetragonal) are very similar. The number of nearest neighbors in each is 9 (6 barium and 3 silicon or germanium, respectively).

7. Metal Halides

7.1. BaF₂

Under the influence of pressure the fluorite phase of BaF₂ transforms irreversibly to the α -PbCl₂-type structure. The transformation was accomplished at 400 °C and 30 kbar [212]. No further transitions were observed up to 150 kbar. The evidence for the α -PbCl₂ phase is based upon 1 bar x-ray data. In an investigation of pressure-induced color centers in BaF₂, Minomura and Drickamer [174] observed that the light was cut off in a 5 kbar range near 30 kbar. This was

interpreted to be due to the occurrence of a polymorphic phase transitions. Samara [212] measured the capacitance of BaF_2 up to 30 kbar and detected a sharp discontinuity at 26.8 kbar in a liquid pressure medium. There is a significant hysteresis associated with this transition. For example, it has the value of 18 kbar at 22 °C and 12.5 kbar at 150 °C. The average slope dP/dT is 2.6×10^{-2} kbar/K.

The transition in BaF_2 is from the cubic-fluorite structure to the orthorhombic $\alpha\text{-PbCl}_2$ phase. Both phases contain four molecules per unit cell. In the $\alpha\text{-PbCl}_2$ structure, each Ba has nine fluorine neighbors, but the distances are not all equal. The volume change at the transition is about 11 percent. The orthorhombic unit cell data is $a = 4.035 \text{ \AA}$, $b = 6.676 \text{ \AA}$, $c = 7.879 \text{ \AA}$ and $Z = 4$.

In the work of Dandekar and Jamieson [89] the $\alpha\text{-PbCl}_2$ phase formed from the simultaneous action of pressure and temperature was retained at 1 bar. The experiments of Samara [212] from room temperature up to 150 °C indicate the transition is readily reversible.

7.2. BeF_2

The normal phase of BeF_2 which is isomorphous with quartz, transforms to a new modification having the coesite-type structure at a pressure of 22 kbar and a temperature of 450 °C [85].

7.3. CaF_2

The high pressure transformation of CaF_2 from the cubic fluorite structure to the $\alpha\text{-PbCl}_2$ -type structure has been reported by Seifert [186] and German et al. [94a]. Seifert [186] reported the $\text{CaF}_2(\text{I})\text{-CaF}_2(\text{II})$ transformation in the region above 100 kbar in a piston-anvil apparatus while German et al. [94a] employing shock techniques reported a pressure of 100 kbar at $-150 \text{ }^\circ\text{C}$. This transformation represents an increase in coordination number from eight to nine and an increase in density of 18.6 percent, based upon atmospheric pressure volumes of both phases.

7.4. CoF_2

CoF_2 undergoes a polymorphic modification from the rutile to a distorted fluorite structure [7]. The transition is sluggish and occurs in the range 130–150 kbar at room temperature. The distortion of the fluorite structure is manifested by a small deviation from the cubic by a c/a ratio less than 1.01. The superlattice reflections (200), (311) and (310) appear in the powder x-ray diffraction pattern.

7.5. EuF_2

EuF_2 which crystallizes in the CaF_2 -type crystal structure at atmospheric pressure and room temperature, transforms to the orthorhombic PbCl_2 -type structure at 114 kbar and 400 °C. The high pressure modification, $\text{EuF}_2(\text{II})$, has unit cell dimensions $a = 3.803 \text{ \AA}$, $b = 6.324 \text{ \AA}$ and $c = 7.435 \text{ \AA}$. The PbCl_2 -type phase of $\text{EuF}_2(\text{II})$ can be retained metastably at atmospheric pressure undergoing an overall volume reduction of 10 percent with respect to the normal volume of $\text{EuF}_2(\text{I})$ [219].

7.6. MnF_2

X-ray investigation of MnF_2 at high pressure and high temperature reveal at least five polymorphic modifications. On the basis of simple crystal chemistry considerations, the ratio of atomic radii is close to the upper limit of stability for the rutile structure and a polymorphic modification of MnF_2 with coordination number eight would be a reasonable assumption [6]. In the early pressure experiments on MnF_2 , a new phase was discovered which is an analogue of the $\alpha\text{-PbO}_2$ -type crystal structure also having the coordination number six (6). This investigation was carried out with quenched phases which made it possible to study the product only after its removal from the pressure chamber. In later studies [133], which permitted x-ray examination of the sample while under pressure, it was shown that the $\alpha\text{-PbO}_2$ -type modification of MnF_2 did not form in the high pressure region on the loading cycle, but was a metastable phase which was formed on the unloading cycle and retained at atmospheric pressure. In another experiment it was shown that the $\alpha\text{-PbO}_2$ -type phase of MnF_2 used as the starting material transforms to the rutile-type structure at approximately 30 kbar and room temperature [133].

In experiments in which rutile-type MnF_2 is used as the starting material three additional polymorphic modifications are observed at high pressure and temperature. NaCl was used as an internal pressure calibrant with an accuracy of ± 2 kbar for pressure up to 40 kbar and ± 3 kbar for pressure greater than 40 kbar. The error in temperature calibration was stated to be less than or equal to ± 5 percent. At room temperature and $P = 33 \pm 4$ kbar $\text{MnF}_2(\text{I})$ [256] transforms to a distorted fluorite phase $\text{MnF}_2(\text{II})$ which is stable up to approximately 150 kbar. At 70 kbar $\text{MnF}_2(\text{II})$ was initially indexed as tetragonal with unit cell parameters $a = 5.18 \text{ \AA}$, $c = 5.01 \text{ \AA}$, $Z = 4$ and $\rho_c = 4.59 \text{ g/cm}^3$. Subsequent studies have never revealed the presence of additional x-ray reflections consistent with an orthorhombic unit cell with $a = b = 5.03 \text{ \AA}$, $c = 5.28 \text{ \AA}$, $Z = 4$ and $\rho_c = 4.62 \text{ g/cm}^3$ [132]. It is assumed that this structure is the same as orthorhombic ZrO_2 [132] which is also a high pressure polymorph with very nearly the same lattice constants. The observed h, k, l of this ZrO_2 phase are consistent with space group $\text{P}2_12_12_1$, however, only powder data are available and the structure has not been solved.

At approximately 150 kbar and room temperature another polymorph, $\text{MnF}_2(\text{III})$ is formed with an increase in density of 6 percent at the $\text{MnF}_2(\text{II})\text{-MnF}_2(\text{III})$ phase boundary [133]. This new phase can be indexed on the assumption of an orthorhombic unit cell with $a = 3.25 \text{ \AA}$, $b = 5.54 \text{ \AA}$, $c = 6.88 \text{ \AA}$, $Z = 4$ and $\rho_c = 4.98 \text{ g/cm}^3$. The h, k, l reflections observed in the x-ray diffraction pattern of $\text{MnF}_2(\text{III})$ are in agreement with space group Pmnb (D_{2h}^{16}) and may be isomorphous with the orthorhombic PbCl_2 structure. A similar transition is observed in CaF_2 , CdF_2 , SrF_2 and BaF_2 at high pressure and room temperature.

The investigation of the polymorphism of MnF_2 was extended to the temperature range up to 400 °C and to a maximum pressure of 80 kbar [133]. In this study a cubic modification $\text{MnF}_2(\text{V})$ with the fluorite structure was confirmed by simultaneous x-ray techniques. At 40 kbar and

400 °C the lattice constant of MnF₂(V) is $a = 5.192 \text{ \AA}$.

The pressure-temperature phase diagram of MnF₂ has a triple point with coordinates at 33 kbar and 210 °C. These values are obtained from an extrapolation of the phase boundaries due to the experimental difficulty of obtaining data in the region of the triple point. In order to determine where the MnF₂(I)-MnF₂(II) phase boundary intersects the temperature axis, a differential thermal analysis of MnF₂ was made at 1 bar. At $710 \pm 5 \text{ °C}$ a thermal arrest was detected which apparently corresponds to the rutile-fluorite phase boundary [133].

7.7. NiF₂

NiF₂ undergoes a polymorphic modification from the rutile to a distorted fluorite structure [7]. The transition temperature decreased from 600 °C at 20 kbar to 375 °C at kbar. The distortion of the fluorite structure is manifested by a small deviation from the cubic by a c/a ratio of less than 1.01. The superlattice reflections (020), (311) and (310) appear in the powder x-ray diffraction pattern.

7.8. PbF₂

In addition to the eight-coordinated cubic fluorite phase, PbF₂ can also exist at normal conditions in the orthorhombic PbCl₂-type structure which is a quasi nine coordinated phase. In both phases there are four atoms per unit cell, but there is a 10 percent increase in density when going from the cubic to the orthorhombic symmetry. The orthorhombic phase should be the stable one at high pressure and such a transition was reported by Schmidt and Vedam [216] to occur at 4.8 kbar at 295 °C. Samara [213] reported that the transition exhibits strong kinetic effects and initiated between 3.93 and 4.75 kbar at room temperature depending on how long the pressure is held constant in the vicinity of the transition. The 3.93 kbar point was determined by increasing the pressure and holding it constant.

Kessler et al. [144] reported the Raman spectrum of PbF₂(II) and confirmed that the structure is orthorhombic PbCl₂-type. Unit cell data [216] are $a = 3.897 \text{ \AA}$, $b = 6.441 \text{ \AA}$, $c = 7.648 \text{ \AA}$, $Z = 4$ and $\rho_c = 8.48 \text{ g/cm}^3$. From neutron powder diffraction data Boldrini and Loopstra [43] determined the atomic positions and the crystal structure of PbF₂(II).

7.9. SrF₂

SrF₂ crystallizes in the fluorite-type structure at normal temperature and pressure. Seifert [219] reported a pressure induced transformation in SrF₂ above 55 kbar to the orthorhombic α -PbCl₂-type structure.

7.10. ZnF₂

In some respects the phase diagram of ZnF₂ is similar to that of MnF₂. One notable correspondence is the existence of ZnF₂(II) which is isostructural with α -PbO₂ [129] and is only found in samples quenched from the high pressure, high temperature conditions $P = 50 \text{ kbar}$ and $T = 1500 \text{ °C}$. This phase reverts to ZnF₂(I) after 2 hours at 400 °C. The transition ZnF₂(I)-ZnF₂(II) is accompanied by a color change from

white to dark gray.

In an x-ray diffraction investigation of ZnF₂ at room temperature up to 130 kbar, a reversible phase transition was observed to take place from the rutile-type structure to a nonclinc phase ZnF₂(III) which is apparently isostructural with the monoclinic phase of ZrO₂. The transition started at 70–80 kbar and was complete at 110 kbar. The unit cell parameters are $a = 5.29 \text{ \AA}$, $b = 4.196 \text{ \AA}$, $c = 5.05 \text{ \AA}$, $\beta = 79.4^\circ$ and $Z = 4$ [131].

Further x-ray investigations at 300 °C in the region 70–80 kbar revealed a cubic phase, ZnF₂(IV) which has the CaF₂-type structure [131]. In all the experiments in which rutile was formed, the quenched product after removal from the pressure cell always showed a mixture of the rutile and α -PbO₂ type phases. Kabalkina and Popova [129] suggested that the α -PbO₂ phase represents an intermediate structure during the transformation from fluorite to rutile.

7.11. FeCl₂

Anhydrous ferrous chloride FeCl₂ exhibits a number of interesting properties and has been extensively studied. It simulates an anisotropic ferromagnet and has a tricritical point. It is quite compressible, has low sound velocities and a strong magnon-phonon coupling. As a result of magnetic studies at high pressure a phase transition has been detected at 5.8 kbar and room temperature [257].

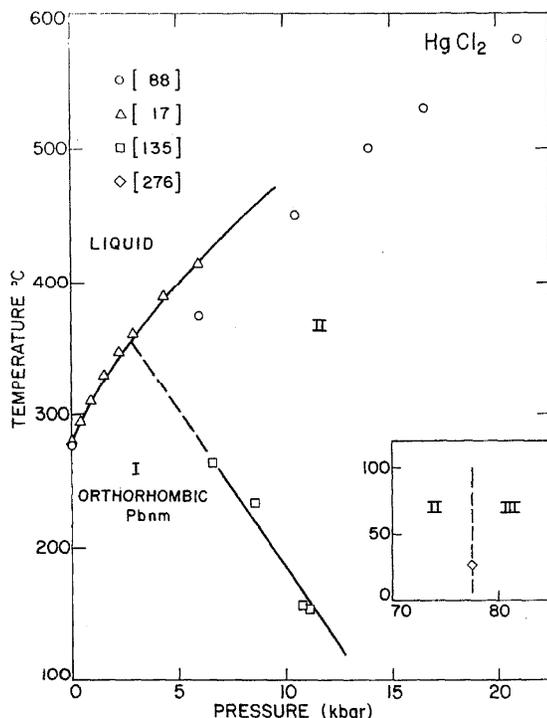
The low pressure form of FeCl₂ is rhombohedral and crystallizes in a close packed layer structure in which hexagonal sheets of iron ions are separated by two layers of chlorine ions. The halide ions have nearly a cubic close packing arrangement. The symmetry is primitive rhombohedral, space group R3m and has unit cell data $a = 3.598 \text{ \AA}$, $c = 17.536 \text{ \AA}$, $Z = 6$ and $\rho = 3.25 \text{ g/cm}^3$ indexed on the more convenient triple hexagonal unit cell. The stacking sequence for the close packed chlorine ions is BAC...BAC with the repeat distance encompassing six chlorine planes along the "c" axis.

At approximately 5.8 kbars the phase transition involved a crystallographic change in which the new c axis $c^* = 1/3c$. The sequence of the chlorine layers is CB...CB in the high pressure phase which has the FeBr₂ structure, space group P3m.

7.12. HgCl₂

Bridgman (51,52) detected a solid-solid transition in HgCl₂ at room temperature near 20 kbar. The HgCl₂(I)-HgCl₂(II) phase boundary was measured more precisely by Kalliomaki and Meisalo [135] from 270 °C at 6 kbar at 140 °C at 11 kbar.

The melting curve of HgCl₂ was originally determined up to 22 kbar by Darnell and McCollum [88] in a piston cylinder apparatus. A second melting determination by Bardoll and Tokheide [18] up to a maximum pressure of 6 kbar resulted in a melting temperature 12 percent higher than found by Darnell and McCollum [88]. The discrepancy is probably accounted for by a difference in pressure calibration. The cell of Darnell and McCollum used solid pressure transmitting medium while Bardoll and Tokheide used argon. Due to the inherent greater accuracy, the latter method

FIGURE 7. Phase diagram for HgCl_2 .

is preferred.

The melting curve determinations [17,88] of HgCl_2 gave no evidence for the existence of a triple point. Extrapolating the $\text{HgCl}_2(\text{I})$ - $\text{HgCl}_2(\text{II})$ phase boundary to the melting curve indicates there should be a triple point at about 348 °C and 2.6 kbar.

A second solid-solid phase transition at room temperature was found at about 90 kbar by Zahner and Drickamer [276]. This boundary was followed to about 300 °C by Kalliomaki and Meisalo [135] where the transition pressure had decreased to 45 kbar. The phase diagram of HgCl_2 is presented in figure 7.

7.13. SrCl_2

Strontium dichloride which crystallizes in the cubic ($\text{Fm}3\text{m}$) symmetry when prepared at 1 bar pressure undergoes a transformation to an orthorhombic structure under the influence of high pressure and high temperature [55]. Since BaCl_2 has a high temperature cubic phase isostructural with $\text{SrCl}_2(\text{I})$ and a low temperature orthorhombic (Pbnm) phase, it was proposed $\text{SrCl}_2(\text{II})$ might have a similar orthorhombic phase at high pressure.

The synthesis of $\text{SrCl}_2(\text{II})$ was carried out in the region of 58 kbar and 800 °C. X-ray diffraction analysis confirms that the high pressure phase is orthorhombic with unit cell dimensions $a = 7.548 \text{ \AA}$, $b = 8.979 \text{ \AA}$ and $c = 4.411 \text{ \AA}$. The space group was determined to be Pnam on the basis of powder diffraction data. These data suggest that $\text{SrCl}_2(\text{II})$ may be isostructural with orthorhombic BaCl_2 since their space groups represent the same symmetry with different axial designations. The calculated density of $\text{SrCl}_2(\text{II})$ is 3.52

g/cm^3 compared to 3.10 g/cm^3 for the cubic phase, an increase of approximately 12 percent. There is no experimental data on the $\text{SrCl}_2(\text{I})$ - $\text{SrCl}_2(\text{II})$ phase boundary.

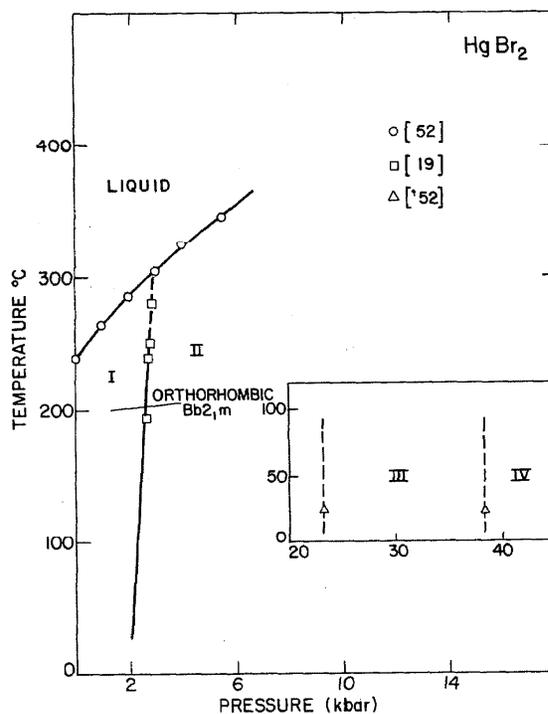
7.14. $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$

The hexahydrate of SrCl_2 melts incongruently at 61.34 °C and atmospheric pressure according to the relation $\text{SrCl}_2 \cdot 6\text{H}_2\text{O} = \text{SrCl}_2 \cdot 2\text{H}_2\text{O} + 4\text{H}_2\text{O}$. Pistorius [191a] investigated the melting curve up to 30 kbar and found it to be a linear function of the pressure expressed by the equation $T(^{\circ}\text{C}) = 61.34 + 5.3 P(\text{kbar})$.

A pressure induced transformation was detected at 32 kbar and 22 °C by a discontinuity in the electrical resistance trace [191a]. This behavior was reversible and the phase boundary was determined at a number of points between 22 and 170 °C. The phase boundary between $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}(\text{I})$ and $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}(\text{II})$ is a linear function of pressure $T = 15.5 P - 470(^{\circ}\text{C})$. The invariant point $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}(\text{I})$ - $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}(\text{II})$ - $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$ is located at $P = 53 \pm 5$ kbar and $T = 345 \pm 30$ °C. Pressures are considered accurate to ± 5 percent and temperatures are within ± 5 °C.

7.15. HgBr_2

Bridgman [52] detected 3 polymorphic transitions along the 50 °C isotherm at 1.7, 23 and 38.7 kbar in HgBr_2 and studied their temperature dependence up to 160 °C. Bridgman [52] also measured the melting curve of HgBr_2 up to 6 kbar. The $\text{HgBr}_2(\text{I})$ - $\text{HgBr}_2(\text{I})$ phase boundary was determined from 200 °C to the triple point at 303 °C and 3 kbar by Bardoll and Tokheide [19]. The intersection of the $\text{HgBr}_2(\text{I})$ -

FIGURE 8. Phase diagram for HgBr_2 .

HgBr₂(II) phase boundary with the melting curve requires a triple point at 3 kbar and 300 °C. These data are summarized in figure 8.

7.16. ZnBr₂

Polymorphic transitions in ZnBr₂ were reported by Bridgman [52] who observed a discontinuity in the high pressure behavior above 25 kbar. The anomalies were attributed to a crystallographic transformation but it was noted that there was some irregularity in the data which suggested the possibility of two closely spaced transitions.

The structure of ZnBr₂ under normal temperature and pressure conditions has not been resolved in detail. Oswald [189a] suggests a large unit cell with 32 molecules. The symmetry assignment is I4₁/acd and there is an almost cubic bimolecular pseudocell.

Meisalo and Kalliomaki [171] examined the high temperature and high pressure regions of ZnBr₂ by means of a polarizing microscope and x-ray diffraction techniques. Investigation in the region 100–200 °C at atmospheric pressure failed to confirm the existence of a high temperature phase suggested by Bridgman [52]. At elevated pressures two polymorphic modifications were observed. The first transition (ZnBr(I)-ZnBr₂(II)) at about 15 kbar was sluggish at room temperature but much more rapid at high temperatures. The second transition (ZnBr₂(II)-ZnBr₂(III)) occurs at 33 kbar at room temperature and has a relatively large volume discontinuity. These two phase boundaries meet at a triple point at 30 kbar and 125 °C. Above the triple point the ZnBr₂(I)-ZnBr₂(II) transition is rapid and easily detected.

The x-ray data for ZnBr₂(II) at 25 kbar [171] can be indexed to a tetragonal unit cell with $a = 10.83$ Å and $c = 21.66$ Å with $c/a = 2$ suggesting a cubic pseudocell. This is based upon 12 reflections from powder data. The x-ray data for ZnBr₂(III) at 80 kbar [171] was indexed on a hexagonal unit cell with $a = 3.65$ Å and $c = 5.73$ Å, which is roughly in agreement with a CdI₂ layered structure.

7.17. GeI₂

Compressibility studies by Bridgman [52] suggest the possibility of a phase transformation in GeI₂ at approximately 18 kbar and room temperature.

7.18. HgI₂

The first high pressure investigation of HgI₂ was performed by Bridgman [48] in 1915. This work consisted of a determination of the pressure-temperature dependence of the α (red)- β (yellow) phase boundary by dilatometric techniques. At room temperature HgI₂(I) (β -form) crystallizes in a tetragonal structure which transforms into the orthorhombic structure of HgI₂(II) (α -form) at 120 °C and atmospheric pressure. Bridgman determined that the HgI₂(I)-HgI₂(II) phase boundary went through a maximum at 5 kbar and 180 °C. Tonkov and Tikhomirova [252] who extended Bridgman's measurements to lower temperatures and higher pressure found evidence for a new high pressure phase HgI₂(II) by DTA techniques. In this work temperatures were recorded with chromel-alumel thermocouples (accuracy ± 3 °C) and pressures with a mangain resistance mano-

meter with an accuracy of ± 100 bars. The HgI₂(I)-HgI₂(III) phase boundary was recorded on both isobaric as well as isothermal cycles. This phase boundary has not been corroborated independently by any other investigator. Brasch et al. [45] claim their research confirms that the HgI₂(III)-HgI₂(II) transition at approximately 13 kbar and room temperature is the same as the α (red) $\rightarrow\beta$ (yellow) transition observed at 127 °C and atmospheric pressure. X-ray examination of HgI₂ by Miller [173] up to a maximum pressure of 120 kbar reveal three polymorphic modifications. According to these data the α (red) tetragonal form is stable up to 13 kbar. The β yellow orthorhombic phase is stable between 13 and 75 kbar. At approximately 75 kbar a new phase appears [173] which can be indexed hexagonal with space group P $\bar{3}$ cl, $Z = 4$ and unit cell dimensions $a = 4.22$ Å and $c = 23.70$ Å.

The melting curve of HgI₂ has been investigated by 3 different groups [18,88,252] Tonkov and Tikhomirova [252] measured the melting curve up to 20 kbars by DTA techniques and present evidence for a high temperature phase which exists between 254 °C and the melting point (332 °C) at atmospheric pressure. Later investigations by Darnell and McCollum [88] and Bardoll and Tokheide [18,19] do not confirm the existence of this high temperature phase and furthermore place the melting curve approximately on the lower boundary of Tonkov and Tikhomirova's high temperature phase. The melting curve of Bardoll and Tokheide agrees very well with that of Darnell and McCollum up to approximately 3.5 kbar. At this point Bardoll and Tokheide report a triple point (338 °C, 3260 bars) between the liquid HgI₂(II) and HgI₂(IV), the latter a new high temperature

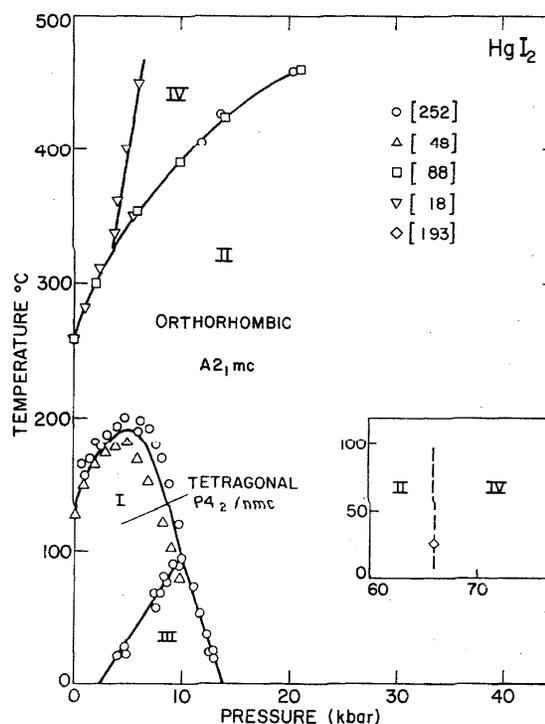


FIGURE 9. Phase diagram for HgI₂.

phase. The liquid-HgI₂(IV) phase boundary was followed to only 6 kbar. In the region above the triple point up to 20 kbar it appears that Darnell and McCallum may have determined the HgI₂(II)-HgI₂(IV) phase boundary. The HgI₂ phase diagram is illustrated in figure 9.

8. Oxides

8.1. Ag₂O

Ag₂O(I), the cuprite form of Ag₂O transforms to a CdI₂-type modification in the range 115–125 kbar and 1400 ± 200°C. The high pressure phase, Ag₂O(II), was quenched and retained metastably at room temperature and atmospheric pressure. The atmospheric pressure values of the hexagonal unit cell dimensions of Ag₂O(II) are $a = 3.072$ Å, $c = 4.941$ Å, with $Z = 1$ and $\rho_c = 9.5$ g/cm³ ($\rho_c = 9.53$ g/cm³). This represents an increase in density of 30 percent between the two phases, both evaluated at atmospheric pressure.

The oxygen atom occupies the position (0,0,0) and the two silver atoms are located at $\pm(1/3, 2/3, z)$ where $z = 0.25$. The transition from Ag₂O(I)-Ag₂O(II) is accompanied by a change in cation(anion) coordination from 2(4) to 3(6). The interatomic distances in Ag₂O(II) are Ag-O, 2.6 Å, and Ag-Ag, 2.86 Å.

8.2. CrO₂

CrO₂ is a transition metal oxide which is strongly ferromagnetic and magnetically ordered above room temperature. It can be prepared in the form of a crystalline powder at atmospheric pressure, but growth of large single crystals at atmospheric pressure has not been successful apparently due to metastability of CrO₂ at low pressures and the relatively high melting point of the oxide.

The first successful synthesis of CrO₂ single crystals was by Chamberlain [69]. Crystals as large as 1.5 mm × 0.3 mm were prepared in the range 900–1300 °C at a pressure 60–65 kbar. A number of flux techniques were tried to improve crystal growth but with no success. The Curie temperature was determined to be 125 °C and the resistivity to be $1.4\text{--}3.8 \times 10^{-4}$ ohm cm which is in the metallic range.

Porta et al. [196] synthesized single crystals of CrO₂ by flux techniques for the purpose of accurate x-ray examination. These crystals were prepared from a mixture of equimolar proportions of CrO₃ and Cr₂O₃ with five percent by weight KOH at 900 °C and 36 kbar.

The space group of CrO₂ is P4₂/mnm with 2 molecules per unit cell which is isostructural with the rutile structure. The tetragonal lattice constants are $a = 4.419$ Å and $c = 2.915$ Å.

8.3. H₂O

H₂O forms more solid phases than any other substance except SiO₂. In addition to the liquid phase there are 9 crystalline phases accessible at pressures below 23 kbar so that the experimental problems are modest compared to many systems. The earliest significant investigation of the H₂O phase diagram was that of Tamman [251] in which he reported the existence of the phases H₂O(II) and H₂O(III).

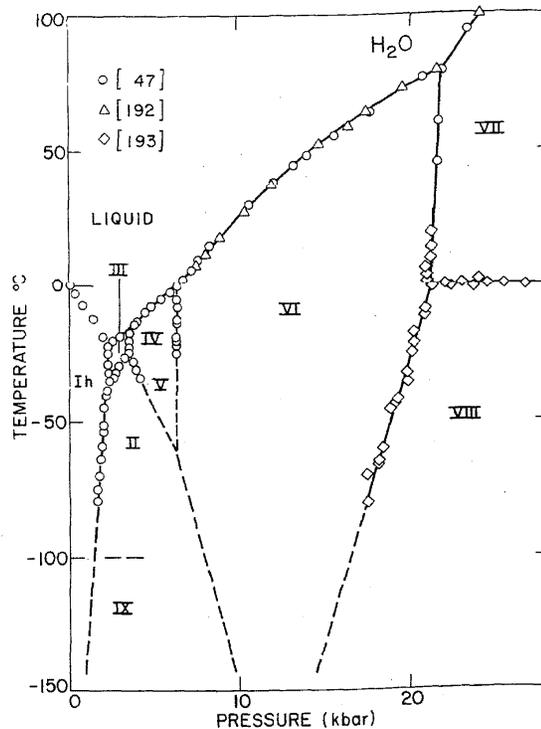


FIGURE 10. Phase diagram for H₂O.

Without doubt the most important single contribution was made by Bridgman [47] in his 1911 paper. In a careful study of the H₂O phases up to 20 kbar he discovered H₂O(V) and H₂O(VI). In this work he reported the determinations of the following phase boundaries: H₂O(L)-H₂O(I), H₂O(I)-H₂O(III), H₂O(L)-H₂O(V), H₂O(L)-H₂O(VI), H₂O(I)-H₂O(II), H₂O(I)-H₂O(III), H₂O(II)-H₂O(III), H₂O(III)-H₂O(IV), H₂O(II)-H₂O(V) and H₂O(V)-H₂O(VI). It is important to note that later investigations in the region up to 20 kbar are in excellent agreement with these results. The data for the phase boundaries are taken from various researchers as indicated in the phase diagram of figure 10.

In 1937 using improved apparatus Bridgman [50] discovered H₂O(VII), H₂O(VIII) and H₂O(IX) were discovered by Whalley et al. in 1966 [267] and 1968 [269], respectively. In 1935 Bridgman investigated the analogous phase diagram of D₂O and detected a new metastable phase D₂O(IV) in the stability field of D₂O(V). He was then able to confirm that this phase was also present in his H₂O data and designated it as H₂O(IV).

Pistorius et al. [192] determined the melting curve of H₂O(VII) up to 200 kbar and fit their data to a Simon equation. It is necessary to know P_0T_0 (the pressure and temperature of the triple point H₂O(L-VI-VII)) very accurately. The H₂O(VI)-H₂O(VIII) transition at room temperature was determined as 21.845 by Bridgman and 21.416 kbar by Kennedy and LaMori [143] and consequently the pressures of Bridgman were lowered by 0.430 kbar. In a later work Pistorius et al. [193] made a determination of the H₂O(VI)-H₂O(VII) phase boundary which at room temperature occurred

at lower pressures than Bridgman's values but agreed at the H₂O(L-VI-VII) triple point. As a result of this, Pistorius et al. [193] corrected their 1963 melting curve for H₂O(VII).

In the early work it was evident that some curvature existed in the H₂O(VI)-H₂O(VII) phase boundary. In a study of the dielectric properties of H₂O(VII), Whalley et al. [267] found that at 0 °C the dielectric constant abruptly decreased suggesting a new phase. Brown and Whalley [56] investigated the H₂O(VI)-H₂O(VII) phase boundary by volumetric techniques and detected a sharp break in the curve at 0 °C and 21 kbar. Pistorius et al. [193] were able to map the H₂O-(VII)-H₂O(VIII) phase boundary from the sharp DTA signals on both heating and cooling cycles.

The normal form of ice with which we are all familiar is ice Ih. For the purpose of this report we choose to designate phases by their chemical symbols instead of mineral names and therefore use the designation H₂O(Ih), H₂O(Ic), which occurs in the region of H₂O(Ih), always appears to be metastable to it. This phase was first reported by König [147].

The crystallography of the various H₂O solid phases is very complex. The presence of disordering in the hydrogen atoms complicates the structural determinations. A combination of probes are necessary to unambiguously determine structures. X-ray diffraction techniques primarily give information on oxygen positions. Infrared and Raman measurements are very important in detecting hydrogen bonding. Dielectric measurements tell something about the type of disorder that might be present. Transformation entropies are important sources of information on the relative configurational entropy which can also be related to relative disorder.

The normal form of ice H₂O(Ih) is hexagonal with space group symmetry P6₃/mmc. H₂O(Ic) is cubic with space group Fd3m. Both of these phases are disordered.

H₂O(III) is the most accessible of the high pressure phases. It is prepared by cooling the liquid phase at 3 kbar pressure, from room temperature down to -40 °C at which point it is quenched in liquid nitrogen. H₂O(III) is the least dense of the high pressure phases of ice ($\rho_c = 1.16 \text{ g/cm}^3$ at -175 °C) and has a tetragonal structure (space group P4₁2₁, $a = 6.73 \text{ \AA}$, $c = 6.83 \text{ \AA}$) involving a tetrahedrally linked hydrogen bond framework. The increase in density relative to H₂O(I) (0.94 g/cm³) is accomplished by a distortion from ideal tetrahedral coordination [137]. There is no decrease in bond length or increase in nearest neighbor coordination, but instead a decrease in next nearest neighbor distance from about 4.5 Å in H₂O(I) to 3.64 Å in H₂O(III).

The hydrogen atoms are ordered in H₂O(II) whereas H₂O(III), H₂O(V), H₂O(VI), H₂O(VII) and H₂O(VIII) are disordered above -40 °C. The absence of disorder in H₂O(II) is demonstrated from entropy measurements [269]. The crystal structure is rhombohedral R3̄ with $a = 7.79 \text{ \AA}$, $\alpha = 113.1^\circ$ and $Z = 12$.

At 6 kbar and -6 °C H₂O(IV) has a density of 1.29 g/cm³ but no structural data are available. In H₂O(V) there are two phases, a high-V and low-V which are disordered and partially ordered, respectively. Both are monoclinic A2/a. The H₂O(VI) structure was reported by Kamb [136,138] to be tetragonal P4₂/nmc with $a = 6.17 \text{ \AA}$ and $c = 5.70 \text{ \AA}$. This phase is disordered and there is also an orthorhombic low-VI

partially ordered phase. The tetragonal structural is built up of hydrogen bonded chains of water molecules that are analogs of tectosilicate chains out of which the fibrous zeolites are constructed. The chains are linked laterally to one another to form an open zeolite like framework. The cavities in this framework are filled with a second framework identical with the first. The two frameworks interpenetrate but do not interconnect. This feature achieves high density in a tetrahedrally linked framework structure.

H₂O(VII) is cubic Pn3m with $a = 3.40 \text{ \AA}$ and $Z = 2$. In this structure each oxygen alone is surrounded by eight instead of the normal four others at the typically H-bonded distance of 2.88 Å (at 25 kbar). Unless the nature of the bonding is greatly altered in this phase each water molecule can have only four hydrogen bonds with its neighbors in tetrahedral directions and, therefore, must be in non-bonded repulsive contact with the other four neighbors.

In H₂O(VIII) which is tetragonal, I4₁/and, an even more unusual situation occurs. Each oxygen atom has two oxygen neighbors at 2.80 Å, four at 2.96 Å, two at 3.15 Å and one at 3.19 Å. The four at 2.96 Å are H-bonded while the others are not. H₂(IX) is the ordered variant of H₂O(III) and is stable below -100 °C.

The thermal conductivity for the nine solid phases of H₂O was measured by Ross et al. [205], Kawai et al. [141] report the dielectric-metal transition in H₂O at a very high unspecified pressure. This was concluded from an abrupt drop in electrical resistance by more than 5 orders of magnitude, a result which has not been duplicated and is questioned by many workers in the high pressure field.

8.4. D₂O

In essential details the phase diagram of D₂O is identical to that of H₂O [49]. The most general characterization is that the triple points in the D₂O diagram all occur at higher temperatures and the transition lines, except those which are approximately vertical, all occur at higher temperatures than in the H₂O diagram. These differences become less, however, at higher pressures.

Pistorius et al. [193] determined D₂O(L)-D₂O(VI), D₂O(L)-D₂O(VIII), D₂O(VI)-D₂O(VII) and the D₂O(VII)-D₂O(VIII) phase boundaries up to 40 kbar. In the region of overlap (i.e., D₂O(L)-D₂O(VI)) his work is in good agreement with that of Bridgman.

Neutron diffraction examination of D₂O polymorphs under helium pressure [5] confirm that the phases Ih, Ic, II, III and IX have the same crystal structures as the H₂O analogs. The presence of helium appears to have affected the locations of the D₂O(I)-D₂O(II) and the D₂O(I)-D₂O(III) phase boundaries.

8.5. GeO₂

At room temperature and atmospheric pressure GeO₂ can exist in two crystallographic forms, the hexagonal α -quartz and the tetragonal rutile structures. The α -quartz form of GeO₂ is a high temperature phase, but due to the sluggishness of the GeO₂ (α -quartz \rightarrow rutile) transformation the α -quartz form is readily obtained at room temperature. The α -quartz form of GeO₂ readily converts to the rutile form when

subjected to high pressures. Sawamoto [215] reported that at high pressure GeO_2 transformed to the orthorhombic $\alpha\text{-PbO}_2$ -type structure. No crystal data is available yet. Liu et al. [160] reported the synthesis of a new hexagonal form of GeO_2 at high pressure from GeO_2 glass by heating with a YAG laser. The new phase has the Fe_2N -type structure (L_3) with unit cell data $a = 2.729 \text{ \AA}$, $c = 4.312 \text{ \AA}$ and $\rho_c = 6.24 \text{ g/cm}^3$.

8.6. HfO_2

The monoclinic-tetragonal phase transformation in HfO_2 has been investigated at high temperatures by Baun [21] and reported to occur in the range 1500 to 1600 °C while the reverse transformation occurs in the range from 1550 to 1450 °C. Curtis et al. [84] and Boganov [40] both place this transition at approximately 1900 °C. Cubic HfO_2 has been obtained by heating pure HfO_2 about 2700 °C [27]. An additional orthorhombic phase was identified by Bendeliani [27]. The new phase was obtained under high pressure in the range 40 to 110 kbar at temperatures of 20 to 1700 °C. X-ray examination of quenched samples give the following crystal data: $a = 5.056 \text{ \AA}$, $b = 5.006 \text{ \AA}$, $c = 5.224 \text{ \AA}$, $\rho_c = 10.58 \text{ g/cm}^3$, and $z = 4$. The space group based on extinctions in the powder data is assumed to be $\text{P}2_12_12_1$. Bocquillon et al. [37] performed a DTA study of the phase boundaries in HfO_2 . In HfO_2 , the monoclinic phase, the tetragonal phase and the orthorhombic phase join in a triple point at approximately 1200 °C and 15 kbar. At present little is known about the tetragonal-cubic phase boundary (fig. 11).

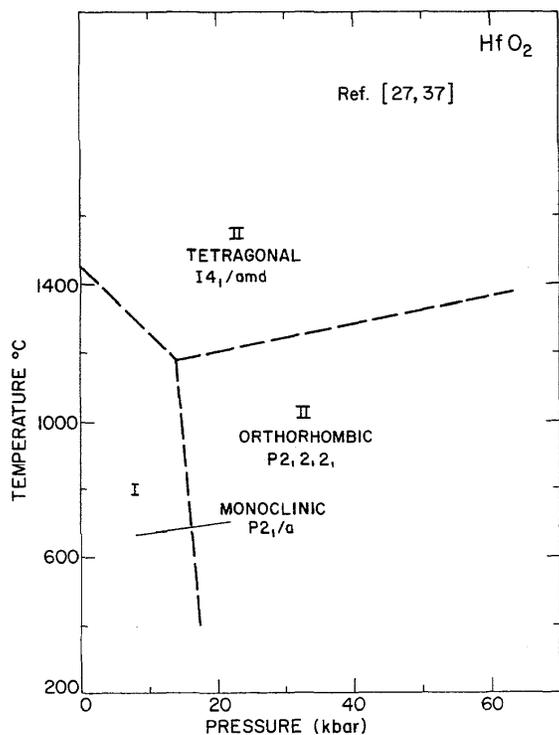


FIGURE 11. Phase diagram for HfO_2 .

8.7. MnO_2

Both amorphous and crystalline (rutile) forms of MnO_2 have been heated by a laser in diamond-anvil pressure cell by Liu [158] resulting in a new metastable high pressure modification. The new phase has been tentatively indexed as cubic with $a = 9.868 \text{ \AA}$. The samples were heated at pressures of 220 to 250 kbar. Clendenen and Drickamer [79] reported the relative volume of MnO_2 up to a pressure of 140 kbar where the MnO_2 underwent a first order phase transition which was not investigated.

8.8. PbO_2

Lead dioxide is known in two forms at atmospheric pressure, the common tetragonal rutile-type and the $\alpha\text{-PbO}_2$ phase [270] which was first prepared under restricted current conditions on the anodes of storage batteries, but has since been prepared by chemical methods [270]. Zaslavskii et al. [277] reported an orthorhombic unit cell with $a = 4.938 \text{ \AA}$, $b = 5.939 \text{ \AA}$ and $c = 5.489 \text{ \AA}$ for $\alpha\text{-PbO}_2$. $\alpha\text{-PbO}_2$ can be prepared easily at high pressure in the region 13–15 kbar and 200–500 °C [249]. This region appears to be the true stability field of $\alpha\text{-PbO}_2$.

Goldschmidt [249] predicted the PbO_2 and MnF_2 would be the most likely rutile-type substances to undergo a phase transformation to a fluorite-type structure since their radius ratios $r_{\text{Pb}}/r_{\text{O}} = 0.65$ ($r_{\text{Mn}}/r_{\text{O}} = 0.61$) are very close to the critical value 0.752 for the fluorite structure derived from simple geometrical considerations.

The crystal structure of $\text{PbO}_2(\text{II})$ ($\alpha\text{-PbO}_2$) is orthorhombic and similar to the columbite structure [277]. The

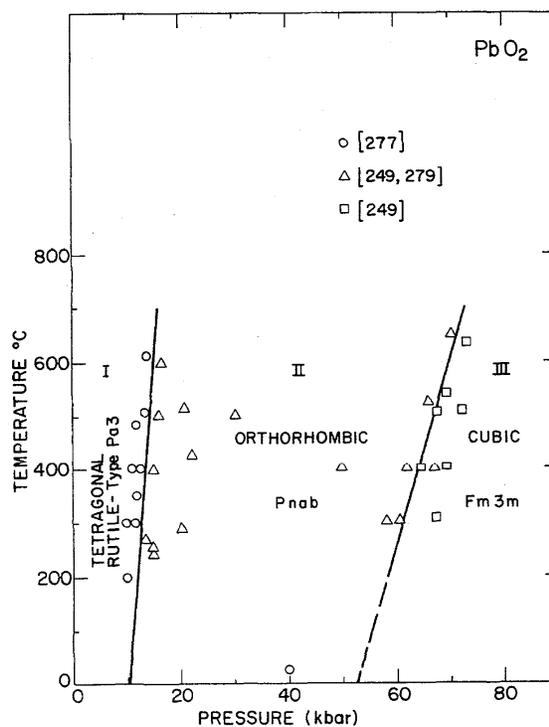


FIGURE 12. Phase diagram for PbO_2 .

PbO₂(I)-PbO₂(II) transformation was shown to be reversible at high temperatures and the phases were confirmed by x-ray diffraction [270]. The high pressure form can be quenched to room temperature and shows no tendency to revert to the rutile phase. After heating at 100 °C for two weeks, a trace of PbO₂(I) appeared. The heat of transition for the PbO₂(II)-PbO₂(I) transition for the PbO₂(II)-PbO₂(I) transition was calculated to be 11 calories per mole and the change in free energy 322 calories per mole [249].

The fluorite-type polymorph of PbO₂ was formed at pressures above 60 kbar in the temperature range 300–600 °C [249]. The cubic cell parameter was determined to be 5.349 Å from x-ray diffraction data obtained from quenched samples at atmospheric pressure. The transformation to PbO₂(III) is very sluggish [249] and the quenched samples are quite metastable undergoing a retrograde transformation to PbO₂(II) at room temperature. A phase equilibrium boundary between PbO₂(II) and PbO₂(III) was determined as $P(\text{kbar}) = 52.5 + 0.30 T(^{\circ}\text{C})$. The density of the fluorite form of PbO₂ is 8.2 percent greater than the rutile form. The phase diagram of PbO₂ is shown in figure 12.

8.9. PtO₂

A distorted rutile-type phase of PtO₂ was synthesized at 700 °C and 3000 bar pressure [233] from the hexagonal phase. High pressure PtO₂(II) is orthorhombic with $a = 4.487 \text{ \AA}$, $b = 4.536 \text{ \AA}$, $c = 3.137 \text{ \AA}$ and $z = 2$. The space group is probably Pnn2 or Pnnm. This is the first example of an orthorhombic distortion among the rutile oxides. It does exist, however, for CaCl₂ and CaBr₂, which have similar unit cells, space group Pnnm. Sahl [211] has shown that perfect close packing of anions results in an orthorhombic distortion of the rutile structure.

8.10. RhO₂

The tetragonal rutile form of RhO₂ was synthesized from the hexagonal RhO₂ at 700 °C and 3000 bar oxygen pressure [223]. The lattice constants are $a = 4.486 \text{ \AA}$, $c = 3.088 \text{ \AA}$ with $Z = 2$. Plotting unit cell volume against ionic radius for several rutile compounds places RhO₂ in the middle of the rutile stability region. Ordinarily, strictly high pressure phases lie at the edge of the stability field.

8.11. SiO₂

SiO₂ in its varied crystalline forms (fig. 13) plays an extremely important role in the crystal chemistry of the earth. The three principal crystalline forms of SiO₂ found in the earth's crust (quartz, tridymite, and cristobalite) have quite distinct crystal structures, each with a well defined field of stability under equilibrium conditions. The transformations from one to another are quite sluggish so the higher temperature forms, cristobalite and tridymite, can exist metastably below their transformation temperatures. Each of these minerals, quartz, metastable tridymite and metastable cristobalite have a low- and high-temperature modification designated α - and β -, respectively. All six crystal structures are built from SiO₄ tetrahedra which are linked by sharing corners with another tetrahedron in a three dimensional framework such that every silicon has four oxygens and ev-

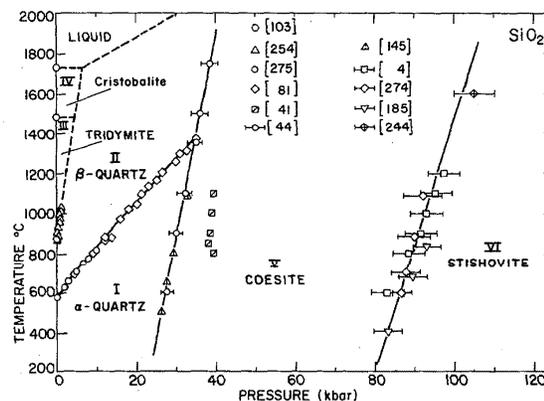


FIGURE 13. Phase diagram for SiO₂.

ery oxygen has 2 silicons as nearest neighbors. While the transformation from α - to β -forms of quartz, tridymite and cristobalite, involves minor atomic displacements, the transformations between quartz, tridymite and cristobalite are reconstructive.

In addition to common SiO₂ minerals just mentioned there are at least five high pressure phases, keatite, coesite, stishovite, a hexagonal Fe₂N-type and a high pressure orthorhombic form. These and possibly other high pressure forms of SiO₂ are very important in the crystal chemistry of the earth in the region from the upper mantle to the lower mantle. Coesite and stishovite are the only high pressure modifications of SiO₂ which have been found in nature. Stoffer and Arndt [245] published an excellent summary of the research involving coesite and stishovite with a very complete list of references. Since the literature pertaining to the various SiO₂ phases is voluminous, this review will be principally concerned with those results which relate to the stability fields in the high pressure region and general information relating to the synthesis and structure of the high pressure phases.

Atmospheric Pressure Phase: For the three SiO₂ phases which occur at atmospheric pressure Fenner [103] determined the transformation temperatures plus the α - β -transformation temperatures for metastable tridymite and metastable cristobalite. In addition to an investigation of the thermodynamic properties of the crystalline forms of SiO₂ Mossman and Pitzer [177] calculated the pressure dependence of the tridymite, cristobalite and liquid SiO₂ phase boundaries a little beyond a kilobar. An analysis of the literature indicates the only high pressure measurements for this part of the SiO₂ phase diagram were the measurements of the tridymite- β -quartz boundary up to 1 kbar by Tuttle and Bowen [254].

The pressure dependence of the α - β quartz boundary was first investigated by Gibson [111] whose pressure data extends to 15 kbar. He states that above 3 kbar the α - β inversion temperatures are extrapolated and their reliability is not comparable to that of the other data. The work of Yoder [275] up to 10 kbar and kbar and that of Cohen and Klement [81] up to 35 kbar agree very well in the region of overlap. Gibson's point (643 °C) at 3 kbar lies 10 °C below that of

Yoder (653 °C). The combined curves of Yoder [275] and Cohen and Klement [81] represent the current best data for the pressure dependence of the quartz α - β inversion temperature.

SiO₂-High Pressure Phases: Coesite, a dense form of SiO₂ was discovered by Coes [80] at high pressures and high temperature. Since the form has a density of 3.01 g/cm³, which is considerably greater than that of quartz, 2.65 g/cm³, this discovery aroused considerable interest. There was some informal speculation that this phase might have six coordination although MacDonald [164] pointed out that this would require an even greater density. A summary of physical properties has been tabulated by Stoffler and Arndt [245] and Sclar et al. [217]. Ramsdell [199] demonstrated that coesite was monoclinic (Pseudo-hexagonal) with space group C2/c with unit cell data $a = 7.17 \text{ \AA}$, $b = 7.17 \text{ \AA}$, $c = 12.38 \text{ \AA}$, $\gamma = 120.0^\circ$ and $Z = 16$. The crystal structure was solved by Zoltai and Buerger [278]. The first natural coesite was found in sheared sandstone samples collected from Meteor Crater, Arizona by Chao et al. [70].

At least 12 studies of the quartz-coesite transition have been reported since Coes [80] first synthesis. The agreement among the workers has not been good. MacDonald [164] reported on the first detailed study of the quartz-coesite stability field. MacDonald's boundary for the quartz-coesite transition was determined in a piston anvil device, for which it was assumed at that time that the pressure was relatively uniform across the anvil face. MacDonald's investigations cover the range 400–600 °C. Griggs and Kennedy [114] traced the quartz-coesite transition from 300–900 °C in apparatus similar to that used by MacDonald [164] and the results agreed with MacDonald's through the overlapping range.

A further study of the quartz-coesite transition in piston anvil apparatus was reported by Dache and Roy [85] who examined the transition over almost the same ranges as MacDonald, 400–600 °C obtaining similar results.

Boyd and England [44] presented a very careful study of the quartz-coesite transition and their results contrast markedly with the results previously presented by MacDonald [164], Griggs and Kennedy [114] and Dache and Roy [85]. Instead of a piston anvil device Boyd and England utilized the more hydrostatic piston cylinder apparatus.

Takahashi [250] also studied the quartz-coesite transition under pressure with a tetrahedral anvil apparatus. This apparatus was calibrated at room temperature without considering the pressure enhancement due to high temperatures. More recent data indicate that this correction may be as great as 1 kbar per 100 °C. Such a correction could easily bring Takahashi's data into agreement with that of Boyd and England. To complicate matters, Boyd and England revised their data up-wards bringing it into fair agreement with Takahashi's uncorrected data. In order to resolve which result is correct Kitahara and Kennedy [145] made a detailed study of the phase boundary using piston cylinder and experimental procedures identical to those described by Boyd and England [44]. By correcting for friction these researchers obtained values for the quartz-coesite phase boundary which agree with the original data published by Boyd and England [44]. Furthermore, the uncorrected data

of Kitahara and Kennedy agree well with Takahashi's published data.

Two further determinations of the quartz coesite boundary by Bell et al. [24] and Roy and Frushour [208] are in fair agreement with Kitahara and Kennedy [145] and Boyd and England [44]. A calculation of the phase boundary by Holm et al. [118] gives a curve which lies about 4 kbar higher than Takahashi's data. Naka et al. [182] examined the effects of shear on the quartz-coesite transition for wet and dry samples and observed a definite shift in the transition to lower pressures.

All the determinations of the quartz-coesite boundary discussed thus far were made with the "quench" method. Bohler and Arndt [41] made a determination of the transition over the temperature range 600°–1100° by in situ x-ray measurements with NaCl as an internal pressure standard. Pressure was determined from the change of the lattice parameter of NaCl by measuring the relative shifts of the strongest two diffraction lines (200) and (220) and by using compression data given by Decker [90] for selected temperatures. The presence of coesite was determined by the (040) and (200) diffraction lines. The authors estimate an accuracy in pressure of ± 1 kbar. As can be seen in the phase diagram, this boundary lies about 8 kbar above the best previous results [44,145].

In evaluating the data for the quartz-coesite phase boundary, the best value appears to be a best fit of the data of Boyd and England [44], Kitahara and Kennedy [145], Bell et al. [24] and Roy and Frushour [208]. This covers a temperature range 350–1750 °C. The set of data (800–1100 °C) of Bohler and Arndt [41], however, cause some concern. The method is inherently superior but reviewers would like to see some independent data covering a larger range of temperature.

Stishovite was originally discovered by Stishov and Popova [242] at pressures in excess of 100 kbar. Stishovite has the rutile-type structure with unit cell data $a = 4.179 \text{ \AA}$, $c = 2.665 \text{ \AA}$, $Z = 2$ [242,243] and the density is 4.29 g/cm³. This form represents a change in coordination from 4 of the coesite phase to 6. Stishovite was found to occur naturally in samples of Coconino Sandstone of Meteor Crater, Arizona [71]. A tabulation of its physical properties was published by Stoffler and Arndt [245] and Sclar et al. [218].

Since stishovite is accepted as a major constituent of the earth's mantle, there has been much interest in determining its properties and stability field. Wentorf [264], Sclar et al. [218], Ringwood and Seabrook [203], Bendeliani and Vereshchagin [26] and Minomura et al. [175] have described the synthesis of stishovite using different types of high pressure apparatus.

The first attempt to determine the coesite-stishovite transformation boundary was made by Stishov [244]. He derived the entropies of stishovite from the entropy and density relations in the rutile-type oxides and estimated the transformation curve passing through an equilibrium point experimentally determined. Experimental determination of the transformation curve was performed by Ostrovskii [185,186] in the temperature range 410–830 °C with the aid of an opposed anvil type high pressure apparatus. His work was followed up by Akimoto and Syono [4] over the tem-

perature range 550–1200 °C using the tetrahedral anvil press. All the above determinations of the coesite-stishovite phase boundary were made with quenching experiments. Yagi and Akimoto [274] made an in situ determination of the phase boundary by means of x-ray diffraction techniques. Pressures were obtained through Decker's NaCl equation of state [90] using the (200) and (220) reflections. The authors estimate an accuracy in pressure measurements of $+2$ kbar at 100 kbar. The equation $P(\text{kbar}) = (80 \pm 2) + (0.011 \pm 0.003)T(^{\circ}\text{C})$ was obtained for the coesite-stishovite equilibrium curve.

In the temperature interval 500–1200 °C, the determinations of Yagi and Akimoto [274] and Ostrovskii [185] fall within the experimental error flags of the data of Akimoto and Syono [4]. Also Stishov's [244] point at 1600 °C and 105 kbar is within the error flags of an extrapolation of Akimoto and Syono [4]. Stishov's calculated phase boundary also lies within this error flag of Akimoto and Syono [4].

Other high pressure phases of SiO₂ not observed in nature have been produced. Keatite [92] is a high pressure synthetic phase of SiO₂. It was prepared at 380–585 °C and 330–1200 bars. Its stability range is unknown.

German et al. [108,109] reported the preparation of an orthorhombic form of SiO₂ in shock wave experiments. This new dense phase was formed using a 350 kbar shock wave and has density of 4.435 g/cm³. The unit cell dimensions of recovered samples are $a = 4.30$ Å, $b = 4.70$ Å and $c = 4.50$ Å. The crystal structure of this orthorhombic phase is unknown.

Liu et al. [160] produced a dense SiO₂ phase at high pressure by heating SiO₂ glass with a YAG laser. The structure is hexagonal Fe₂N type (L₃) with unit cell dimensions $a = 2.561$ Å and $c = 4.112$ Å. The room temperature 1 bar density is 4.26 g/cm³.

8.12. SnO₂

SnO₂ has the tetragonal rutile structure common to many AB₂-type compounds. Suito et al. [248] and Liu [157] synthesized a new dense α PbO₂-type of SnO₂ in the region of 150 kbar and 800 °C. The phase boundary between SnO₂(I) and SnO₂(II) above 700 °C is represented by $P(\text{kbar}) = 140.0 + 0.022 T(^{\circ}\text{C})$. SnO₂(II) is orthorhombic with $a = 4.174$ Å, $b = 5.727$ Å, $c = 5.214$ Å, $\rho_c = 7.11$ g/cm³ and $Z = 4$.

Clendenen and Drickamer [79] measured the room temperature compression of SnO₂ by x-ray techniques up to 250 kbar. At 250 kbar the SnO₂ underwent a first order transition which was investigated by optical techniques. There were no other phase transitions below 250 kbar.

Liu [159] reported the discovery of a new fluorite phase of SnO₂ at very high pressures. The SnO₂ sample was compressed to about 250 kbar and heated by a continuous YAG laser. The cubic unit cell dimension $a = 4.925$ Å was determined at pressure. The density of the fluorite phase is approximately 15.5 percent greater than that of the rutile phase as a result of the coordination number increase from 6 to 8.

8.13. TeO₂

Tellurium dioxide has three known crystalline forms at standard temperature and pressure. Natural TeO₂ crystal-

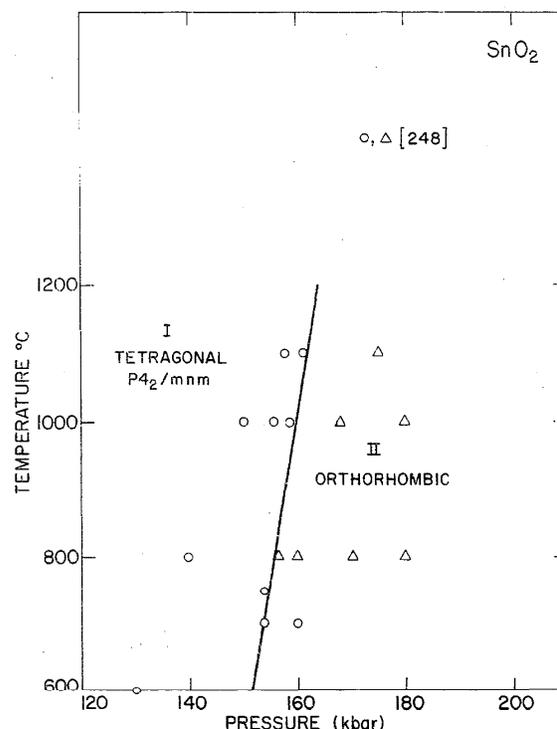


FIGURE 14. Phase diagram for SnO₂.

lizes in both the rutile and brookite structure of TiO₂ whereas all synthetically prepared TeO₂ forms in the paratellurite structure. Paratellurite can also be prepared by heating the tellurite phase above 600 °C. All the high pressure studies on this system have been devoted exclusively to paratellurite which has an interesting second order phase transition.

The paratellurite transition has been studied by a number of investigators and experimental techniques [170,190,191,234,272]. It was first reported by Peercy and Fritz [190] on the basis of Brillouin scattering experiments at pressure. The transition is driven by a pressure dependent transverse acoustic soft mode which decreases smoothly to zero velocity at approximately 9 kbar so it appears to be second order. The phase boundary is very steep with almost negligible temperature dependence. Paratellurite is tetragonal with space group P4₁2₁2 and lattice constants $a = 4.805$ Å, $c = 7.602$ Å and $Z = 4$. The high pressure phase TeO₂(IV) was studied by Worlton and Beyerlein [272] employing neutron diffraction techniques. TeO₂(IV) is orthorhombic with $a = 4.605$ Å, $b = 4.856$ Å, $c = 7.530$ Å and $Z = 4$ at 19.8 kbar. The space group is P2₁2₁2₁ with all atoms in general positions (4a). A phase diagram has not been drawn since the equilibrium relationships of the paratellurite phases to the rutile and brookite phases is not known.

The best value for the paratellurite TeO₂(III)-TeO₂(IV) transition is 8.86 kbar from the work of Peercy et al. [190]. The relationship of these phases to the other phases of TeO₂ (i.e., TeO₂(I), TeO₂(II)) has not been investigated.

8.14. TiO₂

Titanium dioxide occurs in nature in three polymorphic forms as the minerals rutile, anatase, and brookite. Rutile is usually considered to be the high temperature and high pressure phase relative to anatase whereas brookite is often considered to be of secondary origin. When subjected to high pressure all of these three phases transform to a crystallographic structure isomorphous to α -PbO₂ [27,86,183,232].

Several studies have been carried out on the TiO₂ polymorphism. Osborn [184] studied the conversion of anatase to rutile in the presence of water from temperatures of 375 to 660 °C and pressures of 1–3 kbar. He found that pressure lowered the transformation temperature. Dachille et al. [86] reported the existence of a new high pressure form of TiO₂ produced from anatase in the region 15–100 kbar and 25–500 °C which was retained metastably at atmospheric pressure. Bendeliani et al. [27] reported that rutile was converted to a high pressure phase with the α -PbO₂ structure at pressures 40–120 kbars and temperatures 700–1500 °C. Simons and Dachille [232] prepared TiO₂(II) from brookite and did a crystal structure analysis from powder x-ray data. McQueen et al. [168] studied the effect of shock waves on rutile and found the new phase after shocks of about 330 kbar. Later hugoniot measurements by Linde and DeCarli [154] give evidence of a phase transition commencing between 150 and 200 kbar. X-ray diffraction studies of recovered specimens showed the presence of an orthorhombic phase with α -PbO₂ structure.

Dachille et al. [86] made a fairly extensive investigation of the phase boundaries in the TiO₂ system. Runs were made

using rutile, anatase, and brookite as starting materials. In this study no transitions of rutile to other phases were observed. Similarly, no conversion to brookite was observed when TiO₂(II) was the starting material. As a result of this difficulty and the slow reaction kinetics, these "phase" boundaries do not represent equilibrium conditions [86,87,124].

The crystal structures of the TiO₂ polymorphs are as follows [83]: rutile-tetragonal (P4₂/mnm), anatase-Tetragonal (I4₁/amd), brookite-orthorhombic (Pbca) and TiO₂(II)-orthorhombic (Pbcn) of the α -PbO₂-type. Crystallographically TiO₂(II) is very similar to brookite in that the *b* and *c* axes are nearly the same and $a_{II} = \frac{1}{2}a_{br}$. It should be noted that in both MnF₂ and ZnF₂ the α -PbO₂-type structure was retained upon the release of pressure. In these two compounds the α -PbO₂-type phase was not observed at high pressure but only in the quenched material at atmospheric pressure. Jamieson and Olinger [123] performed x-ray diffraction studies at high pressure and showed that the TiO₂(II) phase was the only one observed, therefore the α -PbO₂-type phase of TiO₂ apparently is a quenched form.

Natural ilmenite (Fe,Mg)TiO₃ has been found to transform to the perovskite structure at 140 kbar and then disproportionate to (Fe,Mg)O plus a cubic phase of TiO₂ at 250 kbar in the temperature range of 1400 to 1800 °C. The cubic TiO₂ can be indexed on the basis of space group Fm3m with *Z* = 4 and *a* = 4.455 Å at room temperature and 1 bar. According to the author's calculations the data fit a fluorite (CaF₂-type) structure best.

In an investigation of post rutile phases for TiO₂, Liu [159] discovered a new phase at approximately 250 kbar syn-

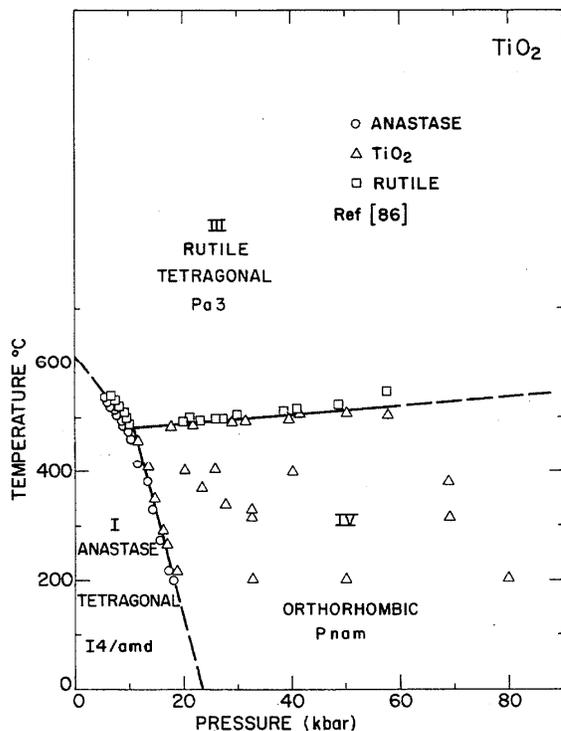


FIGURE 15. Phase diagram for TiO₂ (Anatase).

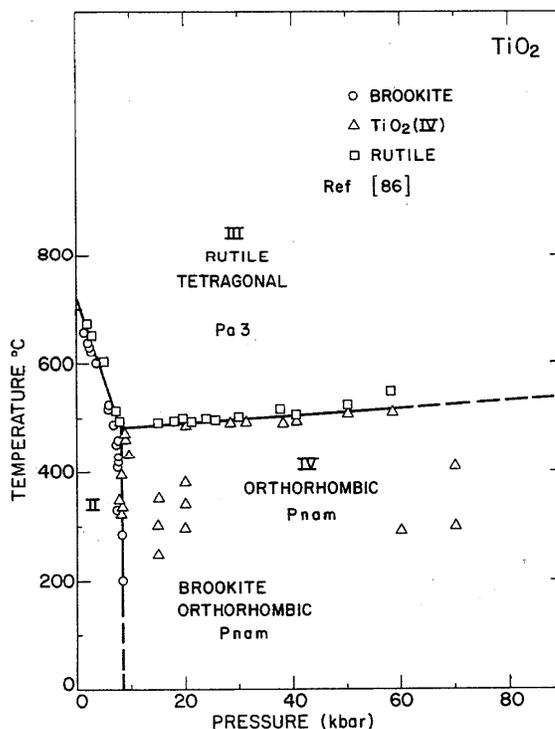


FIGURE 16. Phase diagram for TiO₂ (Brookite).

thesized by laser heating. The diffraction lines were indexed in the hexagonal system with unit cell dimensions $a = 9.22 \text{ \AA}$ and $c = 5.685 \text{ \AA}$ ($Z = 16$). No known structure can yet be assigned to this phase. Its density is about 8.5 percent greater than that of the α -PbO₂ phase of TiO₂.

8.15. ZrO₂

The polymorphism of zirconia was first reported by Ruff and Ebert [209]. A reversible phase transformation from the monoclinic to the tetragonal crystal system was found at about 1000 °C. Lynch et al. [161] place the transition between 1193 °C and 1200 °C. Mumpton and Roy [178], using the differential thermal analysis and x-ray diffraction techniques, obtained a monoclinic-tetragonal transition temperature of 1170 °C. Baun [21] showed that the transition starts at 1000 °C and is complete at 1190–1200 °C. All investigators found a large temperature hysteresis in the reverse transformation from tetragonal to monoclinic.

A number of authors have reported observing the metastable retention of the tetragonal phase at room temperature. It is generally assumed that in these experiments the tetragonal phase was stabilized due to impurities. In high pressure experiments Vahldiek et al. [255] were able to retain the tetragonal phase as a mixture with the stable monoclinic phase at room temperature and atmospheric pressure. The tetragonal form of ZrO₂ was prepared at 15 to 20 kbar and 1200 to 1700 °C and retained after rapid quenching. The high pressure specimens when heated to 1200 °C in air reverted to the monoclinic form.

Whitney calculated the pressure-temperature phase boundary for the monoclinic tetragonal equilibrium transformation. The curve has a negative slope and intersects the pressure axis at 36 kbars. Kulcinski [150] studied this transition by x-ray techniques at room temperature. At 38 kbar a new phase attributed to tetragonal ZrO₂ started to appear which at 46 kbar had increased to 50 percent.

Smith and Cline [235] present some evidence for a cubic ZrO₂ phase at temperatures above the tetragonal phase. This is based on the indirect evidence that a cubic phase can be stabilized by such additives as MgO and CaO, and with solid solution series ZrO₂-ThO₂. This phase is assumed to have the fluorite structure.

Bendeliani et al. [27] prepared an orthorhombic phase of ZrO₂ in the interval 40 to 110 kbar and 20 to 1700 °C. The sample was examined after removal from the press and showed a presence of the monoclinic phase. The unit cell data are $a = 5.110 \text{ \AA}$, $b = 5.073 \text{ \AA}$, $c = 5.267 \text{ \AA}$, $\rho_c = 5.99 \text{ g/cm}^3$, and $Z = 4$. Based upon the observed extinctions in the powder data the space group is assumed to be P2₁2₁2₁. Bendeliani et al. [27] present a tentative phase diagram for ZrO₂ in which the tetragonal, cubic and orthorhombic phases meet a triple point. Using DTA techniques Bocquillon and Susse [37] modify this picture somewhat. Their determinations of the tetragonal orthorhombic phase boundary indicate that it would intersect the monoclinic phase at approximately 600 °C. According to this result the transformation observed by Kulcinski must have been the monoclinic-orthorhombic transition.

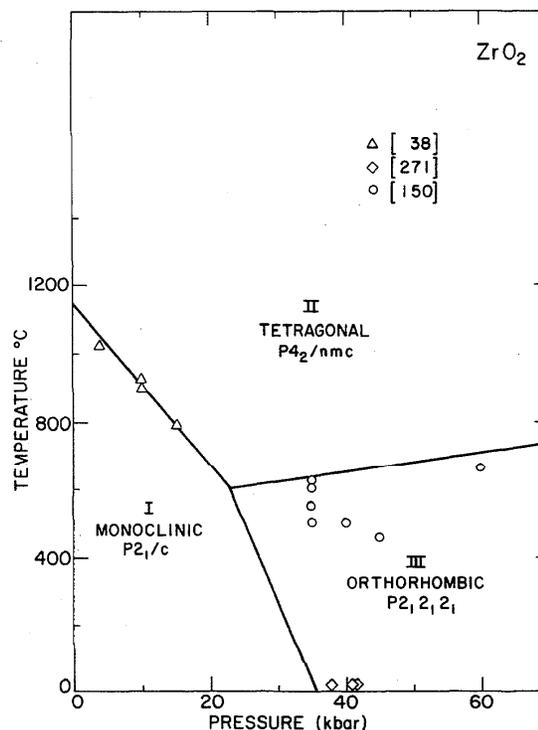


FIGURE 17. Phase diagram for ZrO₂.

8.16. Zn(OH)₂

Zinc hydroxide has several modifications at normal pressures, the most stable of which is the α -form whose crystal structure has been examined in detail. This form is orthorhombic with unit cell data $a = 8.53 \text{ \AA}$, $b = 5.16 \text{ \AA}$, $c = 4.92 \text{ \AA}$, $Z = 4$ and the space group is P222. Each Zn atom is surrounded by four OH groups in a distorted tetrahedron. The disposition of the tetrahedra in the structure is similar to that in various SiO₂ modifications with four-fold coordination, but differs in that the OH groups forming the tetrahedron are not in contact because the Zn atom is too large.

For the other modifications of Zn(OH)₂ there is only limited x-ray data without detailed analysis of their structures. Another orthorhombic form has the cell dimensions $a = 6.73 \text{ \AA}$, $b = 7.33 \text{ \AA}$ and $c = 8.47 \text{ \AA}$ with $Z = 8$. A hexagonal form has the dimensions $a = 3.11 \text{ \AA}$ and $c = 7.80 \text{ \AA}$. Roy and Mumpton [205] prepared a high pressure form of what they consider to be Zn(OH)₂ but could not index the d -spacings to a crystal system.

Baneeva and Popova [11] reported the synthesis of a new CdI₂ form of Zn(OH)₂ at pressures of 110–120 kbar and a temperature of 400 °C from α -Zn(OH)₂. This transformation represents an increase in coordination from 4 to 6. This structure type is already known for mixed hydroxide Zn(OH)₂ + Mg(OH)₂, Co(OH)₂ and Ni(OH)₂. The hexagonal unit cell data for the new CdI₂-form of Zn(OH)₂ are $a = 3.19 \text{ \AA}$, $c = 4.714 \text{ \AA}$, $Z = 1$ and $\rho_c = 3.96 \text{ g/cm}^3$. This represents an increase in density of 30% over the low pressure phase.

9. Phosphides

9.1. CoP₂

The marcasite and arsenopyrite type structures are exhibited by a large number of transition metal di-pnictides. The marcasite structure is most stable for the iron group di-pnictides while the related arsenopyrite type structure has been found for all the cobalt group di-pnictides except CoP₂, CoBi₂, and IrBi₂. Donohue [93] prepared the arsenopyrite type CoP₂ with the reaction of Co + (Ge) + 2P (Ge used only as a flux) between 800 and 1200 °C at a pressure of 65 kbar. The role of the flux in this reaction is not clear, however, without it the new phase could not be synthesized. The structure of the arsenopyrite unit cell is monoclinic with dimensions $a = 5.610 \text{ \AA}$, $b = 5.591 \text{ \AA}$, $c = 5.643 \text{ \AA}$ and $\beta = 116.8$ ($Z = 4$).

9.2. GeP₂

In a study of polymorphism in the Ge-P system Osugi et al. [188] report the synthesis of a cubic phase of GeP₂ in the range 1000–1200 °C and 35–40 kbar. Comparison of the x-ray data of the cubic phase of GeP₂ with that for the pyrite phase of SiP₂ show essentially the same d -spacings but significant discrepancies in their relative intensities. In addition, the cubic cell dimension $a = 5.619 \text{ \AA}$ for GeP₂ is smaller than that of SiP₂ ($a = 5.682 \text{ \AA}$). This latter phenomenon may be due to non-stoichiometry in GeP₂, however.

9.3. NbP_{1.7}

The atmospheric pressure phases in the Nb-P system are NbP and NbP₂. In the pressure range 35–55 kbar a new phase was prepared with the ordered defect PbFCl-type structure having the chemical formula $\sim\text{NbP}_{1.7}$ [126a].

The largest crystals of this new compounds were isolated from samples with Nb:P ratios between 2:3 and 1:2. The samples were heated to 1250 °C at a pressure under 55 kbar, held for 2 hours and quenched while still under pressure. Temperatures were measured with a Pt-Pt/Rh thermocouple placed at the surface of the cylindrical graphite heater enclosing the sample. Under ambient conditions NbP_{1.7} can be kept several years without decomposing or oxidizing.

The chemical composition indicated by the synthesis lies between the mono- and diphosphide. Chemical analysis suggested a composition of NbP_{1.7}. Its measured density was 5.65 g/cm³ which corresponds to NbP_{1.69} assuming partial occupancy of P sites and full occupancy of the metal sites.

Initial identification based on powder x-ray patterns suggest unit cell with $a = 3.339 \text{ \AA}$ and $c = 7.649 \text{ \AA}$. Precession photographs revealed a superstructure with an a -axis which is five times larger than the a -axis of the PbFCl subcell. All reflections were accounted for by Laue Symmetry 4/mmm and $a = 7.468 \text{ \AA}$, $c = 7.649 \text{ \AA}$.

9.4. SiP₂

Silicon diphosphide was synthesized successfully by halogen transport from the elements [94]. The crystal structure is pyrite-type, space group Pa3 with unit cell dimensions $a = 5.705 \text{ \AA}$, $Z = 4$ and $\rho_c = 3.22 \text{ g/cm}^3$.

9.5. VP_{1.75}

The details of the preparation of the high pressure phase VP_{1.75} are identical to those described for Nb_{1.7}. In the V-P system, the stoichiometric compounds VP and VP₂ are the only ones previously known to exist at atmospheric pressure [126a]. VP_{1.75} crystals are black, brittle, and show metallic conductivity.

Powder x-ray diffraction data of the high pressure phase fits a tetragonal cell with $a = 3.162 \text{ \AA}$, $c = 7.267 \text{ \AA}$ and $Z = 8$. The chemical formula VP_{1.75} was determined from the crystal structure determination. From this data the calculated density was 4.80 g/cm³ which is excellent agreement with the measured value of 4.87 g/cm³.

VP_{1.75} crystallizes with a RbFCl-type subshell space group P4m2. The superstructure arises from the ordered arrangement of vacancies of the F site of the PbFCl subcell.

9.6. ZnP₂

A high pressure modification of ZnP₂ was prepared by Osugi and Tanaka [189] by the direct reaction of zinc with phosphorous and also through the polymorphic transitions from both the monoclinic and tetragonal ZnP₂ phases. Application of pressures above 20 kbar with temperatures above 150 °C is required for the synthesis. The new modification of ZnP₂ has a pseudo-cubic symmetry with a cell dimension $a = 5.322 \text{ \AA}$ and measured density 3.55 g/cm³.

10. Silicides

In a study of the effect of pressure and temperature on the disilicides MSi₂ of the divalent metals ($M = \text{Ca, Sr, Ba, Eu}$) new polymorphic modifications have been identified for CaSi₂ [89,169,230] SrSi₂ [101] and BaSi₂ [100]. The alkaline earth metals of calcium, strontium, barium and the divalent rare earth metal europium have two outer s -electrons in their atomic ground state. In many of their compounds similar properties and isotopic structures are found. At atmospheric pressure, however, all of the above disilicides crystallize in four different structure types which differ characteristically in their silicon sublattices.

10.1. BaSi₂

Barium disilicide at atmospheric pressure crystallizes in an orthorhombic structure, space group Pnma (or Pna2₁) with $a = 8.92 \text{ \AA}$, $b = 6.75 \text{ \AA}$, $c = 11.57 \text{ \AA}$ and $Z = 8$. A high pressure modification, BaSi₂(II), was prepared by heating the normal phase of BaSi₂ to 1000 °C at a pressure of 40 kbar. On quenching to ambient conditions the high pressure modification could be stored in the absence of air and moisture for several months. Heating BaSi₂(II) to 400 °C at 1 bar pressure leads to its complete transformation to the original phase. The structure of the high pressure phase of BaSi₂ is rhombohedral, space group P3m1 with $a = 4.047 \text{ \AA}$, $c = 5.330 \text{ \AA}$ and $Z = 1$ [100].

10.2. CaSi₂

Calcium disilicide has a hexagonal layer type structure in which the silicon sublattice consists of corrugated layers, each silicon having three equidistance neighbors. CaSi₂(I)

has a rhombohedral structure, space group R3m with $a = 3.855 \text{ \AA}$, $c = 30.6 \text{ \AA}$, $Z = 6$ and $\rho_c = 2.46 \text{ g/cm}^3$. This represents a volume reduction of 6.9 percent.

CaSi₂(II), a high pressure polymorph, was obtained from rhombohedral CaSi₂(I) in the region 17 to 87 kbar and 700 to 1800 °C. For complete conversion to the high pressure phase in short periods of time, pressures above 40 kbar and temperatures above 1000 °C are required simultaneously [101]. The structure of the high pressure phase is body centered tetragonal, α -ThSi₂-type, space group I4₁/amd with $a = 4.283 \text{ \AA}$, $c = 13.54 \text{ \AA}$ and a calculated density of 2.57 g/cm³. CaSi₂(II) is superconducting at $1.58 \pm 0.01 \text{ K}$ [169].

10.3. EuSi₂

Europium disilicide crystallizes in the body center tetragonal structure [100] identical to those adopted by the high pressure forms of both CaSi₂ and SrSi₂. High pressure and high temperature treatment failed to yield any structure transformations in EuSi₂.

10.4. SrSi₂

Strontium disilicide (SrSi₂-type) is cubic ($a = 6.355 \text{ \AA}$) with silicon atoms forming a three dimensional network. All silicon atoms have three equidistant neighbors in flat trigonal pyramids but twisted against each other. The high pressure phase, SrSi₂(II), also has the α -ThSi₂-type structure identical to CaSi₂(II). The tetragonal unit cell dimensions are $a = 4.438 \text{ \AA}$, $c = 13.89 \text{ \AA}$ with a calculated density of 3.51 g/cm³. This represents a volume reduction by 1.9 percent [100].

11. Sulfides

11.1. Ag₂S

The phase diagram of Ag₂S contains four solid phases, three of which are known at atmospheric pressure and are listed in Table 1. High argentite, the high temperature form of Ag₂S, is stable above 596 °C up to the melting point at 825 °C. The argentite modification, which has a disordered b.c.c. structure, is stable between 177 and 596 °C. The room temperature form Ag₂S(II), known as acanthite, is stable below 177 °C. It crystallizes in a monoclinic unit cell with space group P2₁/n.

The first high pressure study on Ag₂S was a determination of Ag₂S(III) (acathite)-Ag₂S(IV) phase boundary between 82 and 200 °C [52]. The transition is associated with a very small volume change. The Ag₂S(II)-Ag₂S(III) solid-solid phase boundary was determined up to the triple point at approximately 12.3 kbar and 195 °C. From the triple point the Ag₂S(II)-Ag₂S(IV) boundary was extended up to 40 kbar [76]. Previously, the initial slope of the Ag₂S(II)-Ag₂S(III) had been determined up to 1.2 kbar with an initial slope of 4 °C/kbar which appears to be too high [207].

In the work of Clark and Rapoport [76] pressures were generated in a piston cylinder device and phase transitions were detected by means of differential thermal analysis with chromel-alumel thermocouples. Corrections were made for the effect of pressure on the thermocouples [116,117]. Each point on the phase boundary is based upon four separate

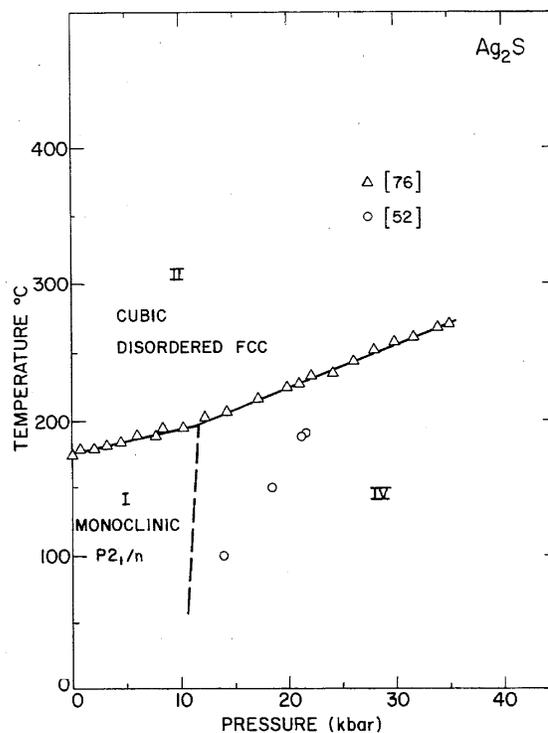


FIGURE 18. Phase diagram for Ag₂S.

determinations on different samples with precision of $\pm 2 \text{ }^\circ\text{C}$. Corrected pressures are stated to be accurate to $\pm 0.5 \text{ kbar}$. Unfortunately, Bridgman's Ag₂S(III)-Ag₂S(IV) phase boundary does not extrapolate to the present triple point (see figure 18 for phase diagram of Ag₂S).

11.2. BiS₂

The preparation of a new polymorph BiS₂ was reported by Silverman [230]. The new material was synthesized at 50 kbar and 1250 °C from a 4:11 atomic mixture of Bi and S, each a purity greater than 99%. The x-ray examination was inconclusive about the crystal system. The published d -values are 3.11 Å(100), 2.97 Å(60), 2.62 Å(65), 2.27 Å(60), 1.88 Å(70), 1.81 Å(70) and 1.504 Å(60).

11.3. CS₂

The earliest pressure studies of CS₂ were by Bridgman [53] who investigated the melting curve and compression up to 35 kbar. At temperatures of 175° or over and at pressures above 45 kbar, CS₂ is transformed slowly and irreversibly into a black solid which is retained under atmospheric conditions. Bridgman suggested that black CS₂ had a structure analogous to SiO₂. Whalley [266] did an infrared study of solid CS₂ prepared at 55 kbar and 185 °C and found a major absorption in this substance at $1063 \pm 5 \text{ cm}^{-1}$. He assigned this to C = S stretching and suggested a linear polymeric structure containing $\begin{matrix} \text{S} \\ \parallel \\ \text{C} - \text{S} \end{matrix}$ units. Other absorptions were much weaker than the 1063 cm^{-1} bond. This conclusion was also confirmed by Silverman and Soulen [226].

More detailed examinations of the phase diagram by Butcher et al. [58,9] revealed that the formation of black CS_2 occurs over a wide range of pressure but over a relatively narrow range of temperature. Above this temperature it decomposes to carbon and sulfur. When heated at atmospheric pressure, black CS_2 softens at about 70°C and decomposes to carbon and sulfur. It is also insoluble in normal laboratory solvents.

X-ray patterns of black CS_2 are broad and diffuse indicating little or no long range order. At room temperature this material has a very low electrical conductivity which increases rapidly with temperature giving an energy gap of 1.15 eV.

Two x-ray studies have been performed on single crystals of CS_2 grown from the melt. The structure determined by Baenziger and Duax [10] is based on an orthorhombic unit cell with space group Cmca and $Z = 4$ at 143 K. The unit cell constants at two different temperatures 158 K and 98 K are $a = 6.455 \text{ \AA}$ (6.215 \AA), $b = 5.596 \text{ \AA}$ (5.404 \AA) and $c = 8.939 \text{ \AA}$ (9.208 \AA). The melting point of CS_2 is 160 K. In this structure the CS_2 molecules are linear S-C-S.

Carbon disulfide freezes at 12.6 kbar at room temperature. The high pressure crystal structure was investigated by Weir et al. [263] and is in agreement with that of Baenziger and Duax [10]. The unit cell dimensions of the orthorhombic cell are $a = 6.16 \text{ \AA}$, $b = 5.38 \text{ \AA}$, and $c = 8.53 \text{ \AA}$. It is of interest to note that with decreasing temperature at 1 bar pressure, c increases from 8.939 \AA (158 K) to 9.280 \AA (98 K). This value appears to decrease with pressure, however. Weir et al. [263] also reported observing an abrupt transition in a single crystal of CS_2 in the vicinity of 30 kbar and -30°C .

11.4. CdS_2

Pyrite-type CdS_2 [33] was prepared from the reaction of CdS or amorphous cadmium polysulfide and sulfur at 65 kbar and $400\text{--}600^\circ\text{C}$. Investigation of the various powder samples by x-ray diffraction showed that all had the pyrite structure with the same unit cell size suggesting a uniform stoichiometry.

11.5. Cu_2S

The polymorphic behavior of Cu_2S is quite complex. In a study of the Cu-S system at high temperature the compounds Cu_2S , $\text{Cu}_{1.96}\text{S}$ and $\text{Cu}_{1.8}\text{S}$ (digenite) have been identified as the products of sintering. All three of these compounds undergo high temperature phase transitions at 1 bar. In Cu_2S the $\text{Cu}_2\text{S(IV)}\text{--Cu}_2\text{S(III)}$ phase transition occurs at 103.5°C . The initial slope of this phase boundary is 0.5°C/kbar [76]. At about 10 kbar new DTA signals were obtained around 240°C and a new transition line followed up to about 40 kbar. DTA signals from the original $\text{Cu}_2\text{S(IV)}\text{--Cu}_2\text{S(III)}$ phase boundary disappeared just above 10 kbar. On decreasing pressure, this behavior is reversed and at 8 kbar the DTA signals from the upper transition disappear and those corresponding to the lower boundary reappear. The upper transition line varies only slightly with pressure and has a shallow maximum in the vicinity of 245°C and 21 kbar.

Serebryanaya [222] reported that $\text{Cu}_{1.96}\text{S}$ could be prepared by heating Cu_2S to 900°C . Clark and Rapoport [76],

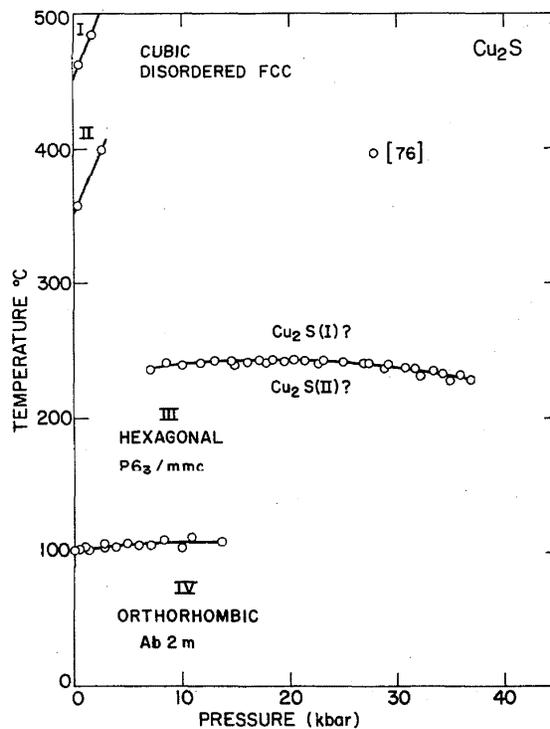


FIGURE 19. Phase diagram for Cu_2S .

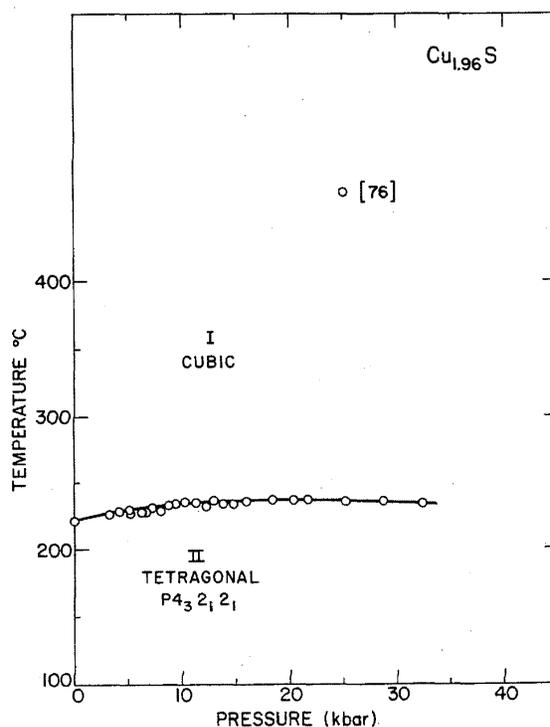


FIGURE 20. Phase diagram for $\text{Cu}_{1.96}\text{S}$.

therefore, heated their Cu₂S sample to approximately 850 °C and below 10 kbar there was no evidence of the transition around 103.5°, whereas in the region 220–230 °C DTA signals were obtained. Clark and Rapoport [76] reported that the upper transition results from the reversible formation of Cu₉S₅ (or Cu₇S₄) by a disproportionation reaction of Cu₂S (See figures 19 and 20 for the phase diagrams of Cu₂S and Cu_{1.96}S, respectively).

11.6. CuS₂

The synthesis of CuS₂ was carried out in a belt apparatus [178a] using a graphite heater and sodium chloride as the pressure transmitting medium. The cell was calibrated at the following fixed points: Bismuth (25.5 kbar; 27 kbar) and Barium (58 kbar). Temperatures were determined from a Pt-Pt10Rh thermocouple present during the runs.

The reaction was carried out with a mixture of CuS(covellite) and sulfur in a 1:1.2 mole ratio at high temperature and high pressure. Chemical analysis of the product, a dark purplish red material, indicated the composition CuS_{1.9} and x-ray analysis confirmed that it had the cubic (NiS₂) pyrite structure with the unit cell dimension $a = 5.796 \text{ \AA}$. The calculated density is 4.44 g/cm³ and the measured density is 4.24 g/cm³. Bither et al. [32] reported $a = 5.790 \text{ \AA}$, $\rho_c = 4.368 \text{ g/cm}^3$ and $\rho_{exp} = 4.354 \text{ g/cm}^3$. Between 200–300 °C in an inert atmosphere CuS₂ decomposes to covellite, digenite, and sulfur. Between 400–475 °C the products further decompose to Cu₂S (chalcocite) and sulfur.

11.7. GeS₂

The synthesis of the tetragonal high pressure form of GeS₂ was investigated by Prewitt and Young [1981]. Single crystals were prepared from stoichiometric ratios of germanium and sulfur held at 1100 °C and 65 kbar for 2–3 hours and then temperature quenched. The tetragonal unit cell dimensions are $a = 5.480 \text{ \AA}$, $c = 9.143 \text{ \AA}$ with $Z = 4$ and $\rho_c = 3.30 \text{ g/cm}^3$ (space group-I $\bar{4}2d$).

The structure of GeS₂(II) is similar to SiS₂(II) and consists of GeS₄ tetrahedra which share vertices to form 3 dimensional networks. GeS₂(I) also has a structure in which the GeS₄ tetrahedra share vertices. Germanium atoms of GeS₂(II) are in positions 4a (0,0,0) while sulfur occupies positions 8d ($x = 0.238$; $y = 0.25$; $z = 0.125$).

11.8. H₂S

The atmospheric pressure phase transitions in H₂S were first observed by Giaouque and Blue [112]. Their specific heat measurements indicated the following transitions: boiling point 212.8 K; melting point 187.6 K; H₂S(I)-H₂S(II) solid-solid transition at 126.2 K and the H₂S(II)-H₂S(III) solid-solid transition at 103.6 K. The measurements indicated a first order transition at 103.6 K and an anomaly occurs at 126.2 K, which is characteristic of a second order transition.

Pressure studies on the H₂S phase diagram were performed by Stevenson who employed volumetric techniques. This work extended to a maximum pressure of 10 kbar. Stevenson [240] detected two new high pressure phases H₂S(V) and H₂S(VI) in the region above 5 and 6 kbars, respectively. In a later study by Stewart [241] these latter two phases were

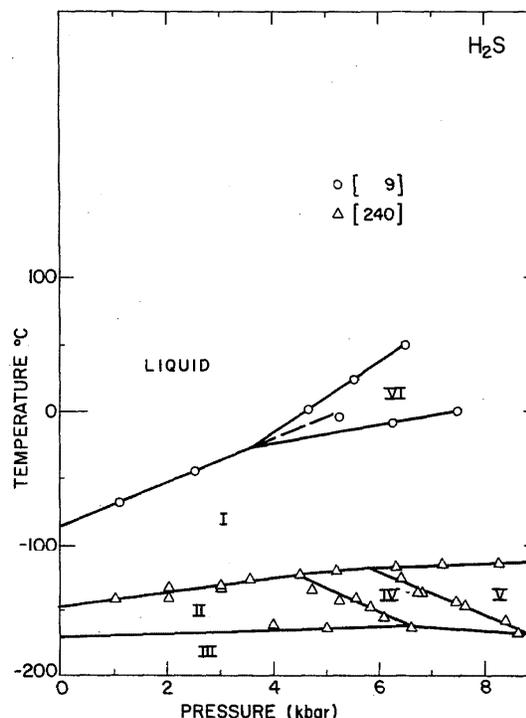


FIGURE 21. Phase diagram for H₂S.

not confirmed. Babb [9] measured the melting curve of H₂S and reported a new solid phase H₂S(IV) which meets H₂S(I) and H₂S(L) in a triple point at -26 °C and 3.6 kbar (see figure 21 for H₂S phase diagram).

The x-ray diffraction studies of Justi and Nitka [128] indicate that the sulfur atoms in all three phases occupy a face-centered cubic lattice which changes less than 1% in lattice constant between 20 and 150 K. The transitions apparently arise from the variation in the positions of the hydrogen atoms. H₂S(III) is ordered while H₂S(I) and H₂S(II) are disordered. The basic cubic structure is quite open so that rearrangements of hydrogen atoms are possible without appreciable changes in lattice constant. There is no crystallographic data for H₂S(IV) nor the questionable phases H₂S(V) and H₂S(VI).

11.9. IrS₂

At atmospheric pressure iridium is known to combine with sulfur to form iridium disulfide having the orthorhombic structure of iridium diselenide. The pyrite structure, space group Pa $\bar{3}$, is in general a densely packed arrangement and tends to be favored when synthesis is attempted between transition metals and groups Va and VIa elements at high pressure. Munson [179] reported the synthesis of a new pyrite phase IrS_{1.9} prepared from a 2:1 mole ratio of sulfur and iridium. The mixture was subjected to 1500 °C at a pressure of 60 kbar. The unit cell dimension of the pyrite-type cell of IrS_{1.9} is $a = 5.68 \text{ \AA}$.

11.10. MoS₂

Bridgman [54] measured the electrical resistance of molybdenite MoS₂ at room temperature up to 100 kbar pressure. The sample, a cleaved single crystal specimen, exhibited reversible electrical resistance discontinuity (drop by a factor of 2.77) at approximately 20 kbar. This result is based upon one run. The crystal structure of MoS₂ is three layered rhombohedral, 3R-MoS₂.

11.11. NbS₂

Niobium disulfide forms two principal phases under normal conditions, one a two layered hexagonal and the other a three layered rhombohedral modification designated 2H-NbS₂ and 3R-NbS₂, respectively. The coordination number of Niobium is 6 but the locations of the sulfur atoms are the corners of a trigonal prism as opposed to octahedral coordination. High pressure synthesis [151] employed stoichiometric mixtures of the niobium and sulfur subjected to a pressure of 90 kbar and various temperatures up to a maximum of 1350 °C. Calibration of the pressure cell was based on the fixed points in bismuth taken at 25.4, 27, and 89 kbar; tin 113–115 kbar.

Below 600 °C there was no reaction, while between 600 and 800 °C a mixture of phases appeared of which the composition and structure could not be identified. In the range 800 to 1000 °C 3R-NbS₂ was formed and from 100 to 1200 °C both 3R-NbS₂ and 2H-NbS₂ were present in the samples. Above 1200 °C a new high pressure form designated NbS₂(II) was synthesized. On the basis of powder x-ray data NbS₂(II) is a new 4 layered hexagonal polytype indexed on the basis of 4H-NbSe₂ but with a different space group. The unit cell parameters are $a = 3.33 \text{ \AA}$, $c = 23.8 \text{ \AA}$ ($c/a = 4.18$). On the basis of the intensity data, NbS₂(II) appears to be isostructural with 4H-TaSe₂ which has the space group $P6_3/mmc$. The atomic coordinates were refined by trial and error to a residual of 0.216. In contrast to trigonal prismatic coordination for the 3R- and 2H-polytypes of NbS₂, the high pressure polytype (4H-NbS₂) of NbS₂(II) has a mixed coordination scheme consisting of both trigonal prismatic and octahedral coordination. NbS₂(II) is stable in air but annealing in a vacuum for 10 hours produces a transformation to the 3R-polytype.

NbS₂(II) has a superconducting transition at 2.9 K. Each of the polytypes 2H-, 3R- and 4H- of NbS₂ exhibit superconductivity.

11.12. PbS₂

Silverman [231] reported the preparation of two high pressure phases of PbS₂. Only the monosulfide had been previously known. A hexagonal CdI₂-type PbS₂ was prepared by reacting PbS + S in the 1:2 ratio at 20 kbar and 1600–1800 °C. The only successful synthesis carried out was with excess sulfur present. The hexagonal CdI₂-type unit cell of PbS₂(I) has the dimensions $a = 3.89 \text{ \AA}$ and $c = 5.91 \text{ \AA}$ ($Z = 4$).

The other phase PbS₂(II) was prepared from a reaction of the Pb:3S elemental mixture at 45 kbar and 1500 °C held for 5 minutes. PbS₂(II) can be indexed as tetragonal with a

KN₃-type structure. The unit cell dimensions are $a = 6.10 \text{ \AA}$ and $c = 7.48 \text{ \AA}$ ($Z = 4$).

11.13. PdS₄

An orthorhombic palladium disulfide may be prepared by heating palladium dichloride and an excess of sulfur in an evacuated quartz tube for 4 days. The structure of PdS₂ prepared in this manner is space group $Pbca$ ($a = 5.46 \text{ \AA}$, $b = 5.54 \text{ \AA}$, $c = 7.53 \text{ \AA}$) and is closely related to the pyrite structure which places the cation in a nearly perfect octahedral environment. Munson and Kasper (180) prepared a second orthorhombic form of PdS₂ ($a = 5.51 \text{ \AA}$, $b = 5.56 \text{ \AA}$, $c = 7.16 \text{ \AA}$) by reacting a mixture of the elements of PdS₂(I) at 1450 °C and 63 kbar for 5 minutes. PdS₂(II) decomposes to PdS and sulfur at 250–300 °C.

The x-ray data of PdS₂ indicates that PdS₂(II) is very similar to PdS₂(I). Both are derived from the pyrite structure by an elongation of the c -axis. However, the elongation of PdS₂(II) is not as great as that of PdS₂(I). The measured and calculated density of PdS₂(II) is 4.92 g/cm³ and 5.17 g/cm³ respectively. PdS₂(II) is not superconducting as is PdS₂(I).

11.14. SiS₂

The synthesis of a high pressure polymorph of SiS₂ has been reported in two separate studies. The first synthesis reported by Silverman and Soulen [230] consisted of a 1Si:2.2S mixture which was subjected to a temperature of 1480 °C at 75 kbar for a duration of 2 minutes. On the basis of x-ray powder patterns SiS₂(II) was indexed in the tetragonal crystal system with $a = 5.43 \text{ \AA}$ and $c = 8.67 \text{ \AA}$. Measured and calculated densities for SiS₂(II) are 2.23 g/cm³ and 2.40 g/cm³, respectively, compared with 2.05 g/cm³ calculated for SiS₂(I). A contemporary study of the silicon-sulfur system by Prewitt and Young (198) reported the synthesis of single crystals of SiS₂(II). The structure of SiS₂(II) consists of SiS₄ tetrahedra which share vertices to form three dimensional networks as compared to SiS₂(I) which contains chains of SiS₄ tetrahedra in which the tetrahedra in each chain shares edges. In this work the unit cell dimensions are $a = 5.420 \text{ \AA}$, $c = 8.718 \text{ \AA}$ and $Z = 4$. Measured and calculated densities are 2.40 and 2.37 g/cm³, respectively. The space group of SiS₂(II) is $I\bar{4}d$. Silicon atoms occupy position 4a (0,0,0) while sulfur occupies positions 8d ($x = 0.227$; $y = 0.25$; $z = 0.125$).

11.15. SrS₂

Polycrystalline SrS₂ was synthesized under normal pressure by Lutz [162,163] who only published d -values with no crystal or structural data. Single crystal SrS₂ was prepared by Kawada et al. [139] by heating a sulphur excess mixture of Sr and S up to 900 °C at a pressure of 20 kbar. SrS₂ is tetragonal ($I4/mcm$) with $a = 6.095 \text{ \AA}$, $c = 7.616 \text{ \AA}$, $Z = 4$ and $\rho_{\text{exp}} = 3.56 \text{ g/cm}^3$. The structure is isotypic with that of the CuAl₂ group intermetallic compounds.

11.16. ZnS₂

Pyrite type ZnS₂ [33] mixed with some unreacted starting materials was obtained as a bright yellow microscopic

powder by the reaction of ZnS + S at 65 kbar for 4–6 hours at 400–600 °C followed by a rapid quench to room temperature. X-ray diffraction powder patterns of all the ZnS₂ compositions prepared showed all samples having the same unit cell size $a = 5.9542 \text{ \AA}$, indicative of ZnS₂ stoichiometry.

11.17. Rare Earth Sulfides

The rare earth disulfides series has been investigated by a number of researchers. Only the disulfides at the lower end of the series can be synthesized at atmospheric pressure. Bilitz [31] reported the synthesis of LaS₂ and CeS₂. Flahaut et al. [104] reported that the disulfides of La, Ce, Pr, Nd, and Sm all had the same “cubic” structure. They also reported the synthesis of the sulfides of Eu, Gd, Dy, and Y which were all nonstoichiometric and having the tetragonal structure. Ring and Tecotzky [202] reported the synthesis of the tetragonal disulfides of Tb, Ho, and Er.

The tetragonal disulfide has the LaS₂ type structure, space group P4/nmm and is related to the ErSe₂ subcell [206] by the relation $a(\text{LaS}_2) = 2a(\text{ErSe}_2)$ and $c(\text{LaS}_2) = c(\text{ErSe}_2)$. The cubic rare earth disulfide structure was indexed on the basis of the close resemblance of its x-ray pattern to that of the tetragonal rare earth disulfide. Both of these structures are assumed to be composed of 4 ErSe₂-type subcells.

On the basis of single crystal data Marcon and Pascard [166] have shown that CeSe₂ and CeS₂ both have a monoclinic structure which is pseudotetragonal and can also be viewed as pseudocubic. It is composed of 2 Fe₂As-type subcells. This apparently bears close resemblance to the structure of the “cubic” LaS₂ which is based upon 4 ErSe₂ subcells since the ErSe₂ subcell has the same structure as Fe₂As.

With the use of high pressure techniques Webb and Hall [262] were able to synthesize rare earth disulfides for the heavier region of the series. Tetragonal rare earth disulfides (P4/nmm) were prepared for Tm, Yb, and Lu. New polymorphs having the apparent cubic “LaS₂”-type structure were prepared for Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y. In this work the identification of the “cubic” and tetragonal phases was based solely upon powder x-ray diffraction data. A few of the weak superlattice reflections could not be indexed either on the basis of the subcell or supercell (figs. 22, 23, and 24).

Eliseev et al. [99] also synthesized the ytterbium disulfide at high pressure. X-ray examination confirmed the existence of two phases whose line positions were in good agreement with the work of Webb and Hall [262]. The phase of YbS₂ which Webb and Hall [262] indexed as cubic was indexed as tetragonal Fe₂As-type Eliseev et al. By refining atomic positions, using an absorption correction and assuming a deficiency of sulfur, they were able to fit the data to YbS_{1.7} with a least squares residual of 0.17 (powder data).

One important fact not mentioned in the literature in that the ErSe₂-type subcell is identical to the Fe₂As-type cell. In all the studies cited in reference to the “cubic” rare earth disulfides one (CeS₂) was based upon single crystal data. All structure determinations and attempts to index powder data were based upon the Fe₂As-type unit cell of subcell. Eliseev et al. did not publish their d -values but attempts to fit the

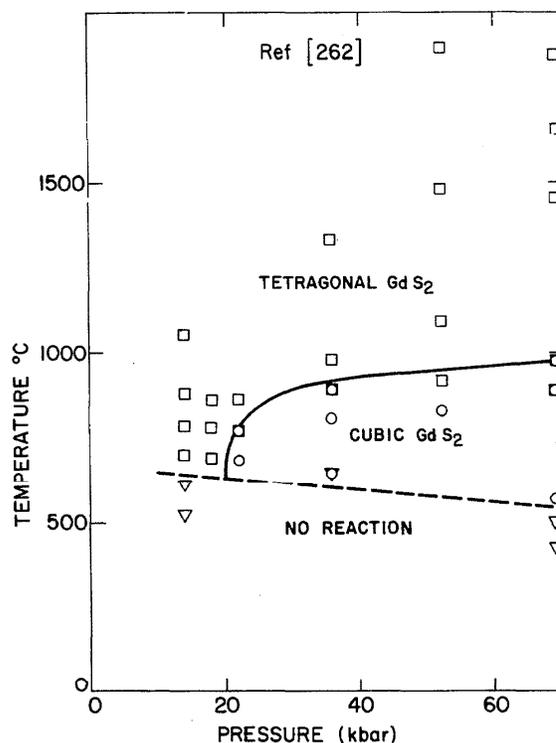


FIGURE 22. Reaction product diagram for Gd + 2S.

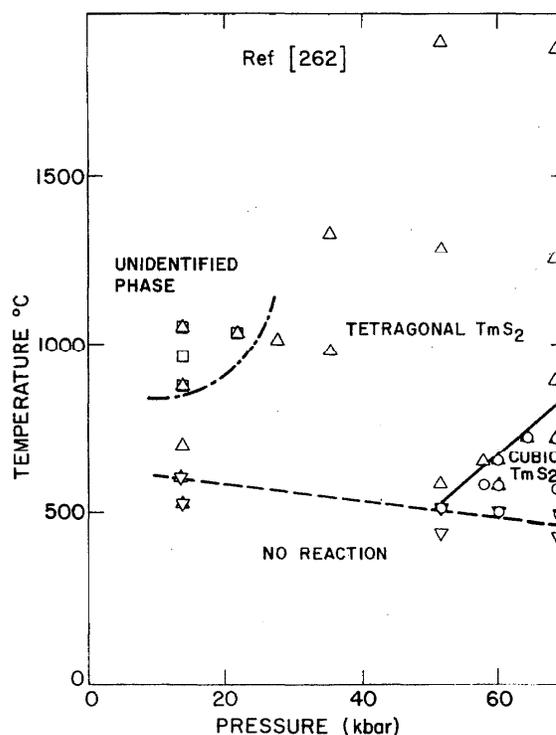


FIGURE 23. Reaction product diagram for Tm + 2S.

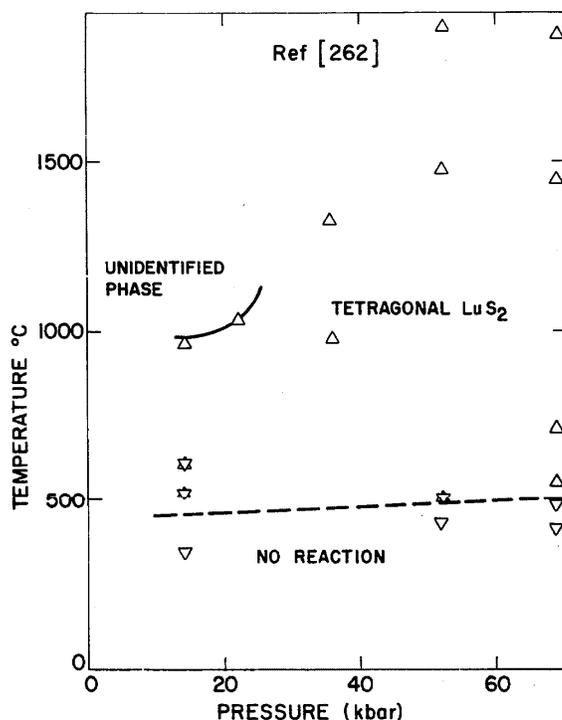


FIGURE 24. Reaction product diagram for Lu + 2S.

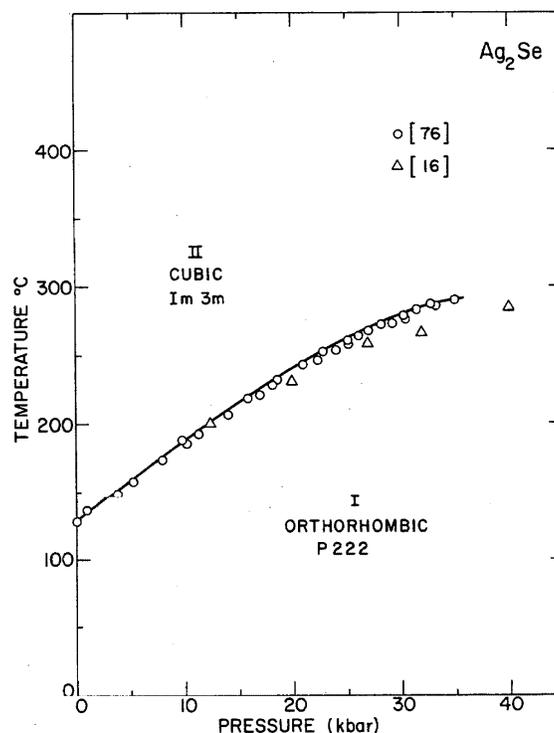
“cubic” data of Webb and Hall [262] with their lattice parameters left 5 of the cubic lines unindexed. In addition to these lines, Webb and Hall [262] mentioned that they were unable to index 3 lines in their “cubic” YbS_2 pattern. It is felt that the work of Eliseev is no more definitive than that of Webb and Hall [262] other than all data seem to point to the view that the Fe_2As -type subcell is basic to the true YbS_2 structure. Certainly further investigation is needed on these compounds.

12. Selenides

12.1. Ag_2Se

The $\text{Ag}_2\text{Se(I)}\text{-Ag}_2\text{Se(II)}$ or commonly known $\alpha\text{-}\beta$ phase boundary has been investigated up to the region of 50 kbar and 300 °C. At atmospheric pressure a sharp change in resistivity occurs when Ag_2Se is transformed from the low temperature orthorhombic ($\alpha\text{-Ag}_2\text{Se}$) to the high temperature body centered cubic form ($\beta\text{-Ag}_2\text{Se}$). This method was employed by Banus [16] to determine the pressure dependence of the phase boundary up to 47 kbar. The samples were polycrystalline and the pressure cells were calibrated with the Bi I-II (25.4 kbar) and the Tl I-II (37 kbar) transitions. The transition temperatures were taken on increasing temperature cycle. The type of thermocouple or information about any thermocouple correction and calibration was not discussed. Up to about 15 kbar the sign of the temperature coefficient of resistivity is negative for $\alpha\text{-Ag}_2\text{Se}$ and positive for $\beta\text{-Ag}_2\text{Se}$. Above 15 kbar the temperature coefficient of resistivity for both phases. Room temperature x-ray patterns showed no phase change up to 45 kbar.

The Ag_2Se ($\alpha\text{-}\beta$) phase boundary was also studied by

FIGURE 25. Phase diagram for Ag_2Se .

Clark and Rapoport [76] up to a pressure of 40 kbar and a temperature of 300 °C by differential thermal analysis. The agreement of this work with Banus (16) is good up to 20 kbars but beyond this, temperatures differ by as much as 15–20 °C. Banus noted temperature hysteresis as high as 15–25 °C while the maximum reported by Clark and Rapoport was 3 °C. As a result of better reproducibility and the additional temperature calibration details, the curve of Clark and Rapoport is considered more accurate (see fig. 25 for Ag_2Se phase diagram).

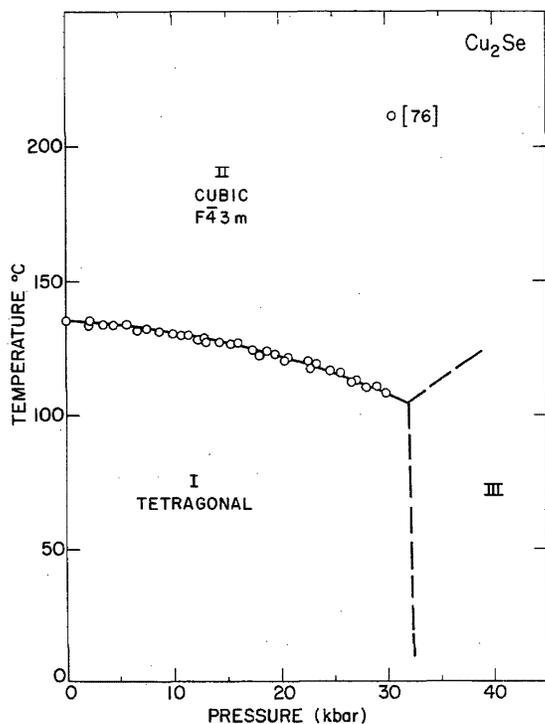
Using the value $dT/dP = 7.0$ °C/kbar reported by Roy et al., Banus [16] determined the heat of transformation as $\Delta H_t = 2.19$ kcal/mol. Taking the most recent value of $dT/dP = 6.02$ °C/kbar, then $\Delta H_t = 2.54$ kcal/mol. The calculated values of ΔH_t range from 1.61 to 2.54 kcal/mol. The high uncertainty arises from the uncertainty in ΔV , and $dT/dP|_{P=0}$.

12.2. BiSe_2

Bismuth diselenide was prepared by the reaction of a 1:2.2 atomic ratio of Bi:Se at a pressure of 45 kbar and 1280 °C [229]. The BiSe_2 crystals were black and are stable in water, aqueous ammonia and HCl at room temperature but reacts vigorously with concentrated HNO_3 . At 275 °C BiSe_2 converts to Bi_2Se_3 . X-ray powder patterns of BiSe_2 contained over 60 lines and have not been indexed.

12.3. Cu_2Se

The atmospheric pressure high temperature phase transition in Cu_2Se was originally reported to occur at 110 °C

FIGURE 26. Phase diagram for Cu₂Se.

[107, 142]. Data published by Clark and Rapoport [76] place the transition at 135 °C. This latter result is attributed to the high purity of the sample. Clark and Rapoport followed the Cu₂Se(I) Cu₂Se(II) phase boundary up to 30 kbar where the DTA signals disappeared completely. This behavior was reversible and repeated from run to run. A thorough search at pressures up to 41 kbar failed to give any indication of additional phase transitions. Clark and Rapoport postulate that in the 30 kbar region the Cu₂Se(I)-Cu₂Se(II) phase boundary has a negative slope with $dT/dP = -0.6$ °C/kbar (fig. 26).

It is impossible to prepare Cu₂Se of stoichiometric composition. The unit cell dimension of the cubic phase decreases considerably with copper deficiency.

Cu₂Se(II) which is the high temperature phase, has a disordered cubic structure with the unit cell dimension $a = 5.840$ Å at 170 °C. The room temperature phase is orthorhombic.

12.4. MoSe₂

A three-layer rhombohedral (3R) polytype of MoSe₂ isostructural with rhombohedral MoS₂ is formed from 2H-MoSe₂ at high pressures and high temperatures [253]. The region in which 3R-MoSe₂ is formed is above 30–40 kbar and above 1400 °C. The unit cell dimensions of 3R-MoSe₂ are $a = 3.292$ Å and $c = 19.392$ Å.

12.5. NbSe₂

Niobium diselenide forms three principal phases under normal conditions, a two layered hexagonal structure (2H-NbSe₂), a three layered rhombohedral structure (3H-NbSe₂)

and a four layered hexagonal structure (4H_p-NbSe₂). The cation coordination is all a six fold trigonal prismatic type as previously discussed for NbS₂. Synthesis conditions are the same as discussed for NbS₂.

The following reaction products were formed [151]: (a) below 600 °C there was no reaction, (b) between 600 and 1000 °C NbSe₄ + Nb was formed, (c) between 1000 and 1200 °C 2H-NbSe₂ was synthesized and (d) above 1200 °C NbSe₂(II), a high pressure phase was obtained. NbSe₂(II) consists of a hexagonal 4 layered cell (4H₀-NbSe₂) isostructural to NbS₂(II). It should be noted that there are now two 4H-polytypes in NbSe₂. For the 4H_p-NbSe₂ polytype the cation coordination is of trigonal prismatic type while the 4H₀-NbSe₂ polytype has octahedral cation coordination. The hexagonal unit cell dimensions are $a = 3.46$ Å, $c = 24.8$ Å, $c/a = 4.18$. The space group is P6₃/mmc with the atoms in the positions: 2Nb(1) in 2(a), 2Nb(2) in 2(b), 4Se(1) in 4(f) and 4Se(2) in 4(f). All four modifications of NbSe₂ are superconducting with the indicated critical superconducting transition temperatures.

2H-NbSe ₂	7.0 K
3R-NbSe ₂	
4H _p -NbSe ₂	6.3 K
4H ₀ -NbSe ₂	3.5 K

12.6. PbSe₂

PbSe₂ which previously had not been prepared in crystalline form was synthesized by Silverman [231]. Thus successful synthesis employed a mixture of PbSe + 2Se with excess selenium which was subjected to temperatures between 600 and 2400 °C at pressures from 20–70 kbar. This crystalline form of PbSe₂ has the tetragonal KN₃-type structure with unit cell dimensions $a = 6.36$ Å and $c = 7.63$ Å. Electrical resistance measurements with increasing pressure from 10–70 kbar showed no significant change.

12.7. PbSSe

The mixed lead dichalcogenide PbSSe which was previously unknown in crystalline form was synthesized by high pressure techniques [231]. The tetragonal KN₃-type structure was prepared by reacting PbS + PbSe + 2S + 2Se at temperatures between 600 and 2400 °C and pressures in the range 20–70 kbar. The unit cell dimensions of KN₃-type PbSSe are $a = 6.27$ Å and $c = 7.57$ Å with $Z = 4$ and $\rho_c = 7.15$ g/cm³.

12.8. SmSe₂

SmSe₂ was prepared from a stoichiometric ratio of the elements at a pressure of 80 kbar in the temperature range 1200 to 2000 °C. The SmSe₂ sample gave a single phase x-ray powder pattern which indexed to a tetragonal structure with $a = 4.100$ Å and $c = 8.275$ Å. The density calculated from these unit cell dimensions is 7.32 g/cm³ and the measured density is 7.23 g/cm³ [13].

12.9. Transition Metal Selenides

Transition metal dichalcogenides of Mn, Fe, Co, Ni, Cd, and Cu have been reported to occur in CdI₂, marcasite,

or pyrite type structures. For a specific composition the density of the transition metal dichalcogenide increases in the order $\text{CdI}_2 < \text{marcasite} < \text{pyrite}$. Several of these MX_2 compounds do not occur normally with the pyrite type structure. Since the pyrite modification is the most dense structure-type, then one would expect that high pressure and high temperature would induce the transformation marcasite of $\text{CdI}_2 \rightarrow \text{pyrite}$.

Bither et al. [32,33,34] reported the synthesis of three series of compounds: CuSSe , CuSe_2 , FeSe_2 , and CdSe_2 , ZnSe_2 all with the pyrite structure. These compounds were prepared from stoichiometric ratios of the elements reacted at 65 kbar and 1000–1200 °C for 1–3 hours. This was followed by a slow cool to 400 °C and a quench to room temperature.

The copper dichalcogenides with one unpaired d-electron show metallic conductivity and superconductivity with critical temperatures ranging from 1.3 to 2.4 K. FeSe_2 is a semiconductor.

12.10. Rare Earth Selenides

The rare earth diselenides of the elements from lanthanum through gadolinium with the exception of Eu were synthesized by Benacerraf et al. [25]. Wang and Steinfink [260] synthesized the compounds of La, Ce, Nd, Gd, Dy, Ho, and Er and attempted the synthesis of YbSe_2 . Kafalas and Finn [134] reported the synthesis of Samarium polyselenide of varying composition ($\text{SmSe}_{1.9}$ to $\text{SmSe}_{2.03}$) at 40 kbar and 600 °C.

Webb and Hall [261] reported the synthesis of TmSe_2 , YbSe_2 , and LuSe_2 in the pressure range 14–70 kbar and temperature range of 400–1900 °C. These compounds crystallize

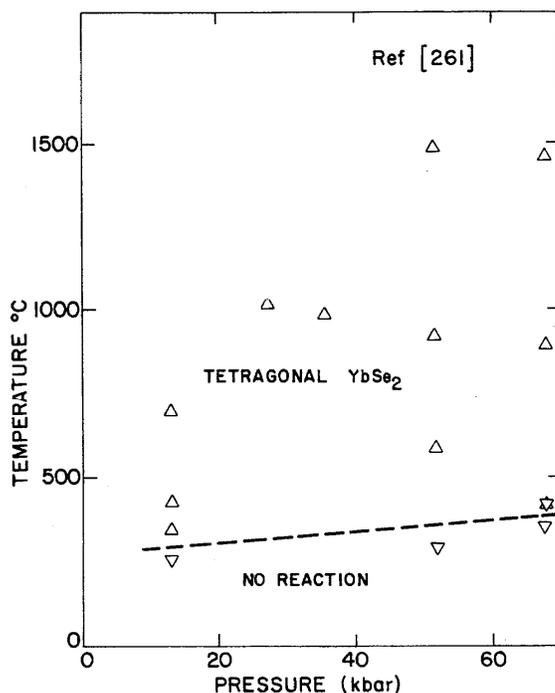


FIGURE 27. Phase diagram for YbSe_2 .

in the ErSe_2 (LaTe_2 -type) structure (fig. 27).

Several different studies have been made of the x-ray crystallography. Eliseev and Kuznetsov [98] reported that $\text{NdSe}_{1.9}$ was isostructural with LaTe_2 which has the tetragonal space group $P4/nmm$. Wang and Steinfink [260] studied ErSe_2 and found it to have a tetragonal subcell of the $P4/nmm$ space group from the strong reflections, but a number of weak reflections which were not observed for LaSe_2 and CeSe_2 . The indexing of these reflections was accomplished on the basis of an orthorhombic supercell composed of 24 tetragonal subcells. Refinement of the structure was accomplished for the subcell but could not be achieved for the supercell. Marcom and Pascarel [166] reported that CeSe_2 is monoclinic with the $P2_1/a$ space group and a pseudo tetragonal structure. Due to the lack of refinement for the supercell of ErSe_2 and the lack of weak supercell reflections in CeSe_2 , the high pressure phases TmSe_2 , YbSe_2 and LuSe_2 have been indexed on the basis of the tetragonal subcell. A number of weak lines consequently do not fit in this indexing scheme.

13. Tellurides

13.1. Ag_2Te

The pressure-temperature phase diagram of Ag_2Te (fig. 28) is fairly complicated and has at least three known atmospheric pressure solid phases from room temperature up to the melting point. The high pressure-high temperature region of Ag_2Te was first investigated by Banus and Finn [17] in the range up to 25 kbar and 250 °C. They employed a combination of techniques: electrical resistivity, differential

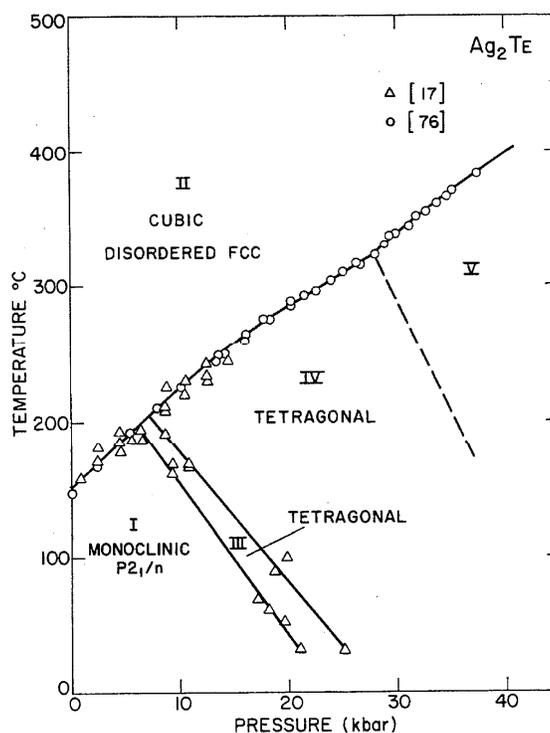


FIGURE 28. Phase diagram for Ag_2Te .

thermal analysis and x-ray diffraction analysis at high pressure.

The Ag₂Te(II)-Ag₂Te(III) boundary was determined by a combination of electrical resistivity and DTA measurements. In the electrical resistivity measurements at approximately 8 kbar an abrupt increase in the slope of the phase boundary was noted which suggested the presence of a triple point. Room temperature resistivity measurements confirmed the new phase boundary at a pressure of 22–25 kbar. The resistivity pressure trace showed a sharp increase at 22.5 kbar and an abrupt drop at 25 kbar confirming the existence of two separate but closely spaced polymorphic transitions. Quasi hydrostatic resistance measurements to 90 kbar duplicated the resistivity trace at 22.5 and 25 kbar. Above 26 kbar the resistivity increased slowly by about 15 percent to a maximum between 44 and 48 kbar and gradually decreased by approximately 20 percent to 90 kbar. The high pressure phases were both indexed as tetragonal on the basis of in situ powder x-ray diffraction data. The proposed unit cells appear to be identical based upon the cell parameters but relative intensities of corresponding lines in the two x-ray patterns do not agree.

Clark and Rapoport [76] extended the study of Banus and Finn [17] up to 40 kbar and 400 °C. In the region of 30 kbar and 325 °C there was a slight upward change in the curvature of the phase boundary which is an indication of a new triple point and a new high temperature high pressure phase region. In these measurements the temperature hysteresis was 4 °C between Ag₂Te(II)-Ag₂Te(III). Along the Ag₂Te(II)-Ag₂Te(V) boundary the hysteresis increased to 20 °C and along the proposed Ag₂Te(II)-Ag₂Te(VI) boundary it reduced to about 12 °C. This behavior is no doubt characteristic of the different phase regions. In the region where the measurements overlap, the data of Clark and Rapoport [76] are considered more accurate due to the significantly lower hysteresis.

13.2. AuTe₂

AuTe₂ exists in nature in two different crystallographic forms, the monoclinic mineral calaverite and the orthorhombic mineral krennerite. Adams and Davis [2] reported a pressure induced polymorphic transition in calaverite at 20 ± 2 kbar. The x-ray data were collected at high pressure resulting in only 4 diffraction peaks. The authors reported two different possible tetragonal unit cells of density 9.94 and 10.74.

The associated unit cell dimensions are $a = 5.25 \text{ \AA}$, $c = 5.48 \text{ \AA}$ and $a = 6.13 \text{ \AA}$, $c = 3.72 \text{ \AA}$, respectively. Correlation with a known structure type was not successful and it is recommended that this transition be re-examined in a diamond anvil pressure cell.

13.3. Transition Metal Tellurides

Transition metal dichalcogenides of Mn, Fe, Co, Ni, and Cu have been reported to occur in CdI₂, marcasite, or pyrite structures. Several of these compounds do not normally occur with the pyrite type structure. Since the pyrite modification is the most dense structure-type then one would expect that high pressure and high temperature

would induce the transformation from marcasite or CdI₂ to pyrite.

Bither et al. [32,33] reported the synthesis of two series of compounds: CuSeTe, CuTe₂ and FeTe₂, CoTe₂, NiTe₂ all with the pyrite structure. These compounds were prepared from stoichiometric ratios of the elements reacted at 65 kbar and 1000–1200 °C for 1–3 hours. This was followed by a slow cool to 400 °C and a quench to room temperature.

The copper dichalcogenides with one unpaired *d*-electron show metallic conductivity and superconductivity with critical temperatures ranging from 1.3 to 2.4 K. FeTe₂ ($a = 6.29 \text{ \AA}$), CoTe₂ ($a = 6.310 \text{ \AA}$), and NiTe₂ ($a = 6.374 \text{ \AA}$) are all metallic.

13.4. Rare Earth Tellurides

Compounds of the type RTe_{2-x} ($0 \leq x < 0.3$) have been reported for the rare earth component R = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, and Yb. These RTe_{2-x} compounds are isomorphous having a tetragonal structure with space group P4/nmm. Since the Te is more compressible than R, high pressure should favor the synthesis of RTe_{2-x} for the smaller end of the series where R = Ho, Er, Rm, and Lu.

Cannon and Hall [60] reported the successful synthesis of these RTe_{2-x} (R = Y, Ho, Er, Tm, Lu) compounds with maximum pressures ranging from 3 to 26 kbar. Increasing pressure is required with increasing atomic number of the rare earth component to form the polymorphs. Synthesis occurred over a fairly broad range of temperature from 450 up to 1500 °C (fig. 29).

Each of the RTe_{2-x} compounds is silver in appearance and unstable. X-ray data showed no decomposition in 15 days but complete decomposition after 80 days. When heat-

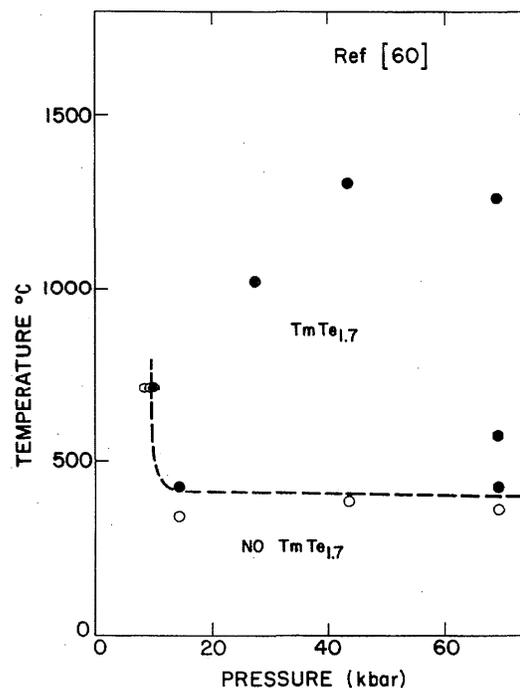


FIGURE 29. Reaction Product diagram for Tm + 1.7Te.

ed in a vacuum HoTe_{2-x} remained stable to 260 °C but decomposed at 340 °C. X-ray studies have shown that these new compounds are isostructural to their lower molecular weight analogs.

14. Mixed Cation Transition Metal Dichalcogenides

Numerous ternary mixed cation transition metal dichalcogenides of the composition $\text{M}_x\text{M}'_{1-x}\text{Y}_2$ ($\text{M}, \text{M}' = \text{Zn}, \text{Cd}, \text{Cu}, \text{Ni}, \text{Mn}, \text{Fe}$) with the pyrite structure have been synthesized by Birther et al. [34].

14.1. $\text{Zn}_x\text{Mn}_{1-x}\text{Y}_2$

Pyrite-type phases were prepared for $\text{Zn}_x\text{Mn}_{1-x}\text{Y}_2$ for $x = 0.35, 0.53,$ and 0.70 . Reactants of the following molar ratios were used: $0.5\text{ZnS}/1.5\text{MnS}/2.5\text{S}$, $\text{ZnS}/\text{MnS}/2.5\text{S}$, and $1.5\text{ZnS}/0.5\text{MnS}/2.5\text{S}$, respectively. The reactions were carried out at 65 kbar and 100 °C for 1 hour followed by a 5 hour cool to 875 °C and quenched to room temperature. The products obtained from these reactions were dark red single crystals with the approximate formula $\text{Zn}_{0.7}\text{Mn}_{0.3}\text{S}_2$.

Black crystals of $\text{Zn}_{0.5}\text{Mn}_{0.5}\text{Se}_2$ having the pyrite-type structure were prepared from a reaction of $0.5\text{Zn}/0.5\text{Mn}/2.2\text{Se}$ at 65 kbar and 800 °C for 1 hour followed by a 2 hour cool to 700 °C and quenched to room temperature. In the telluride system, $\text{Zn}_{0.5}\text{Mn}_{0.5}\text{Te}_2$ was synthesized from $0.5\text{Zn}/0.5\text{Mn}/2\text{Te}$ at 65 kbar and 800 °C for 2 hours. The product was a mixture comprising red crystals of ZnTe adjoined by silver crystals. X-ray examination confirmed the pyrite-type structure for the silver crystalline material.

The $\text{Zn}_x\text{Mn}_{1-x}\text{Y}_2$ compounds are semiconductors with low activation energies. As x ranges from 0 to 1, the unit cell dimension decreases and the crystals range in magnetic properties from antiferromagnetic to diamagnetic.

14.2. $\text{Cd}_x\text{Mn}_{1-x}\text{Y}_2$

The phase relations involved in the formation of the pyrite-type Cd-Mn dichalcogenide appear to be more complex than those of the analogous Zn-Mn systems and only the selenide was obtained in single crystal form suitable for characterization. Synthesis of the Cd-Mn sulfides gave a mixture of phases that comprise (a) pyrite-type $\text{Cd}_{0.35}\text{Mn}_{0.65}\text{S}_2$ ($a = 6.176 \text{ \AA}$), (b) a rock salt type $\text{Cd}_{0.5}\text{Mn}_{0.5}\text{S}$ ($a = 5.340 \text{ \AA}$) and (c) a wurtzite type $\text{Cd}_{0.5}\text{Mn}_{0.5}\text{S}$ ($a = 4.07 \text{ \AA}, c = 6.62 \text{ \AA}$). With the same starting materials and slightly different reaction conditions the product contained pyrite-type $\text{Cd}_{0.6}\text{Mn}_{0.4}\text{S}_2$ ($a = 6.228 \text{ \AA}$) as the main phase mixed with α -MnS and (Mn,Cd)S products as previously described. In the Cd-Mn selenide system high pressure synthesis also resulted in a mixture of phases in the product containing red-brown crystals of wurtzite (Cd,Mn)Se ($a = 4.21 \text{ \AA}, c = 6.94 \text{ \AA}$) and black crystals having the pyrite-type structure with composition $\text{Cd}_{0.45}\text{Mn}_{0.55}\text{Se}_2$. Excess Se was also present. Reaction of (Cd,Mn)Te at high pressure gave a product comprising (a) the pyrite-type and (b) sphalerite-type (Cd,Mn)Te plus unreacted Te. The phases could not be separated for characterization.

14.3. $\text{Zn}_x\text{Cd}_{1-x}\text{Y}_2$

Reaction of equimolar amounts of ZnS/CdS plus excess sulfur at 65 kbar gave a phase mixture comprising (a) pyrite-type $\text{Zn}_x\text{Cd}_{1-x}\text{S}_2$, with (b) unreacted ZnS and CdS. By varying the reaction temperature, cooling rate and quench temperature compositions ranging from $x = 0.5$ to $x = 0.71$ were analyzed. Comparable reactions of Zn/Cd/4Se at 65 kbar gave a microcrystalline product consisting of a mixture of phases comprising (a) ZnSe, (b) CdSe, (c) unreacted Se and (c) $\text{Zn}_x\text{Cd}_{1-x}\text{Se}_2$ (with x ranging from 0.32 to 0.45). The pyrite-type phases had very high electrical resistances in agreement with the semiconducting properties of their end members.

14.4. $\text{Zn}_x\text{Cu}_{1-x}\text{Y}_2$

High pressure synthesis of the Zn-Cu disulfides and diselenides have been achieved over the entire range $x = 0$ to $x = 1$. The $\text{Zn}_x\text{Cu}_{1-x}\text{Y}_2$ compounds are metallic and those with $x < 0.2$ are superconductors.

14.5. $\text{Cd}_x\text{Cu}_{1-x}\text{Y}_2$

Reaction of 0.1 CdS_x (amorphous)/0.9CdS/S at 65 kbar and 700 °C yields a purple microcrystalline product of the pyrite type structure for which $x = 0.04$. Similar reactions for the selenide system result in composition for which $x = 0.04$ to 0.06.

14.6. $\text{Mn}_x\text{Cu}_{1-x}\text{Y}_2$

Pyrite type $\text{Mn}_x\text{Cu}_{1-x}\text{S}_2$ compounds were obtained with compositions ranging from $x = 0.01$ –0.08. In the selenide and telluride systems the compounds $\text{Mn}_{0.55}\text{Cu}_{0.45}\text{Se}_2$ and $\text{Mn}_{0.65}\text{Cu}_{0.35}\text{Te}_2$, respectively, were synthesized at 65 kbar and 800 °C. The $\text{Mn}_x\text{Cu}_{1-x}\text{Y}_2$ compounds are metallic.

14.7. $\text{Cu}_x\text{Fe}_{1-x}\text{S}_2$

Pyrite-type compounds of $\text{Cu}_x\text{Fe}_{1-x}\text{S}_2$ were synthesized for a narrow range in composition ($x = 0.73$ –0.84) suggesting an approximate composition Cu_3FeS_8 . On the basis of microcrystalline samples, qualitative measurements indicated metallic conductivity. A broad superconducting transition was observed to occur below 1.7 K.

14.8. $\text{Ni}_x\text{Fe}_{1-x}\text{Y}_2$

(Ni,Fe) S_2 has been prepared at high pressure with $x = 0.76$ ($a = 5.702 \text{ \AA}$). The analogous pyrite-type diselenides have been prepared with compositions $x = 0.4$ –0.6 ($a = 5.525 \text{ \AA}$ – 5.890 \AA). These Ni-Fe dichalcogenides are metallic conductors.

14.9. $\text{Cr}_x\text{Co}_{1-x}\text{S}_2$

The pyrite-type compound CoS_2 is ferromagnetic. Solid solutions of CoS_2 , FeS_2 , and NiS_2 have been prepared at atmospheric pressure but CrS_2 was unknown. By the use of high pressure-high temperature reactions Donohue et al. [92a] found that it was possible to replace some of the Co in CoS_2 with Cr so as to produce pyrite-type solid solutions

Cr_xCo_{1-x}S₂. The new pyrite phases Cr_xCo_{1-x}S₂ (0 < x < 0.4) were prepared at 65 kbar and 1100–1200 °C held for about 2 hours. Magnetic measurements indicate that the saturation magnetization decreases while the Curie temperature increases dramatically with increasing x. T_c reaches a maximum above temperature at x ~ 0.30. The cubic (pyrite-type) unit cell dimension varies from 5.535 Å for x = 0 to 5.558 for x = 0.39.

15. Alloy and Intermetallic Compounds

15.1. AuX₂ (X = Al, Ga, In)

Gold forms intermetallic compounds of the AB₂ type with Al, Ga, and In having the cubic fluorite structure. Upon melting, these compounds undergo a volume contraction, which is an indication of a negative slope in the fusion curve. In the region of the melting curve minimum one should, therefore, find a triple point and at least one high pressure modification (figs. 30, 31 and 32).

The melting curves for AuAl₂, AuGa₂ and AuIn₂ were measured by differential thermal analysis by Storm et al. [246] in the range up to 50 kbar. The experiments were carried out in the belt press and piston-cylinder type apparatus. Either Chromel alumel (Cr-Al) or Pt, Pt-Rh thermocouples were used depending on the temperature range being covered; however, no correction was made for the pressure effect on the thermal emf. The belt apparatus was calibrated to the transitions in Bi(I-II) at 25.4 kbar, Tl(II-III) at 37 kbar and Ba(I-II) at 58.4 kbar at room temperature as standards.

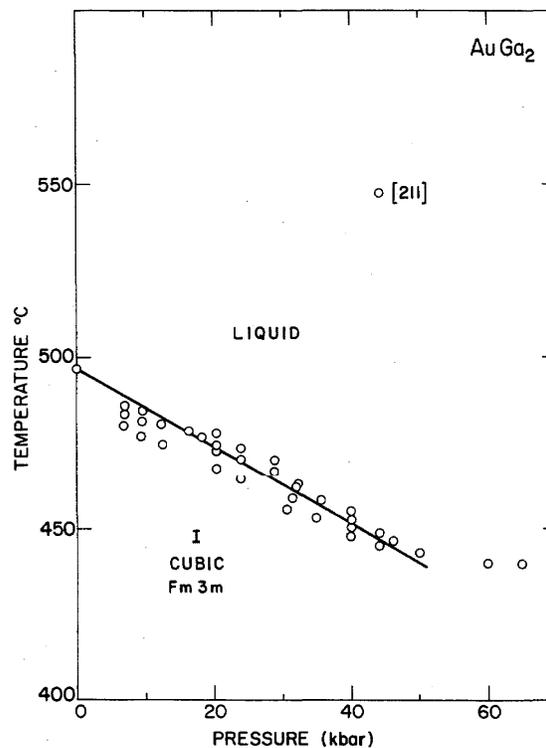


FIGURE 31. Melting curve for AuGa₂.

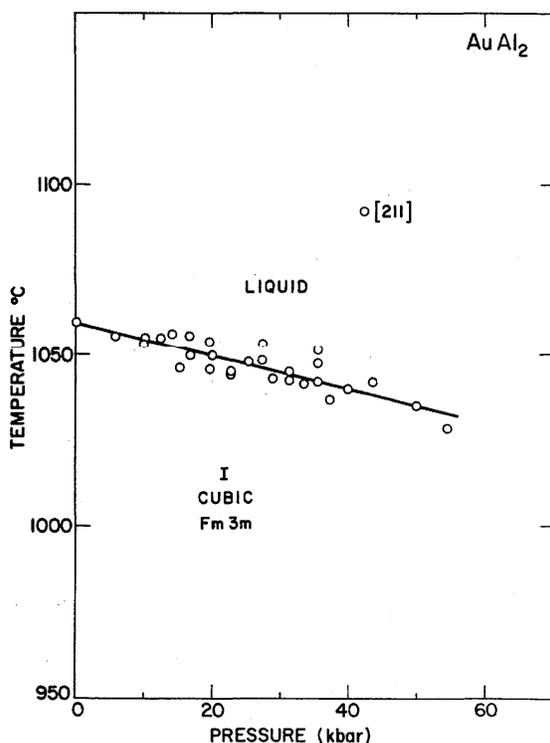


FIGURE 30. Melting curve for AuAl₂.

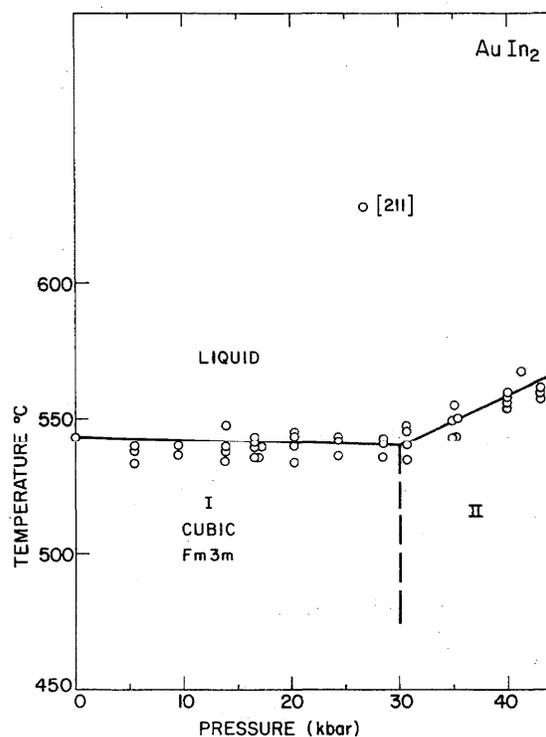


FIGURE 32. Melting curve for AuIn₂.

No correction was made for effect of high temperature on the internal pressure on the sample. The stated accuracies are ± 2 kbar up to 40 kbar, ± 3 kbar above 40 kbar for pressures and ± 2 °C for temperature. These values are overly optimistic since the spread of the data points has an average range of 17 °C for AuAl₂ and 12 °C for AuGa₂ and AuIn₂. Due to the scatter of the data the best fit will be assumed to follow the central tendency of the data points.

The melting curves all initially decrease with increasing pressure but only one, AuIn₂, shows a triple point at the minimum at about 30 kbar and 542 °C. Above 30 kbar the melting curve has a positive slope. There have been no reported attempts to determine the AuIn₂(I)-AuIn₂(II) phase boundary or determine the AuIn₂(II) crystal system.

15.2. LaCo₂

The rare earth cobalt RCo₂ series of compounds crystallize in the face centered cubic MgCu₂-type structure. Attempts to synthesize LaCo₂ at atmospheric pressure were unsuccessful. Using high pressure techniques Robertson et al. [204] were able to synthesize LaCo₂ in the range from 10 to 65 kbar and 1050 to 1350 °C. By x-ray diffraction techniques it was verified that LaCo₂ produced at high pressure and high temperature has the cubic MgCu₂-type structure with a unit cell parameter $a = 7.449$ Å.

15.3. Magnesium Compounds

The dimagnesium compounds Mg₂X (X = Si, Ge, Sn) crystallize in the cubic antiferite structure when prepared at atmospheric pressure conditions [73]. Several researchers have studied various aspects of these compounds at high pressure. Cannon and Conlin [67] reported the existence of a new high pressure modification in each of these compounds. The new high pressure polymorphs Mg₂Si(II) and Mg₂Ge(II) were indexed as hexagonal with unit cell dimensions $a = 7.20$ Å, $b = 8.12$ Å; and $a = 7.2$ Å, $c = 8.24$ Å, respectively, while Mg₂Sn was indexed as a different hexagonal cell with $a = 13.09$ Å and $c = 13.44$ Å. These investigators were unable to assign any structure to these new polymorphs.

The next important investigation was that of Seifert [219]. In this work the metastable high pressure phases for Mg₂X (X = Si, Ge, Sn) were synthesized at 65 kbar and 600–1000 °C. They were indexed in the orthorhombic system with a suggested Ni₂Si-type (anti PbCl₂-type) structure. The range of the a/b ratio is 0.755 to 0.772 and c/b ratio is 1.384 to 1.462 for the new polymorphs. This is in very good agreement with $a/b = 0.746$ and $c/b = 1.412$ for the Ni₂Si structure suggesting that this is a plausible structure and that the high pressure phases are probably isostructural to one another.

Dyuzheva et al. [95a] also examined the structure of Mg₂Sn(II) and demonstrated that the high pressure phase produced at room temperature and 30 kbar is identically the same as the metastable quenched product which was produced at simultaneous high pressure and high temperature.

Dyuzheva et al. [95a] obtained substantially better quality x-ray patterns for Mg₂Sn(II) than the previous investigators and noted that some of their intensities did not agree with the Ni₂-Si-type structure. It was noted that some of the

discrepancies were the absence of extinctions required by space group Pnma and the presence of extra reflections not allowed. The structure proposed by Dyuzheva et al. [95a] is a distortion of the Ni₂Si-type structure indexed as hexagonal with $a = 13.18$ Å and $c = 6.99$ Å with $Z = 15$. The authors stated that the experimentally measured density of Mg₂Sn(II) was 4.1 g/cm³ and upon this basis determined the number of molecules per unit cell as 15. The calculated density for the proposed hexagonal unit cell of Mg₂Sn(II) is 6.19 g/cm³ if it contains 15 molecular units which represents a 72 percent increase in the density over that of the atmospheric pressure phase. If one were to select the number of molecules based upon the calculated density and retain the hexagonal indexing, then $Z = 9$ would yield a density of 3.71 g/cm³ and $Z = 12$ gives a density of 4.95 g/cm³ which amounts to a 3 percent and 37 percent density increase, respectively, over the atmospheric pressure phase. Neither of these values is in good agreement with the measured density. For the present report the orthorhombic Ni₂Si-type cell of Seifert [219] is considered the best selection for the structures of Ng₂Si(II), Mg₂Ge(II), and Mg₂Sn(II) on the basis of currently available experimental data. The x-ray data for these structures need to be re-examined by an independent investigator.

15.4. Rare Earth Iron Compounds

The lanthanide compounds with the formula RFe₂ has been studied by a number of investigators. The known compounds in this series are isomorphic with the MgCu₂-type structure, $Z = 8$, space group Fd3m. In this series attempts to synthesize LaFe₂, PrFe₂, NdFe₂, EuFe₂ and YbFe₂ by high temperature methods alone have been unsuccessful. Of this group, PrFe₂, NdFe₂ and YbFe₂ were successfully synthesized in the MgCu₂-type by Cannon et al., [61] at high pressure. Pressures and temperatures of 90 kbar and 1350 °C failed to produce a similar reaction in La-Fe.

This work indicates that increasing pressure is required for a successful synthesis as the size of the lanthanide component increases suggesting that the size effect is primarily responsible for the previous failures in preparing PrFe₂, NdFe₂ and LaFe₂. Gschneidner and others have suggested that the failure to form certain lanthanide compounds is due to 4f bonding effects. The compounds LaFe₂, PrFe₂, and NdFe₂ have the largest 4f bonding contribution of any of these compounds. However, it is also postulated that pressure increases 4f character and on this basis would tend to impede the function of these compounds contrary to what is observed. It is evident that this behavior is more complex than can be attributed to size effect alone but in this case and several others already discussed the size effect appears to be the major factor.

15.5. Rare Earth Manganese Compounds

The rare earth dimanganese compounds undergo a change in crystal structure as the size of the rare earth component varies. At atmospheric pressure both the light and heavy rare earths form RMn₂ compounds in the MgZn₂ (C14) Laves structure while the intermediate rare earths form RMn₂ compounds in the MgCu₂ (C15) Laves structure.

By application of high pressure simultaneously with

high temperature Eatough and Hall [97a] prepared the MgZn₂-type structure for the dimanganides of Gd, Tb, Dy, Ho, and Y which were previously known only in the MgCu₂-type structure. YbMn₂ which was previously unknown was also synthesized. Synthesis of the MgZn₂-type rare earth dimanganide phases were carried out in the range 1300 to 1400 °C and at pressures ranging from 20 to 50 kbar for the series of compounds HoMn₂ through SmMn₂, respectively. Of interest was the synthesis of SmNn₂ which had reportedly been synthesized in both phases at atmospheric pressure but required a minimum pressure of 50 kbar in this work [97a].

Laves phases of AB₂-type compounds are known with radius ratios $r(A)/r(B)$ varying from 1.05 to 1.68. Since all rare earth dimanganides fall within this range, the existence of structural transitions from hexagonal (MgZn₂-type) to cubic (MgCu₂-type) and back to hexagonal as the size of the rare earth element decreases is indicative that other effects besides radius ratios must be more important in the determination of which Laves structure is stable in this series [97a].

15.6. MnAu₂

The intermetallic compound MnAu₂ has a body centered tetragonal unit cell with the CaC₂ (C11) type structure with $a = 3.363$ Å, $c = 8.592$ Å, $Z = 2$ and $\rho_c = 15.33$ g/cm³. Neutron diffraction investigations have established that the distribution of magnetic moments in MnAu₂ is helical. These atoms lie in planes perpendicular to the c -axis of the tetragonal unit cell. Ferromagnetic ordering is observed within such planes. A magnetic field above a threshold value H_c destroys the helical arrangement and produces ferromagnetic ordering. Grazhdankina and Rodinov [113] investigated the electrical and galvanomagnetic properties of this compound over a wide range of pressures. They determined the pressure dependence of the magnetic transition temperature $dT/dP = 0.68^\circ/\text{kbar}$ and that the critical threshold value H_c decreased linearly with increasing pressure. In an extension of this work Adiatullin and Fakidov [3] found that at 12.5 kbar and 296 K (11.5 kbar at 77 K) the threshold value of the field decreased rapidly to zero. Thus at 12.5 kbar MnAu₂ undergoes a transition to the ferromagnetic state at zero field. The transition varies little with temperature. The pressure induced zero field transition in MnAu₂ was also confirmed by a sudden drop in the electrical resistance trace at high pressure.

15.7. NdRu₂

Synthesis of the hexagonal MgZn₂-type structure of NdRu₂ at high pressures and high temperatures was reported by Cannon et al. [62]. Powdered samples of Nd:Ru in the ratio of 1:2 were reacted at 1300 °C and 88 kbar. Below 78 kbar the cubic MgCu₂-type structure could be prepared while between 78 and 88 kbar both the cubic MgCu₂- and hexagonal MgZn₂-type phases were formed. Above 88 kbar only the hexagonal phase is synthesized.

15.8. SmRu₂

The di-ruthenium compound SmRu₂ crystallizes in the cubic MgCu₂-type structure when prepared at atmospheric

pressure. In the rare earth di-ruthenium series, compounds involving the lowest atomic number rare earth elements crystallize in the MgCu₂-type structure while those with the higher atomic number rare earth adopt the hexagonal MgZn₂-type structure. Since the rare earth element is more compressible than ruthenium, pressure should cause the radius ratio $r(\text{Sm})/r(\text{Ru})$ to decrease and cause samarium and ruthenium to behave more like the higher members of the series.

The hexagonal MgZn₂ form of SmRu₂ was prepared by Cannon et al. [62] under the conditions 1230 °C and 65 kbar. The product was synthesized from the reaction of a mixture of powdered Sm:Ru in the ratio 1:2.

15.9. ROs₂ (R = La,Ce,Pr)

Both CeOs₂ and LaOs₂ exist in the cubic MgCu₂-type structure. Cannon et al. [63] have shown that under a pressure of 70 kbars and temperature of 1000 °C, these compounds transform to the hexagonal MgZn₂-type structure. These synthesis were carried out in the tetrahedral anvil apparatus and x-ray identification was based upon powder samples. Experiments confirmed that the hexagonal form of CeOs₂ and LaOs₂ could be prepared at pressure as low as 6 kbar but could not be prepared at temperature above 1100 °C at any pressure. PrOs₂ can be prepared in either the cubic or hexagonal forms without the aid or pressure.

16. References

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