TABLE IV. Data and parameters for Born–Mayer equation of state.[a]

Material	α	α_r	C_r	C_{cf}	β_0	B	ρ
MnS	4.0	1.7476	···	0	1.25	0.521	0.415
MnO	3.9	1.7476	···	0	0.70	0.487	0.370
FeO	3.9	1.7476	167	43.2	0.65	0.569	0.362
CoO	3.9	1.7476	170	61.5	0.52	1.002	0.324
NiO	4.2	1.7476	190	79.5	0.50	0.961	0.324

[a] Units: $\alpha=10^{-5}$ °K^{-1}, $C_r=10^{-60}$ erg·cm^6, $C_{cf}=10^{-52}$ erg·cm^5, $\beta_0=10^{-3}$ (kbar)$^{-1}$, $B=10^{-8}$ erg, $\rho=$ Å.

TABLE V. Contribution to the "attractive" pressure from the dipole–dipole interaction and from crystal-field stabilization.

Material	Pressure (kbar)	P_{dd}	P_{cf}
FeO	0	11.1%	5.2%
	300	13.8%	6.1%
CoO	0	11.7%	7.5%
	300	13.9%	8.5%
Nio	0	13.6%	9.9%
	300	15.9%	11.1%

TABLE VI. Murnaghan constants for MnS, MnO, FeO, CoO, NiO, and FeS_2.

Material	B_0 (kbar)	B_0'	B_0/B_0' (kbar)
MnS[a]	810	3.3	240
MnO[a]	1440	3.3	430
FeO	1540	3.4	450
CoO	1905	3.9	490
NiO	1990	4.1	480
FeS_2	1480	5.5	270

[a] Low-pressure phase.

TABLE VII. Lattice parameters versus pressure—SnO_2.

V/V_0	c/c_0	a/a_0	$\frac{c/a}{(c/a)_0}$	Press (kbar)
1.00	1.000	1.0000	1.000	0
0.995	1.007	0.9942	1.013	34
0.990	1.009	0.9905	1.019	53
0.985	1.010	0.9875	1.023	68
0.980	1.011	0.9848	1.026	83
0.970	1.010	0.9798	1.031	112
0.960	1.009	0.9753	1.035	140
0.950	1.008	0.9709	1.038	169
0.940	1.006	0.9666	1.040	197
0.930	1.003	0.9629	1.042	226
0.920	0.9998	0.9593	1.042	···
0.910	0.9954	0.9562	1.042	···

Markers: LiF, Ag, Al

TABLE VIII. Lattice parameters versus pressure—MnO_2.

V/V_0	c/c_0	a/a_0	$\frac{c/a}{(c/a)_0}$	Press (kbar)
1.000	1.000	1.0000	1.000	0
0.995	1.008	0.9936	1.015	24
0.990	1.009	0.9900	1.020	38
0.985	1.009	0.9882	1.021	50
0.980	1.007	0.9865	1.021	61
0.975	1.005	0.9851	1.020	71
0.970	1.003	0.9836	1.019	80
0.965	1.000	0.9823	1.018	88
0.960	0.9980	0.9808	1.017	98
0.955	0.9956	0.9794	1.016	107
0.950	0.9935	0.9779	10.16	117
0.945	0.9910	0.9765	1.015	127
0.940	0.9888	0.9750	1.014	140

Markers: LiF, Al

at zero pressure, but here they are treated as empirical constants evaluated to give the best least-squares fit over the entire range of pressure and volume. Therefore they may not correspond exactly to the values obtained at one atmosphere. Furthermore, the calculated pressures are somewhat insensitive to the exact values of B_0 and B_0' if they are properly balanced, so one should not attempt to interpret differences of 10% or so in the constants. The coefficients for the four oxides are close. The agreement between the calculated curve and the experiment is not shown to avoid confusion on the graph. It is not substantially better than the Born–Mayer equation. The constants are listed in Table VI.

MnO and MnS exhibit a small but definite phase transition as shown from the plot of $2\theta_{111}$ vs $2\theta_{220}$ in Fig. 6. Our results could not distinguish between a tetragonal distortion and one of lower symmetry. If it

TABLE IX. Lattice parameters versus pressure—TiO_2.

V/V_0	c/c_0	a/a_0	$\frac{c/a}{(c/a)_0}$	Press (kbar)
1.000	1.000	1.000	1.000	0
0.990	0.996	0.997	0.999	7
0.980	0.992	0.994	0.998	14
0.970	0.987	0.991	0.996	21
0.960	0.982	0.989	0.993	29
0.950	0.977	0.986	0.991	38
0.940	0.973	0.983	0.990	48
0.930	0.968	0.980	0.988	60
0.920	0.963	0.977	0.985	78
0.910	0.958	0.975	0.983	102

Markers: Ag, Al

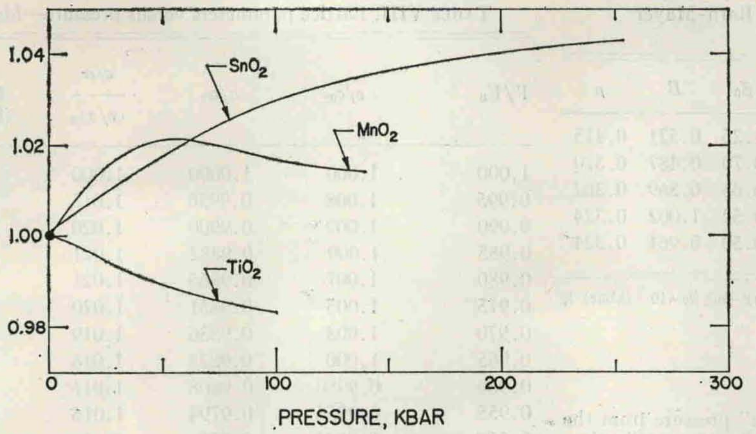

FIG. 11. $(c/a)/(c/a)_0$—SnO$_2$, MnO$_2$, TiO$_2$.

is assumed to be tetragonal, $c/a=0.98$ for both substances, within our accuracy independent of pressure. The p–v curves calculated on this basis are shown in Fig. 7.

FeS$_2$ (PYRITES)

Cubic FeS$_2$ (pyrites) is a transition-metal sulfide of a somewhat different character. It can be thought of as having a fcc structure made up of FeS$_2$ units. There is, however, no obvious valence for the iron of sulfur. Figure 8 shows V/V_0 as a function of pressure. The line represents the p–v curve calculated from the Murnaghan equation using $B_0=1480$ kbar, $B_0'=5.5$; the best least-squares fit our data. These compare very closely to the value of $B_0=1470$, $B_0'=5.3$ obtained from Bridgman's 30-kbar data.[10]

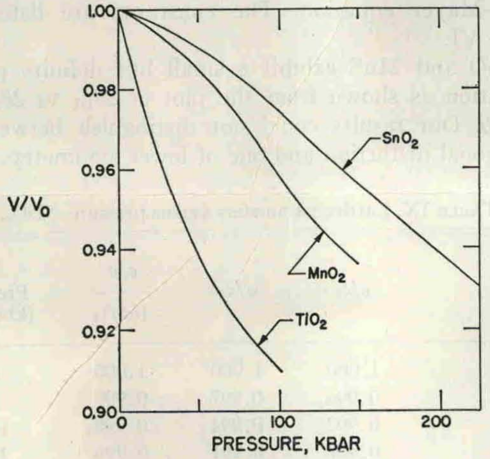

FIG. 12. V/V_0 vs pressure—SnO$_2$, MnO$_2$, TiO$_2$.

The compressibility of FeS$_2$ is much smaller than that of MnS and about the same as FeO. Since most molecular crystals have large compressibilities, at least at low pressure, the binding of FeS$_2$ must be largely covalent.

TETRAGONAL OXIDES

SnO$_2$, MnO$_2$, and TiO$_2$ all crystallize in the tetragonal structure. The 110, 211, and 101 peaks were used to establish the lattice parameters as a function of pressure. The results are shown in Tables VII to IX and in Figs. 9 to 12. The most striking feature is that for SnO$_2$ and MnO$_2$ the c axis actually increases with increasing pressure in the low-pressure region. c passes through a maximum at about 40 kbar for MnO$_2$ and about 80 kbar for SnO$_2$. The a axis decreases smoothly. The anomaly can also be seen in Fig. 12. The compressibility is very low at low pressure and then increases at pressures beyond the maximum in c. TiO$_2$ behaves more normally both as regards change of lattice parameters with pressure and with respect to compressibility. Since ionic binding requires central forces, the unusual compressibilities of MnO$_2$ and SnO$_2$ eliminate the possibility of a major component of ionic character. For all three systems, the pressure was limited by an apparent first-order phase transition. The high-pressure phase was not investigated.

Note added in proof. J. C. Jamieson has informed us that he has unpublished data for the lattice parameters of MnO$_2$, SnO$_2$, and TiO$_2$ at about 75 kbar. His results for MnO$_2$ and SnO$_2$ are in very reasonable agreement with ours, but his measurements on TiO$_2$ give a markedly smaller compressibility. Until this discrepancy is resolved our results for TiO$_2$ must be treated with considerable suspicion.

---

[10] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **77**, 187 (1949).