SnO_2, MnO_2, TiO_2

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Lattice Parameters of Nine Oxides and Sulfides as a Function of Pressure*

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The lattice parameters of seven oxides and two sulfides have been measured as a function of pressure to several hundred kilobars. FeO, CoO, NiO, MnO, and MnS have the NaCl structure or slight distortions thereof. The data can be fit by a Born–Mayer equation. For FeO, CoO, and NiO the crystal-field stabilization term contributes 5% to 15% of the total attractive pressure. FeS_2 (pyrites) has a cubic structure which can be related to the fcc lattice. Its compressibility is much less than MnS and more comparable to the oxides. The binding is apparently covalent.

SnO_2, MnO_2, and TiO_2 all have the same tetragonal structure. For SnO_2 and MnO_2 the c axis actually expands with increasing pressure at low pressure, then passes through a maximum and ultimately contracts. The compressibilities of these two compounds are low at low pressure and increase at pressures beyond the maximum in c. TiO_2 behaves more normally. It is apparent that central forces, and therefore ionic binding, contribute little to the cohesion of these crystals.

THE effect of pressure to several hundred kilobars has been measured on the lattice parameters of seven oxides and two sulfides. Five of these have the cubic NaCl structure, or a distortion of it, one (pyrites) has a different cubic structure, and three have the tetragonal SnO_2 structure. Table I summarizes the materials and sources. Table II contains the atmospheric pressure values of the lattice parameters.

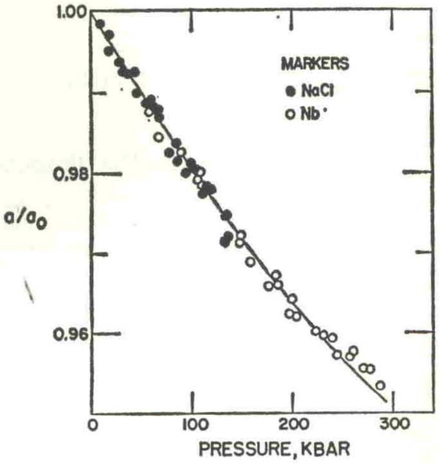

FIG. 1. a/a_0 vs pressure—FeO.

The high-pressure x-ray techniques have been described elsewhere[1] in detail. The pressures were measured by mixing markers of known compressibility mixed with the sample. The markers used are listed in the tables of results. The metal compressibilities were taken from shock-wave data[2,3] corrected to room temperature. The salt compressibilities were from previous x-ray data.[4,5] The results are discussed under the three headings mentioned above.

OXIDES AND SULFIDES WITH NaCl STRUCTURE

The oxides NiO (528°K), FeO (198°K), CoO (291°K), and MnO (126°K) and the sulfide MnS (122°K) are paramagnetic salts above their Neél temperatures which are indicated in parentheses above.

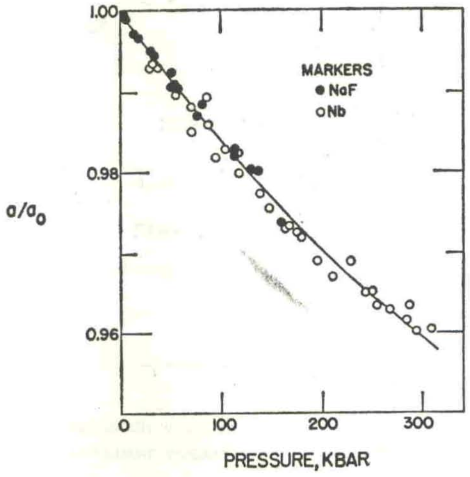

FIG. 2. a/a_0 vs pressure—CoO.

Below the Neél point they are antiferromagnetic and display slight distortions from cubic symmetry. For NiO this distortion is too small for our instruments to detect and it is treated throughout this paper at a cubic crystal. CoO transforms to an antiferromagnetic state at very low pressure.[6] If it is noncubic the distortion is

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* This work was supported in part by the U.S. Atomic Energy Commission.

[1] E. A. Perez-Albuerne, K. F. Forsgren, and H. G. Drickamer, Rev. Sci. Instr. **35**, 29 (1964).

[2] M. H. Rice, R. G. McQueen, and J. M. Walsh, Solid State Phys. **6**, 1 (1958).

[3] R. G. McQueen and S. P. Marsh, J. Appl. Phys. **31**, 1253 (1960).

[4] E. A. Perez-Albuerne and H. G. Drickamer, J. Chem. Phys. **43**, 1381 (1965).

[5] M. Pagannone and H. G. Drickamer, J. Chem. Phys. **43**, 2266 (1965).

[6] C. J. Coston, R. L. Ingalls, and H. G. Drickamer, Phys. Rev. **145**, 409 (1966).

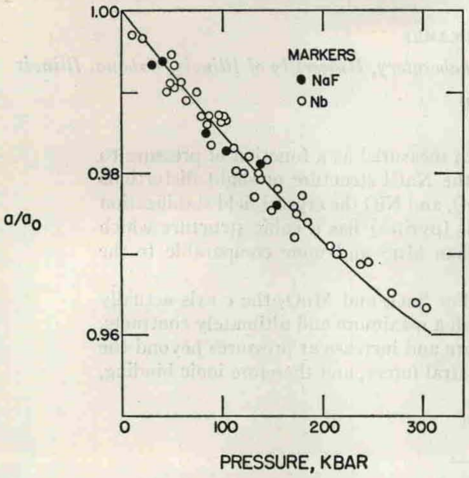

FIG. 3. a/a_0 vs pressure—NiO.

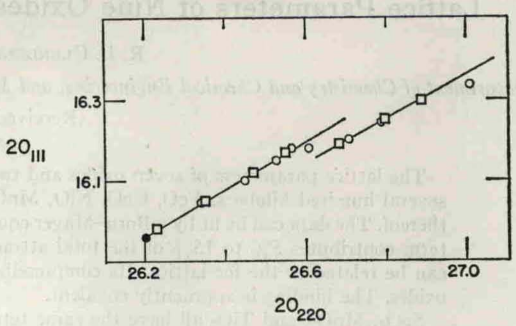

FIG. 6. $2\theta_{111}$ vs $2\theta_{220}$—MnO.

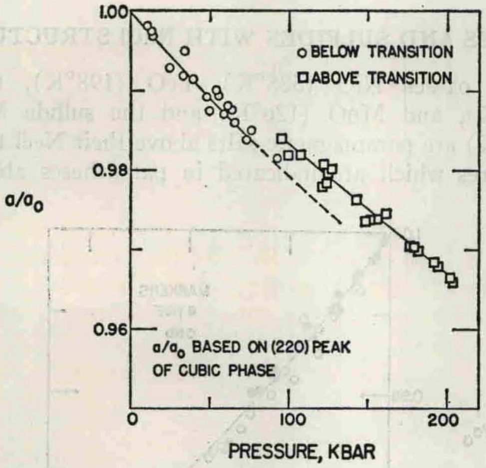

FIG. 4. a/a_0 vs pressure—MnO (calculated from 220 peak).

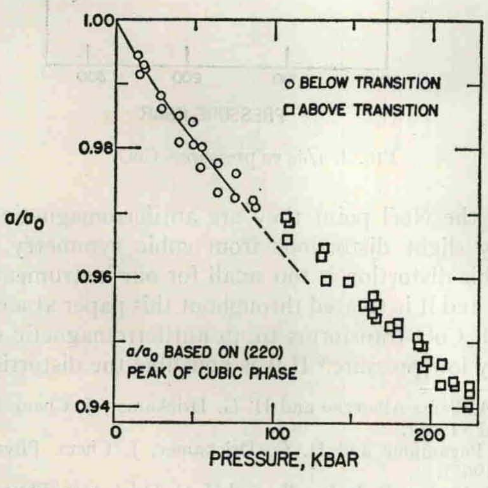

FIG. 5. a/a_0 vs pressure—MnS (calculated from 220 peak).

TABLE I. Sources for oxides and sulfides.

NiO; Fisher Scientific Co. (Lot No. 740463).

MnO; K & K Laboratories (No. 10868).

CoO; The sample was the same as that used by Minomura.[a]

FeO; This was prepared by the decomposition of ferrous oxalate under vacuum at 850°C.[b]

MnS; This was prepared by heating manganese and sulfur in a closed tube at 675°C for 2 h.[c]

FeS_2; Matheson, Coleman & Bell (IX-260).

SnO_2; Allied Chemical and Dye Corp. (Code 2332).

MnO_2; Allied Chemical Corp. (Code 1948).

TiO_2; This sample was the same as that used by Minomura.[a]

[a] S. Minomura and H. G. Drickamer, J. Appl. Phys. **34**, 3043 (1963).

[b] P.L. Gunther and H. Rehaag, Z. Anorg. Allgem. Chem. **243**, 60 (1939).

[c] H. E. Swanson, R. K. Fuyat, and G. M. Ugrinic, Natl. Bur. Std. Circ. No. 539, **4**, 11 (1955).

TABLE II. Atmospheric values of the lattice parameters of the transition-metal oxides and sulfides.

Material	Structure	c(A)	a(A)	c/a
MnO	NaCl	···	4.446	···
FeO	NaCl	···	4.304	···
CoO	NaCl	···	4.258	···
NiO	NaCl	···	4.177	···
MnS	NaCl	···	5.223	···
FeS_2(pyrites)	Cubic	···	5.405	···
SnO_2	tet.	3.188	4.738	0.6729
MnO_2	tet.	2.89	4.44	0.6509
TiO_2	tet.	2.958	4.594	0.6439

TABLE III. a/a_0 versus pressure for MnS, MnO, FeO, CoO, NiO, and FeS_2.

a/a_0	Pressure (kbar)					
	MnS	MnO	FeO	CoO	NiO	FeS_2
1.000	0	0	0	0	0	0
0.995	12	23	23	30	31	23
0.990	26	46	49	62	63	49
0.985	39	70	74	95	96	76
0.980	54	120[b]	101	128	132	107
0.975	70	150	129	162	170	137
0.970	86	180	159	200	217	172
0.965	125[a]	212	229	247	275	218
0.960	146	···	276	308	···	285
0.955	167	···	···	···	···	···
0.950	188	···	···	···	···	···
0.945	208	···	···	···	···	···
0.940	230	···	···	···	···	···
Markers:	Al	NaF	NaCl Nb	NaF Nb	NaF Nb	Ag Al

[a] Below this point a transition to tetragonal structure with $c/a=0.980$ assumed.

[b] Below this point a transition to tetragonal structure with $c/a=0.985$ assumed.

too small for us to detect and it is treated as cubic. FeO either does not transform in our pressure range or the transformation results in negligible lattice distortion. MnO and MnS both transform near 100 kbar to a phase which is tetragonal or of lower symmetry. The high-pressure phase is discussed later in the paper. The experimental results and smoothed data are prescribed in Figs. 1 to 5, and Table III. The equation of state of cubic ionic crystals and the use of a simple semiclassical picture to correlate p–v data have been discussed in detail elsewhere[4,5,7] and are reviewed only briefly here. From simple thermodynamics

$$P=-(\partial A/\partial V)_T, \tag{1}$$

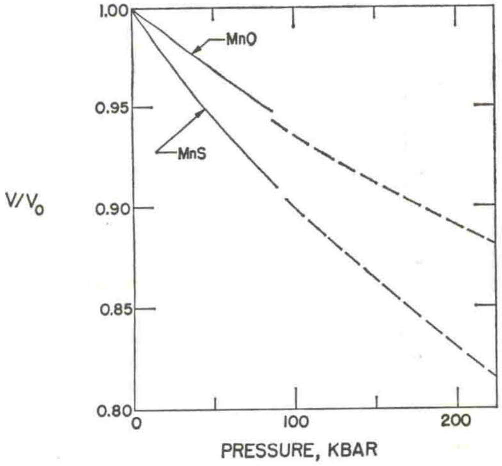

FIG. 7. V/V_0 vs pressure—MnO and MnS.

where P is the pressure and A the work function. As discussed in the above references, one can write

$$A(T,V)=W_L(V)+W_{\text{vib}}(T)-TS(V,T), \tag{2}$$

so

$$P=-(\partial W_L/\partial V)+T[(\alpha/\beta)],$$

where α and β are the thermal expansion coefficient and the isothermal compressibility. The second term on the right seldom contributes more than 3–4 kbar to the pressure and can be approximated in a number of ways.

It has been shown[4,5] that a formulation for W_L of the form

$$W_L=-\frac{\alpha_r(ze)^2}{r}-\frac{C_r}{r^6}+\frac{D_r}{r^8}+Be^{-r/\rho}, \tag{3}$$

where the first term is the Madelung term, the second

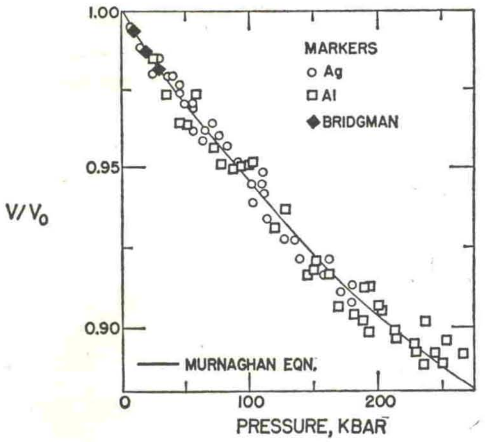

FIG. 8. V/V_0 vs pressure—FeS_2.

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[7] M. P. Tosi, Solid State Phys. **16**, 1 (1965).

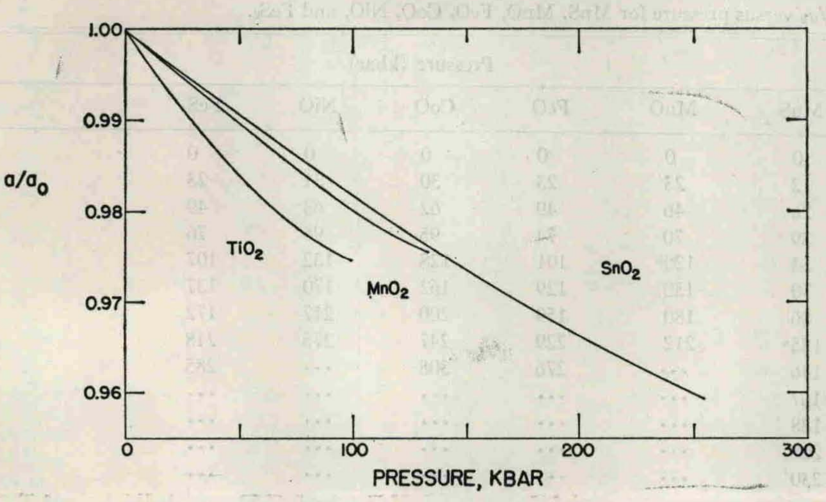

FIG. 9. a/a_0 vs pressure—SnO_2, MnO_2, TiO_2.

and third are the van der Waals' dipole–dipole and dipole–quadrupole terms, and the last one the repulsion term, gives a good fit to p–v data over a large pressure range with alkali halides and other ionic crystals. The dipole–quadrupole term contributes only a small amount to the pressure and could not be evaluated for the transition-metal oxides and so was dropped. On the other hand, Hush and Pryce[8] have shown that there is an additional contribution to the cohesion of crystals containing ions with unfilled d shells, involving crystal-field forces. It is of the form—(C_{cf}/r^5). [r, here, as in Eq. (3) represents the interionic distance.] C_{cf} can be calculated from crystal-field stabilization energies, as shown by Hush and Pryce. Since all constants in the dipole–dipole and Madelung terms can also be evaluated at one atmosphere, this leaves only B and ρ to be evaluated from the initial volume and compressibility. Table IV contains all the constants needed for the calculation.

The agreement between calculation and experiment is shown in Figs. 1–5. It is really very close, although the calculated curve is not quite identical with the "best" smoothed curve through the data, the difference is hardly larger than experimental error. It is of interest to note how much the crystal-field term contributes to the cohesion. In Table V are listed the percent contribution to the "attractive" part of the pressure, (i.e., the part calculated from Madelung, van der Waals, and crystal-field terms) by dipole–dipole and crystal-field stabilization energies. The crystal-field term is always somewhat smaller, but is not negligible.

It is also possible to use a macroscopic equation of state such as that derived by Murnaghan[9]

$$P=(B_0/B_0')[(V_0/V)^{B_0'}-1]. \qquad (4)$$

In the original derivation B_0 and B_0' are the bulk modulus and its pressure derivative, both evaluated

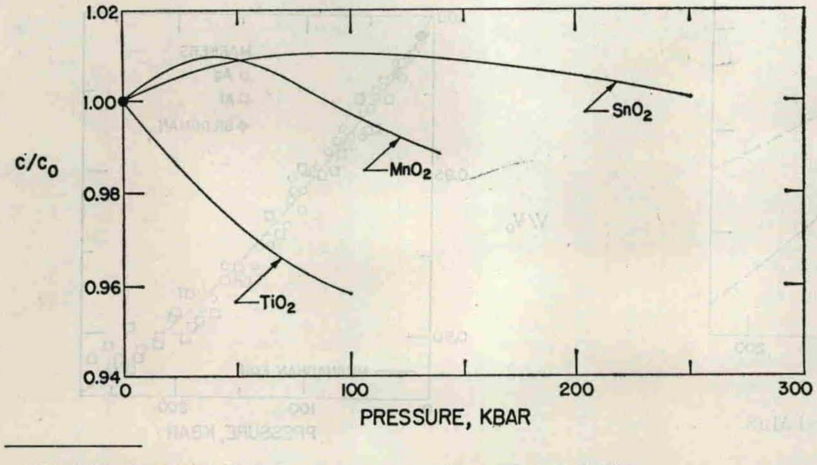

FIG. 10. c/c_0 vs pressure—SnO_2, MnO_2, TiO_2.

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[8] N. S. Hush and M. H. L. Pryce, J. Chem. Phys. **28**, 244 (1958).

[9] F. D. Murnaghan, *Finite Deformation of an Elastic Solid* (John Wiley & Sons, Inc., New York, 1951).

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

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

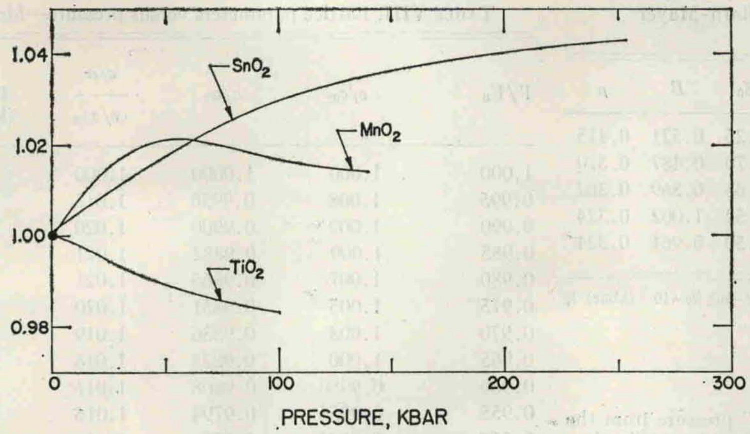

FIG. 11. $(c/a)/(c/a)_0$—SnO$_2$, MnO$_2$, TiO$_2$.

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]

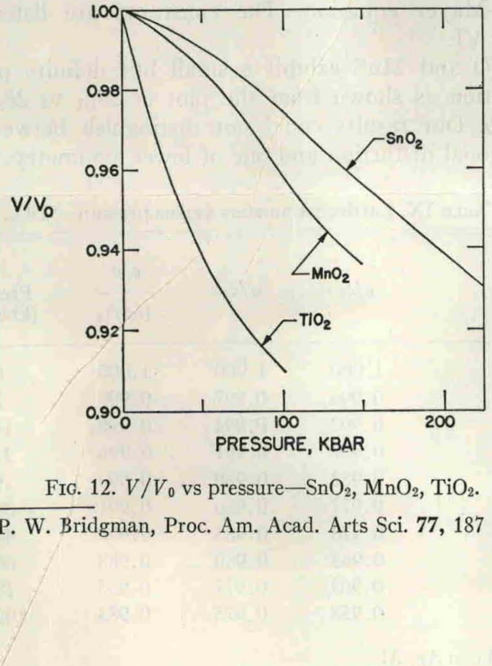

FIG. 12. V/V_0 vs pressure—SnO$_2$, MnO$_2$, TiO$_2$.

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.

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