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

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

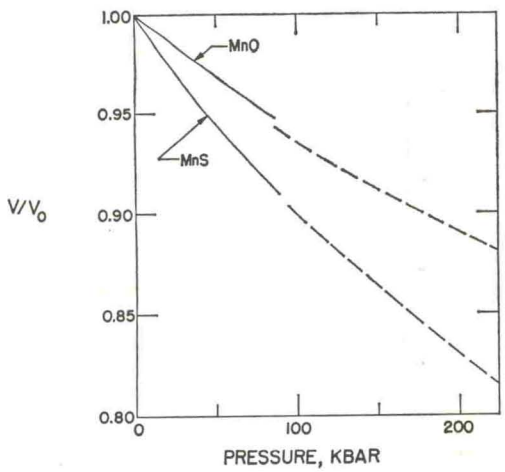

FIG. 7. V/V_0 vs pressure—MnO and MnS.

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

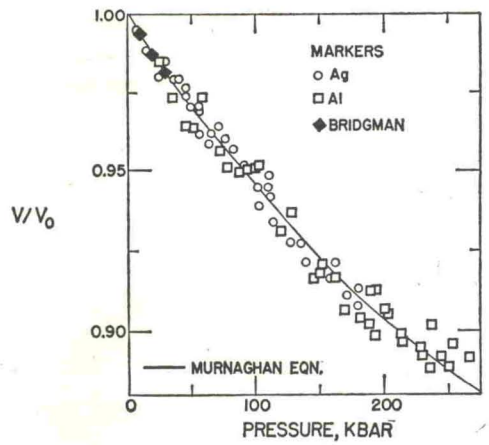

FIG. 8. V/V_0 vs pressure—FeS_2.

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

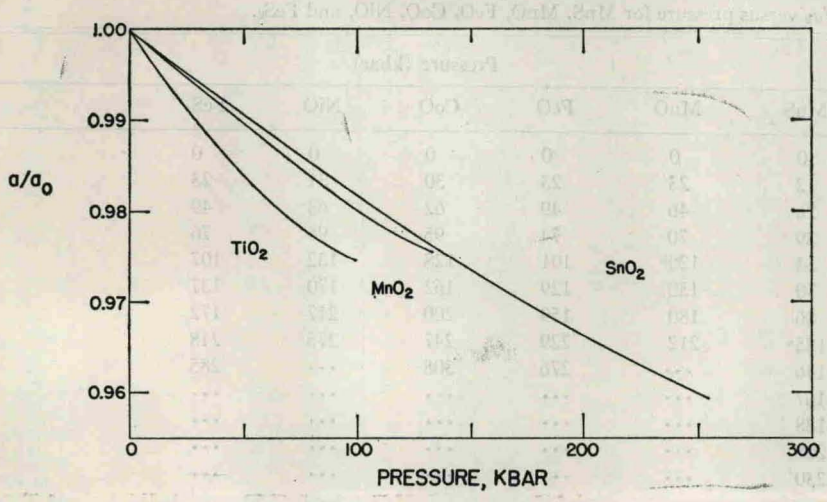

FIG. 9. a/a_0 vs pressure—SnO_2, MnO_2, TiO_2.

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 initia 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

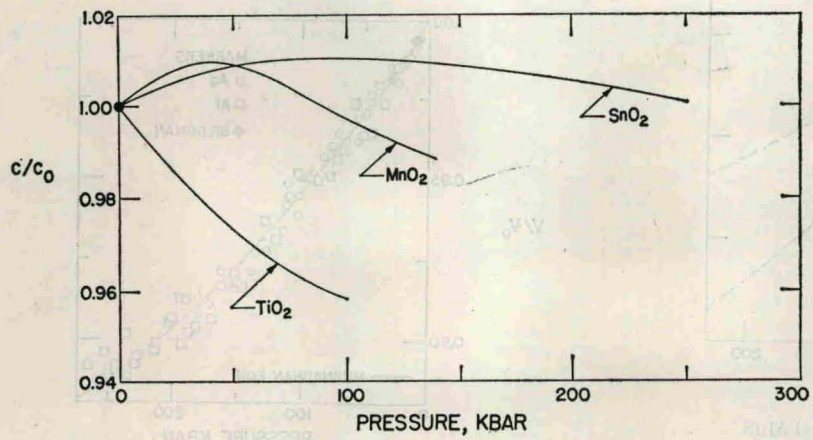

FIG. 10. c/c_0 vs pressure—SnO_2, MnO_2, TiO_2.

[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).