SnO2, MnO2, TiO2

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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 apraently 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.

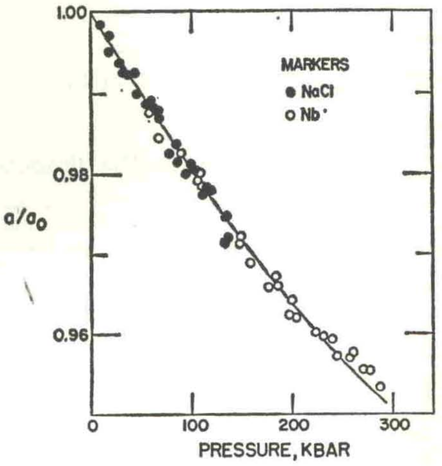

FIG. 1. a/a_0 vs pressure—FeO.

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. 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

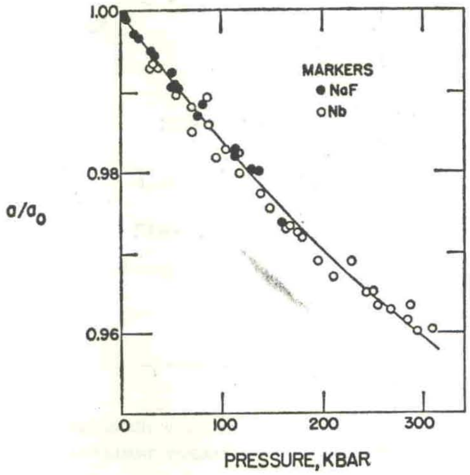

FIG. 2. a/a_0 vs pressure—CoO.

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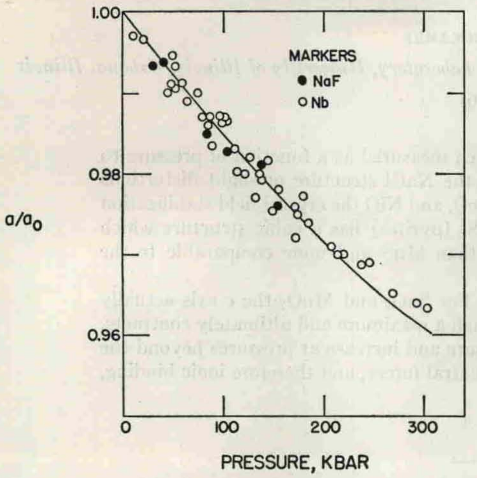

FIG. 3. a/a_0 vs pressure—NiO.

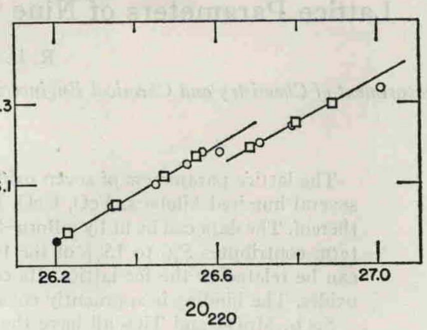

FIG. 6. $2\theta_{111}$ vs $2\theta_{220}$—MnO.

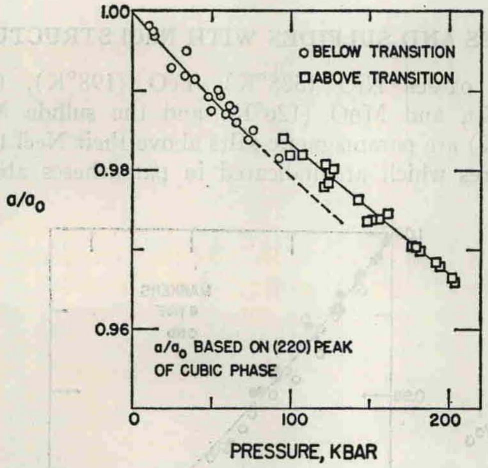

FIG. 4. a/a_0 vs pressure—MnO (calculated from 220 peak).

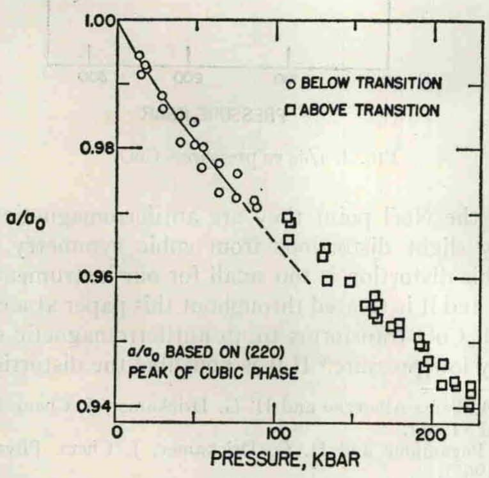

FIG. 5. a/a_0 vs pressure—MnS (calculated from 220 peak).

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]

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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