CHAPTER 4

METAL-OXIDE DEBYE TEMPERATURES AND ELASTIC CONSTANTS: ESTIMATION FROM INTERIONIC SPACING

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ABSTRACT

For cubic metal oxides, we show relationships between crystal-structure-volume properties and elastic-stiffness properties. The interionic distance (or the crystal structure plus volume) gives the bulk modulus B. The product of effective atomic mass and atomic volume gives the Debye temperature Θ_D, which gives the shear modulus G. From B and G, we estimate other elastic constants such as Young modulus E and Poisson ratio ν. We apply this approach to 23 cubic metal oxides where there exists crystal-structure information, but no elastic-constant information. To develop the relationships, we consider elastic and related properties of 17 cubic oxides.

Considering earth oxides, many authors related sound velocities and elastic constants to other physical properties such as mass density, atomic mass, interionic distance, and either atomic volume or unit-cell volume [1–6]. Here, we extend and interrelate these studies to show that we can estimate the bulk modulus B and the shear modulus G from essentially the interionic spacing, which when combined with the crystal structure (rocksalt, perovskite, and so on) gives the atomic volume.

First, we consider the bulk modulus. From the Born model for ionic solids, the bulk modulus is

$$B = \frac{(n-1)}{9V}U \tag{4.1}$$

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Here, n denotes repulsion exponent, V volume, and U potential energy:

$$U = \frac{aM_a}{r_0} \tag{4.2}$$

Here, a denotes a constant, M_a Madelung constant, and r_0 the cation–anion interionic distance. From Eqs. 4.1 and 4.2, we find

$$B = \frac{b}{V_a^{4/3}} \tag{4.3}$$

Here, b denotes a constant and V_a atomic volume. Figure 4.1 shows this relationship for 11 cubic oxides for which monocrystal elastic constants are known from measurement. We got the polycrystalline elastic constants in Table 4.1 by applying Kröner's method [7] and a general cubic-symmetry relationship:

$$B = \frac{(C_{11} + 2C_{12})}{3} \tag{4.4}$$

Here, C_{11}, C_{12}, and C_{44} denote the usual three Voigt second-order elastic stiffnesses. A least-squares fit to the measurements in Figure 4.1 gives $B_n = 1316\ V_a^{-0.939}$ for most oxides, and $B_t = 14188 V_a^{-1.91}$ for oxides containing transition-metal cations. (Subscripts n and t denote nontransition-metal and transition-metal cations.) This fit includes rocksalt, Fe_3O_4, and Cu_2O structure types. Forcing a $V_a^{-4/3}$ dependence gives $B_n = 3525 V_a^{-4/3}$ and $B_t = 3733 V_a^{-4/3}$. We can compare this empirical relationship with a theoretical relationship $B = 1761 r_0^{-3.5}$ derived by Cohen [8] for covalent solids. Thus, from only the interionic spacing r_0 we can estimate B. Perovskite and fluorite crystal structures fail to fit the above relationships.

Second, we consider the Debye temperature, Θ_D. Figure 4.2 shows Θ_D versus a variable suggested by Nakamura [9] and derived from simple lattice-vibration ideas:

$$X = (\overline{m} V_a)^{-1/2} \tag{4.5}$$

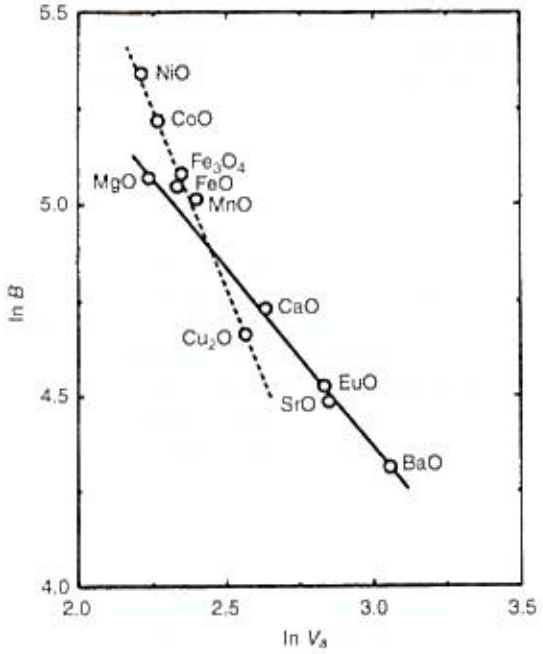

Fig. 4.1. Bulk-modulus–volume relationship for several cubic oxides. Steeper-slope line corresponds to oxides with transition-metal cations.

Table 4.1. For Seventeen Cubic Metal Oxides, Various Physical Properties, Ambient Temperature Except EuO(77 K) and $BaTiO_3$ (424 K); All Measured or Derived Simply from Measurements.

Oxide	ρ (g/cm^3)	G (GPa)	B (GPa)	E (GPa)	ν	V_a (Å^3)	m (10^{-24}g)	X (10^{-22}(g/cm^3)$^{1/2}$)	Θ_D (K)	Ref.
BaO	5.976	35.68	74.30	92.28	0.2930	21.28	127.3	1.921	292.4	1–3
CaO	3.344	80.99	113.3	196.2	0.2114	13.92	46.56	3.928	673.0	2,4–6
CoO	6.411	70.87	185.3	188.5	0.3304	9.651	62.21	4.081	520.0	7–10
EuO	8.203	61.63	92.33	151.2	0.2269	17	139.5	2.054	349.5	11
FeO	5.730	50.58	155.8	136.9	0.3535	10.31	59.65	4.032	455.0	12
MgO	3.581	130.4	159.9	307.5	0.1794	9.338	33.46	5.657	938.2	5,13–22
MnO	5.395	68.09	150.9	177.5	0.3039	11.01	58.90	3.927	531.7	7,23–24
NiO	6.827	46.30	213.6	129.6	0.3990	9.122	62.01	4.204	579.2	25
SrO	4.932	58.21	88.65	143.2	0.2306	17.34	86.03	2.589	436.2	5,23,26–28
$BaTiO_3$	5.999	75.91	164.3	197.3	0.2998	12.91	77.45	3.162	493.9	29–30
$SrTiO_3$	5.113	116.6	175.2	286.3	0.2276	11.91	60.94	3.712	689.6	31–36
Cu_2O	6.085	10.33	105.7	30.03	0.4526	13.02	79.20	3.114	188.1	37
ThO_2	9.860	97.14	193.0	249.5	0.2844	14.51	146.1	2.172	418.4	38
UO_2	10.97	85.12	210.7	225.0	0.3220	13.62	149.5	2.216	381.2	39–40
Sc_2O_3	3.870	80.65	197.3	212.9	0.3201	11.83	45.80	4.295	668.2	41
Y_2O_3	4.980	57.80	167.6	155.5	0.3453	15.06	74.99	2.976	461.2	41
Fe_3O_4	5.175	91.36	161.6	230.6	0.2622	10.47	76.90	4.169	533.9	42

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Here, $\bar{m}$ denotes average atomic mass relationships. Figure 4.2 suggests two linear relationships. For most oxides,

$$\Theta_D = 168.81X \tag{4.6}$$

For oxides containing transition-metal cations,

$$\Theta_D = -946.97 + 363.18X \tag{4.7}$$

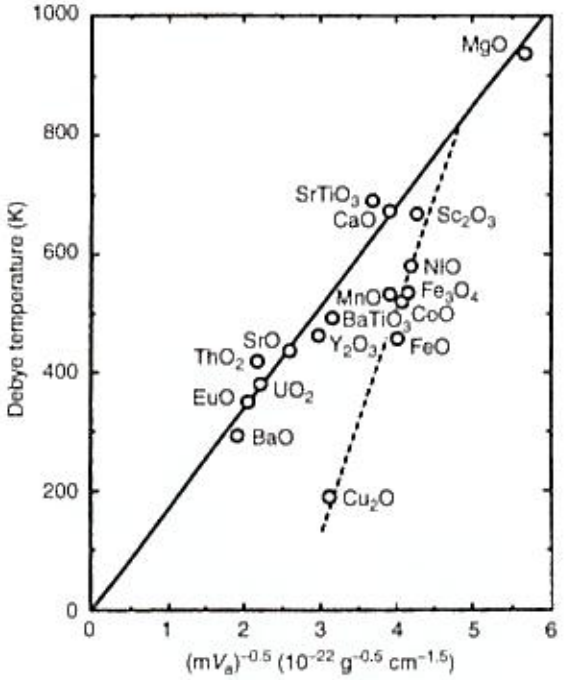

Fig. 4.2. Debye-temperature–mass–volume relationship for several cubic oxides. Steeper-slope line corresponds to oxides with transition-metal cations.

Thus, from only atomic mass and atomic volume, we can estimate the Debye temperature, Θ_D.

Ledbetter [10] showed that, to a good approximation,

$$\Theta_D = 1.122\frac{h}{k}\left(\frac{3}{4\pi V_a}\right)^{1/3}\left(\frac{G}{\rho}\right)^{1/2} \tag{4.8}$$

Here, G denotes shear modulus, ρ mass density, h Planck's constant, and k Boltzmann's constant.

We get G more accurately by considering a general relationship for Θ_D:

$$\Theta_D = 1.122\frac{h}{k}\left(\frac{3}{4\pi V_a}\right)^{1/3} v_m \tag{4.9}$$

Here, v_m denotes a mean sound velocity:

$$3v_m^{-3} = v_l^{-3} + 2v_t^{-3} \tag{4.10}$$

Here, subscripts l and t denote longitudinal and transverse. Recognizing that

$$B = \rho\{[v_l^2 - (4/3)v_t^2]\}, \tag{4.11}$$

and

$$G = \rho v_t^2, \tag{4.12}$$

we solve Eqs. 9–12 for the shear modulus G after we get B from Figure 4.1 and Θ_D from Figure 4.2.

Applying this approach to 25 oxides, Table 4.2 shows estimated values of B, G, and Θ_D. It also contains the relevant mass-volume properties and other elastic constants (E = Young modulus and ν = Poisson ratio) derived by standard relationships.

Table 4.2. For 23 Cubic Oxides: Estimated Debye Temperatures and Elastic Constants.

Oxides	V_a ($Å^3$)	ρ (g/cm^3)	$\bar{m}$ (10^{-24}g)	X [10^{-22}(g/cm^3)$^{1/2}$]	Θ_D (K)	G (GPa)	B (GPa)	E (GPa)	ν
AgO	13.96	7.366	102.84	2.639	445.5	77.73	110.6	188.9	0.2152
Ag_2O	17.61	7.282	128.27	2.104	355.2	56.79	88.89	140.5	0.2366
AmO	15.25	14.095	215.04	1.746	294.7	68.95	101.8	168.7	0.2236
CdO	12.94	8.238	106.62	2.692	454.4	86.11	118.7	208.0	0.2080
Co_3O_4	9.455	6.042	57.122	4.303	615.8	92.44	194.7	239.4	0.2951
Cr_3O_4	9.582	6.005	52.185	4.472	677.2	113.1	189.8	283.1	0.2514
CuO	9.521	6.936	66.044	3.988	501.4	69.99	192.2	187.2	0.3376
K_2O	22.35	2.333	52.139	2.929	494.4	41.16	71.06	103.5	0.2572
Li_2O	8.172	2.023	16.540	8.601	1451.9	160.2	182.8	372.0	0.1610
MnO	7.902	11.759	92.940	3.690	622.9	167.7	188.7	388.1	0.1572
Na_2O	14.32	2.395	34.306	4.511	761.5	75.07	108.0	182.8	0.2177
NbO	12.44	7.269	90.421	2.982	503.4	90.88	123.2	218.8	0.2040
NpO	15.72	13.361	210.10	1.740	293.7	66.20	98.89	162.4	0.2264
PaO	15.26	13.43	205.11	1.787	301.7	68.84	101.7	168.5	0.2238
Pt_3O_4	17.35	8.800	154.01	1.935	326.6	57.47	90.14	142.2	0.2371
PuO	15.23	14.06	215.87	1.744	294.4	68.54	101.9	168.0	0.2252
SmO	15.87	8.701	138.16	2.136	360.6	65.37	98.02	160.4	0.2272
TaO	10.81	15.13	163.52	2.379	401.6	109.9	140.6	261.6	0.1899
TiO	9.555	5.536	53.037	4.442	666.3	100.3	190.9	256.0	0.2765
UO	14.98	14.08	210.91	1.779	300.3	70.68	103.5	172.7	0.2218
VO	8.742	6.357	55.579	4.537	700.8	117.2	240.1	302.4	0.2901
YbO	14.35	10.94	156.95	2.107	355.7	74.92	107.7	182.5	0.2177
ZnO[a]	9.800	6.912	67.575	3.886	464.3	60.81	181.9	164.1	0.3496

[a]Near 100 kbar.

The present study emphasizes the role of volume, and especially of interionic distance, in determining solid-state physical properties. This idea is not new. For example, it formed a cornerstone of Pauling's studies [11, 12] relating chemical bonds to physical properties. Applications of this idea continue. For example, focusing on the $Y_1Ba_2Cu_3O_7$ superconductor, Brown [13] used cation–anion distance to estimate the valences of the copper and oxygen ions; these valences affect the physical properties and probably the normal-superconductive transition.

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