

THE RELATIONSHIP BETWEEN MINERAL HARDNESS AND COMPRESSIBILITY (OR BULK MODULUS)

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ABSTRACT

Hardness has been defined as "the resistance of a mineral to scratching." Compressibility is the isothermal change in volume of a compound with pressure and is dependent upon many of the same factors that determine hardness. Bulk modulus K , the reciprocal of compressibility, has been defined as the second derivative of lattice energy U with change in volume, $K = V(d^2U/dV^2)_{V_0}$. Several authors have demonstrated an empirical correlation between hardness and compressibility for specific groups of minerals. Examination of data for 81 solids representing 11 structure types shows this correlation to be indirect. The hardness of a substance is dependent upon the square of the interatomic distance whereas compressibility and bulk modulus are dependent upon the cube of the interatomic distance. Dependence upon valence is more complex, with the data examined falling into two groups, the Alkali Halide Group and the Sulfide-Oxide Group. Empirical equations developed for the two groups suggest that hardness should be defined as the second derivative of lattice energy with change in interatomic distance, $H = (d^2U/dr^2)_{r_0}$.

Keywords: hardness, compressibility, bulk modulus, lattice energy.

SOMMAIRE

La dureté d'un minéral mesure sa résistance à l'éraflure. La compressibilité d'un composé, le changement isotherme de son volume lorsqu'il est comprimé, dépend de plusieurs des facteurs qui déterminent la dureté. Le module de compression K , qui est l'inverse de la compressibilité, correspond au taux de changement de l'énergie U du réseau avec le changement en volume: $K = V(d^2U/dV^2)_{V_0}$. Plusieurs auteurs ont établi une corrélation empirique entre dureté et compressibilité pour certains groupes de minéraux. Un examen des données pour 81 composés solides qui représentent 11 types de structure montre que cette corrélation est indirecte. La dureté d'une substance dépend du carré de la distance interatomique, tandis que compressibilité et module de compression dépendent du cube de cette distance. La relation avec la valence est plus compliquée; les données définissent deux groupes, celui des halogénures alcalins et celui des sulfures et oxydes. Des relations empiriques pour les deux groupes font penser que l'on devrait défi-

nir la dureté H comme deuxième dérivée de U par rapport à la distance interatomique r , $H = (d^2U/dr^2)_{r_0}$.

(Traduit par la Rédaction)

Mots-clés: dureté, compressibilité, module de compression, énergie du réseau.

INTRODUCTION

Numerous attempts have been made to derive an empirical relationship between hardness and various physical parameters (e.g., Friedrich 1926, Goldschmidt 1926, Plendl & Gielisse 1963, Povarennykh 1964, Julg 1978). Most of these equations incorporate several coefficients that are difficult to determine for a particular substance. Similar attempts at empirical correlations between compressibility or bulk modulus and crystal parameters have been more successful (e.g., Bridgman 1923, Anderson & Nafe 1965, D.L. Anderson 1967, Anderson & Soga 1967, O.L. Anderson 1970, 1972, Plendl & Gielisse 1969, 1970, Anderson & Anderson 1970). Several investigators have demonstrated empirical correlations between hardness and compressibility (e.g., Plendl *et al.* 1965, Beckmann 1971, Scott 1973), suggesting that it might be possible to derive an empirical equation relating hardness to compressibility and, therefore, to other more readily determined physical parameters. The present study was undertaken to test the empirical hardness-compressibility correlation of earlier workers, to determine its theoretical basis and the possibility of using it in a predictive fashion, and to determine an empirical equation for hardness.

CRYSTAL-CHEMICAL FACTORS AFFECTING HARDNESS

Hardness is defined as "the resistance of a mineral to scratching" (Bates & Jackson 1980) or as "resistance to plastic deformation, usually being indentation" (Thrush 1968). It is a complex but poorly defined property dependent upon such factors as the nature of the chemical bond, interatomic distance, valence, atomic density and co-ordination

number. Several methods for approximating the hardness of solids are in common use. The Mohs hardness scale ranks minerals in the order of their ability to scratch one another; numerical values of hardness, ranging from 1 to 10, have been assigned to certain index-minerals. The technical scale is similar and uses many of the same index-minerals, although the range is increased to 1 to 15. The Vickers and Knoop techniques of measuring hardness are more precise; one measures the size of an indentation produced by a diamond stylus under a set load. Other methods include Shore hardness, based upon measurement of the height of rebound of a steel ball or hammer dropped upon the specimen, polishing hardness and Brinnell hardness. Because the Mohs hardness and Vickers hardness are the most commonly used by mineralogists, we have not considered the others.

Many hardness data are expressed as either Mohs or Vickers hardness but not both, so that conversion from one scale to the other is necessary. Two

schemes of conversion, by Beckmann (1971) and by Westbrook & Conrad (1973), are shown in Figure 1, together with published examples for which both Vickers and Mohs hardness are known. The curve of Westbrook & Conrad fits the data better and was used in our study. Whereas there is good agreement in Figure 1 for the Mohs index-minerals upon which the empirical curves are based, there is considerable scatter of the data points (up to 3 H_m units) for non-index minerals. This is at least partly due to the fact that the Vickers-hardness data that we have used are average in ranges of hardness listed in the source literature and, overall, are for different loads (in many cases not included in the source data). For this reason we have used one type of hardness data (H_m , Mohs) where possible.

Several formulae have been proposed for estimating hardness from basic crystal-chemical parameters. Most contain terms involving valence and mean interatomic distance, as well as various constants related to such factors as the crystal structure, the covalency of the bonds, the co-ordination number, and atomic number. None of the formulae proposed to date are particularly useful in predicting hardness because most contain terms that are variable with structure or bulk composition. In an attempt to circumvent this problem, Plendl & Gielisse (1963) proposed that hardness is equal to the volumetric cohesive energy, U/V . In the case of Mohs hardness, they found that:

$$U/V = 24(H_m - 2.7) \text{ for "hard-core" solids,} \\ 4 < H_m < 9, \quad (1a)$$

$$U/V = 48(H_m - 3.3) \text{ for "soft-core" solids,} \\ H_m > 4, \text{ and} \quad (1b)$$

$$U/V = \frac{1}{2} H_m^3 \text{ for all solids, } H_m < 4. \quad (1c)$$

U/V is given in kcal cm^{-3} . They defined as "hard-core" those binary solids either of the AB type in which A or B (or A and B) consist of elements of atomic number less than 10 or of any other type in which one element has an atomic number less than 10 and the other element has an atomic number less than 18. "Soft-core" solids include all others.

CRYSTAL-CHEMICAL FACTORS AFFECTING COMPRESSIBILITY AND BULK MODULUS

Compressibility is the isothermal change in volume of a compound with pressure, $\beta = -(1/V)(dV/dP)_T$ (Birch 1966), and is dependent upon the same factors that determine hardness. Compressibility can be measured directly from the change in volume with confining pressure or can be computed from elastic constants. The bulk modulus is the reciprocal of the compressibility, $K = 1/\beta$, and is more useful than compressibility in the development of predictive models.

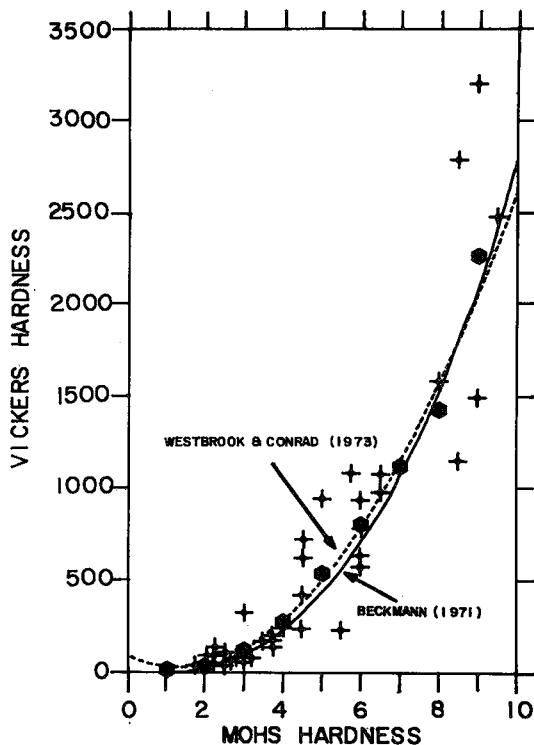


Fig. 1. Comparison of Mohs and Vickers hardness data (+) of Tables 1, 2 and 3. The correlations of Beckmann (1971), $VHN = 86.3 - 90.9 H_m + 34.6 H_m^2$, and Westbrook & Conrad (1973), $VHN = 5.25 H_m^{2.73}$, for the Mohs index minerals (●) are shown as solid and dashed lines, respectively.

The systematics of elastic constants were developed by Birch (1960), who demonstrated that the density and the mean atomic weight are the only variables of importance in describing the compressional velocity of sound of rocks and minerals. Several empirical formulae have been developed, based upon the relationship between bulk modulus and the inverse fourth power of the interatomic distance (e.g., Bridgman 1923, Anderson & Nafe 1965, D.L. Anderson 1967, Anderson & Soga 1967, O.L. Anderson 1970, 1972, Anderson & Anderson 1970, Plendl & Gielisse 1969, 1970). A summary paper by Wang (1978) shows that:

$$K = V(d^2U/dV^2)_{V_0} = V(d^2U/dr^2)(dr/dV)^2_{r_0} \quad (2a)$$

$$= (AZ_a Z_c e^2(n-1))/(9V_0^{4/3}) \quad (2b)$$

where A is the Madelung constant, Z_a the anionic valence, Z_c the cationic valence, e the electronic charge, n the repulsive force parameter, r the mean atomic radius and V_0 the specific volume. If $AZ_a Z_c e^2(n-1)/r_0$ in equation (2b) is assumed to be constant for isostructural compounds, then:

$$KV_m = \text{constant} \quad (2c)$$

where V_m is the molar volume and r_0 is the interatomic distance at equilibrium. Anderson & Nafe

(1965), D.L. Anderson (1967), Anderson & Soga (1967), Anderson & Anderson (1970), and O.L. Anderson (1972) have evaluated equations (2b) and (2c) for a number of different elements and types of compounds.

RELATIONSHIP BETWEEN HARDNESS AND COMPRESSIBILITY (OR BULK MODULUS)

Beckmann (1971) demonstrated empirical correlations between hardness and compressibility for specific groups of minerals. Scott (1973) used a similar empirical correlation for sulfide minerals to predict the compressibility of troilite. In contrast to Beckmann, who fitted straight lines to the data, Scott fitted a curve. Plendl *et al.* (1965) expressed the empirical correlation between hardness and compressibility as:

$$1/\beta = (U/V)(Zm/q) = H/(Zm/q) \quad (3)$$

where β is the compressibility, U/V the volumetric cohesive energy, H the hardness, Z the maximum valence, m the number of component atoms, and q the number of atoms per molecule. If the Mohs hardness from equations (1a), (1b), (1c) is substituted in equation (3), bulk modulus is used in place of inverse

TABLE 1. DATA USED IN DETERMINING THE CONSTANT EMPIRICAL RELATIONSHIPS AMONG BULK MODULUS, MOHS HARDNESS, MOLAR VOLUME AND VALENCE FOR THE SULFIDE-OXIDE GROUP

STRUCTURE TYPE AND COMPOUND	$ Z_{a,c} $	V_m (cm ³ /mole)	U (kcal/mole)	K (Mbar)	H_m	VHN (kg/mm ²)	$KV_m/Z^{3/4}$	$H_m V_m^{2/3}/Z^{2/3}$	H_m (ob-pr)
NaCl AgBr	1	28.9	(217)	0.407	2.5	90	11.76	23.54	0.5
AgCl	1	25.7	(219)	0.442	1.75	32	11.36	15.24	-0.5
ZnS(c) AgI	1	41.3	(213)	0.243	1.5		10.04	17.92	-0.1
CuBr	1	27.7		0.345	2.4		9.56	21.97	0.3
CuCl	1	23.8	(237)	0.398	2.25	74	9.47	18.61	-0.1
CuI	1	33.4		0.333	2.5		11.12	25.92	0.7
NaCl CaO	2	16.8	(900)	1.136	4.5	615	11.35	19.59	-0.1
CoO	2	11.5	(987)	1.852	(4.8)	380	12.66	15.40	-1.2
HgS	2	28.5	(754)	0.230*	2.5	76	3.90*	14.69	-0.8
HgO	2	11.2	(958)	1.538	5.33	1080	10.24	16.81	-0.7
MnO	2	13.2	(953)	1.543	5.5	225	12.11	19.35	0.1
PbS	2	31.4	(810)	0.609	2.65	87	11.28	16.61	-0.4
PbTe	2	40.4	(763)	0.408	3.0	49	9.80	22.24	0.4
SrO	2	20.7	(866)	0.824	3.5	164	10.14	16.62	-0.5
ZnS(c) CdTe	2	41.0	(653)	0.424	2.8	60	10.34	20.97	0.2
HgTe	2	40.0	(662)	0.437	2.5	28	10.39	18.42	-0.1
ZnS	2	23.8	(788)	0.763	3.75	195	10.80	19.54	0.1
ZnSe	2	27.4	(727)	0.595	3.75	135	9.69	21.47	0.4
ZnTe	2	34.0	(686)	0.510	(2.8)	90	10.31	18.71	-0.1
ZnS(h) BeO	2	8.2	(1074)	2.494	8.5	1150	12.16	21.77	1.0
CdS	2	30.1	(746)	0.613	3.2	72	10.97	19.50	0.1
CdSe	2	33.8	(705)	0.537	3.0	110	10.79	19.75	0.1
ZnO	2	13.8	(961)	1.437	4.5	234	11.79	16.31	-0.8
ZnS	2	23.7	(784)	0.767	3.75	178	10.81	19.49	-0.1
ZnS(c) 1/2CuFeS ₂	2	22.0		0.775	3.75	214	10.14	18.54	0.1
NaCl TaC	4	13.3	(2767)	2.169	9.0	1497	10.20	20.05	0.4
TiC	4	12.1	(2500)	2.401	9.0	3200	10.27	18.82	-0.2
TiN	4	11.5		2.941	9.5		11.96	19.21	0.0
UC	4	18.4	(3192)	1.634	(6.1)	724	10.63	16.82	-0.8
ZrC	4	15.4	(2300)	2.231	8.5	2789	12.15	20.88	0.7
ZnS(c) SiC	4	12.4		2.464	9.5	2480	10.80	20.20	0.5

Values in brackets () are estimated. Anomalous values are indicated by asterisks *. H_m (ob-pr) is the difference between the observed Mohs hardness and that predicted using equation (10).

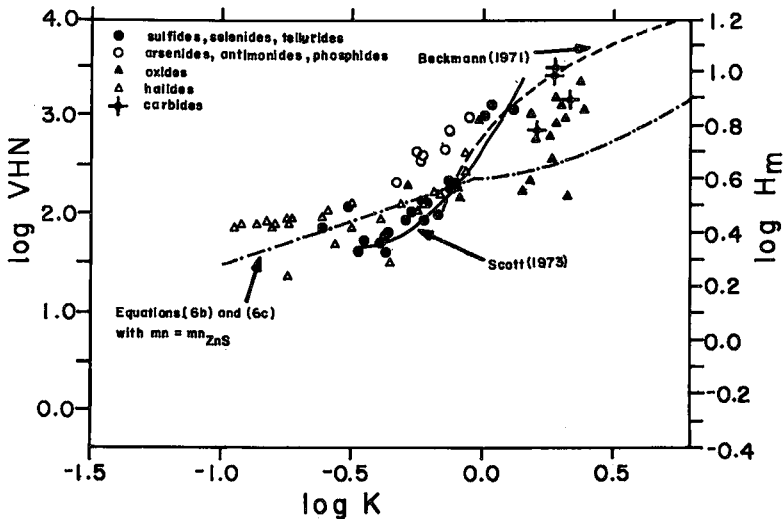


FIG. 2. Bulk modulus and hardness of solids. The curves show correlations for sulfide data by Beckmann (1971) and Scott (1973) as well as a solution to equations (6b) and (6c) with $n = n_{ZnS}$.

TABLE 2. DATA USED IN DETERMINING THE CONSTANT EMPIRICAL RELATIONSHIPS AMONG BULK MODULUS, MOHS HARDNESS, MOLAR VOLUME AND VALENCE FOR THE ALKALI HALIDE GROUP

STRUCTURE TYPE AND COMPOUND	Z _{a,c}	e _l	Z _e	V _m (cm ³ /mole)	U (kcal/mole)	K (Mbar)	H _m	VHN (kg/mm ²)	KV _m /Z ^{3/4}	H _m V _m ^{2/3} /Z ^{2/3}	H _m (ob-pr)	
NaCl	KBr	1	54	1.84	43.3	159.3	0.151	2.0	83	6.54	13.43	-0.3
	KCl	1	36	1.48	37.5	165.4	0.180	2.0	82	6.75	15.16	0.0
	KF	1	28	1.32	23.1	189.7	0.323	2.8	75	7.46	17.21	0.3
	KI	1	72	2.22	53.2	150.8	0.120	2.2	78	6.38	14.17	-0.2
	LiBr	1	38	1.52	25.1	188.5	0.257	2.5	105	6.45	14.12	-0.2
	LiCl	1	20	1.16	20.3	199.2	0.315	3.0	128	6.39	19.26	0.6
	LiF	1	12	1.00	9.8	240.1	0.663	3.75	165	6.50	17.17	0.4
	LiI	1	56	1.88	32.5	174.1	0.188	(2.8)	88	6.11	15.25	0.0
	NaBr	1	46	1.68	32.0	174.5	0.188	2.45	88	6.02	14.72	-0.1
	NaCl	1	28	1.32	26.9	183.1	0.244	2.0	95	6.56	13.61	-0.3
	NaF	1	20	1.16	14.8	213.4	0.490	2.25	130	7.25	11.70	-0.7
	NaI	1	64	2.04	40.8	163.9	0.161	2.3	80	6.57	13.38	-0.3
	RbBr	1	72	2.20	48.4	153.5	0.138	(2.7)	79	6.68	16.33	0.3
	RbCl	1	54	1.84	42.9	160.7	0.160	(2.6)	75	6.86	17.68	0.5
	RbF	1	46	1.68	27.0	181.6	0.273	(2.3)	50	7.37	12.29	-0.6
	RbI	1	90	2.55	59.5	145.3	0.111	(2.7)	76	6.60	15.88	0.1
	BaS	2			39.3		0.345	3.0		6.78	17.33	0.3
	CaS	2			27.7	(725)	0.431	4.0		5.97	18.31	0.6
	PbSe	2			34.5	(763)	0.339	2.7	52	5.85	14.30	-0.2
	SrS	2			32.9		0.417	3.3		6.86	16.94	0.3
	FeS	2			18.2		0.746	4.0	234	6.79	13.84	-0.4
NiAs	AlSb	3			34.8	(1173)	0.593	(4.9)	400	6.88	17.37	0.6
ZnS(c)	GaAs	3			27.2	(1201)	0.756	4.5	717	6.85	13.96	-0.6
	GaP	3			24.4	(1307)	0.887	5.0	942	7.21	14.02	-0.5
	GaSb	3			34.5	(1203)	0.563	4.5	420	6.47	15.89	0.1
	InAs	3			33.1	(1170)	0.579	(4.7)	357	6.39	16.11	0.2
	InP	3			30.4	(1196)	0.725	(5.1)	452	7.35	16.59	0.4
	InSb	3			40.9	(1132)	0.467	3.8	220	6.37	15.03	-0.1

Values in brackets () are estimated.

H_m (ob-pr) is the difference between the observed Mohs hardness and that predicted using equation (12).

compressibility, and the units are converted, we find that:

$$K = [0.574(H_m - 2.7)] / (Z_m/q) \quad (\text{"hard-core", } 4 < H_m < 9) \quad (4a)$$

$$K = [1.147(H_m - 3.3)] / (Z_m/q) \quad (\text{"soft-core", } H_m > 4) \quad (4b)$$

$$K = [0.012(H_m)^3] / (Z_m/q) \quad (\text{all solids, } H_m < 4) \quad (4c)$$

K is given in Mbar⁻¹. Similar relationships can be derived by combining Zhdanov's (1965) equation for the cohesive energy U of an ionic crystal:

$$U = -(Z_a Z_c e^2 N A / r)(1 - 1/n) \quad (5)$$

in which N is Avogadro's number, with equations (1a,b,c) and (2b). N drops out because of differences in definition of volume, giving:

$$(9K/n) = 0.574(H_m - 2.7) \quad (\text{"hard-core", } 4 < H_m < 9) \quad (6a)$$

$$(9K/n) = 1.147(H_m - 3.3) \quad (\text{"soft-core", } H_m > 4) \quad (6b)$$

$$(9K/n) = 0.012(H_m)^3 \quad (\text{all solids, } H_m < 4) \quad (6c)$$

Equations (4) and (6) are identical if (9/n) equals (Zm/q).

We have collected published data for 81 solids in order to test the derived relationships between hardness and bulk modulus or compressibility (Tables 1, 2, 3). Values of hardness are from Palache *et al.* (1944, 1951), Deer *et al.* (1962), Beckmann (1971), Ivan'ko (1971) and Uytendogaardt & Burke (1971). Bulk moduli and compressibilities are taken largely from the compilation of Simmons & Wang (1971), supplemented by data from Birch (1966), Anderson & Anderson (1970), Beckmann (1971), Anderson (1972), Scott (1973) and King (1977). Bulk modulus and compressibility data are averaged values at room temperature and one atmosphere pressure. The data set is plotted in Figure 2 together with Beckmann's (1971) empirical correlation-curve for sulfides and disulfides, Scott's (1973) curve for sulfides, and equations (6b) and (6c) with the value of n as calculated for sphalerite, $n_{ZnS} = 5.1$. Although Scott's curve gives a better "average" fit for the sulfides than does Beckmann's, no single curve satisfies all of the data in Figure 2. On the other hand, there do seem to be trends in the bulk modulus - hardness plots for different types of materials. In order to explore these trends, we have concentrated on the relationships shown for the NaCl and ZnS structures before attempting to expand these relationships to other structural types.

The volumetric cohesive energies U/V for materials having the NaCl and ZnS structures are

listed in Tables 1, 2 and 3, and plotted against hardness in Figure 3. The empirical correlations of Plendl & Gielisse (1963) (equations 1a, b, c) are shown and fit the average data but, for specific structure-types and ionic charges within these structure types, more precise correlations are evident. For example, the alkali halides conform to the expression $U/V = 2.2(H_m - 2.5)$ whereas according to Plendl & Gielisse the relationship should be $U/V = H_m^{3/2}$. Thus, the empirical correlations of Plendl & Gielisse seem to be oversimplified.

Equation 3 demonstrates a correlation between volumetric cohesive energy U/V and bulk modulus K. Equation 3 is shown in Figure 4 (solid line) for

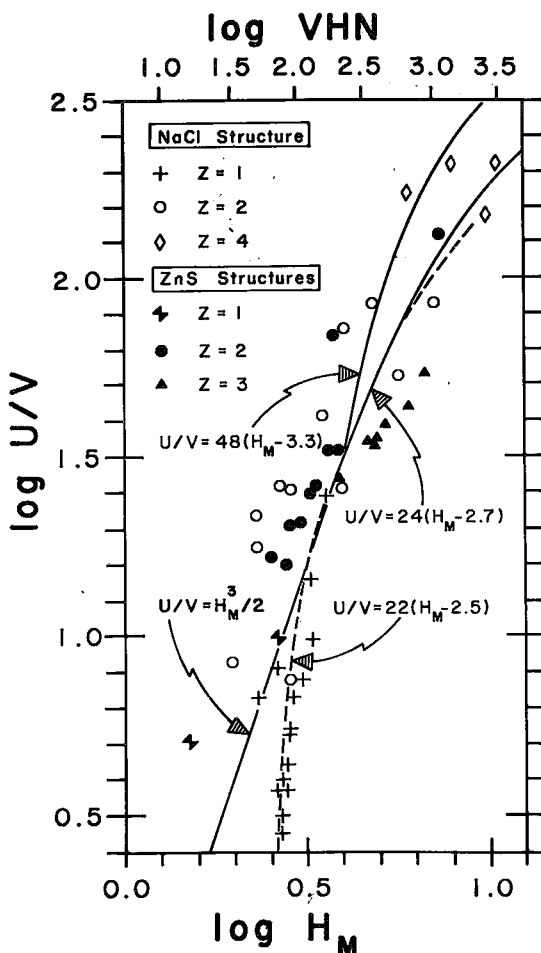


FIG. 3. Hardness and volumetric cohesive energy for the NaCl and ZnS structures. Correlations predicted by Plendl & Gielisse (1963) with equations (1a, b, c) are shown by solid lines; a curve fitted to the alkali halide data is shown as a dashed line.

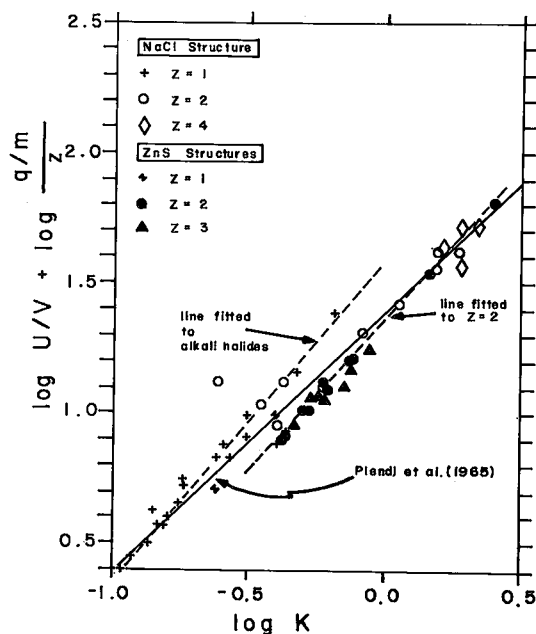


FIG. 4. Bulk modulus and volumetric cohesive energy, compensated for valence, for the NaCl and ZnS structures. The solid line represents the fit of Plendl *et al.* (1965). The dashed lines represent least-squares fits for alkali halide, $Z = 1$, and non-alkali halide, $Z = 2$, data.

materials with the NaCl and ZnS structures. As predicted, there is a good correlation ($R = 0.99$, using a log scale) that is largely independent of structure type. However, for the alkali halides and those materials with divalent cations, a more precise correlation would be $(U/V) \propto K^{1.19 \pm 0.03}$ ($R = 0.997$, log scale used), suggesting that the factor n in equation (6) [or $9q/Zm$ in equation (3)] is approximately inversely proportional to $K^{1/4}$, that is:

$$n = 9q/Zm \propto r/(Z_a Z_c A)^{1/4}. \quad (7)$$

Equation (7) suggests that in order to correct for the effect of ionic charge, K should be multiplied by $Z^{1/2}$ rather than by Z as was done by Plendl *et al.* (1965). In order to evaluate these expressions properly, we must first know the exact correspondence between n and both r and Z . This relationship is also important in empirical expressions used for deriving the bulk modulus (e.g., equation 2) and has been studied by Anderson (1970) and Anderson & Anderson (1970).

AB-type compounds

Tables 1 and 2 and Figures 5 and 6 illustrate the relationship between bulk modulus and volume for AB-type compounds in the halite, sphalerite, wurtzite and niccolite structures. The relationships are

TABLE 3. DATA USED IN DETERMINING THE CONSTANT EMPIRICAL RELATIONSHIPS AMONG BULK MODULUS, MOHS HARDNESS, MOLAR VOLUME AND VALENCE FOR $A_x B_y$ -TYPE COMPOUNDS

STRUCTURE TYPE AND COMPOUND	$ Z_p $	V_m^{**} (cm^3/mole)	K (Mbar)	H_m	VHN (kg/mm^2)	KV_m/z_p^b	$H_m V_m^{2/3}/z_p^c$	H_m (obs-pr)	
ALKALI HALIDE GROUP									
CaF ₂	BaF ₂	1.41	18.0	0.567	3.0	127	7.22	14.47	-0.2
	CaF ₂	1.41	12.3	0.862	4.0	272	7.50	15.07	-0.1
	CdF ₂	1.41	11.8	0.893	4.0		7.45	14.66	-0.2
	PbF ₂	1.41	15.7	0.611	3.2		6.78	14.19	-0.3
	SrF ₂	1.41	14.7	0.699	3.5	163	7.27	14.85	-0.1
TiO ₂	CaCl ₂	1.41	25.6	0.229*	3.0*	317	4.45*	18.42*	0.5
	MgF ₂	1.41	9.8	0.869	5.0		6.02	16.19	0.3
SULFIDE-OXIDE GROUP									
Cu ₂ O	Cu ₂ O	1.41	23.4	0.515	3.75	205	9.29	24.35	0.8
Ag ₂ S	Ag ₂ S	1.41	34.8	0.398	2.25	42	10.68	19.03	0.0
MgAl ₂ O ₄	Fe ₂ O ₄	2.31	11.1	1.872	6.0	575	11.09	17.09	-0.7
	MgAl ₂ O ₄	2.31	9.9	2.020	8.0	1585	10.68	21.11	0.7
	MnFe ₂ O ₄	2.31	11.6	1.851	5.75		11.46	16.86	-0.8
	NiFe ₂ O ₄	2.31	10.9	1.825	5.0		10.61	14.07	-1.8
Al ₂ O ₃	Al ₂ O ₃	2.45	8.5	2.421	9.0	2265	10.51	20.63	0.6
	Cr ₂ O ₃	2.45	9.7	2.237	8.5		11.08	21.28	0.8
	Fe ₂ O ₃	2.45	10.1	2.128	6.0	933	10.98	15.43	-1.5
	FeTiO ₃	2.45	10.6	1.786	6.0	631	9.67	15.93	-1.2
SiO ₂	SiO ₂	2.83	11.3	0.380*	7.0	1120	1.97*	17.62	-0.6
CaF ₂	ThO ₂	2.83	13.2	1.931	6.5	1078	11.69	18.15	-0.4
	UO ₂	2.83	12.3	2.128	6.0	777	12.00	15.99	-1.2
TiO ₂	SnO ₂	2.83	10.8	2.041	7.0		10.11	17.10	-0.8
	TiO ₂	2.83	9.4	2.101	6.5	981	9.06	14.48	-2.1

Anomalous values are indicated by a single asterisk *. V_m^{**} indicates molar volume for a formula unit based upon one anion (e.g. $1/4 \text{Fe}_2\text{O}_4$). b as a Z superscript has the value 1 for the Alkali Halide Group and $3/4$ for the Sulfide-Oxide Group; c used in this way has the value 1 for the Alkali Halide Group and $2/3$ for the Sulfide-Oxide Group. H_m (obs-pr) is the difference between the observed Mohs hardness and that predicted using equations (10) and (12).

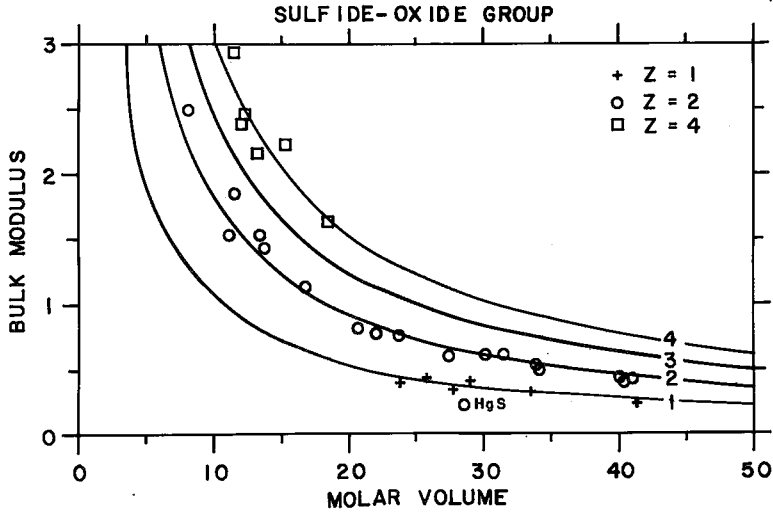


FIG. 5. Bulk modulus - molar volume data for the Sulfide-Oxide Group. The curves represent the equation $K = 10.85 Z^{3/2}/V_m$ with $Z = 1$ (+), $Z = 2$ (O), $Z = 3$ (no symbol), and $Z = 4$ (□). The equation determined by linear regression is in logarithmic form: $\log(KV_m) = 1.025 + 0.781 \log Z$; $R = 0.9765$.

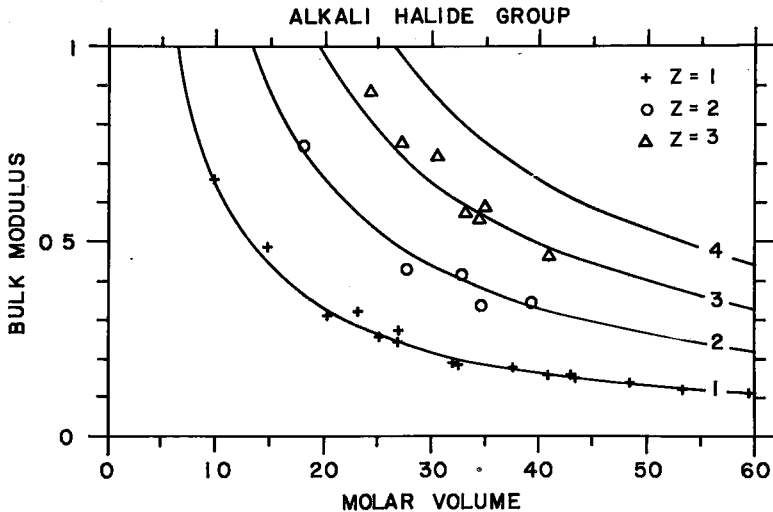


FIG. 6. Bulk modulus - molar volume data for the Alkali Halide Group. The curves represent the equation $K = 6.65 Z/V_m$ with $Z = 1$ (+), $Z = 2$ (O), $Z = 3$ (△), and $Z = 4$ (no symbol). The equation determined by linear regression is in logarithmic form: $\log(KV_m) = 0.821 + 1.010 \log Z$; $R = 0.9919$.

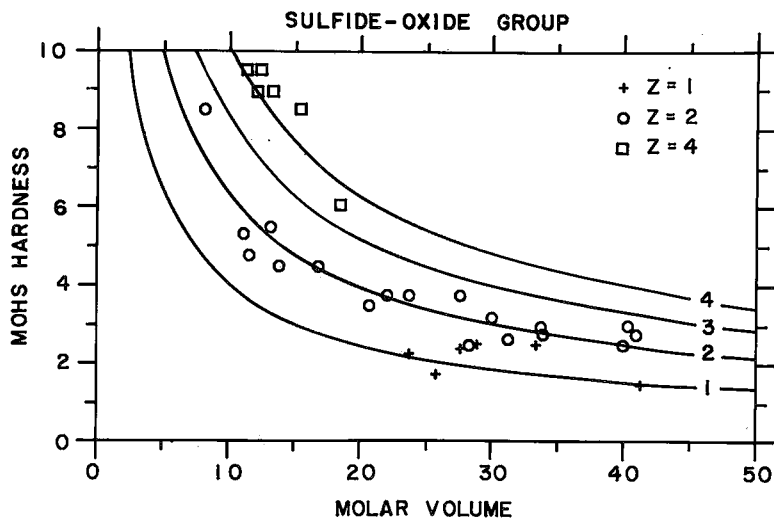


FIG. 7. Mohs hardness - molar volume data for the Sulfide-Oxide Group. The curves represent the equation $H_m = 18.60 Z^{2/3} / V_m^{1/3}$ with $Z = 1$ (+), $Z = 2$ (O), $Z = 3$ (no symbol), and $Z = 4$ (□). The equation determined by linear regression is in logarithmic form: $\log (H_m V_m^{2/3}) = 1.289 + 0.626 \log Z$; $R = 0.9029$.

essentially those shown by Anderson & Anderson (1970), Anderson (1972), Plendl & Gielisse (1969, 1970) and Plendl *et al.* (1965). We have chosen to use molar volume in place of the specific volume or cube of the interatomic distance used by some of these investigators. We have divided our data into two empirical groups, the Alkali Halide Group and the Sulfide-Oxide Group. The group names simply reflect the dominant compounds in each group and are not intended to be exclusive; other types of compounds are included in each group. Figures 5 and 6 show the relationship between bulk modulus and molar volume for these two groups, as well as the equation fitted to the data by linear and nonlinear regression; logarithmic scales were used for these fits. For the Alkali Halide Group the data are described by the equation:

$$KV_m = 6.65 Z_c \quad (8)$$

For the Sulfide-Oxide Group the appropriate equation is:

$$KV_m = 10.84 Z_c^{3/2} \quad (9)$$

In practice the proportionality of K and $1/\bar{V}_m$ was determined separately, and a fit of $\log KV_m$ against $\log Z_c$ was then made. Correlation coefficients of greater than 0.97 confirm that there is a good correlation among bulk modulus, molar volume and valence.

The same groups were used in determining the empirical relationship among Mohs hardness, molar volume and valence. The data for the Sulfide-Oxide Group are shown in Figure 7. The correlation can be described by the equation:

$$H_m V_m^{2/3} = 19.16 Z_c^{2/3} \quad (10)$$

Again, the proportionality of H_m and $V_m^{-2/3}$ was determined separately, and a fit of $\log (H_m V_m^{2/3})$ against $\log (Z_c)$ then made. The correlation coefficient, though not as high as for the KV_m versus Z_c data, is still over 0.90. In the case of the Alkali Halide Group, no immediate correlation of $H_m V_m^{2/3}$ with Z_c is apparent, the data for the alkali halides ($Z_c = 1$) showing considerable scatter. However, if these data are plotted separately against total number of electrons T_e in the formula, a correlation is apparent (Fig. 8), defined by the equation:

$$H_m V_m^{2/3} = 11.41 + 0.30 T_e \quad (11a)$$

This relationship was used to define an "effective valence" Z_e for the alkali halides. This "effective valence" was based upon a minimum of 12 electrons in the alkali halides. Rearranging equation (11a) based on this 12-electron minimum leads to the equation:

$$H_m V_m^{2/3} = 14.99 [1 - (T_e - 12)/50.21] \quad (11b)$$

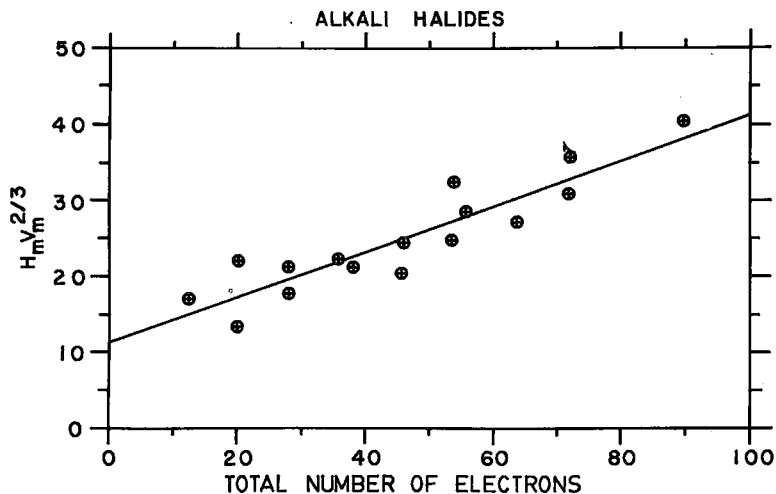


FIG. 8. Dependence of $H_m V_m^{2/3}$ on total number of electrons in the structure for the alkali halides. The line determined by linear regression is: $H_m V_m^{2/3} = 11.41 + 0.299$ (total number of electrons); $R = 0.9096$.

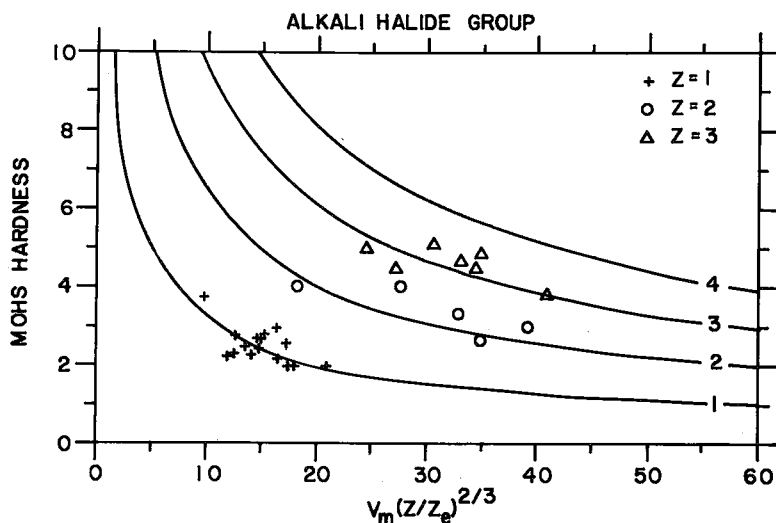


FIG. 9. Mohs hardness - molar volume data for the Sulfide-Oxide Group. Molar volume data for the alkali halides have been adjusted to compensate for the difference between the effective valence, Z_e , and the true valence, Z . For the remaining compounds the effective valence is equal to the true valence, and Z/Z_e equals 1. The curves represent the equation $H_m = 15.01 Z_e / V_m^{2/3}$ with $Z_e = 1$ (+), $Z_e = 2$ (O), $Z_e = 3$ (Δ), and $Z_e = 4$ (no symbol). The equation determined by linear regression is in logarithmic form: $\log (H_m V_m^{2/3}) = 1.176 + 1.023 \log Z_e$; $R = 0.9399$.

where:

$$1 - (T_c - 12) / 50.21 = \text{“effective valence”} = Z_e \quad (11c)$$

Values of Z_e for the alkali halides are tabulated in Table 2; LiF, with 12 electrons, has an effective valence of 1. H_m and V_m data for the Alkali Halide Group are plotted in Figure 9; values of V_m have been adjusted by a quantity $(Z_c/Z_e)^{2/3}$ to permit inclusion of alkali halide data; for the non-alkali halides, $Z_c = Z_e$. The empirical relationship for all data in the Alkali Halide Group is:

$$H_m V_m^{2/3} = 15.38 Z_e \quad (12)$$

The correlation coefficient, using logarithmic scales, is again greater than 0.90.

The empirically derived equations for both the Sulfide-Oxide Group and the Alkali Halide Group are summarized in Table 4. Equations (8), (9), (10) and (12) have been rearranged to put them into common formats in equations (8a), (9a), (10a) and (12a). As can be seen, for the Alkali Halide Group the term $(20 Z_{c,e}/3)$ is common to both the bulk modulus and hardness equations; “effective valence” must be used in place of valence in the hardness equation. For the Sulfide-Oxide Group the term $(24 Z_c)$ is common to both equations, but the exponent on this term differs for the bulk modulus and hardness equations.

Combination of the empirical equations (8) through (12) and (8a) through (12a) results in equations (13), (13a), (14) and (14a) relating hardness to

bulk modulus for the Alkali Halide and Sulfide-Oxide Groups. The approximate term $(9V_m^{1/2}/4)$ is common to the equations for both groups. The equations differ in that the Alkali-Halide-Group equations have a term compensating for the different exponents on the valence term for the hardness and bulk-modulus equations. The latter term may or may not have physical significance; regression analysis of $(H_m / KV_m^{1/2})$ against Z_c shows a dependence on valence, but the correlation coefficient is low. Equations (13) through (14a) show that, as noted by Beckmann (1971) and Scott (1973), there is a relationship between bulk modulus or compressibility and hardness. However, as is shown by these equations, this correlation is not direct but involves other terms as well.

A_xB_y-type compounds

Initially, we restricted ourselves to a consideration of data for AB-type compounds. Table 3 shows the relationship between bulk modulus and molar volume for A_xB_y-type compounds in the fluorite, rutile, quartz, corundum, spinel, cuprite and argentite structures; the ratio x:y is not equal to 1. For the volume term, we have chosen to use the molar volume based upon one anion; for valence we have used the square root of the product of the average cation and anion valences, Z_p . With these definitions, A_xB_y-type compounds fall into two groups corresponding to our original Alkali Halide and Sulfide-Oxide Groups. Table 3 lists observed values of (KV_m/Z_p) and $(H_m V_m^{2/3}/Z_p)$ for the Sulfide-

TABLE 4. SUMMARY OF EMPIRICAL CORRELATIONS

ALKALI HALIDE GROUP		SULFIDE-OXIDE GROUP	
equation	number	equation	number
$K = 6.65 Z_c / V_m$	8	$K = 10.84 Z_c^{3/4} / V_m$	9
$= (20/3) Z_c / V_m$	8a	$= (24 Z_c)^{3/4} / V_m$	9a
$H_m = 15.38 Z_e / V_m^{2/3}$	12	$H_m = 19.16 Z_c^{2/3} / V_m^{2/3}$	10
$= (9/4) (20/3) Z_e / V_m^{2/3}$	12a	$= (9/4) (24 Z_c)^{2/3} / V_m^{2/3}$	10a
$H_m = 2.51 (V_m^{1/3}) (Z_e / Z_c) K$	8+12-13	$H_m = 1.78 (V_m^{1/3}) (1/Z_c) K$	9+10-14
$= (9/4) (V_m^{1/3}) (Z_e / Z_c) K$	13a	$= (9/4) (V_m^{1/3}) (1/24 Z_c) K$	14a

GENERAL RELATIONSHIPS	
equation	number
$K = V(d^2U/dV^2)_{V_0} = V(d^2U/dr^2)(dr/dV)^2$	2a
$= (AZ_a Z_c e^{2(n-1)}) / (9V_m^{0.4/3})$	2b
$H_m = (AZ_e Z_c e^{2(n-1)}) / (4V_m)$	13a+2b-15a
$H_m = (AZ_a Z_c e^{2(n-1)}) / ((4V_m)(24Z_c)^{1/12})$	14a+2b-15b
$H = (d^2U/dr^2)_{r_0} = H_m$	15a+15b-15

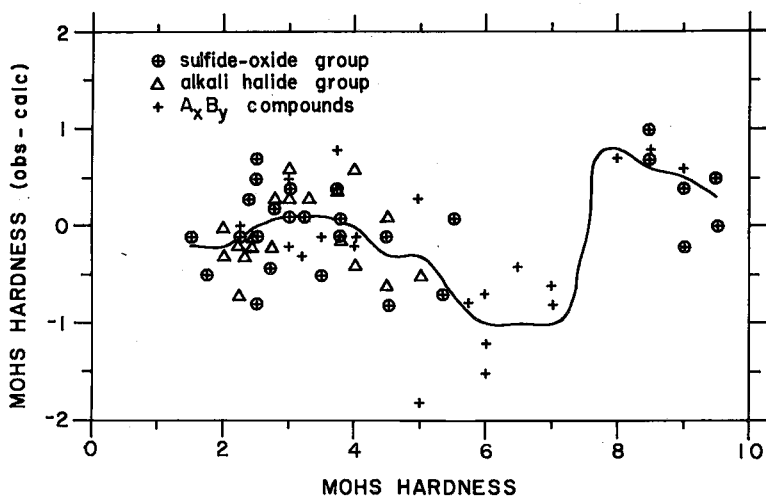


FIG. 10. The difference between observed and calculated Mohs hardness as a function of observed Mohs hardness. Data are shown for the Sulfide-Oxide Group (\oplus), Alkali Halide Group (Δ), and for $A_x B_y$ -type compounds in both groups ($+$). The curve was constructed through points determined by averaging data over one-half unit intervals in Mohs hardness.

Oxide Group. As can be seen, these values are close to the coefficients in equations (8), (9), (10) and (12) and are within the ranges for AB-type compounds shown in Tables 1 and 2, with the exception of two anomalous materials, CaCl_2 and SiO_2 . The fact that quartz, SiO_2 , is anomalous may indicate that this type of correlation will not be applicable to silicates.

CONCLUSIONS

Equations (8), (9), (10) and (12) demonstrate that empirical relationships exist by which bulk modulus and hardness can be modeled for certain groups of minerals. Equations (8a), (9a), (10a) and (12a) further demonstrate that these empirical equations have a number of terms in common; combining equation (8a) with (12a) to derive (13a) and equation (9a) with (10a) to derive (14a) demonstrates the basis for empirical correlations between hardness and bulk modulus (or compressibility) established by previous investigators. Equations (2a) and (2b) show that for bulk modulus these empirical equations can be related to a theoretical concept, that is, bulk modulus is proportional to the second derivative of lattice energy with change of volume, $(d^2U/dV^2)_{V_0}$. Equation (2b) can be combined with equations (13a) and (14a) to produce equations (15a) and (15b) as shown in Table 4; comparison with equation (2a) suggests that the Mohs hardness is proportional to the second derivative of lattice energy with change of interatomic distance, $(d^2U/dr^2)_{r_0}$. "Abso-

lute hardness" could therefore be defined by the equation:

$$H = (d^2U/dr^2)_{r_0} \propto H_m \quad (15)$$

rather than being defined as equal to the volumetric cohesive (lattice) energy, U/V , as proposed by Plendl & Gielisse (1963). The dependence of hardness upon r_0 rather than upon V_0 is a reflection of the directional nature of hardness; *i.e.*, we are stretching and breaking bonds in one direction rather than compressing the structure in three directions.

One of the purposes of this study was to check the possibility of using the empirical Mohs hardness - bulk modulus correlations to estimate compressibilities. Examination of the scatter of data in the various figures and tables shows that, in most cases, application of the empirical equations relating bulk modulus to molar volume would be a more accurate method for estimating bulk modulus. However, the use of the equations relating hardness to molar volume may lie in determining in which group a compound belongs prior to applying the appropriate equation relating compressibility to molar volume.

It is possible that the equations derived could also be used to estimate hardness. Tables 1, 2 and 3 and Figure 10 show the deviation of the values of Mohs hardness estimated by use of equations (10) and (12) from the observed values. The spread is generally about one-half unit about the observed value, but the predicted value is consistently low in the range

6 to 7 and consistently high in the range 8 to 10. In the range 6 to 7 this is probably due to inaccuracies in the data (most of the data points are for A_xB_y compounds); in the range 8 to 10 the discrepancy may be real, since many authors have suggested that the Mohs hardness scale should be expanded between 9 and 10.

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