

The three-dimensional considerations implicit in wall calculations are seldom mentioned. In fact, it is usual to assume that a minimum of  $G$  has been found when, in fact, all that has been found is a solution of the Euler equations (8). Nothing is said about the substitution of another boundary condition for the one that comes, just as unambiguously as does the differential equation, out of the formal variational procedure; and nothing is said about the sign of the second variation, which determines the stability. It does not follow from this that the usual calculations are necessarily not useful, but it does follow that they are lacking in completeness and consistency.

Finally, let us examine, from a three-dimensional point of view, a uniform state that was found stable under the constraint of one-dimensionality. If the magnetization has no component along  $Oz$ , the state is stable with respect to arbitrary three-dimensional variations; for every term in  $G$  is at a minimum with respect to such variations. But if there is a  $z$  component, removal of the constraint may allow a decrease of  $G$  by development of a structure nonuniform in  $x$  and  $y$ ; for such nonuniformity can decrease the magnetostatic energy. Thus domain formation appears to be an essentially two- or three-dimensional phenomenon.

## Hardness of Nonmetallic Solids on an Atomic Basis

JOHANNES N. PLENDL AND PETER J. GIELISSE

*Air Force Cambridge Research Laboratories, Office of Aerospace Research, Bedford, Massachusetts*

(Received July 10, 1961)

Hardness values of 65 nonmetallic crystalline solids of 16 different structures are compared with data of a newly introduced concept: "the volumetric lattice energy." When such solids are classified according to a new interpretation of lattice anharmonicity, a set of linear interrelations is obtained which covers the entire hardness range. Thus, on the basis of interatomic cohesive forces, the over-all hardness of these solids becomes unambiguously defined. Hardness receives the dimension (ergs/cm<sup>3</sup>) or (kcal/cm<sup>3</sup>), and an absolute scale. Such hardness data become independent of anisotropy, structure type, and valency of the atoms. Conversion from relative to absolute hardness, as well as estimation of lattice energy data through appropriate hardness testing, becomes possible. For example, the extremely high hardness value of the rare type-II diamond could be determined to be 1.7 times that of the type-I diamond, purely from atomic data. Analogous treatment of the hardness of metallic solids poses additional problems.

### I. INTRODUCTION

ALL hardness measurements are relative, and the data obtained by the many different methods of hardness testing are for the greater part not comparable with one another.<sup>1</sup> The hardness of a solid is defined by the resistance against lattice destruction and is considered to be a function of the interatomic forces.<sup>2</sup> Attempts towards a physical definition of hardness were made by Friedrich, Goldschmidt and others.<sup>3</sup> Yet hardness has in general defied unambiguous physical

definition.<sup>4</sup> This presentation intends to develop such a definition.

The vast majority of hardness data of crystals are given in numerical units according to Mohs ( $M$  scale). Therefore, the experimental hardness data of this study for the greater part refer to this  $M$  scale. As recent work shows, there is a sound physical basis upon which equal intervals of scratch-hardness can be constructed and, in fact, the  $M$  scale follows it surprisingly well up to the relative hardness  $H=9$ .<sup>5</sup> About 99% of all known materials belong to a hardness range from  $H=1$  to  $H=9$ , while the relative difference in hardness between successive materials is small within this range. Thus the  $M$  scale is quantitatively useful up to  $H=9$ .

However, the complementary range between corundum and diamond (corresponding to  $H=9$  and 10 in

<sup>1</sup> H. Tertsch, *Neues Jahrb. Mineral. Monatsh.*, p. 121 (1955).

<sup>2</sup> C. W. Stillwell, *Crystal Chemistry* (McGraw-Hill Book Company, Inc., New York, 1938), pp. 29, 225–239. R. C. Evans, *An Introduction to Crystal Chemistry* (Cambridge University Press, New York, 1948), pp. 21–23. H. Tertsch, *Festigkeiterscheinungen der Kristalle* (Springer-Verlag, Vienna, 1949), pp. 171–257. H. von Weingraber, *Technische Härtemessung* (C. Hauser-Verlag, Muenchen, 1952). C. Zwicker, *Physical Properties of Solid Materials* (Pergamon Press New York, 1954), pp. 258–261. H. G. F. Winkler, *Struktur und Eigenschaften der Kristalle* (Springer-Verlag, Berlin, 1955), pp. 266–285.

<sup>3</sup> E. Friedrich, *Fortschritte der Chemie, Physik und Physikalischen Chemie* (Verlag Gebr. Borntraeger, Berlin, 1926), Vol. 18, Heft 12, pp. 1–44. V. M. Goldschmidt, *Geochemische Verteilungsgesetze der Elemente* (Jacob Dybwad-Verlag, Oslo, 1927), pp. 102–127.

<sup>4</sup> H. Tertsch, reference 2. D. Tabor, *Endeavour* **13**, 27 (1954). W. F. de Jong, *General Crystallography* (W. H. Freeman & Company, San Francisco, 1959), pp. 236.

<sup>5</sup> E. Troeger, *Neues Jahrb. Mineral. Monatsh.* 233 (1954). D. Tabor, *Proc. Phys. Soc. (London)* **B67**, 249 (1954) (includes a compilation of pertinent literature). D. Tabor, *Endeavour* **13**, 27 (1954).

the  $M$  scale) constitutes a much wider region with great differences in hardness between the few known materials within this range. Therefore, for the region above  $H=9$ , we employ the results of hardness testing according to Wooddell, who measured the relative resistance to abrasion during lapping.<sup>6</sup> Wooddell fixed the hardness values of quartz and corundum at 7 and 9, (in agreement with the  $M$  scale), and extended the relative hardness scale in a linear-proportional sense. Consequently, Wooddell's linear-proportional hardness scale ( $W$  scale), ranging from corundum to diamond ( $H=42.5$  for South American diamonds) covers 80% of the known hardness region, although less than 1% of all solids have a hardness greater than that of corundum. A combination of both the  $W$  scale and the  $M$  scale is justified because of the overlapping interval.

## II. A PHYSICAL DIMENSION OF HARDNESS

The recent first determination of lattice energy data for a number of solids harder than corundum (such as SiC, BN, and the two types of diamond) from their respective infrared spectra,<sup>7</sup> combined with a study on lattice anharmonicity,<sup>7</sup> formed a basis for an examination of hardness from the atomic aspect. In technical hardness testing, hardness can be defined by a pressure or force per square centimeter ( $\text{kg}/\text{cm}^2$ ), and thus be conceived as an energy per volume ( $\text{kgcm}/\text{cm}^3$ ), e.g., the ratio between input energy and abraded volume.

Proceeding now to the atomic aspect, we should likewise have the dimension of an energy per volume for the resistance of the lattice against destruction during hardness testing. Thus we examine this resistance as a function of "the lattice energy per unit volume," and call it "volumetric lattice energy,"  $U/V$ , having the dimension ( $\text{ergs}/\text{cm}^3$ ) or ( $\text{kcal}/\text{cm}^3$ ), where  $U$ =the total cohesive energy of the lattice (lattice energy) per

TABLE I. Data pertinent to  $A$  solids.

No.	Substance	Structure	$X_m$	$V$ ( $\text{cm}^3$ )	$U$ ( $\text{kcal}/\text{mole}$ )	$U/V$ ( $\text{kcal}/\text{cm}^3$ )	$H$ (combined $M$ - $W$ scale)
1	LiF	rock salt	0.27	11.3	246	21.8	3.5
2	LiCl	rock salt	0.31	20.2	203	10.0	3
3	LiBr	rock salt	0.34	25.2	203	8.0	3
4	NaF	rock salt	0.56	15.0	218	14.5	3.3
5	MgF <sub>2</sub>	rutile	0.58	20.1	797	40	4.5
6	BeO	wurtzite	0.31	8.2	1055	129	8.5
7	MgO	rock salt	0.52	11.3	944	84	6.3
8	Al <sub>2</sub> O <sub>3</sub>	$\alpha$ -corundum	0.54	24.5	3620	148	9
9	SiO <sub>2</sub>	$\beta$ -quartz	0.55	26.5	3090	116	7
10	CaO	rock salt	0.62	16.7	823	49	4.5
11	MnO	rock salt	0.67	13.0	923	71	5.5
12	NiO	rock salt	0.68	11.7	960	82	6
13	CaSO <sub>4</sub>	barite <sup>10</sup>	0.62	48.3	667	14	3.2
14	BN	zinc blende	0.33	10.8	5400 <sup>a</sup>	500	~19 <sup>b</sup>
15	SiC	zinc blende	0.45	12.7	4200 <sup>a</sup>	330	14
16	C-C I	type-I diamond	0.32	6.9	9400 <sup>a</sup>	1350	42.5
17	C-C II	type-II diamond	0.32	6.9	17 000 <sup>a</sup>	2450	(71)

<sup>a</sup>  $U$  data determined from pertinent infrared spectra.<sup>7</sup>

<sup>b</sup> The hardness of BN is known to be closer to the hardness of diamond than any other solid except BC. Therefore, it has been assumed that BN, whose  $U$  value was determinable,<sup>7</sup> has approximately the same hardness as BC.<sup>6</sup>

<sup>6</sup> C. E. Wooddell, Trans. Electro. chem. Soc. **68**, 11 (1935).

<sup>7</sup> J. N. Pientl, Phys. Rev. **123**, 1172 (1961).

TABLE II. Data pertinent to  $B$  solids.

No.	Substance	Structure	$X_m$	$V$ ( $\text{cm}^3$ )	$U$ ( $\text{kcal}/\text{mole}$ )	$U/V$ ( $\text{kcal}/\text{cm}^3$ )	$H$ ( $M$ scale)
1	TiO <sub>2</sub>	rutile	0.65	21.0	2900	138	6.3
2	MnO <sub>2</sub>	rutile	0.67	18.2	3100	170	7
3	CuO	tenorite	0.69	12.5	920	73	4.5
4	Cu <sub>2</sub> O	cuprite	0.69	23.9	740	31	4
5	ZnO	wurtzite	0.69	15.1	952	63	4.5
6	Y <sub>3</sub> Fe <sub>5</sub> O <sub>12</sub>	garnet	0.70	145	25 000 <sup>a</sup>	172	7
7	SrO	rock salt	0.73	22.0	790	36	4
8	CdO	rock salt	0.75	18.5	911	49	4.2
9	SnO <sub>2</sub>	rutile	0.76	21.5	2800	130	6
10	BaO	rock salt	0.78	26.8	740	27	3.5
11	PbO <sub>2</sub>	rutile	0.80	29.0	2830	97	5.3
12	KF	rock salt	0.69	23	199	8.7	2.8
13	CaF <sub>2</sub>	fluorite	0.70	24.3	662	27.5	4
14	ZnF <sub>2</sub>	fluorite	0.79	21.3	670	31.5	4
15	SrF <sub>2</sub>	fluorite	0.81	36.4	597	16.4	3
16	CdF <sub>2</sub>	fluorite	0.85	22.5	672	30	4
17	BaF <sub>2</sub>	fluorite	0.90	36.5	564	15.6	3
18	PbF <sub>2</sub>	fluorite	0.94	29.7	599	20.2	3.2
19	MgS	rock salt	0.74	19.5	778	40	4.2
20	CaS	rock salt	0.96	25.8	722	28	3.8
21	MnS	zinc blende	1.09	22	894	40	4
22	FeS	nickel arsenide	1.10	19.4	840	43	4
23	Cu <sub>2</sub> S	antifluorite	1.15	28.4	480	17	3
24	ZnS	zinc blende	1.16	24.2	925	38	4
25	SrS	rock salt	1.27	32.5	687	21	3.3
26	CdS	zinc blende	1.35	30.0	808	27	3.5
27	BaS	rock salt	1.40	40.0	660	16.5	3
28 <sup>b</sup>	SrSO <sub>4</sub>	barite	0.73	46.3	647	14	3
29 <sup>b</sup>	BaSO <sub>4</sub>	barite	0.77	50.5	624	12.5	3
30 <sup>b</sup>	PbSO <sub>4</sub>	barite	0.80	48	642	13	3
31	Si-Si	zinc blende	0.76	24.2	4400 <sup>a</sup>	180	7
32	Ge-Ge	zinc blende	1.96	27.5	3500 <sup>a</sup>	127	6
33	NaCl	rock salt	0.75	27.1	184	7	2.5
34	KCl	rock salt	1.00	37.5	169	4.5	2
35	CaCl <sub>2</sub>	chlorocalcite	1.02	50	546	11	3
36	CuCl	zinc blende	1.23	28.1	236	8.5	2.5
37	RbCl	rock salt	1.35	44	162	4	2
38	SrCl <sub>2</sub>	fluorite	1.36	52	494	9.5	2.8
39	AgCl	rock salt	1.44	25.8	215	8	2.5
40	PbCl <sub>2</sub>	fluorite	1.64	48.5	521	10.5	2.5
41	NaBr	rock salt	0.98	32	172	5.5	2.2
42	KBr	rock salt	1.42	43	160	4	2
43	CuBr	rock salt	1.92	31	232	7.5	2.4
44	AgBr	rock salt	2.45	29.3	212	7	2.4
45	NaI	rock salt	1.05	41	167	4	2
46	KI	rock salt	1.61	53	152	3	2
47	CuI	zinc blende	2.30	33.8	231	7	2.3
48	AgI	zinc blende	3.20	41.5	211	5	2

<sup>a</sup>  $U$  data determined from pertinent infrared spectra.<sup>7</sup>

<sup>b</sup> In determining  $X_m$  for the SO<sub>4</sub> compounds, only adjacent metal and oxygen ions are taken into consideration, since the S ions are shielded by the O ions, as a result of their tetrahedral coordination.

mole,  $V$  = the mole volume, defined as  $M/s$ ,  $M$ =the molecular weight, and  $s$ =the specific weight. Tables I and II show values of "volumetric lattice energy" and relative hardness for 65 minerals and inorganic crystals (semiconductors and nonconductors) of 16 different structure types, for which pertinent data are on hand.<sup>3,8</sup> The vast majority of them are binary compounds and some are either ternary compounds or elements. The number of these crystalline substances is limited by the requirement that data for both relative hardness and lattice energy be known. It should be noted that the above solids have  $H$  values from 2 to 42.5. In Figs. 1 and 2 the  $H$  values of these solids are plotted against their respective  $U/V$  values.

<sup>8</sup> H. H. Landolt and R. Boernstein, *Zahlenwerte und Funktionen* (Springer-Verlag, Berlin, 1955), Vols. I and IV/1. A. Kaputinsky and B. Weselowsky, Z. physik. Chem. **B22**, 261 (1933). Dana's *Manual of Mineralogy*, revised by C. S. Hulbert (John Wiley & Sons, Inc., New York, 1960), 17th ed. A. N. Winchell and H. Winchell, *Elements of Optical Mineralogy* (John Wiley & Sons, Inc., New York, 1951), 4th ed., Part II. The pertinent volumes of *Gmelins Handbuch der Anorganischen Chemie* (Verlag Chemie, GmbH, Berlin).

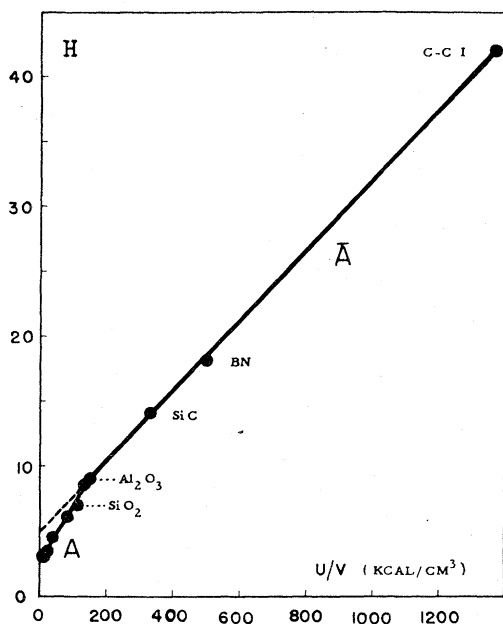


FIG. 1. Proportionality between relative hardness ( $H$ ) and "volumetric lattice energy" ( $U/V$ ) for  $A$  solids. ( $M$  scale:  $H \leq 9$ ,  $W$  scale:  $H \geq 9$ ).

### III. HARDNESS AND "VOLUMETRIC LATTICE ENERGY"

A striking experimental phenomenon is discovered when correlating the  $H$  and  $U/V$  values. An unambiguous linear relationship between both  $H$  and  $U/V$  is established for the entire hardness range of the solids, if properly classified. The maximum limits of error are about  $\pm 0.5$  unit in the  $H$  and  $\pm 5$  percent in the  $U/V$  data. In detail, we obtain from Tables I and II two distinct hardness characteristics:  $A$ - $\bar{A}$  and  $B$ - $\bar{B}$ , as is shown in Figs. 1 and 2, respectively. They correspond to different classes of solids which result from a recent study on lattice anharmonicity by one of us.<sup>7</sup> The mechanical properties of solids appear to be controlled by the amount of anharmonicity of the respective cohesive forces. If the related mass values  $X_m$  of adjacent atom or ion partners<sup>9</sup> decrease substantially below unity, a strong increase of mutual interpenetration or interlinking of the atoms occurs with a corresponding increase of the lattice anharmonicity, represented by  $X_m^{-1/p}$  (see Fig. 3). This results in a very strong resistance against lattice destruction or very high hardness values. (Figure 3 indirectly relates  $X_m^{-1/p}$  to the electronic configurations of the rare gases:  $X_m = \frac{2}{3}$  indicates the neon configuration,  $X_m = \text{unity}$  defines the argon configuration.) Thus, depending upon whether they do or do not have the neon configuration, the nonmetallic solids were divided as follows:

(I) *Class-A Solids*. The atom partners do not have

<sup>9</sup> The "related mass"  $X_m$  is a dimensionless quantity which represents the reduced mass of the vibrating ion (atom) partners related to the reduced mass of the ions of K and Cl (electronic configuration of argon).<sup>7</sup>

the electronic configuration of neon. These solids are defined by related mass values  $X_m < 0.64$  ( $=X_m$  value of  $\text{Sc}_2\text{O}_3$ ) if the atom partners in the solid display different valencies, and  $X_m < 0.69$  ( $=X_m$  value of  $\text{KF}$ ) if they have equal valencies. Pertinent data for 17  $A$ -solids are compiled in Table I and graphically represented by the lines  $A$  and  $\bar{A}$  in Figs. 1 and 2. The  $A$  solids exhibit the steepest hardness characteristic that exists. Since in this case we employ the two relative scales  $M$  and  $W$ , two linear relations result:

$$U/V = 24(H - 2.7) \quad (\text{kcal/cm}^3),$$

corresponding to line  $A$  (1)

and

$$U/V = 36(H - 4.8) \quad (\text{kcal/cm}^3),$$

corresponding to line  $\bar{A}$ . (2)

Equation (2) covers the  $W$  scale between the coordinates ( $H=9$ ,  $U/V=150$ ) and ( $H=42.5$ ,  $U/V=1350$ ), while Eq. (1) covers values from  $H=3$  to  $H=9$ . The change from the first to the second relation (or from the  $M$  scale to the  $W$  scale) results in different slopes of the lines  $A$  and  $\bar{A}$ . A variety of 20 additional  $\bar{A}$  and  $A$  solids (borides, carbides, nitrides), for which  $H$  data but no  $U$  data are available, are tabulated in Table III.

(II) *Class-B Solids*. The atom partners have the electronic configuration of neon. These solids are defined by related mass values  $X_m \geq 0.64$  if the atom partners have different valencies among one another, and  $X_m \geq 0.69$  if they display equal valencies. Pertinent data of 48  $B$  solids are compiled in Table II and graphically represented by the lines  $B$  and  $\bar{B}$  in Fig. 2. The  $B$  solids exhibit a medium hardness characteristic. Since, according to Troeger,<sup>5</sup> the progression ratio increases within the  $M$  scale by a factor  $\sqrt{3}$  when  $H < 4$ , we again

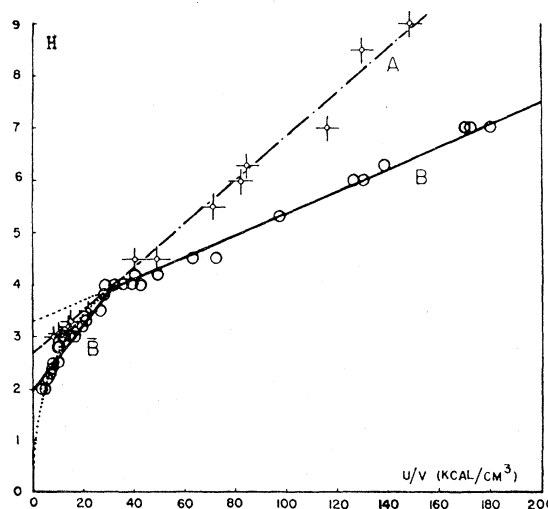


FIG. 2. Proportionality between relative hardness ( $H$ ) and "volumetric lattice energy" ( $U/V$ ). Line  $A$ :  $A$  solids as in Fig. 1, lines  $B$ - $\bar{B}$ :  $B$  solids.

TABLE III. Hardness type classification and lattice energy values ( $U$ ) which are estimated from the data of scratch-hardness ( $M$  scale) or abrasion-hardness ( $W$  scale).

No.	Substance	Structure	$X_m$	$V$ ( $\text{cm}^3$ )	$H$ ( $M$ scale)	$U/V$ ( $\text{kcal}/\text{cm}^3$ )	$U$ ( $\text{kcal}/\text{mole}$ )	Hardness type
1	$\text{B}_4\text{C}$	$\text{CsCl}$ (deformed)	0.31	22.1	19.7 ( $W$ scale)	540	12 000	$\bar{A}$ solids
2	$\text{SiB}_6$		0.43		9-10			
3	$\text{TiB}$		0.48		9-10			
4	$\text{VB}$		0.48		9-10			
5	$\text{ZrB}$		0.52		9-10			
6	$\text{VC}$	rock salt	0.53	10.9	9-10			
7	$\text{NbC}$	rock salt	0.57	13.4	9-10			
8	$\text{VN}$	rock salt	0.59	10.6	9-10			
9	$\text{TaC}$	rock salt	0.60		9-10			
10	$\text{W}_2\text{C}$		0.61	22.1	9-10			
11	$\text{WC}$	(hexagonal)	0.61	12.6	12 ( $W$ scale)	260	3300	
12	$\text{BeS}$	zinc blende	0.38	17.4	7.5	115	2000	$A$ solids
13	$\text{TiC}$	rock salt	0.52	12.2	8-9	139	1700	
14	$\text{Cr}_3\text{C}_2$	$D5_{10}$	0.53	27.0	8-9	139	3800	
15	$\text{ZrC}$	rock salt	0.57	15.3	8-9	139	2100	
16	$\text{MoC}$	(hexagonal)	0.58	12.3	8	127	1600	
17	$\text{ScN}$	rock salt	0.58	13.4	8	127	1700	
18	$\text{TiN}$	rock salt	0.58	11.4	8-9	139	1600	
19	$\text{ZrN}$	rock salt	0.60	14.8	7-8	115	1700	
20	$\text{NbN}$	rock salt	0.60	12.7	9	151	1900	
21	$\text{GeO}_2$	rutile	0.71	16.7	5	82	1400	$B$ solids
22	$\text{Y}_2\text{O}_3$	$D5_3$	0.73	45.2	6	129	5800	
23	$\text{ZrO}_2$	fluorite	0.74	21.7	7-8	202	4400	
24	$\text{Ce}_2\text{O}_3$	$D5_2$	0.78	47.0	5	82	3900	
25	$\text{Yb}_2\text{O}_3$	$D5_3$	0.79	43.0	6	129	5600	
26	$\text{WO}_2$	rutile	0.80	17.8	5-6	106	1900	
27	$\text{ThO}_2$	fluorite	0.81	26.4	6-7	153	4000	
28	$\text{V}_3\text{Si}$	$\beta$ tungsten ( $A15$ )	0.98	23.7	7-8	202	4800	
29	$\text{M}_2\text{Si}$	iron silicide ( $B28$ )	1.00	22.3	6	129	2900	
30	$\text{ZrSi}_2$	$C49$	1.15	30.4	4	33.6	1000	

obtain two linear relations:

$$U/V = 48(H - 3.3) \quad (\text{kcal}/\text{cm}^3),$$

corresponding to line  $B$  (3)

and

$$U/V = 16(H - 2.0) \quad (\text{kcal}/\text{cm}^3),$$

corresponding to line  $\bar{B}$ . (4)

Equation (3) covers the  $M$  scale between the coordinates ( $H=4$ ,  $U/V=35$ ) to ( $H=8$ ,  $U/V=225$ ), while Eq. (4) covers values from  $H=2$  to  $H=4$ . The change from the first to the second relation is again indicated by the different slopes of the lines  $B$  and  $\bar{B}$ . The increase of slope from  $B$  to  $\bar{B}$  (by a factor 3 at  $H < 4$ ) corresponds to the increase of the above mentioned progression ratio (by the factor  $\sqrt{3}$ ). The line  $\bar{B}$  may be conceived as to substitute the real curve, a cubic parabola:  $U/V = H^3/2$ , for which  $H \rightarrow 0$  when  $U/V \rightarrow 0$ . A similar relationship does not appear with the  $A$  solids, however, since their  $H$  values remain  $\geq 3$ . A small variety of 10 additional  $B$  solids (oxides and silicides), of which only the  $H$  data were known,<sup>3</sup> are tabulated in Table III.

The remaining metallic solids have the flattest hardness characteristic that exists for inorganic crystals. They include the metallic and transition elements, their alloys and the conducting compounds. A total examination of these solids, however, poses additional problems, such as a determination of their true lattice energy and

a definition of the indentation hardness on the basis of interatomic forces. Therefore, this subject will be treated as a whole in a forthcoming paper.

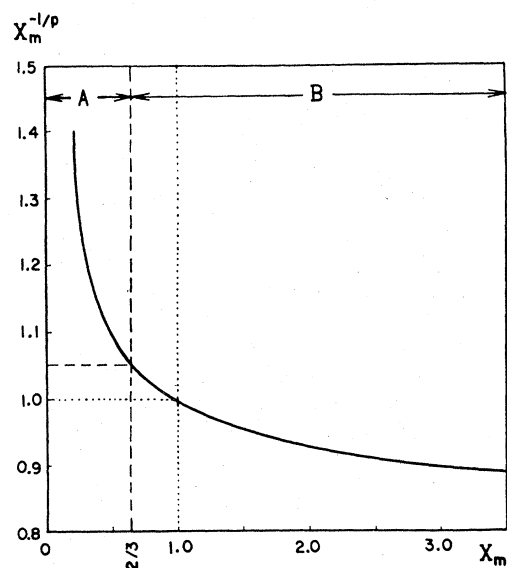


FIG. 3. The two hardness types ( $A$  and  $B$ ) of nonmetallic solids as a consequence of lattice anharmonicity ( $X_m^{-1/p}$ ) and related mass ( $X_m$ ).<sup>7</sup>  $X_m = 1.0$  corresponds to the electronic configuration of argon, and  $X_m = \frac{2}{3}$  corresponds to the electronic configuration of neon; where  $X_m < \frac{2}{3}$  defines the region of the  $A$  solids, and  $X_m \geq \frac{2}{3}$  defines the region of the  $B$  solids.

## IV. COMPILATION OF THE RESULTS

Summarizing the above results, we find that the definition of hardness by means of the "volumetric lattice energy" provides unambiguous scales. Moreover, it gives to hardness the dimension ( $\text{kcal}/\text{cm}^3$ ). Thus instead of using relative hardness scales, such as the combined Mohs-Wooddell scales, we may now employ, with appropriate classification, the new  $U/V$  scales. As for the  $A$  solids, the obtained maximum hardness so far is  $(U/V)_A = 1350 \text{ kcal}/\text{cm}^3$ , while for the  $B$  solids the corresponding  $(U/V)_B$  values extend to about  $225 \text{ kcal}/\text{cm}^3$  only. When compared to the combined  $M$ - $W$  scales, the  $U/V$  scales resolve hardness by a factor of 24 for  $A$ , 36 for  $\bar{A}$ , 48 for  $B$ , and 16 for  $\bar{B}$ .

The  $U/V$  scales give strictly comparable hardness values and avoid any change of the progression ratio. Such a definition of hardness eliminates selective hardness properties (anisotropy), which generally result from differences between the cohesive forces in various crystallographic directions, since the  $U$  values integrate these forces. The  $U/V$  hardness data also appear independent of lattice structure and valency of the atoms, the two already being taken into consideration with  $U$ .<sup>7</sup> Thus, the  $U/V$  hardness, properly classified, could be deemed the absolute over-all hardness.

Hardness data can now be obtained from mole volume and lattice energy values. Vice versa, lattice energy data can be estimated by appropriate scratch or abrasive hardness testing which adds to the various existing methods of lattice energy determination from ionic and structural properties. Table III shows the  $U$  values of 19  $A$  and  $B$  solids, estimated from hardness data  $\leq 9$ , using Eqs. (1) and (3). The  $\bar{A}$  solids of Table III ( $H > 9$ ), however, require a determination of their  $W$  hardness, in order to enable estimation of their  $U$  values in an analogous manner by Eq. (2).

It should be emphasized that the vast majority of the examined solids are binary compounds, except for some ternary compounds and elements, and are all either semiconductors or nonconductors. An investigation of the more complicated compounds was hampered by the fact that either their  $U$  or  $H$  data, or both were unknown. A study of the hardness of the metallic, conducting, solids on an atomic basis is in progress.

Impurities in samples of tested minerals and inorganic crystals may cause some differences in relative hardness values and other experimental data. Consequently, the impurities reduce somewhat the accuracy of the results

and thus may cause the experimental values to deviate from purely linear relationships.

## V. PRACTICAL APPLICATIONS AND CONCLUSIONS

A recent first determination of the lattice energy for the rare type-II diamond from its infrared spectrum gave<sup>7</sup>  $U = 17\,000 \text{ kcal}/\text{mole}$  which results in  $U/V = 2450 \text{ kcal}/\text{cm}^3$ . Using Eq. (1), the relative hardness of the rare type-II diamond is obtained as  $H_{D \text{ II}} = 71$  which is 1.7 times the relative hardness of the type-I diamond. On the basis of these data we obtain the full range of the  $U/V$  scale for the  $A$ - $\bar{A}$  solids as about 10 times larger than that for  $B$  solids. Since the  $H_{D \text{ II}}$  value is extrapolated from line  $\bar{A}$ , a confirmation by testing according to Wooddell's abrasive method seems desirable.<sup>10</sup>

Effects of structure modifications on hardness could not as yet be examined on an atomic basis for substances other than diamond because of lack of pertinent data. However, since data of either  $U$  or  $V$  are known to vary when the modification changes, we may assume until later confirmation that the  $U/V$  values change in accordance with the  $H$  values. The same reasoning should for the time being be applied to temperature effects.

Shortcomings within the  $M$  scale, such as considerable changes in the progression ratio, are indicated by changes of slopes (as for the lines  $A$ - $\bar{A}$  at  $H = 9$ , or the lines  $\bar{B}$ - $B$  at  $H < 4$ ) and to a lesser degree by deviations from the straight line relation (e.g. line  $B$  at  $H = 7$  and  $H = 8$ ). Because of this fact, it appears desirable to subject additional  $\bar{A}$ ,  $A$ , and  $B$  solids (see Table III) to hardness testing according to Wooddell and to determine their  $U$  values (e.g., from their infrared spectra<sup>7</sup>). The samples should be of high purity and the accuracy of measurements of such a degree that the slopes of all curves can be even more accurately fixed. Such work will allow us to form and confirm a uniform experimental scale for the entire hardness range, of nonconducting solids.

An investigation of  $\bar{A}$  solids on the basis of interatomic forces would supply data of value for the ultimate preparation of materials capable of withstanding extreme environmental conditions.

<sup>10</sup> It seems rather unlikely that the very rare type-II diamond was among Wooddell's test specimens, since the differences in the hardness of his diamonds are much less than those observed in the diamond cutting industry.