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Some New Interrelations in the Properties of Solids Based on Anharmonic Cohesive Forces*

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The lattice vibration spectrum of a solid can be characterized by one single frequency, which is defined as "the frequency of the center of gravity" of this spectrum or simply "center frequency." From its equality with the characteristic frequency of specific heat we have recently derived the "center law of the lattice vibration spectra." In assuming now that in a lattice, at equilibrium, the hypothetical maximum of vibrational energy (kinetic energy) of an atom (ion) pair equals the total cohesive energy (potential energy), and at the same time considering the anharmonicity of lattice vibrations, we derive a basic interrelation between center frequency and total cohesive energy. It constitutes a substantial extension of the above "center law." Its validity has been illustrated for 26 solid compounds of six different lattice structures which cover almost the entire range of lattice vibration spectra of solids. This interrelation allows a first determination of thus far inaccessible data of cohesive energy for solids of extremely high sublimation temperatures, such as silicon carbide, boron nitride, and the two types of diamond. Detailed study of the anharmonicity of lattice vibrations results in additional interrelations, such as one between exponent of repulsion and "related mass" [=reduced mass of the vibrating atom (ion) pairs related to argon], one between exponent of repulsion and "relative compressibility" (change of compressibility with pressure over compressibility), and thus one between "relative compressibility" and "related mass." In combining the two interrelations of center frequency, namely that with characteristic temperature and that with cohesive energy, we derive an interrelation between characteristic temperature and total cohesive energy. Examination of the relationship between anharmonicity and atomic behavior suggests a classification of solids according to their different anharmonic force characteristics. The solids can have either a soft or linear or hard force characteristic, dependent on the configuration which they resemble in the periodic chart of the atoms. The underlying concept of anharmonicity deduced in this paper helps to understand the physical properties of solids from an atomistic point of view.

1. INTRODUCTION

LATTICE vibration (infrared) spectra are a very promising means for studying the cohesive forces in solids, since they disclose the magnitude of these forces. Generally speaking, the higher the region of resonance frequencies in the vibrational spectrum, the greater the cohesive energy of a material. It is the aim of the present research to develop this statement into a precise interrelation. We may proceed according to either quantum mechanics or classical mechanics.

In order to simplify the problem, we may characterize the vibrational spectra unambiguously by one single frequency which is adherent to the substance examined. As such a frequency we recently[1] introduced "the frequency of the center of gravity of the lattice vibration spectrum," simply called "center frequency," which is defined by

$$\nu_c=\int_0^\infty \nu f(\nu)d\nu \bigg/ \int_0^\infty f(\nu)d\nu, \quad (\mathrm{sec}^{-1}) \qquad (1)$$

where ν=frequency, $f(\nu)$=either the reflectance R or the absorption coefficient K. The center frequency has the following outstanding properties: (a) Its value remains the same whether it is determined from the reflectance or from the absorption-type spectrum of a solid, although the two types can be very different from one another. (b) Its value remains constant with varying temperature from liquid air to the vicinity of the melting point. (c) Its value is equal to the mean value of Debye's characteristic frequency from specific heat, within the entire range of vibrational spectra of solids. This equality constitutes "the center law of the lattice vibration spectra" which reads:

$$\int_0^\infty \nu f(\nu)d\nu \bigg/ \int_0^\infty f(\nu)d\nu=(k/h)\Theta, \quad (\mathrm{sec}^{-1}) \qquad (2)$$

where Θ=mean value of Debye's characteristic temperature from specific heat, k=Boltzmann's constant, and h=Planck's constant.

In examining the lattice anharmonicity on the basis of these results of a recent study,[1] we have found that we can discriminate the different types of anharmonicity adherent to various solids and define them in simple terms. This knowledge will help us to define, understand, and even predict some physical properties of solid materials from atomic data.

2. COMPUTATION OF THE VIBRATIONAL ENERGY OF A LATTICE

A. According to Quantum Mechanics

In the energy expression for anharmonic vibrations of a lattice we have not only a sum of independent terms corresponding to the different normal vibrations, but also a sum of cross terms containing the vibrational

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* The essence of this paper was presented by the author at the Seventh Annual Science and Engineering Symposium of the U. S. Air Force, Air Research and Development Command, November 30, 1960, at Boston, Massachusetts; also at the Fifth European Congress on Molecular Spectroscopy, Amsterdam, The Netherlands, May 31, 1961.

[1] J. N. Plendl, Phys. Rev. **119**, 1598 (1960). [In Eqs. (2) and (3), read $(k/h)\Theta$ instead of $k/h\Theta$.]

quantum numbers of two or more normal vibrations[2]:

$$(1/hc)U_{v_1,v_2,\ldots}=X_0+\sum_{k=1}^{3N-6}X_k(v_k+\tfrac{1}{2})$$

$$+\sum_{k=1}^{l}\sum_{l=1}^{3N-6}X_{kl}(v_k+\tfrac{1}{2})(v_l+\tfrac{1}{2}),\quad (3)$$

where v_k = the quantum number of the kth mode, $3N-6$ = the number of fundamental frequencies, h = Planck's constant, c = the velocity of light, and X = wavenumbers. The term $X_{kl}(v_k+\frac{1}{2})(v_l+\frac{1}{2})$ arises from the effect of cubic, quartic, and other anharmonic terms of the potential energy. Calculating the X_k's from the cubic and quartic coefficients is, however, a formidable problem which has been solved in only a few of the simplest cases.[2]

B. According to Classical Mechanics

The infrared spectra of lattice vibrations deal with the relatively slow movements of the comparatively heavy nuclei, and, therefore, the quantum mechanical laws closely approach the laws of classical mechanics (Bohr's correspondence principle).[3] In this case we are thus justified in applying the laws of classical mechanics.

Lattice vibrations become strongly anharmonic with increasing amplitude. Their anharmonicity may be due either to lack of proportionality between nuclear displacements and restoring forces, or lack of proportionality between displacements of both the nuclei and the electrical charges.[4] The nonlinearity of the restoring forces as a function of the displacement r can be twofold[5]: (i) *hard*, when the second derivative of $f(r)$ increases with r [see Fig. 1A], (ii) *soft*, when the second derivative of $f(r)$ decreases with r [see Fig. 1C], where $f(r)$ represents the total cohesive energy, $f'(r)$ the restoring force, and $f''(r)$ the stiffness. The *linear* or *harmonic* case occurs when $f''(r)$ = constant [see Fig. 1B]. Since we do not know in advance of trial what type of force characteristic applies to the interatomic forces of various solids, we shall first consider the middle or linear case and develop the two anharmonic modes "soft" or "hard" from it.

For any atom (ion) pair within the lattice of a binary compound which vibrates with frequency ω against its center of gravity, and has the displacements r_x and r_y of its masses M and m, respectively, we have

$$Mr_x=mr_y.\quad (4)$$

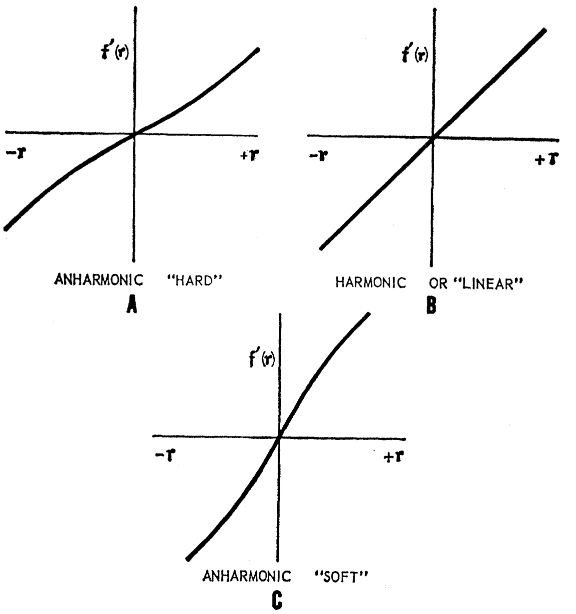

FIG. 1. The different types of anharmonic force characteristic (soft and hard) schematically represented. The linear or harmonic force characteristic indicates the transition from soft to hard force characteristics. [r = interatomic distance, $f'(r)$ = restoring force.]

We compute the vibrational energy of an atom (ion) pair in the linear case simply by the formula

$$U_v=\tfrac{1}{2}\omega^2(Mr_x^2+mr_y^2).\quad (5)$$

The vibrational amplitudes r_x and r_y could in no case be larger than the corresponding nuclear distance r_0 allows. Hence,

$$\max(r_x)+\max(r_y)=r_0\quad (6)$$

is the hypothetical limit for the sum of the two amplitudes, and we accordingly obtain the maximum vibrational energy as

$$\max(U_v)=\tfrac{1}{2}\omega^2m_rr_0^2,\quad (7)$$

where $m_r=Mm/(M+m)$, the reduced mass, and ω an angular frequency as defined below.

3. INTRODUCTION OF A DEFINITE FREQUENCY

In the linear case, ω stands for a definite frequency (ω_d) which represents the vibrational spectrum of the solid in its entirety. In order to determine ω_d from experimental data we equate the maximum of the vibrational energy (kinetic energy) with the total cohesive energy (potential energy) per valency bond (U/z). In this case, U = the total cohesive energy (experimental value) and z = the valency within the molecule.[6] Proceeding in this manner and solving for

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[2] E. Bright Wilson, Jr., J. C. Decius, and Paul C. Cross, *Molecular Vibrations, The Theory of Infrared and Raman Vibrational Spectra* (McGraw-Hill Book Company, Inc., New York, 1955), p. 193.

[3] M. Born, *Optik* (Springer-Verlag, Berlin, 1933), pp. 469 and 537.

[4] F. O. Rice and E. Teller, *The Structure of Matter* (John Wiley & Sons, Inc., New York, 1949), p. 211.

[5] J. J. Stoker, *Nonlinear Vibrations* (Interscience Publishers, Inc., New York, 1950), p. 15.

[6] According to definition, z is the largest common factor of the valencies of all types of ions present in a solid (see H. H. Landolt and R. Börnstein, *Zahlenwerte und Funktionen* (Springer-Verlag, Berlin, 1955), Vol. I, Part 4, p. 534.

TABLE I. Experimental and computed data for 26 solid compounds of

No.	Substance	Structure	α	z	r_0 (10^{-8} cm)	m_r (10^{-24} g)	U (kcal/mole)	λ_d (10^{-4} cm)	λ_c (λ_{rest}) (10^{-4} cm)	λ_d/λ_c
1	LiF	rocksalt	1.748	1	2.01	8.5	246	19	24	0.79
2	NaF			1	2.31	17.3	218	33	34.5	0.95
3	KF			1	2.66	21.4	193	43	(~45)	~0.96
4	NaCl	rocksalt	1.748	1	2.815	23.4	184	51	53	0.96
5	KCl			1	3.14	31.0	169	67	65	1.03
6	RbCl			1	3.27	41.8	162	84	(~79)	~1.06
7	CsCl	cesium chloride	1.763	1	3.56	46.8	157	98	(~95)	~1.03
8	TlCl			1	3.32	50.7	168	92	87	1.06
9	NaBr	rocksalt	1.748	1	2.98	29.7	176	62	(~64)	~0.97
10	KBr			1	3.29	43.9	160	86	84	1.03
11	RbBr			1	3.42	69.0	157	114	(105)	1.09
12	CsBr	cesium chloride	1.763	1	3.70	83.4	153	138	(125)	1.11
13	TlBr			1	3.41	96.2	164	132	(117)	1.13
14	NaI	rocksalt	1.748	1	3.23	32.4	166	72	(~73)	~0.99
15	KI			1	3.52	50.0	152	101	95	1.06
16	RbI			1	3.66	85.6	150	139	(~125)	~1.12
17	TlI	cesium chloride	1.763	1	3.64	131.0	~155	~170	(~150)	~1.14
18	CaF_2	fluorite	5.04	2	2.36	21.6	629	31	31.5	0.98
19	SrF_2			2	2.52	26.2	597	38	(40)	0.95
20	BaF_2			2	2.68	28.0	564	43	(43)	1.00
21	BeO	wurzite	1.639	2	1.65	9.7	1053	11.3	(13)	0.87
22	MgO	rocksalt	1.748	2	2.10	16.1	940	19	19.5	0.97
23	CaO			2	2.40	19.2	842	26	27.5	0.94
24	ZnO	wurzite	1.639	2	1.95	21.5	965	21	22	0.96
25	ZnS	zinc blende	1.638	2	2.34	36.0	853	34	32.5	1.04
26	Al_2O_3	α-corundum	25.03	6	1.91	16.8	3610	16	(17)	0.94

the definite frequency $\omega = \omega_d$, we obtain

$$\omega_d = (1/r_0)(2U/zm_r)^{\frac{1}{2}}, \quad (\text{sec}^{-1}) \tag{8}$$

or

$$\lambda_d = 13.3\times 10^{10}\, r_0(zm_r/U)^{\frac{1}{2}}, \quad (\text{microns}) \tag{9}$$

(all members in cgs units).[7]

Anharmonicity of the lattice vibrations would shift the frequency ω_d away from the linear value. Hence we may conceive the frequency shift to be a function of the anharmonicity and attach the corresponding frequency ratio as a factor, $F(A)$, to ω_d. On the basis of Eq. (9), applying molecular and cohesive energy data (experimental values),[8] the author determined the definite wavelengths λ_d for 26 nonconducting or semiconducting solids. They cover the region from 11 μ to 170 μ and represent the essential part of the lattice vibration spectra of the solid state. From these experimental results, shown in Table I, we may study the definite frequency $(1/\lambda_d)$ in detail and subsequently determine $F(A)$.

4. COMPARISON OF THE DEFINITE FREQUENCY WITH THE CENTER FREQUENCY

A striking phenomenon is discovered when comparing λ_d with the wavelength λ_c which corresponds to the frequency of the center of gravity of solids.[1] For the majority of these solids we establish equality between λ_d and λ_c, considering the over-all inaccuracies of the data used for determination of their values. Table I gives a compilation of values for λ_d and λ_c for 26 solid compounds for which data are now on hand,[8] while Fig. 2 is a graphical presentation.

In Fig. 2 the frequency ratio

$$F(A) = \omega_c/\omega_d = \lambda_d/\lambda_c \tag{10}$$

is plotted against the reduced mass m_r (curve a). The line parallel to the abscissa at 1.00 represents $\lambda_d = \lambda_c$. The limits of experimental error are indicated by dotted parallels at distances of ± 0.05 from the line $\lambda_d = \lambda_c$, while the average inaccuracy of the experimental data is about $\pm 3\%$. With due regard to the above-mentioned factors we establish near equality between ω_d and ω_c for 14 out of 26 solids, ranging in m_r values from 20 to 50×10^{-24} g. Below and above this range, however, we observe deviations which are opposite in the sign and at the same time beyond the limits of data inaccuracy. Thus for the light compounds, such as BeO and LiF ($m_r < 20\times 10^{-24}$ g), the deviation increases rapidly in the minus direction, whereas for the heavy compounds, such as RbI and CsBr ($m_r > 50\times 10^{-24}$ g), the deviation increases slowly in the plus direction. For the heavy compounds λ_d approaches the main resonance wavelength λ_0 (defined as the wavelength of maximum absorption) which here has an average value of $1.10\,\lambda_c$.

Since ω_d is computed on the basis of harmonic vibrations, $\omega_c/\omega_d = $ unity corresponds to the quasi-harmonic or linear case. Consequently, the deviations

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[7] The wavelength scale is chosen instead of frequencies because the original data in pertinent literature are mainly presented in wavelengths.

[8] For detailed representation of experimental data for a great number of solids, and also a comprehensive bibliography of pertinent literature, see Landolt-Börnstein, reference 6; further: O. K. Rice, *Electronic Structure and Chemical Binding* (McGraw-Hill Book Company, Inc., New York, 1940), and J. Sherman, Chem. Rev. 11, 93 (1932).

six different lattice structures (used for the graphs of Figs. 2, 4, and 9).

λ_0 (10^{-4} cm)	n (from measured values)	$X_m=m_r/m_r(A)$	$X_m^{1/p}$	$n=\exp(2.303X_m^{1/p})$	U_C (kcal/mole)	$n=U_C/(U_C-U)$	n (after Sherman)	$\lambda_c=\lambda_d/X_m^{1/p}$ (computed) (10^{-4} cm)
32.6	6.1	0.275	0.81	6.4	291	6.5	6	23.5
40.6	8.9	0.56	0.94	8.7	251	7.6	7	35
...	9.0	0.69	0.96	9.1	218	8.7	8	45
61.1	9.1	0.77	0.97	9.3	206	9.3	8	53
70.7	10.7	1.00	1.00	10.0	186	10.9	9	67
84.8	11.5	1.35	1.03	10.8	177	11.8	9.5	81
102	10.8	1.51	1.05	11.2	160	...	10.5	93
117	11.5	1.64	1.06	11.3	177	(16)	10.5	87
74.7	9.3	0.96	0.99	9.8	195	10.2	8.5	63
88.3	10.8	1.42	1.04	11.0	177	9.6	9.5	83
114	12.3	2.22	1.09	12.3	170	13.0	10	105
134	12.9	2.69	1.11	12.9	158	...	11	124
...	13.5	3.10	1.13	13.8	172	(21)	11	117
85.5	9.8	1.045	1.01	10.1	180	12.8	9.5	73
102	11.5	1.61	1.06	11.3	165	12.7	10.5	95
129.5	13.0	2.76	1.12	13.5	159	17.5	11	124
...	13.5	4.23	1.17	14.8	161	(27)	12	145
51.5	9.5	0.70	0.96	9.1	710	8.8	8	32
69	8.9	0.845	0.98	9.6	670	9.5	8.5	39
73	10.0	0.905	0.99	10.0	625	10.2	9.5	43
...	7.4	0.315	0.86	7.3	1320	5.0	...	13
17.3 24.0	9.3	0.52	0.93	8.5	1110	6.6	7	20.5
...	8.7	0.62	0.95	8.9	965	7.8	8	27.5
...	9.1	0.695	0.96	9.1	1115	7.5	8	22
...	11.0	1.16	1.02	10.4	935	11.4	9	33
...	8.7	0.54	0.93	8.5	4350	6.0	7.5	17

above and below are understood to be caused by the anharmonicity of the lattice vibrations. Combining now Eqs. (9) and (10), we obtain as a general formula for the center frequency

$$\omega_c=F(A)\quad\omega_d=F(A)(1/r_0)(2U/zm_r)^{\frac{1}{2}}. \tag{11}$$

5. ANHARMONICITY OF LATTICE VIBRATIONS AND EXPONENT OF REPULSION

The frequency ratio $F(A)=\omega_c/\omega_d$ represents a unit of measure for the anharmonicity. Strictly speaking, the anharmonicity is inversely proportional to $F(A)$, as shown in curve b of Fig. 2. The anharmonicity is mainly caused by the forces of repulsion, since the repulsive energy increases rapidly when the ions approach one another during vibrations ($r<r_0$), but is close to zero when the ions deviate from one another ($r>r_0$), as Fig. 3 indicates. The repulsive energy is inversely proportional to the exponent of repulsion n. Hence $F(A)$ must be a function of n.

The analytical expression for curve (a) of Fig. 2 obeys the function

$$F(A)=\omega_c/\omega_d=X_m^{1/p}, \tag{12}$$

where $X_m=m_r/m_r(A)$, and $m_r(A)=31\times10^{-24}$ g corresponds to the reduced mass of KCl, with the argon configuration satisfied in all ion partners. The introduction of the dimensionless quantity X_m helps to simplify the equations. We may coin it "the related mass," i.e., the reduced mass of the vibrating atom (ion) pairs related to the reduced mass of K and Cl. For the value of p we have $p=23.0\ X_m$ for the small range of $m_r\leqq12\times10^{-24}$ g, and $p=9=$constant for the large range of $m_r\geqq12\times10^{-24}$ g. In order to determine the n-scale units (Fig. 2) we take into consideration that for $X_m=1$ (KCl), $n=10$, corresponding to $F(A)=1.00$; and for $X_m\rightarrow0$, $n\rightarrow1$, corresponding to $F(A)\rightarrow0$. It thus conveniently follows that

$$X_m^{1/p}=F(A)=\log_{10}n\quad\text{or}\quad n=\exp(2.303X_m^{1/p}). \tag{13}$$

Values of n, determined for the solids of Table I according to Eq. (13), in general agree with the values of n obtained by various other methods, as Table I shows.[9] Thus Eq. (13) gives a useful interrelation between exponent of repulsion and "related mass."

6. EFFECT OF ANHARMONICITY ON THE VIBRATIONAL SPECTRA OF SOLIDS

Nonlinear relationship between restoring force and displacement in free oscillations causes at resonance an increase of amplitude with frequency if the force characteristic is hard, but a decrease of amplitude with frequency if the force characteristic is soft, whereas in the linear case the amplitude is independent of frequency.[4] Therefore, the center of gravity of the vibrational spectrum (1) shifts towards higher fre-

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[9] The values of n, determined from the difference between electrostatic and cohesive energy, deviate considerably for solids with CsCl structure. The reason for this will be discussed in a forthcoming paper. For values of n from compressibility data, see Geiger-Scheel, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1933), Vol. 24, Part II, p. 720, article by M. Born and M. Goeppert-Mayer.

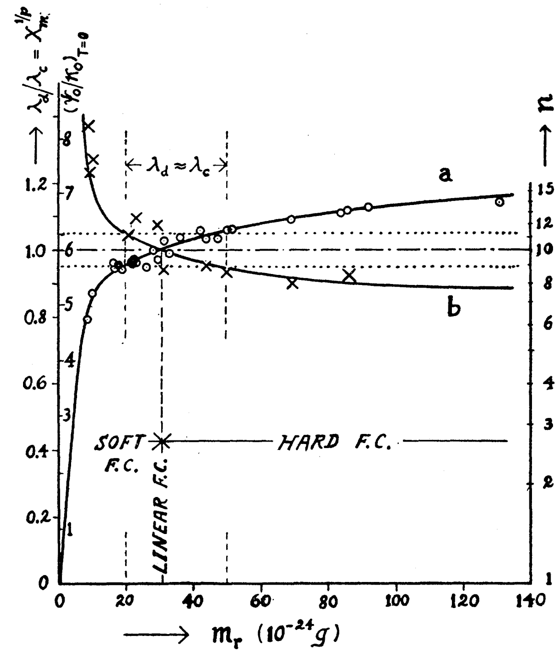

FIG. 2. Anharmonicity data of lattice vibrations (derived from spectral data compiled in Table I) as a function of the reduced mass m_r. Circles: anharmonicity factor $F(A)=\lambda_d/\lambda_c$ (experimentally determined). Curve (a): $F(A)=X_m^{1/p}$ (calculated), also exponent of repulsion n. Curve (b): $1/F(A)=X_m^{-1/p}$ (calculated). Crosses: "relative compressibility" $(\psi_0/\kappa_0)_{T=0}$, (from experimental data compiled in Table II, the scale being $K=6$ times that of $X_m^{-1/p}$). Equality between λ_d and λ_c occurs at $m_r=31\times10^{-24}$ g (KCl). It indicates the linear force characteristic as a transition from soft to hard force characteristics.

quencies ($\omega_c > \omega_d$) if the force characteristic is hard, (2) shifts towards lower frequencies ($\omega_c < \omega_d$) if the force characteristic is soft, and (3) remains unchanged ($\omega_c=\omega_d$) if the force characteristic is linear. This corresponds exactly to the frequency shift observed along curve (a) in Fig. 2, where

$\omega_c > \omega_d$ for heavy solids,

$\omega_c < \omega_d$ for light solids,

$\omega_c = \omega_d$ for the argon configuration (KCl).

Hence we have to assume *three different types of force characteristic* in the solid state:

hard for compounds heavier than KCl,

soft for compounds lighter than KCl,

linear for compounds in the vicinity of KCl.

Here it is essential to note the behavior of $f'(r)$, as indicated in Fig. 1:

For the heavy compounds (hard force characteristic) the curve initially is flat, whereas for the light compounds (soft force characteristic) the curve initially is steep.

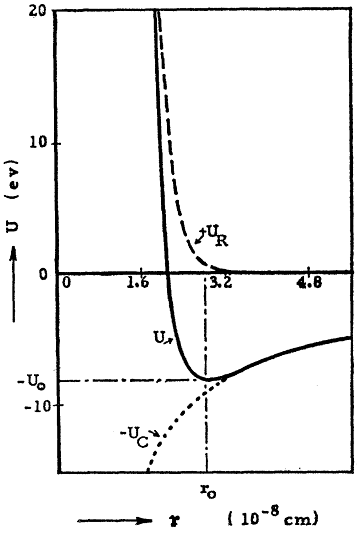

FIG. 3. Diagram of the potential energies for NaCl (calculated) as a function of the interatomic distance r. ···· electrostatic (Coulomb) energy of attraction $(-U_C)$; ---- repulsive energy $(+U_R)$, based on the value of 9 for its exponent n; — total cohesive energy $(-U=-U_C+U_R)$. Equilibrium (=minimum of U) occurs at $r_0=2.815\times10^{-8}$ cm, $U_0=8.0$ ev.

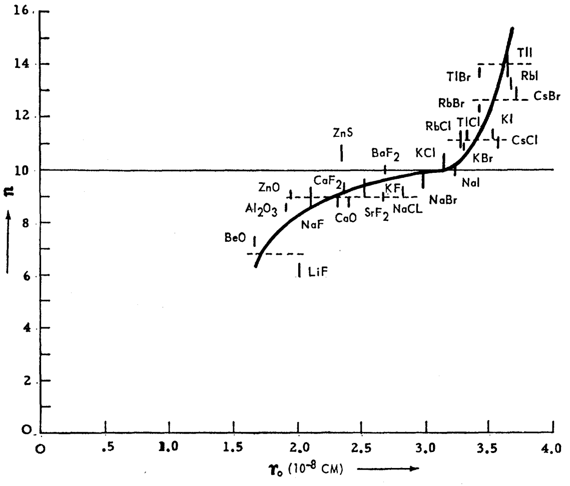

FIG. 4. Experimental data of the exponent of repulsion n as a function of the interatomic distance at equilibrium (r_0) for various solids. The vertical lines indicate data inaccuracies, the dashed horizontal lines correspond to the various n levels. A point of inflection occurs at $r_0=3.14\times10^{-8}$ cm (KCl).

Because of the importance of anharmonicity in understanding the properties of solids from an atomistic point of view, this concept shall be illustrated and confirmed in the following three ways:

(A) By means of *the force characteristic itself:*

Setting $y=r/r_0$, we have

$$U=-(\alpha z_1 z_2 e^2/r_0)(y^{-1}-y^{-n}/n) \quad \text{(cohesive energy)}, \quad (14)$$

$$dU/dr=(\alpha z_1 z_2 e^2/r_0^2)(y^{-2}-y^{-(n+1)}) \quad \text{(restoring force)}, \quad (15)$$

$$d^2U/dr^2=-(\alpha z_1 z_2 e^2/r_0^3)[2y^{-3}-(n+1)y^{-(n+2)}] \quad \text{(stiffness)}, \quad (16)$$

where α = Madelung's constant (e.g., $\alpha = 1.748$ for the rocksalt structure), e = the unit electronic charge, r_0 = the nuclear distance between adjacent atoms at equilibrium, z_1 and z_2 = the valencies of the ion partners, and n = the exponent of repulsion. At equilibrium ($r = r_0$), the repulsive term as compared to the attractive term, is small in (14), becomes equal in (15), and has in (16) a value $(n+1)/r_0$ larger than that in (15). Hence the material constant $(n+1)/r_0$ essentially characterizes the anharmonic portion of the stiffness. As we see from Fig. 4, the exponent n increases with r_0 and, although in various steps of different constant values (n—levels), it may be approximated by a continuous curve which is best defined in the vicinity of KCl ($n = 10$). In plotting $(n+1)/r_0$ against r_0 [see Fig. 5(a)], we notice a distinct minimum at KCl. This indicates a change of stiffness with respect to r_0 from a negative to a positive value, as shown unequivocally through the differential curve $\{d[(n+1)/r_0]/dr_0$ being a function of $r_0\}$ in Fig. 5(b). In this manner, the change of the force characteristic from soft through linear to hard, with increasing value of r_0, is confirmed.

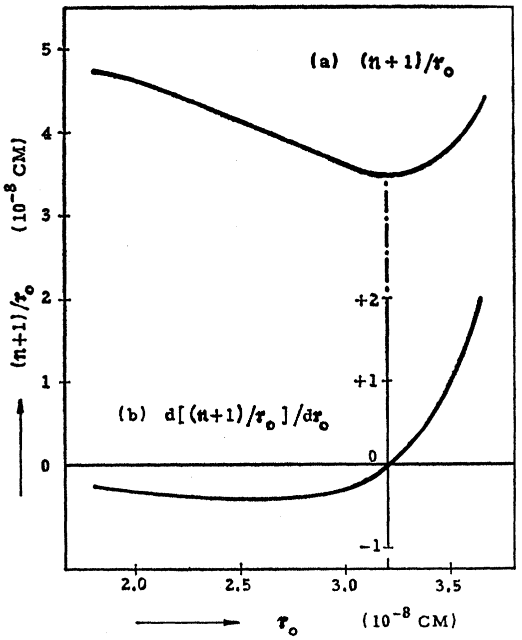

FIG. 5. Curve (a): experimental data of the anharmonic portion of the stiffness coefficient $[(n+1)/r_0]$ for various solids. Curve (b): its differential quotient with respect to r_0, both as a function of r_0. Minimum in (a) corresponds to a change of the sign in (b). They occur at $r_0 = 3.14 \times 10^{-8}$ cm (KCl), indicating a change from soft to hard force characteristics.

(B) By means of *resonance absorption data:*

The resonance curves of anharmonic vibrations have an unsymmetrical shape as Fig. 6 schematically shows. Curve (a) refers to a solid of soft force characteristic, while curve (b) corresponds to a solid of hard force characteristic.[10] As a matter of fact, the experimental absorption curves in Fig. 7 indicate a soft force characteristic for LiF and NaCl, but a hard force characteristic for RbCl, exactly as expected.[11] In

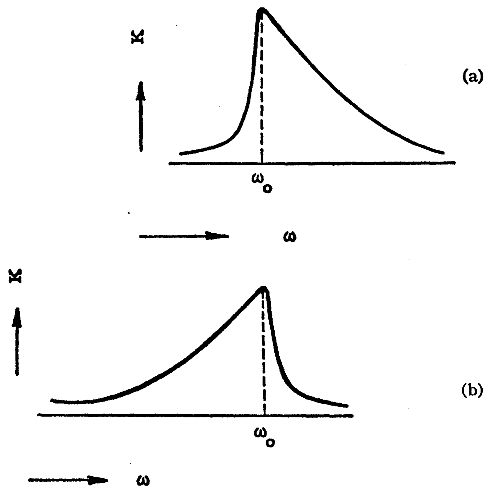

FIG. 6. Principal shape of the resonance absorption curves in relation to the two types of anharmonic force characteristic: (a) soft and (b) hard (schematically represented for the heavily damped lattice vibrations).

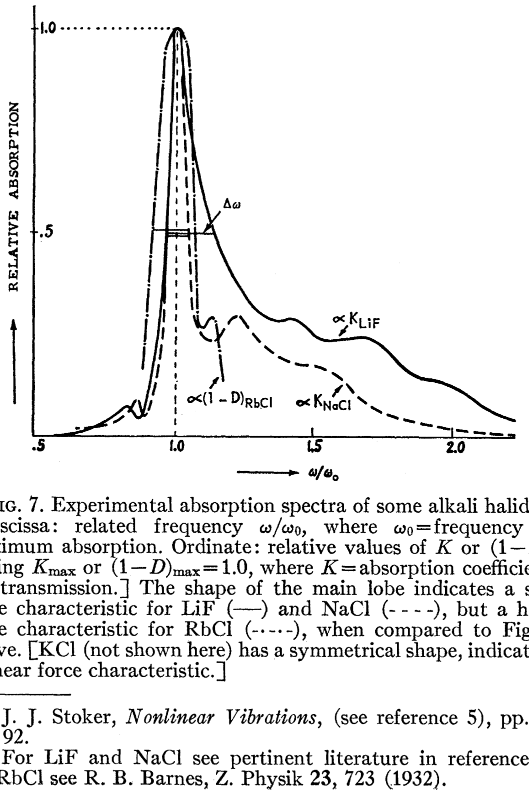

FIG. 7. Experimental absorption spectra of some alkali halides.[1] [Abscissa: related frequency ω/ω_0, where ω_0 = frequency of maximum absorption. Ordinate: relative values of K or $(1-D)$, setting $K_{\max}$ or $(1-D)_{\max} = 1.0$, where K = absorption coefficient, D = transmission.] The shape of the main lobe indicates a soft force characteristic for LiF (—) and NaCl (- - - -), but a hard force characteristic for RbCl (-·-·-), when compared to Fig. 6 above. [KCl (not shown here) has a symmetrical shape, indicating a linear force characteristic.]

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[10] J. J. Stoker, *Nonlinear Vibrations*, (see reference 5), pp. 21 and 92.

[11] For LiF and NaCl see pertinent literature in reference 1; for RbCl see R. B. Barnes, Z. Physik **23**, 723 (1932).

addition, KCl, not shown here, has a nearly symmetrical absorption curve and hence a linear force characteristic. This observation again confirms the above concept.

We should, moreover, observe proportionality between both the deviation from harmonicity of the lattice vibrations and the deviation from symmetry in the absorption curves. Since we define the anharmonicity as a function of ω_c/ω_d, the deviation from harmonicity (="coefficient of anharmonicity") becomes $(1-\omega_c/\omega_d)$. Further, we define the asymmetry of the absorption curve by the ratio (q) between the half-widths at both sides of the maximum; consequently, the deviation from symmetry (="coefficient of asymmetry") by $(1-q)$. In comparing now $(1-\omega_c/\omega_d)$ with $(1-q)$, we obtain the following results:

	$(1-\omega_c/\omega_d)$	$(1-q)$
LiF	0.21	0.75
NaCl	0.04	0.15
RbCl	−0.06	−0.20

The proportionality between the values of the two columns is evident, its factor C being the same ($C\approx 3.5$) for all three solid compounds. Both this proportionality and the change of the sign that occurs when we pass from compounds lighter to those heavier than KCl once again confirm the above concept. In addition, we obtain the relation:

$$F(A)=\omega_c/\omega_d=1-[(1-q)/C] \tag{17}$$

which requires verification by some more solids, once conclusive data become available.

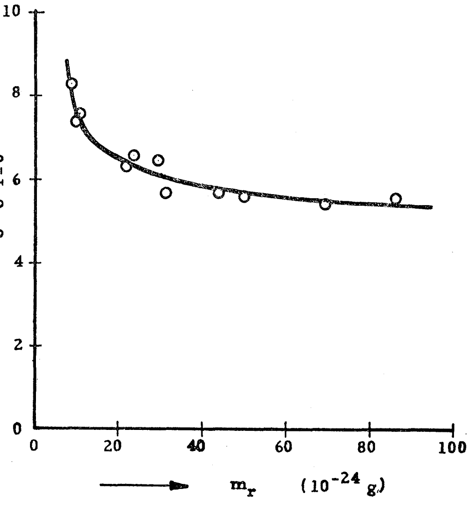

FIG. 8. Experimental data of "relative compressibility" $(\psi_0/\kappa_0)_{T=0}$ [=ratio between change of compressibility with pressure ψ_0 and compressibility κ_0, reduced to the absolute zero] as a function of the reduced mass m_r. For the compilation of pertinent data see Table II.[12] Decrease of the "relative compressibility" indicates hardening of the force characteristic, as m_r increases.

TABLE II. Data of compressibility $(\kappa_0)_{T=0}$ and change of compressibility with pressure ψ_0, according to Slater[12] (applied in determining the data of "relative compressibility" $(\psi_0/\kappa_0)_{T=0}$; reduced to the absolute zero).

No.	Substances	m_r $(10^{-24}$ g)	$-\kappa_0$ $T=30°$C	$-\kappa_0$ $T=0°$K		ψ_0/κ_0 $T=0°$K
			$[1/(10^{12}$ d/cm$^2)]$			
1	LiF	8.5	1.53	1.4	11.7	8.3
2	KF	21.4	3.31	3.2	20.1	6.3
3	LiCl	9.6	3.41	2.7	19.8	7.4
4	NaCl	23.4	4.20	3.3	21.9	6.6
5	KCl	31.0	5.63	4.8	26.5	5.6
6	LiBr	10.6	4.31	3.2	24.5	7.6
7	NaBr	29.7	5.08	3.9	25.5	6.5
8	KBr	43.9	6.70	5.5	31.8	5.7
9	RbBr	69.0	7.94	6.5	35.0	5.4
10	KI	50.0	8.54	7.0	39.1	5.6
11	RbI	85.6	9.58	7.6	43.0	5.6

(C) By means of *compressibility data:*

A striking phenomenon is discovered when we plot against m_r the dimensionless ratio $(\psi_0/\kappa_0)_{T=0}$ (i.e., change of compressibility with pressure over compressibility, reduced to 0°K,[12] for which we propose the notion "relative compressibility." The curve thus obtained (see Fig. 8), in using the data of Table II, is very similar to the anharmonicity curve (b) of Fig. 2, representing $X_m^{-1/p}=f(m_r)$. In fact, by correlation of the two quantities $(\psi_0/\kappa_0)_{T=0}$ and $X_m^{-1/p}$ we find proportionality between them, the coefficient being $K=6$. This is illustrated by the crosses in Fig. 2, fitting the curve (b) within the limits of error [$=\pm 10\%$ for the data of $(\psi_0/\kappa_0)_{T=0}$, due to the extrapolation to 0°K], if the ratio between the two ordinates is chosen as $1/K$. Thus we arrive at the interrelation

$$(\psi_0/\kappa_0)_{T=0}=KX_m^{-1/p}, \tag{18}$$

where the coefficient K equals the coordination number of the rocksalt structure. Since the substances examined here all belong to this structure, and X_m is determined per ion pair, while ψ_0 and κ_0 are volumetric quantities, it seems obvious that K corresponds to the number of ions of opposite sign surrounding each ion within the lattice (=coordination number). However, this statement has to be confirmed for solids of structures other than NaCl, when the corresponding ψ_0 data become available.

From Eq. (18) follows that data for the "relative compressibility" of solids can be determined from "related mass" data, or in other words, that the anharmonicity of lattice vibrations (see Eq. 12) can also be expressed by pure elastic data. Since ψ_0 was found to be independent of temperature,[12] Eq. (18) allows determination of compressibility data (κ_0 values) at the absolute zero without a thus far uncertain extrapolation.

We can obtain another interesting interrelation by

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[12] Data for compressibility and change of compressibility with pressure, reduced the absolute zero, from J. C. Slater, Phys. Rev. 23, 488 (1923).

eliminating $X_m^{1/p}$ and $X_m^{-1/p}$ between Eqs. (13) and (18), respectively. It results in an equation relating the exponent of repulsion (n) and the reciprocal of the "relative compressibility," as follows:

$$\log_{10} n = K(\kappa_0/\psi_0)_{T=0}. \tag{19}$$

As a matter of fact, Fig. 8 or curve (b) in Fig. 2 show that the "relative compressibility" decreases with increasing m_r. This indicates hardening of the force characteristic as m_r increases, and in this manner, once again confirms our concept above.

In summing up the methods used to illustrate and confirm our concept of the anharmonicity of lattice vibrations, we discovered through them useful interrelations and data concerning the anharmonicity, and helped to explain the asymmetry of the main lobe in the absorption spectra, e.g., of alkali halides.

7. CLASSIFICATION OF SOLIDS BASED ON THEIR DIFFERENT ANHARMONIC FORCE CHARACTERISTICS

The concept of anharmonicity of the lattice vibrations, deduced in this paper, allows us to draw certain conclusions concerning the atomic behavior of solid matter. Since for light compounds the values of atomic weight and volume, number and density of the electron shells, also their deformability (polarizability), are small, the atoms experience mutual interpenetration rather than deformation of the electron clouds during vibrations. The mutual repulsion between adjacent atoms, resulting from interpenetration, is initially strong, but increases less than linearly with decreasing distance, because, as Slater and Frank have stated,[13] the part of each atom which penetrates the other finds itself in a field attracting it towards the nucleus of the other, since it is no longer shielded by all the shells of the other. For this reason, the force characteristic is soft for the light compounds (argon configuration not satisfied in at least one ion partner). On the other hand, for the heavy compounds the values of atomic volume, deformability of the ions, etc., are relatively large. During vibrations, therefore, the heavy atoms experience mutual deformation rather than interpenetration of the electron clouds. The mutual repulsion between adjacent atoms, resulting from deformation, is initially weak, but grows stronger than linear with decreasing distance, due to the initial high density of the electron clouds. For this reason, the force characteristic is hard for the heavy compounds (argon configuration satisfied in all ion partners).

Since mutual interpenetration prevails within the light compounds and mutual deformation within the heavy compounds, we conclude that the effects of both interpenetration and deformation are in equilibrium and the force characteristic is linear, when the argon configuration is just attained. The linear or transition state, then, corresponds to the known breaks in grating space, compressibility, and change of compressibility with pressure at argon, when plotted against the rare gas configurations.[12]

The importance of this classification of solids, based on their different anharmonic force characteristics, will be shown through various applications in forthcoming papers.

8. INTERRELATIONS BETWEEN TOTAL COHESIVE ENERGY, LATTICE VIBRATION SPECTRA, AND CHARACTERISTIC TEMPERATURES

From Eqs. (11) and (12) we may now formulate the underlying interrelation between total cohesive energy and lattice vibration spectra for the entire range of nonconducting or semiconducting solids (binary compounds, so far[14]):

$$\omega_c = (X_m^{1/p}/r_0)(2U/zm_r)^{\frac{1}{2}}, \quad (\mathrm{sec}^{-1})$$

or

$$U = (\tfrac{1}{2}) z m_r (\omega_c r_0 X_m^{-1/p})^2. \quad (\mathrm{ergs/mole}) \tag{20}$$

In order to illustrate the validity of this interrelation we plot calculated and experimental values of $1/\lambda_c$ against one another for all 26 solids of Table I (see Fig. 9). We obtain a perfectly straight line of 45° slope, which indicates the equality of the two frequencies. The deviations average ±3% for all these solids, and

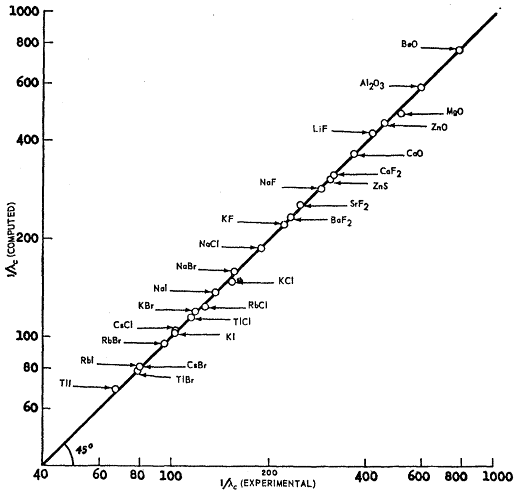

FIG. 9. Equality of experimental data of the center frequency ($1/\lambda_c$) with data of ($1/\lambda_c$) computed from total cohesive energy values. The two types of data of 26 solids (compiled in Table I) are plotted against one another, thus the deviations from the 45° slope stand for deviations from their equality. The fact that they remain within the limits of error (=radius of the circles) indicates the validity of the interrelation between center frequency and total cohesive energy for almost the entire range of center frequencies of solids (in logarithmic scales). In the same manner as a corresponding diagram (showing the equality between center frequency and characteristic frequency from specific heat, see Fig. 6 of reference 1) constitutes the "center law of the lattice vibration spectra," the above diagram illustrates the extension of this "center law" with respect to the total cohesive energy.

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[13] J. C. Slater and N. H. Frank, *Introduction to Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1938), p. 442.

[14] The treatment of a ternary compound, as an example, is shown in Table III and Sec. 9.

TABLE III. First determination of total cohesive energy data for solids of extremely high sublimation temperatures (hence thus far inaccessible) from their infrared spectra.

No.	Substance	Structure	z	r_0 (10^{-8} cm)	m_r (10^{-24} g)	λ_c (10^{-4} cm)	$X_m^{1/p}$	n	U (kcal/mole)	U (kcal/g)
1	SiC	zinc blende	4	1.89	14.1	12.0	0.92	8.2	4200	105
2	BN	zinc blende	3	1.57	10.2	7.0	0.86	7.2	5400	220
3	C−C I	diamond (α)	4	1.54	10.1	5.9	0.86	7.2	9500	395
4	C−C II	diamond (β)	4	1.54	10.1	4.4	0.86	7.2	17 000	710
5	$Y_3Fe_5O_{12}$	garnet	6	2.23	21.5	17.0	0.95	9.0	25 000	34

thus agree exactly with the average inaccuracy of data determination.

Impurities in the investigated nonconducting or semiconducting solids (averaging close to 1%) may cause small deviations in some of the experimental data. However, no changes beyond the over-all inaccuracies of the experimental data are to be expected, either in the total cohesive energy, the center frequency, or the frequency of maximum absorption, provided these impurities do not substantially increase the electric conductivity.

In combining Eq. (20) with Eqs. (1) and (2), we obtain a substantial extension of the center law of the lattice vibration spectra[1] which reads:

$$\int_0^\infty \nu f(\nu)d\nu \Big/ \int_0^\infty f(\nu)d\nu = (X_m{}^{1/p}/2\pi r_0)(2U/zm_r)^{\frac{1}{2}} = (k/h)\Theta. \quad (\text{sec}^{-1}) \qquad (21)$$

In eliminating the center frequency, we arrive at a new interrelation between characteristic temperature and total cohesive energy:

$$\Theta = (hX_m{}^{1/p}/2\pi k r_0)(2U/zm_r)^{\frac{1}{2}}. \quad (°\text{K}) \qquad (22)$$

This equation allows determination of characteristic temperatures from cohesive energy data and vice versa. Its value will be illustrated in a forthcoming paper.

9. PRACTICAL APPLICATIONS OF THE INTERRELATION BETWEEN TOTAL COHESIVE ENERGY AND LATTICE VIBRATION SPECTRA

As such an application we may consider a first determination of thus far inaccessible cohesive energy data for some solids of extremely high sublimation temperatures (e.g. above 4000°K).

On the basis of Eq. (20) the author determined the total cohesive energy of four arbitrarily chosen solids, as shown in Table III. Passing down the list from No. 1 to 4, we observe a successive, strong increase of the total cohesive energy (U) from 105 kcal/g (as for SiC) to 710 kcal/g (as for the diamond of type II). These data may be compared with $U = 35.5$ kcal/g for corundum (Al_2O_3), see Table I, No. 26.

The yttrium iron garnet (No. 5 in Table III) represents an example for a ternary compound. It consists of the two ionic groups Y_2O_3 and Fe_2O_3 of which $z = 6$. They are distributed in the ratio of $1.5/2.5 = 3/5$, in order to satisfy the molecular formula $Y_3Fe_5O_{12}$. Since both ionic groups contribute to the vibrational spectrum, whose center of gravity is at $\lambda_c = 17\,\mu$,[15] we determine the effective mean values $\bar{m}_r$, $\bar{r}_0$, $\bar{z}$, and $\bar{X}_m{}^{-1/p}$ for the combined ionic groups according to their distribution ratio. In introducing them into Eq. (20) we obtain $U = 34$ kcal/g which is close to the U value of Al_2O_3. In addition, Eq. (22) yields $\Theta = 850$°K for the characteristic temperature of the garnet of No. 5.

The results of Table III will be independently confirmed and additional applications will be separately treated in forthcoming papers.

10. CONCLUSION

In both the preceding and the present paper we examined experimental and computed data of a great number of solids. We derived a series of equations which interrelate various physical data of solids. They are: characteristic temperature, total cohesive energy, exponent of repulsion, and a number of new concepts, such as "center frequency," "related mass," "relative compressibility," "factor of anharmonicity," "coefficient of anharmonicity," and "coefficient of asymmetry." These notions define the anharmonicity in various ways, and at the same time, simplify the interrelations. In addition, we deduced a method for classification of solids, based on their different anharmonic force characteristic (soft-linear-hard), and drew certain conclusions concerning the atomic behavior of solid matter. Finally we accomplished a first determination of some so far inaccessible data of total cohesive energy from infrared spectra.

Many practical applications may come from these results, some of them highly important. As a first example, the hardness of minerals and inorganic crystals will be defined and determined on the basis of interatomic forces in the next paper to appear.

It is hoped that the results of this presentation will stimulate experimental and theoretical basic research in the field, in order to provide confirmation and/or modification of them.

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[15] Evaluated from spectral data by P. C. Bailey and A. Goldman, AFCRC-TR-60-147, 1960, Westinghouse Research Laboratories, Pittsburg, Pennsylvania, (unpublished).