

Critical Ionicities of Binary Crystals $A_N B_{8-N}$

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Abstract

We introduce an ionicity parameter f_i based on the symmetric and anti-symmetric form factors of binary and pseudo-binary crystals. A modified Phillips ionicity parameter f_i^{mp} is developed and its maximum deviation from f_i is calculated theoretically which is found to be of the order of few percents. Using the present definition of the ionicity parameter, the ionicity scale is found to be divided into four regions, each for ZnS, Wu, Na Cl, and CsCl structures with three critical ionicities. This is not alike Phillips results in which there is only one critical ionicity that separates all 4-fold from all 6-fold co-ordinated crystals. Calculations are made on a large number of binary and pseudo-binary crystals of the family $A_N B_{8-N}$ and the results are compared with the Phillips ionicity scale .

1. Introduction :

The concept of ionicity of chemical bonds plays an important role for semi-empirical interpretation and predictions of materials properties. The aim of the present work is to develop a better physical understanding of the ionicity from a solid state theoretical point of view .

Pauling¹ defined his ionicity in a thermo-chemical manner from empirical heats of formation. Coulson et al.² used a MO-LCAO scheme for his definition of ionicity. Many other definitions of the ionicity of chemical bonds of solids are based on this approach and reveal the same weakness which is mainly the use of free atom properties. Phillips^{3,4} avoided this weakness and connected between the bond and the band picture in his definition of the ionicity parameter using the energy spectrum of the solid. Since, the band structure of a solid depends in a complicated way on the ionic and electronic potentials, the precise physical nature of the Phillips ionicity has not been well established.

Phillips^{3,4} established a semi-empirical real-space definition of the parameters E_h and C which enter his ionicity through the relation :

$$f_i^P = C^2/E_g^2 = C^2/[E_h^2 + C^2] , \quad (1)$$

as follows :

$$E_h = 39.74 / d^s \text{ eV} \quad (2)$$

and

$$C = 14.4 b e^{-k_s r_0} (Z_\alpha / r_\alpha - Z_\beta / r_\beta) \text{ eV} \quad (3)$$

where E_g is the mean band gap of the electronic band structure E_h and C are the homopolar and heteropolar (ionic) parts of E_g . d is the nearest-neighbor distance in \AA , and s is a

numerical constant of about 2.48. In equation (3), the exponential is the Thomas-Fermi screening factor with $r_0 = d/2$, b is a correction of order unity, and Z_c and Z_p are the numbers of valence electrons on the cation and anion respectively. While it is well known that the group of crystals which have different chemical compositions but with the same lattice structure, has the same physical feature of the electronic band structure and the related properties are determined in terms of their, symmetric and antisymmetric form factors only .

II- Formulation

Since the form factors may be understood as general parameters with a fundamental experimental meaning, the most natural definition of a lattice-vector dependent ionicity follows from these form factors themselves as⁵ ,

$$f_i(\vec{G}) = v_a^2(\vec{G}) / [v_s^2(\vec{G}) + v_a^2(\vec{G})] \quad (4)$$

where V_s and V_a are the symmetric and antisymmetric form factors and \vec{G} is a reciprocal lattice-vector .

In the pure homopolar limit the partial ionicity is zero where $V_a(\vec{G})$ vanishes but it tends to unity in the limit of crystals with predominant ionic character .

Using equation (4), the weighted mean value of the ionicity follows to be :

$$f_i = \sum_{\vec{G}} a_{\vec{G}} f_i(\vec{G}) , \quad (5)$$

where like in the pseudo-potential theory, a rapid convergence of the sum may be assumed⁶. We assume that the sum in equation(5) is equal to the partial ionicity at a certain representative lattice-vector (\vec{G}) determined using the average bonding-antibonding condition from the special geometry of

the Jones-zone⁷, so that :

$$f_i = f_i(\vec{G}^*) = v_a^2(\vec{G}^*) / [v_a^2(\vec{G}) + v_s^2(\vec{G})] \quad (6)$$

Unfortunately, for the extremely important group of zincblende and rocksalt-type crystals $(\vec{G}) = 2\pi/a (2,2,0)$ the antisymmetric form factors cannot be determined from experimental spectroscopical data, since the relevant structure factors vanishes. Phillips^{3,4} actually suggested, for the evaluation of his ionicity, the use of a spherical approximation of the Jones zone, i.e., the Penn model⁸, which is obtained if :

$$\vec{G}^* = -2 k_f \vec{k} / |\vec{k}| \quad , \quad (7)$$

but he did not use such an approximation in the reciprocal-vector space and has established a semi-empirical real-space definition of E_h and C , equations (2) and (3). A characteristic feature of Phillips's theory is that the crystal structure factors nowhere appears explicitly⁹ as for example E_h is taken to be a function of nearest-neighbor distance only.

We proceed as follows: for binary crystals $A_N B_{8-N}$ the Fourier component $V(\vec{G})$ of the crystal potential ,

$$V(\vec{r}) = \sum_{\vec{G}} V(\vec{G}) e^{i\vec{G}\cdot\vec{r}} \quad , \quad (8)$$

can be written, for each reciprocal lattice vector \vec{G} , in terms of the symmetric and antisymmetric form factors as :

$$V(\vec{G}) = v_s(\vec{G}) S_s(\vec{G}) + i v_a(\vec{G}) S_a(\vec{G}) \quad (9)$$

where $S_s(\vec{G})$ and $S_a(\vec{G})$ are the symmetric and antisymmetric structure factors respectively. $V(\vec{G}^*)$ can be written as :

$$V(\vec{G}^*) = v_s(\vec{G}^*) S_s(\vec{G}^*) + i v_a(\vec{G}^*) S_a(\vec{G}^*) \quad (10)$$

and accordingly ,

$$V^*(\vec{G}^*) V(\vec{G}^*) = v_s^2(\vec{G}^*) S_s^2(\vec{G}^*) + v_a^2(\vec{G}^*) S_a^2(\vec{G}^*) \quad (11)$$

Integrating over all angles between wave vector \vec{k} and \vec{C} where $\vec{C} = (a/8)$ (111) for ZnS and $(a/4)$ (111) for rocksalt structures), we get, from equations (11) and (7), the average bonding-antibonding energy gap :

$$E_g = 2 \left[\left\langle V^* (\vec{G}^*) V(\vec{G}^*) \right\rangle_{\theta, \phi} \right]^{\frac{1}{2}} \quad (12)$$

or

$$E_g^2 = 4V_s^2 (2k_f) \left\langle S_s^2(\vec{G}^*) \right\rangle_{\theta, \phi} + 4V_a^2 (2k_f) \left\langle S_a^2(\vec{G}^*) \right\rangle_{\theta, \phi} \quad (13)$$

When this is compared with the Phillips average gap, $E_g^2 = E_h^2 + C^2$, the following relations can be directly obtained :

$$\begin{aligned} E_h &= 2 V_s (2k_f) \left[\left\langle S_s^2(\vec{G}^*) \right\rangle_{\theta, \phi} \right]^{\frac{1}{2}} = \eta V_s (2k_f), \\ C &= 2 V_a (2k_f) \left[\left\langle S_a^2(\vec{G}^*) \right\rangle_{\theta, \phi} \right]^{\frac{1}{2}} = \mu V_a (2k_f) \end{aligned} \quad (14)$$

where η and μ are effective symmetric and antisymmetric crystal structure factors respectively. Inserting equation(14) in equation (1), we get a theoretical expression for the Phillips ionicity parameters :

$$f_i^{mP} = \mu^2 V_a^2 (2k_f) / \left[\eta^2 V_s^2 (2k_f) + \mu^2 V_a^2 (2k_f) \right] \quad (15)$$

where the upper scripts mP refers to a modified Phillips ionicity. Equation (6) gives the proposed ionicity as :

$$f_i = V_a^2 (2k_f) / \left[V_s^2 (2k_f) + V_a^2 (2k_f) \right] \quad (16)$$

in which the Penn model⁸ is used. Equation(15) and (16) give the following relation between f_i and f_i^{mP} in terms of η and μ :

$$f_i = \eta^2 f_i^{mP} / \left[(\eta^2 - \mu^2) f_i^{mP} + \mu^2 \right] \quad (17)$$

It can easily be shown that the maximum deviation (y_m) of f_i^{mP} from f_i reaches the value

$$y_m = (\eta - \mu) / (\eta + \mu) \quad (18)$$

which occurs at the following values of f_i^{mP} and f_i :

$$f_{im}^{mP} = \mu / (\eta + \mu) \quad , \quad f_{im} = \eta / (\eta + \mu) \quad (19)$$

or

$$f_{im}^{mP} = 0.5 - 0.5 y_m \quad , \quad f_{im} = 0.5 + 0.5 y_m$$

III-Calculations and Results :

III-(1) Effective Structure factors :

The calculations of the effective structure factors for the different crystal structures are summarized as follows :

(a) Zinc-blende : $\eta = \sqrt{2(1 + \Delta_s)}$ and $\mu = \sqrt{2(1 - \Delta_a)}$ where
 $\Delta_s = \Delta_a = \sin 4k_f \tau / 4k_f$ with $\tau = \sqrt{3} a / 8$ and a is the lattice constant .

(b) Rock-salt and Cesium Chloride: The same form of equations as the Zinc-blende but with τ different and equal to $\sqrt{3} a / 4$.

(c) Wurtzite: The same expressions for η and μ but with
 $\Delta_s = \sum \sin \theta_i / n_i \theta_i$ and $\Delta_a = \Delta_s - 2(\sin \theta_3) / \theta_3$

where $\theta_1 = 4k_f \tau_1$, $\theta_2 = 4k_f |\vec{\tau}_1 - \vec{\tau}_2|$, $\theta_3 = 2k_f |2\vec{\tau}_1 - \vec{\tau}_2|$,
 $\theta_4 = 4k_f \tau_2$, $n_1 = n_2 = 2$, $n_3 = n_4 = 1$,
 $\vec{\tau}_1 = a [-1/6, 1/6, (\xi/4)(u-1)]$, and $\vec{\tau}_2 = a(0.0, \xi u)$
 with $\xi = c/a = \sqrt{8/3}$ and $u = 3/8$.

Table(1) gives the numerical results for the effective structure factors together with the values of f_{im}^{mP} and f_{im} , and the maximum percentage deviation between them. As can be seen from this table, the percentage deviation between f_i^{mP} and f_i , for all structures, does not exceed 13 %. The maximum deviation occurs at an ionicity of about 0.5 and this is represented for Zinc-blende-type structure as an example, in Fig.(1). A suggested explanation is that the structure effects are somewhat remarkable when the ionicity and covalency are nearly

equal, even these effects are small.

III-(2) Ionicity

The calculations are started by evaluating the average energy gap E_g from the equation ^(9,10) :

$$E_g = \hbar w_p / \sqrt{3(\epsilon_1(0)-1)/2D} , \quad (20)$$

where w_p is the free electron plasma frequency calculated for a density of eight electrons per unit cell, $\epsilon_1(0)$ is the static electronic dielectric constant, and D is the nonlocality factor which is a model dependent and of order unity ^(10,11). The symmetric form factor $V_s(2k_f)$ has been evaluated using the expression⁵ :

$$V_s(2k_f) = V_{si}(2k_f) (a_{si}/a)^{2.5} , \quad (21)$$

where $V_{si}(2k_f)$ and a_{si} is the form factor and lattice constant for silicon while a is the lattice constant of the crystal under considerations. The effective symmetric structure factors are given in table(1). Then using equations (14-17), straight forward calculations of E_h, C, V_a, f_i , and f_i^{mP} are followed.

The ionicities f_i and f_i^{mP} have been calculated for a large number of binary and pseudo-binary crystals of the family $A_N B_{8-N}$. The data are collected in table (II) together with those calculated by Phillips. The relation between E_h and C , obtained from Phillips data ^(3,4), is represented in Fig.(2), to be compared with the relation between $V_s(2k_f)$ and $V_a(2k_f)$, for nearly the same crystals represented in Fig.(3) .

IV-Conclusion :

It is concluded from Fig.(3) that there exist three critical ionicities: the first discriminates between the Zincblende(Zb) and the Wurtzite (Wu)-type structures with

$f_{ic1}(Zb/Wu) = 0.68$; . The second discriminates the Wurtzite from the Rock-salt structures with $f_{ic2}(Wu/R)=0.865$, and the third discriminates between the Rock-salt and Cesium chloride structures with $f_{ic3}(R/CsCl) = 0.965$. This means that our ionicity scale as well as our modified ionicity scale of Phillips distinguish between the four structures ZB, Wu, R and CsCl, while Phillips scale⁴ , and of others^(11,12) , has only one critical ionicity $f_i^{Ph} = 0.785$ which separates all 4-fold from all 6-fold co-ordinated crystals of the family $A_N B_{8-N}$.

The theoretical justification of the success of our ionicity scale in ordering physical properties of $A_N B_{8-N}$ compounds can be understood in terms of using the effective structure factors for the evaluation of the E_h and C rather than relying on purely numerical real-space calculations. Also the extension to more complicated compound seems to be possible¹³ .

Table I : Effective structure factors and maximum
 deviations between f_i and f_i^{mP} .

Structure	Δ_s	Δ_a	γ	μ	f_{im}	f_{im}^{mP}	y_m/f_{im}
Zinc-blende	0.094	0.094	1.48	1.35	0.52	0.48	8.8 %
Rock-salt	0.057	0.057	1.45	1.37	0.51	0.49	5.5 %
Cesium chloride	-0.090	-0.090	1.35	1.48	0.48	0.52	-9.6 %
Wurtzite	0.220	0.080	1.56	1.36	0.53	0.47	12.8 %

Table II : Form Factors and Ionicities of Binary Crystals .

Crystal	a(A) ^c	$\epsilon_1(0)$	$v_s(2k_f)$ Ry	$v_a(2k_f)$ Ry	γ ^{mp}	f_i	f_i^{Ph}
1	2	3	4	5	6	7	8
			Znh				
BN	6.83	5.5	5.581	0.851	0.232	0.267	0.256
AlN	6.26	4.8	0.362	0.344	0.429	0.476	-
P	10.30	8.7	0.208	0.134	0.257	0.294	0.307
As	10.62	10.7	0.193	0.108	0.207	0.239	0.274
Sb	11.59	14.1	0.155	0.075	0.161	0.188	0.426
GaN	8.48	15.9	0.338	0.286	0.372	0.417	-
P	10.30	6.1	0.208	0.148	0.296	0.336	0.327
As	10.68	12.2	0.190	0.100	0.186	0.216	0.310
Sb	11.52	14.4	0.157	0.092	0.220	0.253	0.361
InN	9.35	7.5	0.265	0.218	0.360	0.404	-
P	11.09	9.6	0.173	0.155	0.398	0.444	0.421
As	11.41	12.3	0.161	0.124	0.329	0.371	0.357
Sb	12.24	15.7	0.136	0.090	0.295	0.335	0.321
BeO	7.20	3.0	0.510	0.693	0.604	0.648	-
S	9.17	7.5	0.279	0.157	0.208	0.240	0.286
Se	9.58	8.5	0.249	0.148	0.225	0.260	0.261
Te	10.47	6.0	0.200	0.261	0.587	0.631	0.169
NgTe	12.05	10.6	0.141	0.126	0.401	0.447	-
ZnO	8.61	4.3	0.326	0.419	0.568	0.623	-
S	10.22	5.9	0.212	0.260	0.555	0.601	0.623
Se	10.71	7.3	0.189	0.216	0.521	0.568	0.630
Te	11.51	9.1	0.158	0.177	0.493	0.540	0.609
CdS	11.00	6.2	0.177	0.243	0.610	0.654	0.685
Se	11.43	7.6	0.160	0.207	0.581	0.625	-
Te	12.25	10.2	0.135	0.154	0.518	0.565	0.717
SiC	8.22	6.7	0.366	0.159	0.136	0.159	0.177
			Wu.				
AlN	5.88	4.80	0.356	0.606	0.685	0.744	0.449
ZnO	6.14	4.30	0.319	0.670	0.768	0.815	0.616
InN	6.68	7.50	0.259	0.406	0.649	0.712	0.578
MgS	7.46	5.20	0.196	0.431	0.784	0.829	0.786
MgSe	7.83	6.40	0.173	0.363	0.767	0.814	0.790
GaN	5.97	5.90	0.342	0.533	0.646	0.708	0.500
BeO	5.10	3.00	0.509	1.103	0.780	0.825	0.602

Cont. Table II : Form Factors and Ionicities of Binary Crystals.

1	2	3	4	5	6	7	8
CdS	7.81	6.20	0.174	0.384	0.784	0.829	0.685
MgTe	8.56	10.60	0.139	0.228	0.668	0.729	0.554
CdSe	8.12	7.60	0.138	0.333	0.768	0.815	0.699
ZnSe	7.57	7.30	0.189	0.361	0.732	0.784	0.630
AgI	8.68	6.90	0.134	0.307	0.797	0.839	0.770
ZnS	7.22	5.90	0.212	0.426	0.751	0.801	0.623
CdTe	8.64	10.20	0.136	0.257	0.729	0.782	-
CuBr	7.67	4.80	0.183	0.463	0.828	0.867	0.735
CuCl	7.39	4.83	0.201	0.470	0.804	0.846	0.746
CuI	8.15	5.50	0.151	0.289	0.821	0.859	-
ZnTe	8.15	9.10	0.157	0.289	0.717	0.772	-
NaCl							
CsF	11.361	2.16	0.114	0.547	0.969	0.959	-
Cl	13.270	2.63	0.077	0.365	0.967	0.957	-
MgO	7.958	3.00	0.277	0.660	0.859	0.850	0.841
S	9.837	5.10	0.163	0.326	0.808	0.800	0.786
MgSe	10.301	5.90	0.145	0.289	0.816	0.798	-
CdO	8.822	5.00	0.211	0.407	0.807	0.788	0.785
GaO	9.091	3.30	0.198	0.531	0.889	0.877	0.913
S	10.751	4.50	0.180	0.333	0.879	0.867	-
Se	11.168	5.10	0.119	0.303	0.880	0.867	-
Te	11.990	6.30	0.099	0.245	0.872	0.858	-
SrO	9.751	3.20	0.167	0.506	0.912	0.902	0.926
S	11.376	2.58	0.133	0.485	0.954	0.954	0.914
Se	11.773	4.90	0.104	0.298	0.902	0.891	0.917
Te	12.222	5.80	0.095	0.260	0.894	0.883	0.903
LiF	7.731	1.90	0.311	1.096	0.933	0.925	-
Cl	0.630	2.70	0.169	0.550	0.922	0.914	0.903
Br	10.398	3.20	0.142	0.440	0.915	0.906	0.899
I	11.337	3.80	0.119	0.341	0.909	0.899	0.890
NaCl	10.631	2.30	0.134	0.555	0.960	0.956	0.935
F	8.731	1.70	0.220	1.023	0.951	0.945	0.956
Br	11.288	2.60	0.116	0.464	0.948	0.942	0.934
I	12.232	3.00	0.095	0.367	0.944	0.938	0.927
K F	10.104	1.80	0.152	0.783	0.967	0.963	0 -
Cl	11.891	2.20	0.101	0.500	0.965	0.960	0.953
Br	12.472	2.30	0.090	0.457	0.967	0.963	0.953
I	13.357	2.70	0.076	0.362	0.962	0.958	0.950
Rb	10.688	1.90	0.131	0.678	0.967	0.963	0.960
Cl	12.436	2.20	0.091	0.468	0.968	0.964	0.955
Br	12.952	2.40	0.082	0.418	0.967	0.963	0.957
I	13.875	2.70	0.069	0.345	0.966	0.962	0.951
CsCl							
CsCl	7.77	2.63	0.08	0.40	0.972	0.967	-
CsBr	8.11	2.70	0.07	0.38	0.975	0.970	-
CsI	8.62	3.00	0.06	0.33	0.975	0.970	-
RbCl	7.07	2.18	0.09	0.35	0.976	0.971	-

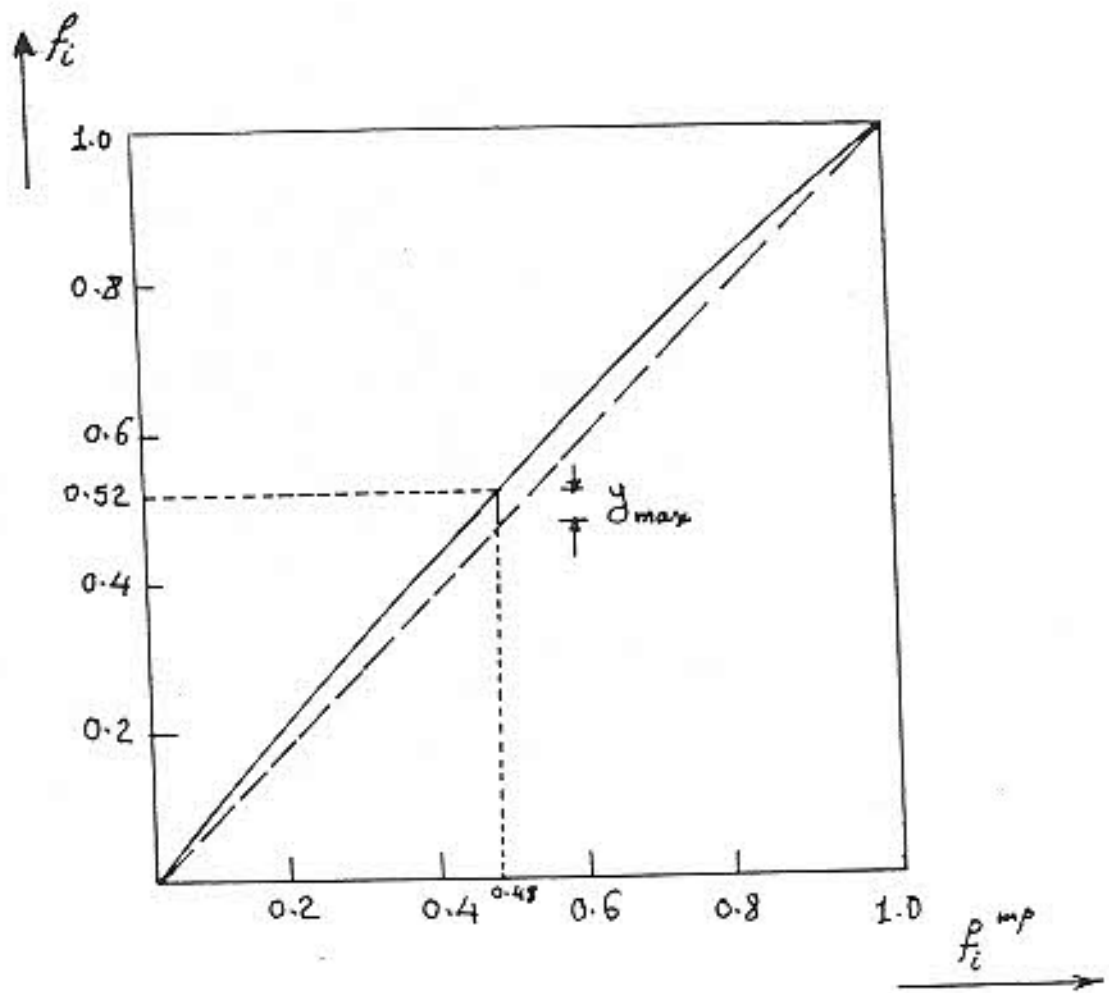


Fig. 1

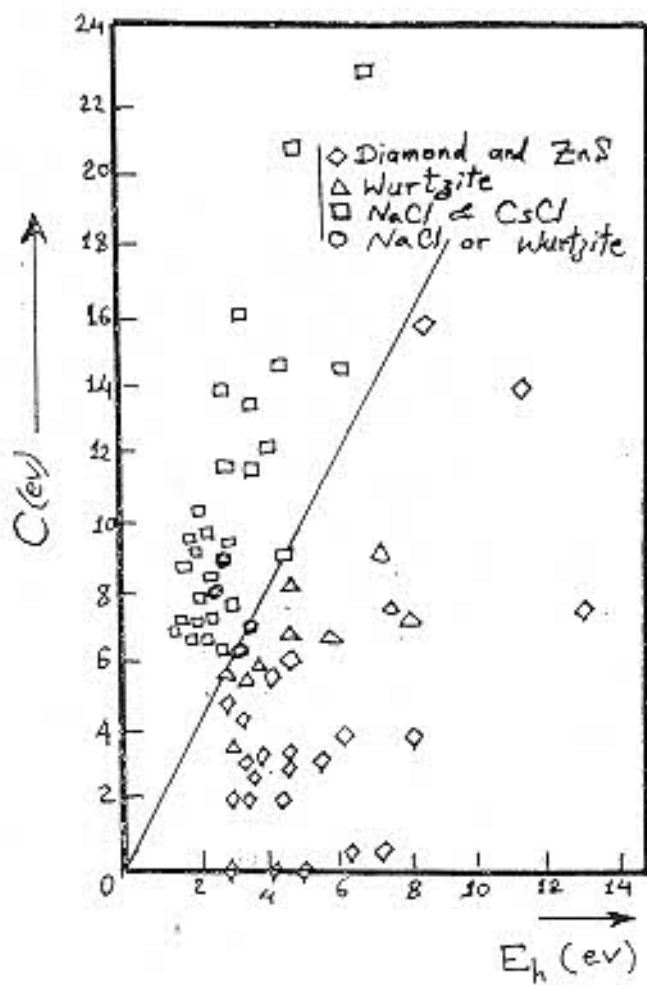


Fig. 2

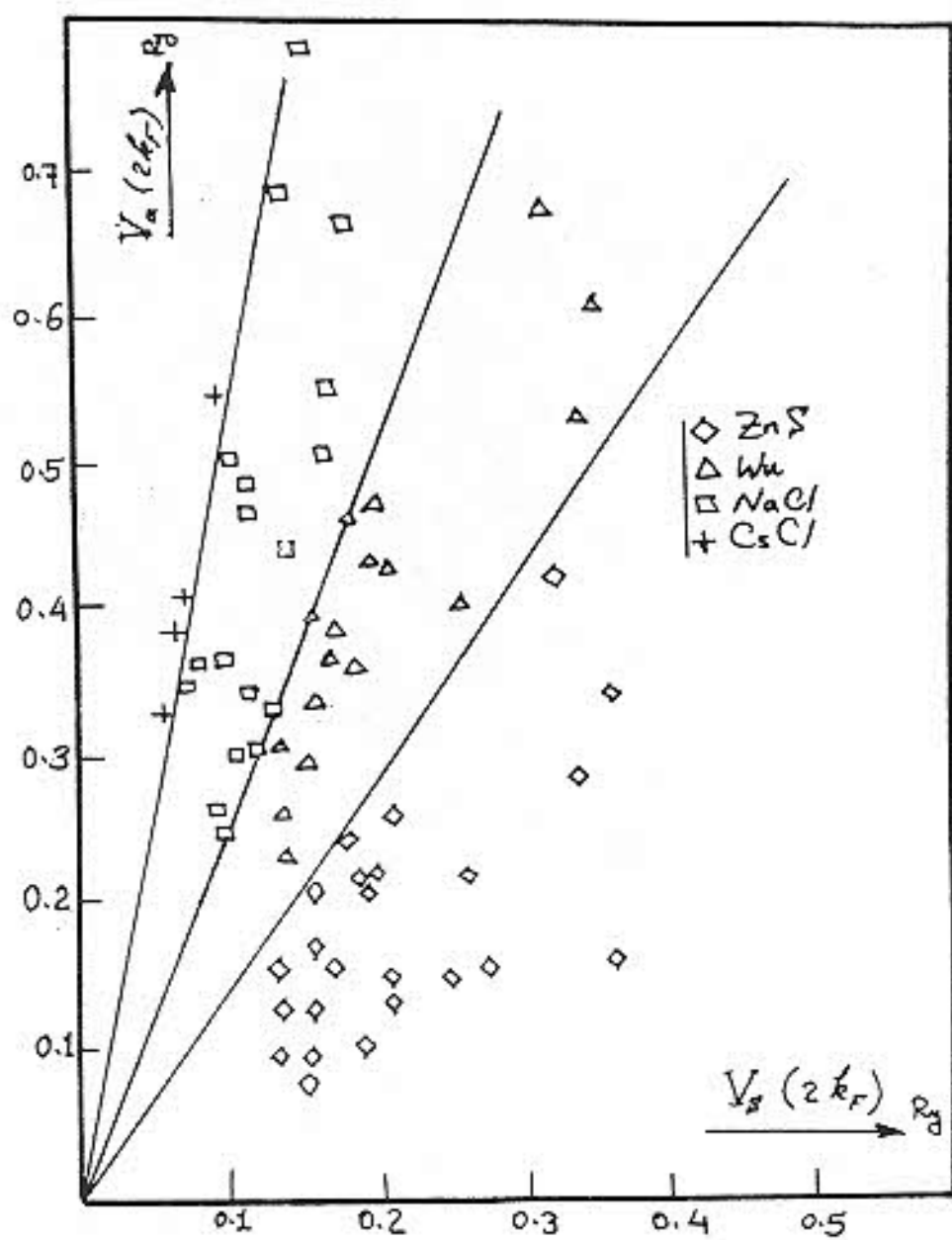


Fig. 3

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