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DISCLAIMER

AN IONICITY SCALE BASED ON X-RAY PHOTOEMISSION VALENCE-BAND SPECTRA OF A^NB^{8-N} AND A^NB^{10-N} TYPE CRYSTALS*

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ABSTRACT

A quantitative scale of ionicity based on x-ray photoemission studies of the valence-band density of states of many A^NB^{8-N} and A^NB^{10-N} crystals is discussed. The scale is empirical. It involves allocating the energy splitting of the two most tightly-bound valence-band peaks between covalent and ionic contributions. Several ternary alloys and chalcopyrite-type crystals were also included in this study. The scale was found to be superior to the molecular orbital approach of Coulson and the thermochemical scale of Pauling because of the symmetrical treatment of covalent and ionic contributions. It appears to have wider applicability than the Phillips-Van Vechten scale. The strengths and weaknesses of the proposed scale are discussed.

I. INTRODUCTION

For several decades the concept of ionicity has been of great practical use in the study of the chemical bond. It is therefore desirable to formulate a quantitative definition of ionicity. There have been many attempts to quantify ionicity, but all have possessed shortcomings.[1] For some time it has been known that the chemical shifts measured by x-ray photoemission spectroscopy (XPS) are related to charge transfer from the cation to the anion in a binary compound; this transfer can of course be related to ionicity.[2,3,4] This approach has been applied to binary solids by Vesely and Langer[5] and more recently by Cardona and co-workers.[6] The measurement of chemical shifts in core-level binding energies in semiconductors and insulators is suspect for two reasons: sample charging (an experimental problem) and lack of a suitable reference energy (a conceptual problem). These problems may both be soluble, but even so it seems questionable whether core-level shifts will yield decisive ionicity information in view of final-state effects, etc.

In this paper we present an alternate approach, also based on XPS results. We have developed a quantitative scale of ionicity from the observed splitting of the lowest (i.e., most tightly-bound) two peaks in the XPS valence-band densities of states (VBDOS) of 41 binary crystals. This scale is compared in detail with the scale of Phillips-Van Vechten based on the single-gap dielectric model. Our scale is tested on the criteria of its ability to predict four-fold versus six-fold coordination for the binary $A^N B^{8-N}$ and $A^N B^{10-N}$ crystals.

Results are given and summarized in Sec. II. They are discussed in Sec. III and conclusions are drawn in Sec. IV.

II. RESULTS

Experiments were performed on a Hewlett-Packard HP 5950A electron spectrometer utilizing monochromatized Al K_α (1486.6 eV) radiation.[7] We have previously reported the XPS-VBDOS of most of the crystals used in this analysis.[8-15] The reader is referred to these publications for experimental details and discussions on the use of XPS as a probe of the VBDOS of solids. We note that these results agree well with recent ultraviolet photoemission (UPS) measurements,[16,17] and theoretical band structure calculations.[18-22]

In general the spectra of the valence band region of A^NB^{8-N} and A^NB^{10-N} crystals show a three-peak structure, occasionally with a sharp core d peak intruding. Figure 1 shows the raw XPS-VBDOS spectra of some typical Group IV and Group V elements, and III-V, II-VI, IA-VII, and IV-VI compounds.

Walter and Cohen[23] calculated electronic charge densities for several diamond zincblende semiconductors from pseudopotential band-structure wavefunctions. These charge densities give the distribution of the valence electrons in each band in real space: they can be related to peaks in our spectra. Peak I (PI) consists of electrons centered around the anion atomic site; i.e., an "s-like" distribution. Peak II (PII) consists of electrons basically centered around the cation, and located in the bonding region. Peak III (PIII) results from electrons concentrated between the atomic sites in the bonding region i.e. a "p-like" distribution. With this in mind, and realizing that the valence-band peaks cannot be truly described with such a simple atomic picture, we shall refer to PI and PII as "s-like" bands and PIII as "p-like". Fuller discussions of the atomic derivation of the valence-band peaks are available in Refs. 10, 15, and 24.

Tables I and II summarize the compounds that have been studied by XPS and give the s-peak splitting ΔE_S^{XPS} in each case. Also given are nearest-neighbor bond distances d and other parameters, discussed below.

III. DISCUSSION

It was noted previously in an XPS study of the VBDOS of the isoelectronic series Ge, GaAs, and ZnSe[9] that ΔE_S^{XPS} increased with increasing ionicity. This increasing splitting was attributed mainly to an increasing localization of electrons around the stronger anion potential. The effect is visually demonstrated by the charge density distributions in Figs. 2, 3, 8, 9, 14, and 15 of Ref. 23. It was related to the antisymmetric form factors of an Empirical Pseudopotential Method (EPM) calculation.[9,23] Later Ley et al.[13] and Grobman et al.[25] discussed the splitting at the symmetry point X (the $X_3 - X_1$ gap) in the Brillouin zone. Increase of the $X_3 - X_1$ gap was related to increasing ionicity and to Phillips' ionicity (heteropolar) parameter C.

Recently, Chadi et al.[26] have studied the various possible relationships between C of the Phillips-Van Vechten theory and atomic pseudopotential in several binary crystals. However, to devise a quantitative scale of ionicity, a covalent fiducial point is necessary. The need to treat ionic and covalent contributions on an equal footing has been cogently put forth in a series of articles by Phillips and Van Vechten.[1,27-37]

Ley et al.[11] in an XPS-VBDOS study of groups IV and V covalent elemental crystals observed a rather simple relationship between the covalent splitting of PI and PII, ΔE_S^C, and the nearest-neighbor distance d. The observed relation is

$$\Delta E_S^C = 8.0 - 2.2\, d \quad , \tag{1}$$

with ΔE_S^C in eV and d in Å. The measured ΔE_S^C and d for these crystals, listed in Table I, are plotted in Fig. 2.

The splitting between the two "s-peaks" corresponds to a splitting at the L ($L_2' - L_1$) points in the diamond structure and at the T ($T_2' - T_1$) point for the A_7 structure of the group V semimetals. The $X_3 - X_1$ gap vanishes by symmetry in homopolar diamond-type crystals. The fact that ΔE_S^C depends on d in such a simple way for the homopolar crystals suggests that it is a strong function of overlap and could serve as a covalent fiducial point. The fact that the group V semimetals fall on the "universal curve" of Fig. 2 suggests that the ionicity of the $A^N B^{10-N}$ as well as the $A^N B^{8-N}$ crystals might well be included in an XPS-derived scale of ionicity. The covalent (homopolar) parameter, E_h, of Phillips' model is a function of d only ($E_h \propto d^{-2.5}$). Grobman et al.[25] have speculated on the possible relationship between E_h and the L gap of homopolar diamond-type crystals.

We are now in a position to decompose our measured splitting of the "s-bands", ΔE_S^{XPS} into an ionic and a covalent contribution. ΔE_S^C is arrived at by simply inserting d(Å) of the crystal under analysis into Eq. (1). To obtain the ionic contribution, ΔE_S^i, we suggest that the relationship

$$\Delta E_S^i = \Delta E_S^{XPS} - \Delta E_S^C \quad , \tag{2}$$

be employed. Now an ionicity number can be simply defined as

$$f_i^{XPS}(AB) \equiv \frac{\Delta E_S^i}{\Delta E_S^{XPS}} \quad . \tag{3}$$

For example let us consider the isoelectronic series Ge, GaAs, and ZnSe, the members of which have nearly constant d. Germanium with d = 2.44 A, is of course purely covalent and $f_i^{XPS}(Ge) = 0.0$. GaAs also has d = 2.44 A and

Eq. (1) or Fig. 2 yields $\Delta E_S^C = 2.6$ eV. ΔE_S^{XPS} was measured to be 4.8 eV, which yields $\Delta E_S^i = 2.2$ and $f_i^{XPS}(GaAs) = 0.46$. In a similar manner for ZnSe (d = 2.45 A), $\Delta E_S^C = 2.6$ eV, $\Delta E_S^{XPS} = 7.8$, $\Delta E_S^i = 5.2$ and $f_i = 0.67$. Figure 3 schematically displays what is happening in the Ge - GaAs - ZnSe series.

The antisymmetric gaps obtained from recent EPM calculations for this series are $V_A(Ge) = 0$ eV, $V_A(GaAs) = 4.5$ eV, and $V_A(ZnSe) = 8.2$ eV.[38] The trend in $V_A(AB)$ follows nicely the trend in $\Delta E_S^i(AB)$ and, since d $\approx$ constant, in $\Delta E_S^{XPS}(AB)$ as well.

Table II summarizes the structures, the various parameters used, and the derived $f_i^{XPS}(AB)$ for the crystals used in this study. Before discussing the results in detail, let us compare this empirical ionicity scale with the dielectric-based scale of Phillips. Our ΔE_S^i, ΔE_S^C, and ΔE_S^{XPS} are analogous to the C, E_h and E_g, respectively, of Phillips. His E_g is the gap between bonding and antibonding states. Here E_h is the homopolar energy and is equal to E_g for homopolar crystals and determined by the empirical relationship

$$E_h \propto d^{-2.5} ,$$

for heteropolar $A^N B^{8-N}$ crystals. C is the ionic contribution to E_g and Phillips has shown it to have the analytic form

$$C(AB) = b[(Z_A/r_A) - (Z_B/r_B)]e^{-K_S R} .$$

This just describes a screened coulomb interaction and, without the screening factor, is similar to a electronegativity difference. With d constant, $C(AB) \propto \Delta Z = 8 - 2N$ so $C(ZnSe)/C(GaAs) \approx 2$, which is close to $\Delta E_S^i(ZnSe)/\Delta E_S^i(GaAs)$. In both scales the homopolar gaps depend only on d. They do have different

parametric dependences on d because of the different bases of the two scales. Phillips' C is related to the $X_3 - X_1$ gap in $A^N B^{8-N}$ tetrahedral crystals. It has been shown that the $X_3 - X_1$ gap can be measured with high resolution (≤ 0.5 eV FWHM) XPS.[13] For the purposes of this study, however, we have chosen to use the PI - PII splitting because: 1) It is consistent with our choice for the covalent fiducial point. 2) It is chemically more appealing to take the peak position in the density of states which contains a large number of electrons rather than an edge of the Brillouin zone. 3) Most XPS spectrometers do not yet possess high enough resolution to pick out the X_3 and X_1 symmetry points. 4) In many cases core d peaks occur in the valence region: it is then hard enough to detect PI or PII, let alone symmetry points. 5) We wish to make our $f_i^{XPS}(AB)$ apply more generally than just to tetrahedral $A^N B^{8-N}$ binary crystals.

For his definition of ionicity, Phillips employed a quadrature relationship,

$$f_i^{DT}(AB) \equiv \frac{C^2}{E_h^2 + C^2} \quad . \tag{4}$$

While this relationship is physically appealing, it is nonetheless arbitrary.[39] We have no a priori reason to define $f_i^{XPS}(AB)$ either linearly, as in (3), or as

$$f_i^{XPS} \equiv \frac{(\Delta E_S^{XPS})^2 - (\Delta E_S^C)^2}{(\Delta E_S^{XPS})^2} \quad , \tag{5}$$

to be similar to Eq. (4). Both Eqs. (3) and (5) give basically the same ordering of $f_i^{XPS}(AB)$. The $f_i^{XPS}(AB)$ defined by Eq. (3) appears to be more useful in that it gives a wider range of ionicities, $0.26 \leq f_i^{XPS}(AB) \leq 1.00$ vs $0.46 \leq f_i^{XPS}(AB) \leq 1.00$ for Eq. (5). A big difference is noted in the $f_i^{XPS}(AB)$ of the alkali halides. The $f_i^{XPS}(AB)$ as defined by Eq. (5) clusters the alkali halides around a very small range of values.

Phillips has discussed in detail the correspondence between ionicity and coordination for the A^NB^{8-N} crystals.[1,32,33] In his study of seventy A^NB^{8-N} crystals Phillips found a critical ionicity F_i such that for $f_i < F_i$ the crystals are four-fold coordinated and for $f_i > F_i$ the crystals are six-fold coordinated. With $F_i = 0.785$, Phillips' scale had 100% accuracy in predicting crystal structure, far superior to any other then available quantitative scale of ionicity. In Fig. 4, we have plotted the ionicities of several A^NB^{8-N} crystals common to studies for each scale, with the structure noted by symbols. We have added to both scales several A^NB^{10-N} crystals, the lead salts and SnTe, which have the rocksalt structure. We have also added to our scale several $Pb_xSn_{1-x}Te$ alloys and two ternary semiconductors. If for the dielectric scale we keep $F_i = 0.785$, the $f_i^{DT}(AB)$ scale will make four wrong predictions with the inclusion of the A^NB^{10-N} crystals. If we lowered F_i to 0.71, $f_i^{DT}(AB)$ would make two errors but would no longer have a perfect score for the 70 A^NB^{8-N} crystals of Ref. 1. The $f_i^{XPS}(AB)$ scale with $F_i = 2/3$ is able to predict 100% of the structures correctly. However, within the accuracy of the data $f_i^{XPS}(ZnSe)$ and $f_i^{XPS}(PbS)$ should be considered equal; thus $f_i^{XPS}(AB)$ makes one error. Thus $f_i^{XPS}(AB)$ appears to be superior to $f_i^{DT}(AB)$ when IV-VI crystals and ternary alloys are included. The lead salts present an interesting case because they can indicate whether the $f_i^{XPS}(AB)$ scale can be generalized beyond A^NB^{8-N} crystals and because both ionic and covalent bonding have been proposed for them.[40] $f_i^{XPS}(AB)$ predicts the lead salts to have the ionic rocksalt structure, which is correct. Recent charge density calculations on PbTe strongly support an ionic interpretation.[41]

The cesium halides have the eight-fold coordinated CsCl structure. Citrin and Thomas have reported XPS data for several of these compounds.[42]

If we apply our treatment to these data we obtain; $f_i^{XPS}(CsF) = 0.93$, $f_i^{XPS}(CsCl) = 0.97$, and $f_i^{XPS}(CsBr) = 1.00$. All these values are in the upper range of the alkali halide data. This is pleasing, although the ionicities of these three salts are ordered opposite to chemical expectations. Phillips did not treat these crystals. In view of the generality of this scale, it would be very useful to enlarge the XPS study, especially to include $A^N B^{10-N}$ crystals.

In Fig. 4 we have also plotted data from two $A^{II}B^{IV}C_2^V$ (chalcopyrite-type) crystals. These are ternary analogs of the binary $A^{II}B^V$ crystals, i.e., $ZnGeP_2$ is the analog of GaP, and $CdSnAs_2$ of InAs.

In Fig. 5 is plotted the bonding charge, as calculated in Ref. 17, vs $f_i^{XPS}(AB)$ for the series Ge - GaAs - ZnSe. This shows that the phase transformation from four-fold to six-fold coordination occurs as the bonding charges get very small.

We shall not discuss the other scales of ionicity in detail since this has already been done by Phillips.[1] The major problems with the other scales, notably Coulson's molecular orbital approach,[43] $f_i^{CRS}(AB)$, and Pauling's thermochemically based scale,[44] $f_i^{P}(AB)$, derive from the lack of symmetrical treatment of ionic and covalent contributions. The covalent contribution is neglected in Pauling's definition and is an order of magnitude smaller in Coulson's approach. As an example let us consider GaAs and InAs. Both $f_i^{CRS}(AB)$ and $f_i^{P}(AB)$ predict the same ionicity for each set of crystals $f_i^{CRS}(GaAs) = 0.37 = f_i^{CRS}(InAs)$, $f_i^{P}(GaAs) = 0.26 = f_i^{P}(InAs)$. We can see they both have nearly the same ionic contribution but the covalent contribution is different in both $f_i^{XPS}(AB)$ and $f_i^{DT}(AB)$. Hence the values $f_i^{XPS}(GaAs) = 0.46$, $f_i^{XPS}(InAs) = 0.51$, $f_i^{DT}(GaAs) = 0.31$, $f_i^{DT}(InAs) = 0.36$. Coulson's scale is limited only to

tetrahedrally coordinated $A^N B^{8-N}$ crystals. Both Pauling's and Coulson's scales tend to bunch groups of crystals with respect to ΔZ; i.e., III-V crystals are clustered at one value and II-VI at another. Phillips stated that his dispersion theory does not work too well for crystals such as alkali halides with $f_i \gtrsim 0.9$, which is where Pauling's scale is best because the covalent contribution is very small. The Phillips-Van Vechten theory uses optical and dielectric data. Optical data are not always straightforward to interpret and this approach includes some approximations.

Finally we point out problems with the XPS-derived scale: (1) For a series with a given cation, the ordering of $f_i^{XPS}(AB)$ is not what one would expect from chemical intuition. However, within a series with a given anion the ordering is much better. For isoelectronic series that have d essentially constant, $f_i^{XPS}(AB)$ works out much better, so there may be a size effect which should be taken into account. (2) For the alkali halides of a given cation in particular, the ordering of $f_i^{XPS}(AB)$ is exactly the inverse of what chemical intuition expects. For a given anion, the ordering is the expected one. Possible sources of this discrepancy could arise from being at the ionic limit where the anion s peak (PI) is essentially a core peak; the effect of cation core peaks at lower binding energies; or a size effect which would be greatest for the alkali halide series. If we divide $f_i^{XPS}(AB)$ by the anion radius, r_a, to obtain

$$f_i^{*XPS}(AB) = f_i^{XPS}/r_a \quad , \tag{6}$$

the resulting ordering of $f_i^{*XPS}(AB)$ is the intuitively correct one for both cation series and anion series. This is summarized in Table III. If Eq. (6)

is applied to III-V compounds one gets mixed results. The size effect should be studied further as more results become available.

IV. CONCLUSIONS

This has been a first attempt to obtain a quantitative experimental measure of ionicity using XPS. An ionicity parameter $f_i^{XPS}(AB)$ was derived from the splitting of the lowest two "s-like" valence bands, ΔE_S^{XPS}. First a covalent fiducial line was established from the "universal curve" of ΔE_S^C vs d. The energy ΔE_S^{XPS} was then decomposed into an ionic and covalent contribution and an ionicity number f_i^{XPS} was defined. This scale was applied to over 40 crystals. The crystals included not just A^NB^{8-N} binary crystals but also A^NB^{10-N}, ternary alloys and chalcopyrite-type $A^MB^NC_2^{8-(M+N)/2}$. It was able to predict quite well the transformation from four-fold to six-fold coordination solely on the basis of $f_i^{XPS}(AB)$. The scale was compared to other scales. It was found superior to Coulson's M-O approach and Pauling's thermochemical ionicity because it treated covalent and ionic contributions symmetrically. $f_i^{XPS}(AB)$ also appeared to have wider applicability than the Phillips scale which was limited to A^NB^{8-N} crystals. It appears that $f_i^{XPS}(AB)$ needs a correction factor for the anion size. The question of d-band mixing with valence bands also requires further attention. There is need for further work especially in the expansion of classes of crystals studied. This study shows promise in the application of XPS to study of the problem of the nature of the chemical bond in solids. The approach taken in this work bypasses the difficulties associated with core-level shift studies by measuring splittings rather than shifts.

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FOOTNOTES AND REFERENCES

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Table I. Nearest-neighbor distance and ΔE_S^C splitting for group IV and group V elemental crystals.

Crystal	Structure	d(Å)	ΔE_S^C(eV)	Ref.
C	diamond	1.54	4.7	10
Si	diamond	2.34	2.6	8
Ge	diamond	2.44	3.1	8
α-Sn	diamond	2.80	1.8[b]	--
As	A7	2.50	2.6	11
Sb	A7	2.86	1.7	11
Bi	A7	3.10	1.2	11

[a] R. W. G. Wyckoff, Crystal Structures (Wiley, Interscience, New York, 1963).

[b] Predicted value from Eq. (1)).

Table II. Nearest-neighbor distances, energy of XPS splitting of lowest two valence bands ΔE_S^{XPS}, the covalent splittings ΔE_S^C, ionic splitting ΔE_S^i and ionicity number $f_i^{XPS}(AB)$. These parameters are explained in the text. All energies are given in eV.

Crystal	d(Å)[a]	Structure[b]	ΔE_S^{XPS}	ΔE_S^{C}[c]	ΔE_S^i	$f_i^{XPS}(AB)$[d]	Ref.
GaAs	2.44	Z	4.8	2.6	2.2	0.46	13
ZnSe	2.45	Z	7.8	2.6	5.2	0.67	13
InSb	2.81	Z	4.1	1.8	2.3	0.56	13
CdTe	2.81	Z	∿ 5.2	1.8	∿ 3.4	∿ 0.65	13
GaSb	2.65	Z	3.6	2.2	1.4	0.39	13
ZnTe	2.64	Z	6.5	2.2	4.3	0.66	13
KI	3.53	R	8.3	0.2	8.1	0.97	15
InAs	2.61	Z	4.7	2.3	2.4	0.51	13
CdSe	2.63	W	∿ 5.7	2.2	∿ 3.5	0.61	13
InP	2.54	Z	4.3	2.4	1.9	0.44	13
CdS	2.53	W	∿ 5.5	2.4	∿ 3.1	∿ 0.56	13
RbCl	3.29	R	10.7	0.7	10.0	0.94	h
AlSb	2.66	Z	4.3	2.2	2.1	0.49	g
NaI	3.24	R	8.1	0.9	7.2	0.89	15
NaBr	2.99	R	9.9	1.4	8.5	0.86	15
GaP	2.36	Z	3.8	2.8	1.0	0.26	13
ZnS	2.34	Z	7.5	2.9	4.6	0.61	13
KCl	3.15	R	11.8	1.1	10.7	0.91	15
ZnO	1.95	W	9.1	3.7	5.4	0.59	13
KF	2.67	R	20.9	2.1	18.7	0.90	15
MgO	2.10	R	13.5	3.4	10.1	0.75	g
NaF	2.32	R	21.1	2.9	18.3	0.86	15
PbS	2.97	R	4.4	1.5	2.9	0.67	12
PbSe	3.06	R	4.3	1.3	3.0	0.70	12
PbTe	3.25	R	3.5	0.9	2.6	0.74	12
SnTe	3.14	R	4.4	1.1	3.3	0.75	g

(continued)

Table II. (continued)

Crystal	d(Å)[a]	Structure[b]	ΔE_S^{XPS}	ΔE_S^{C}[c]	ΔE_S^{i}	$f_i^{XPS}(AB)$[d]	Ref.
$Pb_{0.8}Sn_{0.2}Te$	3.23	R	3.1	0.9	2.2	0.70	g
$Pb_{0.4}Sn_{0.6}Te$	3.18	R	3.5	1.0	2.5	0.71	g
$Pb_{0.2}Sn_{0.8}Te$	3.16	R	4.3	1.1	3.2	0.74	g
LiF	2.01	R	19.7	3.6	16.1	0.82	15
KBr	3.30	R	15.0	0.7	14.3	0.95	15
NaCl	2.82	R	10.0	1.8	8.2	0.82	15
$CdSnAs_2$	2.64[e]	Z[f]	∿ 5	2.2	∿ 2.8	∿ 0.56	14
$ZnGeP_2$	2.37[e]	Z[f]	4.8	2.8	2.0	0.42	14
CsCl	3.51	CsCl	10.6	0.3	10.3	0.97	42
CsF	3.00	R	20.9	1.4	19.5	0.93	42
CsBr	3.71	CsCl	9.6	-0.2	9.6	1.00	42
HgTe	2.76	Z	∿ 3.5	1.9	1.6	∿ 0.46	13
SrO	2.57	R	∿ 13	2.4	10.6	∿ 0.82	g

[a] R. W. G. Wyckoff, Crystal Structures (Wiley-Interscience, Inc., New York, 1963).

[b] Z - zinc-blende, R - rocksalt, W - wurtzite, CsCl - cesium chloride.

[c] From Eq. (1).

[d] From Eq. (3).

[e] A. S. Borschevskii, N. A. Goryvnova, and F. P. Kesamanly, Phys. Stat. Sol. B 21, 9 (1967).

[f] Chalcopyrite structure is analogous to zincblende structure with the cation site being occupied alternately by group II and group IV cation.

[g] Unpublished work of this laboratory.

[h] C. J. Veseley, D. L. Kingston, and D. W. Langer, Phys. Letters 44A, 137 (1973).

Table III. Anion size correction applied to alkali halide crystals.[a]

Crystal	ΔE_S^{XPS}[b]	ΔE_S^{C}[c]	ΔE_S^{i}[d]	$\mathcal{F}_i^{XPS}(AB)$[e]	$\mathcal{F}_i^{*XPS}(AB)$[f]	r_a (Å)
LiF	19.68	3.57	16.11	0.819	1.14	0.72
NaF	21.14	2.90	18.24	0.863	1.20	0.72
NaCl	9.98	1.80	8.18	0.820	0.83	0.99
NaBr	9.88	1.42	8.46	0.856	0.75	1.14
NaI	8.06	0.87	7.19	0.892	0.69	1.33
KF	20.86	2.13	18.73	0.898	1.25	0.72
KCl	11.8	1.07	10.73	0.909	0.92	0.99
KBr	14.97	0.74	14.23	0.951	0.83	1.14
KI	8.26	0.23	8.03	0.972	0.73	1.33

[a] Energies in eV.

[b] From Ref. 15.

[c] From Eq. (1).

[d] From Eq. (2).

[e] From Eq. (3).

[f] From Eq. (5).

FIGURE CAPTIONS

Fig. 1. (a) X-ray photoemission valence band spectra of several typical $A^N B^{8-N}$ type crystals, Ge, GaAs, ZnSe, and KBr and (b) $A^N B^{10-N}$ type crystals, Sb and PbS.

Fig. 2. Plot of ΔE_S^C(eV) vs d(Å) for group IV and V crystals which yields Eq. (1). Figure is taken from Ref. 11.

Fig. 3. Schematic display of the ΔE_S^{XPS} splitting of the isoelectronic series Ge, GaAs, and ZnSe. The relevant parameters in determining $f_i^{XPS}(AB)$ are denoted.

Fig. 4. Comparison of the XPS-derived scale of ionicity, $f_i^{XPS}(AB)$ from Table II and the Phillips-Van Vechten ionicity, $f_i^{DT}(AB)$ (Ref. 1) illustrating the ability to predict structural phase transformation. $f^{DT}(AB)$ for crystalline materials of average V valence was obtained from P. J. Stiles, Solid State Commun. 11, 1063 (1972). Vertical line indicates critical ionicity, F_i. Dashed vertical line for $f^{DT}(AB)$ is the F_i derived in Ref. 1. Crystals with diamond, zincblende or chalcopyrite structure are indicated by ◊, wurtzite structure by ▲ and rocksalt structure by O.

Fig. 5. Plot of bonding charge determined as in Ref. 23 vs $f_i^{XPS}(AB)$ for the series Ge, GaAs, and ZnSe.

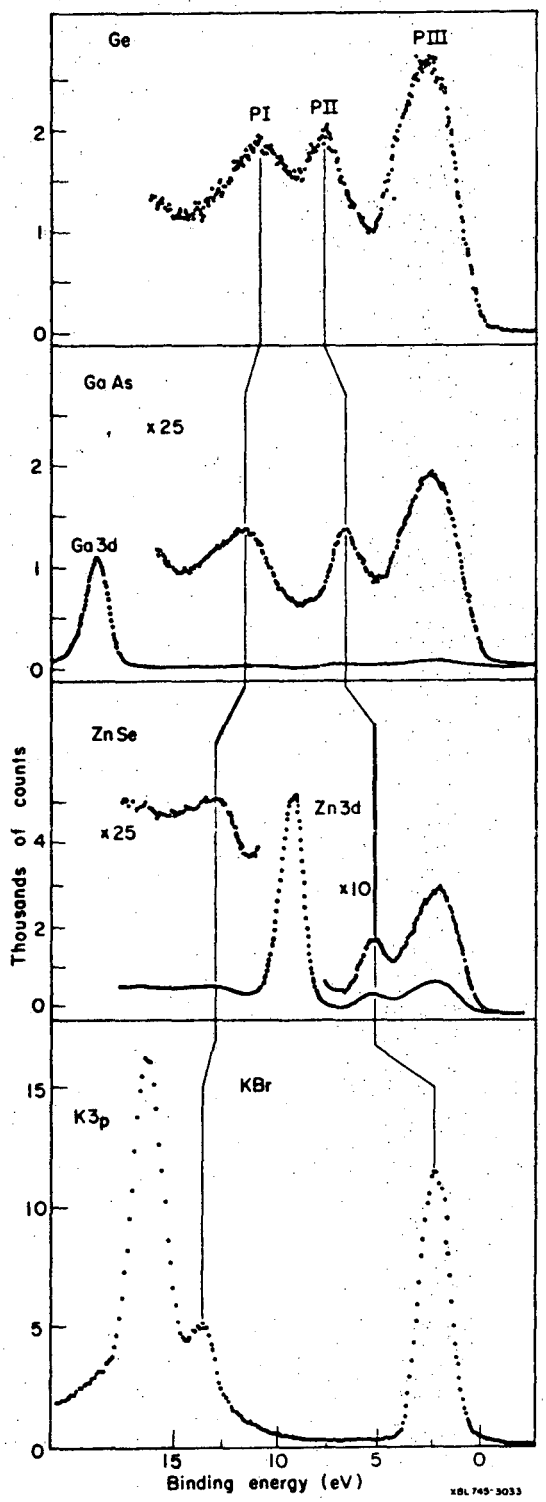
Ge
PI
PII
PIII
GaAs
x25
Ga3d
ZnSe
x25
Zn3d
x10
KBr
K3p
Thousands of counts
Binding energy (eV)
XBL 745-3033

Fig. 1a.

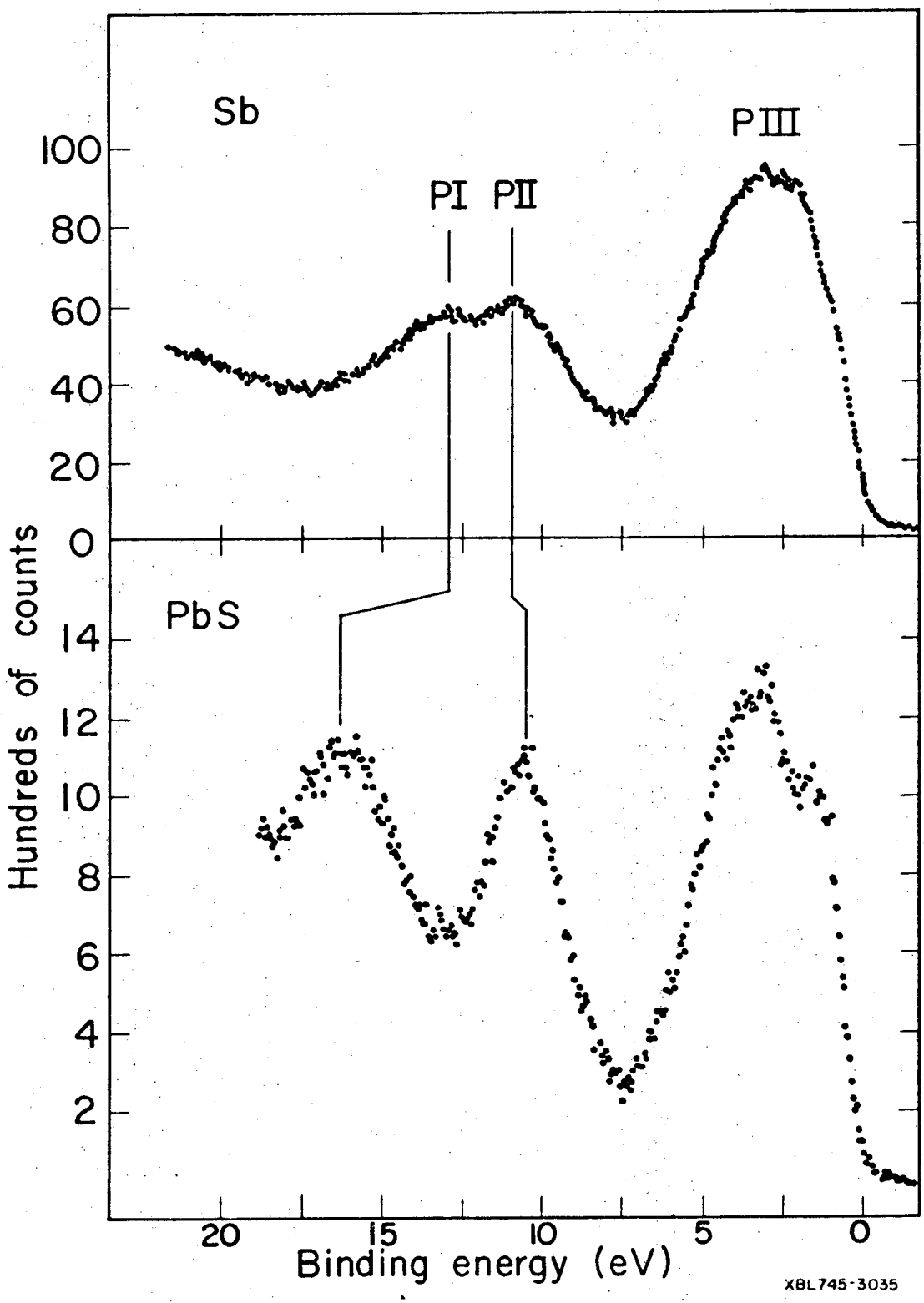
Sb
PIII
PI PII
100
80
60
40
20
0
PbS
14
12
10
8
6
4
2
Hundreds of counts
20
15
10
5
0
Binding energy (eV)
XBL745-3035

Fig. 1b.

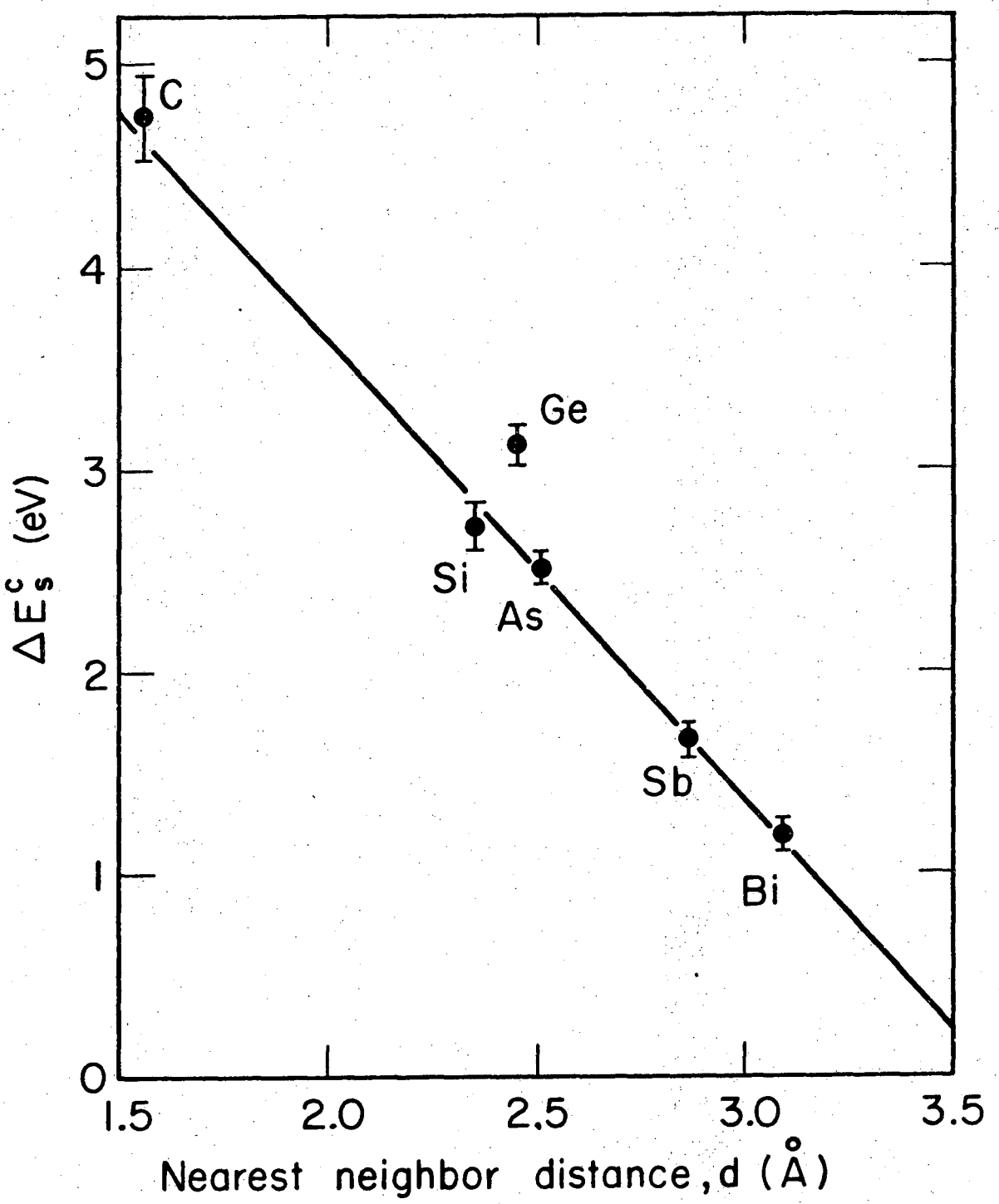
5
4
3
2
1
0
C
Ge
Si
As
Sb
Bi
ΔE_s^c (eV)
1.5
2.0
2.5
3.0
3.5
Nearest neighbor distance, d (Å)
XBL 744-2886

Fig. 2.

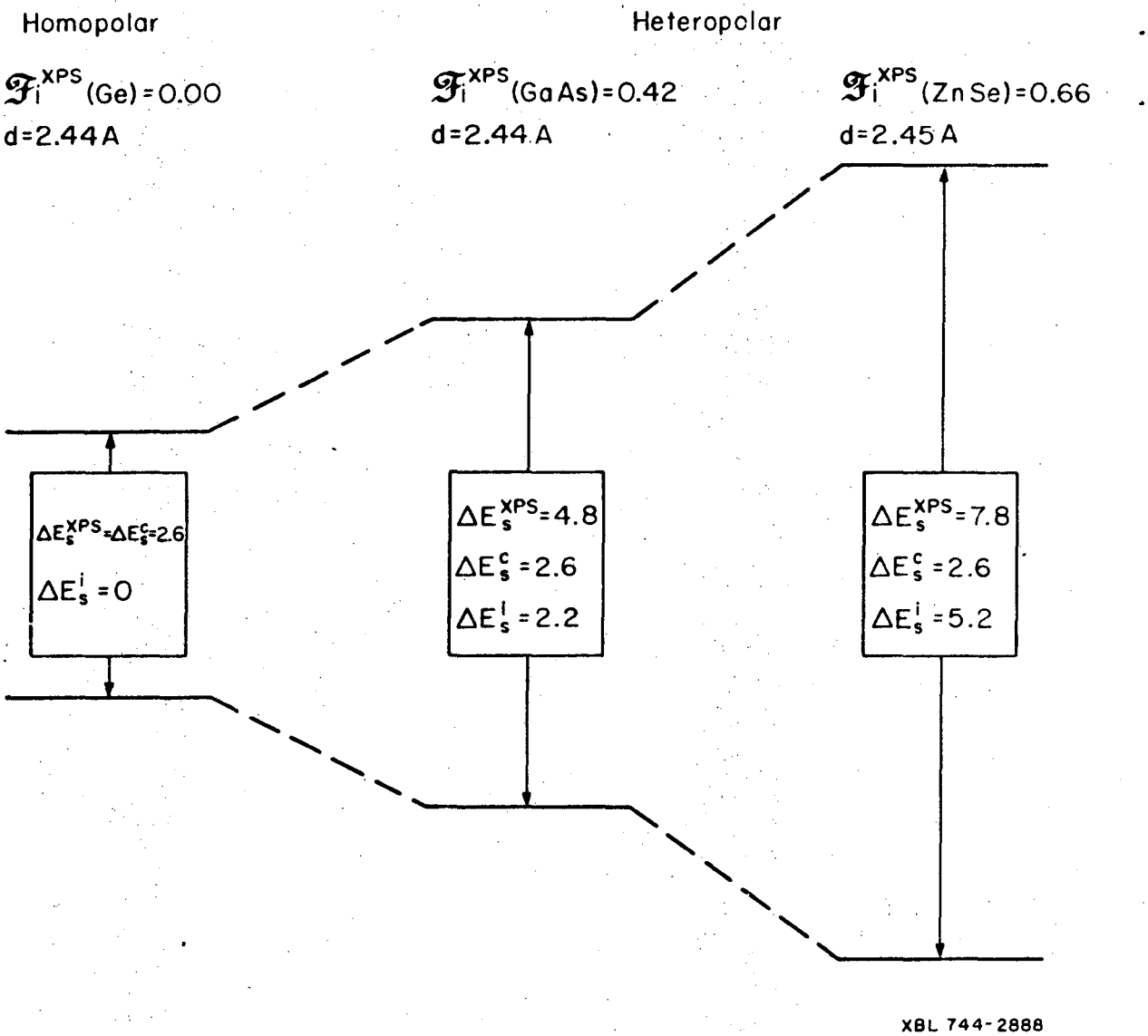
Homopolar
Heteropolar
$\mathcal{F}_i^{XPS}$(Ge) = 0.00
d = 2.44 A
$\mathcal{F}_i^{XPS}$(GaAs) = 0.42
d = 2.44 A
$\mathcal{F}_i^{XPS}$(ZnSe) = 0.66
d = 2.45 A
$\Delta E_s^{XPS} = \Delta E_s^c = 2.6$
$\Delta E_s^i = 0$
$\Delta E_s^{XPS} = 4.8$
$\Delta E_s^c = 2.6$
$\Delta E_s^i = 2.2$
$\Delta E_s^{XPS} = 7.8$
$\Delta E_s^c = 2.6$
$\Delta E_s^i = 5.2$
XBL 744-2888

Fig. 3.

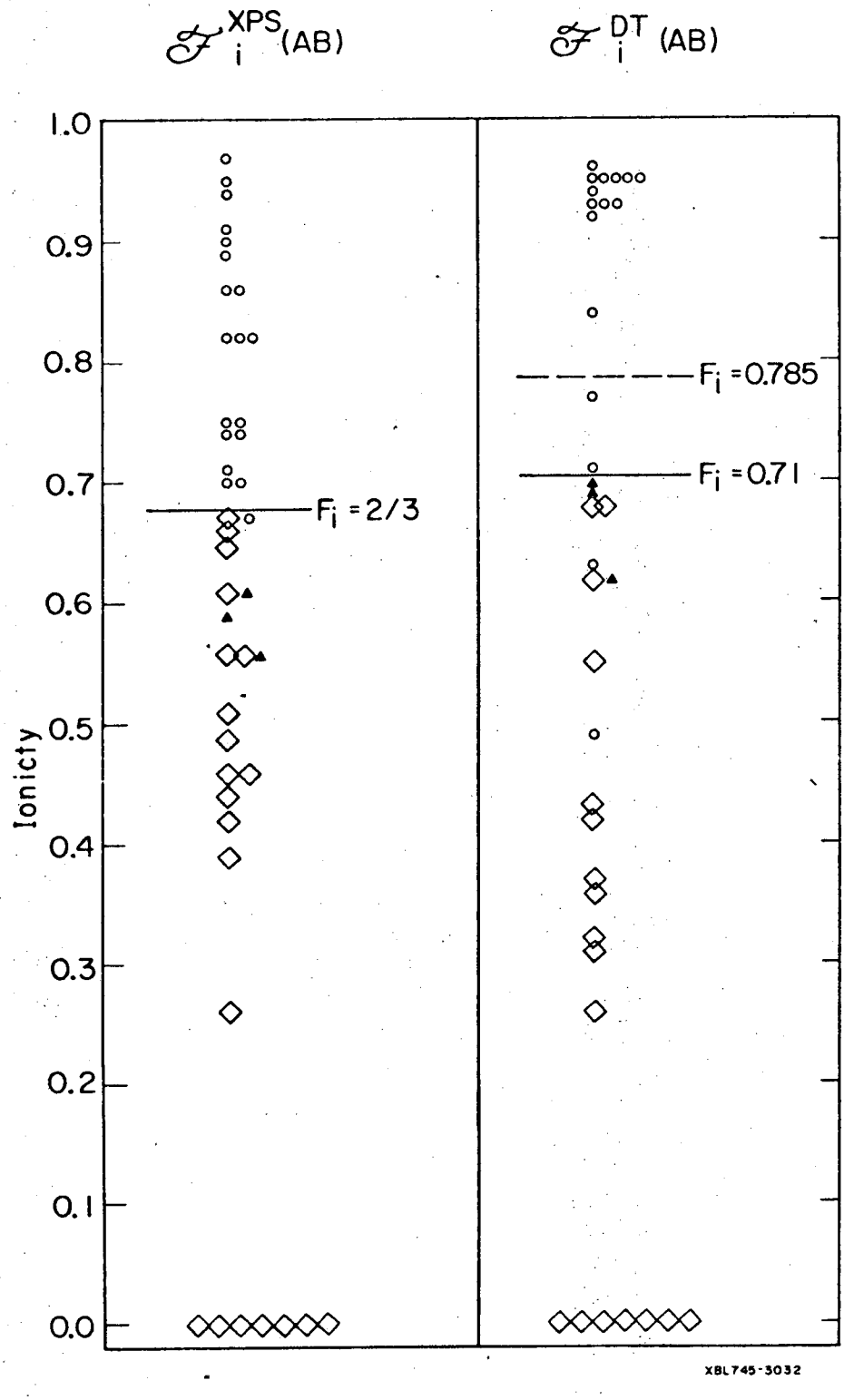
$\mathcal{F}_i^{XPS}$(AB)
$\mathcal{F}_i^{DT}$ (AB)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
Ionicty
F_i = 2/3
F_i = 0.785
F_i = 0.71
XBL745-3032

Fig. 4.

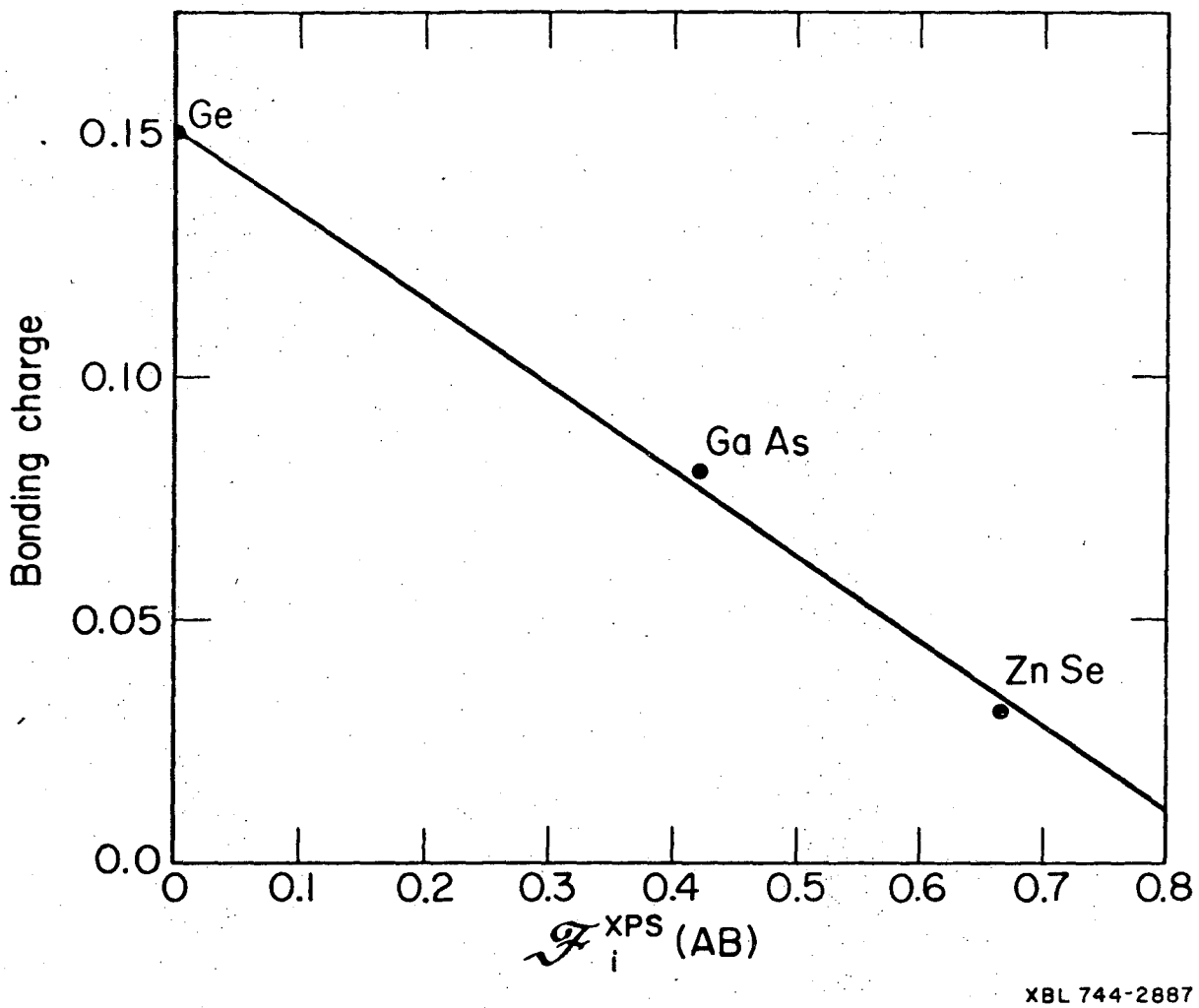
Bonding charge
0.15
0.10
0.05
0.0
Ge
Ga As
Zn Se
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
$\mathcal{F}_i^{XPS}$ (AB)
XBL 744-2887

Fig. 5.

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